

# **Structural and electronic control of the photoluminescence properties of $\text{Mn}^{2+}$ in inorganic solids for potential lighting applications**

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Ich versichere an Eides Statt, dass die Dissertation von mir selbständig und ohne unzulässige fremde Hilfe unter Beachtung der „Grundsätze zur Sicherung guter wissenschaftlicher Praxis an der Heinrich-Heine-Universität Düsseldorf“ erstellt worden ist. Die Dissertation wurde in der vorliegenden oder in ähnlicher Form noch bei keiner anderen Institution eingereicht und ich habe bisher keinen erfolglosen Promotionsversuch unternommen. Die experimentellen Arbeiten für diese Dissertation wurden am Institut für Anorganische Chemie in der Arbeitsgruppe für Anorganische Photoaktive Materialien an der Heinrich-Heine-Universität Düsseldorf durchgeführt.

Düsseldorf, den 25. Juni 2026

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# Zusammenfassung

Moderne leuchtstoffkonvertierte Weißlicht-emittierende Dioden (engl. "*phosphor-converted white light-emitting diodes*", *pc-wLEDs*) sind effiziente Beleuchtungslösungen, die durch ihre energieschonende Konversion elektrischer Energie in Licht maßgeblich zur Reduzierung der vom Menschen verursachten CO<sub>2</sub>-Emissionen beitragen. Jedoch basieren die meisten der derzeit in diesem Anwendungsfeld verwendeten kommerziellen Leuchtstoffe auf Elementen aus der Gruppe der Seltenen Erden, welche eine Reihe von wirtschaftlichen, geopolitischen und ökologischen Problemen mit sich bringen. Das global häufiger vorkommende Übergangsmetallion Mn<sup>2+</sup> könnte eine potentielle Alternative zu Seltenen Erden in *pc-wLEDs* darstellen.

Diese Dissertation liefert Einblicke in die Funktionsweise moderner *pc-LEDs* und die verbleibenden Herausforderungen, insbesondere im Hinblick auf die Nachhaltigkeitsproblematik von Seltenen Erden. Es werden die vielfältigen Anforderungen beschrieben, die anorganische Leuchtstoffe für eine mögliche Anwendung in *pc-wLEDs* erfüllen müssen. Darauf aufbauend werden Leitlinien für die Entwicklung nachhaltiger Mn<sup>2+</sup>-aktivierter Leuchtstoffe abgeleitet. Diese Designprinzipien wurden im Rahmen von drei wissenschaftlichen Manuskripten demonstriert.

Die erste Arbeit (Kapitel 3) befasst sich mit Mn<sup>2+</sup>-aktivierten Borosulfaten. Diese Verbindungen zeichnen sich durch eine ungewöhnliche Emission im orangen Spektralbereich aus, trotz oktaedrischer Oxido-Koordination der Mn<sup>2+</sup>-Ionen, die sonst typischerweise eher rote Lumineszenz dieser Ionen hervorruft. Im Rahmen einer detaillierten Untersuchung wurde diese Beobachtung auf eine ungewöhnlich schwache Koordinationsfähigkeit der O<sup>2-</sup>-Liganden zurückgeführt, wie auch eine Analyse der interelektronischen Racah-Repulsionsparameter nahelegte. Die Ergebnisse zeigen, dass die Lumineszenz der Mn<sup>2+</sup>-Ionen empfindlich auf solche elektronischen Effekte reagiert und dass die Verwendung solch besonderer Liganden Emissionsfarben hervorrufen kann, deren Eigenschaften für Beleuchtungs- und Displayanwendungen von Vorteil sind.

In einer zweiten Arbeit (Kapitel 4) wurden die Photolumineszenzeigenschaften Mn<sup>2+</sup>-aktivierter Alkalilithooxidosilicate untersucht. Diese Gruppe von hochgradig kondensierten Verbindungen mit Strukturen, die sich aus dem UCr<sub>4</sub>C<sub>4</sub>-Typ ableiten, ist bekannt für ihre hervorragenden Emissionseigenschaften bei Aktivierung mit Eu<sup>2+</sup>. Die Einführung anderer Aktivatorionen als Eu<sup>2+</sup> war jedoch zum Zeitpunkt dieser Arbeit nahezu noch nicht beschrieben. Aufgrund der Anwesenheit sowohl kuboidal als auch tetraedrisch koordinierter Lagen und der kleinen Größe des 3d<sup>5</sup> high-spin Ions Mn<sup>2+</sup> führt eine Einlagerung dieses Aktivators in solche Alkalilithooxidosilicate zu zwei Emissionsbanden im grünen und roten Spektralbereich. Die Besetzung der verfügbaren Lagen durch Mn<sup>2+</sup> wird auf deren Größe zurückgeführt, die aus Einkristallstrukturdaten abgeleitet wurden. Die Ergebnisse werden vor dem Hintergrund einer möglichen Anwendung in Einkomponenten-*pc-wLEDs* diskutiert.

Die letzte Arbeit (Kapitel 5) befasst sich mit Mn<sup>2+</sup>-aktivierten Boraciten mit der Zusammensetzung M<sub>3</sub>B<sub>7</sub>O<sub>13</sub>X (M = Zn, Mg; X = F, Cl, Br, I), welche eine bisher nicht beobachtete thermisch robuste Nahinfrarotemission der Mn<sup>2+</sup>-Ionen bei etwa 800 nm zeigen. Diese Beobachtung kann durch eine besonders starke Verzerrung der sowohl

durch Halogenido- als auch Oxido-Liganden gebildeten Koordinationspolyeder erklärt werden, welche die Entartung des angeregten, dreifach bahnentarteten  $^4T_{1g}(^4G)$ -Zustands aufhebt. Temperaturabhängige stationäre und zeitaufgelöste Spektren der untersuchten Verbindungen zeigen eindeutig ungewöhnlich hohe thermische Quenching-Temperaturen über 500 K, die sowohl auf die hochkondensierte Struktur der Boracit-Wirtsverbindungen als auch auf ihre hohen Bandlücken ( $> 5$  eV) zurückgeführt werden können. Darüber hinaus wurde festgestellt, dass die Absorption von blauem Licht mit steigender Ordnungszahl der Halogenido-Liganden  $F \rightarrow Cl \rightarrow Br \rightarrow I$  zunimmt, was auf einen Einfluss der zunehmenden Stärke der Spin-Bahn-Kopplung hindeutet, welche die Spin-Auswahlregel abschwächt.

Insgesamt zeigen die vorgestellten Arbeiten das Potenzial der Nutzung fortgeschrittener Konzepte der Ligandenfeldtheorie, um die Lumineszenz von  $Mn^{2+}$  im Festkörper in ungewöhnliche Spektralbereiche zu verschieben und dieses Aktivatorion somit zu einer wettbewerbsfähigen Alternative zu Seltenen Erden in anorganischen Leuchtstoffen zu machen.

# Abstract

Modern phosphor-converted white light-emitting diodes (pc-wLEDs) are efficient lighting solutions that significantly contribute to the reduction of man-made CO<sub>2</sub> emissions through their energy-saving conversion of electrical energy into light. However, most commercially used phosphors in this application area are based on rare-earth elements, which pose a number of economic, geopolitical, and environmental problems. The abundant transition metal ion Mn<sup>2+</sup> could be a potential alternative to rare-earth elements in pc-wLEDs.

This thesis provides insights into the working principles of modern pc-LEDs and the remaining challenges, particularly with regard to the sustainability issues associated with rare-earth elements. The diverse requirements that inorganic phosphors must meet for possible application in pc-wLEDs are described. Based on this, guidelines for the development of sustainable Mn<sup>2+</sup>-activated phosphors are derived. These design principles have been demonstrated in three scientific manuscripts.

The first work (Chapter 3) deals with Mn<sup>2+</sup>-activated borosulfates. These compounds are characterized by an unusual emission in the orange spectral range despite the octahedral oxido-based coordination of the Mn<sup>2+</sup> ions, which more typically causes a red luminescence of those ions. This observation is attributed to the unusually weak coordination behavior of the O<sup>2-</sup> ligands, as suggested by an analysis of the interelectronic Racah repulsion parameters. The results show that the luminescence of the Mn<sup>2+</sup> ions is sensitive to such electronic effects and that the use of such rather unusual ligands can induce emission colors with properties that are beneficial for lighting and display applications.

In a second work (Chapter 4), the photoluminescence properties of Mn<sup>2+</sup>-activated alkali lithofoxidosilicates were investigated. This group of highly condensed compounds with structures derived from the UCr<sub>4</sub>C<sub>4</sub> type is known for its excellent emission properties when activated with Eu<sup>2+</sup>. However, the introduction of activator ions other than Eu<sup>2+</sup> had hardly been described at the time of this work. Due to the presence of both cuboidally and tetrahedrally coordinated sites and the small size of the 3d<sup>5</sup> high-spin ion Mn<sup>2+</sup>, incorporation of this activator into these alkali lithofoxidosilicates results in two emission bands in the green and red spectral region in these compounds. The occupation of the available sites by Mn<sup>2+</sup> is attributed to their size derived from single-crystal structure data. The results are discussed in the context of a possible application in single-component pc-wLEDs.

The final work (Chapter 5) concerns Mn<sup>2+</sup>-activated boracites of the composition M<sub>3</sub>B<sub>7</sub>O<sub>13</sub>X (M = Zn, Mg; X = F, Cl, Br, I) that showed a hitherto non-observed thermally robust near-infrared emission at around 800 nm. This observation can be explained by a particularly strong distortion of the coordination polyhedra formed by both halide and oxide ligands, which lifts the degeneracy of the triply orbitally degenerate <sup>4</sup>T<sub>1g</sub>(<sup>4</sup>G) excited state. The temperature-dependent steady state and time-resolved spectra of the investigated compounds clearly reveal unusually high thermal quenching temperatures above 500 K, which can be related to both the highly condensed structure of the boracite hosts as well as their high band gaps (> 5 eV). Additionally, the blue-light absorption was found to gradually increase with increasing atomic number of the halide

ligands,  $F \rightarrow Cl \rightarrow Br \rightarrow I$ , which indicates an impact of increasing spin-orbit coupling strength relieving the spin selection rule.

Overall, the presented studies demonstrated the potential of the exploitation of advanced ligand field theoretical concepts to tailor the luminescence of  $Mn^{2+}$  in the solid state towards unusual spectral ranges and thus, indicate first steps how to make this activator a competitive alternative to rare-earth activators in inorganic phosphors.



# Table of Contents

|          |                                                                               |            |
|----------|-------------------------------------------------------------------------------|------------|
| <b>1</b> | <b>Introduction</b>                                                           | <b>15</b>  |
| 1.1      | Modern lighting                                                               | 16         |
| 1.2      | Sustainability concerns of recent phosphors                                   | 16         |
| 1.3      | Mn <sup>2+</sup> as a potential substitute for <i>REE</i> in pc-LED phosphors | 18         |
| 1.4      | Scope of this thesis                                                          | 21         |
| <b>2</b> | <b>Theory</b>                                                                 | <b>29</b>  |
| 2.1      | Working principle of an LED                                                   | 30         |
| 2.2      | Phosphors for pc-wLEDs                                                        | 31         |
| 2.2.1    | Correlated color temperature                                                  | 31         |
| 2.2.2    | Human perception of light, luminous efficacy and color rendering              | 31         |
| 2.2.3    | Color gamut and display applications                                          | 32         |
| 2.2.4    | Bandwidth                                                                     | 33         |
| 2.2.5    | Thermal quenching                                                             | 34         |
| 2.2.6    | Radiative decay                                                               | 36         |
| 2.3      | Mn <sup>2+</sup> as activator ion                                             | 37         |
| 2.3.1    | The free Mn <sup>2+</sup> ion                                                 | 38         |
| 2.3.2    | Crystal field splitting                                                       | 39         |
| 2.3.3    | Interelectronic repulsion and covalency                                       | 40         |
| 2.3.4    | Selection rules                                                               | 41         |
| 2.4      | Optimization strategies for Mn <sup>2+</sup> -activated phosphors             | 41         |
| <b>3</b> | <b>Borosulfates</b>                                                           | <b>53</b>  |
| <b>4</b> | <b>Alkali Lithooxidosilicates</b>                                             | <b>75</b>  |
| <b>5</b> | <b>Boracites</b>                                                              | <b>97</b>  |
| <b>6</b> | <b>Conclusion &amp; outlook</b>                                               | <b>125</b> |
| 6.1      | Conclusion                                                                    | 126        |
| 6.2      | Outlook                                                                       | 128        |
| 6.3      | Closing remarks                                                               | 130        |
| <b>7</b> | <b>Appendix</b>                                                               | <b>133</b> |
| 7.1      | List of Publications                                                          | 134        |
| 7.2      | List of Presentations                                                         | 134        |

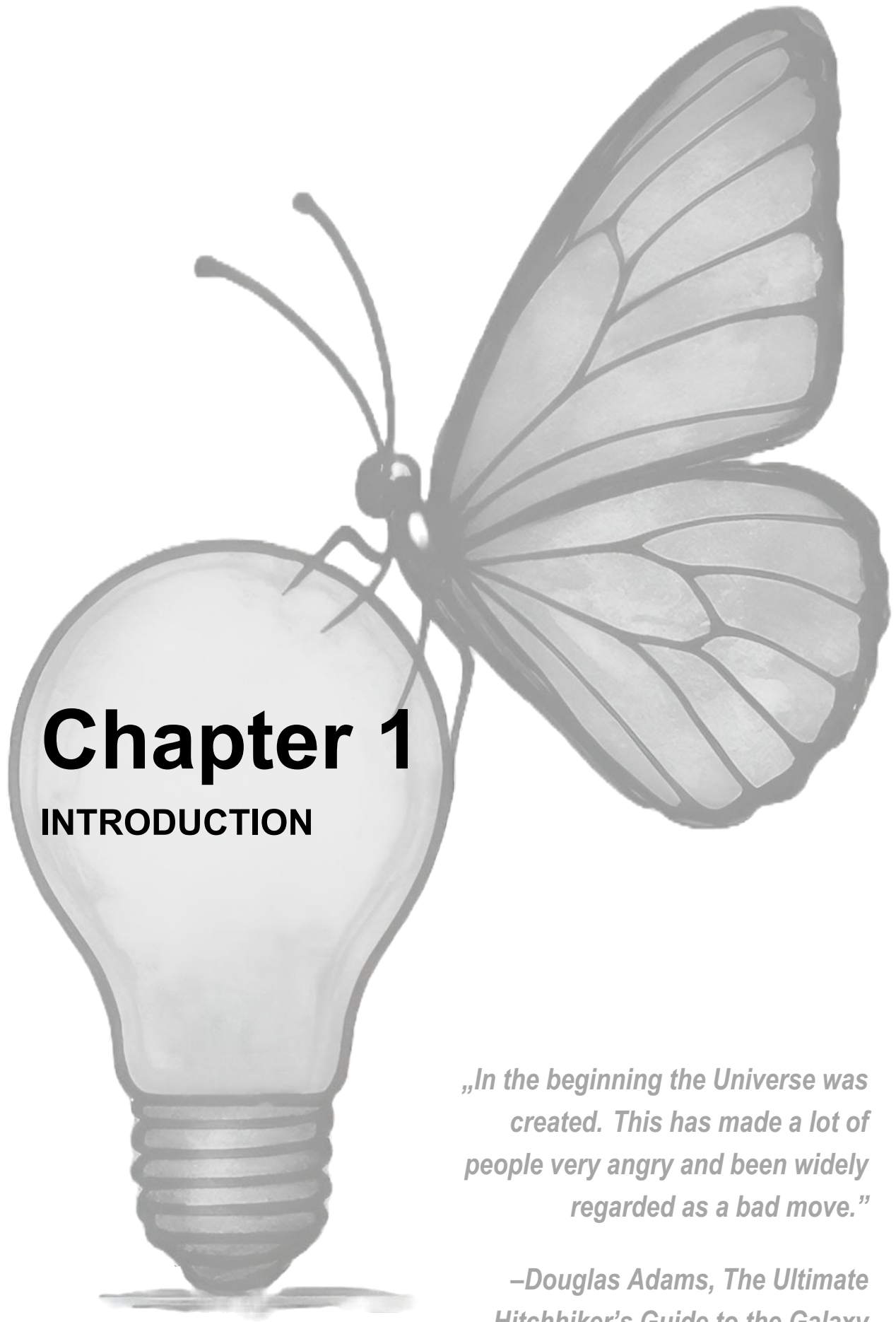




*“You should enjoy the little detours  
to the fullest. Because that’s where  
you’ll find the things more  
important than what you want.”*

*– Yoshihiro Togashi*





# Chapter 1

## INTRODUCTION

*„In the beginning the Universe was created. This has made a lot of people very angry and been widely regarded as a bad move.”*

*–Douglas Adams, The Ultimate Hitchhiker’s Guide to the Galaxy*

## 1.1 Modern lighting

We are currently witnessing a technological revolution of the lighting market due to the rapid replacement of outdated or potentially harmful technologies like incandescent lamps and mercury-containing fluorescent lamps by semiconductor based light-emitting diodes (LEDs).<sup>[1,2]</sup> This ongoing progress was initiated by the development of an efficient blue-emitting (In,Ga)N LED by Shuji Nakamura in 1991, who was also honored with a Nobel Prize in Physics together with Isamu Akasaki and Hiroshi Amano in 2014.<sup>[3–8]</sup> Nakamura's finding finally allowed to produce a white light-emitting diode by combining his blue-emitting (In,Ga)N LED with a blue-excitable, broad yellow-emitting phosphor, usually  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  (YAG: $\text{Ce}^{3+}$ ), originally developed by George Blasse and Alfred Bril at Philips Laboratories in 1967.<sup>[9,10]</sup> Such a phosphor-converted white LED (pc-wLED) produces cold-white light by additive color mixing. Optionally, orange/red conversion phosphors like  $\text{CaAlSiN}_3:\text{Eu}^{2+}$  or  $\text{K}_2[\text{SiF}_6]:\text{Mn}^{4+}$  might be added to create a warm-white impression (see Section 2.1 for a detailed depiction of the working principle of a pc-wLED).<sup>[11–13]</sup> It is this simple optimization capability paired with potentially near unity efficiency that is key for the recent success of pc-wLEDs.<sup>[1,2,8]</sup>

The spreading of LEDs is not only relevant from an economic point of view, but most importantly necessary to face the human-made climate change. In 2010 a share of 19% of the worldwide electricity consumption was used for lighting applications.<sup>[14]</sup> It is predicted that LED lighting will have a market penetration of 84% by 2030 and thus, will potentially reduce the overall energy consumption of lighting technologies by 70%.<sup>[15,16]</sup> For more details on the theoretical background of the luminous efficacy of modern LEDs, see Section 2.2.2.

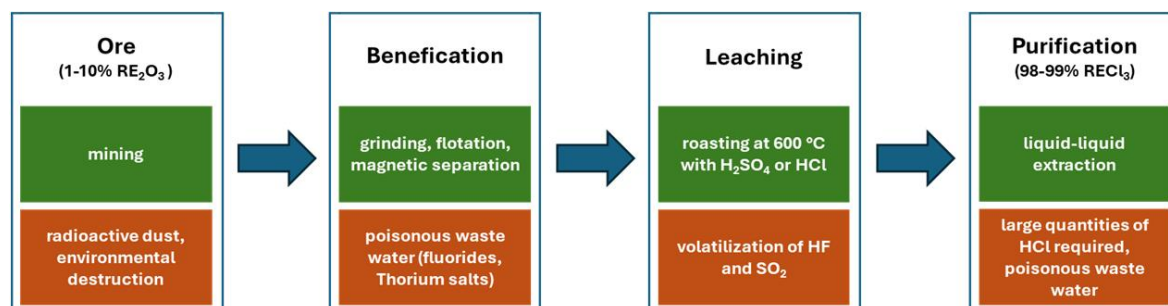
## 1.2 Sustainability concerns of recent phosphors

Pc-wLEDs offer great potential for energy savings. However, the currently used conversion phosphors almost always contain rare-earth elements (*REE*; referring to Sc, Y and the elements with atomic number 57–71 (La–Lu))<sup>[17]</sup>, which come with a series of economic, geopolitical and environmental issues. The term "rare-earth elements" is somewhat misleading as some of those elements are in fact quite abundant in the Earth's crust. To give an example: cerium (60 ppm), lanthanum (30 ppm) and neodymium (27 ppm) are about as abundant as zinc (65 ppm), copper (25 ppm) or lead (14.8 ppm) and even the least abundant stable *REE* (lutetium and thulium, 350 and 300 ppb) are still more abundant than cadmium (100 ppb) or silver (70 ppb).<sup>[18]</sup> However, unlike many other elements, *REE* have a very small tendency to form higher concentrated ores. As a result, usable *REE* deposits are rare and of high strategic value. The mining and purification of *REE* poses a special challenge, both from a chemical and ecological perspective.<sup>[19]</sup>

### Environmental impact of rare-earth mining

*REE* are typically recovered from phosphate or carbonate ores.<sup>[20]</sup> The most abundant *REE* bearing minerals are bastnaesite  $\text{Y}, \text{REE}[(\text{OH}, \text{F})\text{CO}_3]$ , monazite  $(\text{La}, \text{REE})\text{PO}_4$  and xenotime  $(\text{Y}, \text{REE})\text{PO}_4$ , with bastnaesite and monazite typically carrying larger  $\text{RE}^{3+}$  ions and xenotime carrying smaller  $\text{RE}^{3+}$  ions.<sup>[21,22]</sup> However, those *REE* bearing min-

erals usually make up only a small fraction of the mined ores. For instance, even the high quality ores of the Bayan Obo mine in China or the Mountain Pass mine in California have rare-earth oxide ( $RE_2O_3$ ) contents of only 5-9wt%.<sup>[25-27]</sup> This is why an extensive processing routine is necessary, which includes mechanical (e.g. mining, grinding) and chemical (e.g. leaching, roasting) treatment of the ores (Figure 1.1).<sup>[23,24]</sup> That, however,



**Figure 1.1** | Simplified processing chain from ore to specific *REE* chlorides. The green boxes give a brief overview on the applied methods and orange boxes summarize possible environmental hazards. Adopted according to the literature.<sup>[23,24]</sup>

comes with a series of ecological concerns. First of all, *REE* are often accompanied by radioactive elements, especially thorium and uranium, which are particularly prominent in monazite and xenotime ores.<sup>[19,28]</sup> Those potentially hazardous elements are enriched during the processing of *REE* ores and have to be carefully separated and disposed in appropriate repositories, which is cost-intensive.<sup>[28,29]</sup> Therefore, large-scale *REE* producers were repeatedly reported to avoid appropriate handling of radioactive waste. Radioactive dust and wastewater from *REE* production were shown to leak into the environment on several occasions.<sup>[30-33]</sup> There are numerous reports that criticize the radioactive-waste management of the Chinese Bayan Obo mine in particular, which stores most of its waste in open-pit tailing ponds.<sup>[34,35]</sup> In the USA, the repeated leakage of radioactive wastewater between 1984 and 1998 even led to a contemporary shutdown of the Mountain Pass mine between 2000 and 2015, which was the biggest *REE* mine at that time.<sup>[22,31,36,37]</sup>

Other concerns are specifically addressing the leaching and purification process for its toxic side products and resource consumption. For instance, the production of one ton of *REE* in the Bayan Obo mine is estimated to consume 4.4 t  $H_2SO_4$ , 1.6 t  $NaOH$  and 1.2 t  $HCl$ , while producing 60,000 m<sup>3</sup> of waste gas, that contains hydrogen fluoride and sulfur dioxide, 200 m<sup>3</sup> of toxic wastewater and 1.0-1.4 tons of radioactive waste.<sup>[38,39]</sup> However, the exact amounts and compositions of the waste from *REE* production vary heavily, depending on the ore and the purification process. Generally, waste gas emission can be reduced if acid roasting is substituted with alkaline leaching and by the implementation of suitable filter systems.<sup>[40,41]</sup> Wastewater can be recovered in specialized treatment plants and radioactive waste may be stored in deep geological repositories.<sup>[24,42]</sup> Those measures are, however, not commonly employed, as they come with increasing costs. It is therefore still a common practice to store wastewater from *REE* production in tailing ponds, which poses substantial risks for the environment due to possible leakage, seepage into the groundwater, or dust formation.<sup>[34]</sup>

## Supply chain risks

The global demand for rare-earth containing products is constantly rising. However, this demand is currently only covered by a few countries, with China being the globally leading exporter. In 2023, China accounted for 70% of the world's rare-earth production alone. Other important producers are the USA (14.3%), Australia (6%) and Myanmar (4%).<sup>[43]</sup>

The possible consequences of the *de facto* monopoly of China on rare-earths became explicitly noticeable during the 2010 rare-earth crisis, when rare-earth prices skyrocketed after China announced reduced export quotas. One reason for this government-dictated turnaround was a dispute with Japan over the Diaoyu/Senkaku Islands.<sup>[44,45]</sup> Those export restrictions were withdrawn in 2014 after an intervention of the World Trade Organization. However, the 2010 rare-earth crisis emphasized the world's reliance on Chinese rare-earth exports and showcased China's willingness to use its market position for political purposes. More recently, the USA showed similar tendencies by granting major tax credits for electric vehicles with batteries that primarily contain critical minerals produced in the USA or allied states, governed in the Inflation Reduction Act of 2022, thereby discriminating against political opponents (referred to as „Foreign Entities of Concern“, e.g. China or Russia).<sup>[46,47]</sup> Moreover, the USA is currently displaying a very volatile foreign policy, also towards its allies and therefore, the reliability of rare-earth supplies from the USA is questionable.<sup>[48,49]</sup>

## 1.3 $\text{Mn}^{2+}$ as a potential substitute for *REE* in pc-LED phosphors

The previously-mentioned environmental and political concerns of *REE* significantly mitigate the benefits of current pc-LEDs as modern and sustainable light sources. This situation is one of the reasons why there is a growing interest in alternative, non-*REE* activator ions for pc-LEDs. One such emitter, which has recently experienced a renaissance, is the abundant transition metal ion  $\text{Mn}^{2+}$ .<sup>[50–52]</sup>

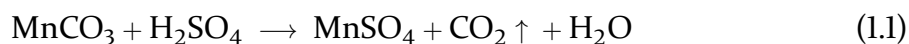
### Manganese: mineralogy, abundance, and refinement

Manganese is found in various minerals. The most important are the oxides pyrolusite ( $\text{MnO}_2$ ), psilomelane ( $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ ), manganite ( $\text{MnO}(\text{OH})$ ), the (oxy-)silicates braunite ( $\text{Mn}^{2+}\text{Mn}_6^{3+}[(\text{SiO}_4)_8\text{O}_8]$ ), piemontite ( $\text{Ca}_2(\text{Mn}, \text{Fe})\text{Al}_2[(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})]$ ), and the carbonate rhodochrosite ( $\text{MnCO}_3$ ).<sup>[53]</sup> Deposits of manganese-containing ores with high manganese contents of 15–50wt% exist on every continent.<sup>[53–55]</sup> Manganese is found with an average concentration of 716 ppm in the Earth's crust, making it the 12th most abundant element and 8th most abundant metal.<sup>[18]</sup> About 85–90% of the world supply of manganese is currently used as alloying element in steel production. It is the 4th most produced metal (after iron, aluminum, and copper).<sup>[56,57]</sup>

High-quality manganese oxide ores are used directly in some industrial processes, such as metallurgy<sup>[58]</sup>. However, oxide ores with lower manganese content as well as silicate and carbonate ores have to be refined before they can be used. It is common to start with a physical separation by washing, gravity, magnetism, or flotation. The subsequent processing steps depend on the composition of the ores.

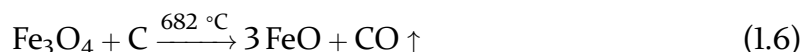
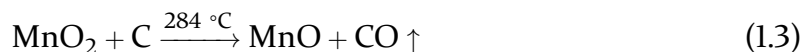
**Reduction leaching** is most common for carbonate and oxide ores with low iron con-

tent. It is performed by dissolving the ore concentrate in H<sub>2</sub>SO<sub>4</sub> in the presence of a reducing agent. MnSO<sub>4</sub> is precipitated afterwards:[54,58]



A fundamental issue of this process is the co-leaching of manganese and iron, which makes further purification steps necessary.[58]

Ores with higher iron content can be refined by **reductive roasting and magnetic separation**.<sup>[54,58]</sup> This process utilizes both the different reduction temperatures of iron and manganese and the different magnetic behavior of MnO and Fe<sub>3</sub>O<sub>4</sub>/Fe. The ores are first crushed and subsequently roasted inside a rotary kiln in the presence of coal. The roasting temperatures are typically adjusted between 400 °C and 1000 °C to produce ferromagnetic Fe<sub>3</sub>O<sub>4</sub> or Fe and antiferromagnetic MnO, which can be separated in a subsequent magnetic separation to reach manganese concentrations up to 95%.<sup>[59,60]</sup>



**High-temperature reduction smelting** is particularly common for manganese silicate ores and primarily relies on the fusibility differences of the manganese silicates slag and molten iron.<sup>[59]</sup> The raw ores are inserted into a high-temperature furnace and heated to 1250-1350 °C in the presence of coal. These conditions are sufficient to reduce Fe<sub>2</sub>O<sub>3</sub>, PbO and Ag<sub>2</sub>O to the respective metals and evaporate undesired impurities like zinc and phosphorus.<sup>[54]</sup> Higher oxidation states of manganese are reduced to Mn<sup>2+</sup> and enriched in the slag, from which it is recovered after the process.<sup>[54,58]</sup> The aforementioned processes produce crude products, which can be used in industrial processes with moderate purity demands, like metallurgy. However, they may be supplemented by further purification steps, like electrolysis, ion exchange, precipitation or solvent extraction if a higher purity is required.<sup>[58,61-63]</sup>

## Environmental impact of manganese vs. REE production

The mining and purification process of manganese is considerably less resource-draining than for REE. This comes from a number of reasons:



### Higher ore qualities

Manganese has a strong tendency to conglomerate in ores due to its versatile redox chemistry.<sup>[64]</sup> Regularly used ores for manganese refinement contain 15-50wt% manganese.<sup>[53-55]</sup> In contrast, high-quality REE bearing ores contain only 5-9wt% of RE<sub>2</sub>O<sub>3</sub>.<sup>[25-27]</sup>

### Simple purification

Manganese-containing ores typically also contain larger amounts of iron ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) as a main impurity.<sup>[53,54,56,65]</sup> Other common impurities include  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ba}^{2+}$ .<sup>[54,65]</sup> The vastly different chemical and physical properties of those impurity ions allow for a simple separation by precipitation and magnetic sorting.<sup>[54,63,65]</sup> *REE*, on the other hand, are chemically fairly similar, which makes their purification energy-consuming and not an easy task. So far, resource draining liquid-liquid chromatography is one of the most common methods to separate the individual *REE*.<sup>[23,24]</sup>

### Waste management

Waste from manganese production are highly versatile, depending on the specific purification process. However, the most important sources of waste are usually slag from the ore reduction process and wastewater that may occur at various stages of the production process.<sup>[66,67]</sup> Slag is usually stored at landfills and wastewater is precipitated, filtered and discarded into rivers.<sup>[68]</sup> The environmental effects of this procedure are not clear and still subject of discussion. However, the environmental toxicity of manganese is comparably low.<sup>[68,69]</sup> The disposal of waste from *REE* production, on the other hand, is a special challenge, as they are frequently contaminated with radioactive elements like thorium and uranium as well as toxic fluids, e.g. hydrofluoric acid.<sup>[38,39]</sup>

## A history of $\text{Mn}^{2+}$ lighting

$\text{Mn}^{2+}$  has been widely used in commercial phosphors for mercury discharge lamps and fluorescent tubes, e.g. as green-emitting willemite ( $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ ) or white emitting halophosphate ( $\text{Ca}_5(\text{PO}_4)_3\text{F}, \text{Cl}:\text{Sb}^{3+}, \text{Mn}^{2+}$ ).<sup>[70–74]</sup> Those phosphors are characterized by a good excitability by the mercury UVC line at 253.7 nm, either due to a  $\text{Sb}^{3+} \rightarrow \text{Mn}^{2+}$  energy transfer or an excitation over the band gap.<sup>[75]</sup> They thereby successfully bypassed a fundamental issue of  $\text{Mn}^{2+}$ , which is the poor absorption cross section based on its spin-forbidden  $3d^5 \leftrightarrow 3d^5$  transitions, making a direct excitation inefficient. However, modern pc-LEDs require excitation with blue or near-UV light, which is challenging for the aforementioned phosphors. This was a major reason for the transition to *REE*-activated phosphors like YAG: $\text{Ce}^{3+}$  and  $\text{CaAlSiN}_3:\text{Eu}^{2+}$  with intrinsically strong absorption cross sections in the blue spectral range.

## The renaissance of $\text{Mn}^{2+}$

The usage of *REE* in phosphors for pc-LEDs is a historical success story of materials development. However, researchers kept the idea of  $\text{Mn}^{2+}$ -activated phosphors alive. Over time, numerous new materials with improved luminescence properties have been introduced that frequently rival or even surpass commercial *REE*-activated phosphors in terms of luminescence temperature stability<sup>[76–79]</sup>, color purity<sup>[76,78–81]</sup>, and quantum yield<sup>[82]</sup>. Yet, the poor blue light absorption remains a major obstacle that, however, can be overcome by co-activation with sensitizers with allowed transitions, such as  $\text{Sn}^{2+}$ <sup>[83,84]</sup>,  $\text{Pb}^{2+}$ <sup>[84–86]</sup>,  $\text{Sb}^{3+}$ <sup>[82]</sup>,  $\text{Bi}^{3+}$ <sup>[87]</sup> or excitons<sup>[88,89]</sup> (see Section 2.4). But also *RE* ions like  $\text{Ce}^{3+}$ <sup>[90,91]</sup> and  $\text{Eu}^{2+}$ <sup>[92,93]</sup> are promising sensitizers for  $\text{Mn}^{2+}$ , which could



be an intriguing, yet simple way to reduce the *REE* content in pc-LEDs.

## 1.4 Scope of this thesis

This dissertation aims for a better understanding of the luminescence of the  $\text{Mn}^{2+}$  ion in inorganic solids, with the ultimate goal to derive guidelines for the development of sustainable, competitive  $\text{Mn}^{2+}$ -activated phosphors for pc-LEDs and displays. This is achieved by the introduction of  $\text{Mn}^{2+}$  into host compounds that stand out due to their electronic or structural features and a careful investigation of their photoluminescence properties. The features to be investigated comprise (see Section 2.3 for theoretical background):

### Structural rigidity and condensation

It is well known that structural rigidity facilitates narrow emission bandwidths and high thermal quenching temperatures of phosphors. Generally, this is the case for "condensed" compounds (i.e., with a small anion to cation ratio), often also prepared under high pressure.

### Crystal field splitting

The most common way to tune the emission color of  $\text{Mn}^{2+}$  from green to red is by a change from a weak tetrahedral to a strong octahedral crystal field. However, the luminescence of  $\text{Mn}^{2+}$  in other coordination geometries (e.g. cubic, square-planar, distorted octahedron) is barely encountered in literature. Such features could be a missed opportunity as a distortion of the crystal field should expectedly result in a lifting of orbital degeneracy of the excited states and thereby enable an unusually strong red-shift of the emission. This could be a promising design strategy for  $\text{Mn}^{2+}$ -activated near-infrared-emitting phosphors.

### Covalency of the metal–ligand interaction

Adjusting the covalency of the metal–ligand interaction by the usage of particularly soft ( $\text{N}^{3-}$ ,  $\text{S}^{2-}$ ,  $\text{I}^-$ ) or hard ( $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) ligands offers a simple way to tune the emission color of  $\text{Mn}^{2+}$ . Hosts like AlN or ZnS show a narrow orange/red emission, despite the weak crystal field splitting in tetrahedral coordination, which can be explained by means of the covalency of the Mn–ligand bond and the consequent reduction of the interelectronic repulsion by the nephelauxetic effect.

### Spin-orbit coupling

The poor absorption and long luminescence decay times of  $\text{Mn}^{2+}$  are among the biggest obstacles to overcome for a potential application in phosphors for pc-LEDs and bright displays with low reaction times. A promising strategy to achieve this is by the usage of heavy, electron-rich ligands like  $\text{I}^-$  or  $\text{Te}^{2-}$  that enable a spin-orbit coupling and thus lower the restrictions based on the spin selection rule of electronic transitions of  $\text{Mn}^{2+}$ .

### Band gap

The quenching temperatures of  $\text{Mn}^{2+}$  are known to correlate with the band gap

of the respective host compounds.<sup>[77]</sup> This experimental observation is explained by means of thermal photoionization as the main quenching mechanism. It is therefore recommendable to use host compounds with wide band gaps ( $E_g > 5$  eV) in the design of  $\text{Mn}^{2+}$ -activated phosphors, which is usually the case for compounds composed of small and highly charged anions like  $\text{O}^{2-}$  or  $\text{F}^-$  and cations like  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{P}^{5+}$ , or  $\text{S}^{6+}$ . However, this strategy complicates the aforementioned utilization of soft and heavy ligands, which are usually associated with small band gaps.

**Chapter 2** of this thesis aims to provide a theoretical background for the reader. It starts with a brief depiction of the working principle of a pc-wLED, followed by a closer look at the conversion phosphors and the key features they need for a possible application. The luminescence characteristics of common activator ions, like  $\text{Eu}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  are discussed in this context. The final part of this chapter is devoted to an in-depth description of the photophysical properties of the  $d^5$  high-spin ion  $\text{Mn}^{2+}$ . The influence of structural and electronic effects on the luminescence of  $\text{Mn}^{2+}$  is discussed and optimization strategies for the development of functional  $\text{Mn}^{2+}$  phosphors are given.

In **Chapter 3** of this thesis, the  $\text{Mn}^{2+}$ -activated zinc borosulfates in the solid solution  $\text{Zn}_{(1-x)}\text{Mn}_x[\text{B}_2(\text{SO}_4)_4]$  ( $x = 0.5, 1, 2, 3, 4, 5, 10$ ) are presented. Borosulfates are a class of silicate-analogous compounds, however, the stronger electron withdrawing character of the  $[\text{SO}_4]^{2-}$  groups makes them intriguing hosts for our studies. The samples showed an orange emission around 590 nm, which is an unusually short wavelength for octahedrally coordinated  $\text{Mn}^{2+}$  and indicates an uncommonly weak crystal field. This suspicion was confirmed by the estimation of the interelectronic Racah repulsion parameters from photoluminescence excitation spectra. The results show that  $\text{Mn}^{2+}$  can be used as a tool to detect weak coordination behavior of ligands and emphasize that electronic control over the metal–ligand bond can be an effective lever to tune the emission of  $\text{Mn}^{2+}$  to unusual spectral ranges.

In **Chapter 4**, we present the photoluminescence properties of  $\text{Mn}^{2+}$ -activated alkali lithooxidosilicates. This group of highly condensed  $\text{UCr}_4\text{C}_4$ -type compounds is characterized by a rigid anionic backbone, comprising tetrahedral  $[\text{LiO}_4]^{7-}$  and  $[\text{SiO}_4]^{4-}$  building units.<sup>[94]</sup> Those tetrahedra are arranged in *vierer-ring* channels around cuboidally coordinated alkali cations.  $\text{Eu}^{2+}$ -activated alkali lithooxidosilicates have become interesting candidates for thermally robust, narrow-band-emitting phosphors in the context of display applications. However, the introduction of other activator ions besides  $\text{Eu}^{2+}$  is rather new to this group of compounds. Our results showed that  $\text{Mn}^{2+}$  can be incorporated into those compounds, resulting in two emission bands in the green and red spectral range. This observation is discussed on the basis of the size of the available  $\text{Li}^+$  and  $\text{Na}^+$  sites, which is derived from single crystal diffraction data. The study provides insights into the site preference of  $\text{Mn}^{2+}$  if more than one possible cation site is available. This might be a valuable trait for a possible application in one-component pc-wLEDs.

**Chapter 5** of this thesis deals with  $\text{Mn}^{2+}$ -activated boracites, which showed some rather unexpected, thus intriguing luminescence features. These compounds with the general molecular formula  $M_3\text{B}_7\text{O}_{13}X$  ( $M = \text{Zn}, \text{Mg}$ ;  $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) show the unique feature to possibly incorporate any stable halide anion, while being structurally and chemically stable. This makes them ideal candidates for a trend analysis on the impact of spin-orbit coupling induced by heavy ligands. However, our results showed that this effect is rather small compared to other literature known compounds. Another intriguing feature of these  $\text{Mn}^{2+}$ -activated boracites, however, was the observation of an emission in the near-infrared (NIR) range at around 800 nm, hitherto not assessed for any  $\text{Mn}^{2+}$ -related emission in inorganic solids so far. This finding is explained by a strong asymmetry of the ligand field in the six-fold coordinated cation sites thus lifting the orbital degeneracy of the emissive  $^4\text{T}_{1g}(^4\text{G})$  state that results in an unusual red-shift of the luminescence. In addition, this broad-band emission is accompanied by vibronic fine structure at low temperatures and high thermal quenching temperatures for these NIR phosphors, especially for the new compound  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$ . By that strategy, the paradigm of broad-banded NIR emitters accompanied with low thermal quenching temperatures could be structurally mitigated, while the introduction of heavy halide anions helped enhance the absorption cross section at 450 nm. With this host design strategy, it was possible to extend the spectral range for  $\text{Mn}^{2+}$ -based emission for the first time without introducing any of the other disadvantages usually accompanying such an approach.

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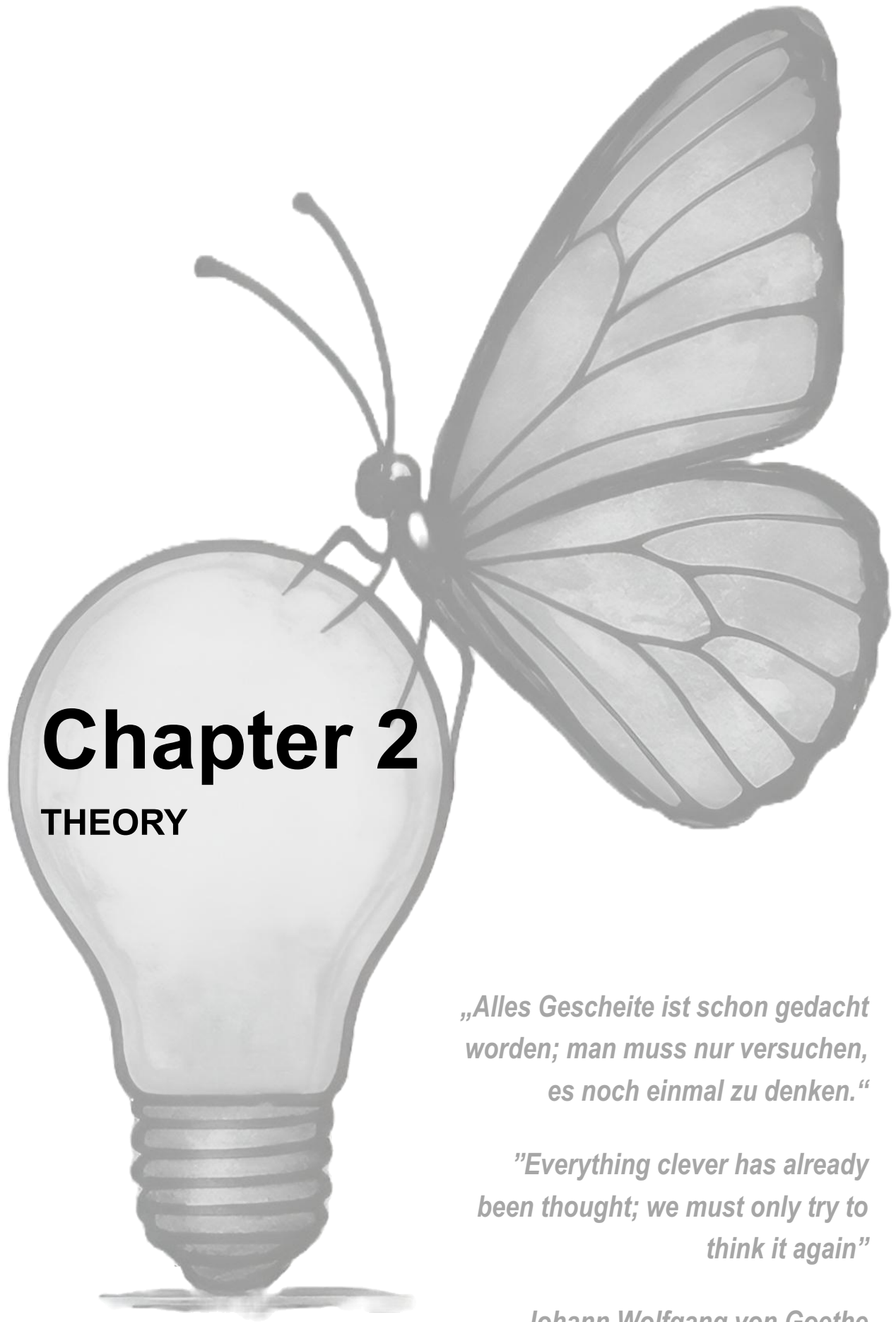
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# Chapter 2

## THEORY

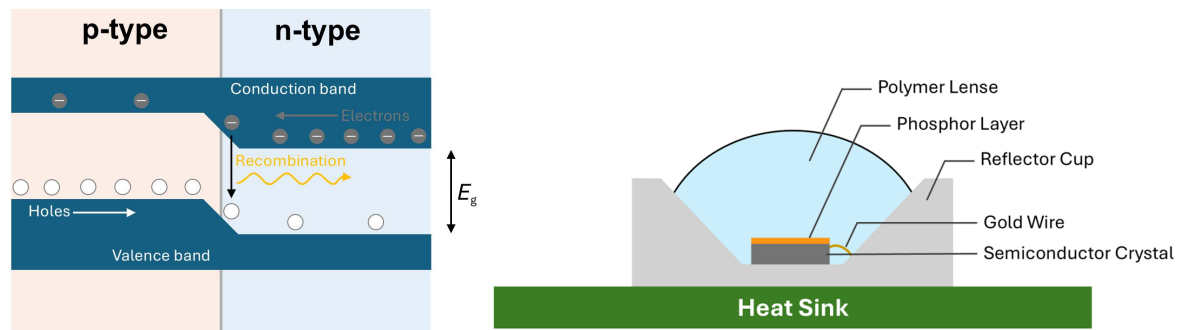
*„Alles Gescheite ist schon gedacht worden; man muss nur versuchen, es noch einmal zu denken.“*

*”Everything clever has already been thought; we must only try to think it again”*

*– Johann Wolfgang von Goethe*

## 2.1 Working principle of an LED

A light-emitting diode (LED) is an electroluminescent device that is constructed from two layers of semiconductor material, one of which contains additional positive charge carriers (holes) in its valence band (p-type), while the other contains additional negative charge carriers (electrons) in its conduction band (n-type). Those carriers start moving to the p-n-junction, if a forward bias is applied and eventually recombine upon releasing that energy as light.<sup>[1-3]</sup> The working principle of an LED is depicted in Figure 2.1.



**Figure 2.1** | Basic LED operation and structure. Left: Working principle of a LED. Electrons recombine at the p-n junction if a forward current is applied. The energy difference is released in the form of light. Right: Schematic construction of a pc-LED.

The emission color of an LED only depends on the band gap  $E_g$  of the specific semiconductor material. By that approach, light of any color can be produced by LEDs with semiconductors with appropriate band gaps in principle. However, there are practical limitations to this concept. First of all, semiconductors with a direct band gap are favorable over those with indirect band gap. A direct band gap basically means that the electron in the conduction band and the hole in the valence band have approximately the same momentum, which dramatically increases the probability of a radiative recombination. It should also be possible to grow high-quality n-doped and p-doped single crystals of the desired material.<sup>[2]</sup> This turned out to be particularly challenging for semiconductors with large band gaps, which are required for blue and UV-LEDs.<sup>[4,5]</sup> As a result, the development of an efficient (In,Ga)N blue LED was delayed until 1991, while red and green LEDs had already been technologically mature for 20+ years at that time.<sup>[6-8]</sup> The breakthrough was achieved by Shuji Nakamura at Nichia in 1992, who was awarded the Nobel Prize in Physics together with Isamu Akasaki and Hiroshi Amano from Nagoya University in Japan for laying the foundations that ultimately led to the development of white LEDs.<sup>[1-3,9-12]</sup>

### Phosphor-converted white LEDs

The technological advance in the processing of bright blue LEDs allowed to create a white-light impression by additive color mixing of blue, green and red light from LEDs (RGB-LED) for the first time. However, most LEDs have a tendency to degrade over time, which may result in an unfavorable color shift and alters the product lifetime of RGB-LEDs. Additionally, the quantum efficiencies of current green LEDs are comparatively low ("green gap").<sup>[13,14]</sup> An alternative approach for the creation of white light is

achieved by the combination of a blue LED with one or multiple blue-excitable conversion phosphors with high internal quantum efficiency.<sup>[5,15]</sup> The color impression of light from phosphor-converted white LEDs (pc-wLEDs) can be widely tuned by simply changing the conversion phosphor. This simplicity and robustness significantly contributed to the success of pc-wLEDs.<sup>[1,5]</sup>

## 2.2 Phosphors for pc-wLEDs

Pc-wLEDs are a simple, yet effective solution for many lighting applications. However, their performance is closely related to the applied conversion phosphors. The following section is dedicated to give an overview on the features that a conversion phosphor should possess for an application in pc-wLEDs. Both the state-of-the-art, as well as future challenges will be addressed.

### 2.2.1 Correlated color temperature

The **color temperature** is defined as the temperature of a Planckian radiator whose radiation has the same chromaticity as that of a given light source.<sup>[16]</sup> However, artificial white-light sources will never exactly match the radiation profile of a Planckian radiator, which is why the **correlated color temperature (CCT)** is used much more frequently for lighting devices. The CCT represents the temperature of a Planckian radiator having the chromaticity closest to the chromaticity associated with the given spectral distribution in a color coordinate diagram.<sup>[16,17]</sup> Generally, white light with a low CCT (e.g. 2700 K) is perceived as yellowish/reddish and often referred to as "warm" white light usually applied in residential lighting. White light with a high CCT (e.g. 6500 K), on the other hand, appears bluish-white and is referred to as "cold" light more typically applied in commercial indoor lighting, in which bright light is required.<sup>[18]</sup>

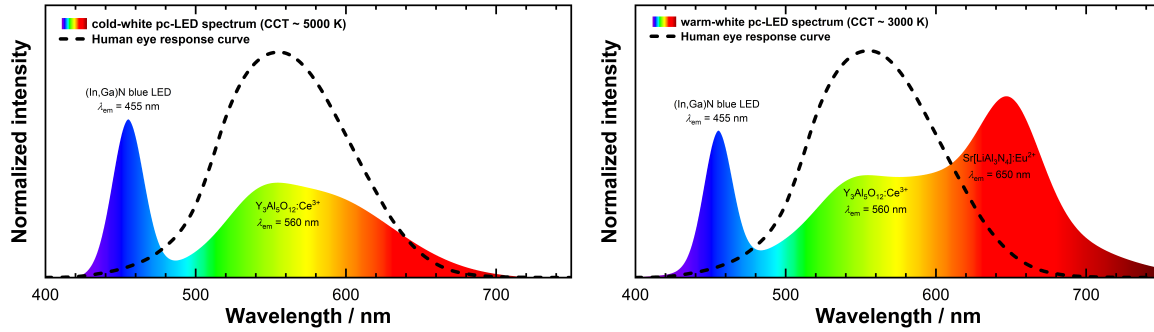


**Figure 2.2** | Comparison of several light sources with different correlated color temperatures. Light sources with lower correlated color temperatures (left) give a yellowish color impression, whereas higher correlated color temperatures (right) result in a bluish color impression. Figure taken from the literature.<sup>[19]</sup>

### 2.2.2 Human perception of light, luminous efficacy and color rendering

The first pc-wLEDs used broad-band yellow emitting  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  (YAG: $\text{Ce}^{3+}$ ) as conversion phosphor.<sup>[20,21]</sup> This, however, gave a cold-white impression, due to a missing portion of emission in the red spectral range. Cold-white light is generally unfavorable for human-centered lighting, as it is perceived as "artificial" or "clinical".<sup>[5]</sup> Moreover,

there is strong evidence that exposure to cold-white light in the evening disrupts the circadian rhythm and causes sleep disorders.<sup>[22–24]</sup> These facts caused a growing demand for orange-red emitting conversion phosphors to create a warm-white light impression, which finally led to the discovery of orange/red-emitting nitride phosphors like  $(\text{Sr}, \text{Ba})\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ <sup>[25–27]</sup>,  $\text{CaAlSiN}_3:\text{Eu}^{2+}$ <sup>[28,29]</sup> and  $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ .<sup>[30]</sup>



**Figure 2.3** | Comparison of the electroluminescence spectra of a cold-white pc-LED with high luminous efficacy but poor color rendering (left) and a warm-white pc-LED with improved color rendering but slightly worse luminous efficacy. The spectra were modeled using Lorentzian-functions to resemble real spectra, according to the literature.<sup>[31]</sup> The dashed line indicates the human eye spectral luminous efficiency for photopic vision, according to a dataset provided by the International Commission on Illumination (CIE).<sup>[32]</sup>

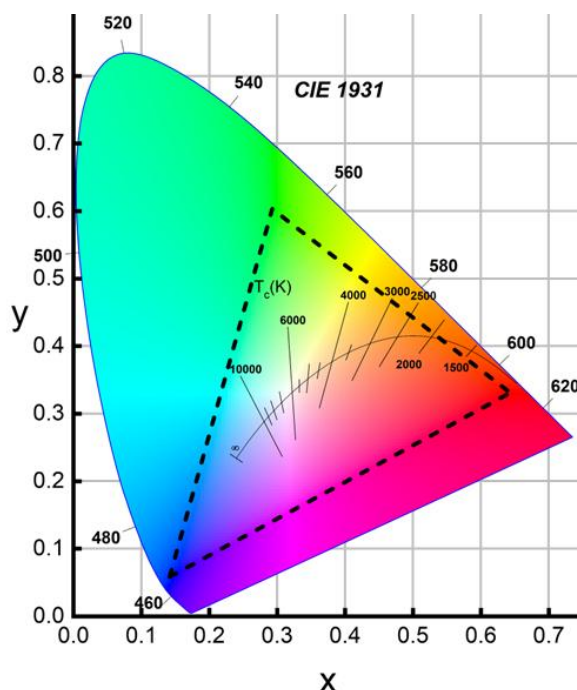
Those, however, suffer from losses in the deep-red to near-infrared (NIR) region, for which the human eye is barely sensitive. This fundamental bias of lighting efficiency vs. quality might be expressed by the comparison of two measures:

The **luminous efficacy** (in units of lm/W) relates the perceived luminous intensity to the electric power input. The highest theoretically possible luminous efficacy of 683 lm/W could only be achieved from monochromatic green-yellow light at 555 nm, at which the human eye has the highest sensitivity.<sup>[13,32,33]</sup>

The **color rendering index (CRI)** essentially compares an artificial light source with sunlight or incandescent light to give a measure of how “natural” colors are rendered under its illumination. By definition, sunlight and incandescent light have a fixed CRI value of 100 and warm-white halophosphate fluorescent lamp light has a CRI of 50.<sup>[34]</sup> Modern pc-LEDs can reach a luminous efficacy of  $\geq 235$  lm/W with high CRI  $\geq 80$  (e.g. ams OSRAM OSCONIQ<sup>TM</sup>).<sup>[35]</sup> Such a high CRI of  $\geq 80$  is mandatory for indoor lighting purposes, which is regulated by directives of the European Commission.<sup>[36]</sup>

### 2.2.3 Color gamut and display applications

A common application for pc-wLEDs is in backlighting for liquid crystal displays (LCDs), which has very specific demands on the used conversion phosphors. In contrast to general illumination purposes, where broad emission bands are favorable for a high CRI, display applications demand narrow emission bandwidths.<sup>[37,38]</sup> This is explained by the working principle of an LCD, which essentially consists of a white backlight and a multitude of microscopic color filters (pixels) that selectively transmit the blue, green, or red light components.<sup>[39]</sup> A thin liquid crystal layer together with two polarization filters acts as a light switch for every pixel.<sup>[40]</sup> Ideally, the emission spectrum of a backlight should peak precisely at the transparency window of the color filters to avoid intensity losses. In addition, a display should be able to reproduce a wide range of colors, which is usually quantified by a comparison of its **color gamut** with a stan-



**Figure 2.4** | The 1931 CIE color space.<sup>[41]</sup> The boundaries of the diagram assign a perceived color to the wavelength of a monochromatic emitter. The correlated color temperature of a black body emitter is indicated by the Planckian locus. The sRGB color space is depicted as dashed triangle.

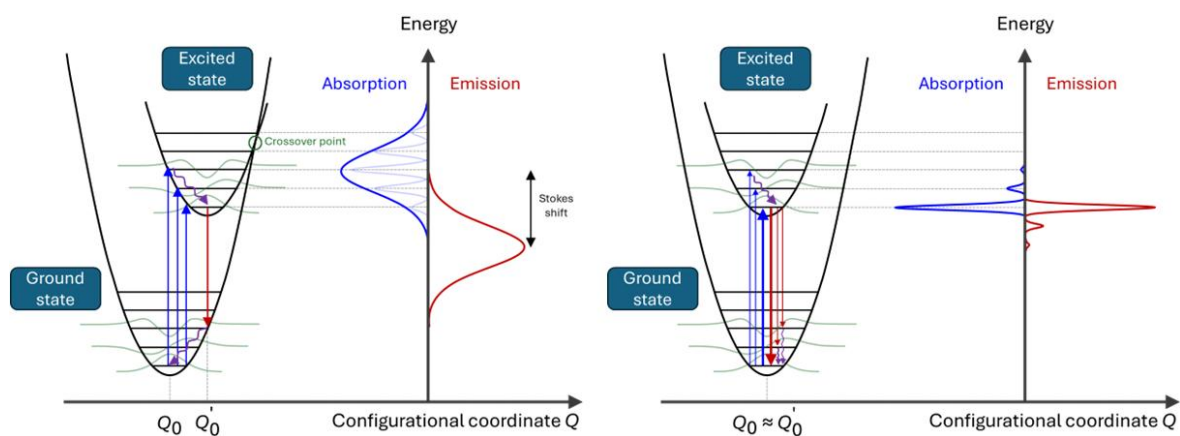
dard, e. g. the sRGB color space (introduced by HP Inc. and Microsoft Corporation) or the National Television Standard Committee (NTSC) standard.<sup>[42,43]</sup> The color gamut describes a triangular surface in color space where any color with a desired saturation within the gamut can potentially be reproduced (see Figure 2.5). Therefore, wide color gamuts are crucial for vivid color rendering of modern displays. Phosphors with narrow bandwidths and carefully optimized emission wavelengths meet the demands for both efficiency and maximizing the gamut.

#### 2.2.4 Bandwidth

Phosphors with narrow bandwidths are not only important for display applications, but also for efficient pc-LEDs. The spectral overlap of the emission from conventional broad-band orange/red phosphors like  $(\text{Sr}, \text{Ba})\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ <sup>[25–27]</sup> or  $\text{CaAlSiN}_3:\text{Eu}^{2+}$ <sup>[28,29]</sup> with the deep-red to NIR region causes non-negligible efficacy losses. One possible solution to this issue is the development of red phosphors with narrower emission bands and limited overlap with the NIR spectral region. This might be achieved by two strategies. One approach consists in the utilization of emitter ions with intrinsically narrow emission bandwidths, e. g.  $\text{Mn}^{4+}$  in fluoridic hosts or  $\text{Eu}^{3+}$ . Famous narrow-band red emitters that follow this strategy are  $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ <sup>[44]</sup> or  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ <sup>[45]</sup>. However, those phosphors are generally more prone to excited state saturation due to the low transition rate of the respective  $3d^3 \leftrightarrow 3d^3$  and  $4f^7 \leftrightarrow 4f^7$  transitions (see Section 2.2.6 for details). Moreover, many  $\text{Mn}^{4+}$ -activated phosphors suffer from distinct thermal quenching at the working temperature of pc-wLEDs of approx. 150 °C and  $\text{Eu}^{3+}$  is hardly excitable at the desired wavelength of 450 nm.<sup>[44,46]</sup> However, alternative strategies employing non-radiative interparticle energy transfer are investigated to overcome this obstacle.<sup>[47]</sup> An



alternative approach is the usage of broad-band emitters and limitation of any changes of the activator–ligand distance, which can be explained using the so-called configurational coordinate diagram (Figure 2.5). In general, the width of an emission band

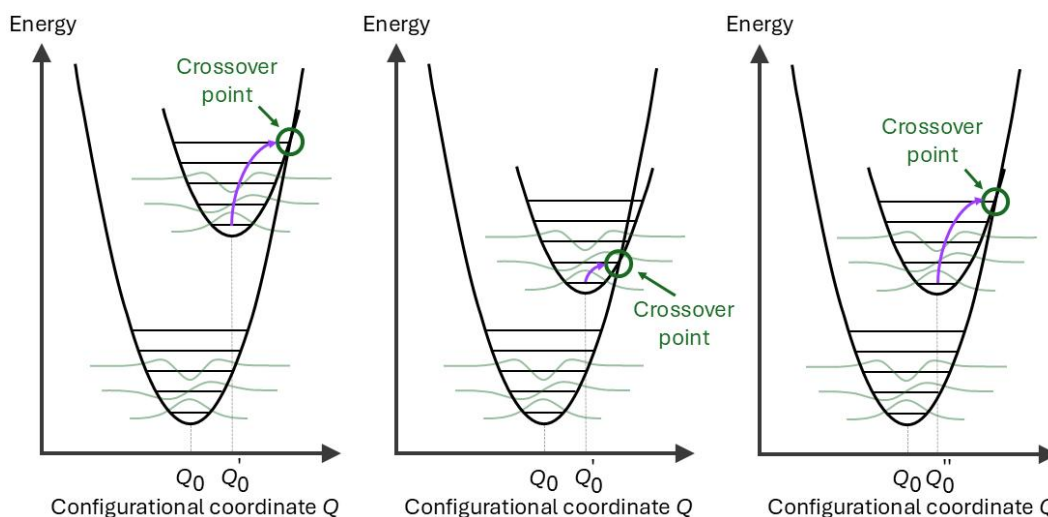


**Figure 2.5** | Configurational coordinate diagrams of a typical broad-band emitter (left) and a narrow-band emitter (right). The vertical blue arrows depict an excitation from the vibrational ground level of the electronic ground state into different vibrational levels of the excited state, followed by a fast non-radiative relaxation into the vibrational ground level of the excited state. The hypothetical absorption and emission spectra are shown, and the vibrational fine structure is indicated. Illustration created according to the literature.<sup>[48,49]</sup>

correlates with the offset of the equilibrium geometries of the ground state and the excited state.<sup>[48]</sup> This offset is a consequence of changes in the nature of the activator–ligand bond due to a reorganization of electron density in the excitation process that may affect the nature of the chemical bond (making it either more bonding or antibonding).<sup>[50,51]</sup> Naturally, interconfigurational transitions (e.g. f–d or s–p transitions) with a change in the type of orbitals naturally cause a stronger reorganization of electron density and thus, result in Stokes shifted broad-band emission compared to intraconfigurational transitions (e.g. f–f transitions) that rather rely on a rotation of charge density and barely affect the nature of the chemical bond in many cases. It is therefore a successful strategy to incorporate emitters with intrinsically broad, interconfigurational transitions (e.g.  $\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Mn}^{2+}$ ) into hosts with condensed, mechanically rigid structures that structurally restrain any change in the metal–ligand distance. Famous luminescent materials that follow this strategy are  $\text{Eu}^{2+}$ -activated oxido- or nitridosilicates with  $\text{UCr}_4\text{C}_4$ -derived structure, such as  $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ <sup>[30]</sup>,  $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]:\text{Eu}^{2+}$ <sup>[52]</sup>,  $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2:\text{Eu}^{2+}$ <sup>[53,54]</sup>, and  $\text{K}_{1.6}\text{Na}_{2.1}\text{Li}_{0.3}[\text{Li}_3\text{SiO}_4]_4:\text{Eu}^{2+}$ <sup>[55,56]</sup>.<sup>[57,58]</sup>

### 2.2.5 Thermal quenching

The efficiency of any pc-LED is fundamentally determined by the control over the non-radiative relaxation from the excited state to the ground state of the incorporated activators in the inorganic conversion-phosphors. In the case of broad-band emitters, this process can be thermally activated and leads to so-called *thermal quenching*. This is particularly decisive in the context of an application in pc-LEDs as their working temperatures can usually reach 150 °C. There are several known mechanisms leading to thermal quenching of phosphors: **Thermal crossover** is a consequence of a thermally driven population of higher vibronic levels within the excited state. With reference to the configurational coordinate diagram, the parabolas of the excited state and the

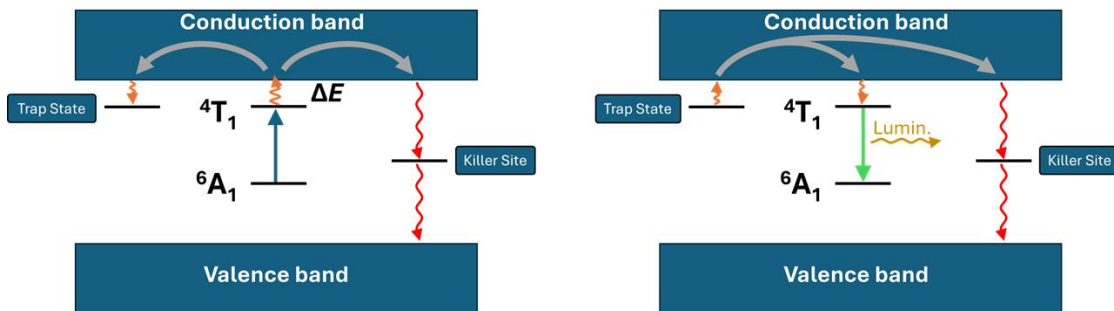


**Figure 2.6** | Correlation of crossover point, transition energy and configurational coordinate: Lower transition energies (middle) are associated with a lower crossover barrier, given equal vibrational energies and configurational coordinates (left). A smaller offset of the configurational coordinates correlates with a higher crossover barrier (right; note that  $Q'_0 < Q_0$ ).

ground state may cross at a certain energy, referred to as *crossover point*. This crossing results in a non-radiative relaxation into the electronic ground state. Generally, thermal crossover quenching is particularly common for emitters with large configurational coordinate offset (broadband emitters) and becomes particularly problematic at ambient temperatures if the transition energy is low (red and NIR emitters) (see Figure 2.6).<sup>[59]</sup> Emitters with narrow bands (e.g. most trivalent lanthanides), on the other hand, are usually less prone to thermal quenching. The dominating quenching mechanism for those is **multiphonon relaxation**, which resembles a depopulation of the excited state by the emission of multiple lattice vibrations (phonons).<sup>[60]</sup> This process depends primarily on the interplay between the frequency of lattice vibrations of the host compound and the energy gap of the involved states.

Another major quenching mechanism is **thermally assisted photoionization** into the conduction band, which is primarily observed for oxidation-labile emitters like  $\text{Eu}^{2+}$ ,  $\text{Ce}^{3+}$  or  $\text{Mn}^{2+}$ .<sup>[61–63]</sup> It occurs when sufficient thermal energy is available to promote an electron from an excited state into the conduction band. Once there, energy migration to defective sites or other electron-accepting impurities may occur, which can ultimately lead to quenching (see Figure 2.7).<sup>[63]</sup> A possible strategy to avoid quenching by thermally assisted photoionization is the usage of host compounds with wide band gaps ( $E_g > 5$  eV).

It can be challenging to differentiate between thermally activated photoionization and thermal crossover. However, thermoluminescence measurements are a valuable tool in this regard.<sup>[62,63]</sup> Thermoluminescence occurs when a material emits light as a result of the release of energy stored in trap states by thermal heating.<sup>[48]</sup> Those trap states are typically filled by electrons that were previously excited into the band gap, which is the case with thermally activated photoionization, but not with thermal crossover. Thermoluminescence measurements are typically started by heating the sample to a temperature much higher than the thermal quenching temperature to thermally empty the trap states. It is irradiated for several minutes with a wavelength that matches an



**Figure 2.7** | Schematic depiction of thermally assisted photoionization (left) and thermoluminescence (right).  $6A_1$  and  $4T_1$  represent the electronic ground state and lowest excited state of  $Mn^{2+}$ , which is a typical example for an emitter liable for thermally activated photoionization. Figure adapted according to the literature.<sup>[63]</sup>

excitation band of the emitter ion, and rapidly cooled afterwards. The sample is then gradually heated while the emission intensity is recorded over a broad spectral range. The emission intensity reaches its maximum value when there is enough thermal energy to empty the traps. A coincidence of this de-trapping temperature and the thermal quenching temperature is a strong indication for thermally activated photoionization as quenching mechanism.<sup>[62,63]</sup>

### 2.2.6 Radiative decay

The depopulation of an excited state is usually referred to as decay. It may involve two major pathways: **Radiative decay** (emission of a photon) and **non-radiative decay / quenching** (emission of phonons or non-radiative energy transfer to an impurity or defect). Non-radiative decay is usually unfavorable, as it reduces the efficiency of a phosphor. It can be promoted by many factors, e.g. small band gaps<sup>[61–63]</sup>, lattice defects<sup>[64,65]</sup>, impurities<sup>[65,66]</sup> or presence of functional groups with high vibrational energy (O–H, N–H, C–H, B–O, etc.) in the case of narrow-line emitters<sup>[67–69]</sup>. The radiative decay probability, on the other hand, is primarily determined by selection rules and the mechanism of the electronic transition. In general, the nature of radiative transitions might be categorized into **electric dipole transitions** (ED-type) and **magnetic dipole transitions** (MD-type), which refer to the component of the electromagnetic field of light that couples with the transition dipole moment of the respective emitter.<sup>[48]</sup> ED transitions involve a linear displacement of charge density, typically associated with a transition in a different kind of orbital, e.g.  $f \rightarrow d$  or  $s \rightarrow p$  transitions. MD transitions, on the other hand, involve a rotation of charge density, typically associated with a preservation of the occupied orbital type, e.g.  $f \rightarrow f$  or  $d \rightarrow d$  transitions.<sup>[49]</sup> Generally, ED-transitions are more likely by a factor of  $10^5$ .<sup>[49,70]</sup> This can also be observed experimentally in the decay times  $\tau$ , which are defined as:

$$\tau = \frac{1}{k_r + k_{nr}} \quad (2.1)$$

where  $k_r$  and  $k_{nr}$  are the radiative and non-radiative transition rate [ $s^{-1}$ ], respectively.<sup>[71]</sup> As a rule of thumb, ED-type transitions have radiative decay times in the order of several ns, whereas MD-type transitions typically exhibit decay times in the ms range.<sup>[71]</sup> However, it is important to notice, that the presence of heavy elements can cause a



significant deviation from this trend due to a magnetic coupling between the spinning electrons and the magnetic field caused by the orbital motion of the electrons around the atomic nucleus, referred to as *spin-orbit coupling*.<sup>[72]</sup> In that case, different energetically adjacent levels with similar total angular momentum  $J$ , but different total spins  $S$  and orbital angular momenta  $L$  may admix into each other thus complicating selection rules. A well-known example of this is the ED-type  $4f^6 5d^1 \leftrightarrow 4f^7$  transition of  $\text{Eu}^{2+}$  with a typical decay time in the  $\mu\text{s}$  range, due to an admixture of excited spin octet ( $S = 7/2$ ) and spin sextet ( $S = 5/2$ ) levels compared to the rather pure spin octet ground level  $^8S_{7/2}$ .

The rate at which spontaneous emission occurs can be described by the Einstein coefficient for spontaneous emission, given by:

$$A_{eg} = \frac{n \omega_0^3}{3\pi \hbar \varepsilon_0 c_0^3} |\mu|^2 = \frac{8\pi^2 n}{3\varepsilon_0 \hbar \lambda^3} |\langle \mu_{eg} \rangle|^2 \quad (2.2)$$

where  $n$  is the refractive index of the medium,  $\omega_0$  corresponds to the transition frequency of the system,  $|\langle \mu_{eg} \rangle|^2$  represents the transition dipole moment,  $c_0$  is the speed of light in a vacuum and  $\varepsilon_0$  is the vacuum permittivity.<sup>[48,49]</sup>  $A_{eg}$  is equal to the radiative rate constant if only spontaneous emission is assumed, following:

$$A_{eg} = k_{rad} = \frac{1}{\tau_{rad}} \quad (2.3)$$

Equations 2.2 and 2.3 show that, first: The spontaneous transition rate is proportional to  $|\langle \mu_{eg} \rangle|^2$ , which aligns with the spin selection rule, as the transition dipole moment of MD-type transitions is much smaller than for ED-type transitions.<sup>[48,70]</sup> In addition, a  $\lambda^3$ -dependence of the radiative decay times is readily indicated, which was also experimentally observed on the  $4f^n \leftrightarrow 4f^{n-1} 5d^1$  transitions of  $\text{Ce}^{3+}$  and  $\text{Pr}^{3+}$ .<sup>[73,74]</sup> This increase of the radiative decay times at longer emission wavelengths poses a particular challenge in the development of efficient NIR phosphors, as the non-radiative channel becomes proportionally more important.

Overall, a short radiative decay time is favorable for most applications as it is often accompanied by high absorption cross sections of the respective transition and minimizes the risks of saturation at high pump powers and non-radiative decay.

## 2.3 Mn<sup>2+</sup> as activator ion

The previous section gave an overview of the key features that conversion phosphors should fulfill for a potential application in pc-wLEDs for indoor lighting and LCD back-lighting. With those in mind, the luminescence features of  $\text{Mn}^{2+}$  and possible optimization strategies can be investigated more closely. Therefore, the following section will first impart a fundamental understanding of the transitions of  $\text{Mn}^{2+}$  as a free ion and in a crystalline host. Subsequently, key factors of the emission properties will be highlighted and guidelines for the optimization of  $\text{Mn}^{2+}$  for a potential application in pc-wLEDs will be derived.

### 2.3.1 The free $\text{Mn}^{2+}$ ion

Any electron in a microscopic system (e.g. an activator ion) can be described by a unique set of four quantum numbers:

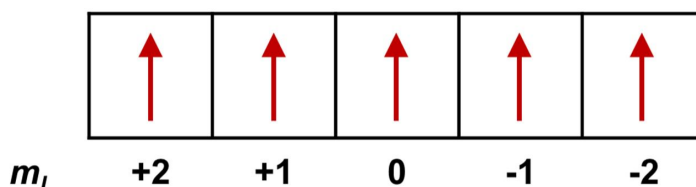
- Principal quantum number  $n$
- Orbital angular momentum quantum number  $l$
- Magnetic quantum number  $m_l$
- Spin magnetic quantum number  $m_s$

No two electrons are allowed to share the same values for all four quantum numbers (*Pauli exclusion principle*). In chemistry, the electronic configuration of an ion is conveniently denoted by  $n, l$  (indicated by the letters s, p, d, f, ... according to its values 0, 1, 2, 3, ...) and the number of electrons in superscript. For example: The  $\text{Mn}^{2+}$  ion has an  $[\text{Ar}]3d^5$  electron configuration, with five valence electrons that share the same values for  $n = 3$  and  $l = 2$ . By that means, all electrons within this configuration have to differentiate by a unique combination of  $m_l$  and  $m_s$ . Thereby,  $m_l$  can take any value between  $-l, -l+1, \dots, l-1, l$  and  $m_s$  can take the values  $-1/2$  and  $+1/2$ , resulting in 252 possible ways to arrange the electrons in the five degenerated 3d orbitals.<sup>[75]</sup> However, not all of those arrangements of electrons are equally favorable as the negatively charged electrons are subject to (direct) Coulomb repulsion and exchange interactions. These two interactions lead to the formation of *terms*. The energetically lowest term is referred to as ground term and can be determined using *Hund's rules*:

$$S = \max \sum_i m_{s,i} \quad (2.4)$$

$$L = \max \sum_i m_{l,i} \quad (2.5)$$

where  $S$  and  $L$  are the total spin and angular magnetic momentum of all electrons in a given configuration. Conventionally, capital letters are used for variables that describe multiple electrons. The energy levels are labeled by *Russell-Saunders term symbols* with the general notation  $^{2S+1}L$  where  $2S+1$  is the spin multiplicity (number of degenerated states with the same  $S$ , but different  $M_s$ ).  $L$  is denoted by the letters S, P, D, ... in analogy to s, p, d, ... for  $l$ . The ground state configuration of  $\text{Mn}^{2+}$  may be depicted by the following box scheme:



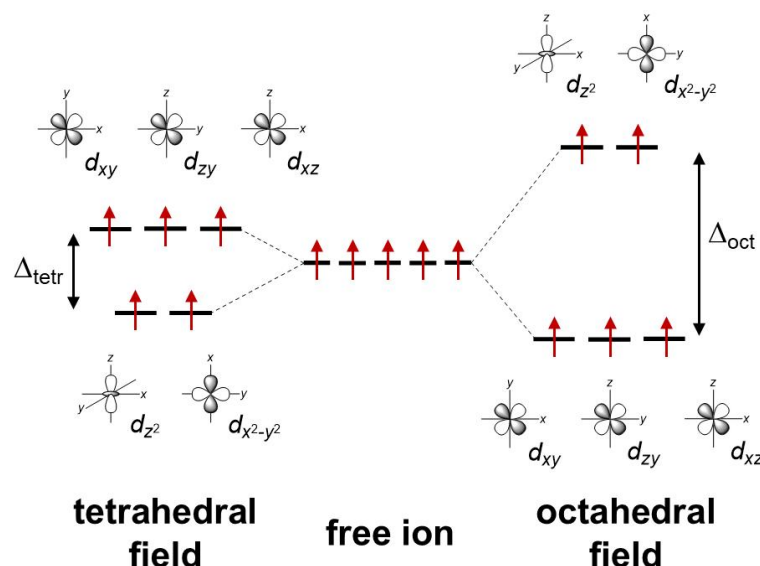
**Figure 2.8** | Box scheme for the occupation of the five 3d orbitals by five electrons in the electronic groundstate of  $\text{Mn}^{2+}$ . Each box represents one d-orbital. The arrows shall visualize the occupation of each orbital with electrons and their spin.

According to Hund's rules,  $S$  is maximized first to  $S = 5/2$  and therefore,  $2S+1 = 6$ .  $L$

equals zero as the values for  $m_l$  lead to a  $M_{L\max} = 0 = L$ . It follows a  ${}^6S$  ground term for the free Mn<sup>2+</sup> ion.

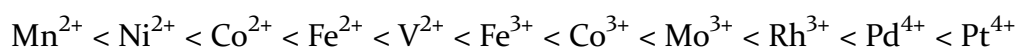
### 2.3.2 Crystal field splitting

Activator ions are typically incorporated into crystalline host compounds, where they are subject to rich interactions with their nearest neighbors, called ligands. In a purely



**Figure 2.9** | Crystal field splitting scheme for Mn<sup>2+</sup> in a tetrahedral and octahedral field. The splitting in a tetrahedral field is 4/9 of the value in an octahedral field. The shape and orientation of the d orbitals is depicted. Adapted according to the literature.<sup>[76]</sup>

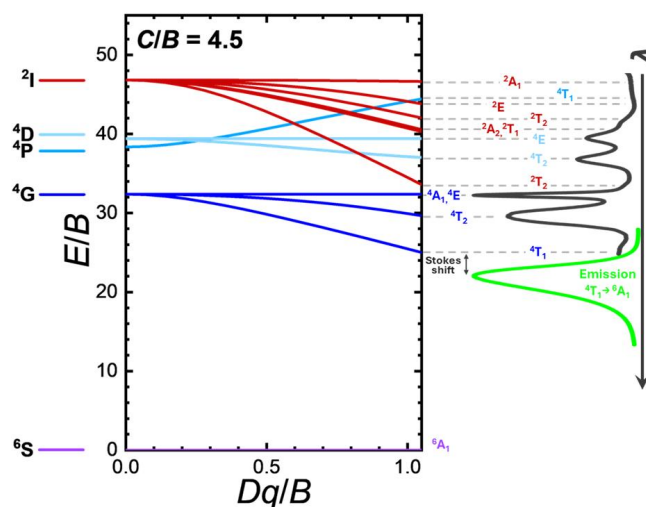
ionic model, the mutual repulsion of negatively charged electrons of the activator ion and the ligands increases the energy of those orbitals in close proximity to the ligand. The shape and orientation of the d orbitals in a Cartesian coordinate system is depicted in Figure 2.9. It can be seen that the  $z^2$  and  $x^2-y^2$  orbitals are oriented along the three axes, which is particularly unfavorable in an octahedral crystal field, as they point directly towards the ligands. The  $xy$ ,  $yz$  and  $xz$  orbitals, on the other hand, lie in between the axes, which is advantageous in octahedral coordination. Those two sets of orbitals are referred to as  $t_{2g}$  and  $e_g$  levels (the subscript "g" indicates the parity and is only added in centrosymmetric crystal fields) and the energy gap between both levels is called crystal field splitting  $\Delta$  or  $10Dq$ . Their sequence is reversed in tetrahedral and cubic crystal fields, due to a reduced interference of the  $z^2$  and  $x^2-y^2$  orbitals with the ligands, which also reduces the overall crystal field splitting, so that  $\Delta_{\text{tetr}} = 4/9 \Delta_{\text{oct}}$  and  $\Delta_{\text{cub}} = 8/9 \Delta_{\text{oct}}$ . However, the actual magnitude of the crystal field splitting is not only governed by the symmetry, but also by the distance and nature of both the ligands and the activator ion. It can be estimated from so-called *spectrochemical series*, in which ligands and metal ions are ordered with increasing associated crystal field strength.<sup>[77]</sup>



Herein, highly charged metal ions and ligands are usually associated with a strong crystal field splitting. Crystal field splitting gives rise to several new energy levels, that originate from the free-ions states. Those crystal field levels are conventionally labeled with *Mulliken-Herzberg* symbols  $^{2S+1}\Gamma_i$ .  $\Gamma$  is a symmetry-specific representation with a degeneracy  $g$  (given as A or B for  $g = 1$ , E for  $g = 2$  and T for  $g = 3$ ).

### 2.3.3 Interelectronic repulsion and covalency

We established a purely electrostatic model for the description of the crystal field splitting in the previous subsection, which provides a good qualitative estimate for the number of crystal field states as well as the overall energy separation of the  $e_g$  and  $t_{2g}$ -type orbitals. However, crystal field splitting alone is not sufficient to explain the experimentally observed transition energies of transition metal ions, which can be derived from absorption spectra. The interelectronic repulsion has to be taken into account as well, which is expressed by the interelectronic *Racah repulsion parameters*  $A$ ,  $B$  and  $C$ .<sup>[72]</sup>  $A$  accounts for a constant average interelectronic repulsion and contributes equally to all energy levels. In spectroscopy, however, the relative distance of electronic levels is of greater interest, so that  $A$  is usually ignored.  $B$  and  $C$ , on the other hand, represent the repulsion of the individual d electrons. Their value is highest for a free ion and decreases, if electron density shifts away from the metal ion, e.g. by a covalent bond (this is known as *nephelauxetic effect*). By those means, the Racah parameters  $B$  and  $C$  account for a covalent contribution to the metal–ligand interaction. The combined



**Figure 2.10** | Simplified Tanabe-Sugano diagram of a  $d^5$  configured transition metal ion with a  $C/B$  ratio of 4.5. The excitation (grey) and emission spectrum (green) of  $MgAl_2O_4:Mn^{2+}$  is shown as an example for tetrahedrally coordinated  $Mn^{2+}$  with a  $Dq/B$  ratio of approx. 1.1. Horizontal lines in the Tanabe-Sugano diagram represent crystal field independent transitions and give narrow excitation bands. An extended version of this diagram that also covers greater  $Dq/B$  ratios is given in Chapter 4.

effects of crystal field splitting and interelectronic repulsion / covalency on the energy levels of an octahedrally coordinated transition metal ion were originally calculated by Yukito Tanabe and Satoru Sugano in 1954.<sup>[78,79]</sup> The results are visualized in so-called *Tanabe-Sugano diagrams*, in which the energy  $E$  of a state is plotted against the ratio between the crystal field splitting  $Dq$  and interelectronic Racah repulsion  $B$  given a fixed  $C/B$  ratio, for which the diagram holds. Tanabe-Sugano diagrams can be set up for any

possible  $C/B$  ratio, but it is most common to assume  $C/B = 4.5$ , which is a valid approximation for many 3d elements.<sup>[75]</sup> They were originally designed for octahedrally coordinated ions, but can also be used for tetrahedrally and cubically coordinated  $d^{10-n}$  ions by means of the electron-hole analogy. The left hand side of the diagram gives the states of a free ion. Those states split in the presence of a crystal field ( $Dq/B \neq 0$ ) into crystal field states. The slope of the individual lines in the Tanabe-Sugano diagram reflects the nature of the electronic transition: Transitions characterized by a spin inversion within one and the same orbital (commonly referred to as "spin-flip transitions") are independent of the crystal field strength, which results in horizontal lines and narrow spectral bands. Sloping lines, on the other hand, represent transitions in which electrons are transferred between the  $t_{2g}$ - and  $e_g$ -type orbitals. Those transitions are connected to a change in the nature of the chemical bond and thus, result in broad spectral bands. The qualitative correlation between the slope of a line in the Tanabe-Sugano diagram and spectral bandwidth is depicted in Figure 2.10.

### 2.3.4 Selection rules

The probability of electronic transitions is governed by so-called selection rules. Two of those are particularly important for transition metal ions: The *spin selection rule* and the *Laporte selection rule*.<sup>[80]</sup> The spin selection rule states that transitions between states with equal spin multiplicity are much more likely to occur. This rule is often relieved for heavier activators by means of spin-orbit coupling. The  $3d^5$  high-spin configured transition metal ion  $\text{Mn}^{2+}$  is a special case in this regard, as any possible electronic transition from or to the  ${}^6A_1$  ground state is formally spin-forbidden. This is also experimentally observed by an overall small absorption cross section and considerably long radiative decay times in the order of several milliseconds. The Laporte selection rule, on the other hand, only applies to environments with inversion symmetry, but is essentially a more specific symmetry selection rule for ED-type transitions. It states that the probability of a transition is low if the parity of the involved states does not change. This affects all d–d transitions, due to the strictly *gerade* parity of the involved d orbitals given their even  $l = 2$  orbital angular momentum quantum number. As a result, the radiative decay times of  $\text{Mn}^{2+}$  in octahedral or cubic coordination are typically in the range of 50–200 ms<sup>[81,82]</sup>, whereas for tetrahedrally coordinated  $\text{Mn}^{2+}$  (with no inversion center), shorter radiative decay times of 1–10 ms<sup>[83,84]</sup> are much more common.

## 2.4 Optimization strategies for $\text{Mn}^{2+}$ -activated phosphors

Based on the fundamental electronic properties of  $\text{Mn}^{2+}$  in a ligand field, the following section combines these properties with the previously alluded requirements for the application in pc-LEDs and LCD displays and is dedicated to offering guidelines for the design of successful  $\text{Mn}^{2+}$ -activated phosphors in general. Advantages and remaining challenges of the respective strategies will be emphasized.

### Degree of condensation and structural rigidity

The term "condensation" refers to the ratio of network building cations to anions.<sup>[85]</sup> Generally, a high degree of condensation  $\kappa$  goes in hand with an in-

creased coordination number of the respective anions, which results in more cross-connections within the anionic framework and, ultimately, in an increased structural rigidity. This structural rigidity is usually associated with a mechanically limited offset in the configurational coordinates between ground state and excited state, resulting in narrower emission bandwidths and inhibition of crossover processes (see Sections 2.2.4 and 2.2.5). This optimization strategy is particularly well established for *REE*-activated phosphors, giving rise to several narrow-band emitting and thermally stable materials including garnets<sup>[21]</sup>, (oxo)-nitridoberyllates<sup>[86–89]</sup> and nitrides<sup>[27,28,90,91]</sup>. A particularly promising

**Table 2.1** | Correlation of the cation/anion ratio with the coordination number of the anion for some binary nitrides.

| Compound                         | Si <sub>3</sub> N <sub>4</sub> | AlN | Mg <sub>3</sub> N <sub>2</sub> | Li <sub>3</sub> N |
|----------------------------------|--------------------------------|-----|--------------------------------|-------------------|
| Degree of condensation $\kappa$  | 0.75                           | 1   | 1.5                            | 3                 |
| Coordination number of the anion | 3                              | 4   | 6                              | 8                 |

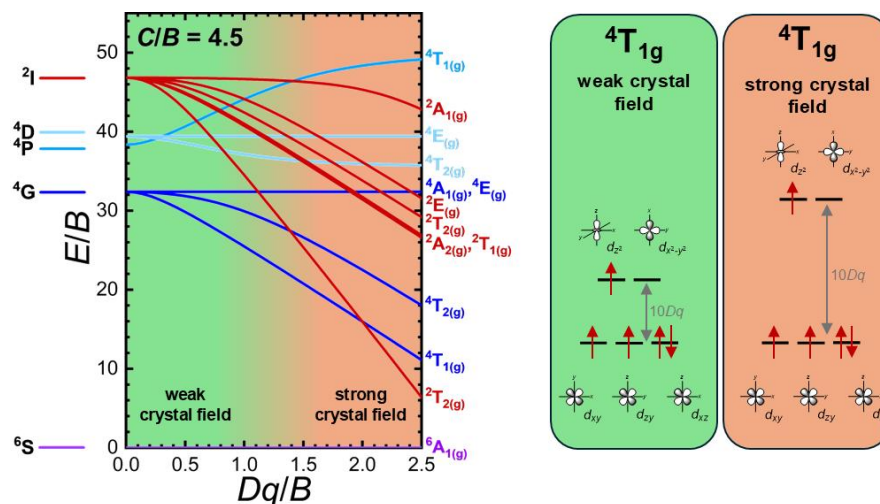
class of highly condensed Eu<sup>2+</sup>-activated compounds are (ultra-)narrow emitting UC<sub>4</sub>C<sub>4</sub>-type nitrides and oxidosilicates/ -aluminates, which attracted much attention within the last decade (see Chapter 4). However, the same fundamental principles were successfully employed for Mn<sup>2+</sup>-activated phosphors. Examples for highly condensed Mn<sup>2+</sup>-activated phosphors with narrow emission bandwidths include aluminates like BaZnAl<sub>10</sub>O<sub>17</sub>:Mn<sup>2+</sup> ( $\lambda_{\text{em}} = 516 \text{ nm}$  / FWHM = 1170 cm<sup>-1</sup>)<sup>[92]</sup>, borates like sodalite-type Zn<sub>4</sub>B<sub>6</sub>O<sub>13</sub>:Mn<sup>2+</sup> ( $\lambda_{\text{em}} = 540 \text{ nm}$  / FWHM = 1100 cm<sup>-1</sup>)<sup>[93]</sup>, nitrides like wurtzite-type AlN:Mn<sup>2+</sup> ( $\lambda_{\text{em}} = 600 \text{ nm}$  / FWHM = 1220 cm<sup>-1</sup>)<sup>[94]</sup> or sulfides like Ba<sub>2</sub>ZnS<sub>3</sub>:Mn<sup>2+</sup> ( $\lambda_{\text{em}} = 611 \text{ nm}$  / FWHM = 1350 cm<sup>-1</sup>)<sup>[95,96]</sup>. This optimization strategy was pursued in the design of Mn<sup>2+</sup>-activated alkali lithooxidosilicate phosphors with UC<sub>4</sub>C<sub>4</sub>-related structure within the scope of this thesis (see Chapter 4).<sup>[97]</sup>

### Crystal field splitting

The energy levels of most excited states of Mn<sup>2+</sup> are highly dependent on the surrounding crystal field, due to the spatially extended nature of the involved d orbitals (see Section 2.3.2). For emitters for pc-LEDs, however, usually the energy difference between the lowest excited state (<sup>4</sup>T<sub>lg</sub>) and the ground state (<sup>6</sup>A<sub>lg</sub>) is most important, as it determines the emission wavelength of a compound. This energy gap decreases if Mn<sup>2+</sup> is embedded into stronger crystal fields, due to a stabilization of the excited <sup>4</sup>T<sub>lg</sub> state. As a result, Mn<sup>2+</sup> shows a red-shifted emission in strong crystal fields, or, alternatively, hosts with strongly covalent Mn–ligand bonds and thus, reduced Racah parameters (see below), which is also indicated by the corresponding Tanabe-Sugano diagram (Figure 2.11). It is thus, a common strategy to tune the emission color of Mn<sup>2+</sup>-activated phosphors from green to red *via* a transition from tetrahedral to octahedral coordination.<sup>[98]</sup> Other coordination geometries, on the other hand, are comparably rare in literature.<sup>[99]</sup> However, less symmetric activation sites can potentially lift the orbital triple degeneracy of the lowest excited state (<sup>4</sup>T<sub>lg</sub>) and thus,



induce an additional red-shift of the luminescence. This is best known from  $\text{Mn}^{2+}$ -activated pyrophosphates  $\text{ABP}_2\text{O}_7$  ( $A = \text{Sr}, \text{Ba}$ ;  $B = \text{Mg}, \text{Zn}$ ) with  $\text{Mn}^{2+}$  in square-planar (bi-)pyramidal coordination<sup>[99,100]</sup> and hexagonal  $\text{CsNiCl}_3$ -type halides  $\text{CsCdX}_3$  ( $X = \text{Cl}, \text{Br}$ ) with trigonally distorted  $[\text{CdX}_6]^{4-}$  octahedra.<sup>[101–103]</sup>



**Figure 2.11** |  $d^5$  Tanabe-Sugano diagram (left) and one possible electronic configuration within the triply orbitally degenerated  ${}^4\text{T}_{1g}$  state, depicted for two octahedrally coordinated ions in crystal fields of varying strength. The wider gap between the  $e_g$  and  $t_{2g}$  levels in a strong crystal field stabilizes the lowest excited state  ${}^4\text{T}_{1g}$ , thereby causing a red shift of the emission.

Noticeably, most lines in the Tanabe-Sugano diagram show a considerably lower slope at small  $Dq/B$ , which readily indicates a lower crystal field-dependence of the excited states in weak crystal fields. Consequently, narrower emission bandwidths are expected in that regime. This is also experimentally observed, as tetrahedrally coordinated  $\text{Mn}^{2+}$  generally shows smaller FWHMs and higher energies of the emission bands than octahedrally coordinated  $\text{Mn}^{2+}$  with a given type of ligands due to the different crystal field strength.<sup>[63,83]</sup>

In the context of this thesis, both strategies for crystal field optimization were demonstrated: Chapter 4 covers a series of narrow-band green emitting phosphors and broad-band red-emitting phosphors comprising  $\text{Mn}^{2+}$  in weak tetrahedral and strong cubic crystal fields.<sup>[97]</sup> Chapter 5 presents the first near-infrared emitting  $\text{Mn}^{2+}$ -activated phosphors, in which  $\text{Mn}^{2+}$  occupies a highly distorted [5+1] coordinated lattice site<sup>[104,105]</sup> within a series of compounds with boracite-type structure.<sup>[106]</sup>

### 💡 Covalency of the metal–ligand interaction

The energy of the states in the Tanabe-Sugano diagram is not only dependent on the crystal field splitting  $Dq$  but also on the Racah parameter  $B$ , which essentially parametrizes the degree of electron density localization within a Mn–ligand bond. The highest value for  $B$  is observed in the free ion, while any chemical bond will reduce  $B$  due to a delocalization of electron density between the emitter ion and the ligand, ultimately leading to a red-shifted emission (see Section 2.3.3). This effect is particularly prominent in host compounds with rather covalent metal–ligand bonds, like nitrides

or sulfides. Examples of such  $\text{Mn}^{2+}$ -activated phosphors comprise  $\text{AlN}:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 600 \text{ nm}$  /  $\text{FWHM} = 1220 \text{ cm}^{-1}$ )<sup>[94]</sup>,  $\text{ZnGeN}_2:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 610 \text{ nm}$  /  $\text{FWHM} = 1320 \text{ cm}^{-1}$ )<sup>[107]</sup>,  $\text{Ba}_2\text{ZnS}_3:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 611 \text{ nm}$  /  $\text{FWHM} = 1350 \text{ cm}^{-1}$ )<sup>[95,96]</sup>, or  $\alpha\text{-ZnS}:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 580 \text{ nm}$  /  $\text{FWHM} = 1570 \text{ cm}^{-1}$ )<sup>[63,108]</sup>, which show an orange-red emission from  $\text{Mn}^{2+}$ , despite tetrahedral weak-field coordination. The opposite effect is observed in highly ionic compounds such as  $\text{CaF}_2:\text{Mn}^{2+}$ , that even shows emission in the cyan spectral range  $\lambda_{\text{em}} = 495 \text{ nm}$ <sup>[81,109]</sup> despite cubic coordination of the incorporated  $\text{Mn}^{2+}$  ions. The potential of a careful optimization of the crystal field covalency in phosphor design is demonstrated in Chapter 3, using the example of borosulfates of the solid solution  $\text{Zn}_{1-x}\text{Mn}_x[\text{B}_2(\text{SO}_4)_4]$  ( $x = 0, 0.03, 0.04, 0.05, 0.1$ ) with particularly ionic Mn–O interactions.<sup>[110]</sup>

The band gap of the host is another important aspect in phosphor design that correlates with the covalency of the chemical bonds within a given host compound. As a rule of thumb, larger band gaps are observed for ionic compounds with highly polar ligands (e.g. oxides or fluorides), whereas softer ligands (e.g. nitride, sulfide, iodide) induce smaller band gaps.<sup>[63,111]</sup> This is particularly important for  $\text{Mn}^{2+}$  as larger band gaps are usually associated with lower liability to thermal quenching *via* thermally assisted photoionization (see Section 2.2.5).<sup>[63,112]</sup> This concept is explicitly demonstrated in Chapter 5 for a series of compounds with a boracite-type structure, comprising an ultra-wide band gap and low thermal quenching.<sup>[106]</sup>



### Co-activation with sensitizer ions

A common strategy to overcome the small absorption cross section of the spin- and parity-forbidden d–d transitions of  $\text{Mn}^{2+}$  (see Section 2.3.4) is by co-activation with sensitizer ions with electric dipole-allowed transitions. This has been extensively studied in the past and successfully applied in the so-called halophosphate phosphors ( $\text{Ca}_5(\text{PO}_4)_3\text{F}, \text{Cl}:\text{Sb}^{3+}, \text{Mn}^{2+}$ ) using an efficient  $\text{Sb}^{3+} \rightarrow \text{Mn}^{2+}$  energy transfer.<sup>[113–116]</sup> There are several other ions besides  $\text{Sb}^{3+}$  known to sensitize  $\text{Mn}^{2+}$ , e.g.  $\text{Sn}^{2+}$ <sup>[117,118]</sup>,  $\text{Pb}^{2+}$ <sup>[118–120]</sup>,  $\text{Sb}^{3+}$ <sup>[113]</sup>,  $\text{Bi}^{3+}$ <sup>[121]</sup> or excitons<sup>[122,123]</sup>. However, these sensitizers exhibit only weak absorption in the blue spectral range, which is unfavorable for a possible application in pc-wLEDs. It is therefore a widespread approach to use RE ions with allowed  $4f^n \rightarrow 4f^{n-1}5d^1$  transitions like  $\text{Ce}^{3+}$ <sup>[124,125]</sup> or  $\text{Eu}^{2+}$ <sup>[126,127]</sup> as sensitizers for  $\text{Mn}^{2+}$ , which frequently show strong absorption in the blue spectral range. However, the exact mechanisms of the sensitizer  $\rightarrow \text{Mn}^{2+}$  energy transfer are often not fully understood despite their use in numerous examples. A representative example in this regard may be the  $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$  energy transfer. Several authors proposed dipole–quadrupole interactions to be the sensitization mechanism based on concentration-dependent measurements.<sup>[128–132]</sup> However, a possible dipole–quadrupole interaction would suggest an  $r^{-8}$  distance dependence, which could not be found conclusively.<sup>[89,126,133]</sup> Recently, conclusive experimental evidence for a Dexter-type exchange interaction was given based on concentration-dependent, time resolved luminescence studies on  $\text{Ba}_2\text{MgSi}_2\text{O}_7: 3.5\% \text{Eu}^{2+}, x\% \text{Mn}^{2+}$  ( $x = 0 - 10$ ) and combination with a shell model of energy transfer.<sup>[89]</sup> The sensitization efficiency depends on several factors that have to be carefully optimized in phosphor design. First, donor–acceptor



distances should be as close as possible, considering the exponential distance dependence of the energy transfer rate  $k_{\text{ET}}$  of Dexter-type exchange interactions:<sup>[134]</sup>

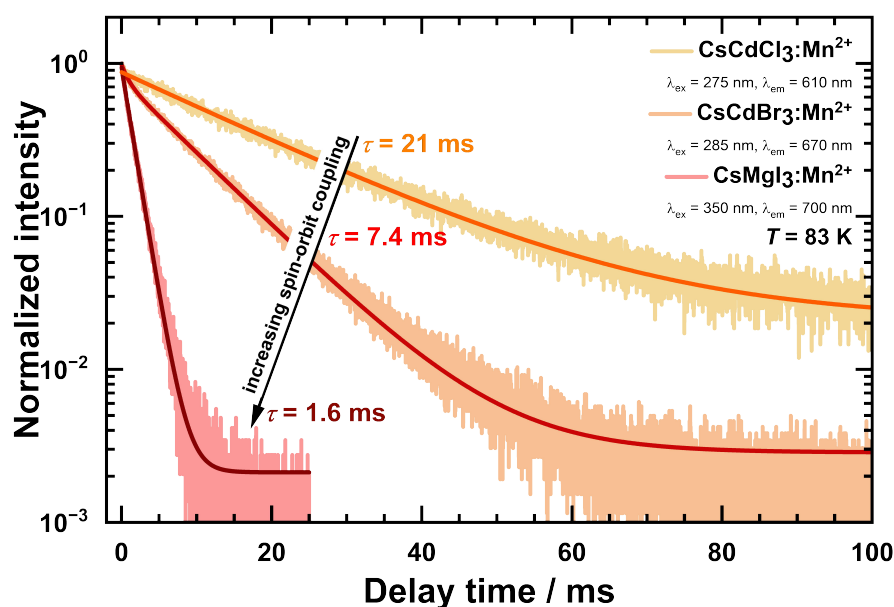
$$k_{\text{ET}} \propto \exp\left(\frac{-2r}{l}\right) \quad (2.6)$$

Here,  $r$  represents the average interelectronic separation and  $l$  is the average Bohr radius of the excited state of the sensitizer (such as Eu<sup>2+</sup>) and Mn<sup>2+</sup> in its <sup>6</sup>S ground term. Generally, Eu<sup>2+</sup>–Mn<sup>2+</sup> distances below 5 Å are recommended to realize an efficient energy transfer.<sup>[89]</sup> In addition, the emission of the sensitizer should overlap with the absorption bands of Mn<sup>2+</sup> ("resonance condition").<sup>[72]</sup> One consequence of this is a large offset between the excitation radiation and the Mn<sup>2+</sup> emission, which essentially represents the accumulated Stokes shift of both the sensitizer and the Mn<sup>2+</sup> ion. This makes sensitization for green-emitting, blue-excitable Mn<sup>2+</sup>-activated phosphors particularly challenging as extremely small Stokes shifts would be required from both the sensitizer and the Mn<sup>2+</sup> ion.

A fundamental issue of this optimization strategy is the occurrence of saturation effects at high excitation intensities.<sup>[135]</sup> This is especially the case for octahedrally coordinated Mn<sup>2+</sup>, which exhibits longer radiative decay times related to Laporte's parity selection rule.

### 💡 Spin-orbit coupling

Another possible strategy to improve the absorption cross section and simultaneously decrease radiative decay times of the <sup>4</sup>T<sub>1g</sub>(<sup>4</sup>G) state of Mn<sup>2+</sup> can be the introduction into host compounds with heavy, electron-rich ligands that mediate



**Figure 2.12** | Low-temperature photoluminescence decay curves of Mn<sup>2+</sup>-activated halides CsMX<sub>3</sub> ( $M = \text{Mg, Cd}$ ;  $X = \text{Cl, Br, I}$ ) with hexagonal perovskite structure, comprising octahedrally coordinated Mn<sup>2+</sup> ions. The amplitude-weighted decay times were extracted from single-exponential fit functions for CsCdCl<sub>3</sub>:Mn<sup>2+</sup> and CsMgI<sub>3</sub>:Mn<sup>2+</sup> and a bi-exponential fit function for CsCdBr<sub>3</sub>:Mn<sup>2+</sup>. A significant shortening of the decay times is observed depending on the type of ligand in the order Cl<sup>−</sup> → Br<sup>−</sup> → I<sup>−</sup>, due to an increasing spin-orbit coupling.

spin-orbit coupling and thereby weaken the spin-forbidden character of the intra-configurational d–d transitions. The composition dependent decay times of  $\text{Mn}^{2+}$ -activated halides  $\text{CsMX}_3$  ( $M = \text{Mg}, \text{Cd}$ ;  $X = \text{Cl}, \text{Br}, \text{I}$ ) with hexagonal perovskite structure may serve as an example here (Figure 2.12). The decay times at 83 K gradually decrease upon change of the ligand in the order  $\text{Cl}^- \rightarrow \text{Br}^- \rightarrow \text{I}^-$ , in line with the increasing extent of spin-orbit coupling. Comparable observations were also made for tetrahedrally coordinated  $\text{Mn}^{2+}$  in benzyl-1-trimethylammonium manganese(II) halides  $[\text{Bz}(\text{Me})_3\text{N}]\text{MnX}_4$  with  $X = \text{Cl}, \text{Br}, \text{I}$ , in which decay times of 3.79 ms, 0.34 ms and 0.045 ms were found for  $X = \text{Cl}^-, \text{Br}^-, \text{I}^-$ , respectively.<sup>[83]</sup> This aligns with observations from *Zinkblende*-type zinc chalcogenides ( $\text{ZnCh}$ ), where decay times of 1.77 ms, 0.3 ms and 0.045 ms were found for  $\text{Ch} = \text{S}^{2-}, \text{Se}^{2-}, \text{Te}^{2-}$  at 4.2 K, respectively.<sup>[108,136,137]</sup> However, heavy ligands are usually also associated with smaller band gaps and thus also increase the liability for quenching by thermally assisted photoionization, which can also shorten the decay times.<sup>[63]</sup> A clear distinction of both effects would require measurements of the temperature-dependent quantum yields. However, quenching by thermally activated photoionization should be rather weak at cryogenic temperatures, which is also indicated by the temperature dependency of the emission intensities as well as the temperature-dependent decay times of the aforementioned compounds.<sup>[138,139]</sup>

### Exchange interactions

Exchange interactions with paramagnetic neighboring ions (e.g.  $\text{Gd}^{3+}$  or  $\text{Mn}^{2+}$ ) were shown to be another potential tool to induce a partial release of the spin- and parity restriction and decrease the radiative decay times by about one order of magnitude. This effect was found to be comparatively weak for  $\text{Gd}^{3+}$ – $\text{Mn}^{2+}$  pairs ( $\tau = 24$  ms in  $\text{YF}_3$  vs.  $\tau = 22$  ms in  $\text{GdF}_3$ ,  $T = 298$  K), but stronger for  $\text{Mn}^{2+}$ – $\text{Mn}^{2+}$  pairs ( $\tau = 7.2$  ms in  $\text{MgAl}_2\text{O}_4$ : 0.2%  $\text{Mn}^{2+}$  vs.  $\tau = 4.2$  ms in  $\text{MgAl}_2\text{O}_4$ : 10%  $\text{Mn}^{2+}$ ,  $T = 298$  K).<sup>[84]</sup> Other host compounds showed an even stronger shortening of the radiative decay times due to the formation of exchange-coupled  $\text{Mn}^{2+}$ – $\text{Mn}^{2+}$  pairs, e.g.  $\tau = 15$  ms in  $\text{Zn}_2\text{SiO}_4$ : 0.05%  $\text{Mn}^{2+}$  vs.  $\tau = 1.75$  ms in  $\text{Zn}_2\text{SiO}_4$ : 12.5%  $\text{Mn}^{2+}$  ( $T = 300$  K), or  $\tau = 8.5$  ms in  $\text{CaS}$ : 0.1%  $\text{Mn}^{2+}$  vs.  $\tau = 0.55$  ms in  $\text{CaS}$ : 2%  $\text{Mn}^{2+}$  ( $T = 80$  K)<sup>[140]</sup>, most likely caused by shorter closest  $\text{Mn}^{2+}$ – $\text{Mn}^{2+}$  distances.<sup>[84]</sup>

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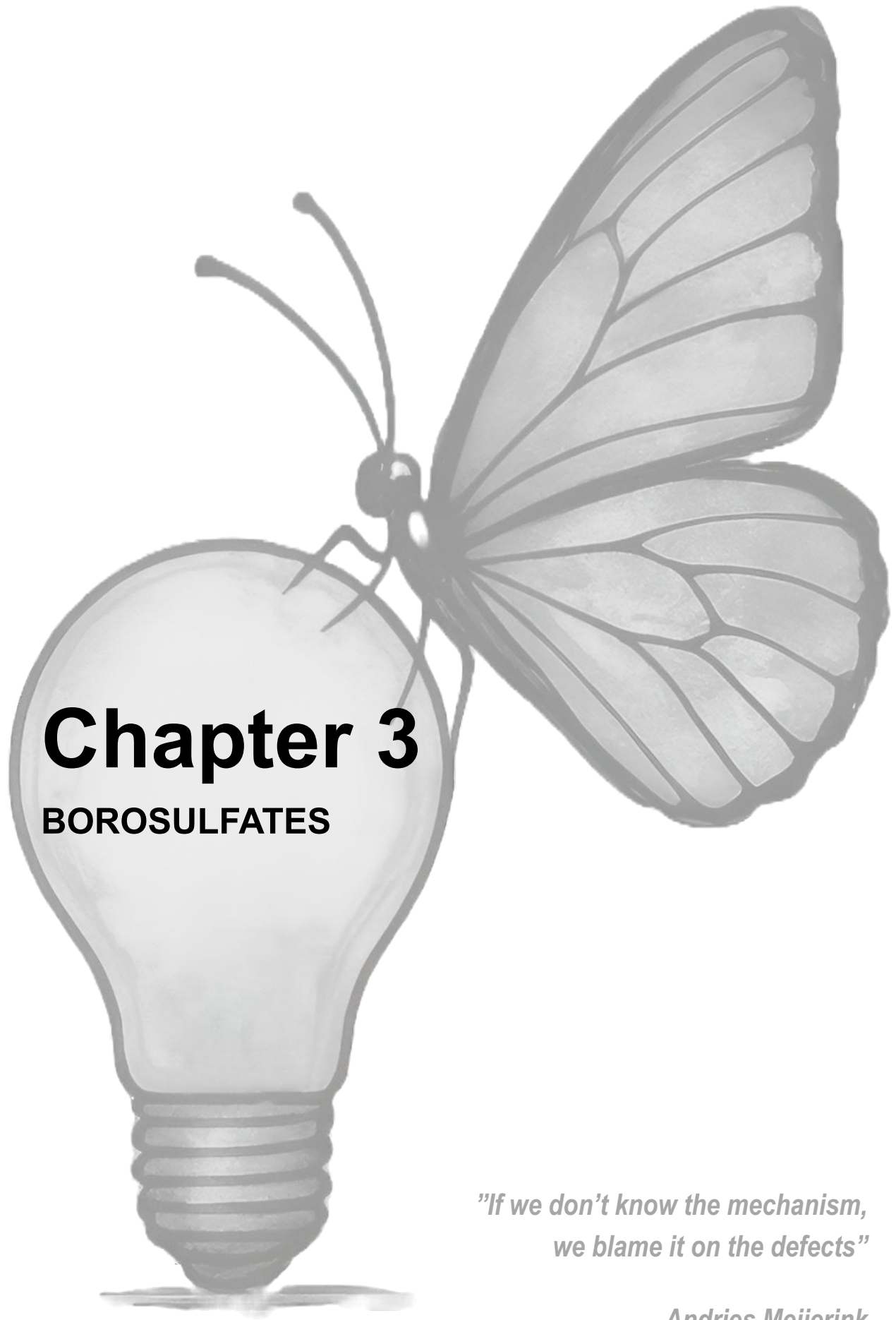
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# Chapter 3

## BOROSULFATES

*"If we don't know the mechanism,  
we blame it on the defects"*

*—Andries Meijerink*

**Photoluminescence of  $\text{Mn}^{2+}$  in the Borosulfate  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] : \text{Mn}^{2+}$ —A Tool to Detect Weak Coordination Behavior of Ligands**

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**Author contributions:**

**L. M. Träger** reviewed the relevant literature, performed the photoluminescence measurements, evaluated and visualized the spectroscopic data, performed the calculations and wrote the major part of the manuscript. He also prepared the table of contents graphic and the German translation of the manuscript. **L. C. Pasqualini** synthesized the investigated compounds, checked the phase purity by X-ray powder diffraction and Rietveld refinement. He wrote the first paragraph of the "Results and Discussion" section and designed the cover picture. **J. Bruns, H. Huppertz** and **M. Suta** conceptualized the project, acquired funding and reviewed the manuscript. M. Suta supervised the whole project, assisted in the data interpretation and finalized the manuscript.

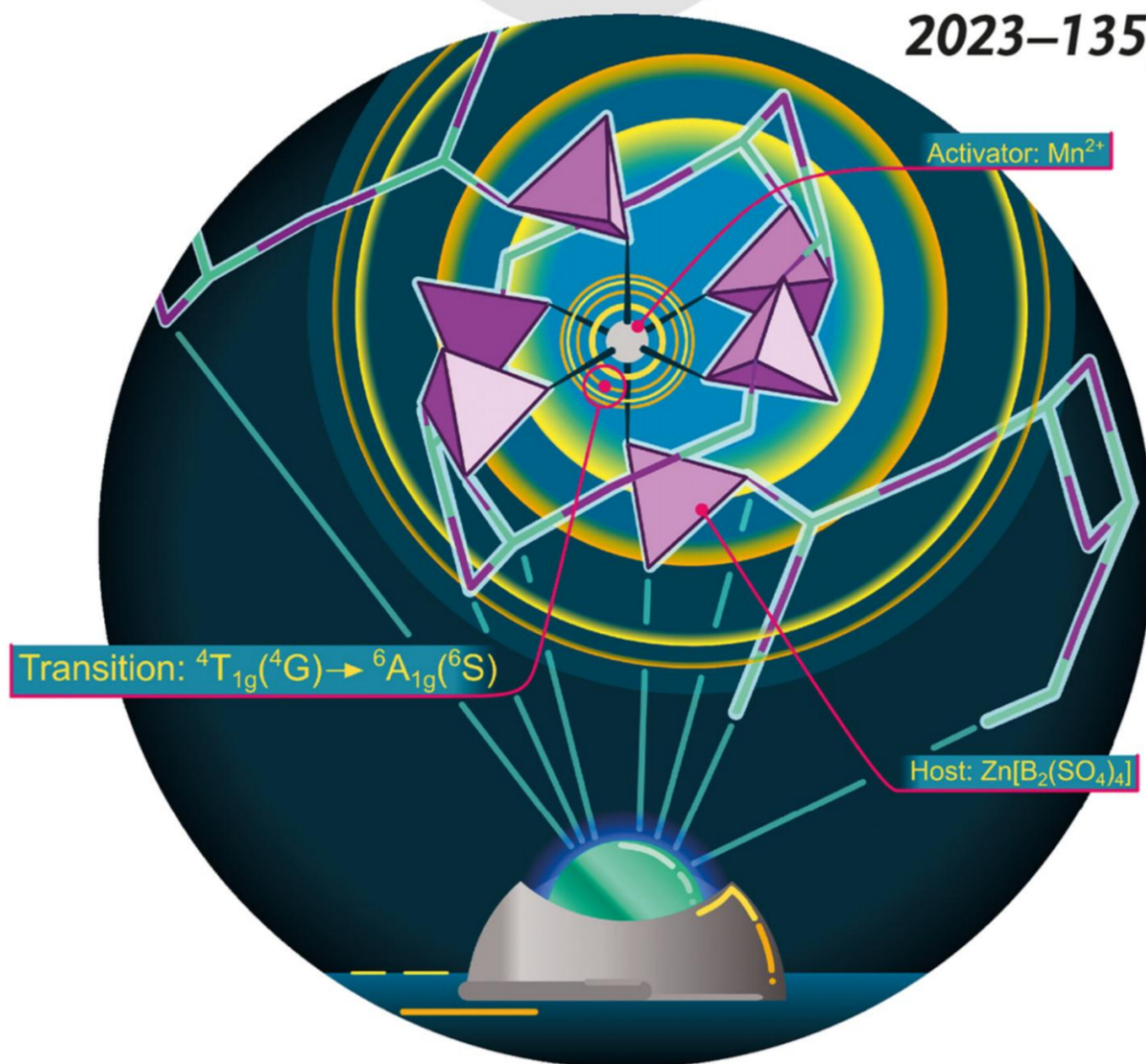
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## Titelbild

Jörn Bruns, Markus Suta et al.

Photoluminescence of  $\text{Mn}^{2+}$  in the Borosulfate  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ :  $\text{Mn}^{2+}$

- A Tool to Detect Weak Coordination Behavior of Ligands

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## Photoluminescence

**Photoluminescence of  $\text{Mn}^{2+}$  in the Borosulfate  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] : \text{Mn}^{2+}$  – A Tool to Detect Weak Coordination Behavior of Ligands**Lukas M. Träger<sup>+</sup>, Leonard C. Pasqualini<sup>+</sup>, Hubert Huppertz, Jörn Bruns,<sup>\*</sup> and Markus Suta<sup>\*</sup>

**Abstract:** The impact of the surrounding ligand field is successfully exploited in the case of  $\text{Eu}^{2+}$  to tune the emission characteristics of inorganic photoactive materials with potential application in, e.g., phosphor-converted white light-emitting diodes (pc-wLEDs). However, the photoluminescence of  $\text{Mn}^{2+}$  related to intraconfigurational  $3d^5-3d^5$  transitions is also strongly dependent on local ligand field effects and has been underestimated in this regard so far. In this work, we want to revive the idea how to electronically tune the emission color of a transition metal ion in inorganic hosts by unusual electronic effects in the metal-ligand bond. The concept is explicitly demonstrated for the weakly coordinating layer-like borosulfate ligand in the  $\text{Mn}^{2+}$ -containing solid solutions  $\text{Zn}_{1-x}\text{Mn}_x[\text{B}_2(\text{SO}_4)_4]$  ( $x = 0, 0.03, 0.04, 0.05, 0.10$ ).  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] : \text{Mn}^{2+}$  shows orange narrow-band luminescence at 590 nm, which is an unusually short wavelength for octahedrally coordinated  $\text{Mn}^{2+}$  and indicates an uncommonly weak ligand field. On the other hand, the analysis of the interelectronic Racah repulsion parameters reveals ionic Mn–O bonds with values close to the Racah parameters of the free  $\text{Mn}^{2+}$  ion. Overall, this strategy demonstrates that electronic control of the metal-ligand bond can be a tool to make  $\text{Mn}^{2+}$  a potent alternative emitter to  $\text{Eu}^{2+}$  for inorganic phosphors.

**Introduction**

In recent years, an overwhelming amount of new phosphor materials has emerged to meet versatile industrial and scientific requests. Most of these phosphors are  $\text{Ce}^{3+}$ - or  $\text{Eu}^{2+}$ -doped oxide or nitride-based ceramics, which show luminescence based on electric dipole-allowed  $4f^{N-1}5d^1 \rightarrow 4f^N$  transitions ( $N=1$  for  $\text{Ce}^{3+}$ ,  $N=7$  for  $\text{Eu}^{2+}$ ).<sup>[1–6]</sup> In order to meet the numerous requirements for applications in light-emitting devices and displays, the employed host compounds for these activator ions usually combine structural rigidity and high coordination number with high chemical and thermal resistance to induce desirable luminescence features

like narrow-band emission, high quenching temperatures and high quantum efficiency. Famous commercialized examples are  $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}^{3+}$  (YAG:  $\text{Ce}^{3+}$ ),<sup>[7]</sup>  $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ ,<sup>[8]</sup>  $\text{Sr}[\text{LiAl}_3\text{N}_4] : \text{Eu}^{2+}$  (SLA:  $\text{Eu}^{2+}$ )<sup>[9]</sup> and  $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2] : \text{Eu}^{2+}$  (SALON:  $\text{Eu}^{2+}$ ).<sup>[10]</sup> Besides those,  $\text{Eu}^{2+}$  activated  $\text{CaAlSiN}_3$ ,<sup>[11]</sup> alkali litho-oxidosilicates,<sup>[12–17]</sup> (oxo–)nitridoberyllates<sup>[18–21]</sup> and oxynitrides<sup>[22,23]</sup> have attracted attention due to their favorable luminescence characteristics. Despite the promising photoluminescence properties of  $\text{Eu}^{2+}$  for next-generation phosphor-converted white light-emitting diodes (pc-wLEDs), the more abundant transition metal ion  $\text{Mn}^{2+}$  could be a potential alternative in this field. Since the photoluminescence of  $\text{Mn}^{2+}$  relies on electronic transitions within the spatially less extended 3d subshell compared to the diffuse 5d orbitals of  $\text{Eu}^{2+}$ , narrower and more color-pure emission bands can generally be expected from  $\text{Mn}^{2+}$  if appropriately optimized. Moreover, given the spatially extended nature of the 3d orbitals, the emission color of  $\text{Mn}^{2+}$  can be as easily controlled by the coordination geometry and type of surrounding ligands as for  $\text{Eu}^{2+}$ . Tetrahedrally coordinated  $\text{Mn}^{2+}$  usually exhibits narrow-band green luminescence, e.g. in  $\text{MgAl}_2\text{O}_4 : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 525 \text{ nm}$ ),<sup>[24]</sup>  $\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 525 \text{ nm}$ ),<sup>[25,26]</sup>  $\text{ZnGa}_2\text{O}_4 : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 500 \text{ nm}$ ),<sup>[27]</sup>  $\text{BaZnAl}_{10}\text{O}_{17} : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 516 \text{ nm}$ ),<sup>[28]</sup>  $\text{LaMgAl}_{11}\text{O}_{19} : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 517 \text{ nm}$ ),<sup>[29]</sup>  $\text{Sr}_2\text{MgAl}_{22}\text{O}_{36} : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 518 \text{ nm}$ ),<sup>[30]</sup>  $\text{Zn}_4\text{B}_6\text{O}_{13} : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 540 \text{ nm}$ ).<sup>[31]</sup> In contrast, octahedrally coordinated  $\text{Mn}^{2+}$  typically shows red emission, e.g.  $\text{MgSiO}_3 : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 661 \text{ nm}$ ),<sup>[32]</sup>  $\text{Mg}_4\text{Ta}_2\text{O}_9 : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 659 \text{ nm}$ ),<sup>[26]</sup>  $\text{Ba}_2\text{M}(\text{BO}_3)_2 : \text{Mn}^{2+}$  ( $\text{M} = \text{Mg, Ca}$ ;  $\lambda_{\text{em}} = 615 \text{ nm, } 630 \text{ nm}$ ),<sup>[33,34]</sup>  $\text{NaZn}(\text{PO}_3)_3 : \text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 613 \text{ nm, } 643 \text{ nm}$ ).<sup>[35]</sup> This is related to a stronger ligand field splitting in an octahedral field and accompanied by larger emission bandwidths as well as generally lower quenching temperatures ( $T_{50}$ ).<sup>[36]</sup> The

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marked difference in the emission properties for tetrahedrally and octahedrally coordinated  $\text{Mn}^{2+}$  is understandable from the  $d^5$  Tanabe-Sugano diagram valid for both cases (see Figure 1). The lowest energetic excited ligand field state  ${}^4\text{T}_{1(g)}$  ( ${}^4\text{G}$ ) of a  $d^5$  ion decreases in energy relative to the ground state  ${}^6\text{A}_{1(g)}$  ( ${}^6\text{S}$ ) with increasing ligand field strength. The spin-forbidden nature of the optical transitions of  $\text{Mn}^{2+}$  in a  $3d^5$  high-spin configuration leads to a generally long emission decay time, which may pose problems to high-power pc-wLEDs based on saturation effects (*cf.* the related emitter  $\text{Mn}^{4+}$ ).<sup>[37]</sup> The decay time can be, however, shortened upon incorporation into hosts with heavier atoms due to enhanced spin-orbit coupling or upon exploitation of magnetic exchange interaction in Mn–Mn pairs.<sup>[39]</sup> Often is only an ionic picture of the crystal field interaction considered and its strength is generally enhanced by decreasing Mn–ligand distances as well as a transition from tetrahedral to octahedral coordination geometry. However, the impact of covalency and a decrease in the interelectronic repulsion parametrized by the Racah parameters  $B$  and  $C$  is as important and can also be used to tune the ligand field strength. Nitrides with tetrahedrally coordinated doping sites for  $\text{Mn}^{2+}$  serve as an illustrative example here.  $\text{AlN}:\text{Mn}^{2+}$  ( $\lambda_{\text{em}}=600\text{ nm}$ ),<sup>[40]</sup>  $\text{ZnGeN}_2:\text{Mn}^{2+}$  ( $\lambda_{\text{em}}=610\text{ nm}$ )<sup>[41]</sup> and  $\text{MgSiN}_2:\text{Mn}^{2+}$  ( $\lambda_{\text{em}}=630\text{ nm}$ )<sup>[42]</sup> are red-emitting phosphors despite tetrahedral coordination of the doped  $\text{Mn}^{2+}$  ions, which is a consequence of the strong  $\sigma$ -donating nature of the  $\text{N}^{3-}$  ligands and the resulting strong degree of covalency of the Mn–N bonds. In contrast, one would expect a blue-shifted luminescence of octahedrally coordinated  $\text{Mn}^{2+}$  ions if the surrounding ligands were weakly coordinating with a high degree of ionicity in the Mn–ligand bond. This strategy has so far only been scarcely

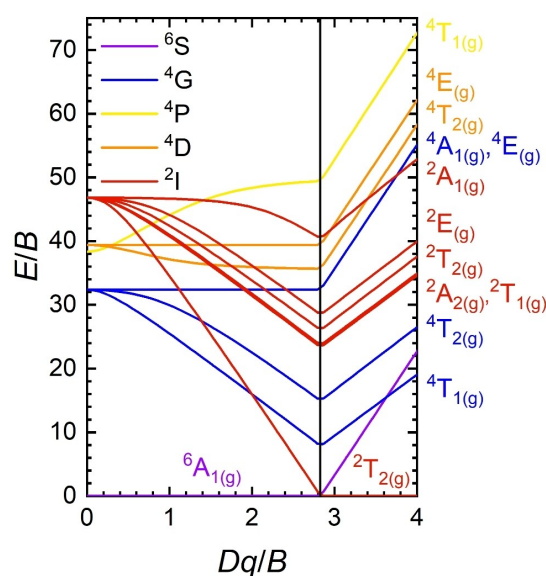
regarded. An alternative approach to obtain narrow-band emitting phosphors based on  $\text{Mn}^{2+}$  with other emission colors than green is thus to embed them in an octahedral ligand field with only weakly coordinating ligands. Similar effects are already known for  $\text{Eu}^{2+}$  in selected borates e.g.  $\text{SrB}_4\text{O}_7$ ,<sup>[43,44]</sup> and aluminates<sup>[45]</sup> or very ionic fluorides such as  $\text{AMgF}_3$  ( $A=\text{K}, \text{Rb}$ ),<sup>[46,47]</sup> for which in the latter example, even the observation of  $4f^7\text{--}4f^7$  narrow-line luminescence of  $\text{Eu}^{2+}$  was possible.

Years ago, borosulfates as a new class of silicate-analogue compounds started to gain increasing interest and in recent years some borosulfate anions were characterized as weakly coordinating, making them promising candidates for our investigations.<sup>[48–50]</sup> Typically, the anionic substructures of borosulfates consist of vertex-connected  $(\text{BO}_4)^-$ - and  $(\text{SO}_4)^-$ tetrahedra formally substituting the  $(\text{SiO}_4)$ tetrahedra in silicates.<sup>[51]</sup> The anionic substructures comprise e.g. oligomeric anions (like nesosilicates),<sup>[52,53]</sup> infinite chains (like inosilicates),<sup>[53,54]</sup> layers (like phyllosilicates)<sup>[50,55–57]</sup> or 3D network structures (like tectosilicates).<sup>[58,59]</sup> The weak coordination behavior was also demonstrated by the stabilization of  $(\text{L}_4)^{2+}$ -cations.<sup>[60]</sup> The latter can also be obtained in presence of a sufficiently powerful oxidizer and weakly coordinating anions such as  $[\text{AsF}_6]^-$  and  $[\text{SbF}_6]^-$ .<sup>[61]</sup> The special reaction conditions during the synthesis as well as the weak coordination behavior of the borosulfate anions are most likely also the reason for the stabilization of the cluster-like heteropolycations in  $[\text{Au}_3\text{Cl}_4][\text{B}(\text{S}_2\text{O}_7)_2]$  and the chain-like heteropolycations in  $[\text{Au}_2\text{Cl}_4][\text{B}(\text{S}_2\text{O}_7)_2](\text{SO}_3)$ .<sup>[62]</sup> Spectroscopic evidence for the weak coordination behavior of borosulfates has so far been mainly related to the luminescence of lanthanoid ions such as  $\text{Ce}^{3+}$  or the UV/Vis absorption of transition metal ions such as  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$ .<sup>[48,50,63]</sup>

Based on these promising findings, it was our goal to demonstrate that weakly coordinating ligands can be beneficially employed to tune the photoluminescence properties of  $\text{Mn}^{2+}$  for alternative lighting sources in a desirable manner and that the covalency of the Mn–ligand bond plays an equally important role in controlling of the ligand field strength.

## Results and Discussion

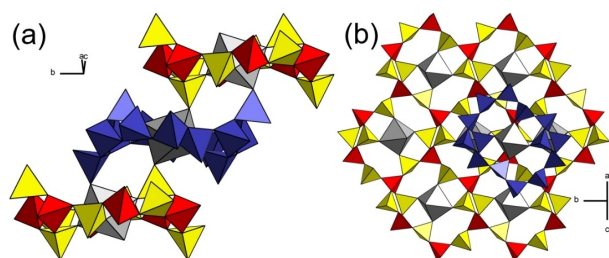
$\text{Zn}[\text{B}_2(\text{SO}_4)_4]$  crystallizes in the space group  $P2_1/n$  (no. 14), with the lattice parameters  $a=7.8338(4)$ ,  $b=8.0967(4)$ ,  $c=9.0399(4)\text{ \AA}$  and  $\beta=111.26(1)^\circ$ .<sup>[57]</sup> It features heteropolyanionic layers of alternating  $(\text{BO}_4)^-$ - and  $(\text{SO}_4)^-$ tetrahedra sharing a common vertex. Each  $(\text{BO}_4)$ -tetrahedron is connected to four  $(\text{SO}_4)$ -tetrahedra, which themselves are connected only to two  $(\text{BO}_4)$ -tetrahedra, thus exhibiting two terminal oxygen atoms. The layers consist of *vierer-* and *zwoelfer-* rings of alternating tetrahedra, a structural motif which can be found in a lot of conventional phyllosilicate-analogue borosulfates. Inside the twelve-membered rings the charge compensating  $\text{Zn}^{2+}$  cations reside, octahedrally coordinated by six oxygen atoms; four belonging to the surrounding ring and two denote to the adjacent polyanionic



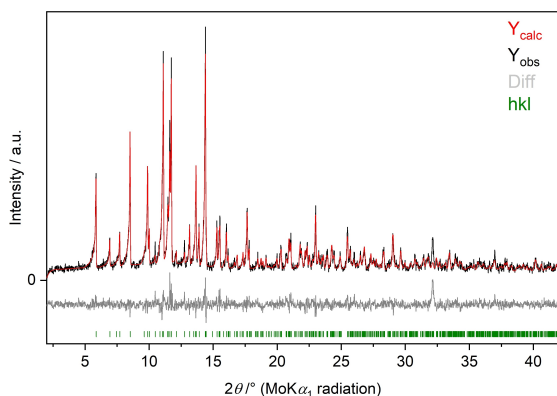
**Figure 1.** Tanabe-Sugano diagram ( $C/B=4.5$ ) for octahedrally coordinated  $d^5$  ions.<sup>[38]</sup>  $B$  and  $C$  denote the interelectronic repulsion Racah parameters.



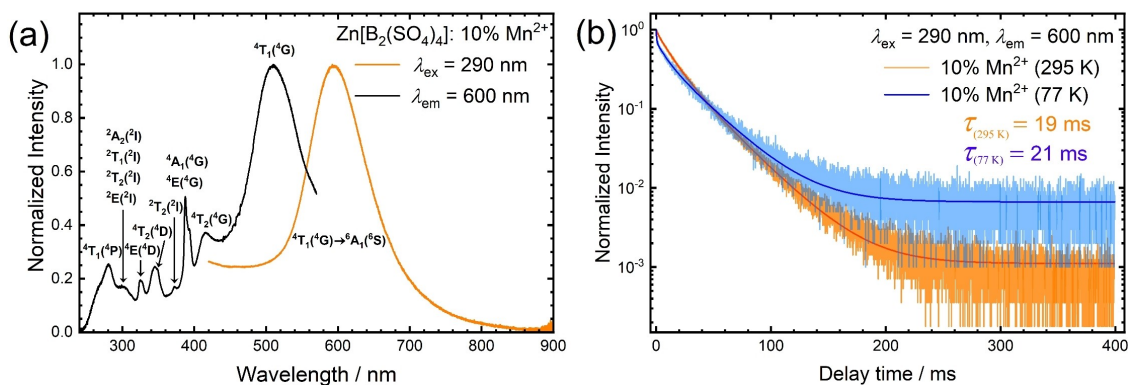
layers. All oxygen atoms coordinating the  $\text{Zn}^{2+}$  cation are terminal oxygen atoms of the  $(\text{SO}_4)$ -tetrahedra. Figure 2 depicts the structure and coordination of the cation in  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] \cdot \text{Mn}^{2+}$ , both within the layer (Figure 2b) and by two oxygen atoms of adjacent layers, which are situated



**Figure 2.** Structural features of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ . (a) View parallel to the layers. (b) View orthogonal to the layers. Color code: yellow— $(\text{SO}_4)$ -tetrahedra, red— $(\text{BO}_4)$ -tetrahedra, gray— $(\text{Zn/Mn})\text{O}_6$ -octahedra. One layer is colored blue as a guide for the eye.



**Figure 3.** Rietveld-refined XRPD pattern of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] \cdot 10\% \text{Mn}^{2+}$  ( $\text{MoK}\alpha_1$  radiation). For details on the quality parameters of the refinement, see the Supporting Information.



**Figure 4.** Photoluminescence properties of  $\text{Mn}^{2+}$  in  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ . (a) PL and PLE spectra of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] \cdot 10\% \text{Mn}^{2+}$  at room temperature. Assignment of states according to the Tanabe-Sugano diagram. The  $10\% \text{Mn}^{2+}$ -activated compound was chosen as representative sample due to its favorable ratio of  $\text{Mn}^{2+}$ -based to host-based luminescence. Note that the parity of the states was omitted for representational reasons. (b) PL decay curves of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] \cdot 10\% \text{Mn}^{2+}$  at 295 K (orange) and 77 K (blue). Excitation and emission wavelength are indicated in the graph. Decay times are averaged values extracted from multiexponential fit functions.

in a *trans* arrangement within the coordination octahedron (Figure 2a).

Figure 3 shows a representative Rietveld refinement of the solid solution series  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] \cdot x\% \text{Mn}^{2+}$  ( $x = 0.5, 1, 2, 3, 4, 5, 10$ ). The percentage of dopant was fixed during the refinement. Further details of the synthesis and the fitting quality parameters of the Rietveld refinement are given in the Supporting Information.

### Luminescence Spectroscopy

All of the  $\text{Mn}^{2+}$ -activated  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$  samples, enclosed in quartz ampoules, with high optical quality, showed luminescence upon excitation with UV light. Figure 4a depicts the photoluminescence emission (PL) and excitation (PLE) spectra of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4] \cdot 10\% \text{Mn}^{2+}$  at room temperature. An intense, broad orange emission is observed under excitation with 290 nm. The emission band is located at 595 nm with a full width at half maximum (FWHM) of  $2960 \text{ cm}^{-1}$  ( $\approx 103 \text{ nm}$  in the wavelength domain) and the emission is assigned to the  ${}^4\text{T}_{1g}({}^4\text{G}) \rightarrow {}^6\text{A}_{1g}({}^6\text{S})$  transition according to the Tanabe-Sugano diagram. The PL and PLE spectra were also recorded at 77 K but no additional information could be gained due to limited emission intensity of the compounds in evacuated quartz ampoules. Figure 4b depicts the luminescence decay trace of the  ${}^4\text{T}_{1g}({}^4\text{G}) \rightarrow {}^6\text{A}_{1g}({}^6\text{S})$  transition of  $\text{Mn}^{2+}$ . It shows multiexponential decay with an average decay time of 21 ms. The luminescence characteristics agree with the structural feature of octahedrally coordinated  $\text{Mn}^{2+}$ . The decay time of 21 ms is longer than the commonly reported decay times for tetrahedrally coordinated  $\text{Mn}^{2+}$  (e.g.  $\text{MgAl}_2\text{O}_4$ : 3%  $\text{Mn}^{2+}$ :  $\tau = 6.5 \text{ ms}$  at room temperature;<sup>[24,39]</sup>  $[\text{Bz}(\text{Me})_3\text{N}]_2[\text{MnCl}_4]$ :  $\tau = 3.8 \text{ ms}$  at room temperature ( $[\text{Bz}(\text{Me})_3\text{N}]^+$ : Benzyltrimethylammonium);<sup>[64]</sup>  $\text{Zn}_2\text{SiO}_4$ : 0.05%  $\text{Mn}^{2+}$ :  $\tau = 13 \text{ ms}$  at room temperature).<sup>[65]</sup> Even if the regarded high doping fraction of 10%  $\text{Mn}^{2+}$  is taken into account, the extracted

decay time of 19 ms at room temperature already indicates that violation of the spin selection rule cannot be the sole reason for the slow decay, but the transition must be also parity-forbidden. This goes in line with examples of octahedrally coordinated  $\text{Mn}^{2+}$  ions in inorganic host compounds such as  $\text{KMgF}_3$ : 0.5 %  $\text{Mn}^{2+}$  ( $\tau=100$  ms at room temperature) or selected perovskite-derived chlorides  $\text{AMCl}_3\text{:Mn}^{2+}$  ( $\text{A}=\text{K, Rb, Cs}$ ;  $\text{M}=\text{Mg, Ca, Sr}$ ) ( $\tau\approx 20$  ms at room temperature) with slightly distorted octahedral doping sites for the  $\text{Mn}^{2+}$  ions.<sup>[66,67]</sup> In contrast, the FWHM of the  $\text{Mn}^{2+}$ -related emission band in  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]\text{:Mn}^{2+}$  is comparably small and in a similar order of magnitude compared to reported values for the FWHMs of emission bands for tetrahedrally coordinated  $\text{Mn}^{2+}$  (in halides:  $1400\text{ cm}^{-1}$ – $2000\text{ cm}^{-1}$  at room temperature).<sup>[64]</sup> Moreover, the emission wavelength is comparably short for octahedrally coordinated  $\text{Mn}^{2+}$ , which usually extends beyond 600 nm (e.g.  $\text{MgSiO}_3\text{:Mn}^{2+}$ :  $\lambda_{\text{em}}=661\text{ nm}$ ,<sup>[32]</sup>  $\text{CsMnBr}_3$ :  $\lambda_{\text{em}}=680\text{ nm}$ ,<sup>[68]</sup>  $\text{Ba}_2\text{Ca}(\text{BO}_3)_2\text{:Mn}^{2+}$ :  $\lambda_{\text{em}}=630\text{ nm}$ <sup>[33]</sup>) and only becomes orange in weak octahedral ligand fields ( $\text{AMCl}_3\text{:Mn}^{2+}$ :  $\lambda_{\text{em}}\approx 560\text{ nm}$ ,<sup>[67]</sup>  $\text{CsPbCl}_3\text{:Mn}^{2+}$ :  $\lambda_{\text{em}}=586\text{ nm}$ ,<sup>[69]</sup>  $\text{MgF}_2\text{:Mn}^{2+}$ :  $\lambda_{\text{em}}=586\text{ nm}$ <sup>[70]</sup>). Altogether, these properties demonstrate that the  $\text{Mn}^{2+}$  ions are octahedrally coordinated in  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]\text{:Mn}^{2+}$  but with only weakly coordinating ligands. This is in agreement with earlier findings by Höpfe *et al.* on lanthanoid-activated borosulfates.<sup>[48,71]</sup> The weak coordination behavior is understandable given the presence of the strongly electron-withdrawing  $\text{S}^{\text{VI}}$  atoms that compete with  $\text{Mn}^{2+}$  about the electron density at the 2p lone pair of a coordinating O atom. In agreement with this interpretation, the luminescence decay time barely changes between 77 K and room temperature (see Figure 4b). The photoluminescence excitation spectra (PLE) of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]\text{:Mn}^{2+}$  shows characteristic transitions of  $\text{Mn}^{2+}$  that can be assigned according to the  $d^5$  Tanabe-Sugano diagram (see Figure 1). All these transitions are spin- and parity-forbidden in an octahedral ligand field. Furthermore, a weak bluish emission is also observed, which is attributed to host-related luminescence but could not be specified further. Even in nominally undoped  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ , a broad-banded emission peaking at around 550 nm can be observed at room temperature (see Supporting Information). The intensity of this host emission

is small upon excitation with 290 nm and is only dominant in samples with low  $\text{Mn}^{2+}$  content (3 mol % or below, see Supporting Information). Figure 5 shows the PL properties of  $\text{Mn}^{2+}$ -activated  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$  with varying  $\text{Mn}^{2+}$ -concentrations. The  $^4\text{T}_{1g}(^4\text{G})\rightarrow^6\text{A}_{1g}(^6\text{S})$ -based emission band of the  $\text{Mn}^{2+}$  ions is slightly red-shifted for the higher doped samples, which is a consequence of exchange interaction between different  $\text{Mn}^{2+}$  ions.<sup>[38]</sup> However, given a relatively long closest Zn–Zn distance of  $6.2707(2)\text{ \AA}$  in  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ ,<sup>[56]</sup> the effect of mutual interactions between the incorporated  $\text{Mn}^{2+}$  ions is limited. Exchange interaction between the  $\text{Mn}^{2+}$  ions is usually accompanied by an increasing FWHM and a gradual decrease of the decay time together with increasingly multi-exponential decay behavior.<sup>[38]</sup> Both the dependence of the emission FWHM and average luminescence decay times show that exchange coupling and concentration quenching is weak up to the regarded doping concentrations of 10 mol %.

It should be noted that also an effect due to a change in the average Mn–O bond length is imaginable, which could affect the ligand field splitting based on its  $R^{-5}$  dependence for d-elements.<sup>[72,73]</sup> Since  $\text{Mn}^{2+}$  in its  $3d^5$  high-spin configuration has, however, a larger ionic radius than  $\text{Zn}^{2+}$  with a  $3d^{10}$  configuration, one would expect an overall decreasing ligand field strength giving rise to an observable blue-shift of the emission based on the  $d^5$  Tanabe-Sugano diagram (see Figure 1). Since this is not experimentally observed, we conclude that this contribution is not the dominant one.

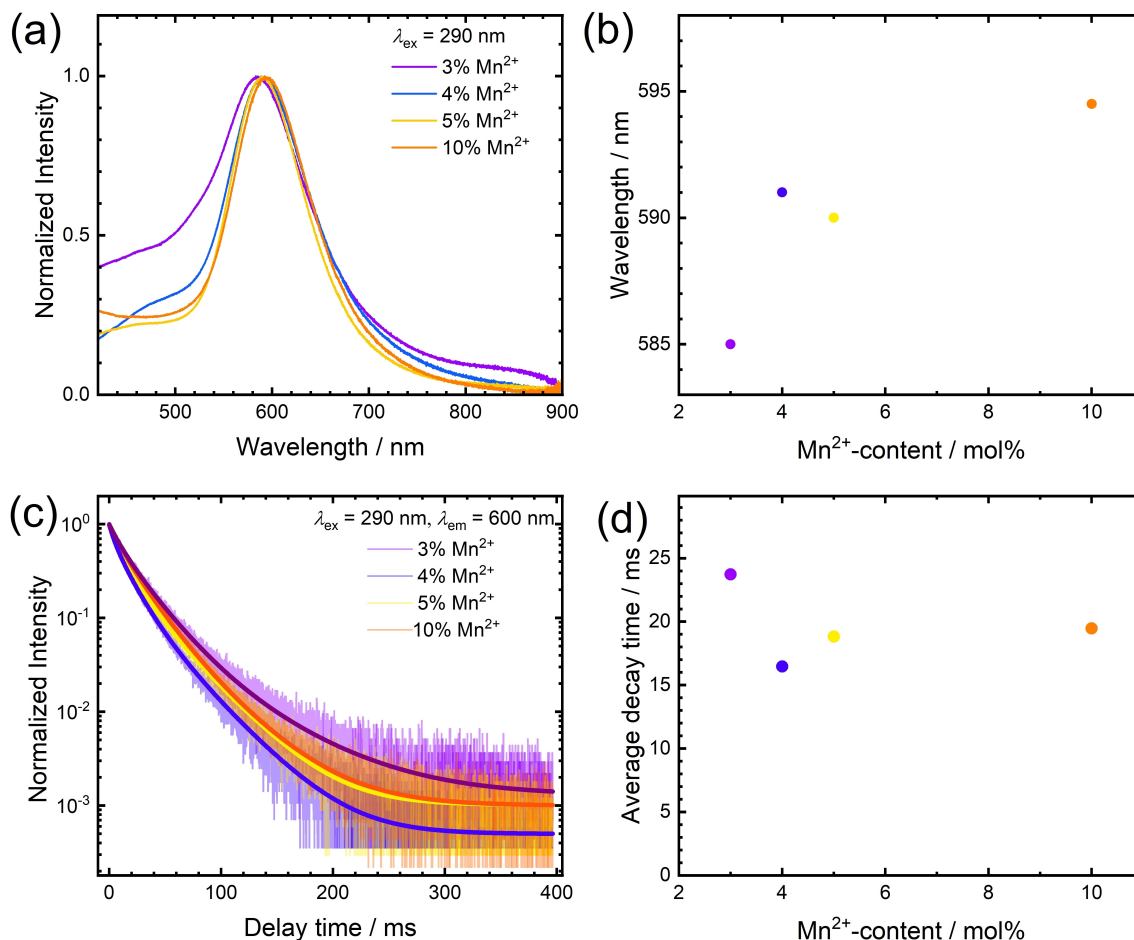
#### Racah parameters and ligand field analysis

From the energies of the electronic transitions, it is possible to estimate the Racah parameters  $B$  and  $C$  and the ligand field splitting  $10Dq$  as  $B=729\text{ cm}^{-1}$ ,  $C=3660\text{ cm}^{-1}$  and  $10Dq=9430\text{ cm}^{-1}$  respectively (a detailed description of the calculations is given in the Supporting Information).<sup>[74]</sup> The same approach was applied for some other selected compounds with  $\text{Mn}^{2+}$  in halides with octahedrally coordinated sites with the results being compared in Table 1. It should be noted that this semi-empirical approach only offers estimate values for interelectronic repulsion and ligand field parame-

**Table 1:** Racah parameters  $B$  and  $C$ , ligand field splitting  $10Dq$ , lowest energetic excitation energy  $E_{\text{ex}}$  of the  $^4\text{T}_{1g}(^4\text{G})\leftarrow^6\text{A}_{1g}(^6\text{S})$  transition (at room temperature), and related emission energy  $E_{\text{em}}$  (at room temperature) of  $\text{Mn}^{2+}$  in  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$  and selected chlorides and fluorides with octahedrally coordinated doping sites for  $\text{Mn}^{2+}$ .

|                                      | $\text{Zn}[\text{B}_2(\text{SO}_4)_4]\text{:Mn}^{2+}$ | $\text{CsCaCl}_3\text{:Mn}^{2+}$ <sup>[79]</sup> | $\text{KMgCl}_3\text{:Mn}^{2+}$ <sup>[79,80]</sup> | $\text{CsCaF}_3\text{:Mn}^{2+}$ <sup>[81]</sup> | $\text{KZnF}_3\text{:Mn}^{2+}$ <sup>[82]</sup> |
|--------------------------------------|-------------------------------------------------------|--------------------------------------------------|----------------------------------------------------|-------------------------------------------------|------------------------------------------------|
| $B/\text{cm}^{-1}$ <sup>[a]</sup>    | 729                                                   | 631                                              | 619                                                | 702                                             | 696                                            |
| $C/\text{cm}^{-1}$ <sup>[a]</sup>    | 3663                                                  | 3579                                             | 3537                                               | 3666                                            | 3651                                           |
| $10Dq/\text{cm}^{-1}$ <sup>[a]</sup> | 9427                                                  | 8583                                             | 8629                                               | 9844                                            | 11285                                          |
| $Dq/B$                               | 1.29                                                  | 1.36                                             | 1.39                                               | 1.40                                            | 1.62                                           |
| $C/B$                                | 5.0                                                   | 5.7                                              | 5.7                                                | 5.2                                             | 5.2                                            |
| $E_{\text{ex}}/\text{cm}^{-1}$       | 19430                                                 | 20095                                            | 19440                                              | 19880                                           | 18530                                          |
| $E_{\text{em}}/\text{cm}^{-1}$       | 16680                                                 | 18190                                            | 17530                                              | 18350                                           | 17100                                          |

[a] Values were derived from excitation spectra without Racah-Trees or seniority correction and may therefore differ from values in the respective reference.



**Figure 5.** Photoluminescence of different doping concentrations of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]:\text{Mn}^{2+}$ . a) PL emission spectra at room temperature. The excitation wavelength is indicated in the graph. b) Plot of the wavelength at maximum emission intensity versus  $\text{Mn}^{2+}$  concentration. c) Time-resolved luminescence of  $\text{Mn}^{2+}$  at room temperature. Excitation and emission wavelengths are indicated in the graph. d) Plot of the average decay time at room temperature versus  $\text{Mn}^{2+}$  content.

ters of  $\text{Mn}^{2+}$ , which allows, however, a quantitative comparison between the regarded compounds. More elaborate *ab initio* methods would be required to gain additional accuracy in especially the Racah parameters, which are, however not trivial for open-shell systems and usually requires wavefunction-based approaches.<sup>[75–78]</sup> Nonetheless, clear trends are already visible at this stage that also agree with the experimentally found emission and lowest excitation energies. The Racah parameter  $B$  for  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]:\text{Mn}^{2+}$  is exceptionally high, even in comparison with highly ionic fluorides. Consequently, the Mn–ligand bond may be regarded as strongly ionic. The ligand field splitting caused by the borosulfate anion ( $10Dq = 9430 \text{ cm}^{-1}$ ) is in between the values calculated for chlorides ( $10Dq \approx 8500 \text{ cm}^{-1}$ ) and fluorides ( $10Dq \approx 10000\text{--}11000 \text{ cm}^{-1}$ ). Together with the strong ionic degree of the Mn–ligand bond, the borosulfate anion indeed shows characteristic weak coordination behavior that is directly reflected in the photoluminescence properties of the incorporated  $\text{Mn}^{2+}$  cations.

## Conclusion

$\text{Mn}^{2+}$  is a so-far underestimated potential emitter for inorganic phosphors given its less spatially extended 3d orbitals compared to the 5d orbitals exploited in the celebrated case of  $\text{Eu}^{2+}$ . In most studies, the emission color is varied by changes in either the metal–ligand distances or the coordination geometry. Tetrahedrally coordinated  $\text{Mn}^{2+}$  typically emits in the green, octahedrally coordinated  $\text{Mn}^{2+}$  typically in the red range. An alternative concept to tune the emission color of transition metal ions can be electronic control of the nature of the metal–ligand bond. This concept was explicitly demonstrated in the phyllosilicate-analogous borosulfates  $\text{Zn}_{1-x}\text{Mn}_x[\text{B}_2(\text{SO}_4)_4]$  ( $x = 0, 0.03, 0.04, 0.05, 0.10$ ) with weakly-coordinating borosulfate ligands.  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]: x\% \text{ Mn}^{2+}$  ( $x = 3, 4, 5, 10$ ) shows an orange  ${}^4\text{T}_{1g}({}^4\text{G}) \rightarrow {}^6\text{A}_{1g}({}^6\text{S})$  emission at  $\approx 590 \text{ nm}$ , which is unusually high in energy for  $\text{Mn}^{2+}$  in an octahedral coordination of an oxidic compound and indeed implies a weak coordination behavior of the ligands according to the  $d^5$  Tanabe–Sugano



diagram. By comparison with literature-known examples of  $\text{Mn}^{2+}$ -activated symmetric fluorides and chlorides with octahedrally coordinated doping sites for this activator, we were able to place the borosulfate ligands into the commonly known spectrochemical series of ligands just between  $\text{Cl}^-$  and  $\text{F}^-$ . These studies give an insight into more sophisticated possibilities to tailor the emission color of  $\text{Mn}^{2+}$  in inorganic phosphors by electronic means with chemically more uncommon ligands.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Borosulfates •  $\text{Mn}^{2+}$  • Photoluminescence • Weak Coordination

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## Supporting Information

### **Photoluminescence of $\text{Mn}^{2+}$ in the Borosulfate $\text{Zn}[\text{B}_2(\text{SO}_4)_4] : \text{Mn}^{2+}$ — A Tool to Detect Weak Coordination Behavior of Ligands**

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### Calculation of the Racah parameters and ligand field splitting

The Racah parameters  $B$  and  $C$  and the ligand field splitting  $10Dq$  are estimated from equations (1) - (4) by the following procedure:<sup>[1]</sup> First, the transition energies according to (1) - (4) were extracted from the photoluminescence excitation (PLE) spectrum of the 10%  $\text{Mn}^{2+}$  doped  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ ,\* giving:

$$\Delta E_{(1)} = 25600 \text{ cm}^{-1}$$

$$\Delta E_{(2)} = 30700 \text{ cm}^{-1}$$

$$\Delta E_{(3)} = 19400 \text{ cm}^{-1}$$

$$\Delta E_{(4)} = 24200 \text{ cm}^{-1}$$

\*The 10%  $\text{Mn}^{2+}$  doped compound was chosen as representative sample due to its favorable ratio of  $\text{Mn}^{2+}$ -based to host-based luminescence, allowing for clear assignment of  $\text{Mn}^{2+}$ -associated transitions.

Then,  $B$  was estimated from (1) - (2) =  $7B$ , giving  $B = 729 \text{ cm}^{-1}$ .  $B$  was inserted in either (1) or (2) to determine  $C = 3662 \text{ cm}^{-1}$ .  $10Dq$  was calculated by inserting  $B$  and  $C$  in (3) or (4) giving two values for  $10Dq = 11090 \text{ cm}^{-1}$  and  $9430 \text{ cm}^{-1}$  of which the first one should be discarded as the designated  ${}^4\text{T}_{1g}({}^4\text{G}) \leftarrow {}^6\text{A}_{1g}({}^6\text{S})$  band is assumed to show significant overlap with the excitation band of the host-based luminescence.

$$E({}^4\text{A}_{1g}, {}^4\text{E}_g({}^4\text{G}) \leftarrow {}^6\text{A}_{1g}({}^6\text{S})) = 10B + 5C \quad (1)$$

$$E({}^4\text{E}_g({}^4\text{D}) \leftarrow {}^6\text{A}_{1g}({}^6\text{S})) = 17B + 5C \quad (2)$$

$$E({}^4\text{T}_{1g}({}^4\text{G}) \leftarrow {}^6\text{A}_{1g}({}^6\text{S})) = -10Dq + 10B + 6C - \frac{26B^2}{10Dq} \quad (3)$$

$$E({}^4\text{T}_{2g}({}^4\text{G}) \leftarrow {}^6\text{A}_{1g}({}^6\text{S})) = -10Dq + 18B + 6C - \frac{26B^2}{10Dq} \quad (4)$$

### Experimental Section

**Caution:** Oleum is a strong oxidant and must be handled with care. During and even after the reaction, the ampoules may be under considerable pressure. It is essential to cool the ampoules with liquid nitrogen before opening.

**Synthesis of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ :** We followed a similar route described earlier by some of us.<sup>[2]</sup>  $\text{H}_3\text{BO}_3$  (300.0 mg (4.85 mmol), Carl Roth, Karlsruhe, Germany,  $\geq 99.8\%$ ),  $\text{ZnO}$  (56.4 mg (0.69 mmol), Merck, Darmstadt, Germany, 99%) and 1 ml oleum (65%  $\text{SO}_3$ ,

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Merck, Darmstadt, Germany) were placed in a thick-walled glass ampoule ( $l = 300$  mm,  $\phi = 16$  mm, wall thickness = 1.8 mm). For the solid solutions  $\text{Zn}_{1-x}\text{Mn}_x[\text{B}_2(\text{SO}_4)_4]$  ( $x = 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.10$  and  $1$ ), the respective stoichiometric amount of ZnO was replaced by  $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$  (0.7, 1.4, 2.7, 4.1, 5.5, 6.8, 13.7 and 137.3 mg (0.003, 0.007, 0.0014, 0.021, 0.028, 0.035, 0.069 and 0.69 mmol), Fluka, Seelze, Germany, >99%). After torch-sealing the ampoules under reduced pressure (0.01 mbar), they were placed in a block-shaped resistance furnace and the following heating program was applied: heating to 523 K within 270 min, holding the maximum temperature for 96 h and cooling to 298 K within 96 h. After separating the mother liquor from the precipitated products by decantation, they were transferred into a glove box and further strictly handled under inert conditions due to the moisture sensitivity of the products. Adhesive mother liquor was removed by washing with dry  $\text{CH}_3\text{CN}$  and finally the solvent was removed under vacuum.

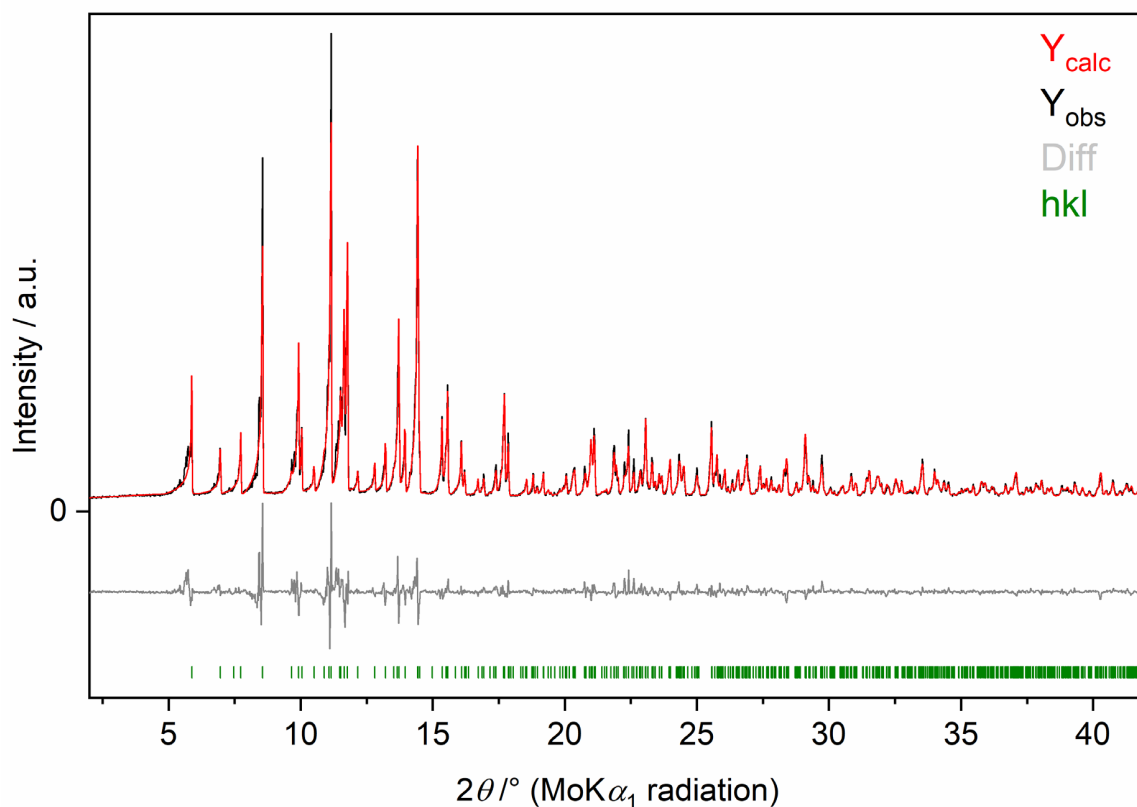
## Characterization and methods

**X-ray powder diffraction (XRPD):** The purity of the products was determined by XRPD using a Stoe Stadi P powder diffractometer in transmission geometry. Glass capillaries ( $\phi = 0.3$  mm) were packed with washed, thoroughly ground products and irradiated with Ge(111)-monochromatized  $\text{MoK}\alpha_1$ -radiation ( $\lambda = 0.7093$  Å), which was detected with a Dectris Mythen 1K detector. Rietveld refinement was performed with the program TOPAS 4.2 (Bruker, Germany, 2009). The starting point for the refinement was the single-crystal structure of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ . The peak shape was fitted with modified Thompson-Cox-Hastings pseudo-Voigt profiles.<sup>[3, 4]</sup> A  $\text{LaB}_6$  standard was used to adjust for the contribution of the diffractometer and background corrections were performed with Chebychev polynomials with the 20<sup>th</sup> order. The diffraction patterns are displayed in Figures S1-S8. The high, unexplained Bragg reflection in Figure S2 and S3 at  $2\theta = 18.4^\circ$ , as well as the reflection at  $2\theta = 32.1^\circ$  in Figure S8 are due to the use of a not calibrated collimator during the irradiation. The smaller maximum angle in these three measurements is a result of the substances decomposing in the capillaries before a longer range could be measured, due to imperfect sealing of the capillaries (bulk material was not affected). For these samples, a  $2\theta$  range from  $2$  to  $42^\circ$  with a step size of  $1.05^\circ$  and 15 s exposure time was measured. The longer measurements were performed with a  $2\theta$  range from  $2$  to  $72^\circ$

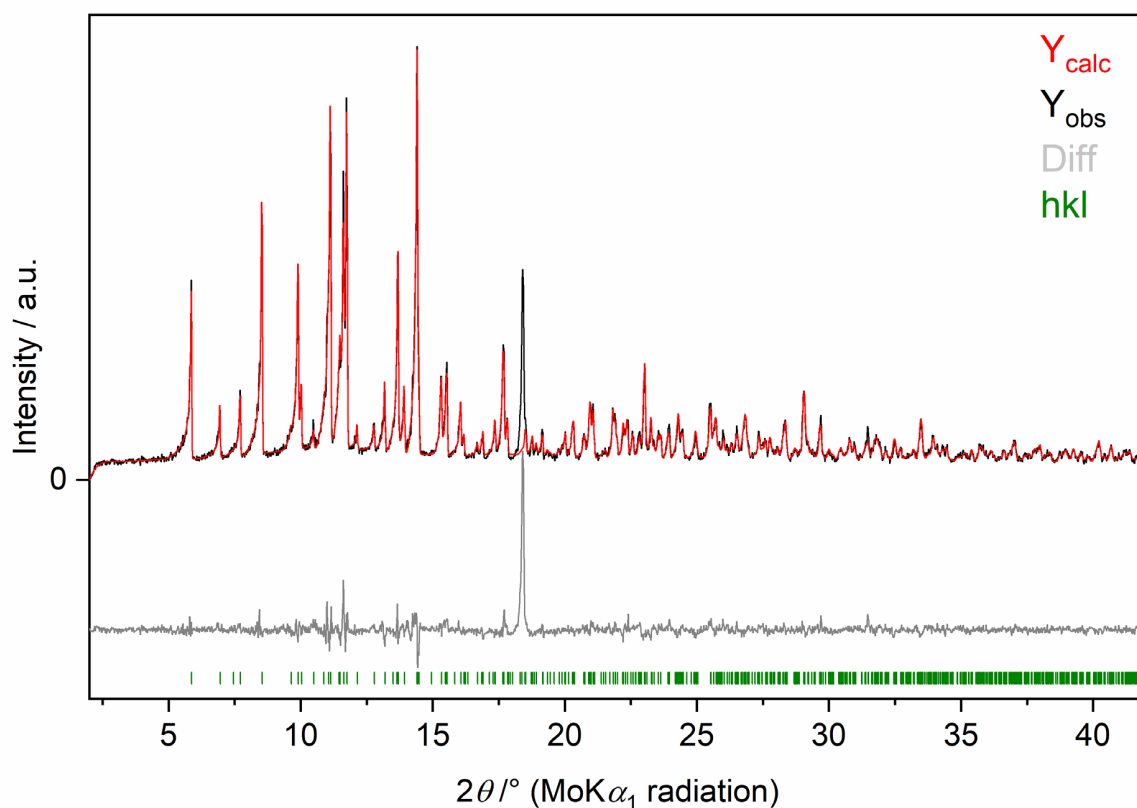
with a step size of  $0.15^\circ$  and 10 s exposure time. The refinement parameters are given in Table S1.

**Luminescence Spectroscopy:** Due to the air-sensitivity, all samples were treated under inert Ar atmosphere and subsequently enclosed in evacuated thin, optically transparent quartz ampoules (ilmasil® quality). Optical measurements were performed on an Edinburgh Instruments FLS1000 photoluminescence spectrometer equipped with a 450 W Xe arc lamp as an excitation source, double excitation and emission monochromators in Czerny-Turner configuration and a thermoelectrically cooled ( $-20^\circ\text{C}$ ) photomultiplier tube PMT-980 (Hamamatsu). The emission spectra were corrected with respect to the grating efficiency and PMT sensitivity, while excitation spectra were additionally corrected with respect to the lamp intensity. Photoluminescence decays were recorded using an Edinburgh Instruments  $\mu\text{F2}$  microsecond flash lamp with a 60 W pulsed Xe arc lamp as light source and adjustable trigger frequency (0.1...1000 Hz). The detection mode for time resolved measurements was single-photon multichannel scaling.

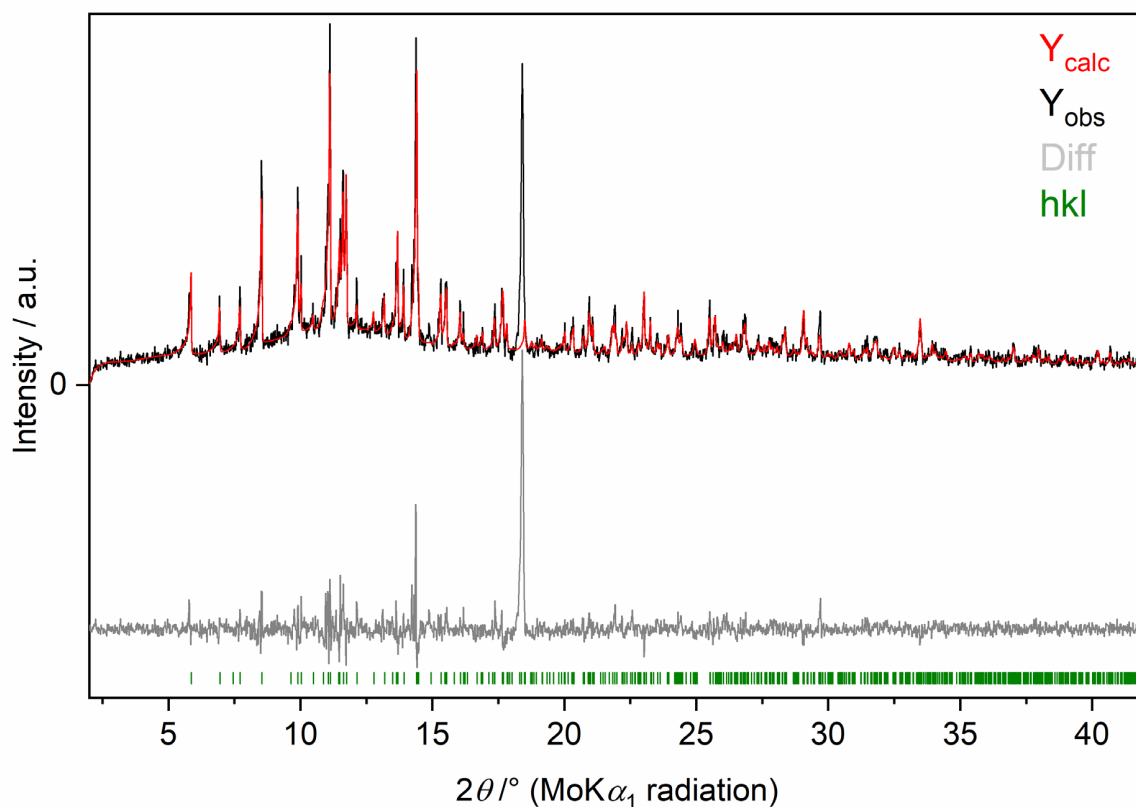
### **X-ray powder diffraction patterns of the $\text{Zn}_{1-x}\text{Mn}_x[\text{B}_2(\text{SO}_4)_4]$ solid solution**



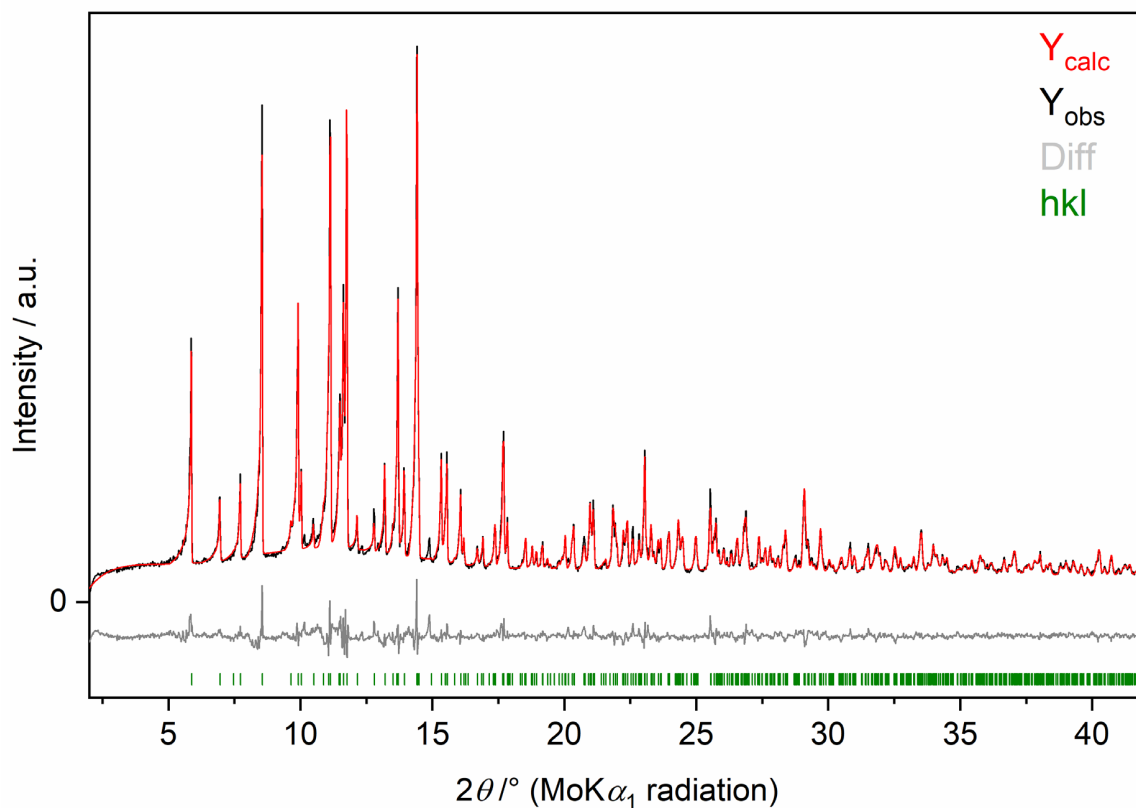
**Figure S1.** Rietveld refined X-ray powder diffraction (XRPD) pattern of undoped  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ .



**Figure S2.** Rietveld-refined XRPD pattern of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ : 0.5%  $\text{Mn}^{2+}$ . The strong, unexplained reflection at  $2\theta = 18.4^\circ$  is due to the use of a non-calibrated collimator during the irradiation.

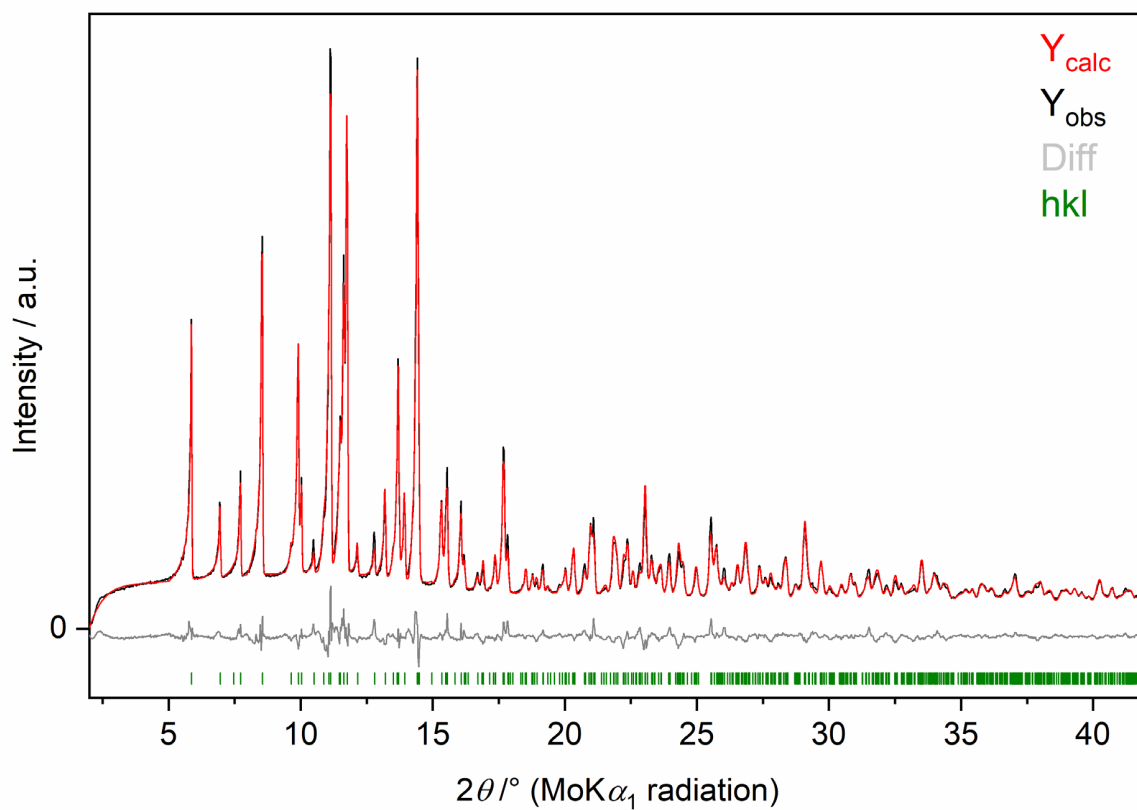


**Figure S3.** Rietveld-refined XRPD pattern of Zn[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]: 1% Mn<sup>2+</sup>. The strong, unexplained reflection at  $2\theta = 18.4^\circ$  is due to the use of a non-calibrated collimator during the irradiation.

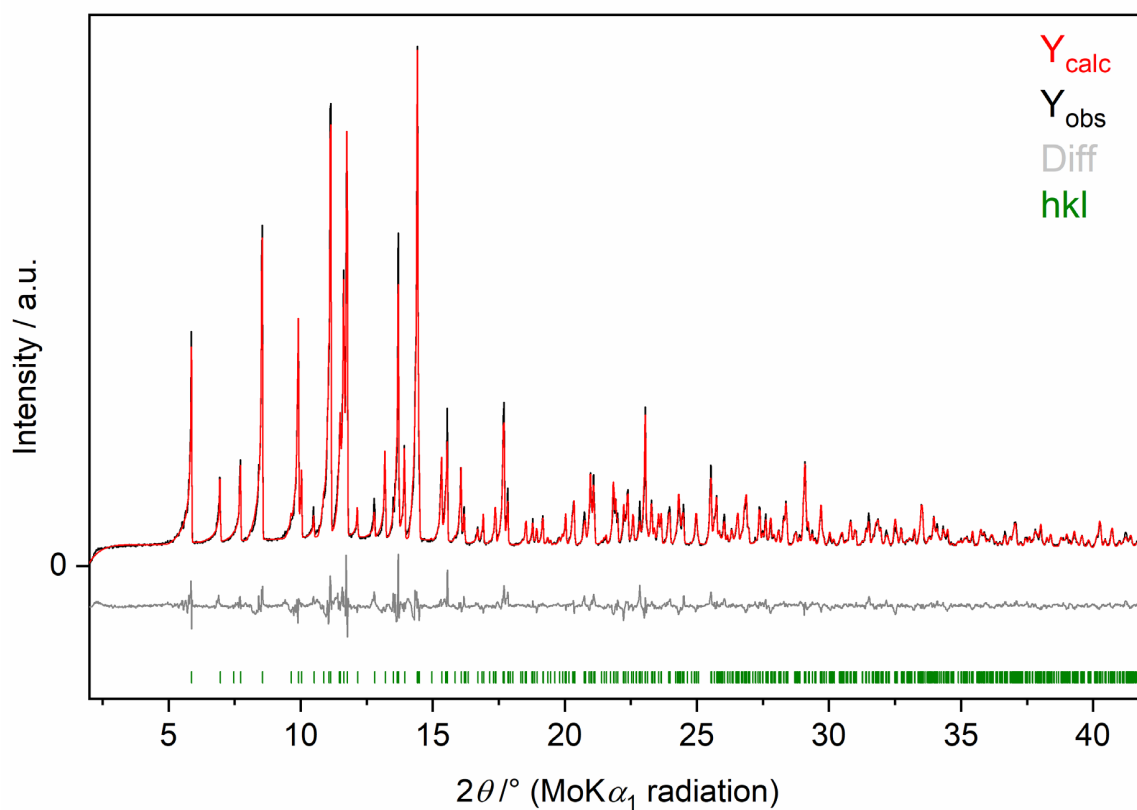


**Figure S4.** Rietveld-refined XRPD pattern of Zn[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]: 2% Mn<sup>2+</sup>.

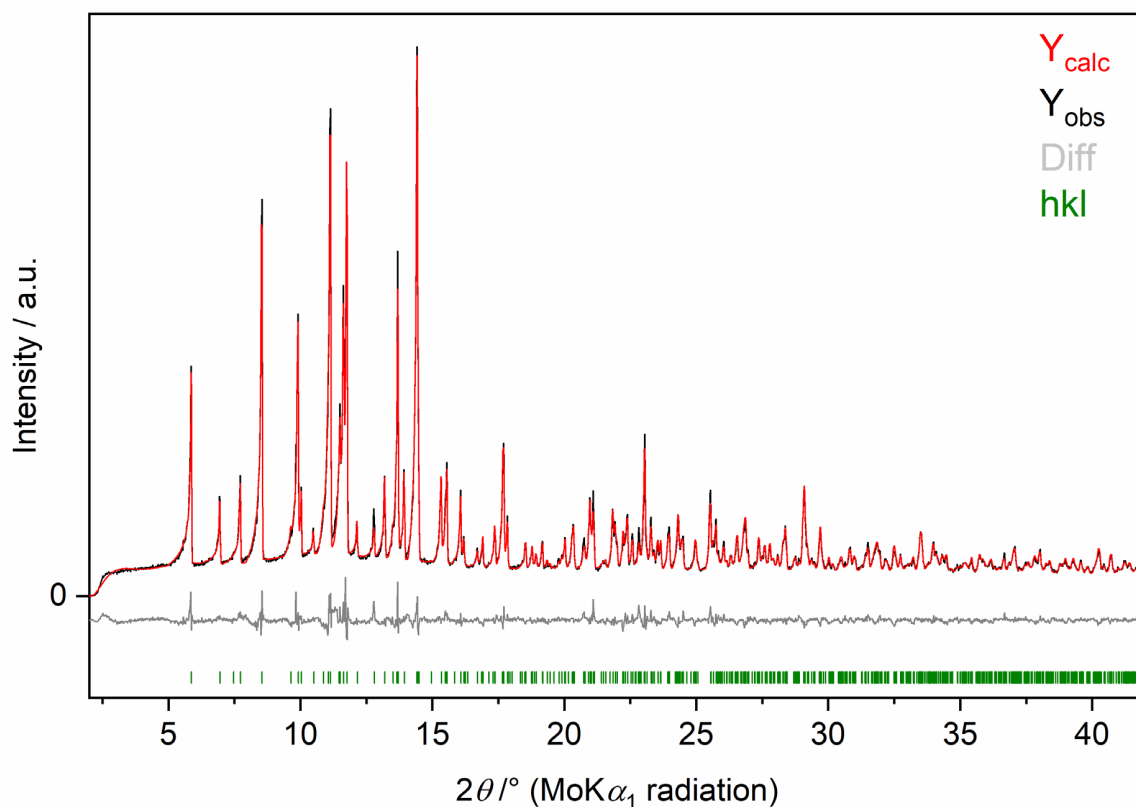




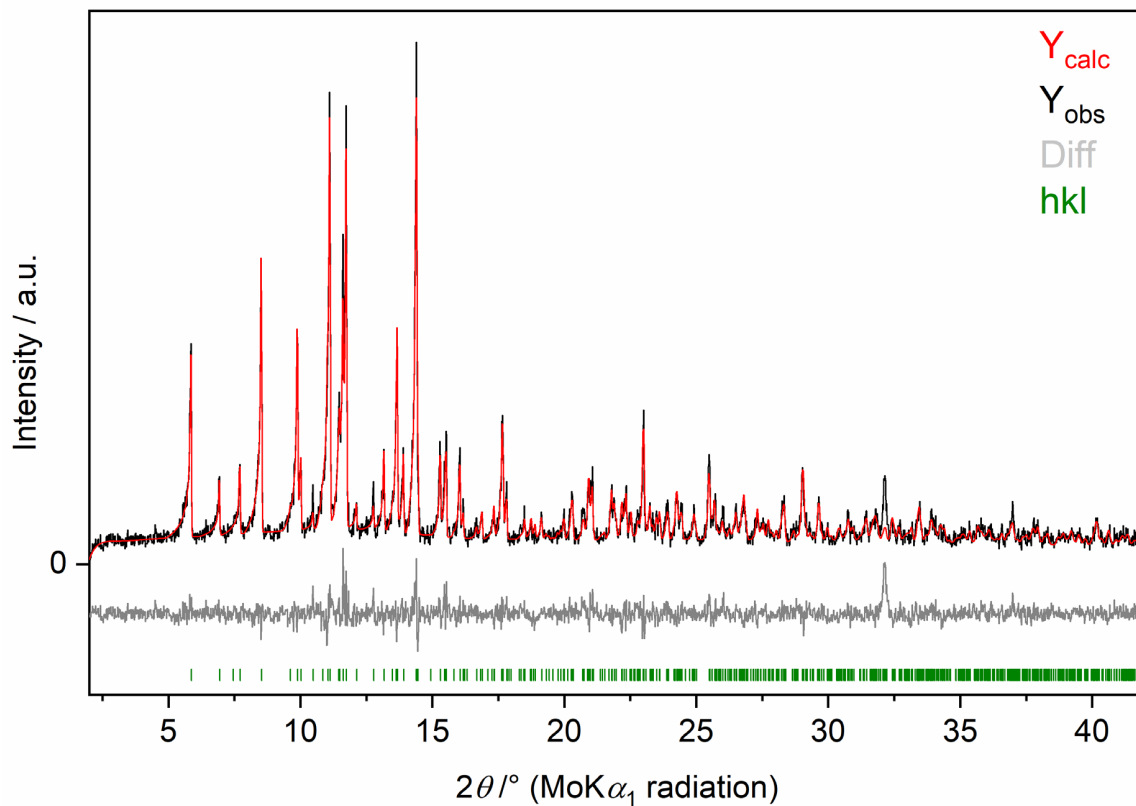
**Figure S5.** Rietveld-refined XRPD pattern of Zn[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]: 3% Mn<sup>2+</sup>.



**Figure S6.** Rietveld-refined XRPD pattern of Zn[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]: 4% Mn<sup>2+</sup>.



**Figure S7.** Rietveld-refined XRPD pattern of Zn[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]·5% Mn<sup>2+</sup>.

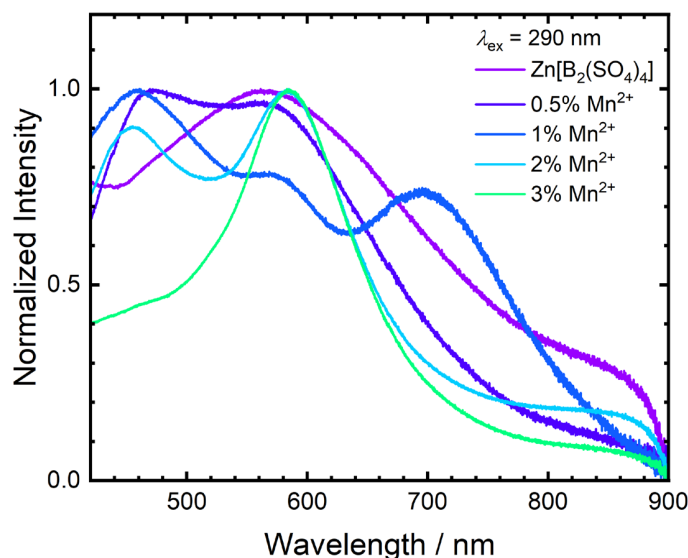


**Figure S8.** Rietveld-refined XRPD pattern of Zn[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]·10% Mn<sup>2+</sup>. The unexplained reflection at 2θ = 32.1° is due to the use of a non-calibrated collimator during the irradiation.

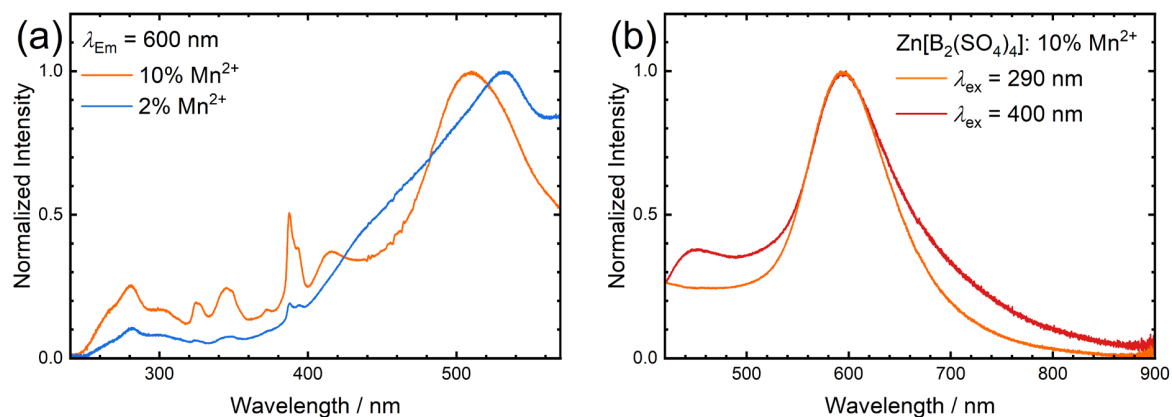
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**Table S1:** Parameters of the Rietveld Refinement of  $\text{Zn[B}_2(\text{SO}_4)_4]$ :  $x\%$   $\text{Mn}^{2+}$

| $x$ (mol% $\text{Mn}^{2+}$ ) | $R_{\text{Bragg}}$ / % | $R_{\text{exp}}$ / % | $R_{\text{wp}}$ / % | $R_p$ / % | G.o.o.F. |
|------------------------------|------------------------|----------------------|---------------------|-----------|----------|
| 0                            | 3.03                   | 3.65                 | 8.49                | 5.94      | 2.32     |
| 0.5                          | 3.45                   | 6.65                 | 12.88               | 7.83      | 1.94     |
| 1                            | 5.96                   | 12.26                | 17.90               | 12.39     | 1.46     |
| 2                            | 2.09                   | 3.20                 | 5.56                | 4.20      | 1.74     |
| 3                            | 2.61                   | 1.48                 | 4.61                | 3.40      | 3.12     |
| 4                            | 3.23                   | 2.95                 | 6.58                | 4.91      | 2.23     |
| 5                            | 2.13                   | 3.31                 | 5.34                | 4.05      | 1.61     |
| 10                           | 4.53                   | 15.22                | 15.18               | 11.65     | 1.00     |

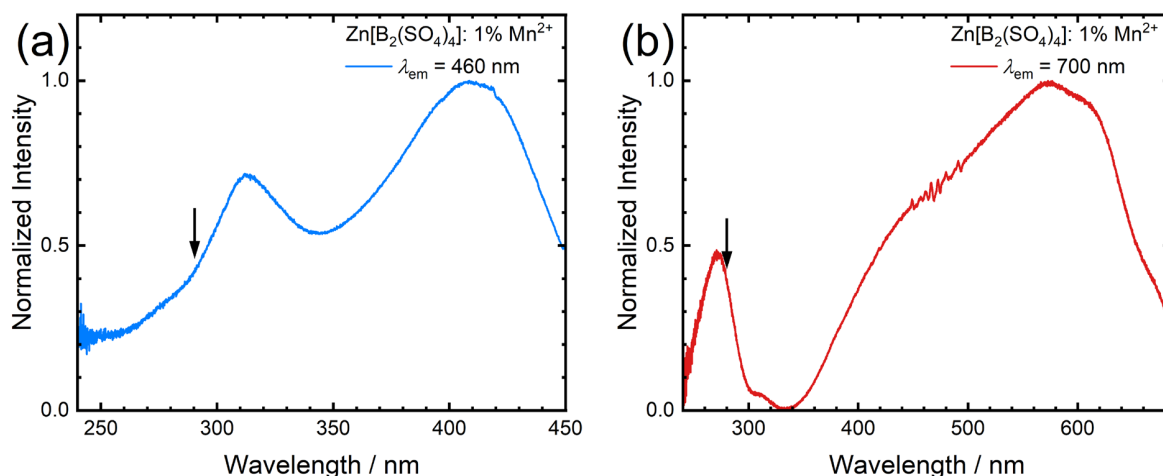
Photoluminescence spectra of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$  doped with  $< 4\%$   $\text{Mn}^{2+}$ 

**Figure S9.** Photoluminescence emission spectra of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ :  $x\%$   $\text{Mn}^{2+}$  ( $x = 0.5, 1, 2, 3$ ) at room temperature. The narrow emission around 600 nm is attributed to the  ${}^4\text{T}_{1g}({}^4\text{G}) \rightarrow {}^6\text{A}_{1g}({}^6\text{S})$  transition of  $\text{Mn}^{2+}$ . The blue emission centered at 480 nm is assigned to host-related luminescence. The deep red emission band at 700 nm was solely observed in the 1 mol%-doped sample and not additionally characterized.

Appearance of excitation and emission spectra of  $\text{Mn}^{2+}$ -activated  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ 

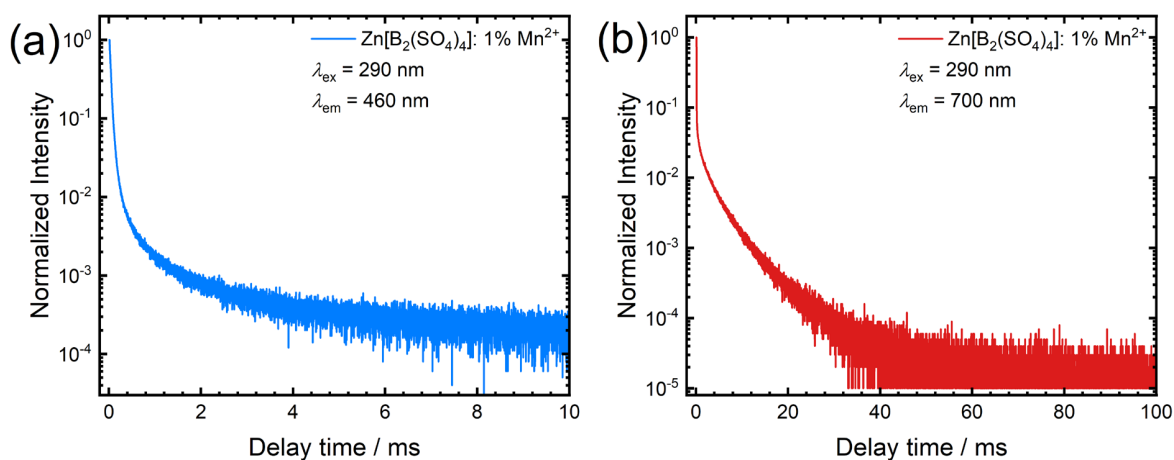
**Figure S10.** (a) Photoluminescence excitation spectra of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ :  $x\%$   $\text{Mn}^{2+}$  ( $x = 2, 10$ ) at room temperature. The characteristic transitions of  $\text{Mn}^{2+}$  are more pronounced in the 10 %-doped sample and thus, the broad excitation band around 500 nm is assigned to be host-related. (b) Photoluminescence emission spectra of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ : 10%  $\text{Mn}^{2+}$  with different excitation wavelengths. The host-related emission around 460-480 nm is stronger for the 400 nm excitation.

## Excitation spectra upon detection of nominally intrinsic luminescence of $\text{Zn}[\text{B}_2(\text{SO}_4)_4]: 1\% \text{Mn}^{2+}$



**Figure S11.** Photoluminescence excitation spectra of  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]: 1\% \text{Mn}^{2+}$  at room temperature under detection of the host-related luminescence at 460 nm (a) and 700 nm (b). The arrows depict the 290 nm excitation, which was chosen as a compromise for an excitation wavelength in the main manuscript as it shows low overlap with both host-excitation bands.

## Decay curves of the intrinsic emission bands of $\text{Zn}[\text{B}_2(\text{SO}_4)_4]: 1\% \text{Mn}^{2+}$

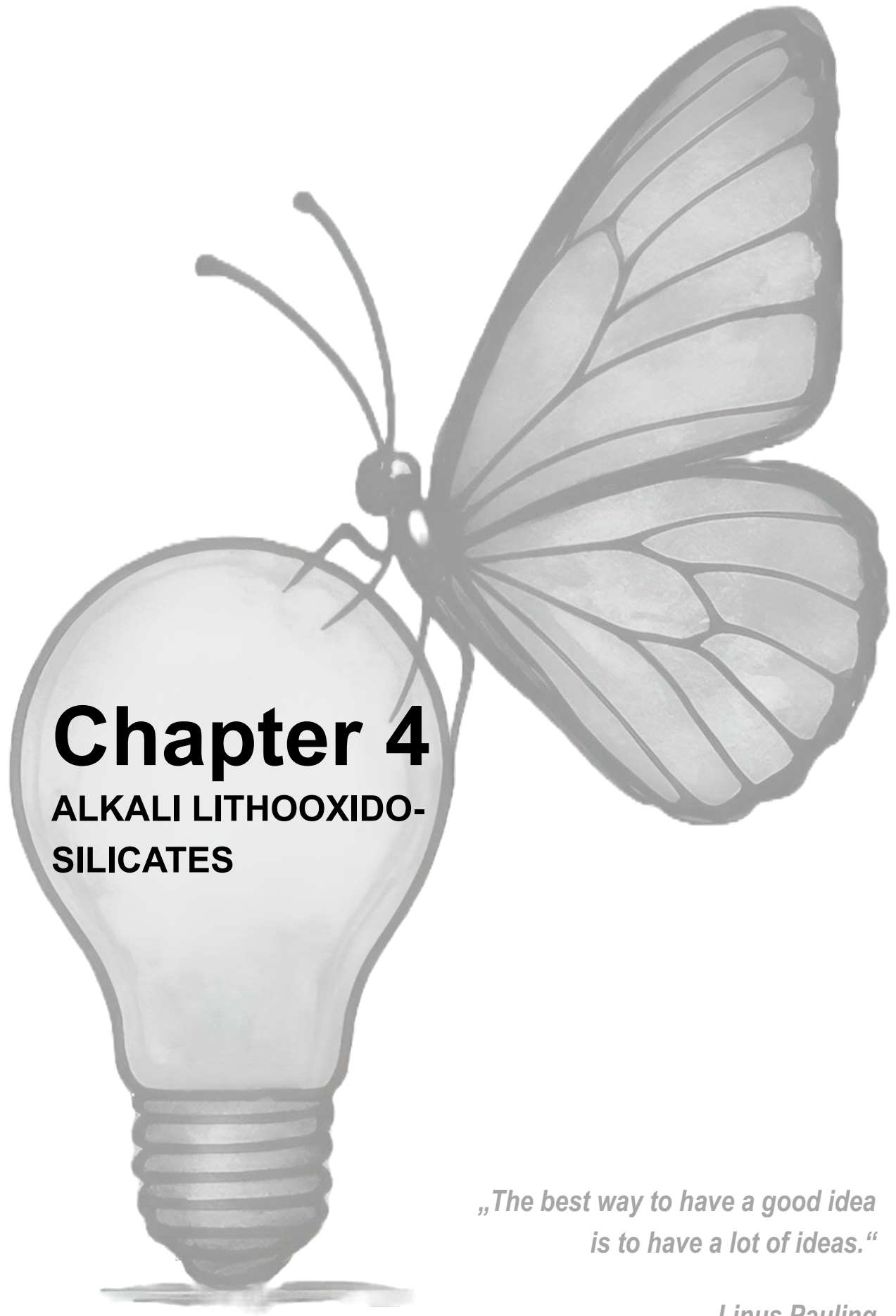


**Figure S12.** Photoluminescence decay curves ( $\lambda_{\text{ex}} = 290 \text{ nm}$ ) of the host-related luminescence at 460 nm (a) and 700 nm (b) recorded at room temperature.

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# **Chapter 4**

## **ALKALI LITHOOXIDO- SILICATES**

*„The best way to have a good idea  
is to have a lot of ideas.“*

*–Linus Pauling*

### **Mn<sup>2+</sup>-Activated Alkali Lithooxidosilicate Phosphors as Sustainable Alternative White-Light Emitters**

#### **Full citation:**

L. M. Träger, J. I. Ekeya, A. Liesenfeld, M. Wiczorek, H. Huppertz, M. Suta, *Angew. Chem. Int. Ed.* **2025**, 64, e202504078. <https://doi.org/10.1002/anie.202504078>

Also published in German:

### **Mn<sup>2+</sup>-aktivierte Alkalilithooxidosilikat-Leuchtstoffe als nachhaltige alternative Weißlichtemitter**

#### **Full citation:**

L. M. Träger, J. I. Ekeya, A. Liesenfeld, M. Wiczorek, H. Huppertz, M. Suta, *Angew. Chem.* **2025**, 137 (25), e202504078. <https://doi.org/10.1002/ange.202504078>

#### **Author contributions:**

**L. M. Träger** discovered the possibility of Mn<sup>2+</sup>-doping for the covered class of compounds and optimized the synthesis. He synthesized four of the seven investigated compounds, checked the phase purity by X-ray powder diffraction and Rietveld refinement, performed the photoluminescence measurements, evaluated and visualized the data, performed the calculations and wrote the major part of the manuscript. He also prepared the table of contents graphic and the German translation of the manuscript. **J. I. Ekeya**, **A. Liesenfeld** and **M. Wiczorek** synthesized the remaining three compounds and acquired spectroscopic data under the supervision and instruction of L. M. Träger and M. Suta. **H. Huppertz** reviewed the manuscript and contributed to the project with his expertise for the investigated class of compounds. **M. Suta** supervised the project, acquired funding and assisted in the data interpretation. He also conceptualized, reviewed and finalized the manuscript.



# Mn<sup>2+</sup>-Activated Alkali Lithooxidosilicate Phosphors as Sustainable Alternative White-Light Emitters

Lukas Maximilian Träger, Judith Ifeoma Ekeya, Annika Liesenfeld, Marc Wieczorek, Hubert Huppertz,\* and Markus Suta\*

**Abstract:** Eu<sup>2+</sup>-activated alkali lithooxidosilicates have emerged as promising candidates for narrow-band cyan and green-emitting phosphors for human-centered lighting. Despite the vivid research on Eu<sup>2+</sup>-activated alkali lithooxidosilicates, little to nothing is known about the possible luminescence with other activator ions than Eu<sup>2+</sup>. The more abundant transition metal ion Mn<sup>2+</sup> is a potential alternative emitter with tunable emission over the visible spectral range. Mn<sup>2+</sup>-activated alkali lithooxidosilicates show two emission bands in the green and red spectral range, respectively, making them intriguing candidates for one-component phosphor-converted white light-emitting diodes. A total of seven Mn<sup>2+</sup> activated compounds were prepared to elucidate possible trends. The results show that the ratio between green and red emission correlates to the size of the available activator sites and is easily controlled by the composition of the alkali lithooxidosilicate host compounds. Temperature-dependent luminescence studies reveal that thermal quenching occurs slightly above room temperature for those compounds, which may be connected to the comparably low band gaps for silicates ( $E_g < 6$  eV) and a consequent thermal ionization of excited electrons into the conduction band. Overall, this study comprises the first class of compounds with efficient tailored white-light emission based on Mn<sup>2+</sup> within one host compound.

## Introduction

The quest for new, sustainable light sources is considered one major task to reduce human-centered CO<sub>2</sub> emissions. In recent years, phosphor-converted light-emitting diodes (pc-LEDs) have emerged as promising candidates in this field as they combine low energy consumption and wide color tunability. Pc-LEDs are usually constructed from an efficient blue-emitting In<sub>1-x</sub>Ga<sub>x</sub>N chip, coated with one or more layers of phosphor materials, that convert the blue excitation radiation to light of longer wavelength.<sup>[1–5]</sup> Today, an overwhelming number of phosphors for application in pc-LEDs were introduced, including famous commercialized materials like Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup> (YAG:Ce<sup>3+</sup>/λ<sub>em</sub> = 532 nm),<sup>[6,7]</sup> M<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (M = Ca, Sr, Ba/λ<sub>em</sub> = 580–610 nm),<sup>[8–10]</sup>

CaAlSiN<sub>3</sub>:Eu<sup>2+</sup> (λ<sub>em</sub> = 660 nm),<sup>[11]</sup> K<sub>2</sub>SiF<sub>6</sub>:Mn<sup>4+</sup> (λ<sub>em</sub> = 620 nm),<sup>[12]</sup> and β-SiAlON:Eu<sup>2+</sup> (λ<sub>em</sub> = 535 nm).<sup>[13]</sup> A particularly prominent emerging class of efficient phosphors are Eu<sup>2+</sup>-activated UC<sub>4</sub>C<sub>4</sub>-type oxido- or nitridosilicates/-aluminates, which have recently attracted much attention due to their (ultra-)narrow emission bands with full widths at half maximum (FWHMs) below 2500 cm<sup>-1</sup> at room temperature and amazing color-tunability over the whole visible spectral range. Prominent representatives of this material class are Sr[LiAl<sub>3</sub>N<sub>4</sub>]:Eu<sup>2+</sup> (SLA:Eu<sup>2+</sup>/λ<sub>em</sub> = 654 nm/FWHM = 1180 cm<sup>-1</sup>),<sup>[14]</sup> M[Mg<sub>2</sub>Al<sub>2</sub>N<sub>4</sub>]:Eu<sup>2+</sup> (M = Ca, Sr, Ba/λ<sub>em</sub> = 607–666 nm/FWHM = 1820–2330 cm<sup>-1</sup>),<sup>[15]</sup> Sr[Mg<sub>3</sub>SiN<sub>4</sub>]:Eu<sup>2+</sup> (λ<sub>em</sub> = 615 nm/FWHM = 1170 cm<sup>-1</sup>),<sup>[16,17]</sup> Sr[Li<sub>2</sub>Al<sub>2</sub>O<sub>2</sub>N<sub>2</sub>]:Eu<sup>2+</sup> (SALON:Eu<sup>2+</sup>/λ<sub>em</sub> = 614 nm/FWHM = 1290 cm<sup>-1</sup>)<sup>[18]</sup> and blue to green emitting alkali lithooxidosilicates like Na[Li<sub>3</sub>SiO<sub>4</sub>]:Eu<sup>2+</sup> (λ<sub>em</sub> = 469 nm/FWHM = 1460 cm<sup>-1</sup>),<sup>[19]</sup> RbLi[Li<sub>3</sub>SiO<sub>4</sub>]<sub>4</sub>:Eu<sup>2+</sup> (λ<sub>em</sub> = 530 nm/FWHM = 1500 cm<sup>-1</sup>),<sup>[20,21]</sup> RbKLi<sub>2</sub>[Li<sub>3</sub>SiO<sub>4</sub>]:Eu<sup>2+</sup> (λ<sub>em</sub> = 474 nm, 532 nm/FWHM = 1100 cm<sup>-1</sup>, 1560 cm<sup>-1</sup>),<sup>[22]</sup> and K<sub>1.6</sub>Na<sub>2.1</sub>Li<sub>0.3</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>4</sub>:Eu<sup>2+</sup> (λ<sub>em</sub> = 486 nm/FWHM = 890 cm<sup>-1</sup>).<sup>[23,24]</sup> Most recently, the solid solution Sr[Li<sub>3</sub>(Al<sub>1-x</sub>Ga<sub>x</sub>)O<sub>4</sub>] was discovered, being the first oxolithoaluminates and -gallates with UC<sub>4</sub>C<sub>4</sub>-related structure (λ<sub>em</sub> = 554 nm/FWHM = 1589 cm<sup>-1</sup> (x = 0), λ<sub>em</sub> = 572 nm/FWHM = 1446 cm<sup>-1</sup> (x = 1)).<sup>[25,26]</sup> Their formidable luminescence characteristics are closely related to the structural rigidity of the condensed anionic backbone that is made up from vertex- and edge-sharing [MX<sub>4</sub>]-tetrahedra (M = Li, Mg, Al, Si; X = O, N) forming *vierer*-ring cation channels. The larger alkali or alkaline earth cations are located within these channels, occupying cuboidally coordinated sites.

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Despite the success of  $\text{Eu}^{2+}$ -activated  $\text{UCr}_4\text{C}_4$ -typed phosphors, reports on the introduction of other activator ions into  $\text{UCr}_4\text{C}_4$ -typed materials are scarce and solely focused on trivalent lanthanides (typically  $\text{Ce}^{3+}$ ).<sup>[16,27–31]</sup> In view of more sustainable and abundant emitters, the  $3d^5$  high spin (HS) configured transition metal ion  $\text{Mn}^{2+}$  is a competitive alternative. The less extended nature of the 3d orbitals of  $\text{Mn}^{2+}$  compared to the 5d orbitals of  $\text{Eu}^{2+}$  could formally result in even narrower emission bands. Upon tetrahedral coordination by  $\text{O}^{2-}$  ligands, it can show thermally inert, narrow green emission, often with quenching temperatures above 600 K.<sup>[32]</sup> Examples include  $\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 525 \text{ nm/FWHM} = 1270 \text{ cm}^{-1}$ ),<sup>[33]</sup>  $\text{ZnAl}_2\text{O}_4:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 510 \text{ nm/FWHM} = 820 \text{ cm}^{-1}$ ),<sup>[32,34]</sup>  $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 525 \text{ nm/FWHM} = 1530 \text{ cm}^{-1}$ ),<sup>[35,36]</sup>  $\text{BaZnAl}_{10}\text{O}_{17}:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 516 \text{ nm/FWHM} = 1170 \text{ cm}^{-1}$ ),<sup>[37]</sup>  $\text{Zn}_4\text{B}_6\text{O}_{13}:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 540 \text{ nm/FWHM} = 1100 \text{ cm}^{-1}$ ).<sup>[38]</sup> In corresponding cubic or octahedral ligand fields, the  $\text{Mn}^{2+}$ -related emission shifts toward the red spectral range as the lowest excited  ${}^4\text{T}_{1(\text{g})}({}^4\text{G})$  state becomes stabilized due to occupation of the  $t_{2\text{g}}$ -type 3d orbitals by an additional electron. The stronger ligand field and necessary vibronic coupling to break the parity selection rule also results in higher FWHMs for octahedrally or cubically coordinated  $\text{Mn}^{2+}$  than for the case of tetrahedral coordination. Representative examples for luminescent compounds with octahedrally coordinated  $\text{Mn}^{2+}$  are  $\text{MgSiO}_3:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 661 \text{ nm/FWHM} \approx 2100 \text{ cm}^{-1}$ ),<sup>[39]</sup>  $\text{Mg}_4\text{Ta}_2\text{O}_9:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 670 \text{ nm/FWHM} \approx 2000 \text{ cm}^{-1}$ ),<sup>[36,40]</sup>  $\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 620 \text{ nm/FWHM} = 1650 \text{ cm}^{-1}$ )<sup>[41]</sup> or  $\alpha\text{-Na}_2\text{CaMg}(\text{PO}_4)_2:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 620 \text{ nm/FWHM} = 2100 \text{ cm}^{-1}$ ).<sup>[42]</sup>  $\text{Mn}^{2+}$  usually occupies Mg or Zn sites as they match in terms of ionic radius and charge. However,  $\text{Mn}^{2+}$  is also known to substitute sites occupied by aliovalent ions like  $\text{Al}^{3+}$ ,<sup>[43–48]</sup>  $\text{Sc}^{3+}$ ,<sup>[49]</sup> or  $\text{Li}^{+}$ <sup>[44,50–52]</sup> and may therefore be considered an activator ion in alkali lithooxidosilicates as well. Especially Li sites should be well suited for  $\text{Mn}^{2+}$  substitution as its ionic radius of 59 pm is de facto identical with those of  $\text{Mg}^{2+}$  (57 pm) and  $\text{Zn}^{2+}$  (60 pm) in tetrahedral coordination.<sup>[53]</sup> This idea is also promoted by the known capability of most alkali lithooxidosilicates to compensate a significant amount of charge-defects, e.g. caused by aliovalent  $\text{Eu}^{2+}$  activation or  $\text{Si}^{4+}$  deficit.<sup>[19,54]</sup> Given the comparably small size of  $\text{Mn}^{2+}$ , a higher coordination number than six for this ion is rather uncommon, as also suggested by Pauling's radius ratio rule. Such an example is  $\text{CaF}_2:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 495 \text{ nm/FWHM} \approx 1640 \text{ cm}^{-1}$ ) with a comparably high quenching temperature of 580 K related to the large band gap of the compound.<sup>[55,56]</sup> In this work, we follow up on these ideas and investigate the successful class of  $\text{UCr}_4\text{C}_4$ -type alkali lithooxidosilicates as possible host compounds for  $\text{Mn}^{2+}$ . The structures of these compounds comprise both tetrahedrally coordinated sites for the  $\text{Li}^{+}$  ions and cuboidally coordinated sites for the larger alkali cations that both could be potentially occupied by  $\text{Mn}^{2+}$ . This is not only interesting from a fundamental perspective. In fact, the presence of two potential activator sites that give rise to both green and red emission could lead to warm white light-emitting phosphors without the need of mixing two different compounds, which

is an additional benefit to a more sustainable approach to phosphors.

A series of seven  $\text{Mn}^{2+}$ -activated alkali lithooxidosilicates was prepared to gain a better understanding of their luminescence properties and to reveal possible trends. We therefore considered exclusively those known compounds featuring cation ordering and excluded those with complex disorders (e.g.,  $\text{K}_{1.6}\text{Na}_{2.1}\text{Li}_{0.3}[\text{Li}_3\text{SiO}_4]_4$  or  $\text{CsKNaLi}[\text{Li}_3\text{SiO}_4]_4$ ) as a defined coordination environment is crucial for our analysis.<sup>[24,57]</sup>

## Results and Discussion

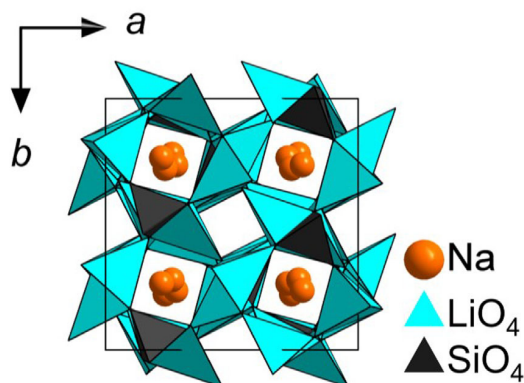
### Structural Features

The alkali lithooxidosilicates are structurally derived from the  $\text{UCr}_4\text{C}_4$  structure type ( $I4/m$ , no. 87).<sup>[58,59]</sup> Their structure is composed of corner and edge sharing  $[\text{LiO}_4]$ - and  $[\text{SiO}_4]$ -tetrahedra, which are arranged in *vierer-ring* channels. The larger alkali metal ions ( $\text{Na}^+$ - $\text{Cs}^+$ ) are situated within these channels, occupying sites with distorted cuboidal symmetry. In some cases,  $\text{Li}^+$  is not only part of the tetrahedral backbone but also incorporated within these channels. However, due to the small size of these cations, cubic coordination is avoided and the  $\text{Li}^+$  ions are displaced in an off-centered fashion to allow square-planar, fourfold coordination by  $\text{O}^{2-}$  ligands.<sup>[22,57,60,61]</sup> There are only two known compounds in which all channels are filled with exclusively one sort of alkaline metal ion:  $\text{Na}[\text{Li}_3\text{SiO}_4]$  ( $I4_1/a$ , no. 88) and  $\text{K}[\text{Li}_3\text{SiO}_4]$  ( $P\bar{1}$ , no. 2).<sup>[59,62]</sup> Noticeably, the exchange of  $\text{Na}^+$  for the bigger  $\text{K}^+$  leads to a significant symmetry lowering, which can be related to lattice distortions. Any other alkali lithooxidosilicates contain two different channel types, with one primarily accommodating smaller cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ) and the other hosting larger cations ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ). Complex disordering for the  $\text{Li}^+$  ions is observed if these ions share a channel with larger cations as  $\text{Li}^+$  prefers the sites with approximately square-planar coordination, whereas the heavier alkaline metal ions occupy the distorted cubic sites.<sup>[57,61]</sup> However, a full occupation of both sites is not feasible due to a too short hypothetical  $\text{Li}^+ \leftrightarrow \text{A}^+$  distance (where  $\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ). A representative depiction of the  $\text{UCr}_4\text{C}_4$ -typed alkali lithooxidosilicate  $\text{Na}[\text{Li}_3\text{SiO}_4]$  is given in Figure 1.

Regarding the incorporation of possible activator ions, it is well-known that  $\text{Eu}^{2+}$  occupies exclusively the cuboidally coordinated positions due to its relatively large ionic radius.  $\text{Mn}^{2+}$  on the other hand is much smaller and may therefore also occupy the tetrahedral  $\text{Li}^+$  positions. Table 1 summarizes the composition and space groups of the phosphors investigated in this study.

### Luminescence Spectroscopy

All investigated  $\text{Mn}^{2+}$ -activated alkali lithooxidosilicates ( $\text{Mn}^{2+}$  content 0.1–0.25 mol%) presented in this work show two distinguishable emission bands located at 515–530 and 610–635 nm, respectively. This indicates that  $\text{Mn}^{2+}$



**Figure 1.** Structural depiction of Na[Li<sub>3</sub>SiO<sub>4</sub>] (view along crystallographic *c* direction) as a representative example of a UCr<sub>4</sub>C<sub>4</sub>-type compound.

**Table 1:** Composition and space groups of the investigated Mn<sup>2+</sup>-activated alkali lithooxidosilicates.

| Compound                                                                                    | Space group                      | Reference |
|---------------------------------------------------------------------------------------------|----------------------------------|-----------|
| RbNa <sub>3</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.25% Mn <sup>2+</sup> | <i>I4/m</i> (no. 87)             | [57]      |
| Na[Li <sub>3</sub> SiO <sub>4</sub> ]: 0.1% Mn <sup>2+</sup>                                | <i>I4<sub>1</sub>/a</i> (no. 88) | [62]      |
| NaK <sub>7</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>8</sub> : 0.1% Mn <sup>2+</sup>   | <i>I4<sub>1</sub>/a</i> (no. 88) | [19, 63]  |
| CsKNa <sub>2</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.2% Mn <sup>2+</sup> | <i>I4/m</i> (no. 87)             | [57]      |
| RbKLi <sub>2</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.1% Mn <sup>2+</sup> | <i>I4/m</i> (no. 87)             | [22]      |
| K[Li <sub>3</sub> SiO <sub>4</sub> ]: 0.1% Mn <sup>2+</sup>                                 | <i>P1</i> (no. 2)                | [59]      |
| RbNa[Li <sub>3</sub> SiO <sub>4</sub> ] <sub>2</sub> : 0.17% Mn <sup>2+</sup>               | <i>C2/m</i> (no. 12)             | [57]      |

occupies two crystallographically independent sites with different coordination number (CN) based on the dependence of the energy of the  ${}^4T_{1(g)}({}^4G) \rightarrow {}^6A_{1(g)}({}^6S)$  transition of Mn<sup>2+</sup> on the ligand field strength. In general, green emission is observed from Mn<sup>2+</sup> in tetrahedral O<sup>2-</sup>-based coordination, whereas coordination numbers of six or eight lead to a red emission. We therefore assign the green emission to Mn<sup>2+</sup> occupying the tetrahedrally coordinated Li sites and the red emission to Mn<sup>2+</sup> occupying the cuboidally coordinated alkali sites. This is also in agreement with the width of the emission bands as the comparably large cuboidal sites lead to some flexibility in the Mn–O bonds. The tetrahedrally coordinated Li sites, on the other hand, are particularly small. Any change in the Mn–O distance is thus sterically already limited generally resulting in a comparably narrow emission band. In addition, tetrahedral coordination of Mn<sup>2+</sup> generally leads to barely any dependence of the energy of the  ${}^4T_1({}^4G)$  state on the ligand field strength according to the Tanabe–Sugano diagram for a 3d<sup>5</sup> HS ion (Figure S8). This is also indicated by the comparably narrow lowest energetic excitation bands, generally observed for tetrahedrally coordinated Mn<sup>2+</sup>.<sup>[64,65]</sup> However, the intensity ratio of these two bands at both 77 K and room temperature differs drastically, showcasing different site occupation preferences of Mn<sup>2+</sup> within the investigated compounds. If random occupation of both Li and Na sites is assumed based on the lacking ligand field stabilization energy for a d<sup>5</sup> HS ion, a more dominant green emission is to be expected as there are more Li sites than Na sites in any of the regarded UCr<sub>4</sub>C<sub>4</sub>-

type alkali lithooxidosilicates. Nevertheless, most considered Mn<sup>2+</sup>-activated alkali lithooxidosilicates in this work show intense red emission. This may indicate a general preference of Mn<sup>2+</sup> to occupy the slightly larger Na sites. Another possible explanation for this observation is non-radiative Mn<sup>2+</sup><sub>(tetrah.)</sub> → Mn<sup>2+</sup><sub>(cubic)</sub> energy transfer. This, however, seems less likely since the critical distance of the energy transfer for acceptors with strongly forbidden transitions is generally low.<sup>[66]</sup> Moreover, the restriction by both the spin and Laporte selection rule for the  ${}^4T_{1(g)}({}^4G) \leftarrow {}^6A_{1(g)}({}^6S)$  transition of the cuboidally coordinated Mn<sup>2+</sup> ions implies a Dexter-type energy transfer with an exponential distance dependence.<sup>[67]</sup> A possible Mn<sup>2+</sup><sub>(tetrah.)</sub> → Mn<sup>2+</sup><sub>(cubic)</sub> energy transfer could be identified by concentration-dependent measurements within future experiments and was not in the scope of this work. Figure 2 compares the emissions of the investigated samples upon 450 nm excitation at 83 and 283 K. The spectra clearly reveal noticeable differences in the intensity ratio between the green and red emission dependent on the composition of the alkali lithooxidosilicate hosts.

Generally, most samples show a predominantly red emission, which is rather surprising if the size mismatch between Na<sup>+</sup> (*r*<sub>Na<sup>+</sup></sub> = 1.18 Å) and Mn<sup>2+</sup> (*r*<sub>Mn<sup>2+</sup></sub> = 0.96 Å) according to the Shannon radii is considered.<sup>[53]</sup> This might be due to electrostatic repulsion by nearby cations, thereby leading to a preferential occupation of bigger voids with larger mutual cation–cation distances by the higher charged Mn<sup>2+</sup> ions. However, this apparent mismatch motivated us to have a closer look on the mean effective ionic radii (MEFIR) of the available substitution sites within the investigated compounds. These were calculated in an iterative process starting with M–O distances derived from single-crystal X-ray diffraction data.<sup>[68]</sup> The results are summarized and compared in Table 2, showcasing some clear correlations of the emission profiles and the MEFIR of the possible activator sites. First, if effectively smaller Na sites are available, the red component of the emission is dominant, e.g., in Na[Li<sub>3</sub>SiO<sub>4</sub>]:Mn<sup>2+</sup> (MEFIR(Na<sup>+</sup>) = 111.6 pm) and RbNa<sub>3</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>4</sub>:Mn<sup>2+</sup> (MEFIR(Na<sup>+</sup>) = 115.4 pm). On the other hand, the absence of smaller Na sites enhances green emission, e.g., in K[Li<sub>3</sub>SiO<sub>4</sub>]:Mn<sup>2+</sup> (MEFIR(K<sup>+</sup>) = 127.6 pm), RbNa[Li<sub>3</sub>SiO<sub>4</sub>]<sub>2</sub>:Mn<sup>2+</sup> (MEFIR(Na<sup>+</sup>) = 118.5 pm) and RbKLi<sub>2</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>4</sub>:Mn<sup>2+</sup> (MEFIR(K<sup>+</sup>) = 142.4 pm). In addition, the red emission band is shifted to longer wavelengths for smaller Na sites. This observation is expected given a stronger ligand field acting at smaller Na sites that should result in a stabilization of the excited  ${}^4T_{1(g)}({}^4G)$  state. Another possible explanation for a red-shifted emission of Mn<sup>2+</sup> could be an increased degree of covalency in the Mn–O bond.<sup>[69]</sup> However, this is not the case for the Mn<sup>2+</sup>-activated alkali lithooxidosilicates as the location of the ligand field-independent  ${}^4A_{1(g)}, {}^4E_{(g)}({}^4G) \leftrightarrow {}^6A_{1(g)}({}^6S)$  transition at 427–430 nm barely changes among the investigated compounds (see Figure S11), which usually reacts sensitively to subtle changes in the interelectronic repulsion and thus, the covalency of the metal–ligand bond.<sup>[70]</sup>

However, those compounds with exceptionally large activation sites (MEFIR ≥ 122 pm) derive from both trends as they show surprisingly intense red emission. We therefore

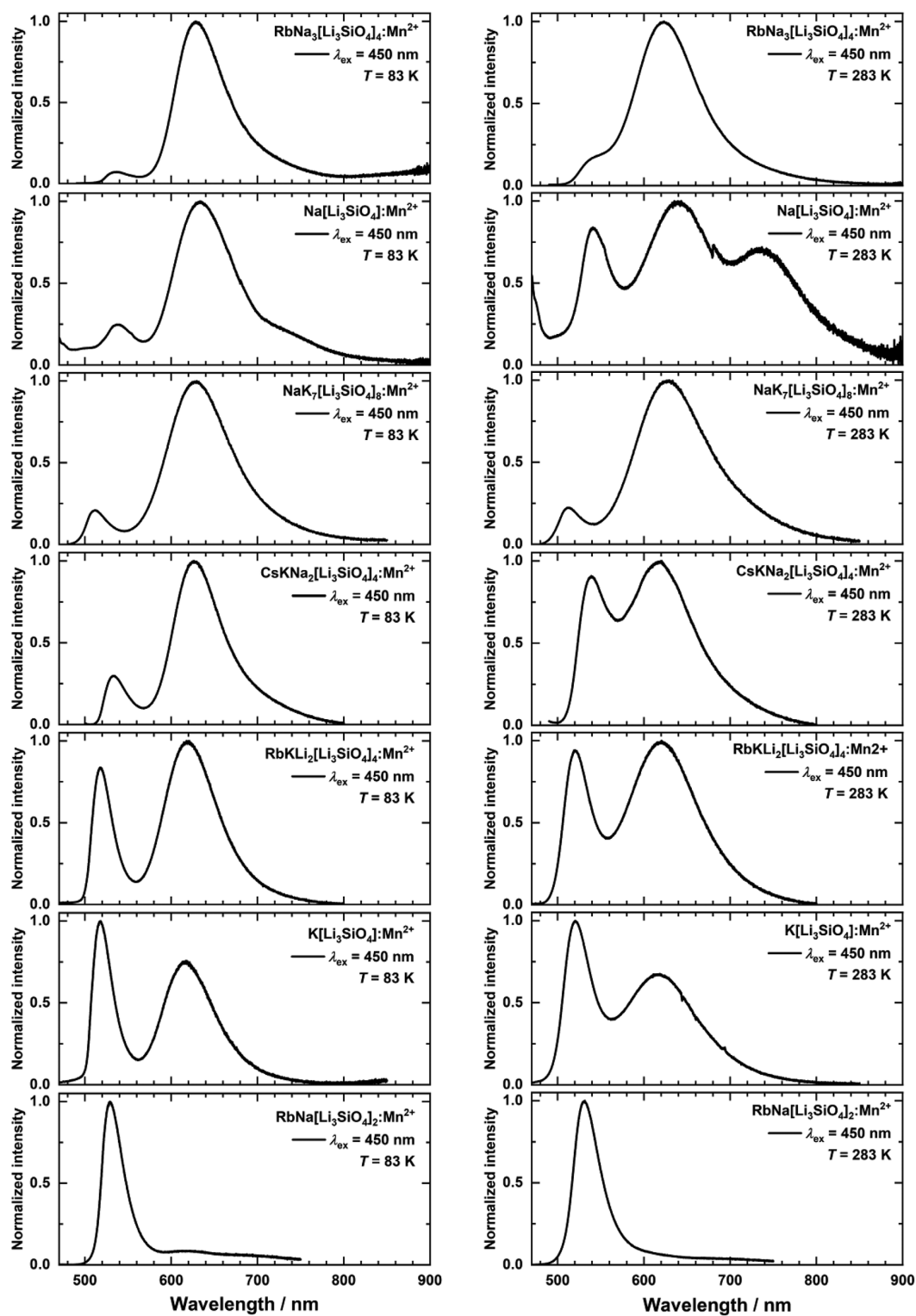
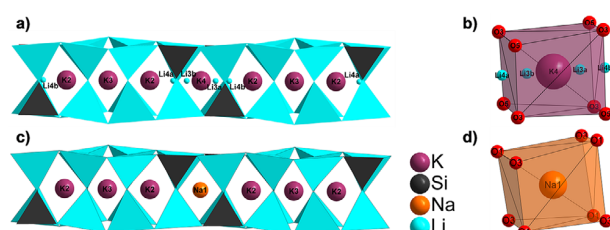


Figure 2. Photoluminescence emission spectra of Mn<sup>2+</sup>-activated alkali lithooxidosilicates at 83 K (left) and 283 K (right).



**Table 2:** Mean effective ionic radii (MEFIR) of the smallest channel sites of the investigated alkali lithooxidosilicates as well as characteristic luminescence properties. Decay times are amplitude-weighted average values derived from triexponential fit functions. The quenching temperatures  $T_{1/2}$  were estimated from temperature dependent decay curves.

| Compound                                                                                    | MEFIR (pm)                 | FWHM (cm <sup>-1</sup> )<br>( $T = 83$ K)<br>green/red | $\lambda_{em}$ (83 K)<br>(nm)<br>green/red | $\tau_{green}$ (ms)<br>( $T = 83$ K)<br>green/red | Stokes shift (cm <sup>-1</sup> )<br>( $T = 83$ K) green/red | $T_{1/2}$ (K)<br>green/red |
|---------------------------------------------------------------------------------------------|----------------------------|--------------------------------------------------------|--------------------------------------------|---------------------------------------------------|-------------------------------------------------------------|----------------------------|
| RbNa <sub>3</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.25% Mn <sup>2+</sup> | 132.0 (Na1)<br>115.4 (Na2) | 830/1670                                               | 536/629                                    | 3.5/15.5                                          | 2400/3130                                                   | –/470                      |
| Na[Li <sub>3</sub> SiO <sub>4</sub> ]: 0.1% Mn <sup>2+</sup>                                | 111.6 (Na1)                | 940/2070                                               | 538/634                                    | 3.2/5.5                                           | 1930/3830                                                   | 380/325                    |
| NaK <sub>7</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>8</sub> : 0.1% Mn <sup>2+</sup>   | 122.0 (Na1)                | 930/2120                                               | 511/629                                    | 5.1/4.2                                           | 1190/3040                                                   | 330/375                    |
| CsKNa <sub>2</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.2% Mn <sup>2+</sup> | 117.0 (Na1)<br>145.8 (K1)  | 920/1790                                               | 533/626                                    | 4.4/16.5                                          | 2270/3220                                                   | 585/500                    |
| RbKLi <sub>2</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.1% Mn <sup>2+</sup> | 142.4 (K1)                 | 1060/1920                                              | 518/620                                    | 5.3/4.3                                           | 1700/3920                                                   | 280/355                    |
| K[Li <sub>3</sub> SiO <sub>4</sub> ]: 0.1% Mn <sup>2+</sup>                                 | 127.6 (K4)                 | 1070/1910                                              | 518/616                                    | 5.7/4.1                                           | 1700/3880                                                   | 320/370                    |
| RbNa[Li <sub>3</sub> SiO <sub>4</sub> ] <sub>2</sub> : 0.17% Mn <sup>2+</sup>               | 118.5 (Na1)                | 890/–                                                  | 529/610–620                                | 5.0/9.7                                           | 2050/–                                                      | 490/–                      |



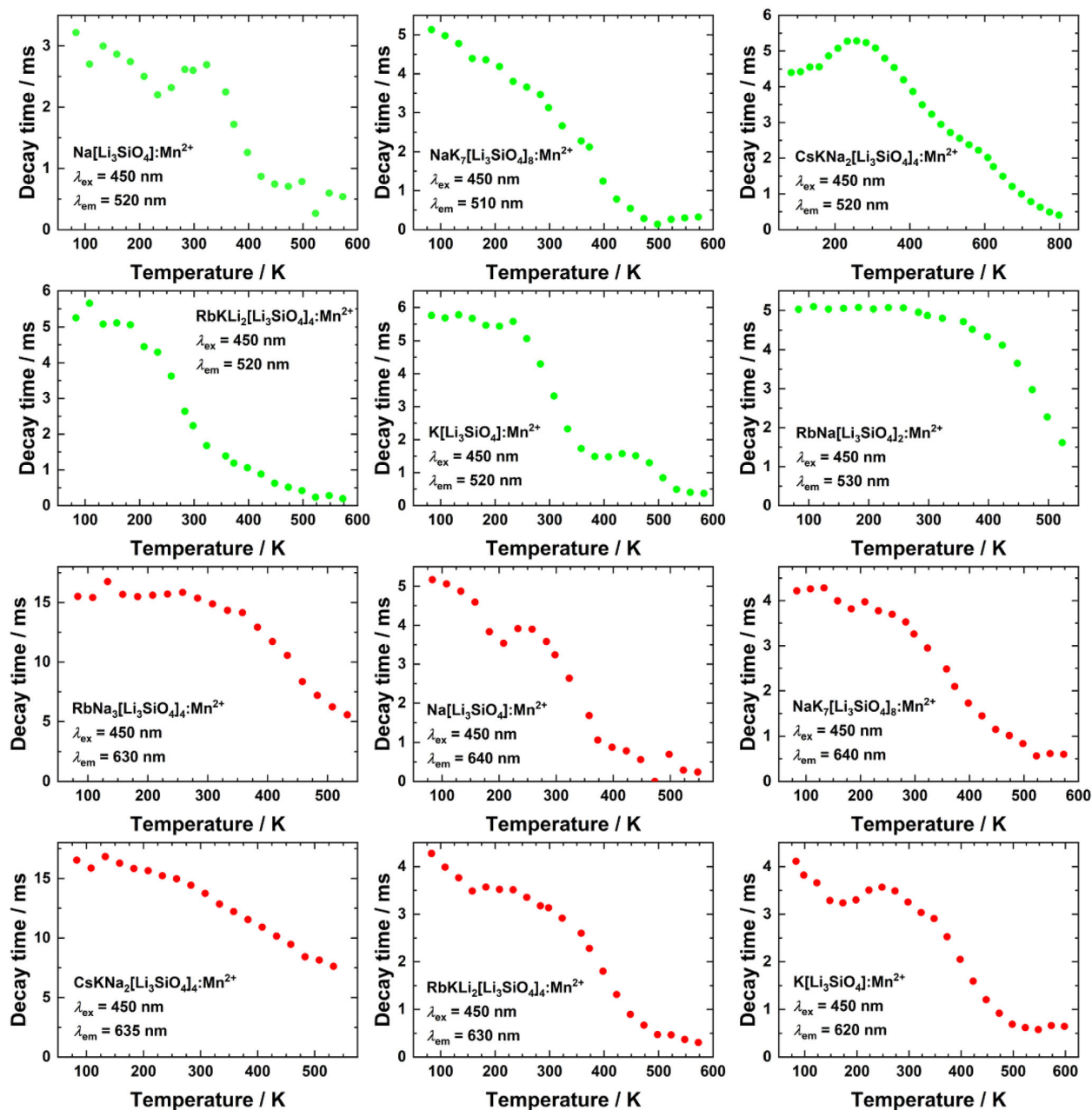
**Figure 3.** View perpendicular to the *vierer*-ring channels and depiction of the cations in the cuboidal voids of LiK<sub>7</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>8</sub> (a+b) and NaK<sub>7</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>8</sub> (c+d). The Li<sub>3</sub>, Li<sub>4</sub> and K<sub>4</sub> sites in a) and b) are only partially occupied.

assume that Mn<sup>2+</sup> occupies a site that deviates from the cuboidally coordinated Na or K sites. This phenomenon is also well known from Mn<sup>2+</sup>-activated fluorite-type compounds, in which the local environment of Mn<sup>2+</sup> is formally strictly cubic only for CaF<sub>2</sub> ( $r_{Ca^{2+}} = 112$  pm) and CdF<sub>2</sub> ( $r_{Cd^{2+}} = 110$  pm).<sup>[56]</sup> Diverging coordination geometries with lower symmetry in SrF<sub>2</sub> ( $r_{Sr^{2+}} = 126$  pm), PbF<sub>2</sub> ( $r_{Pb^{2+}} = 129$  pm) and BaF<sub>2</sub> ( $r_{Ba^{2+}} = 142$  pm) were derived from electron paramagnetic resonance (EPR) data and luminescence spectra, indicating an off-centered positioning of the Mn<sup>2+</sup> ion.<sup>[71–74]</sup> In the alkali lithooxidosilicates, a similar behavior is known from the Li<sup>+</sup> ions, which is comparable in size to Mn<sup>2+</sup> ( $r_{Li^+} = 92$  pm,  $r_{Mn^{2+}} = 96$  pm).<sup>[53]</sup> Single-crystal X-ray diffraction data showed that Li<sup>+</sup> (if incorporated into the channel) seemingly avoids the cubic sites and occupies sites with square planar symmetry or off-centered positions without inversion symmetry, respectively.<sup>[22,57,60,61]</sup> A particularly noteworthy example are the otherwise isotypic alkali lithooxidosilicates MK<sub>7</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>8</sub> ( $M = Li, Na$ ), where  $M = Na$  occupies the center of the distorted cubic position and  $M = Li$  moves to an off-centered position (see Figure 3).<sup>[19,61]</sup> Arguably, Mn<sup>2+</sup> is expected to preferentially occupy the Li sites given the stronger similarity in the ionic radii compared to the difference in ionic radii of eightfold coordinated Mn<sup>2+</sup> and Na<sup>+</sup>.

Figure 4 depicts the time-resolved luminescence data of the regarded Mn<sup>2+</sup>-activated alkali lithooxidosilicates. The green emission in the range of 520–530 nm for each sample is characterized by decay times in the order of 3–6 ms, which is typical for the spin-forbidden 3d<sup>5</sup> (HS)  $\leftrightarrow$  3d<sup>5</sup> (HS)

transitions of tetrahedrally coordinated Mn<sup>2+</sup> due to a relieve in the parity selection rule.<sup>[75,76]</sup> However, the decay times of most red components (Table 1 and Figure 4) are significantly larger ( $\tau \sim 10$ –20 ms) and thus, rather comparable to values known from Mn<sup>2+</sup> in a centrosymmetric environment, like octahedrally or cubically coordinated Mn<sup>2+</sup> ( $\tau \sim 50$ –200 ms at 77 K).<sup>[56,77]</sup> However, the cuboidally coordinated sites in any of the herein investigated compounds are distorted and thus, the parity restrictions of the 3d<sup>5</sup> HS  $\leftrightarrow$  3d<sup>5</sup> HS transitions are weakened. In ultimate consequence, the observed decay time is in between values known from tetrahedrally and undistortedly cubically coordinated Mn<sup>2+</sup>. In addition to selection rules affecting the radiative decay, the total decay times might be shortened due to additional nonradiative decay processes such as thermally induced crossover or thermal ionization via the conduction band with subsequent charge carrier trapping. The latter mechanism is also known to correlate with the bandgap of the host compound, due to photoionization as a major quenching mechanism.<sup>[32]</sup> The relatively small bandgap of alkali lithooxidosilicates of  $\sim 5.5$ –6.0 eV may thus also promote a low thermal quenching temperature.<sup>[21,78]</sup> In Na[Li<sub>3</sub>SiO<sub>4</sub>]:Mn<sup>2+</sup>, the cuboidal symmetry at the Na sites is particularly strongly distorted resulting in an unusually short decay time ( $\tau = 5.2$  ms) at 83 K. The same general trend is observed in alkali lithooxidosilicates with uncommonly large available cuboidally coordinated cation sites in the *vierer*-ring channels (NaK<sub>7</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>8</sub>, MEFIR = 122.0 pm), RbKLi<sub>2</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>4</sub>, MEFIR = 142.4 pm and K[Li<sub>3</sub>SiO<sub>4</sub>], MEFIR = 127.6 pm). The red luminescence of Mn<sup>2+</sup> in those compounds is characterized by decay times in the order of  $\sim 4$ –5 ms.

According to temperature-dependent luminescence measurements (Figure S9), most of the regarded Mn<sup>2+</sup>-activated alkali lithooxidosilicates show the highest emission intensity in the range of 200 K to 300 K, which is rather unexpected. It may, however, be explained by the participation of trap states that are emptied at a certain temperature and, thus, contribute to the excitation of Mn<sup>2+</sup>, which is also known from defect-rich halides like Rb<sub>4</sub>CdCl<sub>6</sub>:Mn<sup>2+</sup>.<sup>[79]</sup> Such an interpretation complies with the necessary presence of charge-compensating vacancies or defects based on the presented aliovalent activation strategy in the alkali lithooxidosilicates. Future experiments will be necessary to elucidate



**Figure 4.** Temperature-dependent photoluminescence decay times of  $\text{Mn}^{2+}$ -activated alkali lithooxidosilicates. Decay times are amplitude-weighted average values derived from triexponential fit functions.

the impact of adjacent vacancies/defects. Another aspect that may contribute to the observed temperature dependencies of both the decay times and the emission intensities is a weakening of the Laporte restriction caused by pronounced vibronic coupling with increasing temperatures. This is particularly prominent in compounds with centrosymmetric lattice sites, like highly symmetric fluoridoperovskites (e.g.,  $\text{KMgF}_3\text{:Mn}^{2+}$ ) or fluorite ( $\text{CaF}_2\text{:Mn}^{2+}$ ).<sup>[56,77,80]</sup> In all regarded  $\text{Mn}^{2+}$ -activated alkali lithooxidosilicates within this work, thermal quenching already becomes significant in the range of room temperature or slightly above ( $T_{1/2} \sim 300\text{--}500 \text{ K}$ ),

which is unusual compared to many other  $\text{Mn}^{2+}$ -activated phosphors or  $\text{Eu}^{2+}$ -activated alkali lithooxidosilicates with quenching temperatures much above  $500 \text{ K}$ .<sup>[21,32,33,38,47]</sup> This could be an immediate consequence of the comparably low band gaps and the related thermal ionization-based quenching processes. Two particularly promising candidates within this series are, however,  $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2\text{:Mn}^{2+}$  and  $\text{CsKNa}_2[\text{Li}_3\text{SiO}_4]_4\text{:Mn}^{2+}$ , which show thermal quenching temperatures above  $450 \text{ K}$  for the green and red emission, respectively and, thus, could be promising candidates for future developments of white-light emitting phosphors.

## Conclusion

The luminescence of seven  $\text{Mn}^{2+}$ -activated alkali lithooxidosilicates was investigated characterized by a dual-band emission at both around 530 nm and 620 nm due to the ligand-field dependent  ${}^4\text{T}_{1(\text{g})}({}^4\text{G}) \rightarrow {}^6\text{A}_{1(\text{g})}({}^6\text{S})$  transitions of  $\text{Mn}^{2+}$  occupying both tetrahedrally and cuboidally coordinated alkali sites. The intensity ratio of the two emission bands is shown to be controlled by the composition of the alkali lithooxidosilicate host. There is a general trend that  $\text{Mn}^{2+}$  has a tendency to occupy the cuboidally coordinated Na sites if they are sufficiently small. The absence of small Na sites, on the other hand, results in the preferred occupation of tetrahedrally coordinated Li sites and a consequent observation of narrow green emission. The unique feature of dual-band green and red emission makes  $\text{Mn}^{2+}$  activated alkali lithooxidosilicates intriguing candidates for sustainable one-component phosphor-converted white light-emitting diodes. Notably, many of the herein investigated compounds suffer from a distinct luminescence temperature quenching below 150 °C, which is technologically relevant for that type of application. In that regard, the dual-band emitting  $\text{CsKNa}_2[\text{Li}_3\text{SiO}_4]_4:\text{Mn}^{2+}$  and the narrow-band green-emitting  $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2:\text{Mn}^{2+}$  only show minor thermal quenching relevant for pc-wLEDs and displays, respectively.

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## Mn<sup>2+</sup>-Activated Alkali Lithooxidosilicate Phosphors as Sustainable Alternative White-Light Emitters

### Experimental Section

**Table S1.** Chemicals used in the preparation of alkali lithooxidosilicates.

| Compound                               | Quality  | Manufacturer          | Comment              |
|----------------------------------------|----------|-----------------------|----------------------|
| Li <sub>2</sub> CO <sub>3</sub>        | 99.999 % | Thermo Scientific     |                      |
| Na <sub>2</sub> CO <sub>3</sub>        | 99.5 %   | Grüssing              | Dehydrated at 400 °C |
| K <sub>2</sub> CO <sub>3</sub>         | 99.8 %   | J. T. Baker Chemicals | Dehydrated at 400 °C |
| Rb <sub>2</sub> CO <sub>3</sub>        | 99 %     | Alfa Aesar            | Dehydrated at 400 °C |
| Cs <sub>2</sub> CO <sub>3</sub>        | 99.9 %   | Aldrich               |                      |
| SiO <sub>2</sub>                       | 99.99 %  | chemPUR               | D50<1µm              |
| Ethanol                                | p.a.     | Supelco               |                      |
| N <sub>2</sub> :H <sub>2</sub> (90:10) | 3.0      | Messer                |                      |

MnC<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O:

2.2124 g (15.6 mmol) (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · H<sub>2</sub>O were dissolved in 100 ml deionized water and a solution of 2.5383 g (15.0 mmol) MnSO<sub>4</sub> · H<sub>2</sub>O in 50 ml deionized water was added. A pinkish precipitate forms within 15 minutes. The batch was then stirred and boiled for 15 minutes after which a colorless precipitate remained. The solid was separated by filtration, washed several times with water and dried in a drying cabinet for 12 hours. MnC<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O was received as colorless powder.<sup>[1]</sup>

#### General procedures

Any of the investigated Mn<sup>2+</sup>-activated alkali lithooxidosilicates were synthesized by solid state reactions of the corresponding alkali carbonates, SiO<sub>2</sub> and MnC<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O. Li<sub>2</sub>CO<sub>3</sub> was used deficient to open vacancies for occupation by Mn<sup>2+</sup>. The educts were ground in an agate mortar together with some ethanol as dispersing aide. The samples were then dried in a drying cabinet at 80 °C and ground once more. Two or three sintering steps were applied with intermediate grinding. This was found to be necessary as the starting mixtures have a strong tendency to melt if heated immediately over ~ 600 °C. The heating and cooling rates were fixed at 100 °C/h.

Notes on the synthetic procedures

It was found beneficial for phase purity to use slightly excessive amounts of the heavier alkali carbonates (esp.  $\text{Rb}_2\text{CO}_3$ ). This might be due to the incorporation of small amounts of water or volatilization of the alkali oxides.<sup>[2]</sup> A reasonable suspicion for volatilization is that prolonged annealing of  $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2$  leads to the formation of  $\text{RbNa}_3[\text{Li}_3\text{SiO}_4]_4$  as side phase whereas even longer annealing of  $\text{RbNa}_3[\text{Li}_3\text{SiO}_4]_4$  finally leads to the formation of  $\text{Na}[\text{Li}_3\text{SiO}_4]$  as side phase.

**Table S2.** Educt stoichiometries and temperature programs used for the synthesis of the investigated  $\text{Mn}^{2+}$  activated alkali lithooxidosilicates. Heating and cooling rates were fixed at 100 °C/h.

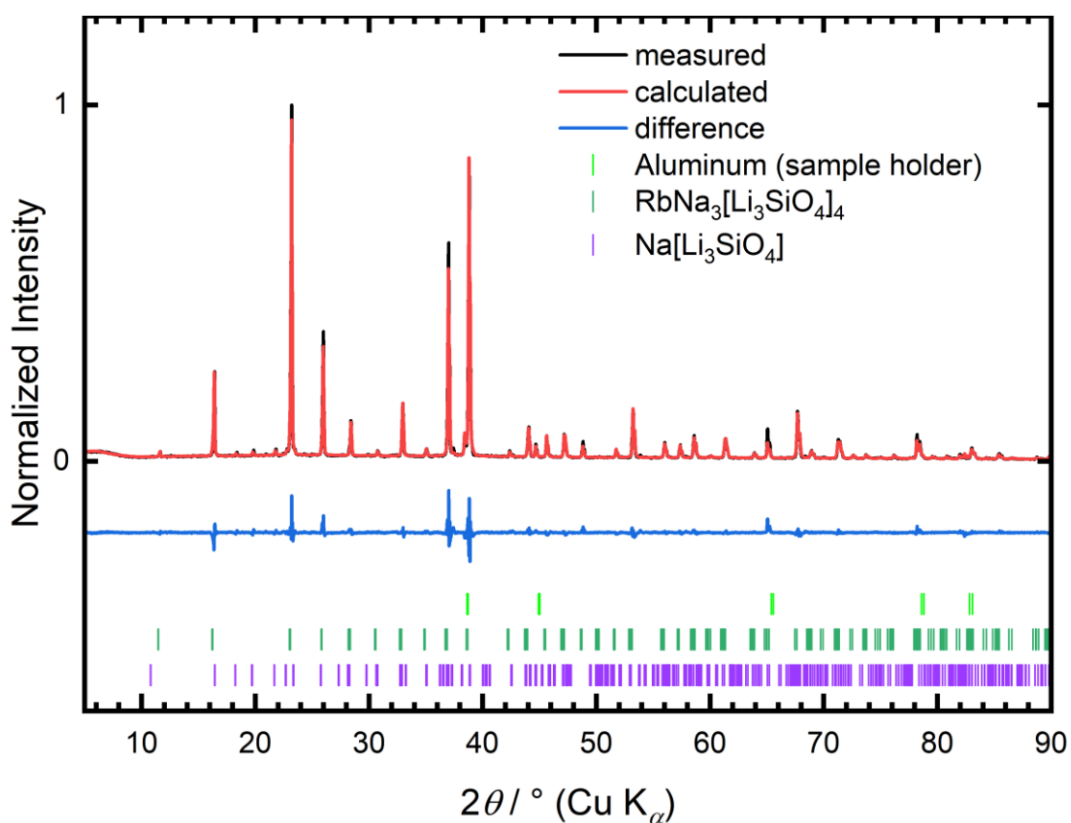
|                                                                | $\text{Na}[\text{Li}_3\text{SiO}_4]$ | $\text{NaK}_7[\text{Li}_3\text{SiO}_4]_8$ | $\text{RbNa}_3[\text{Li}_3\text{SiO}_4]_4$ | $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2$ | $\text{RbKLi}_2[\text{Li}_3\text{SiO}_4]_4$ | $\text{CsKNa}_2[\text{Li}_3\text{SiO}_4]_4$ | $\text{K}[\text{Li}_3\text{SiO}_4]$ |
|----------------------------------------------------------------|--------------------------------------|-------------------------------------------|--------------------------------------------|------------------------------------------|---------------------------------------------|---------------------------------------------|-------------------------------------|
| $\text{Li}_2\text{CO}_3$ / mg (mmol)                           | 442.4 (5.988)                        | 442.6 (6.988)                             | 443.4 (6.0)                                | 221.7 (2.988)                            | 516.6 (6.993)                               | 441.6 (5.976)                               | 442.4 (5.988)                       |
| $\text{Na}_2\text{CO}_3$ / mg (mmol)                           | 221.1 (2.0)                          | 27.7 (0.26)                               | 154.2 (1.46)                               | 51.9 (0.5)                               |                                             | 106.0 (1.0)                                 |                                     |
| $\text{K}_2\text{CO}_3$ / mg (mmol)                            |                                      | 266.2 (1.93)                              |                                            |                                          | 73.6 (0.527)                                | 69.1 (0.5)                                  | 331.5 (2.4)                         |
| $\text{Rb}_2\text{CO}_3$ / mg (mmol)                           |                                      |                                           | 138.6 (0.6)                                | 138.6 (0.6)                              | 130.6 (0.57)                                |                                             |                                     |
| $\text{Cs}_2\text{CO}_3$ / mg (mmol)                           |                                      |                                           |                                            |                                          |                                             | 171.1 (0.525)                               |                                     |
| $\text{SiO}_2$ / mg (mmol)                                     | 240.0 (4.0)                          | 240.3 (4.0)                               | 240.3 (4.0)                                | 120.2 (2.0)                              | 240.3 (4.0)                                 | 240.3 (4.0)                                 | 240.2 (4.0)                         |
| $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ / mg (mmol) | 2.2 (0.012)                          | 2.1 (0.012)                               | 5.4 (0.03)                                 | 1.8 (0.010)                              | 2.5 (0.014)                                 | 4.3 (0.024)                                 | 2.2 (0.012)                         |
| 1. Sintering (air) / °C                                        | 550                                  | 500                                       | 650                                        | 550                                      | 550                                         | 700                                         | 550                                 |
| Dwell / h                                                      | 20                                   | 2                                         | 5                                          | 5                                        | 20                                          | 5                                           | 20                                  |
| 2. Sintering (air) / °C                                        |                                      | 650                                       |                                            |                                          |                                             |                                             |                                     |
| Dwell / h                                                      |                                      | 3                                         |                                            |                                          |                                             |                                             |                                     |
| 1. Sintering ( $\text{N}_2:\text{H}_2$ ) / °C                  | 750                                  | 725                                       | 725                                        | 725                                      | 750                                         | 750                                         | 750                                 |
| Dwell / h                                                      | 10                                   | 1                                         | 1                                          | 1                                        | 10                                          | 1                                           | 10                                  |

## X-ray powder diffraction (XRPD) of $\text{Mn}^{2+}$ -activated alkali lithooxidosilicates

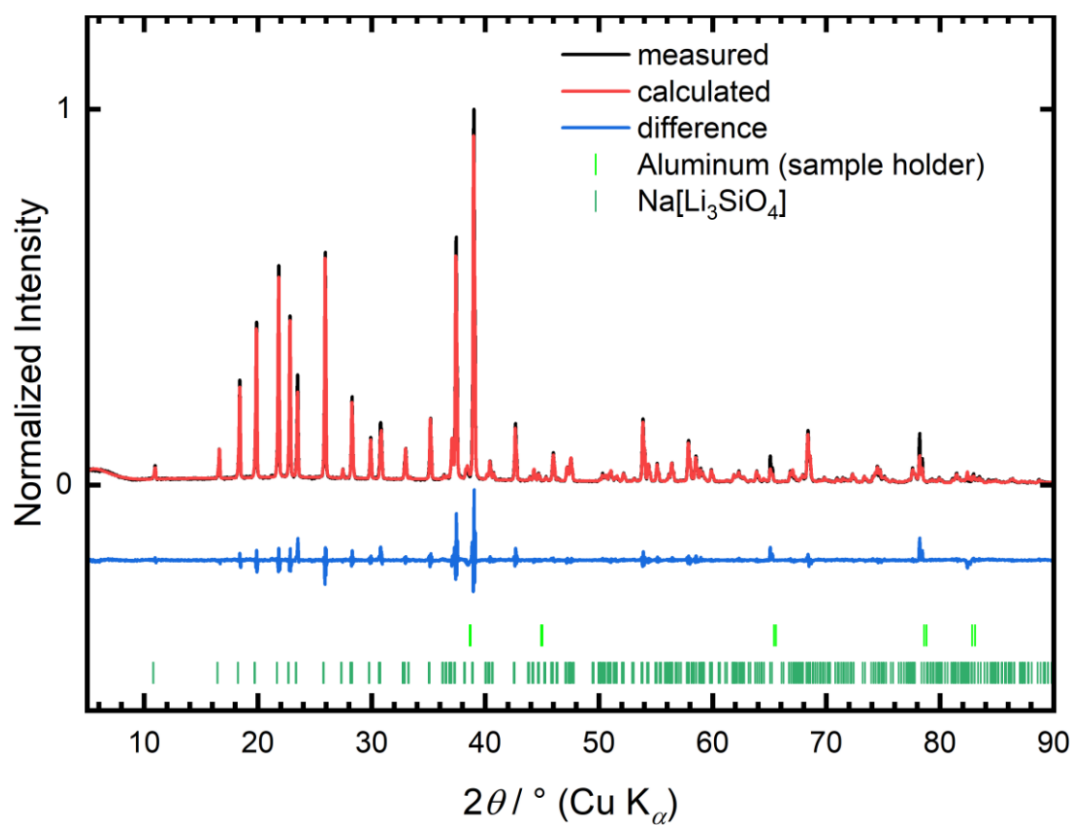
The purity of the products was determined by XRPD using a Malvern Panalytical X'Pert Pro diffractometer in Bragg-Brentano / reflection geometry ( $\text{Cu K}\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ). Samples were prepared on an aluminum disc. Rietveld refinement was performed with the program Topas 7.0.0.7 (Bruker ASX, 2022, Germany). Single-crystal diffraction data of  $\text{K}[\text{Li}_3\text{GeO}_4]$  were used as starting model for the refinement of  $\text{K}[\text{Li}_3\text{SiO}_4] \cdot \text{Mn}^{2+}$ . The powder diffraction patterns of the other compounds were refined based on the single-crystal structural data of the respective compounds. Background corrections were performed with Chebychev polynomials of the 20<sup>th</sup> order. Peak shapes were fitted using the `LVol_FWHM_CS_G_L` and `e0_from_Strain` commands, that comprises both Voight and Gaussian components. The diffraction patterns are displayed in Figure S1-7. Common side phases are  $\text{Li}_4\text{SiO}_4$  and other alkali lithooxidosilicates. The refinement parameters are given in Table S 3.

**Table S3.** Parameters of the Rietveld refinements of the investigated alkali lithooxidosilicates and database code of the structures used for the refinements.

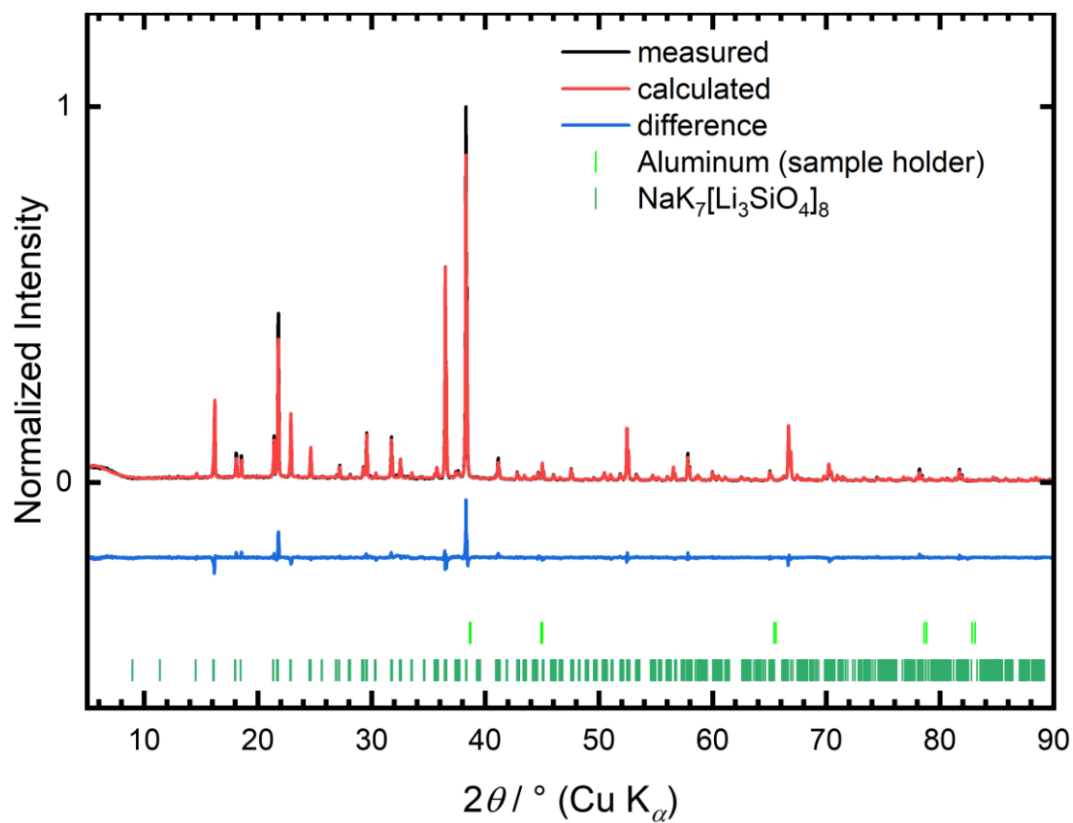
| Compound                                                                                     | $R_{\text{Bragg}}$ / % | $R_{\text{exp}}$ / % | $R_{\text{wp}}$ / % | $R_p$ / % | G.o.o.F. | Database code |
|----------------------------------------------------------------------------------------------|------------------------|----------------------|---------------------|-----------|----------|---------------|
| RbNa <sub>3</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.25 % Mn <sup>2+</sup> | 3.45                   | 3.80                 | 10.52               | 7.64      | 2.77     | CCDC 1635539  |
| Na[Li <sub>3</sub> SiO <sub>4</sub> ]: 0.1 % Mn <sup>2+</sup>                                | 3.35                   | 4.16                 | 11.03               | 7.84      | 2.66     | COD 1518159   |
| NaK <sub>7</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>8</sub> : 0.1 % Mn <sup>2+</sup>   | 6.19                   | 5.46                 | 10.58               | 8.24      | 1.94     | CCDC 1861384  |
| CsKNa <sub>2</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.2 % Mn <sup>2+</sup> | 6.73                   | 5.28                 | 13.89               | 9.77      | 2.63     | CCDC 1635538  |
| RbKLi <sub>2</sub> [Li <sub>3</sub> SiO <sub>4</sub> ] <sub>4</sub> : 0.1 % Mn <sup>2+</sup> | 6.10                   | 4.16                 | 12.04               | 8.27      | 2.90     | CCDC 1936593  |
| K[Li <sub>3</sub> SiO <sub>4</sub> ]: 0.1 % Mn <sup>2+</sup>                                 | 8.76                   | 5.24                 | 16.49               | 11.18     | 3.15     | COD 1536511   |
| RbNa[Li <sub>3</sub> SiO <sub>4</sub> ] <sub>2</sub> : 0.17 % Mn <sup>2+</sup>               | 7.09                   | 5.35                 | 14.67               | 10.92     | 2.74     | CCDC 1635540  |



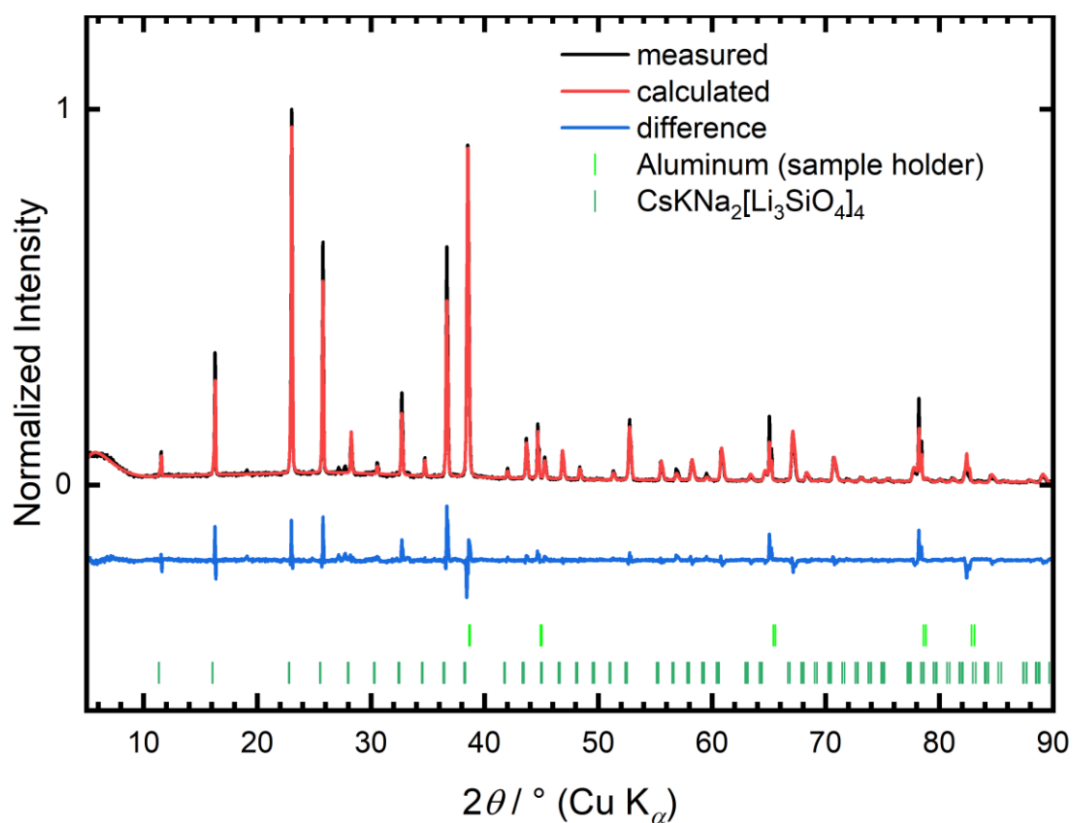
**Figure S1.** Rietveld refined X-ray powder diffraction (XRPD) pattern of RbNa<sub>3</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>4</sub>: 0.25% Mn<sup>2+</sup>.



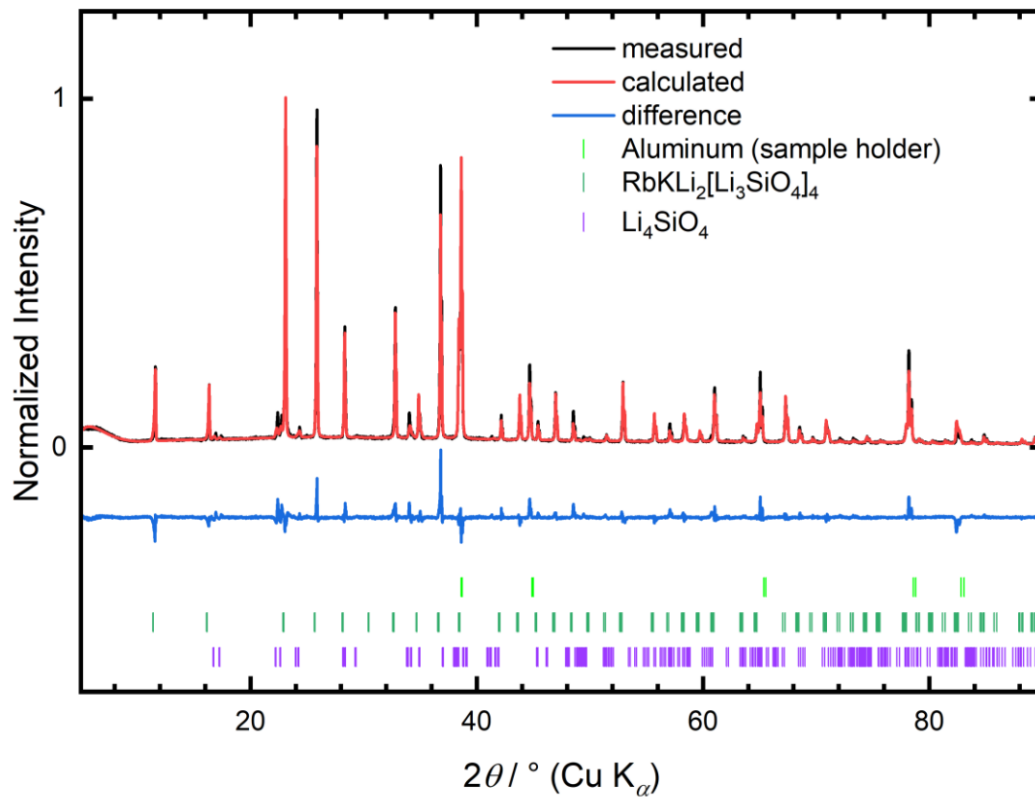
**Figure S2.** Rietveld refined X-ray powder diffraction (XRPD) pattern of Na[Li<sub>3</sub>SiO<sub>4</sub>]: 0.1% Mn<sup>2+</sup>.



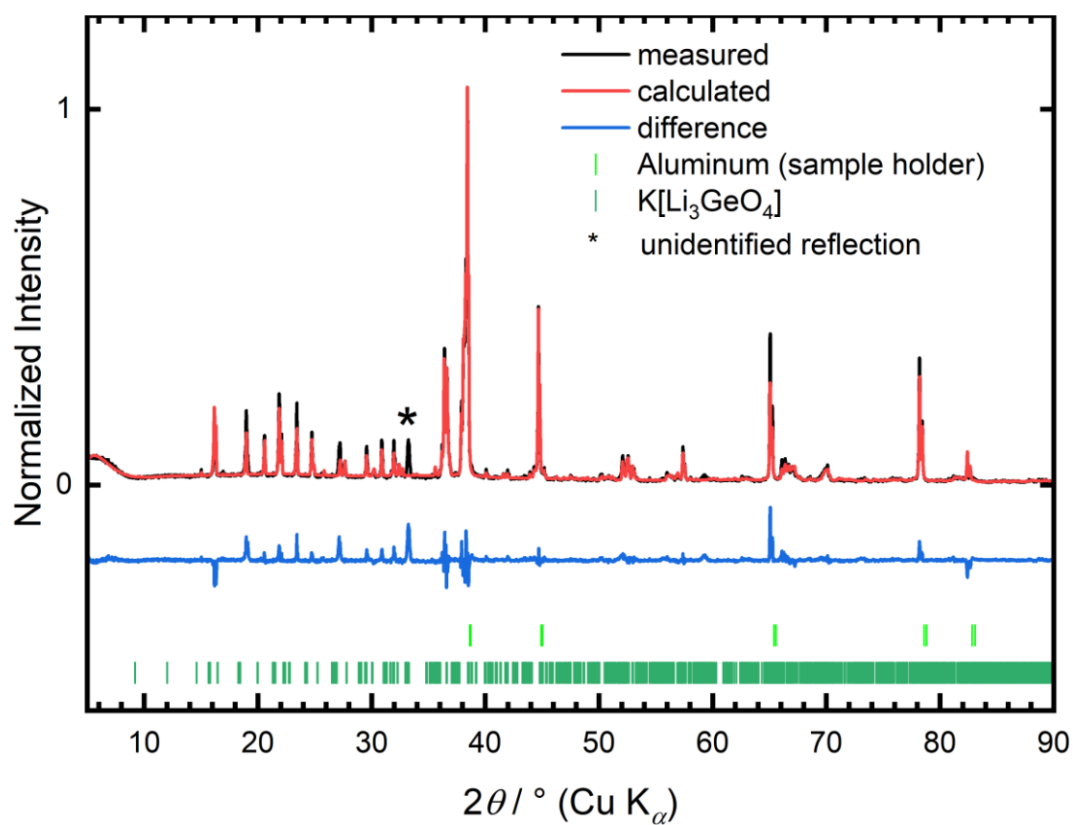
**Figure S3.** Rietveld refined X-ray powder diffraction (XRPD) pattern of NaK<sub>7</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>8</sub>: 0.1% Mn<sup>2+</sup>.



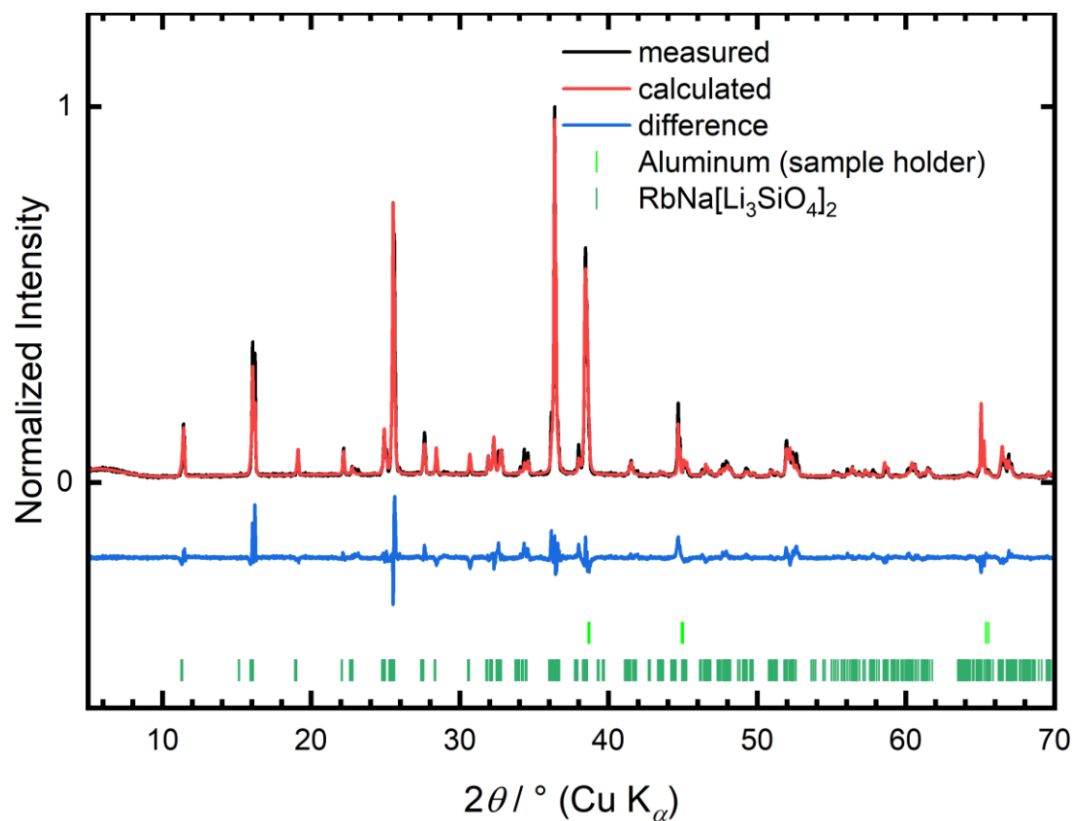
**Figure S4.** Rietveld refined X-ray powder diffraction (XRPD) pattern of CsKNa<sub>2</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>4</sub>: 0.1% Mn<sup>2+</sup>.



**Figure S5.** Rietveld refined X-ray powder diffraction (XRPD) pattern of RbKLi<sub>2</sub>[Li<sub>3</sub>SiO<sub>4</sub>]<sub>4</sub>: 0.1% Mn<sup>2+</sup>.



**Figure S6.** Rietveld refined X-ray powder diffraction (XRPD) pattern of  $\text{K}[\text{Li}_3\text{SiO}_4]: 0.1\% \text{Mn}^{2+}$ .

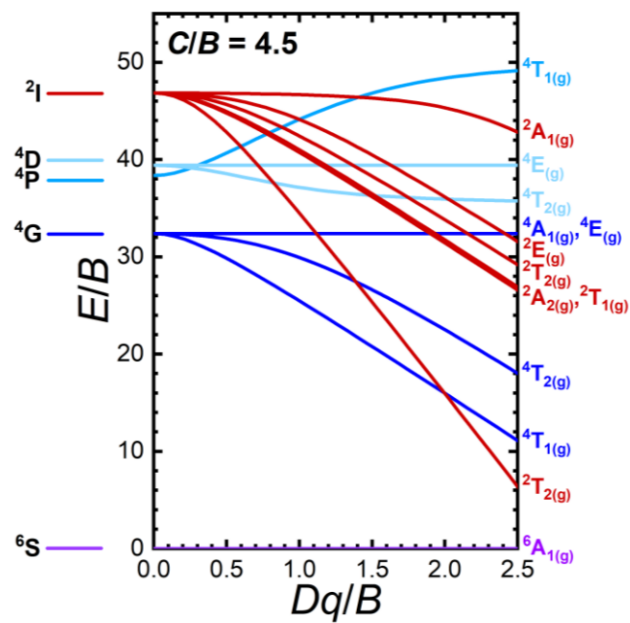


**Figure S7.** Rietveld refined X-ray powder diffraction (XRPD) pattern of  $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2: 0.17\% \text{Mn}^{2+}$ .

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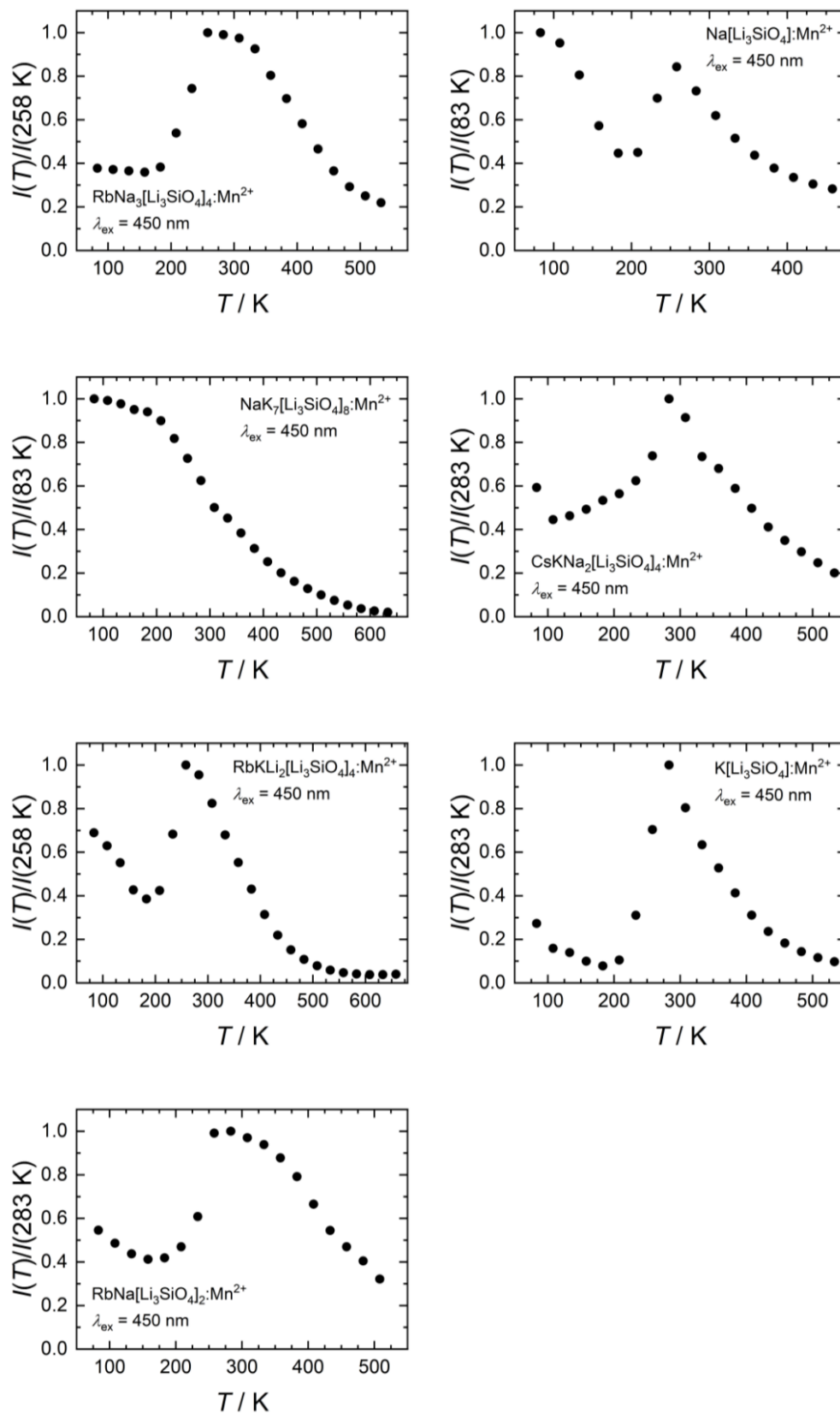
## Luminescence Spectroscopy

All samples were sealed in evacuated thin, optically transparent quartz ampoules (ilmasil® quality) to avoid extensive contact of the samples to air and humidity. Optical measurements were performed on an Edinburgh Instruments FLS1000 photoluminescence spectrometer equipped with a 450 W Xe arc lamp as a wavelength-variable excitation source for excitation spectra, double excitation and emission monochromators in Czerny-Turner configuration and a thermoelectrically cooled ( $-20\text{ }^{\circ}\text{C}$ ) photomultiplier tube PMT-980 (Hamamatsu). The emission spectra were corrected with respect to the grating efficiency and PMT sensitivity, while excitation spectra were additionally corrected with respect to the lamp intensity. The decay traces were measured with a laser diode VPL-450 (Edinburgh Instruments, 53.0 mW average incident peak power,  $\lambda = 450.9\text{ nm}$ ) with adjustable temporal pulse width ( $0.1\text{ }\mu\text{s} \dots 1\text{ ms}$ ) and variable trigger frequency ( $0.1\text{ Hz} \dots 5\text{ MHz}$ ) as the pulsed excitation source. The laser was also used in a continuous wave excitation mode for recording emission spectra. The detection mode for time resolved measurements was single-photon multichannel scaling. Temperature-dependent measurements were performed with a Linkam Scientific THMS600 temperature cell with temperature accuracy of  $\pm 0.1\text{ }^{\circ}\text{C}$  in the regarded temperature range between  $-190\text{ }^{\circ}\text{C}$  and  $525\text{ }^{\circ}\text{C}$ . Sample-ampoules were mounted in a custom-made solid silver sample holder with some thermal conductive grease. After each heating or cooling step, a five-minute equalization time was set before a measurement was started.

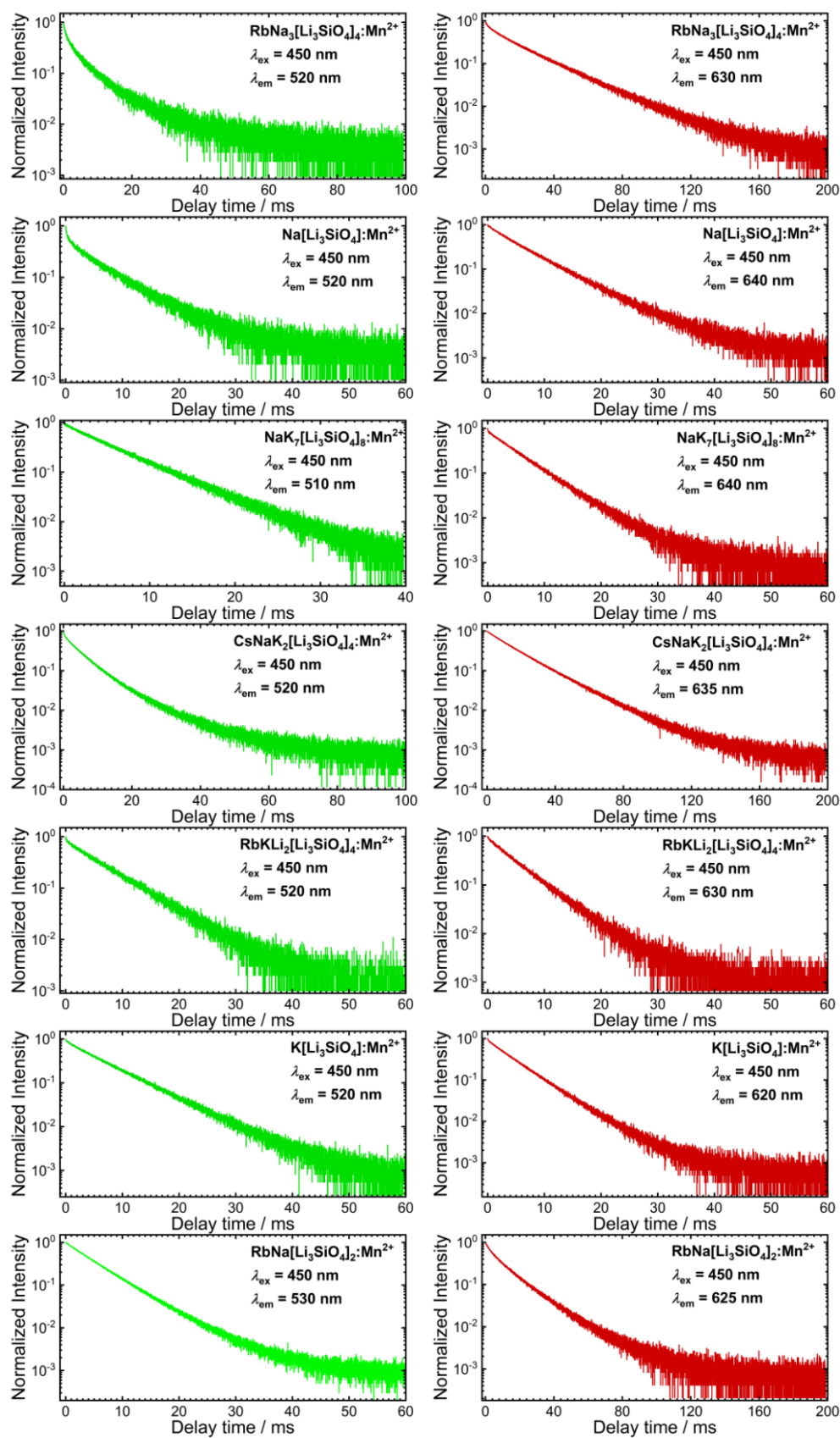


**Figure S8.** Tanabe-Sugano diagram for octahedrally coordinated d<sup>5</sup> ions.  $B$  and  $C$  denote the interelectronic repulsion Racah parameters.





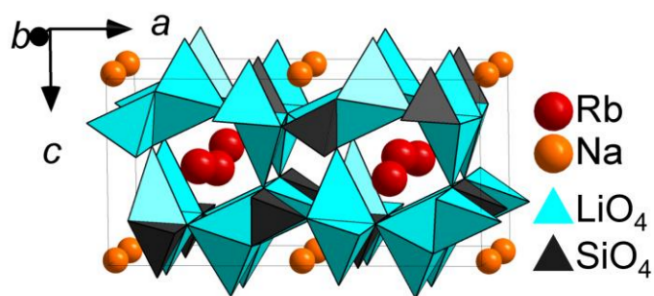
**Figure S9.** Temperature dependence of the emission intensity (full emission range used for integration).



**Figure S10.** Photoluminescence decay curves of  $\text{Mn}^{2+}$ -activated alkali lithooidosilicates at 83 K. Excitation and emission wavelengths are indicated in the graph.

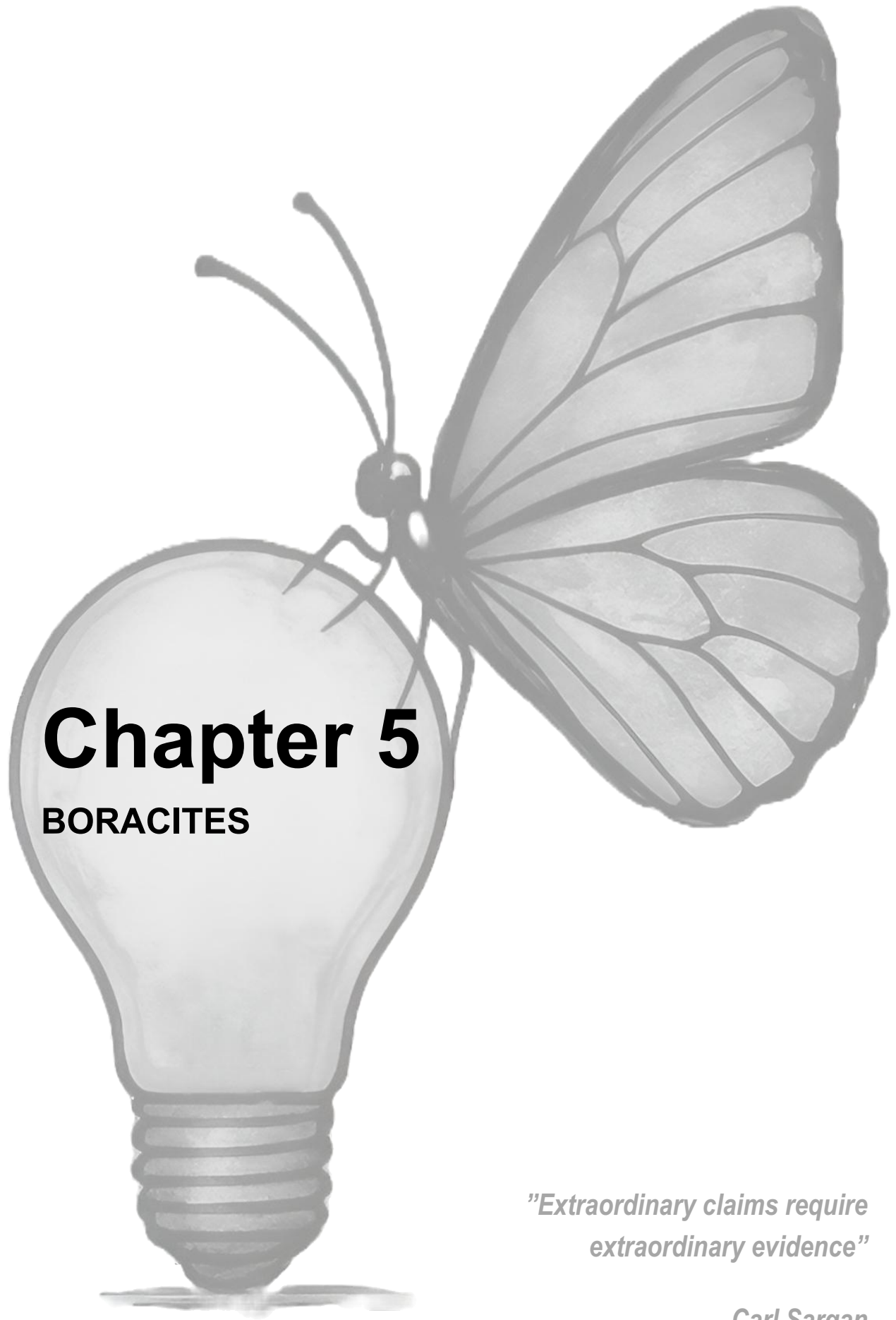


### Structural depiction of $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2$



**Figure S12.** Structural depiction of  $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2$  as a representative example of a  $\text{UCr}_4\text{C}_4$ -type compound with lower symmetry and different occupation of the channel positions.

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- [2] R. H. Lamoreaux, D. L. Hildenbrand, "High Temperature Vaporization Behavior of Oxides. I. Alkali Metal Binary Oxides" *J. Phys. Chem. Ref. Data* **1984**, 13, 151–173.



# Chapter 5

**BORACITES**

*"Extraordinary claims require  
extraordinary evidence"*

*—Carl Sagan*

## **Thermally robust near-infrared broad-band emission of Mn<sup>2+</sup> in boracites with fine-tuned absorption strength**

### **Full citation:**

L. M. Träger, A. Shagova, B. J. Schöpper, M. Stremel, P. Pandey, A. Meijerink, H. Huppertz, M. Suta, *manuscript in finalization 2026*.

### **Author contributions:**

**L. M. Träger** discovered and interpreted the unusual near-infrared emission of the investigated class of Mn<sup>2+</sup>-activated phosphors and optimized the synthesis. He synthesized three of the seven investigated compounds, including the previously only vaguely known compound Mg<sub>3</sub>B<sub>7</sub>O<sub>13</sub>I. He also checked the phase purity of the samples by Rietveld refinement, performed the photoluminescence measurements, evaluated and visualized the data and wrote the major part of the manuscript. **B. J. Schöpper** synthesized three of the investigated compounds and acquired spectroscopic data under supervision and instruction of L. M. Träger and M. Suta. **M. Stremel** recorded the X-ray powder diffraction patterns. **P. Pandey** acquired spectroscopic data at temperatures below 77 K. **A. Meijerink** assisted those measurements and supplied the required equipment and liquid helium. He also reviewed the manuscript and contributed to the project with his expertise. **A. Shagova** performed high-pressure experiments for the preparation of Zn<sub>3</sub>B<sub>7</sub>O<sub>13</sub>F and Mg<sub>3</sub>B<sub>7</sub>O<sub>13</sub>F. She also checked the phase purity of the products of those experiments and wrote the "Structural depiction" part of the manuscript. **H. Huppertz** reviewed the manuscript and contributed to the project with his expertise in high-pressure chemistry and the structural chemistry of borates. **M. Suta** supervised the whole project, acquired funding and assisted in the data interpretation. He also conceptualized, reviewed and finalized the manuscript.



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# Thermally robust near-infrared broad-band emission of $\text{Mn}^{2+}$ in boracites with fine-tuned absorption strength

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## Abstract

Broad-band emitting NIR phosphors are typically liable towards thermal quenching at room temperature and above. So far,  $\text{Cr}^{3+}$  has been the primary activator for that purpose in inorganic emitters. In this work, we demonstrate how to use targeted structural distortion within the rigid, highly condensed network of boracites  $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$  ( $M = \text{Mg}, \text{Zn}$ ;  $X = \text{F} - \text{I}$ ) to make  $\text{Mn}^{2+}$  show thermally stable NIR emission in the range between 780 nm and 795 nm for the first time. Variation of the halide ion  $X^-$  does not only introduce additional internal structural rigidity but also positively affects the absorption strength in the blue range at 435 nm based on increased spin-orbit coupling. Based on these combined electronic and structural design concepts, we managed to increase thermal quenching temperatures  $T_{50}$  up to 560 K in the case of  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$ . Moreover, it is demonstrated that  $T_{50}$  correlate very well with the phase transition temperatures to the cubic polymorphs of the investigated boracites, which is in turn affected by the radius ratio  $r(\text{M}^{2+})/r(\text{X}^-)$  thus offering simple structural guidelines for the conceptualization of NIR-emitting phosphors based on  $\text{Mn}^{2+}$ .

**Keywords:**  $\text{Mn}^{2+}$ , boracites, NIR emission, thermal quenching

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## Introduction

Broad-band near-infrared (NIR) phosphors find versatile applications in fields like plant-growth<sup>[1–3]</sup>, active night vision<sup>[4–5]</sup>, medicals<sup>[6–7]</sup> or non-destructive analysis<sup>[8–10]</sup>. However, there is still ongoing search for an efficient NIR light source. Conventional NIR tungsten halogen lamps suffer from low efficiency, heat production, short lifetimes and very limited down-scalability.<sup>[11]</sup> The traditional semiconductor chip-based light-emitting diodes (LEDs) with emission in the NIR range (e.g. based on GaInP or GaAs)

struggle from low external quantum efficiencies (EQE) (usually < 1%), narrow emission bandwidths and toxicity.<sup>[12-13]</sup> Recently, NIR-emitting perovskite-based LEDs with increased EQE have attracted much attention.<sup>[14-17]</sup> However, despite the tremendous progress on this field, their EQE still barely exceed 20%. Moreover, many of the produced devices have low lifetimes (usually < 50 h) or contain toxic elements like lead. A well-established strategy to overcome the aforementioned issues is the usage of a phosphor-converted LED (pc-LED), constructed from an efficient blue-emitting LED chip as excitation source and a NIR emitting phosphor.<sup>[11, 18-22]</sup> Based on the success in the field of red-emitting phosphors for pc-wLED technology,<sup>[23-24]</sup> Eu<sup>2+</sup>-activated compounds like Sr<sub>0.5</sub>Ba<sub>0.5</sub>Y<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> ( $\lambda_{\text{em}} = 773 \text{ nm}$ )<sup>[25]</sup> and K<sub>3</sub>LuSi<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup> ( $\lambda_{\text{em}} = 740 \text{ nm}$ )<sup>[26]</sup> with a drastically increased ligand field splitting due to a structural distortion of the (Y/Lu)O<sub>6</sub> substitution sites as well as a Ce<sup>3+</sup>-activated metal-organic composite C<sub>78</sub>H<sub>132</sub>N<sub>9</sub>S<sub>6</sub>Ce · 2 CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{\text{em}} = 740 \text{ nm}$ )<sup>[27]</sup> with highly covalent Ce–S-bonds have been recently discussed. However, the comparably high ionization potentials of both Ce<sup>3+</sup> as well as Eu<sup>2+</sup> due to its half-filled 4f<sup>7</sup> ground configuration already imposes high energies of the excited 4f<sup>*n*-1</sup>5d<sup>1</sup> configurations (*n* = 1 for Ce<sup>3+</sup>, *n* = 7 for Eu<sup>2+</sup>) that require challenging chemical design to induce a substantial redshift of that excited configuration by means of the nephelauxetic effect.

Out of that reason, much more common NIR-emitting activators are the transition metal ions. Among the most commonly used ones is the 3d<sup>3</sup> ion Cr<sup>3+</sup>, as it combines spin-allowed, effective excitability with blue light and great spectral tuneability of the broad <sup>4</sup>T<sub>2g</sub>(<sup>4</sup>F) → <sup>2</sup>A<sub>2g</sub>(<sup>4</sup>F) transition with peak emission wavelengths in the 700 – 1000 nm range by means of a sufficiently weak ligand field.<sup>[28-30]</sup> On the other hand, many Cr<sup>3+</sup>-activated phosphors already suffer from significant thermal quenching at the operating temperature of pc-LEDs (~ 150 °C), which can be explained by a thermally activated crossover from the <sup>4</sup>T<sub>2g</sub>(<sup>4</sup>F) excited state to the <sup>4</sup>A<sub>2g</sub>(<sup>4</sup>F) ground state.<sup>[29, 31-32]</sup> This is a general fate to broad-band emitters at low emission energies. A classic mitigating design strategy to overcome that obstacle is a limitation in the change of the equilibrium geometry in the excited state thus invoking low Stokes shifts, and high thermal crossover barriers. Rigid, condensed structures have been demonstrated to work very well for that purpose and the combination with sufficiently covalent metal-ligand bonds contributed to the success of red-emitting phosphors for pc-wLEDs such as SLA:Eu<sup>2+</sup> or SALON:Eu<sup>2+</sup> (*vide supra*).<sup>[23-24]</sup> In the case of Cr<sup>3+</sup>, however, this design strategy often provokes too strong ligand fields that ultimately lead to the observation of spin-forbidden narrow-line emission from the spin doublet states instead. An insightful example in this regard is the “molecular ruby” [Cr(dppd)<sub>2</sub>][BF<sub>4</sub>]<sub>3</sub> (dppd = *N,N'*-dimethyl-*N,N'*-dipyridine-2-ylpyridine-2,6-diamine) with covalent Cr–N bonds, rigidified structure, and narrow-line emission at around 775 nm.<sup>[33]</sup>

In this work, we follow the idea to tune the emission wavelength of a broad-band emitter by a careful utilization of ligand field effects and host compounds with high structural rigidity. The 3d<sup>5</sup> high-spin (HS) ion Mn<sup>2+</sup> is a so far rarely explored activator for this purpose. Unlike Cr<sup>3+</sup>, its broad-band luminescence shifts to the red range with increasing ligand field strength based on the stronger stabilization of the emissive excited <sup>4</sup>T<sub>1g</sub>(<sup>4</sup>G) state in that case. Such a situation is typically encountered in octahedral coordination geometries. Excited state radiative decay times are then often above 100 ms related to both a spin- and parity-forbidden nature of the



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${}^4T_{1g}({}^4G) \rightarrow {}^6A_{1g}({}^6S)$  transition.<sup>[34-35]</sup> In contrast, in weak-field tetrahedral coordination, the equilibrium geometry of the excited  ${}^4T_1({}^4G)$  state barely differs from that of the ground state, generally resulting in rather narrow emission bands of  $Mn^{2+}$  with recorded radiative decay times in the order of 10 ms.<sup>[36-38]</sup> In both cases, a decrease of the cubic coordination symmetry induces additional splitting of the excited state based on a lift in the triple orbital degeneracy of the excited  ${}^4T_{1(g)}$  state that may lead to a structurally induced redshift of the luminescence. Thus, an alternative strategy peculiar to  $Mn^{2+}$  can be to provoke structurally induced symmetry lowering at the cation site in combination with a rigid, condensed structural template. Such an approach has been successfully demonstrated, e.g. in sodalite-type  $Zn_4B_6O_{13}:Mn^{2+}$ <sup>[38]</sup>, wurzite-type  $AlN:Mn^{2+}$ <sup>[39]</sup>, or  $Mg_4Ta_2O_9:Mn^{2+}$  in an ordered corundum-type superstructure.<sup>[40]</sup>

Another fundamental issue of  $Mn^{2+}$ -activated phosphors is the weak absorption cross section related to its spin-forbidden  $3d^5(HS) \leftrightarrow 3d^5(HS)$  transitions. The absorption strength at desirable wavelengths can be increased by incorporation into host compounds with heavy ligands, which enables spin-orbit coupling and thereby weakens the spin-forbidden character of the electronic transitions of  $Mn^{2+}$ .<sup>[36, 41-42]</sup> Halide ligands are usually a simple choice for that purpose. From a materials perspective, however, heavy halides tend to be hygroscopic and show limited long-time durability thus preventing a clear-cut application. In addition, it has been shown that in the special case of  $Mn^{2+}$ , a wide band gap is as important to limit thermal quenching by ionization of excited electrons into the conduction band.<sup>[43]</sup> This is usually problematic for heavy halides as the increased degree of covalency of the chemical bonds typically also lowers a band gap of the host compound.

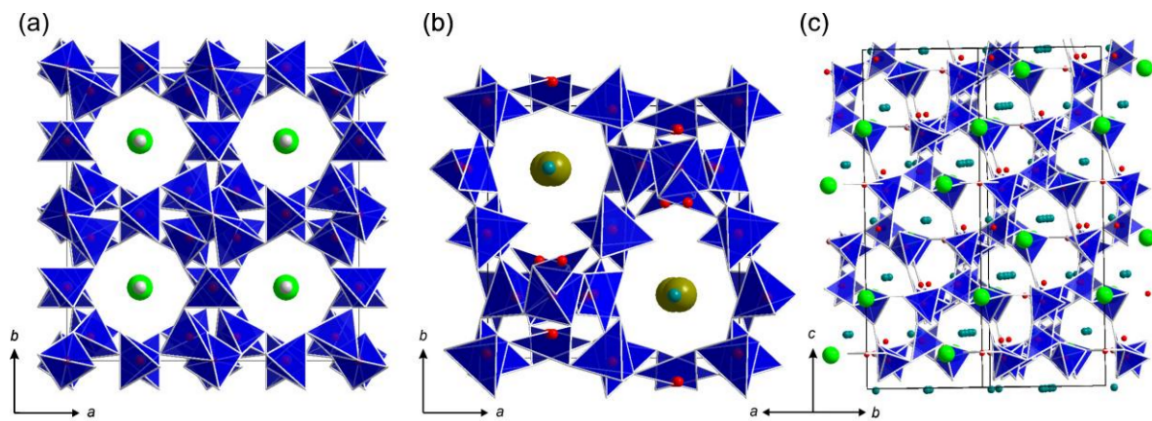
A compound class that combines the desirable properties of wide band gaps with highly condensed structures and by the same virtue allow introduction of heavy atoms are boracites with the general composition  $M_3B_7O_{13}X$  ( $M = Mg, Zn$ ;  $X = F - I$ ). In their structures, the metal site shows an asymmetric coordination pattern consisting of four equatorial  $O^{2-}$  ligands with two axial  $X^-$  ligands. Moreover, the condensed structure and ultra-wide band gap ( $\sim 6.5 - 8$  eV)<sup>[44-45]</sup> of those compounds readily suggests promisingly high thermal quenching temperatures.<sup>[43]</sup> A series of six  $Mn^{2+}$ -activated boracites was prepared *via* conventional solid-state reactions. The thus prepared compounds show broad NIR luminescence in a hitherto unreported range of 800 nm for  $Mn^{2+}$  with unusually high thermal quenching temperatures above 400 K. In addition, their absorption cross section in the range of 430 – 450 nm increases with introduction of heavier halide ions without sacrificing any air stability. Both the emission full width at half maximum (FWHM) and luminescence decay times are in between values that are common for tetrahedrally and octahedrally coordinated  $Mn^{2+}$  in solids and imply that such a targeted approach may help design NIR-emitting phosphors on the basis of abundant transition metal emitters more generally.

## Results and Discussion

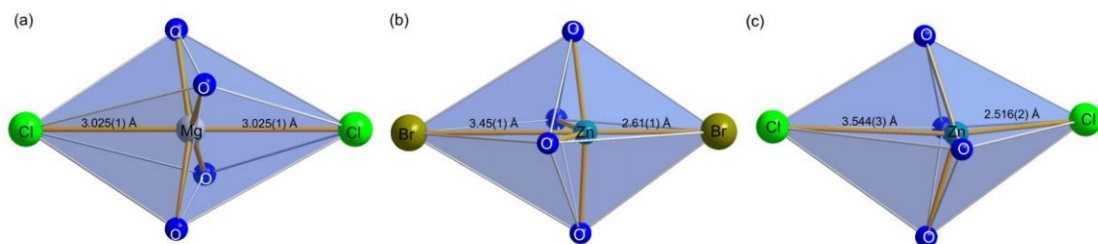
### Structural depiction

Boracites ( $M_3B_7O_{13}X$ , where  $M = Mg$ , 3d metal and  $X = F, Cl, Br, I, OH$  or  $NO_3$ ) are a well-known class of minerals with structural diversity. They crystallize in three stable

modifications at room temperature: a cubic one (space group type  $F\bar{4}3c$ , no. 219)<sup>[46-48]</sup>, an orthorhombic variant (space group type  $Pca2_1$ , no. 29)<sup>[49-51]</sup>, and a trigonal polymorph (space group type  $R3c$ , no. 161)<sup>[52-53]</sup>. For several boracites, these modifications are connected via phase transitions with an increase of the symmetry towards the cubic modification under rising temperatures.<sup>[54-56]</sup> Table 1 summarizes the crystal structures with the corresponding space groups and potential phase transitions of the boracites investigated in this study. The structure of a cubic boracite can be described as a 3D framework of corner-sharing  $[\text{BO}_4]$  tetrahedra (Figure 1a), while in the orthorhombic (Figure 1b) and trigonal (Figure 1c) modifications, some of the B atoms are still coordinated in a trigonal planar fashion. For the cubic and the orthorhombic boracites, these borate frameworks form channels, inside which the  $M^{2+}$  and  $X^-$  ions are located, while for the trigonal boracites the channels are also formed, but  $M^{2+}$  and  $X^-$  are no longer within the same line. Accordingly, the coordination of the metal cations depends on the boracite modification. In the cubic boracites, the  $M$  sites are sixfold coordinated by four oxide and two halide anions (Figure 2a) in form of a distorted octahedron with  $S_4$  symmetry according to Schoenflies notation. In the orthorhombic and trigonal boracites (Figure 2b-c), the central  $M^{2+}$  ion is even more off-centered towards one of the halogen anions. This causes a so-called  $[5 + 1]$  local environment of the metal cations with  $C_1$  symmetry and is considered responsible for many of the magnetic and piezoelectric properties of boracites.<sup>[56-57]</sup> In first approximation, however, all  $[\text{MO}_4\text{X}_2]$  ( $M = \text{Mg}, \text{Zn}$ ;  $X = \text{F} - \text{I}$ ) polyhedra can be considered to derive from an idealized (centrosymmetric)  $D_{4h}$  symmetry, which will become important in the discussion of the photoluminescence properties of the incorporated  $\text{Mn}^{2+}$  ions. Given the similar ionic radii of  $\text{Mn}^{2+}$  ( $r_{\text{Mn}^{2+}} = 0.83 \text{ \AA}$  (HS)),  $\text{Mg}^{2+}$  ( $r_{\text{Mg}^{2+}} = 0.72 \text{ \AA}$ ) and  $\text{Zn}^{2+}$  ( $r_{\text{Zn}^{2+}} = 0.74 \text{ \AA}$ ) for C.N. = 6, it is expected that both Mg- and Zn-based boracites could be successfully activated with  $\text{Mn}^{2+}$  ions that are known to show photoluminescence all over the visible range.<sup>[58-60]</sup>



**Figure 1.** Structural depiction of the general structures of cubic<sup>[61]</sup> (a), orthorhombic<sup>[51]</sup> (b) and trigonal boracites<sup>[53]</sup> (c). The  $[\text{BO}_3]$  and  $[\text{BO}_4]$  polyhedra are shown in blue,  $\text{B}^{3+}$  ions in red,  $\text{Mg}^{2+}$  ions in grey,  $\text{Zn}^{2+}$  ions in green-blue,  $\text{Cl}^-$  ions in green, and  $\text{Br}^-$  ions in brown-green.



**Figure 2.** Local environment of  $M^{2+} = \text{Mg/Zn}$  ions in the structure of cubic<sup>[61]</sup> (a), orthorhombic<sup>[51]</sup> (b) and trigonal boracites<sup>[53]</sup> (c).

**Table 1.** Space groups, known phase transitions and symmetries of the local environments of the  $M$  site of the investigated  $\text{Mn}^{2+}$  activated  $\text{Mg-X}$  and  $\text{Zn-X}$  ( $X = \text{F, Cl, Br, I}$ ) boracites.

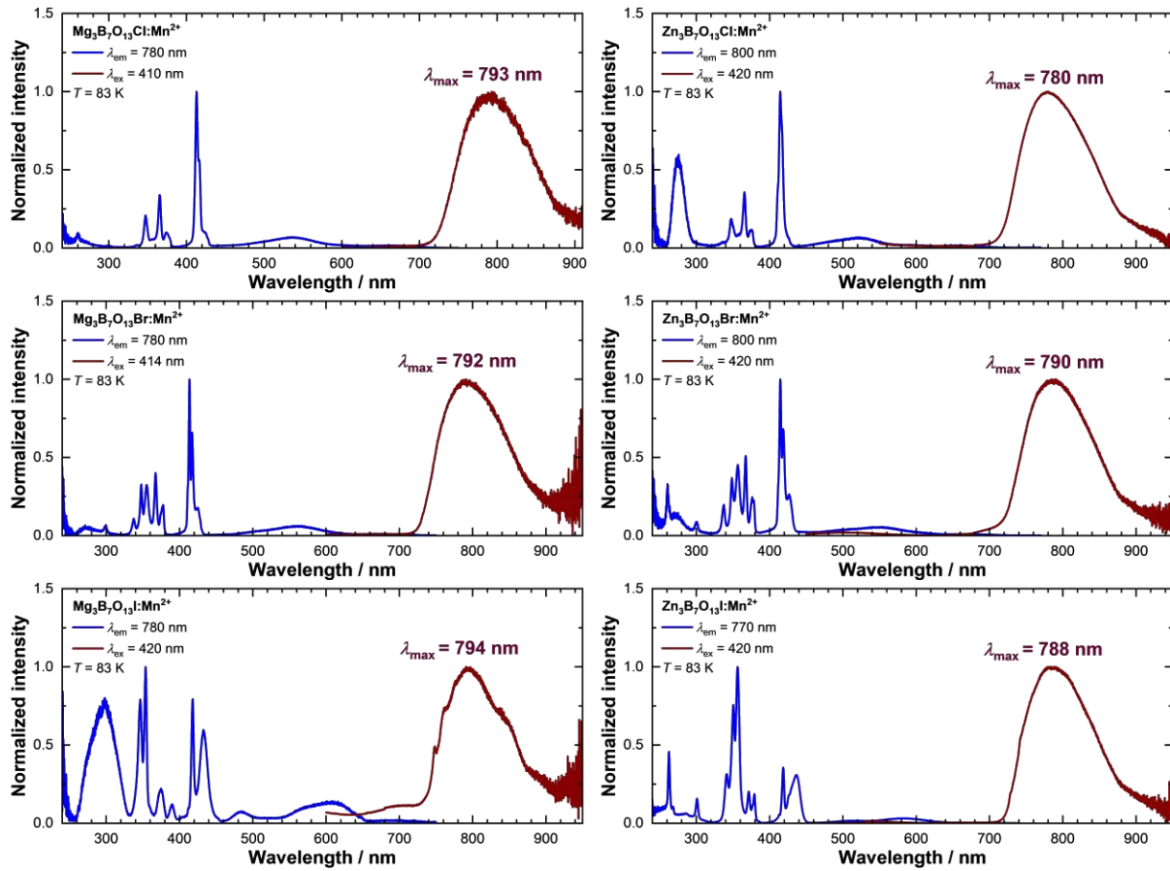
| $M\text{-X}$ | Space group (298 K)    | Phase transitions                                                                                                    | Site symmetry (298 K) | Reference |
|--------------|------------------------|----------------------------------------------------------------------------------------------------------------------|-----------------------|-----------|
| Mg-Cl        | $Pca2_1$ (no. 29)      | 538 K $\rightarrow F\bar{4}3c$                                                                                       | $C_1$                 | [48, 62]  |
| Mg-Br        | $F\bar{4}3c$ (no. 219) | $\approx 293$ K $\rightarrow F\bar{4}3c$                                                                             | $S_4$                 | [63-64]   |
| Mg-I         | $F\bar{4}3c$ (no. 219) | —                                                                                                                    | $S_4$                 | This work |
| Zn-F         | $R3c$ (no. 161)        | $\sim 1100$ K $\rightarrow$ decomposition                                                                            | $C_1$                 | [65]      |
| Zn-Cl        | $R3c$ (no. 161)        | $\approx 473$ K $\rightarrow Pa$<br>$\approx 563$ K $\rightarrow Pca2_1$<br>$\approx 723$ K $\rightarrow F\bar{4}3c$ | $C_1$                 | [53, 66]  |
| Zn-Br        | $Pca2_1$ (no. 29)      | 586 K $\rightarrow F\bar{4}3c$                                                                                       | $C_1$                 | [51]      |
| Zn-I         | $Pca2_1$ (no. 29)      | 375 K $\rightarrow F\bar{4}3c$                                                                                       | $C_1$                 | [55, 64]  |

## Luminescence Spectroscopy

The photoluminescence (PL) emission and excitation spectra at 83 K of the investigated  $\text{Mn}^{2+}$ -activated boracites are depicted in Fig. 3. All investigated  $\text{Mn}^{2+}$ -activated boracites  $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$  ( $M = \text{Mg, Zn}$ ;  $X = \text{Cl, Br, I}$ ) show broad-band (FWHM = 1680 – 1990  $\text{cm}^{-1}$ ) emission in the NIR range centred between 744 – 794 nm at that temperature, which has so far not been observed for  $\text{Mn}^{2+}$  and is actually much more typically observed in  $\text{Cr}^{3+}$ -activated phosphors. The emission FWHMs are in between the typical ranges observed for tetrahedrally and octahedrally coordinated  $\text{Mn}^{2+}$  in solid-state compounds.<sup>[43]</sup> Additional confirmation can be gained from the long decay times at 83 K in the range between 50 ms ( $M = \text{Mg}$ ;  $X = \text{Cl}$ ) and 71 ms ( $M = \text{Mg}$ ;  $X = \text{I}$ ) that also match spin- and parity-forbidden transitions of  $\text{Mn}^{2+}$ . They clearly differ from the expectations for emissive impurities like broad-band emitting  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$  or defects.<sup>[30-31, 67-68]</sup> Additional confirmation can be gained from electron spin resonance (ESR) spectra at 100 K, as the estimated  $g$  factor is close to the free electron value ( $g = 2.0023\dots$ ), as should be expected for a  $^6\text{S}$  ground term of a  $3d^5$  HS ion in a crystal field (see Fig. S7). While  $\text{Mn}^{4+}$  and  $\text{Mn}^{5+}$  give rise to spin-forbidden narrow-line emission in the red ( $\text{Mn}^{4+}$ ) or deep NIR ( $\text{Mn}^{5+}$ ) range and can already be optically distinguished, potentially NIR broad-band emitting  $\text{Mn}^{3+}$  ( $d^4$  HS) should be characterized by  $g < 2$  based on its  $^5\text{E}_g(^5\text{D})$  ground state in an octahedral field and partial quenching of the spin-only magnetic moment.<sup>[69]</sup>

Usually,  $\text{Mn}^{2+}$  shows green emission in tetrahedral coordination and orange to red emission in octahedral coordination in the solid state.<sup>[36, 40, 70]</sup> An additional redshift to the NIR can be achieved upon additional distortion of those cubic symmetries. In those cases, the lowest excited triply orbitally degenerate state  $^4\text{T}_{1g}(^4\text{G})$  ultimately splits and

leads to an additional structurally induced redshift. Such a loss of degeneracy of excited  $3d^n$  states has also been reported for the absorption spectra of transition metal-based boracites  $M_3B_7O_{13}X$  ( $M = \text{Co}, \text{Ni}$ ;  $X = \text{Cl}, \text{Br}, \text{I}$ ).<sup>[71]</sup> Another example includes the ligand field splitting and unusually redshifted luminescence of  $\text{Mn}^{2+}$  in the pyrophosphates  $AM'P_2O_7:\text{Mn}^{2+}$  ( $A = \text{Sr}, \text{Ba}$ ;  $M' = \text{Mg}, \text{Zn}$ ) with the activator in square-planar (bi-)pyramidal coordination.<sup>[72-73]</sup> Finally, also the hexagonal  $\text{CsM}''\text{X}_3$  ( $M'' = \text{Mg}, \text{Cd}$ ;  $X = \text{Cl}, \text{Br}$ ) with face-sharing  $[\text{M}''\text{X}_6]$  octahedra constitute examples, in which incorporated  $\text{Mn}^{2+}$  ions show unusually redshifted luminescence beyond 650 nm due to the non-negligible (structurally induced) trigonal distortion at the  $M''$  sites.<sup>[74-76]</sup>



**Figure 3.** PL excitation (blue) and emission (red) spectra of  $\text{Mn}^{2+}$ -activated boracites at 83 K.

There are also discernible trends among the investigated  $\text{Mn}^{2+}$ -activated boracites. Generally, the emission spectra of the Mg-based boracites are red-shifted compared to those of the Zn-based ones. This is assigned to a stronger ligand field splitting related to the slightly smaller ionic radius of  $\text{Mg}^{2+}$  ( $r_{\text{Mg}^{2+}} = 0.72 \text{ \AA}$ , C.N. = 6) compared to that of  $\text{Zn}^{2+}$  ( $r_{\text{Zn}^{2+}} = 0.74 \text{ \AA}$ , C.N. = 6).<sup>[60]</sup> Interestingly, the luminescence spectra of the  $\text{Mn}^{2+}$ -activated iodide-containing boracites even show vibronic fine structure at already 83 K, which is a typical signature of host compounds with extremely rigid structures such as garnets or nitrides.<sup>[38, 77-78]</sup> The extracted phonon replica is  $\hbar\omega = (249 \pm 9) \text{ cm}^{-1}$  in both  $M_3B_7O_{13}I:\text{Mn}^{2+}$  ( $M = \text{Mg}, \text{Zn}$ ) compounds. This observation is in line with a comparably small Stokes shift below  $2000 \text{ cm}^{-1}$  in both compounds and unusually high thermal quenching temperatures beyond 423 K (see Table 2) that is necessary for reasonable performance in phosphor-converted light-emitting devices



(pc-LEDs). For better resolution, measurements at 4.2 K were conducted. Indeed, in all regarded boracites vibronic fine structure can be resolved (Figure S6). The extracted phonon replicas of the compounds  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{X}:\text{Mn}^{2+}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Br}:\text{Mn}^{2+}$  are in the range of  $\hbar\omega = 77 - 96 \text{ cm}^{-1}$ , which aligns very well with the lowest phonon frequencies of orthorhombic boracites known from Raman spectra.<sup>[55]</sup> However, the extracted phonon replica of the new compound  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$  are significantly higher ( $\hbar\omega \approx 241 \text{ cm}^{-1}$ ), in agreement with the lowest phonon frequencies of known cubic boracites.<sup>[55]</sup>

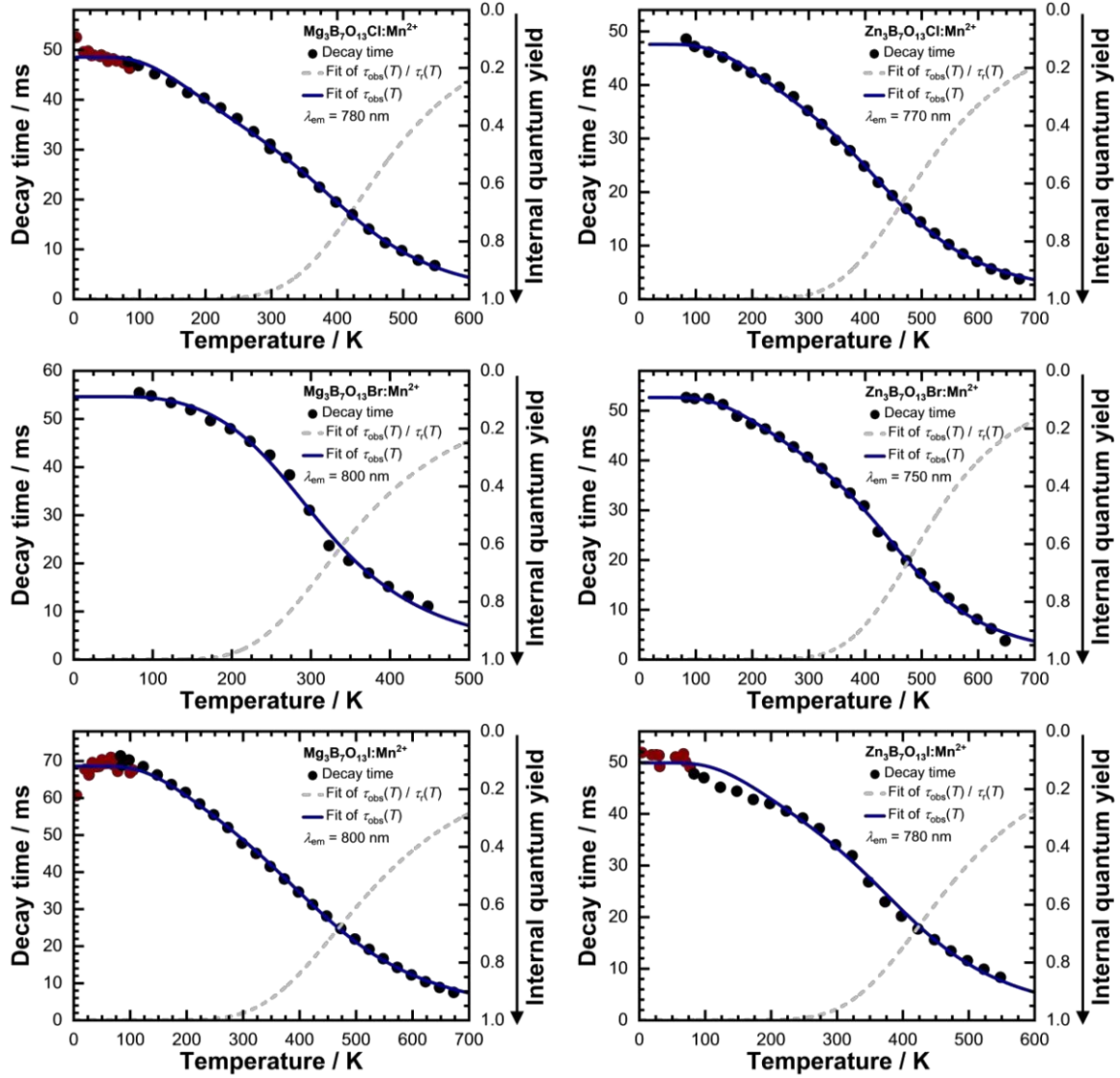
The PL excitation spectra show a distinct splitting of the excited states, which is particularly prominent for the bromide and iodide-containing boracites. This is a direct result of the loss of orbital degeneracy in the low-symmetric  $[5 + 1]$  ligand field.<sup>[72-73]</sup> It is particularly noteworthy that there is an increasing intensity of the excitation band at around 430 nm from the chloride- to the iodide-based boracites. This observation must be related to an increasing impact of spin-orbit coupling that enhances the absorption cross section at that particular wavelength.

**Table 2.** PL properties of  $\text{Mn}^{2+}$ -activated boracites.

| Compound                                                     | FWHM / $\text{cm}^{-1}$<br>( $T = 83 \text{ K}$ ) | $\lambda_{\text{em}} / \text{nm}$<br>( $\lambda_{\text{ex}} = 410\text{-}420 \text{ nm}$ ,<br>$T = 83 \text{ K}$ ) | Zero phonon<br>line / $\text{cm}^{-1}$<br>( $T = 4.2 \text{ K}$ ) | Stokes shift / $\text{cm}^{-1}$<br>( $T = 83 \text{ K}$ ) | $T_{50} / \text{K}$ |
|--------------------------------------------------------------|---------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|-----------------------------------------------------------|---------------------|
| $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}:\text{Mn}^{2+}$ | 1790                                              | 793                                                                                                                | Not observed                                                      | 2440                                                      | 476                 |
| $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Br}:\text{Mn}^{2+}$ | 1790                                              | 792                                                                                                                | 13660                                                             | 2170                                                      | 372                 |
| $\text{Mg}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$  | 1680                                              | 794                                                                                                                | 13360                                                             | 1860                                                      | 562                 |
| $\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}:\text{Mn}^{2+}$  | 1990                                              | 744                                                                                                                | Not observed                                                      | 3050                                                      | 494                 |
| $\text{Zn}_3\text{B}_7\text{O}_{13}\text{Cl}:\text{Mn}^{2+}$ | 1850                                              | 780                                                                                                                | 13770                                                             | 2520                                                      | 522                 |
| $\text{Zn}_3\text{B}_7\text{O}_{13}\text{Br}:\text{Mn}^{2+}$ | 1820                                              | 790                                                                                                                | 13720                                                             | 2340                                                      | 525                 |
| $\text{Zn}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$  | 1810                                              | 788                                                                                                                | 13710                                                             | 1990                                                      | 468                 |

A sharp break is found in the temperature-dependent intensity evolution of  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Br}:\text{Mn}^{2+}$  and  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$  at around 300 K and 360 K, respectively (see Fig. S3), which is associated with an orthorhombic  $\rightarrow$  cubic phase transition, reportedly occurring at 291 – 294 K and 370 – 380 K.<sup>[55, 64, 71, 79]</sup> Interestingly, an initially increasing photoluminescence intensity with increasing temperature is observed in  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{Cl}:\text{Mn}^{2+}$ ,  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$ , and  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$ . This is a consequence of vibronic coupling to low energetic odd-parity modes that lift the parity selection rule in centrosymmetric environments and thus, thermally accelerate the radiative decay pathway, which is a well-known feature in the luminescence of transition metal ions.<sup>[35, 71, 80-82]</sup> In line with that interpretation, the photoluminescence decay time also gradually decreases at temperatures between 4.2 K and 500 K. This observation can be understood in the regarded  $\text{Mn}^{2+}$ -activated boracites starting from an idealized centrosymmetric  $D_{4h}$  symmetry at the  $M$  sites. An additional hint on the validity of this hypothesis is the fact that the radiative decay time at 4.2 K is particularly long (see Fig. 5 and Table S7) in the boracites with a  $S_4$  symmetric  $M$  site ( $M = \text{Mg}, \text{Zn}$ ) such as  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Br}:\text{Mn}^{2+}$  and  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$  (see Table 1), which deviates less from that approximated idealized  $D_{4h}$  symmetry than the  $C_1$  site symmetry in the other boracites. It is typical that the much more spatially extended 3d orbitals react less sensitive to

slight symmetry distortions than, e.g., more shielded 4f orbitals such as in the case of  $\text{Eu}^{3+}$ , which is comparably sensitive to tiny symmetry distortions.



**Figure 5.** Temperature-dependent decay times of  $\text{Mn}^{2+}$ -activated boracites. The red and black color coding indicates different measurement setups (see SI for details). Decay times are amplitude-weighted average values derived from triexponential fit functions. The blue lines denote to a fit of the full decay probability according to (1). The dashed grey lines represent the temperature dependence of the IQY according to (3).

In turn, the photoluminescence quenching temperature  $T_{50}$  is an important measure in phosphor design, typically derived from temperature-dependent luminescence intensity plots or temperature-dependent decay times. However, this approach does not account for the influence of vibronic coupling on the radiative rates, which induces a decreasing decay time and an increasing luminescence intensity with increasing temperatures, without necessarily causing an alteration of the overall efficiency. It is therefore more accurate to model and compare the contributions of radiative and nonradiative decay processes to the observed decay time  $\tau_{\text{obs}}$ , according to<sup>[83]</sup>

$$\tau_{\text{obs}}(T) = \frac{\tau_r(T)}{1 + \left(\frac{\tau_r(T)}{\tau_{\text{nr}}(0)}\right) \exp\left(-\frac{\Delta E}{k_B T}\right)} \quad (1)$$

with

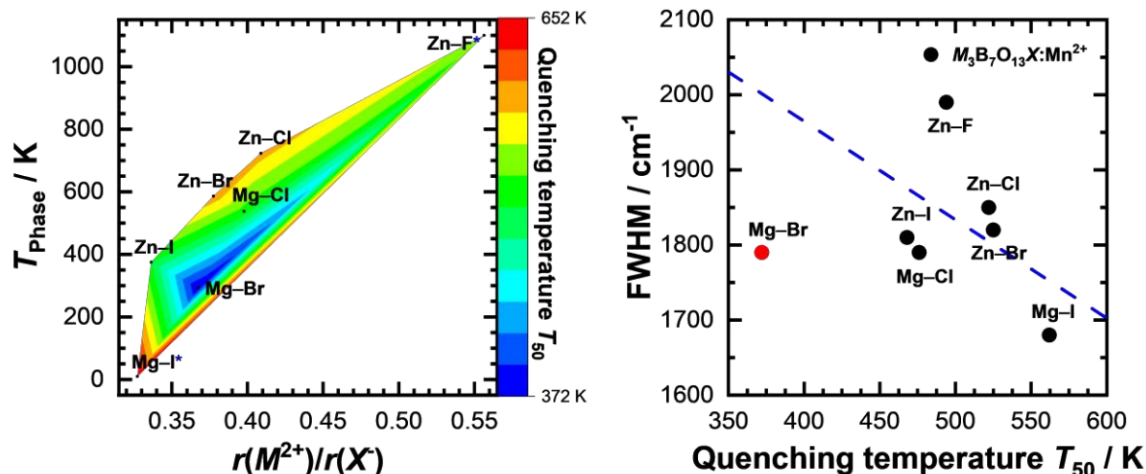
$$\tau_r(T) = \frac{\tau_r(0)}{\coth\left(\frac{\hbar\omega}{2k_B T}\right)} \quad (2)$$

where  $k_B = 0.695\,034\,800\,486\,127\text{ cm}^{-1}\text{ K}^{-1}$  is the Boltzmann constant (defined as being exact according to the International System of Units),  $T$  is the absolute temperature,  $\hbar\omega$  is the effective odd-parity phonon energy coupled to,  $\Delta E$  is the activation energy for thermal quenching,  $\tau_r(0)$  is the intrinsic radiative decay time of the excited state and  $k_{nr}(0) = 1/\tau_{nr}(0)$  the connected intrinsic crossover rate for thermal quenching. The fitting parameters are summarized in Table S7. The ratio of the observed decay time vs. the radiative decay time allows for an estimation of the theoretically expected internal quantum yield (IQY) per  $\text{Mn}^{2+}$  emitter according to:

$$\text{IQY} = \frac{\tau_{\text{obs}}(T)}{\tau_r(T)} \quad (3)$$

The temperature dependence of the IQY finally allows a more realistic estimate of the photoluminescence quenching temperature  $T_{50}$ . The fitting results from Fig. 5 agree very well with the results from the temperature-dependent emission spectra, validating a negligible contribution of nonradiative processes up to temperatures higher than 300 K for all investigated  $\text{Mn}^{2+}$ -activated boracites due to vibronic coupling contributions. At higher temperatures, thermal quenching becomes noticeable. Usually, broad-band emitters in solid-state structures can undergo thermal quenching by thermally activated nonradiative crossover of the potential energy curves of the excited state and the ground state in configurational coordinate space. Alternatively, also thermally induced ionization of excited electrons *via* the conduction band of the host compound is a possible quenching pathway that has been demonstrated to be relevant in  $\text{Mn}^{2+}$ -activated phosphors. The band gaps of the investigated boracites are very wide, typically in the order of 6.5 eV for the Zn-based boracites or even close to 8.0 eV for the Mg-based boracites.<sup>[44-45]</sup> These values are comparable to band gaps of ionic fluoride host compounds and also generally disfavour thermal ionization as an alternative quenching mechanism. Variation of the halide ion is not expected to have a significant impact on these band gaps since their p orbital contributions to the uppermost valence band of such ionic compounds is negligible compared to the 2p contribution of the O atoms in those compounds according to density of states (DOS) calculations.<sup>[45]</sup> Thus, thermally activated crossover is a plausible quenching mechanism for the luminescence of  $\text{Mn}^{2+}$  in the regarded boracites. In such a case, the quenching temperatures  $T_{50}$  should show a correlation with structural features such as the radius ratio  $r(\text{M}^{2+})/r(\text{X}^-)$  being a reasonable qualitative descriptor for the internal chemical pressure in inorganic structures. A plot of the estimated thermal quenching temperatures  $T_{50}$  according to a temperature-dependent decay analysis against the radius ratio  $r(\text{M}^{2+})/r(\text{X}^-)$  does indeed imply such a correlation (Fig. 6). It is noteworthy that the same trend is expected for the phase transition temperature to the cubic polymorphs.<sup>[64]</sup>  $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Br}:\text{Mn}^{2+}$  shows an unexpectedly low  $T_{50}$ , which is ascribed to the occurrence of a  $Pca2_1$  (no. 29)  $\rightarrow$   $F\bar{4}3c$  (no. 219) phase transition within the investigated temperature range. Next to the quenching temperatures and emission FWHMs, also the radiative contributions to the decay times show such a correlation and become gradually longer along the series  $Pca2_1$  (no. 29) /  $R3c$  (no. 161) with  $\tau_r \sim 50 - 55\text{ ms}$  to  $F\bar{4}3c$  (no. 219) with  $\tau_r \sim 70\text{ ms}$  (see Figure 5 and Table S7) clearly

demonstrating the impact of the off-centered position of the  $M$  site and thus, lowered local site symmetry (see Figure 2) on the photoluminescence decay time at cryogenic temperatures.



**Figure 6.** Left: Contour plot of the  $Pca2_1$  (no. 29)  $\rightarrow$   $F\bar{4}3c$  (no. 219) phase transition temperature against the ratio of the ionic radii of the respective  $M^{2+}$  and  $X^-$  sites. The thermal quenching temperatures  $T_{50}$  of the respective compounds are denoted by a color plot. \*Mg-I does not show a definite phase transition in the investigated temperature range, according to photoluminescence measurements. This is in line with observations made on  $Cu_3B_7O_{13}I$  with an identical  $r(M^{2+})/r(X^-)$  ratio.<sup>[84]</sup> Zn-F does not show a structural transition up to the decomposition temperature of 1100 K according to the literature.<sup>[65]</sup> Right: Plot of the FWHM at 83 K against the respective thermal quenching temperatures  $T_{50}$ . Smaller FWHMs are associated with higher quenching temperatures. The dashed line is added to indicate the trend. Mg-Br was not included in the trend, due to the influence of a phase transition within the investigated temperature range.

## Conclusion

In this work, we present hitherto unreported  $Mn^{2+}$ -activated air-stable boracites  $M_3B_7O_{13}X:Mn^{2+}$  ( $M = \text{Mg, Zn}$ ;  $X = \text{Cl, Br, I}$ ) compounds with (for that activator) so far non-encountered efficient broad-band NIR emission close to 800 nm, vibronic fine structure at low temperatures and connected unusually high thermal quenching temperatures up to 560 K ( $Mg_3B_7O_{13}I:Mn^{2+}$ ). The photoluminescence decay times are in the order of 50 – 70 ms and in between common values for tetrahedrally and octahedrally coordinated  $Mn^{2+}$  in solid-state phosphors. We ascribe the unusually long emission wavelength as well as the connected decay times to the highly unsymmetric [5+1] coordination pattern of the  $M$  sites ( $M = \text{Mg, Zn}$ ) in the structure of the  $Mn^{2+}$ -activated boracites. The wide band gaps above 6.5 eV exclude thermal ionization as a relevant thermal quenching mechanism and offer leverage in the desired control of the thermal quenching properties of the NIR emission of  $Mn^{2+}$  in these compounds by the structural concepts of chemical pressure. Beneficially, the absorption cross section at 430 – 450 nm of the incorporated  $Mn^{2+}$  ions also increases with increasing atomic number of the halide ions implying a stronger impact of spin-orbit coupling. These combined effects show that the presented  $Mn^{2+}$ -activated boracites could pave a first way to interesting alternative phosphors for NIR-emitting pc-LEDs with earth-abundant elements.



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## Supporting Information

# Thermally robust near-infrared emission of $\text{Mn}^{2+}$ in boracites with fine-tuned absorption strength

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## 1. Experimental Section

**Table S1.** Chemicals used in the preparation of  $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$  ( $M = \text{Mg}, \text{Zn}, \text{Mn}$ ;  $X = \text{Cl}, \text{Br}, \text{I}$ ).

| Compound          | Quality          | Manufacturer      |
|-------------------|------------------|-------------------|
| ZnCl <sub>2</sub> | 99.99%           | Thermo Scientific |
| ZnBr <sub>2</sub> | 99.999%          | abcr              |
| ZnI <sub>2</sub>  | 99.99%           | Sigma Aldrich     |
| MgO               | 99.999%          | Roth              |
| ZnO               | 99.999%          | Thermo Scientific |
| MnO               | 99.99%           | Alfa Aesar        |
| HBr               | 48%, p.a.        | Honeywell         |
| HI                | 57%, p.a.        | Acros             |
| I <sub>2</sub>    | z.S.             | Unknown           |
| Mg                | p.a., oxide free | Unknown           |
| EtOH              | p.a.             | CHEMSOLUTE        |

## B<sub>2</sub>O<sub>3</sub>

H<sub>3</sub>BO<sub>3</sub> (≥99.5%, CHEMSOLUTE) was dehydrated stepwise at 100 °C, 150 °C and 250 °C in a dynamic vacuum. The final temperature of 250 °C was held for 12 h. B<sub>2</sub>O<sub>3</sub> was received as colorless powder. The product was stored in an argon filled glovebox.

## MgCl<sub>2</sub>

5 g (24.6 mmol) MgCl<sub>2</sub> · 6 H<sub>2</sub>O (99%, Merck) and 1.975 g (36.9 mmol) NH<sub>4</sub>Cl (99.7%) were dissolved in 12 ml of water, evaporated till dryness and subsequently dried for 12 h in a drying cabinet. The remaining powder was reground with another 1.975 g of NH<sub>4</sub>Cl and tempered for 4 h at 600 °C in a dynamic vacuum. The remaining off-white powder was distilled at 900 °C for 48 h in a flame sealed, evacuated silica ampoule. The colorless product was reground and stored in an Ar filled glovebox.

## MgBr<sub>2</sub>

MgBr<sub>2</sub> (98%, anhydrous, Thermo Scientific) was sealed in an evacuated fused silica tube and distilled at 950 °C. The colorless product was reground and stored in an Ar filled glovebox.

## MgI<sub>2</sub>

Mg and I<sub>2</sub> were filled in a long, fused silica tube, with a small excess of the metal. The ampoule was sealed under vacuum and its bottom was inserted into a tubular furnace. The mixture was heated with a rate of 200 °C/h to 550 °C and held for 12 h. The remaining elemental I<sub>2</sub> was sublimed to the end of the ampule and torch sealed. The colorless product was then distilled twice at 900 °C in fused silica ampoules. MgI<sub>2</sub> was received in form of colorless plates. The product was reground and stored in an Ar filled glovebox.

**Table S2.** Chemicals used in the preparation of Zn<sub>3</sub>B<sub>7</sub>O<sub>13</sub>F:Mn<sup>2+</sup>

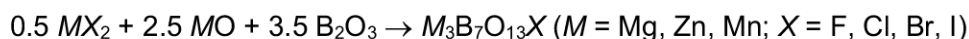
| Compound                      | Quality | Manufacturer   |
|-------------------------------|---------|----------------|
| ZnF <sub>2</sub>              | 99.9%   | Thermo Fischer |
| B <sub>2</sub> O <sub>3</sub> | 99.9%   | Alfa Aesar     |

## MnF<sub>2</sub>

MnF<sub>2</sub> has been prepared from MnCO<sub>3</sub> and HF, as described in the literature.<sup>[1-2]</sup>

## Preparation of M<sub>3</sub>B<sub>7</sub>O<sub>13</sub>X (M = Mg, Zn, Mn; X = Cl, Br, I)

Any of the investigated Mn<sup>2+</sup>-activated boracites were synthesized by solid-state reactions of the respective oxides and halides according to:



In some cases, an excess of both the halide and B<sub>2</sub>O<sub>3</sub> was necessary to receive phase pure products (see Table S3). The educts were carefully ground with an agate mortar in an argon filled glovebox and subsequently sealed in evacuated silica ampoules. The ampoules were sintered and opened in air. The Br<sup>-</sup> and I<sup>-</sup>-containing boracites were subsequently washed with distilled water, ethanol and a 1:1 mixture of concentrated HBr or HI and water. The Cl<sup>-</sup>-containing boracites were used without washing.

**Preparation of  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}:\text{Mn}^{2+}$** 

For synthesis of  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}:\text{Mn}^{2+}$ , the corresponding starting materials ( $\text{ZnF}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{MnF}_2$ ) in the form of powders were mixed in the ratio 3.96:7:0.04, respectively, and put into a Pt capsule. The experiment was carried out via high-pressure/high-temperature methods using a Walker-type multianvil module within a 1000 t hydraulic press (Max Voggenreiter GmbH) in an 18/11 assembly. Further details concerning this kind of setup are described in the literature.<sup>[3-5]</sup> The pressure of 2.5 GPa was built up in 60 min, followed by heating to the temperature of 400 °C within 5 min. The maximum temperature of the reaction was held for 20 min, then reduced to 80 °C with a cooling rate of 3.2°C/min. Afterwards, the reaction was quenched to room temperature within a few minutes. Decompression to ambient conditions was performed within 180 min.

**Table S3.** Stoichiometric amounts of the starting compounds and sintering conditions used for the synthesis of  $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$  ( $M = \text{Mg}, \text{Zn}, \text{Mn}$ ;  $X = \text{Cl}, \text{Br}, \text{I}$ ).

|                                    | $\text{Mg-Cl}:\text{Mn}^{2+}$ | $\text{Mg-Br}:\text{Mn}^{2+}$ | $\text{Mg-I}:\text{Mn}^{2+}$ | $\text{Zn-F}:\text{Mn}^{2+}$ | $\text{Zn-Cl}:\text{Mn}^{2+}$ | $\text{Zn-Br}:\text{Mn}^{2+}$ | $\text{Zn-I}:\text{Mn}^{2+}$ |
|------------------------------------|-------------------------------|-------------------------------|------------------------------|------------------------------|-------------------------------|-------------------------------|------------------------------|
| MgO / mg (mmol)                    | 50 (1.24)                     | 24.7 (0.613)                  | 27.3 (0.677)                 |                              |                               |                               |                              |
| ZnO / mg (mmol)                    |                               |                               |                              |                              | 50.6 (0.621)                  | 50.6 (0.621)                  | 50.4 (0.619)                 |
| $\text{B}_2\text{O}_3$ / mg (mmol) | 122 (1.75)                    | 67.0 (0.963)                  | 80.1 (0.869)                 | 119.0 (1.709)                | 61.1 (0.878)                  | 61.0 (0.876)                  | 60.9 (0.863)                 |
| $\text{ZnF}_2$ / mg (mmol)         |                               |                               |                              | 100.0 (0.967)                |                               |                               |                              |
| $\text{ZnCl}_2$ / mg (mmol)        |                               |                               |                              |                              | 34.2 (0.259)                  |                               |                              |
| $\text{ZnBr}_2$ / mg (mmol)        |                               |                               |                              |                              |                               | 42.1 (0.187)                  |                              |
| $\text{ZnI}_2$ / mg (mmol)         |                               |                               |                              |                              |                               |                               | 79.9 (0.25)                  |
| $\text{MgCl}_2$ / mg (mmol)        | 30 (0.31)                     |                               |                              |                              |                               |                               |                              |
| $\text{MgBr}_2$ / mg (mmol)        |                               | 24.2 (0.121)                  |                              |                              |                               |                               |                              |
| $\text{MgI}_2$ / mg (mmol)         |                               |                               | 109 (0.392)                  |                              |                               |                               |                              |
| $\text{MnF}_2$ / mg (mmol)         |                               |                               |                              | 0.91 (0.0098)                |                               |                               |                              |
| MnO / mg (mmol)                    | 1 (0.015)                     | 1.1 (0.016)                   | 0.9 (0.013)                  |                              | 1 (0.015)                     | 0.8 (0.011)                   | 1 (0.015)                    |
| Sintering / °C                     | 850                           | 950                           | 950                          |                              | 700                           | 700                           | 700                          |
| Dwell / h                          | 24                            | 16                            | 16                           |                              | 16                            | 16                            | 16                           |

## 2. Energy dispersive X-ray spectroscopy

The chemical composition of all compounds was investigated with a field emission gun scanning electron microscope (FEG-SEM) Clara Ultra High Resolution (UHR) from TESCAN equipped with an energy dispersive X-ray spectroscopy (EDX) detector Ultim Max, 65 mm<sup>2</sup> from OXFORD. Imaging and EDX measurements were performed in analysis mode at an acceleration voltage of 20 keV and a beam current of 3 nA at a working distance of 9.5 mm. Boron, oxygen, and hydrogen were not quantifiable with reasonable accuracy.

**Table S4.** Dopant concentration of the investigated samples according to EDX.

| $M-X$ | Mg-Cl / % | Mg-Br / % | Mg-I / % | Zn-F / % | Zn-Cl / % | Zn-Br / % | Zn-I / % |
|-------|-----------|-----------|----------|----------|-----------|-----------|----------|
| Mn/M  | 2.2(3)    | 4.9(7)    | 1.0(6)   | 0.7 (3)  | 0.8(1)    | 0.7(2)    | 0.6(4)   |



### 3. X-ray powder diffraction (XRPD)

The purity of the products was determined by XRPD using a STOE Stadi P2 diffractometer in Debye-Scherrer mode and transmission geometry with Ge(111)-monochromatized Mo  $K_{\alpha 1}$  radiation ( $\lambda = 0.7093 \text{ \AA}$ ) within a range of  $2\theta = 2 - 50^\circ$ , a step size of  $0.015^\circ$  and a Mythen 1K silicon strip detector (Dectris, Baden-Dättiswil, Switzerland). Rietveld refinement was performed with the program Topas 7.0.0.7 (Bruker ASX, 2022, Germany).<sup>[6]</sup> Background corrections were performed with Chebychev polynomials of the 20<sup>th</sup> order. Peak shapes were fitted using the LVol\_FWHM\_CS\_G\_L and e0\_from\_Strain commands, that comprises both Voigt and Gaussian components. The diffraction patterns are displayed in Figure S1. An identified side phase was the sodalite type  $\text{Zn}_4\text{B}_6\text{O}_{13}$  that occurred frequently in the synthesis of  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{I}$ . The refinement parameters are given in Table S5 and S6.

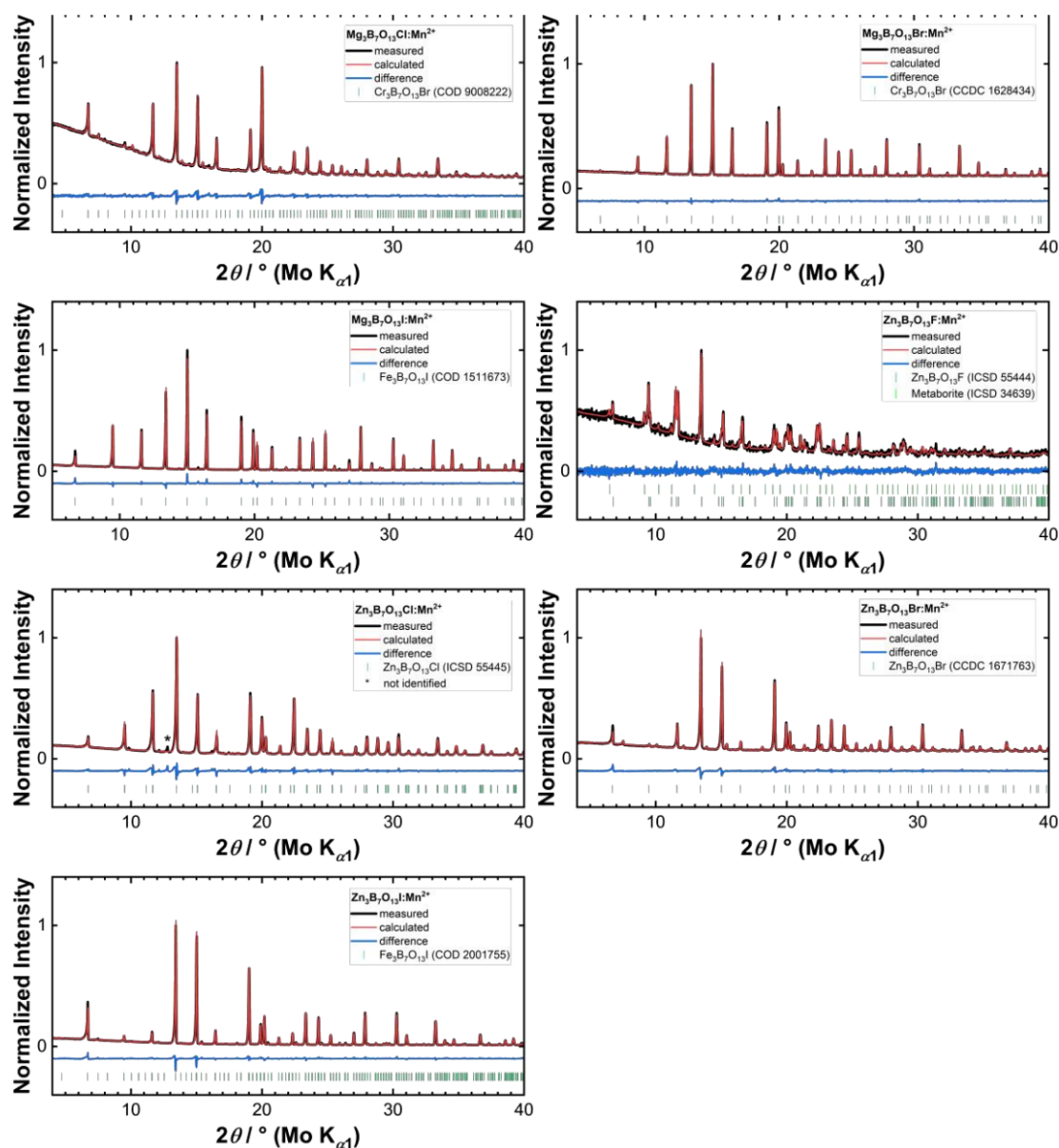
$\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}:\text{Mn}^{2+}$  was analyzed by powder X-ray diffraction on a STOE Stadi P powder diffractometer. Measurements were performed in transmission geometry with Ge(111)-monochromatized Mo  $K_{\alpha 1}$  radiation ( $\lambda = 0.7093 \text{ \AA}$ ) within a range of  $2\theta = 2 - 60^\circ$ , a step size of  $0.015^\circ$  and a Mythen 1 K detector. Rietveld refinement was performed with the program Topas 4.2 (Bruker ASX, 2009, Germany). Background corrections were performed with Chebychev polynomials of the 20<sup>th</sup> order. Peak shapes were fitted using FP, Cry size L and Strain G commands. The diffraction pattern is displayed in Figure S1. An identified side phase was metaboric acid ( $\text{HBO}_2$ ). The refinement parameters are given in Table S5 and S6.

**Table S5.** Parameters of the Rietveld refinements of the investigated  $\text{Mn}^{2+}$ -activated boracites and database code of the structures used for the refinements.

| Compound                                                                                          | $R_{\text{Bragg}} / \%$ | $R_{\text{exp}} / \%$ | $R_{\text{wp}} / \%$ | $R_p / \%$ | G.o.F. | Database code |
|---------------------------------------------------------------------------------------------------|-------------------------|-----------------------|----------------------|------------|--------|---------------|
| <b><math>\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}:</math> 2.2% <math>\text{Mn}^{2+}</math></b> | 0.97                    | 2.05                  | 3.67                 | 2.43       | 1.79   | COD 9008222   |
| <b><math>\text{Mg}_3\text{B}_7\text{O}_{13}\text{Br}:</math> 4.9% <math>\text{Mn}^{2+}</math></b> | 1.34                    | 1.19                  | 1.36                 | 1.03       | 1.14   | CCDC 1628434  |
| <b><math>\text{Mg}_3\text{B}_7\text{O}_{13}\text{I}:</math> 1.0% <math>\text{Mn}^{2+}</math></b>  | 5.38                    | 2.43                  | 7.07                 | 4.92       | 2.91   | COD 1511673   |
| <b><math>\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}:</math> 0.7% <math>\text{Mn}^{2+}</math></b>  | 2.57                    | 7.95                  | 7.07                 | 5.50       | 0.89   | ICSD 34639    |
| <b><math>\text{Zn}_3\text{B}_7\text{O}_{13}\text{Cl}:</math> 0.8% <math>\text{Mn}^{2+}</math></b> | 2.04                    | 1.57                  | 6.42                 | 4.29       | 4.10   | ICSD 55445    |
| <b><math>\text{Zn}_3\text{B}_7\text{O}_{13}\text{Br}:</math> 0.7% <math>\text{Mn}^{2+}</math></b> | 1.89                    | 1.31                  | 3.52                 | 2.26       | 2.70   | CCDC 1671763  |
| <b><math>\text{Zn}_3\text{B}_7\text{O}_{13}\text{I}:</math> 0.6% <math>\text{Mn}^{2+}</math></b>  | 3.36                    | 1.85                  | 6.08                 | 4.35       | 3.29   | COD 2001755   |

**Table S6.** Structure parameters of the investigated Mn<sup>2+</sup>-activated boracites, received from Rietveld refinement.

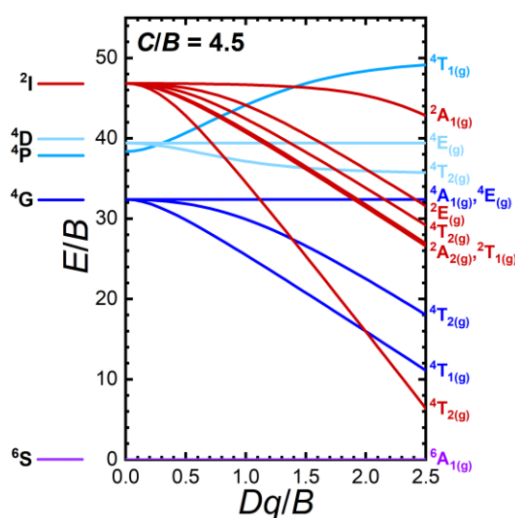
| Compound                                                                 | Space Group (no.)                       | <i>a</i> / Å | <i>b</i> / Å | <i>c</i> / Å | <i>V</i> / Å <sup>3</sup> | <i>Z</i> |
|--------------------------------------------------------------------------|-----------------------------------------|--------------|--------------|--------------|---------------------------|----------|
| Mg <sub>3</sub> B <sub>7</sub> O <sub>13</sub> Cl: 2.2% Mn <sup>2+</sup> | <i>Pca</i> 2 <sub>1</sub> (no. 29)      | 8.5456       | 8.5417       | 12.10        | 882.10                    | 4        |
| Mg <sub>3</sub> B <sub>7</sub> O <sub>13</sub> Br: 4.9% Mn <sup>2+</sup> | <i>F</i> $\bar{4}$ 3 <i>c</i> (no. 219) | 12.10        |              |              | 1772.6                    | 8        |
| Mg <sub>3</sub> B <sub>7</sub> O <sub>13</sub> I: 1.0% Mn <sup>2+</sup>  | <i>F</i> $\bar{4}$ 3 <i>c</i> (no. 219) | 12.14        |              |              | 1788.5                    | 8        |
| Zn <sub>3</sub> B <sub>7</sub> O <sub>13</sub> F: 0.7% Mn <sup>2+</sup>  | <i>R</i> 3 <i>c</i> (no. 161)           | 8.477        |              | 21.12        | 1314.0                    | 6        |
| Zn <sub>3</sub> B <sub>7</sub> O <sub>13</sub> Cl: 0.8% Mn <sup>2+</sup> | <i>R</i> 3 <i>c</i> (no. 161)           | 8.542        |              | 20.97        | 1324.8                    | 6        |
| Zn <sub>3</sub> B <sub>7</sub> O <sub>13</sub> Br: 0.7% Mn <sup>2+</sup> | <i>Pca</i> 2 <sub>1</sub> (no. 29)      | 8.562        | 8.569        | 12.11        | 888.71                    | 4        |
| Zn <sub>3</sub> B <sub>7</sub> O <sub>13</sub> I: 0.6% Mn <sup>2+</sup>  | <i>Pca</i> 2 <sub>1</sub> (no. 29)      | 8.600        | 8.584        | 12.15        | 896.84                    | 4        |

**Figure S1.** Rietveld refined X-ray powder diffraction (XRPD) patterns of Mn<sup>2+</sup>-activated boracites.

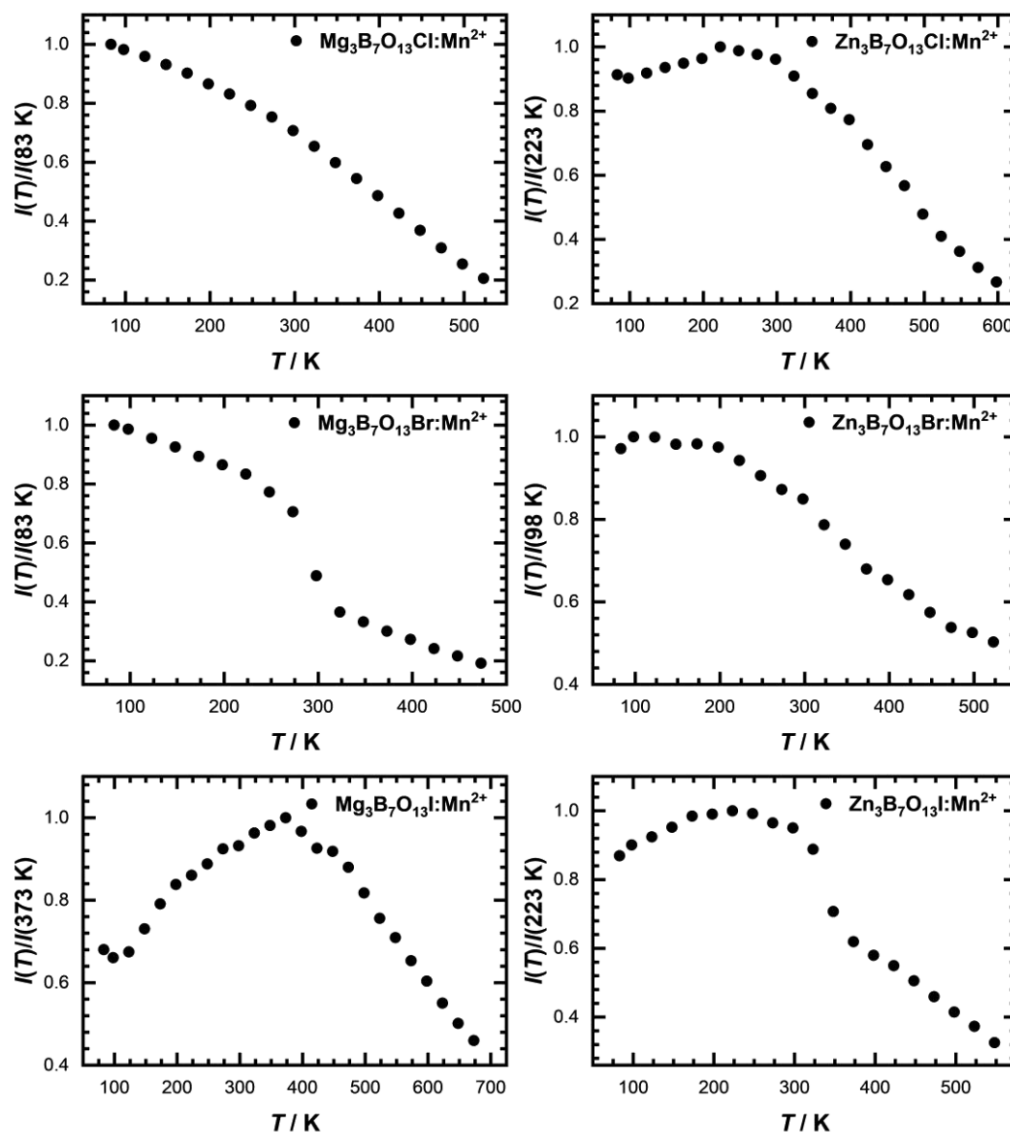
#### 4. Luminescence spectroscopy

Optical measurements between 83 K and 700 K were performed on an Edinburgh Instruments FLS1000 photoluminescence spectrometer equipped with a 450 W Xe arc lamp as a wavelength-variable excitation source for excitation spectra, double excitation and emission monochromators in Czerny-Turner configuration and a thermoelectrically cooled ( $-20\text{ }^{\circ}\text{C}$ ) photomultiplier tube PMT-980 (Hamamatsu). The excitation spectra were corrected with respect to the grating efficiency, PMT sensitivity with respect to the lamp intensity. The decay traces were measured with a laser diode VPL-420 (Edinburgh Instruments, 70.0 mW average incident peak power,  $\lambda = 423.6\text{ nm}$ ) with adjustable temporal pulse width ( $0.04\text{ }\mu\text{s} \dots 1\text{ ms}$ ) and variable pulse repetition rate ( $0.1\text{ Hz} \dots 5\text{ MHz}$ ) as the pulsed excitation source. The laser was also used in a continuous wave excitation mode for the recording of emission spectra. The detection mode for time resolved measurements was single-photon multichannel scaling. Temperature-dependent measurements were performed with a Linkam Scientific THMS600 temperature cell with temperature accuracy of  $\pm 0.1\text{ }^{\circ}\text{C}$  in the regarded temperature range between  $-190\text{ }^{\circ}\text{C}$  and  $525\text{ }^{\circ}\text{C}$ . Sample were prepared on fused silica sample holders. After each heating or cooling step, a two-minute equalization time was set before a measurement was started.

Optical measurements below 83 K were performed with an Ekspla NT342B OPO laser (10 Hz) and an Opotek Opolette 355 HE II tunable laser with 5 ns pulse width and variable pulse repetition rate (1 Hz...20 Hz) as a wavelength-variable excitation source for steady-state emission spectra and time-resolved measurements, respectively. Temperature-dependent measurements were carried out using an Oxford Instruments liquid-helium flow cryostat (Oxford, UK) equipped with an external temperature controller. The powder samples were mounted on a copper holder within the cryostat, and the temperature was monitored by a thermocouple in direct contact with the sample holder. Emission spectra were recorded with a liquid N<sub>2</sub>-cooled Ocean Optics QE Pro CCD detector, while luminescence decay traces were collected using a thermoelectrically cooled (−20 °C) Hamamatsu R928 photomultiplier tube attached to an Edinburgh Instruments FLS920 photoluminescence spectrometer with single grating emission monochromator.



**Figure S2.** Tanabe-Sugano diagram for octahedrally coordinated  $d^5$  ions.  $B$  and  $C$  denote the interelectronic repulsion Racah parameters.

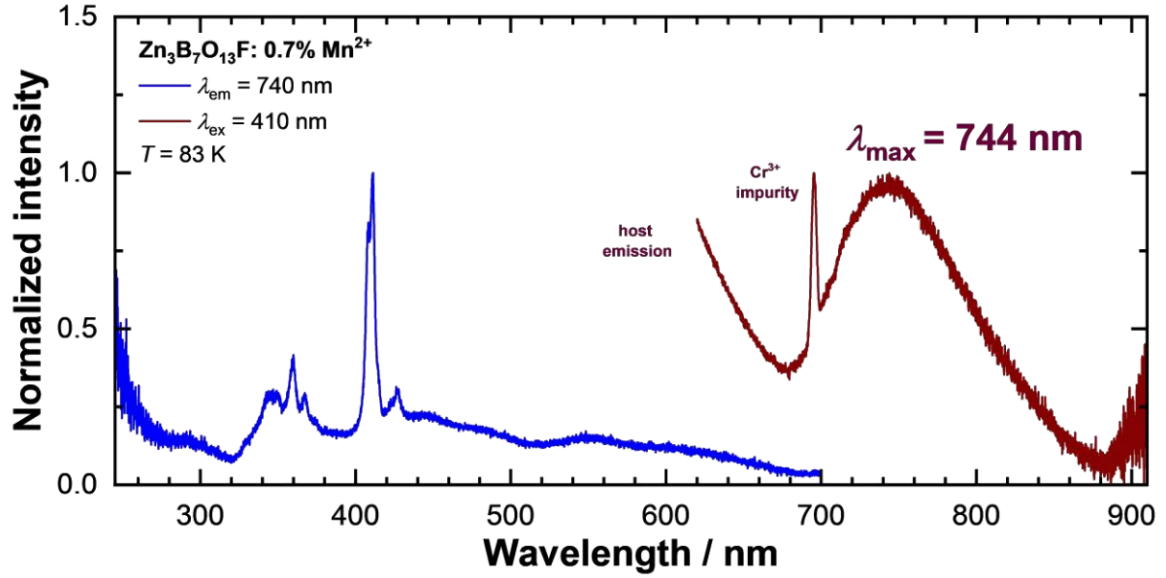


**Figure S3.** Temperature dependence of the emission intensity of  $\text{Mn}^{2+}$ -activated boracites (full emission range used for integration, see Fig. 3).

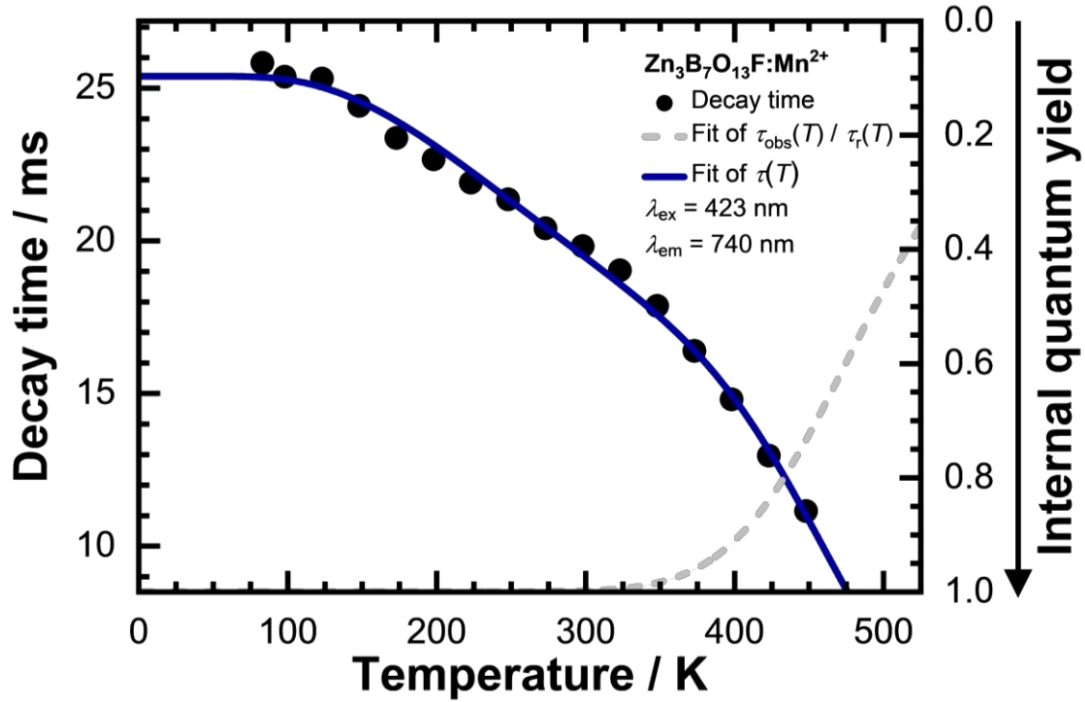
**Table S7.** Fitting parameters of the total decay probability. Errors are given in brackets.

| Compound                                                     | $\tau_r(0)$ / ms | $\tau_{nr}(0)$ / ms | $\hbar\omega$ / $\text{cm}^{-1}$ | $\Delta E$ / $\text{cm}^{-1}$ |
|--------------------------------------------------------------|------------------|---------------------|----------------------------------|-------------------------------|
| $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}:\text{Mn}^{2+}$ | 48.5(3)          | 0.16(10)            | 321(8)                           | 1930(210)                     |
| $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Br}:\text{Mn}^{2+}$ | 54.6(9)          | 0.6(3)              | 412(45)                          | 1150(130)                     |
| $\text{Mg}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$  | 68.6(3)          | 0.9(4)              | 386(13)                          | 1662(175)                     |
| $\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}:\text{Mn}^{2+}$  | 25.4(2)          | 0.001(3)            | 423(10)                          | 3380(720)                     |
| $\text{Zn}_3\text{B}_7\text{O}_{13}\text{Cl}:\text{Mn}^{2+}$ | 47.6(3)          | 0.18(4)             | 400(8)                           | 2020(80)                      |
| $\text{Zn}_3\text{B}_7\text{O}_{13}\text{Br}:\text{Mn}^{2+}$ | 52.63(2)         | 0.09(2)             | 426(6)                           | 2320(100)                     |
| $\text{Zn}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$  | 49.9(5)          | 0.3(2)              | 359(18)                          | 1744(315)                     |

## 5. Luminescence spectroscopy of $\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}: 0.7\% \text{Mn}^{2+}$

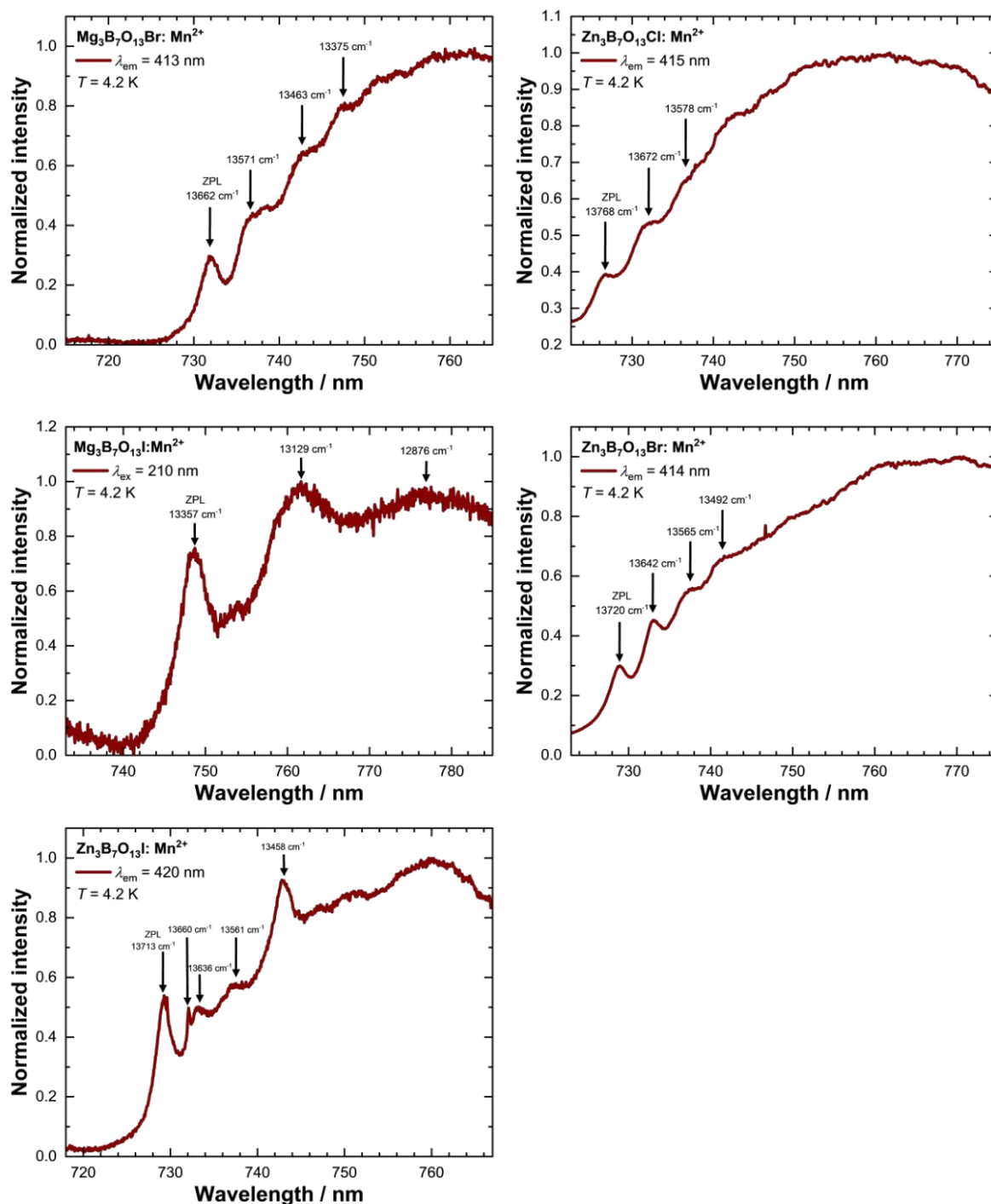


**Figure S4.** PL excitation (blue) and emission (red) spectra of  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}: 0.7\% \text{Mn}^{2+}$  at 83 K.



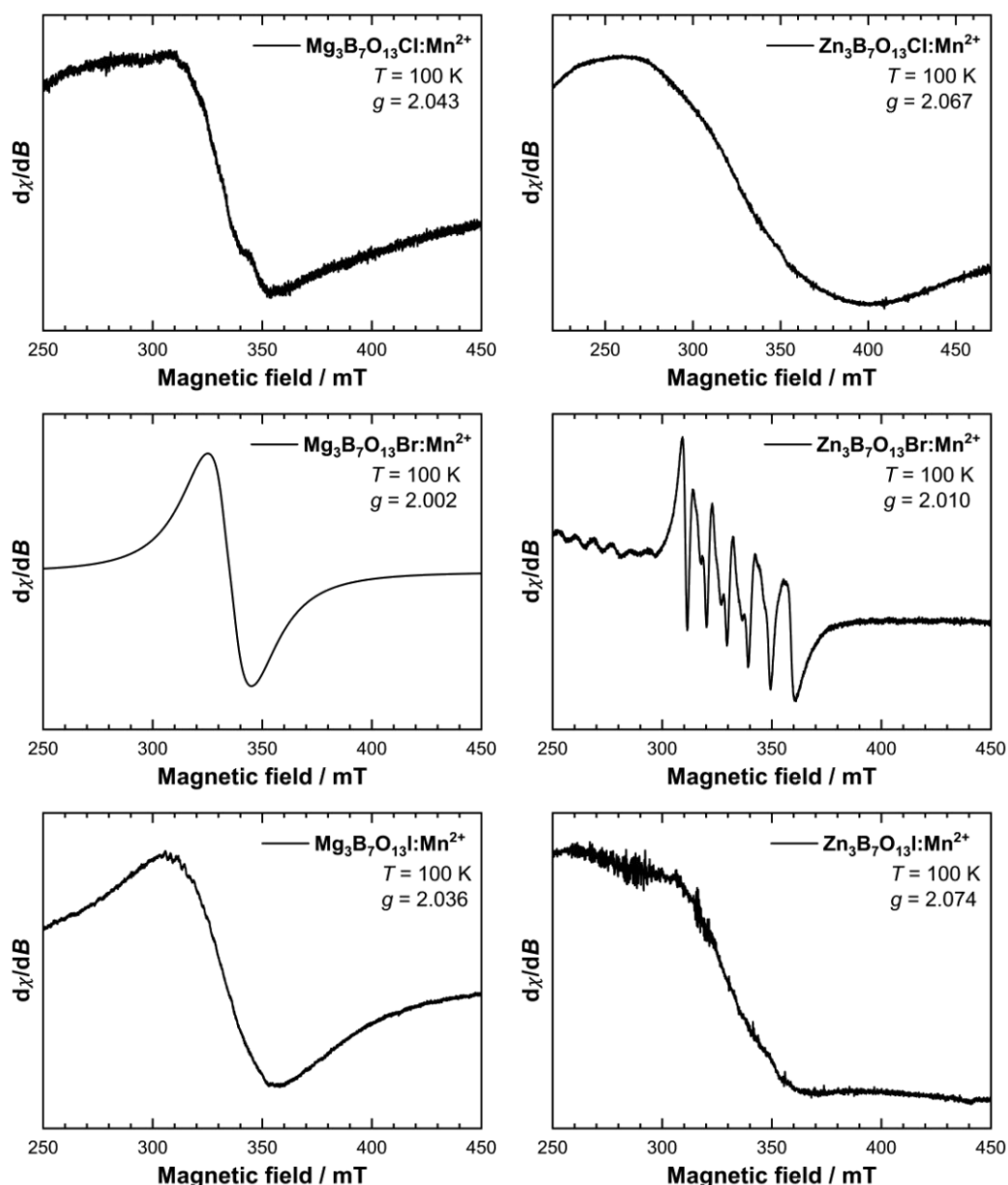
**Figure S5.** Temperature dependent decay times of  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{F}:\text{Mn}^{2+}$ . Decay times are amplitude-weighted average values derived from triexponential fit functions. The blue line denotes to a fit of the full decay probability according to eq. (1) in the main text. The grey line represents the temperature dependence of the IQY according to eq. (3) in the main text.

## 6. Luminescence spectra at 4.2 K

Figure S6. High-resolution emission spectra of  $\text{Mn}^{2+}$ -activated boracites at 4.2 K.

## 7. Electron spin resonance (ESR) spectra

Low-temperature electron spin resonance (ESR) measurements were performed using a Bruker Magnetech ESR5000 bench-top spectrometer at  $T = 100$  K operating with an X band ( $\nu = 9.4$  GHz). The results confirm the presence of  $\text{Mn}^{2+}$  in the samples with  $g$ -factors of 2.002–2.074. The ESR spectra of the  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{Cl}:\text{Mn}^{2+}$  and  $\text{Zn}_3\text{B}_7\text{O}_{13}\text{I}:\text{Mn}^{2+}$  samples used for photoluminescence measurements showed very weak resolution, which might be related to the low dopant concentration, the sample adjustment or possible impurities. Therefore, samples with a higher nominal  $\text{Mn}^{2+}$  concentration of 10% were prepared for recording the ESR spectra of these two compounds.

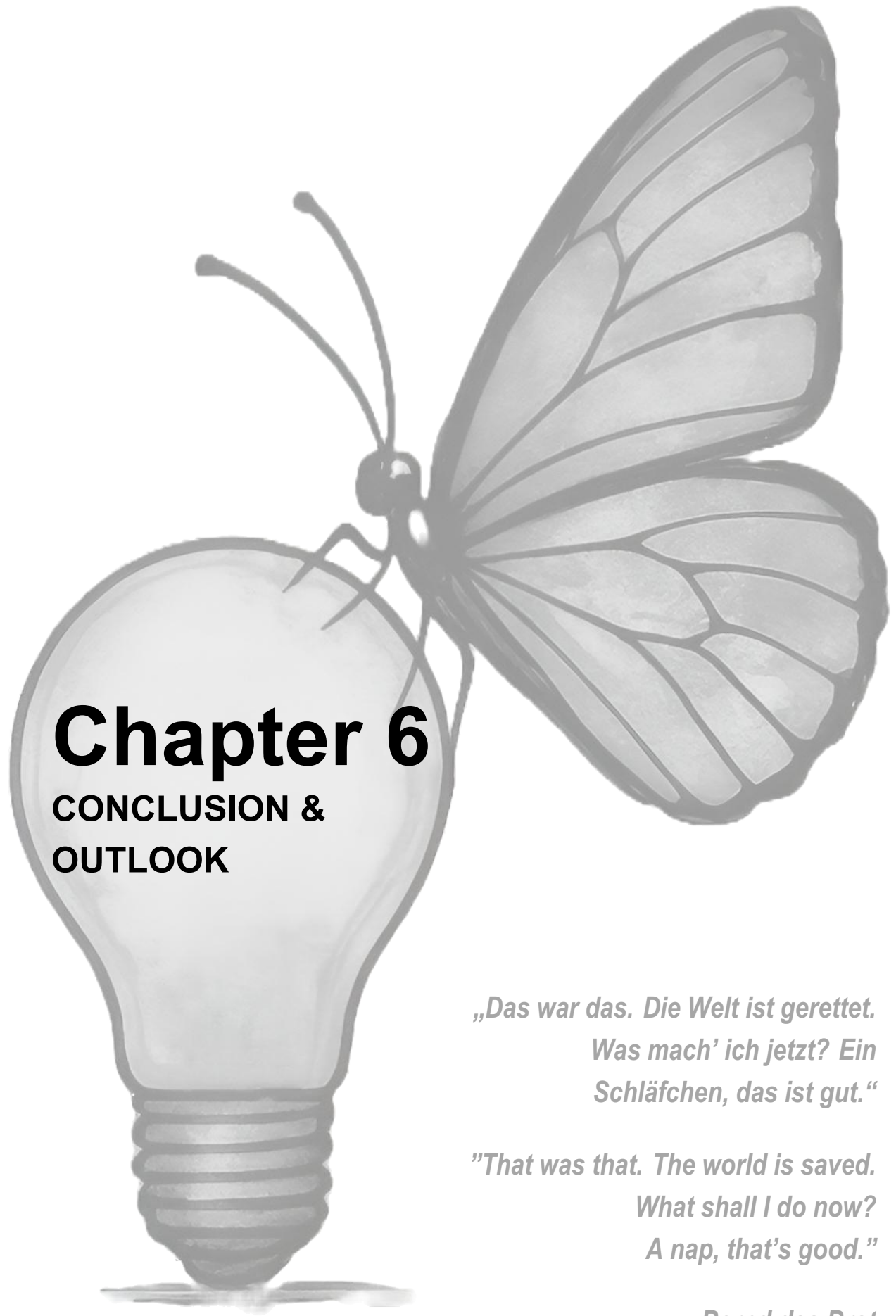


**Figure S7.** Low-temperature ( $T = 100$  K) X band ESR spectra of the investigated  $\text{Mn}^{2+}$ -activated boracites. Powder-averaged electron  $g$  factors according to the position of the resonance are given in the respective graphs.

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# Chapter 6

## CONCLUSION & OUTLOOK

*„Das war das. Die Welt ist gerettet.  
Was mach' ich jetzt? Ein  
Schläfchen, das ist gut.“*

*”That was that. The world is saved.  
What shall I do now?  
A nap, that’s good.”*

*– Bernd das Brot*

## 6.1 Conclusion

Modern pc-wLED are mature, sustainable lighting solutions. However, the ecologically positive implications of their energy efficiency are diminished by the environmental impact of the incorporated *REE*. The mining and refinement of *REE* is usually accompanied by the production of toxic byproducts, including corrosive gases, sewage and radioactive waste (see Section 1.2). Moreover, the worldwide increasing demand for *REE* is currently only covered by a few countries, with China being the globally leading exporter. In 2023, China alone accounted for  $\approx 70\%$  of the worldwide *REE* production.<sup>[1]</sup> Environmental and political concerns caused a growing interest in alternative, non-*REE* activator ions for pc-LEDs. One such emitter could be the abundant transition metal ion  $\text{Mn}^{2+}$ , which, in fact, has already been widely applied in commercial phosphors for mercury discharge lamps and fluorescence tubes, e.g. as green-emitting willemite ( $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ ) or white-emitting halophosphate ( $\text{Ca}_5(\text{PO}_4)_3\text{F,Cl:Sb}^{3+}, \text{Mn}^{2+}$ ).<sup>[2–6]</sup>

This thesis established optimization strategies for the design of effective  $\text{Mn}^{2+}$ -activated phosphors with the ultimate goal to create additional stimuli for an application in pc-wLEDs and display technology. These concepts were explicitly demonstrated by the introduction of  $\text{Mn}^{2+}$  into rather unusual host compounds and a careful investigation of the photoluminescence properties of the resulting activated compounds. The results contribute to a better scientific understanding of how to target an efficient luminescence of  $\text{Mn}^{2+}$  in solids by means of structural and electronic control parameters:

### Covalency of the metal–ligand interaction

The energy of the states in the Tanabe-Sugano diagram depends on the Racah parameter  $B$ , which essentially parametrizes the degree of covalency of a Mn–ligand bond. A larger value of  $B$  is associated with an increased energy separation of the lowest excited state ( ${}^4\text{T}_{1g}({}^4\text{G})$ ) and the ground state ( ${}^6\text{A}_{1g}({}^6\text{S})$ ) of  $\text{Mn}^{2+}$ , which ultimately leads to blue-shifted emission.

In **Chapter 3**, this correlation of the Racah parameter  $B$  with the spectral energy of the excitation bands of  $\text{Mn}^{2+}$  was used to gain information about the nature of the chemical bond in  $\text{Mn}^{2+}$ -activated zinc borosulfates in the solid solution  $\text{Zn}_{(1-x)}\text{Mn}_x[\text{B}_2(\text{SO}_4)_4]$  ( $x = 0.5, 1, 2, 3, 4, 5, 10$ ). These silicate-analogous compounds contains particularly electron-withdrawing  $[\text{SO}_4]^{2-}$  groups next to  $[\text{BO}_4]^{5-}$  tetrahedra making them interesting candidates for our studies. The investigated samples showed an orange emission around 590 nm, despite octahedral strong-field coordination, which readily indicates highly ionic Mn–ligand bonds and potentially weak coordinating behavior of the borosulfate ligand. This suspicion was confirmed by the extraction of the interelectronic Racah repulsion parameters and the ligand field splitting  $10Dq$  from photoluminescence excitation spectra. The results were discussed and compared to literature-known  $\text{Mn}^{2+}$ -activated metal-halide perovskites, which share the structural feature of octahedral coordination. By that, it was possible to place the borosulfate ligand in the spectrochemical series in between chloride and fluoride. Moreover, the results were also affirmed by other studies using Mössbauer spectroscopy on antimony

borosulfates as well as UV/vis and magnetic studies on transition metal and rare-earth borosulfates.<sup>[7–9]</sup>

This study shows that  $\text{Mn}^{2+}$  can be a potential tool to detect weak coordination behavior of ligands and to gather additional insights into the nature of the Mn–ligand interaction. The results also emphasize to consider chemically more uncommon ligands to tailor the emission color of  $\text{Mn}^{2+}$  by electronic means.

#### **Degree of condensation and structural rigidity of the host**

Structural rigidity is usually associated with a mechanically limited offset in the configurational coordinates between ground state and excited state, which results in narrower emission bandwidths and inhibition of crossover processes.

This idea was followed in **Chapter 4** by introducing  $\text{Mn}^{2+}$  into a series of alkali lithooxidosilicates, which stand out by their highly condensed  $\text{UCr}_4\text{C}_4$ -related structures, comprising a rigid anionic backbone with tetrahedral  $[\text{LiO}_4]^{7-}$  and  $[\text{SiO}_4]^{4-}$  building units and cuboidally coordinated alkali cations.<sup>[10]</sup> The luminescence of seven  $\text{Mn}^{2+}$ -activated alkali lithooxidosilicates was investigated, characterized by a dual-band narrow-green and broad-red emission at around 530 nm and 620 nm. Temperature-dependent emission and lifetime measurements allowed us to assign both emissions to the radiative  ${}^4\text{T}_{1g} \leftrightarrow {}^6\text{A}_{1g}$  transition of  $\text{Mn}^{2+}$  occupying different sites within the alkali lithooxidosilicate host: The green emission was assigned to  $\text{Mn}^{2+}$  occupying tetrahedrally coordinated Li sites with only weak crystal field splitting and the red emission was assigned to  $\text{Mn}^{2+}$  occupying cuboidally coordinated Na or K sites with effectively stronger crystal field splitting. However, the ratio of both emission bands was found to change among the respective compounds from almost purely green-emitting  $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2:\text{Mn}^{2+}$  to red-emitting  $\text{RbNa}_3[\text{Li}_3\text{SiO}_4]_4:\text{Mn}^{2+}$ . This observation was taken as an opportunity to investigate the site occupation preferences of  $\text{Mn}^{2+}$  if more than one possible substitution site is available. Calculations of the mean effective ionic radii (MEFIR) of the available Li, Na and K substitution sites in the investigated compounds revealed the following trends: First, if effectively smaller Na sites are available, the red component of the emission is dominant, e.g., in  $\text{Na}[\text{Li}_3\text{SiO}_4]:\text{Mn}^{2+}$  ( $\text{MEFIR}(\text{Na}^+) = 111.6 \text{ pm}$ ) and  $\text{RbNa}_3[\text{Li}_3\text{SiO}_4]_4:\text{Mn}^{2+}$  ( $\text{MEFIR}(\text{Na}^+) = 115.4 \text{ pm}$ ). Conversely, the absence of smaller Na sites enhances green emission, e.g., in  $\text{K}[\text{Li}_3\text{SiO}_4]:\text{Mn}^{2+}$  ( $\text{MEFIR}(\text{K}^+) = 127.6 \text{ pm}$ ),  $\text{RbNa}[\text{Li}_3\text{SiO}_4]_2:\text{Mn}^{2+}$  ( $\text{MEFIR}(\text{Na}^+) = 118.5 \text{ pm}$ ) and  $\text{RbKLi}_2[\text{Li}_3\text{SiO}_4]_4:\text{Mn}^{2+}$  ( $\text{MEFIR}(\text{K}^+) = 142.4 \text{ pm}$ ). In addition, the red emission band is shifted to longer wavelengths for smaller Na sites, which is in line with an expectedly increasing crystal field strength.

It was concluded that the site preference of  $\text{Mn}^{2+}$  is closely related to the size of the available substitution sites, which allows for a careful optimization of the overall color impression of the dual-band green and red emission. Our work provides insights into the site preference of  $\text{Mn}^{2+}$  if more than one possible cation site is available. This might be a valuable asset for a possible application in sustainable one-component pc-wLEDs.

### 💡 Crystal field splitting

The energy separation of the lowest excited state ( ${}^4T_{1g}({}^4G)$ ) and the ground state ( ${}^6A_{1g}({}^6S)$ ) of  $Mn^{2+}$  is strongly correlated with the crystal field strength. Generally, stronger crystal fields are associated with a red-shifted emission due to a stabilization of the excited  ${}^4T_{1g}({}^4G)$  state. It is thus a common way to tune the emission color of  $Mn^{2+}$  from green to red by transitioning from a weak tetrahedral to a strong octahedral crystal field. However, less symmetric activation sites should expectably result in a lifting of orbital degeneracy of the excited states and thereby enable an unusually strong red-shift of the emission.

In **Chapter 5**, we have studied the photoluminescence of  $Mn^{2+}$ -activated boracites  $M_3B_7O_{13}X$  ( $M = Zn, Mg$ ;  $X = F, Cl, Br, I$ ) with highly asymmetric [5+1] coordinated cation sites. Photoluminescence emission spectra of the as-prepared samples revealed an unprecedented bathochromic shift of the emission of  $Mn^{2+}$  approaching 800 nm. This observation is discussed on the basis of an increased orbital triple degeneracy of the lowest excited state ( ${}^4T_{1g}({}^4G)$ ), induced by the asymmetric [5+1] coordinated  $M$  sites. This is also reflected in the photoluminescence excitation spectra, which show a distinct splitting of the excited states as a direct result of the loss of orbital degeneracy. Additionally, temperature-dependent measurements revealed a high luminescence temperature stability with quenching temperatures above 300 K for any of the investigated compounds. The quenching mechanism is discussed on the basis of a trend analysis, consulting structural and luminescence features. The wide band gap of the investigated compounds ( $E_g > 6.5$  eV) makes thermally assisted photoionization unlikely. Instead, thermally activated crossover is a more plausible quenching mechanism for this specific group of  $Mn^{2+}$ -activated phosphors, which must, however, also be structurally limited as the observation of vibronic fine structure in the low temperature spectra ( $T = 77$  K) indicated.

Our study presents the first group of  $Mn^{2+}$ -activated NIR-emitting phosphors with emission wavelengths approaching nearly 800 nm. With this, our results extend the effective working range of  $Mn^{2+}$ -activated phosphors into a range that was previously reserved for  $Cr^{3+}$ -activated phosphors. The unique combination of a very wide band gap, distinct structural rigidity, and spin-orbit facilitated absorption makes  $Mn^{2+}$ -activated boracites an interesting alternative in this regard.

## 6.2 Outlook

LED lighting is expected to reduce the overall energy consumption of lighting technologies by 70% until 2030.<sup>[11,12]</sup> This energy saving greatly contributes to reducing CO<sub>2</sub> emissions and helps slow down the human-made climate change. However, the current reliance of pc-LEDs on *REE* is also liable to supply chain uncertainties and environmental pollution based on their extraction from ores. One possible solution for this issue can be the exploration of new *REE* deposits in developed countries, such as the recently discovered deposit in Kiruna, Sweden. However, according to an official statement by the mining company LKAB, it will take at least 10 to 15 years from the discovery to the start of mining.<sup>[13]</sup> Therefore, a substitution of *REE* with alternative

emitters might be a more viable solution for the current issues with *REE*. The abundant transition metal ion  $\text{Mn}^{2+}$  is a particularly promising candidate in this regard, with temperature-stable and comparably narrow emission bands, making it particularly interesting for low-power applications like backlighting for liquid crystal displays or indoor lighting. Scientists have already developed several functioning  $\text{Mn}^{2+}$ -based pc-wLED devices with appreciable efficiency, but several drawbacks such as lowered absorption strength and expectable droop at higher current densities compared to established  $\text{Ce}^{3+}$ - or  $\text{Eu}^{2+}$ -activated phosphors limit clear-cut commercial applications.<sup>[14–17]</sup> It is therefore a reasonable strategy to create new incentives for a transition to *REE*-free lighting by the development of new  $\text{Mn}^{2+}$ -activated phosphors with further improved luminescence characteristics. The following is intended to highlight some of the remaining challenges:

#### **Cyan narrow-band emission from $\text{Mn}^{2+}$**

The search for efficient cyan phosphors with narrow emission bandwidths centered around 490 nm is a particularly active research field.<sup>[18–20]</sup> However, only a few  $\text{Mn}^{2+}$ -activated phosphors with peak emission wavelengths below 505 nm are known, including  $\text{CaF}_2:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 495 \text{ nm}$ )<sup>[21,22]</sup> or  $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 505 \text{ nm}$ )<sup>[23]</sup>. Those compounds combine highly ionic Mn–ligand interactions and a tetrahedral or cubic coordination environment with comparably low ligand field splitting. The greatest challenge in the design of cyan-emitting  $\text{Mn}^{2+}$ -activated phosphors is the search for suitable host compounds. In principle, ionic host compounds like fluorides, phosphates, or borosulfates with tetrahedrally coordinated activation sites could enable a cyan emission. Two such compounds are the scheelite-type fluorides  $\text{CaZnF}_4$  and  $\text{SrZnF}_4$ <sup>[24]</sup>. However, first tests within the preparations for this thesis indicated an occupation of the heavier alkaline earth sites in both compounds.

#### **Deeper NIR emission**

Broad-band NIR-emitting phosphors are used in many technical areas, including plant-growth, active night vision, medicine, and non-destructive analysis. However, a fundamental issue of many NIR phosphors is their liability to thermal quenching, either due to a thermal crossover, or, alternatively, due to thermal ionization (see Section 2.2.5). It is thus a promising approach to use host compounds with large band gaps and profound structural rigidity in the design of thermally stable broad-band NIR-emitting phosphors. Chapter 5 of this thesis presented the first  $\text{Mn}^{2+}$ -activated near-infrared phosphors. This unique emission property is related to the unsymmetrical [5+1] coordination, which lifts the triple orbital degeneracy of the excited states and thus causes an additional red-shift of the luminescence. An even larger bathochromic shift might be conceivable through the introduction of covalent ligands or even more unconventional coordination symmetries, e.g. square-planar coordination. The fact that square-planar coordinated  $\text{Li}^+$  is known from some alkali lithooxidosilicates like  $\text{RbLi}[\text{Li}_3\text{SiO}_4]_2$  or  $\text{RbKLi}_2[\text{Li}_3\text{SiO}_4]_4$  supports this idea.<sup>[25–27]</sup>

#### **Narrow-band red phosphors**

A common strategy to tune the emission color of  $\text{Mn}^{2+}$  from green to red is by a

transition from tetrahedral to octahedral coordination with an overall stronger crystal field splitting. However, octahedrally coordinated  $\text{Mn}^{2+}$  suffers from a weaker absorption and higher sensitivity to saturation effects as the Laporte restriction becomes effective. Moreover, the stronger crystal field splitting readily implies larger emission bandwidths according to the Tanabe-Sugano diagram, which is unfavorable for many applications. Another strategy to achieve orange-red emission from  $\text{Mn}^{2+}$  with narrow bandwidths is a higher degree of covalency of the Mn–ligand bond in host compounds like nitrides or sulfides (see Section 2.4). This is particularly challenging from a synthetic point of view as total exclusion of moisture and air is often necessary during the preparations to avoid the formation of oxygen-defects. Moreover, increased covalency of the chemical bonds is often accompanied by smaller band gaps of the host compounds which facilitates thermal quenching at comparably low temperatures. However, this strategy holds great potential upon careful selection of the host systems. Generally, compounds composed of small and highly charged main-group cations (e.g.  $\text{P}^{5+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Be}^{2+}$ ) tend to have larger band gaps, which is preferable for a possible activation with  $\text{Mn}^{2+}$  (see Section 2.4). Successful examples include  $\text{AlN}:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 600 \text{ nm}$  /  $\text{FWHM} = 1220 \text{ cm}^{-1}$  /  $E_{\text{g}} = 6.2 \text{ eV}$ )<sup>[16]</sup>,  $\text{ZnGeN}_2:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 610 \text{ nm}$  /  $\text{FWHM} = 1320 \text{ cm}^{-1}$  /  $E_{\text{g}} = 3.3 \text{ eV}$ )<sup>[28]</sup> and  $\text{Ba}_2\text{ZnS}_3:\text{Mn}^{2+}$  ( $\lambda_{\text{em}} = 611 \text{ nm}$  /  $\text{FWHM} = 1350 \text{ cm}^{-1}$  /  $E_{\text{g}} = 3.4 \text{ eV}$ )<sup>[29,30]</sup>.

### 6.3 Closing remarks

The abundant transition metal ion  $\text{Mn}^{2+}$  has great potential to substitute *REE* in phosphors for pc-wLEDs for low-power applications. However, the industry has not yet adopted this idea due to the maturity of the well-established *REE*-activated phosphors. It is therefore up to the academic research to stimulate a technological transition by the development of new and improved  $\text{Mn}^{2+}$ -activated phosphors that could foster a sustainable transition to competitive rare-earth-free alternatives for lighting and display technology.

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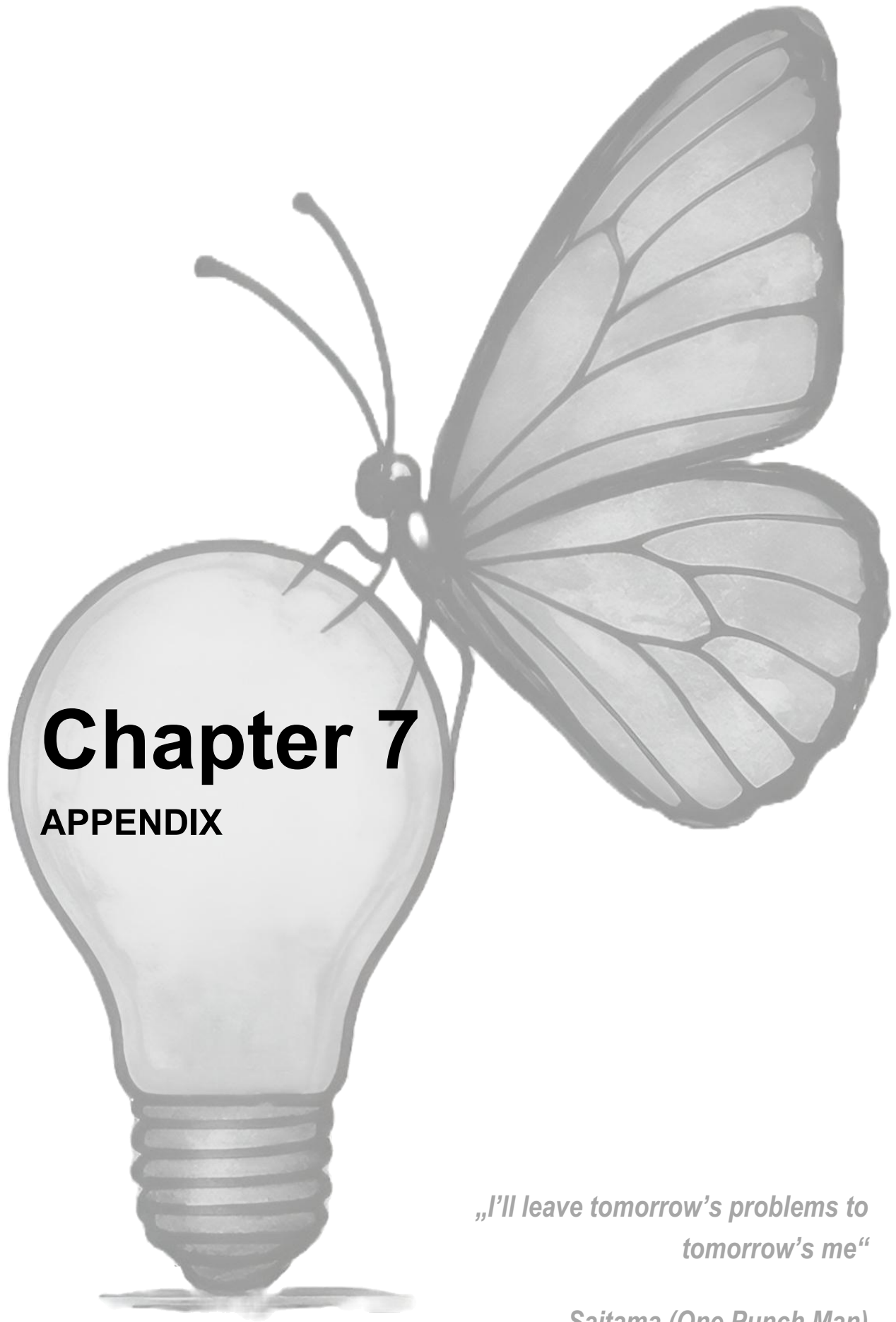
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# Chapter 7

## APPENDIX

*„I'll leave tomorrow's problems to  
tomorrow's me“*

*– Saitama (One Punch Man)*

## 7.1 List of Publications

### **Photoluminescence of $\text{Mn}^{2+}$ in the Borosulfate $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ : $\text{Mn}^{2+}$ —A Tool to Detect Weak Coordination Behavior of Ligands**

**Full citation:**

L. M. Träger, L. C. Pasqualini, H. Huppertz, J. Bruns, M. Suta, *Angew. Chem. Int. Ed.* **2023**, 62, e202309212. <https://doi.org/10.1002/anie.202309212>

Also published in German:

### **Photolumineszenz von $\text{Mn}^{2+}$ in dem Borosulfat $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$ : $\text{Mn}^{2+}$ – Eine Möglichkeit zum Nachweis schwach koordinierender Liganden**

**Full citation:**

L. M. Träger, L. C. Pasqualini, H. Huppertz, J. Bruns, M. Suta, *Angew. Chem.* **2023**, 135 (45), e202309212. <https://doi.org/10.1002/ange.202309212>

### **$\text{Mn}^{2+}$ -Activated Alkali Lithooxidosilicate Phosphors as Sustainable Alternative White-Light Emitters**

**Full citation:**

L. M. Träger, J. I. Ekeya, A. Liesenfeld, M. Wiczorek, H. Huppertz, M. Suta, *Angew. Chem. Int. Ed.* **2025**, 64, e202504078. <https://doi.org/10.1002/anie.202504078>

Also published in German:

### **$\text{Mn}^{2+}$ -aktivierte Alkalilithooxidosilikat-Leuchtstoffe als nachhaltige alternative Weißlichtemitter**

**Full citation:**

L. M. Träger, J. I. Ekeya, A. Liesenfeld, M. Wiczorek, H. Huppertz, M. Suta, *Angew. Chem.* **2025**, 137 (25), e202504078. <https://doi.org/10.1002/ange.202504078>

### **Thermally robust near-infrared broad-band emission of $\text{Mn}^{2+}$ in boracites with fine-tuned absorption strength**

**Full citation:**

L. M. Träger, A. Shagova, B. J. Schöpfer, M. Stremel, P. Pandey, A. Meijerink, H. Huppertz, M. Suta, *manuscript in finalization* **2026**.

## 7.2 List of Presentations

### **Obergurgl-Seminar Solid-State Chemistry 2024**

*Omnipresent – Using abundant emitters as alternatives for pc-LED phosphors*

Obergurgl (Austria), 01.02.2024

**7<sup>th</sup> International Conference on the Physics of Optical Materials and Devices (ICOM) 2024**

*Photoluminescence of  $Mn^{2+}$  in the Borosulfate  $Zn[B_2(SO_4)_4]$  :  $Mn^{2+}$  – A Tool to Detect Weak Coordination Behavior of Ligands*

Budva-Bečići, (Montenegro), 27.08.2024

**Obergurgl-Seminar Solid-State Chemistry 2025**

*Pushing the limits – Luminescence of  $Mn^{2+}$  in unusual ligand fields*

Obergurgl (Austria), 29.01.2025

