

THESIS FOR THE DEGREE OF LICENCIATE OF ENGINEERING

Local structure and luminescence in Cs-based metal halide double perovskites

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Abstract

Metal halide double perovskites are currently attracting large interest, because of their luminescent properties and application potential for various optoelectronic devices. However, fundamental questions surrounding the relationship between local structure and luminescence remain unresolved for these materials, which limits the rational design of better materials and devices. This thesis concerns investigations of the local structure and luminescence in two important metal halide double perovskites, namely $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaEuCl}_6$, by using a combination of thermoluminescence, photoluminescence, and Raman spectroscopy techniques.

The investigations of $\text{Cs}_2\text{AgInCl}_6$ focus on how Na^+ substitution at the Ag^+ site and Bi^{3+} doping at the In^{3+} site, i.e. $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$ ($x = 0 - 1$; $y = 0, 0.025$), affect the local structure, luminescence and charge-trapping defects in the materials. Up to six energetically different families of charge-trapping defects are identified. Na^+ substitution changes the charge-trapping landscape in a non-systematic way, while complete replacement of Ag^+ by Na^+ suppresses both charge trapping and the characteristic broadband luminescence as commonly observed in these materials. Bi^{3+} doping promotes deeper trapping states while simultaneously enhancing the intensity of broadband luminescence. The results from Raman spectroscopy indicate that these deeper traps originate from Ag^+ vacancies associated with nearby BiCl_6 clustering. Increased BiCl_6 clustering may therefore provide a route to materials combining deeper charge trapping with intense broadband luminescence.

The investigations of $\text{Cs}_2\text{NaEuCl}_6$ focus on the nature of phonon-induced hypersensitive transitions due to Eu^{3+} . The doubly degenerate e_g vibrational mode, corresponding to axial distortions of the EuCl_6 octahedra, progressively relaxes the parity restriction and enhances the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition by a factor of 2 – 3 relative to the magnetic-dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition. Direct excitation of the Eu^{3+} $^5\text{L}_{6-7}$ manifold is shown to bypass host-mediated reverse energy transfer through a defect state, resulting in a photoluminescence quantum yield approaching 70%, which is comparable to that of state-of-the-art Eu^{3+} -doped phosphors. These findings expand the possibilities for designing hypersensitive-transition-based emitters and provide insight into the competing processes that ultimately limit their efficiency.

Keywords:

thermoluminescence spectroscopy, Raman spectroscopy, photoluminescence spectroscopy, self-trapped exciton, metal halide double perovskite

List of Papers

Appended papers

This thesis is based on the following papers:

- [**Paper I**] P. Pakmehr, M. Zhang, J. M. Jedon, G. G. Gkikas, A. Martinelli, F. Gao, M. Karlsson, *Thermoluminescence and local structure of $Cs_2AgInCl_6:Na^+,Bi^{3+}$ double perovskite* *In Manuscript*.
- [**Paper II**] M. Zhang, S. Khamkaeo, U. Singh, X. Cai, P. Pakmehr, K. Moupoung, Y. Li, J. Morat, K. Chernenko, A. Kivimäki, W.-X. Ni, M. Karlsson, I. A. Buyanova, W. M. Chen, S. I. Simak, I. A. Abrikosov, Y. Puttisong, F. Gao, *Phonon-Induced Hypersensitive Transitions in Lanthanide Double Perovskites* *Phys. Rev B*, 2026, **114**, 084308.

My contributions to the papers

Paper 1

I performed the photoluminescence, thermoluminescence and Raman spectroscopy measurements and performed the first analysis and evaluation of the data. I also wrote the first complete draft of the manuscript. The attached version of the manuscript has been worked on by all authors.

Paper 2

I performed the temperature-dependent photoluminescence excitation and emission measurements and the powder X-ray diffraction measurements, and took part in the writing of the manuscript together with all other authors.

List of acronyms:

HST	Hypersensitive transition
MHP	Metal halide perovskite
MHDP	Metal halide double perovskite
PL	Photoluminescence
PLE	Photoluminescence excitation
PLQY	Photoluminescence quantum yield
STE	Self-trapped exciton
TL	Thermoluminescence
UV	Ultraviolet

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Contents

Abstract	i
List of Publications	iii
List of Acronyms	v
Acknowledgments	vi
1 Introduction	1
2 Metal halide double perovskites	5
2.1 Crystal structure	5
2.2 Electronic and optical properties	6
2.2.1 Self-trapped excitons	8
2.2.2 Lanthanide luminescence	9
2.2.3 Charge-trapping defects	11
2.2.4 Thermal quenching of luminescence	11
2.3 $\text{Cs}_2\text{AgInCl}_6$	13
2.4 $\text{Cs}_2\text{NaEuCl}_6$	14
3 Experimental techniques	17
3.1 Structural and chemical analysis	17
3.1.1 Powder X-ray diffraction	17
3.1.2 Energy-dispersive X-ray spectroscopy	18
3.1.3 Ultraviolet–visible absorption spectroscopy	19
3.1.4 Raman spectroscopy	20
3.2 Analysis of luminescence	22
3.2.1 Photoluminescence excitation and emission spectroscopy	22
3.2.2 Photoluminescence quantum yield	23
3.2.3 Time-resolved photoluminescence spectroscopy	23
3.2.4 Thermoluminescence spectroscopy	23
4 Results and Discussion	27
4.1 Local structure and luminescence in $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$	27
4.1.1 Discussion of the results	31

4.2	Local structure and luminescence in	
	$\text{Cs}_2\text{NaEuCl}_6$	31
4.2.1	Discussion of the results	35
5	Conclusions	37
6	Outlook and future work	39
	Bibliography	40

Chapter 1

Introduction

Artificial lighting accounts for approximately 15% of the world’s annual electricity consumption, making the continued development of energy-efficient lighting technologies an important scientific and technological objective [1, 2]. Incandescent and fluorescent lamps dominated artificial lighting for much of the twentieth century, but both suffer from substantial energy losses through heat generation or gas-discharge processes which limit their energy efficiency [3]. Light-emitting diodes (LEDs) now constitute a standard lighting technology and offer higher luminous efficacy, longer operational lifetimes and increased design flexibility than these older generations of lighting technologies [2, 3].

A LED is a semiconductor device that generates light through the radiative recombination of electrons and holes within a semiconductor. Depending on the semiconductor material, LEDs can emit light over a broad spectral range. However, many lighting applications require emission characteristics that cannot readily be achieved by the semiconductor chip alone, such as broadband white-light emission, narrowband emission in specific spectral regions or high color-rendering performance [3, 4]. These properties are commonly realized by combining a LED chip with one or more phosphors [3, 5].

A phosphor is a luminescent material that absorbs part of the radiation emitted by the LED chip and subsequently re-emits light at a different wavelength [3, 5]. One of the most widely used phosphor-converted LED architectures consists of a blue InGaN LED chip coated with the yellow-emitting phosphor Ce^{3+} -doped yttrium aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) [3, 5]. The combination of the residual blue emission from the LED chip and the broad yellow emission resulting from the excitation of YAG: Ce^{3+} with blue light, produces white light [3, 5], as depicted in Figure 1.1. Alternatively, near-ultraviolet LED chips may be combined with red-, green- and blue-emitting phosphors, enabling tuning of the emission spectrum and improved color-rendering performance [3, 5].

To satisfy the diverse requirements of modern LED lighting, numerous phosphor materials have been developed. Their performance is commonly evaluated using the photoluminescence quantum yield (PLQY), defined as the ratio between the number of emitted and absorbed photons, together with character-

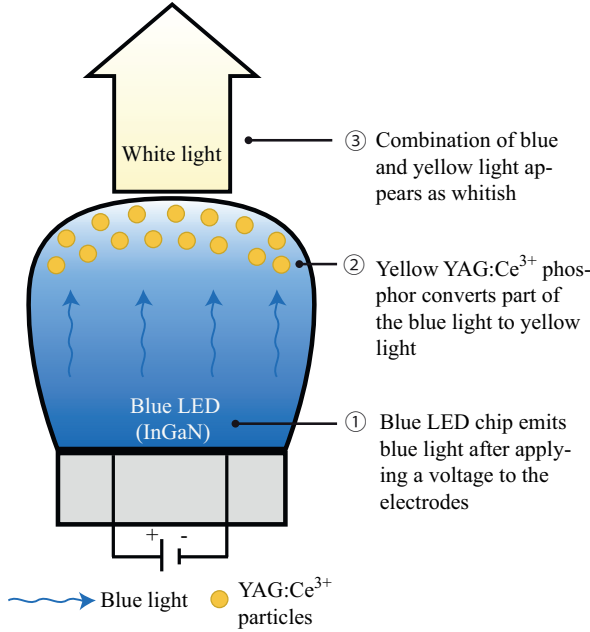


Figure 1.1: Schematic illustration of a phosphor-converted white LED based on a blue InGaN LED chip and a YAG:Ce³⁺ phosphor layer.

istics such as the emission wavelength, thermal stability, chemical stability and long-term operational stability [2–4, 6, 7]. Commercial phosphors are predominantly based on oxide-, nitride- and silicate-based host materials doped with rare-earth ions [5]. Besides the yellow-emitting phosphor YAG:Ce³⁺, representative examples include the red-emitting nitride phosphor (Sr, Ca)₂AlSiN₃:Eu²⁺, and the green-emitting silicate phosphor (Ba, Sr)₂SiO₄:Eu²⁺ [5, 8, 9]. Collectively, these phosphors have enabled modern phosphor-converted LED lighting owing to their high PLQYs and thermal stability [5, 8, 9]. However, none of these phosphors simultaneously combine high PLQY, spectral tunability, excellent color quality, long-term stability, environmental sustainability and low-cost and facile synthesis, motivating the continued search for new energy-efficient phosphor materials [5–9].

Among the emerging phosphor materials for next-generation energy-efficient lighting technologies, metal halide perovskites (MHPs), with the general formula ABX₃, where A is a monovalent cation, B is a divalent metal cation and X is a halide anion, have attracted considerable attention owing to their optical properties, such as their high PLQYs and tunable emission [4, 6, 7, 10]. One of the most studied materials is CsPbBr₃, which exhibits green emission with a high PLQY ($\sim 90\%$) upon excitation with 365 nm ultraviolet (UV) light and can be readily synthesized using solution-processing methods [11, 12]. The emission wavelength of MHPs can easily be tuned across the visible spectrum through compositional modifications, making MHPs attractive for phosphor-

converted LEDs [6, 7]. However, despite intense research for more than 15 years, the presence of toxic Pb^{2+} , together with limited long-term chemical and thermal stability, remains a major obstacle to their widespread implementation in lighting applications [4, 6, 7].

One of the most promising lead-free MHPs are based on the double perovskite structure $\text{A}_2\text{BB}'\text{X}_6$, where the divalent B-site cation in ABX_3 -type materials is now replaced by a pair of monovalent (B) and trivalent (B') cations [4, 6, 7, 13–16]. In contrast to ABX_3 -based MHPs, the presence of two chemically distinct B and B' site cations introduces an additional degree of compositional freedom, allowing the two metal cation sites to be independently modified through substitution or doping. Thus, together with their reduced toxicity, these metal halide double perovskites (MHDPs) retain many of the attractive optical properties of conventional ABX_3 -based MHPs, including high PLQYs, broad spectral tunability and facile synthesis, while offering considerably increased flexibility for compositional engineering [4, 6, 7, 13–16]. Furthermore, several MHDPs have been shown to exhibit near-unity PLQY white luminescence as a single phosphor, thereby offering the potential to simplify phosphor-converted white LED architectures and reduce manufacturing costs compared with conventional white LEDs [4, 6, 7, 13].

Despite these attractive characteristics, MHDP-based phosphors have yet to find widespread commercial application in lighting technologies. Although they retain many of the favorable optical properties of MHP-based phosphors, their practical implementation is limited by pronounced thermal quenching of the luminescence, i.e. the loss of luminescence intensity with increasing temperature, together with reduced long-term operational stability compared with conventional LEDs [6, 7, 13]. Consequently, considerable research efforts have focused on improving these limitations through compositional engineering.

$\text{Cs}_2\text{AgInCl}_6$ has emerged as the prototypical MHDP phosphor for lighting applications, owing to its broadband 400–800 nm emission upon excitation with UV light, and ability to accommodate a wide range of alloying and dopant ions [7, 13–15]. In particular, partial substitution of Ag^+ by Na^+ and doping of ns^2 cations such as Bi^{3+} and Sb^{3+} on the In^{3+} -site have been shown to substantially modify the luminescence, leading to significant improvements in both the PLQY and thermal stability [13, 14, 17–20]. Additionally, lanthanide-based MHDPs, such as $\text{Cs}_2\text{NaEuCl}_6$, have attracted considerable interest owing to their narrowband high color-purity emission, making them promising phosphors for applications that require spectrally pure emission [21–24]. Collectively, these two materials clearly demonstrate that the luminescence of MHDPs is highly sensitive to the choice of B and B' cations. However, it is still not fully understood how changes in the local crystal structure, i.e. the immediate atomic environment of the metal-halide octahedra, including the metal-halide bond lengths, octahedral distortions, and lattice vibrations, govern the luminescence of these materials. Developing a better understanding of the relationship between local crystal structure and luminescence is therefore expected to be useful for the rational development of MHDPs with properties optimized for certain applications.

The work presented in this thesis addresses this challenge by investigating

two complementary Cs-based MHDPs that prove different aspects of the relationship between local crystal structure and luminescence. The first is the compositional series $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$; $y = 0, 0.025$), which is employed as a model system to determine how systematic cation substitution modifies the local crystal structure and how these structural changes influence charge-trapping states that may act as luminescence killer centers and broadband luminescence. The second is the lanthanide-based $\text{Cs}_2\text{NaEuCl}_6$, which acts as a model system for investigating how local lattice distortions and lattice vibrations influence the characteristic Eu^{3+} emission.

To address the research questions in this thesis, photoluminescence (PL), PL excitation (PLE), thermoluminescence (TL), and Raman spectroscopy techniques are employed. By combining these complementary techniques, changes in the charge-trapping states, excitation pathways, and radiative emission of Cs-based MHDPs can be correlated with changes in the local crystal structure. In doing so, this work advances our understanding of how local structure governs the nature of luminescence in these technologically important materials.

Chapter 2

Metal halide double perovskites

2.1 Crystal structure

The term perovskite originally referred to the calcium titanate mineral CaTiO_3 , discovered by Gustav Rose in 1839 in the Ural Mountains of Russia and named after the Russian mineralogist Lev A. Perovski [25, 26]. Today, the term perovskite is used more broadly to describe a large family of compounds that adopts the same (or similar) fundamental crystal structure as CaTiO_3 .

In this ABX_3 type structure, smaller B-site cations are octahedrally coordinated by six X anions, forming a three-dimensional framework of corner-sharing BX_6 octahedra, while larger A-site cations occupy the cuboctahedral cavities formed by the octahedra. Depending on the chemistry of the material, X may represent oxygen, as in oxide perovskites such as CaTiO_3 and BaTiO_3 , or a halide ion, giving rise to the family of MHPs. In MHPs, the A site is occupied by a monovalent inorganic or organic cation, such as Cs^+ or CH_3NH_3^+ , the B site by a divalent metal cation, such as Pb^{2+} or Sn^{2+} , and the X site by a halide ion, such as Cl^- , Br^- , and I^- [(Figure 2.1 (a)) [4, 6, 7, 14].

Mixed organic-inorganic MHPs such as the prototypical $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) possesses a band gap close to optimum for solar-energy conversion and a high optical absorption coefficient, and have been predominantly researched in view of its application in solar cells [4]. All-inorganic MHPs, such as CsPbBr_3 and CsPbI_3 have been predominantly researched in view of applications in lighting, owing to their high PLQYs and narrow emission linewidths [7, 10–12]. However, the toxicity of Pb^{2+} and its potential effects on human health and environment remain major concerns for the widespread use of lead-based MHPs [4, 6, 7]. Although replacement of toxic Pb^{2+} by other divalent cations provides a direct route towards lead-free MHPs, finding a suitable substitute has proven to be challenging. Most research has focused on Sn^{2+} -based MHPs, however Sn^{2+} readily oxidizes to Sn^{4+} under ambient conditions, which degrades their performance [4, 7, 14].

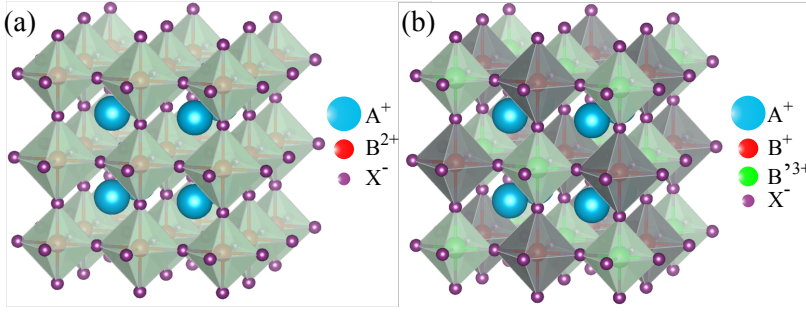


Figure 2.1: Crystal structures of (a) a MHP with the general formula ABX_3 and (b) a MHDP with the general formula $A_2BB'X_6$. Notice the alternating arrangement of $[BX_6]^{5-}$ and $[B'X_6]^{3-}$ octahedra for the MHDP.

Compared with MHPs, MHDPs retain the three-dimensional framework of corner-sharing octahedra but with alternating corner-sharing $[BX_6]^{5-}$ and $[B'X_6]^{3-}$ octahedra [(Figure 2.1 (b))]. This ordered arrangement preserves the overall perovskite structure while providing substantially increased compositional flexibility for tuning emission properties, such as the PLQY and emission wavelength, through independent substitution or doping on both the monovalent B and trivalent B' cation sites [4, 6, 7, 13–16].

Whereas the average crystal structure describes the long-range periodic arrangement of atoms throughout the crystal, the local crystal structure refers to the immediate atomic environment surrounding a particular atom or structural unit, such as the metal-halide octahedra in MHPs and MHDPs. This includes the local coordination geometry of the atoms, metal-halide bond lengths, bond angles, octahedral distortions and lattice vibrations. These structural characteristics determine the overlap between the metal and halide orbitals and therefore influence the electronic structure of the material. Consequently, modifications of the local crystal structure arising from various cation/anion substitutions (in small amounts typically referred to as "doping") or octahedral distortions can alter the luminescence properties of these materials, including their absorption and emission [4, 6, 7, 13–16, 24].

2.2 Electronic and optical properties

The electronic and optical properties of MHPs and MHDPs are governed by their electronic band structure and the interaction between electronically excited states and the crystal lattice. In these materials, the electronic band structure consists of a valence band (VB), a conduction band (CB), and the energy separation between the VB and CB, known as the band gap, E_g . The highest occupied electronic state within the VB is referred to as the VB maximum (VBM), whereas the lowest unoccupied electronic state within the CB is referred to as the CB minimum (CBM).

When a photon with an energy equal or higher than the band gap is absorbed,

an electron is excited from the VB to the CB, leaving behind a positively charged hole, corresponding to the absence of an electron, in the VB, as illustrated schematically in Figure 2.2. The electrostatic attraction between the negatively charged electron and the positively charged hole may subsequently lead to the formation of a bound electron-hole pair, referred to as an exciton. Radiative recombination of the exciton results in the emission of a photon of energy $h\nu_{em}$, where $h \approx 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ is Planck's constant, and ν_{em} is the emission frequency, giving rise to photoluminescence (PL). Alternatively, the excited state may relax non-radiatively, whereby the excitation energy is transferred to the crystal lattice, for example through lattice vibrations (phonons), without the emission of a photon. The competition between radiative and non-radiative relaxation pathways therefore determines the luminescence efficiency of MHPs and MHDPs [13, 20].

Although these fundamental processes of optical absorption and radiative recombination are common to both MHPs and MHDPs, the electronic states involved in optical absorption and emission differ because the VBM and CBM originate from different combinations of metal and halide orbitals. In typical Pb-based MHPs, the VBM and CBM are primarily derived from hybridized Pb 6s, Pb 6p and halide p orbitals, whereas the electronic structure of MHDPs is formed by the orbitals of two chemically distinct B and B' site cations together with the halide orbitals [27, 28]. As a consequence, replacing the single divalent B-site cation of a MHP with two chemically distinct monovalent and trivalent cations can substantially modify the electronic structure and subsequently the optical properties of MHDPs. Depending on the constituent cations, MHDPs can therefore exhibit large differences in band gap, optical transition probability and luminescence compared with MHPs [7, 10, 27, 28]. The additional compositional flexibility of having two different B and B' site cations in MHDPs, compared with MHPs, also provides a means of modifying these properties through substitution and doping, to create a wide variety of MHDP compositions for different optoelectronic applications such as LED lighting.

The mechanism responsible for luminescence consequently varies between different MHP and MHDP compositions. In many Pb-based MHPs, such as CsPbBr_3 and CsPbI_3 , luminescence predominantly originates from radiative recombination of excitons, resulting in narrowband emission [7, 10–12]. However, narrowband emission is not characteristic of all MHPs. Several MHPs, such as MAPbI_3 instead exhibit broadband luminescence commonly associated with self-trapped excitons (STE), a luminescence mechanism that is also believed to be present in many MHDPs, such as in $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaInCl}_6$ [4, 7, 10, 13, 20, 28, 29]. In addition, luminescence in MHPs and MHDPs can originate from electronic transitions localized on specific metal ions. Lanthanide-containing MHDPs, for example, can exhibit characteristic narrowband emission arising from intra-4f transitions of trivalent lanthanide ions such as Eu^{3+} in $\text{Cs}_2\text{NaEuCl}_6$ [21–24].

The materials investigated in this thesis, $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$; $y = 0, 0.025$) and $\text{Cs}_2\text{NaEuCl}_6$, have in common that they have the same A and X site ions, but differ in the B and B' site cations,

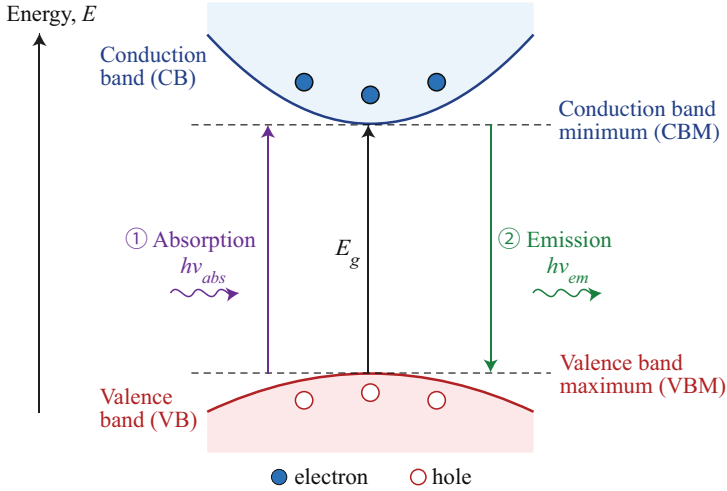


Figure 2.2: Schematic illustration of photon absorption and emission in a MHP.

which therefore provides a mean to systematically investigate the effect of the type of B and B' site cations and alloying on the B/B' site on both the local structure and luminescence.

2.2.1 Self-trapped excitons

STE refers to an exciton that becomes localized within a lattice distortion, and arises because, following photoexcitation, strong coupling between the electronic excitation and lattice vibrations (phonons) can cause the surrounding atoms to move away from their equilibrium positions [7, 13, 20, 30]. The relatively soft (easily deformable) lattices of MHPs and MHDPs facilitate these lattice distortions and therefore promote self-trapping when the electron-phonon coupling is sufficiently strong [7, 13, 20, 30].

Optical excitation can be described according to the Franck-Condon principle, whereby an electronic transition occurs on a much shorter timescale than the motion of the atomic nuclei. Absorption therefore occurs approximately vertically from the equilibrium electronic ground-state configuration without an immediate change in the atomic positions, and may initially populate free-carrier or free-exciton states. These excited states can subsequently undergo non-radiative vibrational relaxation toward lower-energy configurations; see Figure 2.3 (a) for a schematic. When the electron-phonon coupling is sufficiently strong, the lattice distorts toward a STE configuration, lowering the energy of the electronically excited state and localizing the exciton. Radiative recombination subsequently occurs from the STE state, producing a photon of lower energy than that initially absorbed. The resulting difference in energy between the absorption and emission maxima is referred to as the Stokes shift. Owing to the substantial lattice distortion associated with self-trapping, STE-

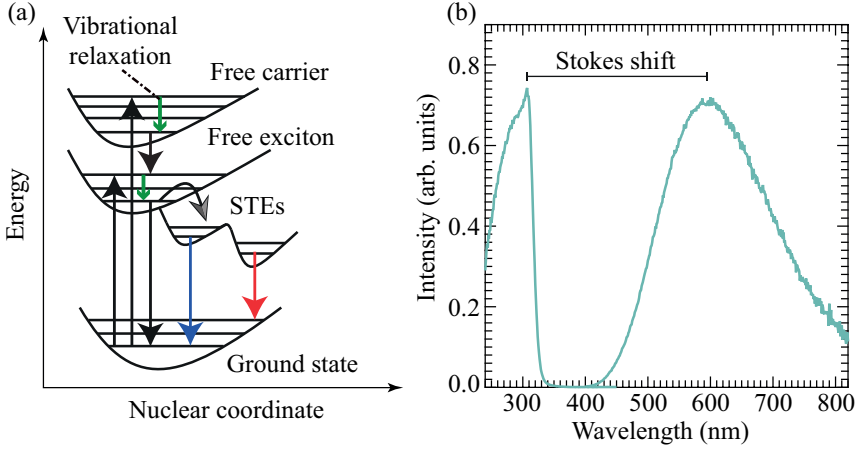


Figure 2.3: (a) Schematic configurational-coordinate diagram illustrating the formation and radiative recombination of STEs. (b) Example of the large Stokes shift and broadband STE emission in $\text{Cs}_2\text{Na}_{0.8}\text{Ag}_{0.2}\text{InCl}_6$ at 300 K, measured as part of this thesis, showing excitation and emission bands centered at approximately 310 nm and 600 nm, respectively.

emitting materials commonly exhibit large Stokes shifts, which can correspond to several hundred nanometers between the excitation and emission maxima [7, 10, 19, 20, 30], as shown in Figure 2.3 (b).

Because the local lattice distortions associated with self-trapping can differ slightly in magnitude, an ensemble of STE configurations with different energies may be formed. Furthermore, according to the Franck-Condon principle, radiative recombination from the STE configurations can occur into multiple vibrational levels of the electronic ground state. Together, these effects result in emission over a broad range of photon energies, giving rise to the characteristic broadband emission associated with STEs.

2.2.2 Lanthanide luminescence

A second luminescence mechanism relevant to MHDPs arises when trivalent lanthanide ions (e.g., Eu^{3+} , Tb^{3+} , Er^{3+}) are incorporated into the double perovskite lattice. In contrast to the broadband emission commonly associated with STEs, lanthanide ions can exhibit spectrally sharp emission originating from electronic transitions within their partially filled $4f$ shell [21–24, 31, 32]. Eu^{3+} is a well-known example, exhibiting a series of characteristic $4f - 4f$ emission lines [21–24, 31, 32]. The $4f$ electrons are strongly shielded by the outer $5s$ and $5p$ orbitals and are therefore highly localized, meaning that they do not participate significantly in bonding with neighboring ions or the host lattice [24, 33]. As a result, the energies of the $4f$ states are comparatively weakly affected by the surrounding crystal lattice, allowing lanthanide ions to largely retain their characteristic emission energies when incorporated into

different host lattices [24].

Despite this localization, the intensities of the $4f - 4f$ transitions remain strongly dependent on the local coordination environment of the lanthanide ion. Electric-dipole (ED) $4f - 4f$ transitions are formally parity forbidden, unlike magnetic-dipole (MD) transitions, but interactions with the surrounding crystal field and coupling to phonons can partially relax this restriction and increase their transition probability [24, 34–37]. Certain ED transitions are particularly sensitive to changes in the local chemical and structural environment and are therefore referred to as *hypersensitive transitions* (HSTs) [24, 34–41]. Their transition probabilities can change substantially in response to changes in local symmetry, lattice distortions and vibrational coupling [24], making their emission intensities sensitive probes of the local environment surrounding the lanthanide ions. Conventionally, HST emission is often realized by incorporating lanthanide ions as dilute dopants into a suitable host material, where the host can both modify the probability of the HST and participate in the excitation of the lanthanide ion [24, 34–37].

As illustrated schematically in Figure 2.4, excitation of the lanthanide ion can occur either directly into the $4f$ states, or indirectly through absorption by the host followed by energy transfer to the lanthanide $4f$ states [24, 34–37]. Such host-mediated “sensitization” enables efficient population of the emitting $4f$ states [24]. However, the additional energy-transfer pathway can introduce losses including defect-induced quenching which reduces the emission intensity [24].

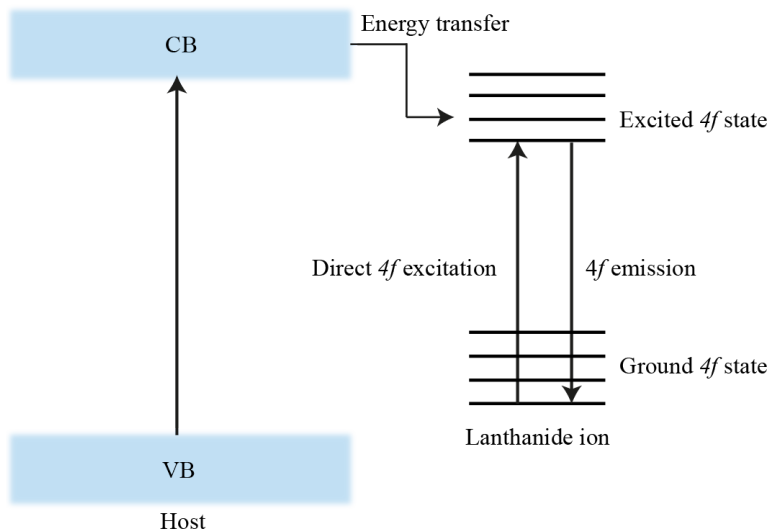


Figure 2.4: Schematic illustration of direct and host-mediated excitation pathways for lanthanide $4f$ luminescence in a host. Excitation can occur directly into the lanthanide $4f$ states or indirectly through absorption by the host, followed by energy transfer to the lanthanide ion.

Lanthanide-containing MHDs provide a different platform for $4f$ luminescence. Their comparatively soft lattices can undergo local distortions and symmetry breaking that influence the probability of HSTs [13, 24, 42, 43], while their $A_2BB'_6X_6$ structure can accommodate trivalent lanthanide ions at high concentrations within a charge-balanced lattice [22, 24, 44], as exemplified by the prototypical lanthanide-containing MHD $Cs_2NaEuCl_6$ [21–24, 31, 32]. In such materials, the high concentration of optically active lanthanide ions can make direct $4f$ excitation a significant excitation pathway alongside host-mediated energy transfer to $4f$ states [24].

2.2.3 Charge-trapping defects

In addition to the intrinsic electronic states of ideal crystal lattices, structural defects such as vacancies, interstitials, antisite defects and impurities modify the electronic structure and introduce localized states within the band gap [45, 46]. If these states capture photoexcited electrons or holes, they act as charge-trapping states, or traps. An electron trap can be represented as a localized state below the CBM, whereas a hole trap can be represented as a localized state above the VBM, as illustrated schematically in Figure 2.5. The energy required to release a trapped charge carrier is referred to as the trap depth, and determines how strongly the charge carrier is confined [47, 48]. Accordingly, states close to the band gap edges are generally described as shallow traps, whereas states located further within the band gap are referred to as deeper traps [47, 48].

Charge trapping at defects introduces additional, plausible, relaxation pathways for photoexcited carriers and can therefore strongly influence the luminescence. A charge carrier captured by a trap remains trapped until sufficient energy is provided for it to escape, with deeper traps requiring higher thermal energy for detrapping at defects [47, 48]. Following detrapping, the charge carrier may return to an emissive recombination pathway, or decay non-radiatively, thereby reducing the PLQY [13, 49, 50]. These competing relaxation pathways are also illustrated in Figure 2.5.

In STE-emitting MHDs, charge trapping at defects can compete with the formation and radiative recombination of STEs. For example, it has recently been shown that reducing the density of defect-related trapping states in $Cs_2Ag_{0.6}Na_{0.4}In_{0.8}Bi_{0.2}Cl_6$, through partial Br^- doping on the Cl^- -site, suppresses trap-mediated non-radiative relaxation and enhances STE emission [50]. At higher Br^- contents, however, the formation of additional trapping states was accompanied by increased non-radiative recombination and a reduction in PLQY, demonstrating that compositional modification can either suppress or promote charge trapping depending on the local crystal structure [50].

2.2.4 Thermal quenching of luminescence

The luminescence of MHPs and MHDs is often strongly temperature dependent. Increasing the temperature commonly results in thermal quenching of luminescence, i.e. reduction of the PL intensity [5, 13, 51]. Thermal quench-

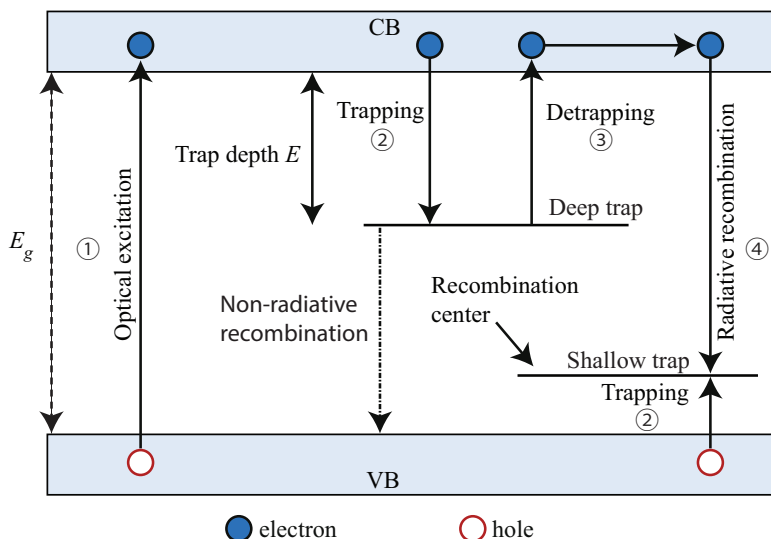


Figure 2.5: Energy-level diagram illustrating charge trapping and recombination in a MHDP. (1) Optical excitation promotes electrons from the VB to the CB, generating electron-hole pairs. (2) Photoexcited electrons and holes become localized at defect-related trapping states within the band gap. An electron captured at a trapping state undergoes non-radiative recombination, whereby the excitation energy is dissipated to the lattice (in the form of lattice vibrations) rather than emitted as a photon. Alternatively, (3) a trapped electron is thermally released back to the CB and subsequently (4) recombine radiatively with a trapped hole at a recombination center.

ing is an unwanted phenomenon and represents an important limitation for phosphors intended for most lighting applications, since high PLQY must be retained not only at low temperature but also at and above room temperature.

On a fundamental level, thermal quenching is associated with thermally activated processes that increase the probability of non-radiative relaxation relative to radiative recombination of the photoexcited excitons [5, 51]. Phonons play an important role in this process by providing the thermal energy required to access such competing non-radiative relaxation pathways [5]. The microscopic mechanism is, however, material dependent and not fully understood. In conventional phosphors such as YAG:Ce^{3+} , thermal quenching may occur through thermally activated crossover between excited- and ground-state potential-energy surfaces or through thermal ionization of an excited carrier into the conduction band, or through charge trapping at defects acting as luminescence "killer centers" [5].

In MHPs and MHDPs, their comparatively soft lattices make the excited-state relaxation particularly sensitive to lattice vibrations and local structural distortions [7, 13, 20]. In $\text{Cs}_2\text{AgInCl}_6$ -type materials, for example, strong electron-phonon coupling drives the local lattice distortion associated with STE formation [7, 13, 20, 50, 51]. Increasing temperature can therefore modify

the balance between radiative STE recombination and thermally activated non-radiative relaxation pathways. For example, temperature-dependent PL measurements of $\text{Cs}_2\text{AgInCl}_6:\text{Al}^{3+}$ show that the STE emission becomes substantially stronger upon cooling as non-radiative decay pathways are suppressed [51].

2.3 $\text{Cs}_2\text{AgInCl}_6$

$\text{Cs}_2\text{AgInCl}_6$ exhibits broadband luminescence, commonly ascribed to STE emission, and is a prototypical phosphor for lighting applications [7, 13–15, 20, 28]. A major limitation of the material is, however, its very low PLQY, which has been measured to be below 0.1% at room temperature (297 K) [13]. This weak emission is primarily associated with the parity-forbidden nature of the lowest-energy optical transition, since the VBM and CBM both possess even parity [13, 20, 52]. In addition to the intrinsically low radiative transition probability, the luminescence is further reduced by thermal quenching [13, 51], as illustrated in Figure 2.6. This has motivated efforts to improve the PLQY through compositional modification on the B, B' and X-sites.

Partial substitution of Ag^+ by Na^+ has been shown to strongly enhance the STE emission by introducing odd-parity character to the VBM, thereby breaking the parity-forbidden restriction and increasing the probability of radiative recombination [13, 14, 20]. The enhancement is strongly dependent on the concentration of Na^+ , with particularly high room temperature PLQY reported near 40% Na^+ substitution [13]. Doping of small amounts of Bi^{3+} on the In^{3+} site can further enhance the emission, which has been attributed to improved exciton localization, better crystal quality, and suppression of non-radiative recombination [13, 19, 53]. When Na^+ substitution and Bi^{3+} doping are combined, high room temperature PLQYs approaching 86% have been reported [13].

The composition-dependent luminescence of $\text{Cs}_2\text{AgInCl}_6$ -based MHDPs has consequently been investigated in numerous studies, including materials containing different Na^+ concentrations, Bi^{3+} contents and other compositional modifications [13, 14, 18, 20, 49, 50, 53–62]. Collectively, these studies show that compositional modification strongly affect the luminescent properties, such as the PLQY, thermal stability and emission intensity of $\text{Cs}_2\text{AgInCl}_6$ -based materials. However, less is known about the presence and role of charge-trapping defects, which may as well influence very strongly the luminescent properties of MHDPs [13, 45, 46, 49, 50]. In this regard, results from density functional theory calculations have predicted several intrinsic defects in $\text{Cs}_2\text{AgInCl}_6$ that introduce localized electronic states within the band gap that may trap charge carriers [13, 45, 46, 49]. In particular, In^{3+} vacancies have been predicted to form deep charge-trapping states within the band gap, while Bi^{3+} doping increases its formation energy, thereby reducing its concentration and contributing to the enhanced STE emission intensity [13, 49]. While these calculations provide important insight into the possible microscopic origin of charge trapping, experimental studies of the trap states have generally been

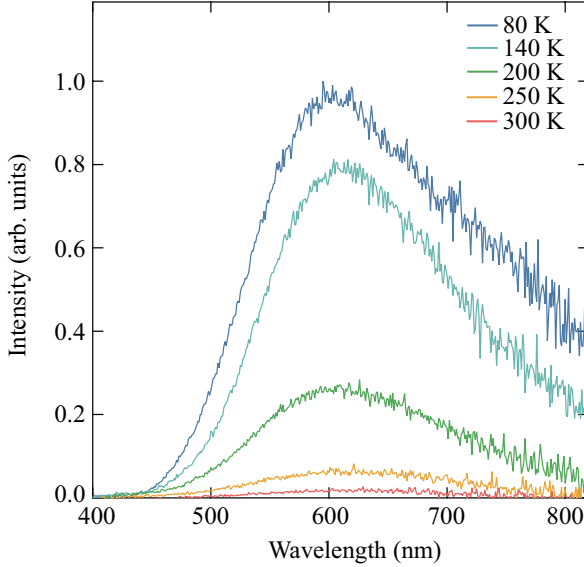


Figure 2.6: Temperature-dependent PL spectra of $\text{Cs}_2\text{AgInCl}_6$. The PL spectrum was recorded under 375 nm excitation, as part of this thesis.

limited to selected compositions, and how the overall charge-trapping landscape evolves with Na^+ substitution and Bi^{3+} doping remains poorly understood. The $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1; y = 0, 0.025$) series investigated in this thesis was therefore selected to systematically examine how Na^+ substitution, with and without Bi^{3+} doping, modifies the charge-trapping landscape and local crystal structure, and how these changes relate to luminescence.

2.4 $\text{Cs}_2\text{NaEuCl}_6$

Whereas the study of $\text{Cs}_2\text{AgInCl}_6$ examines how composition, local structure and charge trapping influence STE emission, $\text{Cs}_2\text{NaEuCl}_6$ provides a system in which local structural distortions can be directly related to the transition probabilities of localized Eu^{3+} 4*f* emission. $\text{Cs}_2\text{NaEuCl}_6$ was therefore selected as a complementary system to the $\text{Cs}_2\text{AgInCl}_6$ -based materials for investigating the relationship between local crystal structure and luminescence in MHDPS. As observed in Figure 2.7, the emission at 297 K is dominated by the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ MD transition and the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ HST, while weaker emission arises from the remaining $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0, 3-6$) transitions [21–24, 63–65].

Because the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ HST is strongly restricted by parity, distortions that lower the local symmetry and coupling to lattice vibrations can increase its transition probability, whereas the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ MD transition is considerably less sensitive to such changes [21–24, 63–65]. Previous studies of $\text{Cs}_2\text{NaEuCl}_6$ have shown that the intensities of the Eu^{3+} emission transitions change with

temperature [63, 64, 66, 67]. However, the origin of the pronounced temperature dependence of the HST remained unclear. Although local symmetry breaking and vibronic coupling are known to increase the transition probability of HSTs [24, 63, 64, 66, 67], no direct relationship had been established between the temperature-dependent HST in $\text{Cs}_2\text{NaEuCl}_6$ and specific local structural distortions. It was therefore not known which structural distortions were responsible for enhancing the HST and how the distortions depend on temperature.

The temperature dependence of $\text{Cs}_2\text{NaEuCl}_6$ is also characterized by thermal quenching, meaning that the increase of the HST with temperature occurs together with thermally activated processes that eventually reduce the Eu^{3+} emission [24, 66, 67]. $\text{Cs}_2\text{NaEuCl}_6$ also differs from conventional dilute lanthanide-doped phosphors in that Eu^{3+} is an intrinsic constituent of the lattice, rather than a dilute dopant, enabling efficient direct absorption into the Eu^{3+} 4*f* states [24, 68, 69]. This provides the possibility of generating HST emission without relying on host-to-4*f* energy transfer and thereby avoiding losses associated with this intermediate transfer step [24].

The goal of the $\text{Cs}_2\text{NaEuCl}_6$ study was therefore to determine the microscopic origin of the temperature-dependent HST enhancement and to establish whether efficient HST could be achieved through a host-transfer-independent excitation pathway [24]. More specifically, the study aimed to identify which local distortions of the EuCl_6 octahedra enhance the HST and how these distortions evolve with temperature, while determining how direct 4*f* excitation and thermally activated relaxation processes influence the resulting Eu^{3+} emission.

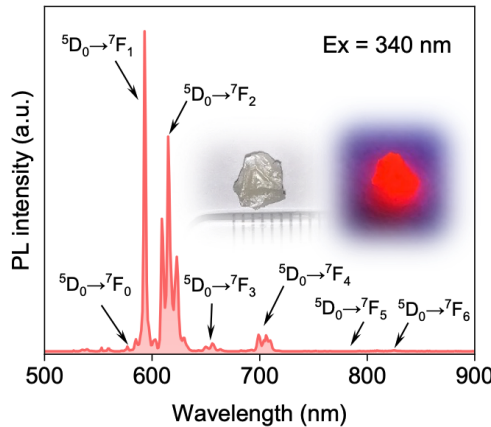


Figure 2.7: Room-temperature PL spectrum of $\text{Cs}_2\text{NaEuCl}_6$ under 340 nm excitation, showing the characteristic Eu^{3+} emission arising from the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions. Insets show a millimeter-sized $\text{Cs}_2\text{NaEuCl}_6$ single crystal under visible light and 365 nm UV illumination [24] (**Paper 2**). Reproduced from M. Zhang *et al.*, "Phonon-induced hypersensitive transitions in lanthanide double perovskites", *Phys. Rev. B*, 2026, **114**, 084308, DOI: 10.1103/ss4k-zyd6, under the Creative Commons Attribution 4.0 International License.

Chapter 3

Experimental techniques

The experimental techniques employed in this thesis were selected to provide complementary information on the structure, chemistry, and luminescence of the investigated MHDPs. Structural analyses were performed using powder X-ray diffraction (PXRD) together with Raman spectroscopy. PXRD was used to obtain information on the long-range crystal structure, whereas Raman spectroscopy was used to probe the structure on a shorter length scale, and to investigate inhomogeneities in the studied materials. Chemical analysis was performed using energy-dispersive X-ray spectroscopy (EDX). Luminescence was investigated using PL and PLE techniques, together with PLQY and time-resolved photoluminescence spectroscopy measurements (TRPL) to examine the emission, excitation pathways and excited-state dynamics. The TL technique was employed to probe the presence and nature of charge-trapping states. Additionally, Ultraviolet–visible (UV–vis) absorption spectroscopy was used to probe the electronic states involved in optical absorption, and to measure the optical band gap. In the following, the general concept of each technique is described in brief. For more details of the techniques used, the reader is referred to the cited references and appended papers.

3.1 Structural and chemical analysis

3.1.1 Powder X-ray diffraction

The PXRD technique uses a beam of monochromatic X-rays which is directed on the sample [70]. The X-rays are then scattered elastically by the periodically arranged atoms in the crystal lattice [70]. Constructive interference between X-rays scattered from crystallographic planes occurs when the Bragg condition is satisfied,

$$n\lambda = 2d \cdot \sin(\theta), \quad (3.1)$$

where n is an integer number, λ is the X-ray wavelength, d is the spacing between the crystallographic planes and θ is the angle of incidence [Figure 3.1

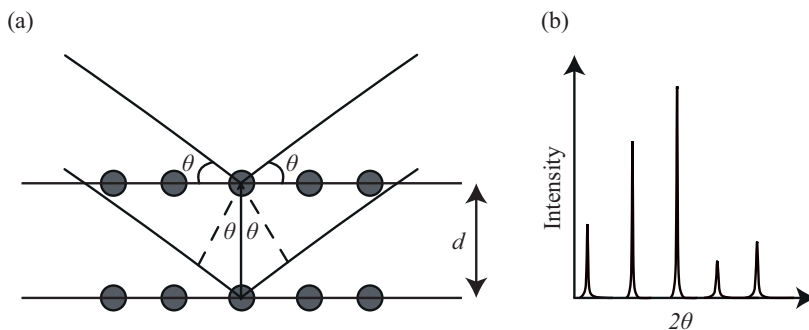


Figure 3.1: Schematic illustration of PXRD. (a) Bragg diffraction from parallel crystallographic planes separated by the interplanar distance d . (b) PXRD pattern showing reflections at characteristic 2θ angles.

(a)] [70]. The resulting diffraction pattern consists of reflections at characteristic 2θ angles corresponding to different sets of crystallographic planes [Figure 3.1 (b)] [70].

Generally, a comparison of the experimentally determined diffraction pattern with calculated or reference diffraction patterns provides a means of identifying the crystal structure and possible phase-impurities in a material [70]. The quality and interpretation of PXRD data can, however, be affected by several factors, including the crystallinity and particle size of the sample. Low crystallinity and small crystallite sizes can result in broadened diffraction peaks, while large particles and preferred orientation can affect the measured peak intensities and complicate phase identification [70]. In addition, the overlap of reflections represents an inherent limitation of PXRD, as it can reduce the amount of structural information that can be extracted from the diffraction pattern [70].

3.1.2 Energy-dispersive X-ray spectroscopy

EDX uses a focused beam of high-energy electrons that is directed onto the sample surface. When these incident electrons interact with the atoms in the material, they can eject electrons from inner atomic shells, leaving vacancies [71]. Electrons from higher-energy shells subsequently relax into these vacancies, and the energy difference between the electronic levels is released as X-rays [71] (Figure 3.2). Since the electronic energy levels are characteristic of each element, the energies of the emitted X-rays can be used to identify the elements present in the irradiated volume [71]. An EDX spectrum therefore contains characteristic X-ray peaks associated with the constituent elements, while the relative intensities of these peaks can be used to estimate their relative concentrations [71]. By scanning the electron beam across the sample and recording the characteristic X-ray signal at each position, elemental maps can be obtained to evaluate the spatial distribution of the elements and homogeneity of the probed sample. EDX thus complements the structural information

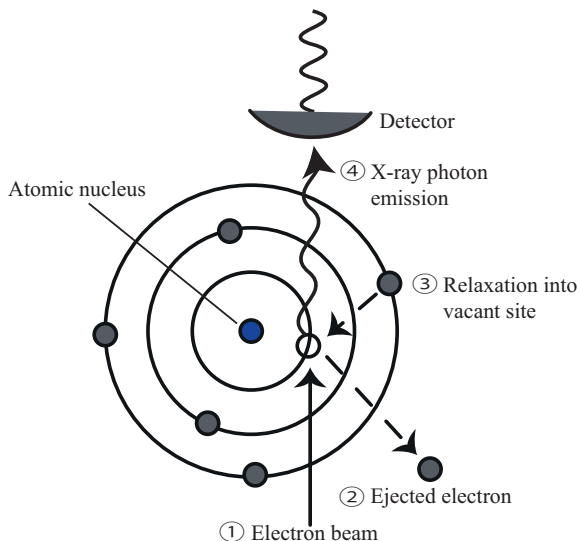


Figure 3.2: Schematic illustration of EDX.

obtained from PXRD by providing information on the elemental composition and allowing comparison with the expected stoichiometry [71].

3.1.3 Ultraviolet–visible absorption spectroscopy

UV–Vis absorption spectroscopy measures the attenuation of UV and visible light as a function of photon energy or wavelength [72]. When light passes through a material, photons whose energies correspond to electronic transitions may be absorbed, reducing the transmitted intensity [72]. The absorbance, A , can be expressed as $A = -\log_{10} \frac{I}{I_0}$, where I_0 and I are the incident and transmitted light intensities, respectively [72]. The resulting absorption spectrum therefore provides information on the energies of optically accessible electronic transitions.

The optical absorption edge can additionally be used to estimate the optical band gap through Tauc analysis [72, 73]. In this approach, the absorption coefficient, α , and photon energy, $h\nu$, are related according to $(\alpha h\nu)^2 = A(h\nu - E_g)$, where E_g is the optical band gap, A is a proportionality constant, and r depends on the type of electronic transition [72, 73]. For an allowed direct transition, $(\alpha h\nu)^2$ is plotted as a function of $h\nu$, whereas for an allowed indirect transition, $(\alpha h\nu)^{1/2}$ is plotted as a function of $h\nu$ [73]. Near the absorption edge, the approximately linear part of the corresponding plot is extrapolated to $(\alpha h\nu)^r = 0$, and its intercept with the photon-energy axis provides an estimate of E_g [73].

3.1.4 Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopic technique widely used to investigate the local structural properties of a wide range of materials [20, 74–77]. The technique is based on the inelastic scattering of monochromatic light, typically from a laser source, through interactions with vibrational modes involving the chemical bonds within a material [77]. When the incident photons interact with the crystal lattice, the majority of them are elastically scattered without exchanging energy with the material, a process known as Rayleigh scattering [77]. A much smaller fraction of the photons scatter inelastically and exchange energy with phonons, resulting in Raman scattering [77]. Since the energy shift of the scattered photons corresponds to the vibrational energies of the material, Raman spectroscopy provides direct information on the vibrational modes and local bonding environment of the crystal lattice [77].

Depending on whether energy is transferred from the photon to the lattice or from the lattice to the photon, Raman scattering is classified as either Stokes or anti-Stokes scattering [77], respectively (Figure 3.3). In Stokes scattering, the incident photon loses energy by exciting a vibrational mode, resulting in scattered light of lower energy (longer wavelength). Conversely, in anti-Stokes scattering, the incident photon gains energy from an already thermally populated vibrational state, producing scattered light of higher energy (shorter wavelength). Since anti-Stokes scattering requires the vibrational state to be populated before the scattering event, its intensity is typically much lower than that of Stokes scattering [77]. The difference in their relative intensities depends on temperature and on the vibrational energies of the material. Consequently, Stokes scattering is commonly used for Raman spectral analysis [77].

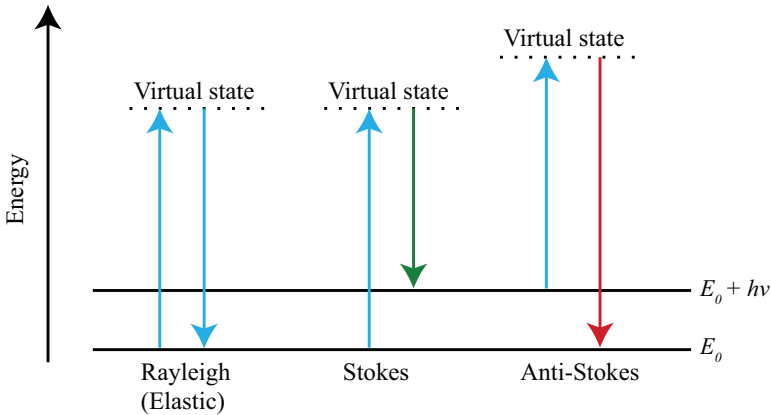


Figure 3.3: Schematic illustration of the Rayleigh, Stokes, and anti-Stokes scattering processes. E_0 denotes the energy of the initial state, while $E_0 + hv$ represents the energy of the first vibrationally excited state. Transitions to higher vibrational states (higher-order transitions) can also occur, but with lower probability.

Not all vibrational modes are Raman active. For a vibrational mode to give rise to Raman scattering, the vibration must induce a change in the polarizability of the bond during the vibration [77]. The Raman selection rule can therefore be expressed as $\frac{\partial \alpha}{\partial Q} \neq 0$, where α denotes the polarizability and Q is the normal vibrational coordinate. Physically, the polarizability describes the ease with which the electronic charge distribution surrounding the atoms can be distorted by the oscillating electric field of the incident light. The magnitude of the Raman signal depends on how strongly the polarizability changes during the vibration [77]. Vibrations that do not produce such a change are Raman inactive, although they may instead be active to infrared radiation if they induce a change in the dipole moment [77]. These selection rules determine which of the lattice vibrations can be observed in a Raman spectrum.

The frequencies (energy) of the lattice vibrations are determined by the masses of the participating atoms and by the effective force constants associated with their displacements. A soft lattice is characterized by comparatively small effective force constants, resulting in low-energy phonon modes [20, 74–76]. MHDPs are generally characterized by relatively soft ionic lattices and can therefore exhibit several low-frequency vibrational modes involving the metal-halide octahedra [20, 74–76, 78, 79]. Representative examples include bending, asymmetric stretching and symmetric stretching vibrations [20, 74–76], as schematically illustrated in Figure 3.4.

Changes in the Raman spectrum upon compositional modification can be related to changes in the local crystal structure. Shifts in vibrational frequencies reflect changes in bond lengths of the vibrational moieties [18, 20, 61]. The linewidth provides additional information on the lifetime and energetic distribution of vibrational states. A broader band either means a shorter lifetime of the vibration (homogeneous broadening) or a wider distribution of local bonding environments (inhomogeneous broadening). Changes in the intensity reflects changes in the polarizability, which is strongly affected by the symmetry of the vibration. Studying how the Raman spectra change with the polarization of the incident and scattered light can therefore provide information about the symmetry and orientation of vibrational modes in a material.

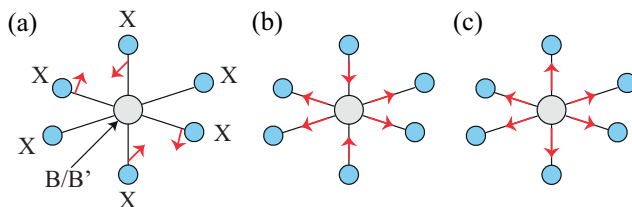


Figure 3.4: Schematic illustration of representative $\{B/B'\}X_6$ vibrational modes of $A_2BB'X_6$ -type MHDPs: (a) bending, (b) asymmetric stretching, and (c) symmetric stretching. Blue circles represent halides (X), grey circles represent the central metal cations (B/B'), and red arrows indicate the principal atomic displacements.

3.2 Analysis of luminescence

The fundamental processes underlying the luminescence of the investigated MHDPs were described in Chapter 2.2. The following sections describe how PL- and TL-based techniques were employed to experimentally probe some of these processes.

3.2.1 Photoluminescence excitation and emission spectroscopy

In steady-state PL and PLE spectroscopy, a sample is excited by a light source at a selected wavelength and the emitted luminescence is collected by a detector [80] (Figure 3.5). The distinction between PL and PLE measurements lies in which wavelength is varied during the measurement. In a PL measurement, the excitation wavelength is kept fixed while the emitted intensity is recorded as a function of emission wavelength [80]. The resulting PL spectrum therefore shows the spectral distribution of the radiative emission produced under a particular excitation condition, including the positions, shapes and relative intensities of the observed emission bands. In a PLE measurement, the emission wavelength is instead fixed while the excitation wavelength is varied [80]. The resulting PLE spectrum identifies the excitation energies that efficiently lead to the monitored emission. PL and PLE spectroscopy consequently provide complementary information: PL determines how a material emits light following excitation at a selected energy, whereas PLE determines which excitation energies efficiently populate the state or relaxation pathway responsible for light emission [80]. In contrast to UV – Vis absorption spectroscopy, which measures the attenuation of incident light regardless of the subsequent relaxation process, PLE selectively probes excitation processes that result in light emission [80].

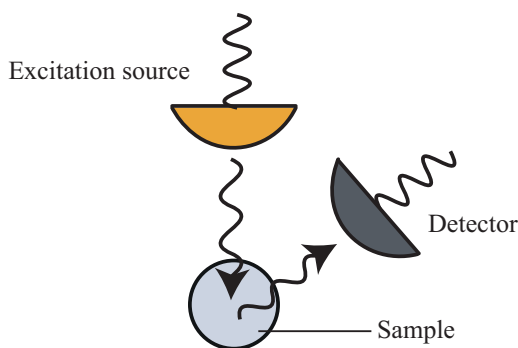


Figure 3.5: Schematic illustration of the general measurement geometry used for PL and PLE spectroscopy.

3.2.2 Photoluminescence quantum yield

PLQY measurements are commonly performed using an integrating sphere, which collects both the luminescence emitted in different directions and the excitation light that is not absorbed by the sample [80]. Comparison of the excitation signal with and without absorption by the sample allows the number of absorbed photons to be determined, while integration of the emitted luminescence provides the number of emitted photons. PLQY measurements can therefore be used to determine how efficiently absorbed excitation energy is converted into light emission.

3.2.3 Time-resolved photoluminescence spectroscopy

TRPL spectroscopy is used to investigate the temporal evolution of luminescence following excitation. In contrast to conventional steady-state PL, TRPL measurements use a short excitation pulse and record how the emission intensity evolves after the pulse [80]. The resulting decay profiles provide information on the characteristic lifetimes of the excited states and can reveal changes in the competing radiative and non-radiative relaxation pathways [13, 80]. An increased contribution from non-radiative relaxation shortens the excited-state lifetime, which leads to luminescence quenching [51]. By monitoring the emission at different wavelengths, the relaxation of different excited states can be followed.

3.2.4 Thermoluminescence spectroscopy

TL spectroscopy monitors the luminescence generated when previously trapped charge carriers are thermally released [47, 48, 81]. The fundamental processes of charge trapping, thermal detrapping and subsequent radiative or non-radiative recombination are described in Section 2.2 and illustrated schematically in Figure 2.5. A schematic overview of a TL measurement sequence is shown in Figure 3.6. In a TL measurement, the sample is first excited to populate available trapping states [47, 48, 81]. The excitation source is subsequently removed and the sample is heated at a constant rate while the emitted luminescence is continuously recorded as a function of temperature [47, 48, 81]. The resulting TL glow curve consists of one or more emission maxima corresponding to the thermal release and subsequent radiative recombination of trapped charge carriers [47, 48, 81].

Less thermally stable trapping states are generally emptied at lower temperatures, whereas more stable and deeper trapping states require higher thermal energy for detrapping and therefore tend to give rise to glow peaks at higher temperatures [47, 48, 81]. The temperature, intensity and shape of the glow peaks therefore provide information on the thermal stability and relative population of the trapping states. A representative TL glow curve of $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{InCl}_6$ is shown in Figure 3.7.

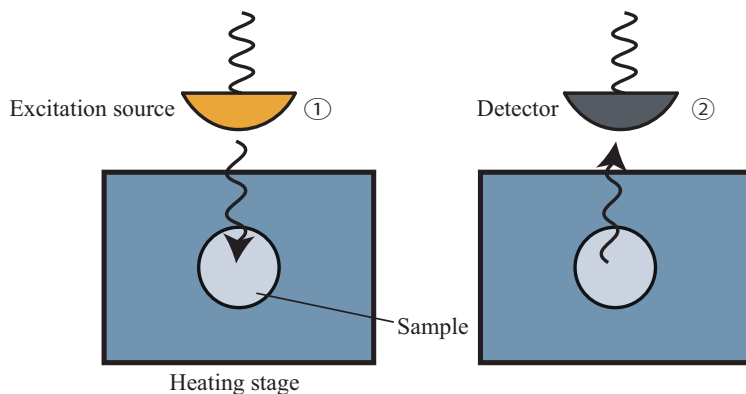


Figure 3.6: Schematic illustration of the TL measurement sequence. (1) The sample is first irradiated with an excitation source to populate available charge-trapping states. (2) The excitation source is then switched off and the sample is heated, while the emitted luminescence is recorded with a detector as a function of increasing temperature.

In charging-dependent TL measurements, the duration of the excitation period is varied before the sample is heated [82]. This changes the extent to which available trapping states are populated prior to the TL measurement. By comparing the resulting glow curves as a function of charging time, changes in the intensity and shape of the TL glow peaks can be used to assess how the trapping states are progressively populated and whether saturation is approached [82].

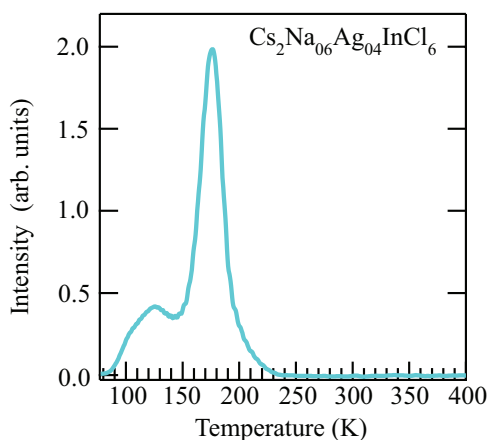


Figure 3.7: TL glow curve of $\text{Cs}_2\text{Na}_{0.6}\text{Ag}_{0.4}\text{InCl}_6$, as measured following 1 min of 345 nm UV charging at 77 K and subsequent heating to 400 K at a constant heating rate of 1 K/s (**Paper 1**).

In fading measurements, the waiting time between the end of excitation and the subsequent heating is varied [83]. During this period, trapped charge carriers may be released before the TL measurement begins, causing the population of less stable trapping states to decrease with increasing waiting time. Comparing the glow-peak intensities as a function of waiting time therefore provides information on the stability of the populated trapping states and allows more rapidly fading states to be distinguished from those that retain trapped charge carriers for longer periods [83].

Chapter 4

Results and Discussion

In this chapter, I will summarize and discuss the main results obtained from the studies in this thesis. The chapter begins with a presentation of the results related to the study of $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$; $y = 0, 0.025$), and then on $\text{Cs}_2\text{NaEuCl}_6$.

4.1 Local structure and luminescence in $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$

The study of $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{1-y}\text{Bi}_y\text{Cl}_6$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$; $y = 0, 0.025$), focuses on unraveling the effect of x and y on local structure and luminescence. Figure 4.1 shows, as an example, the PL and PLE spectra of the investigated compositions. Increasing the Na^+ concentration from $x = 0$ to $x = 0.8$ produces relatively small changes in the PL emission, with all compositions retaining the broad 500 – 800 nm emission characteristic of STE emission in $\text{Cs}_2\text{AgInCl}_6$ -type MHDPs [13, 14, 20, 30]. Bi^{3+} doping results in substantially stronger luminescence throughout this compositional range. This is particularly evident for $x = 0$, where the Bi^{3+} -containing sample gives much stronger emission and consequently a substantially improved signal-to-noise ratio compared with $\text{Cs}_2\text{AgInCl}_6$. The clearest change in the PL is observed at $x = 1$, where complete substitution of Ag^+ by Na^+ suppresses the characteristic broadband $\text{Cs}_2\text{AgInCl}_6$ -type emission and gives rise instead to blue emission centered near 450 nm. PLE measurements show that increasing the Na^+ concentration from $x = 0$ to $x = 0.8$ shifts the excitation bands towards shorter wavelengths, whereas Bi^{3+} doping results in considerably broader excitation bands that extend further towards longer wavelengths.

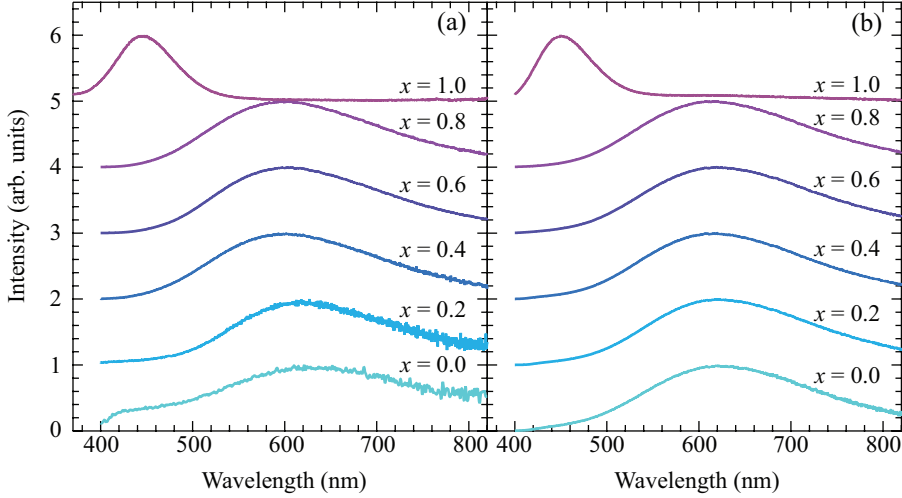


Figure 4.1: PL spectra of (a) $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{InCl}_6$ ($x = 0 - 1$) and (b) $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{0.975}\text{Bi}_{0.025}\text{Cl}_6$ ($x = 0 - 1$). All spectra were normalized to a maximum intensity of 1 and vertically offset by 1 (arb. units) for clarity (**Paper 1**).

TL measurements aimed to determine whether the composition-dependent changes observed in the luminescence are accompanied by corresponding changes in the charge-trapping landscape. The results reveal up to six thermally distinguishable families of charge-trapping defects, with glow-peak maxima within approximately 90 – 110 K (*trap 1*), 115 – 125 K (*trap 2*), 130 – 155 K (*trap 3*), 165 – 185 K (*trap 4*), 210 – 225 K (*trap 5*) and 230 – 260 K (*trap 6*). Upon increasing the Na^+ concentration, the occurrence of the different trap families changes in a non-systematic manner with x . Despite this, there is an overall tendency towards deeper trapping states with increasing x . Bi^{3+} doping further promotes this tendency, generally increasing the depth of the charge-trapping defects and giving rise to the additional deep trap families, *trap 5* and *trap 6*, as illustrated in Figure 4.2. At $x = 1$, however, complete substitution of Ag^+ by Na^+ results in a strong suppression of the charge-trapping defects, with no distinct glow peaks observed in the Bi^{3+} -free material and only a weak, broad TL signal remaining upon Bi^{3+} doping.

To investigate whether these composition-dependent changes in luminescence and charge trapping are related to any local structural differences between the studied materials, Raman spectroscopy was used. In $\text{Cs}_2\text{AgInCl}_6$, the Raman spectrum shows bands at around 142, 166 and 300 cm^{-1} , assigned to the $\text{T}_{2g}(\text{In})$ bending/breathing, $\text{E}_g(\text{In})$ asymmetric stretching and A_{1g} symmetric stretching vibrations of the $\{\text{In,Ag}\}\text{Cl}_6$ octahedra, respectively [18, 20, 74, 76, 78, 79]. Upon Bi^{3+} doping, an additional weak band appears near 113 cm^{-1} , assigned to the $\text{T}_{2g}(\text{Bi})$ bending vibration of the BiCl_6 octahedra [18, 61, 74, 78], as shown in Figure 4.3.

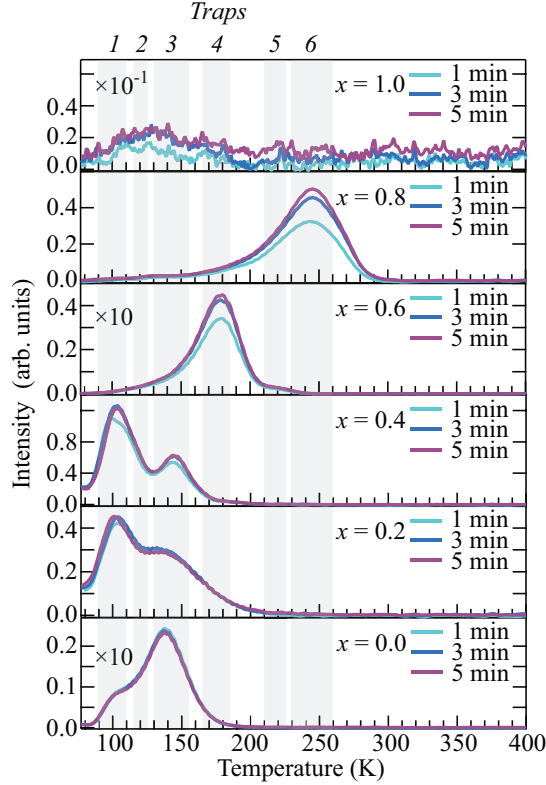


Figure 4.2: TL glow curves for $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{In}_{0.975}\text{Bi}_{0.025}\text{Cl}_6$ ($x = 0 - 1$) under 1, 3, and 5 minutes of charging. (**Paper 1**).

Upon increasing the Na^+ concentration, the A_{1g} mode systematically shifts towards lower frequencies, whereas the $E_g(\text{In})$ mode shifts towards higher frequencies and progressively decreases in relative intensity. The $T_{2g}(\text{In})$ mode remains nearly unchanged in frequency, although its relative intensity increases with increasing x . The same Na^+ -dependent shifts and intensity changes are observed for the Bi^{3+} -containing compositions. The most pronounced change occurs at $x = 1$, where the $E_g(\text{In})$ mode is almost completely suppressed.

In order to investigate the spatial homogeneity of the Bi^{3+} distribution, we performed Raman mapping measurements over an extended surface area. A key result is the significant variation in the intensity of the $T_{2g}(\text{Bi})$ mode across the sample, with localized regions of substantially higher intensity (Figure 4.4). This indicates significant variations in the distribution of Bi^{3+} on a length-scale of some micrometers, possibly related to the presence/nature of charge-trapping defects in the material.

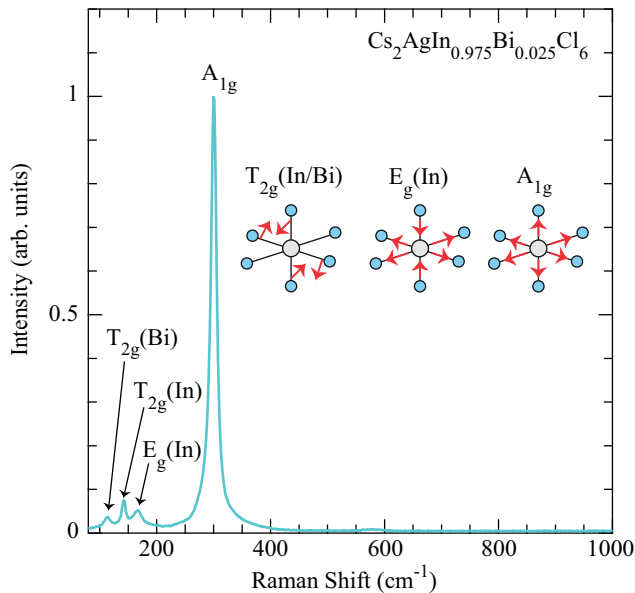


Figure 4.3: Raman spectrum of $\text{Cs}_2\text{AgIn}_{0.975}\text{Bi}_{0.025}\text{Cl}_6$, together with the assignments of the vibrational bands. Blue circles represent Cl^- ions, grey circles represent the central metal cation ($\text{Ag}^+/\text{In}^{3+}/\text{Bi}^{3+}$), and red arrows indicate the principal atomic displacements. (**Paper 1**).

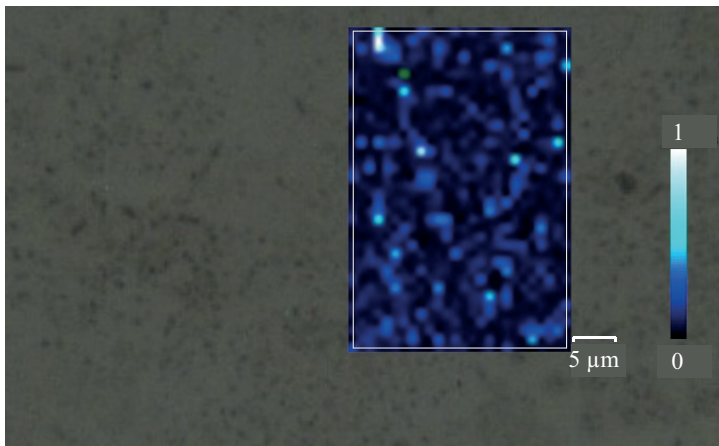


Figure 4.4: Raman mapping of $\text{Cs}_2\text{Na}_{0.2}\text{Ag}_{0.8}\text{In}_{0.975}\text{Bi}_{0.025}\text{Cl}_6$, showing the spatial distribution of the $T_{2g}(\text{Bi})$ mode. The spatially resolved Raman intensity map is overlaid on an optical image of the crystal surface, with the color scale representing the intensity of the mode. (**Paper 1**).

4.1.1 Discussion of the results

One of the most important findings is that the enhanced broadband luminescence upon Bi³⁺ doping coexists with charge-trapping defects of higher energetic depth. This contrasts with the commonly proposed picture in which improved luminescence is associated primarily with suppression of charge-trapping states in Cs₂AgInCl₆-type MHDPs [13, 49, 50]. The present results instead show that Bi³⁺ modifies the charge-trapping landscape towards deeper states while simultaneously increasing the luminescence intensity and broadening the excitation range.

The Raman spectroscopy results provide a possible structural origin for these deeper traps. The locally inhomogeneous distribution of Bi³⁺—here manifested in the T_{2g}(Bi) bending mode—is consistent with local BiCl₆ clustering, while previous calculations show that Bi³⁺ doping lowers the formation energy of Ag⁺ vacancies in Cs₂AgInCl₆ [49]. Together, these observations suggest that local BiCl₆ clustering may promote the formation of nearby Ag⁺ vacancies, which could account for the appearance of deeper trapping states observed upon Bi³⁺ doping.

The behavior at $x = 1$ further highlights the importance of Ag⁺ in Cs₂AgInCl₆-type MHDPs. The simultaneous loss of the characteristic broadband STE emission, strong suppression of the E_g(In) Raman mode and near disappearance of resolved charge trapping upon complete Ag⁺ substitution indicate that Ag⁺ is central not only to STE formation, but also to the charge-trapping processes in these materials. Taken together, these findings suggest that the local arrangement of BiCl₆ octahedra may provide a means of controlling trap depth while retaining strong broadband luminescence.

4.2 Local structure and luminescence in Cs₂NaEuCl₆

The studies of Cs₂NaEuCl₆ focused on identifying the mechanisms governing the temperature-dependent Eu³⁺ luminescence, particularly the enhancement of the HST and the thermal quenching of luminescence at higher temperatures, and on determining how the excitation pathway influences the resulting luminescence efficiency. This was investigated using a combination of PL, PLE, PLQY and TRPL techniques [24]. Figure 4.5 shows, as an example, data from the temperature-dependent PL measurements. A key result is that the HST ⁵D₀ → ⁷F₂ is progressively enhanced relative to the MD ⁵D₀ → ⁷F₁ transition with increasing temperature [24].

The origin of this behavior can be understood from the relative contributions of two distortion modes of the EuCl₆ octahedra [Figure 4.5 (a)] [24, 84, 85]. The doubly degenerate e_g mode corresponds to axial elongation or compression of the EuCl₆ octahedra, whereas the triply degenerate t_{2g} mode is primarily associated with tilting or rotation of the octahedra [24, 84, 85]. The I(e_g)/I(t_{2g}) ratio increases steadily with temperature and, since this ratio is expected to remain constant for an ideal cubic Eu³⁺ site, indicates an increasing relative

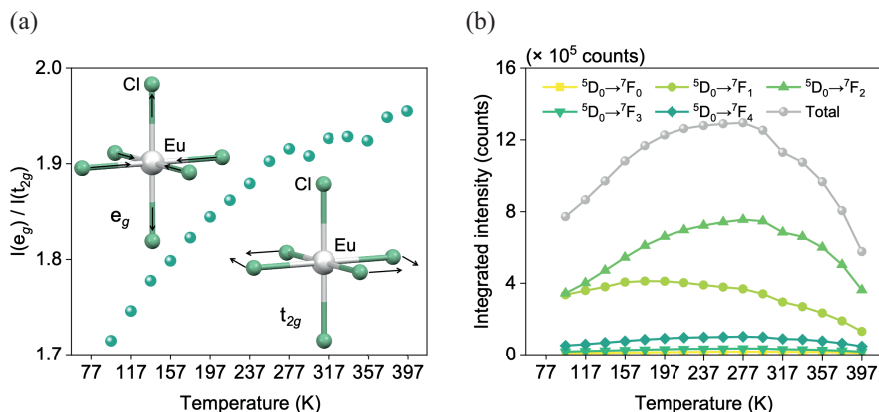


Figure 4.5: Temperature dependence of the local EuCl_6 distortions and Eu^{3+} emission in $\text{Cs}_2\text{NaEuCl}_6$ under 394 nm excitation between 77 and 397 K. (a) Intensity ratio $I(e_g)/I(t_{2g})$ as a function of temperature. The insets illustrate the corresponding distortions of the EuCl_6 octahedra, where the e_g component represents axial elongation or compression and the t_{2g} component represents primarily octahedral tilting or rotation. (b) Integrated intensities of the Eu^{3+} $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0 - 4$) transitions and the total emission as a function of temperature. The figure is adapted from Ref. [24] (**Paper 2**): M. Zhang *et al.*, "Phonon-induced hypersensitive transitions in lanthanide double perovskites", *Phys. Rev. B*, 2026, **114**, 084308, DOI: 10.1103/ss4k-zyd6, under the Creative Commons Attribution 4.0 International License.

contribution from thermally activated e_g -type axial distortions [24]. These axial distortions lower the local symmetry around Eu^{3+} and relax the parity restriction of the HST, thereby increasing its transition probability [24].

The corresponding temperature dependence of the Eu^{3+} emission is shown in Figure 4.5 (b) [24]. The integrated intensity of the MD $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition increases with temperature and reaches a maximum at approximately 177 K, whereas the HST $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition continues to increase up to approximately 277 K [24]. The HST is therefore progressively enhanced relative to the MD transition over the same temperature range in which the contribution from axial EuCl_6 distortions becomes increasingly pronounced [24]. Above approximately 277 K, all of the Eu^{3+} emission transitions decrease in intensity due to thermal quenching [24]. The comparable thermal-quenching behavior of the different transitions indicates that they are affected by a common thermally activated non-radiative pathway [24].

Evidence for the origin of this common non-radiative quenching pathway is obtained from excitation-dependent PL measurements [24]. A weak defect-related emission band centered near 420 nm is observed at room temperature for excitation wavelengths shorter than approximately 380 nm (> 3.26 eV), but disappears below approximately 250 K [24]. The temperature dependence of this emission is consistent with the thermal-quenching behavior of the Eu^{3+}

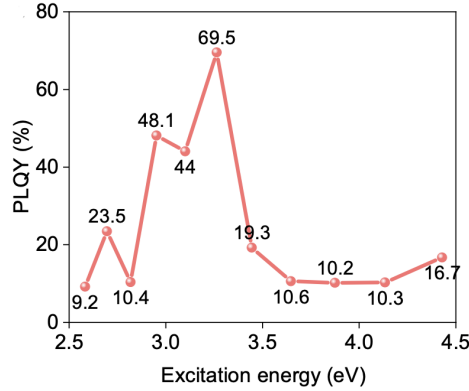


Figure 4.6: Excitation-energy-dependent PLQY of Cs₂NaEuCl₆ measured between approximately 2.5 – 4.5 eV. The PLQY reaches a maximum of 69.5% at an excitation energy of approximately 3.25 eV. The figure is adapted from Ref. [24] (**Paper 2**): M. Zhang *et al.*, "Phonon-induced hypersensitive transitions in lanthanide double perovskites", *Phys. Rev. B*, 2026, **114**, 084308, DOI: 10.1103/ss4k-zyd6, under the Creative Commons Attribution 4.0 International License.

transitions, supporting the presence of a defect-related state involved in the reverse energy-transfer process [24].

The luminescence efficiency is strongly dependent on the excitation energy, as shown in Figure 4.6 [24]. The PLQY reaches a maximum of 69.5% at approximately 3.25 eV, within a narrow excitation range of approximately 3.1 – 3.3 eV [24]. This energy range lies below the conduction-band minimum at approximately 3.5 eV and allows direct excitation of the Eu³⁺ 4*f* states, particularly the ⁵L_{6–7} manifold [24]. At higher excitation energies above the band gap, the PLQY decreases as excitation instead proceeds through the host before the energy is transferred to the Eu³⁺ 4*f* states [24]. The substantially higher PLQY obtained near 3.25 eV therefore shows that direct excitation of the Eu³⁺ manifold provides a more efficient route to the emissive states than host-mediated excitation [24].

TRPL measurements provide further information on the relaxation of the Eu³⁺ excited states after different parts of the 4*f* manifold are populated [24]. The results shows that population of the higher-lying states is followed by sequential relaxation through the ⁵D₂ → ⁵D₁ → ⁵D₀ levels, with emission from the upper states appearing at shorter times before the long-lived ⁵D₀ emission becomes dominant [24]. This shows that excitation of higher Eu³⁺ 4*f* states is efficiently funneled towards the ⁵D₀ state from which the dominant Eu³⁺ emission occurs [24].

This behavior is further supported by synchrotron-excited PL measurements [24]. Increasing the excitation energy from the band-to-band regime to substantially higher photon energies strongly enhances emission from the upper ⁵D₁ states, whereas the ⁵D₀ → ⁷F_J emission remains comparatively unchanged

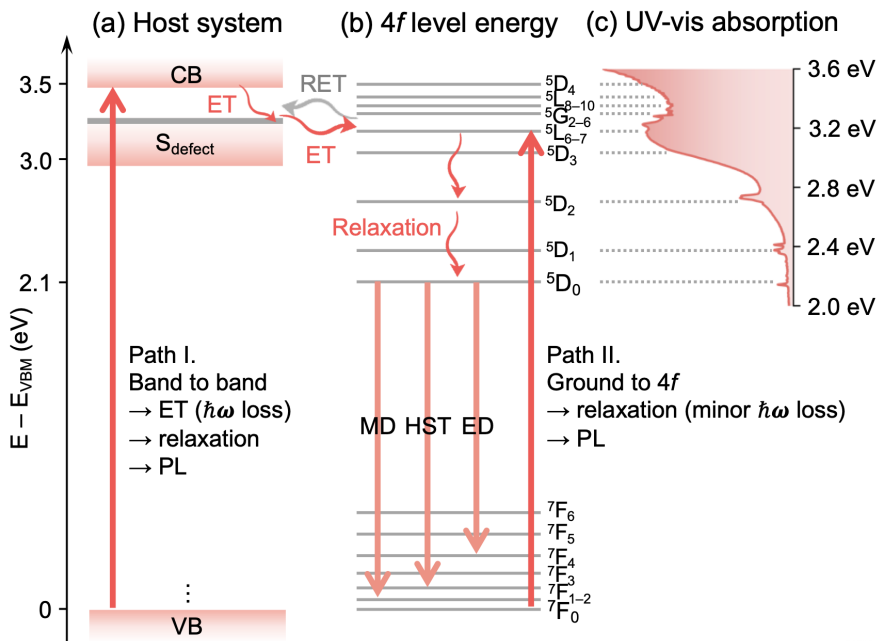


Figure 4.7: Proposed energy-level diagram illustrating the two excitation pathways in $\text{Cs}_2\text{NaEuCl}_6$. (a) Host-system band structure showing the valence band (VB), conduction band (CB) and defect-related intermediate state, S_{defect} . (b) Eu^{3+} $4f$ energy levels and the principal radiative transitions from the emissive $5D_0$ state: the MD $5D_0 \rightarrow 7F_1$ transition, the $5D_0 \rightarrow 7F_2$ HST, and the remaining ED transitions. (c) UV-vis absorption spectrum indicating the excitation energies associated with the Eu^{3+} $4f$ states and the host absorption edge [24] (**Paper 2**). Reproduced from M. Zhang *et al.*, "Phonon-induced hypersensitive transitions in lanthanide double perovskites", *Phys. Rev. B*, 2026, **114**, 084308, DOI: 10.1103/ss4k-zyd6, under the Creative Commons Attribution 4.0 International License.

[24]. Thus, changing the excitation energy primarily alters the population of the higher-lying Eu^{3+} states, but not the intensity of the $5D_0$ emission [24].

The resulting excitation and relaxation pathways are summarized in Figure 4.7 [24]. In Path I, above-band-gap excitation generates charge carriers in the host lattice, after which energy is transferred to the Eu^{3+} $4f$ manifold through the defect-related intermediate state. This host-mediated pathway is associated with thermalization losses and provides a route for reverse energy transfer [24]. In Path II, direct excitation near 3.2 eV directly populates the Eu^{3+} $5L_{6-7}$ manifold and is followed by rapid intra- $4f$ relaxation towards the emissive $5D_0$ state [24]. The substantially higher PLQY obtained for excitation near 3.2 eV is therefore associated with bypassing the host-mediated energy-transfer pathway and the corresponding energy losses [24].

4.2.1 Discussion of the results

Previous studies had established a pronounced temperature dependence of the Eu³⁺ emission and the sensitivity of the HST to vibronic coupling [63, 64, 66, 67], but the specific origin of the HST enhancement remained unclear. The present results provide a more microscopic understanding by showing that increasing temperature progressively strengthens the axial e_g distortion of the EuCl₆ octahedra, thereby lowering the local Eu³⁺ symmetry and relaxing the parity restriction of the HST [24]. At higher temperatures, however, this beneficial effect is eventually overcome by thermally activated reverse energy transfer through a defect-related state [24]. The temperature dependence of the luminescence therefore reflects a competition between lattice-induced enhancement of the HST and non-radiative energy loss [24].

The excitation-dependent results provide a complementary route for overcoming this efficiency limitation [24]. Conventional lanthanide emitters commonly rely on dilute doping and host-to-4*f* energy transfer, for which defect-induced quenching and transfer losses can limit the luminescence efficiency [24, 34–37]. In Cs₂NaEuCl₆, Eu³⁺ is instead an intrinsic constituent of the lattice, enabling efficient direct excitation of the 4*f* manifold and thereby bypassing the host-mediated pathway associated with reverse energy transfer [24]. The resulting PLQY approaching 70% is comparable to that reported for state-of-the-art Eu³⁺-doped phosphors [24], showing that high luminescence efficiency can be achieved in an intrinsic Eu³⁺-containing MHDP without relying on host-mediated sensitization [24].

Chapter 5

Conclusions

This thesis has reported on studies of the relationship between local structure and luminescence in $\text{Cs}_2\text{AgInCl}_6$ and $\text{Cs}_2\text{NaEuCl}_6$, which represent two of the most important MHDPs currently available. In particular, the effects of Na^+ substitution at the Ag^+ site and Bi^{3+} doping at the In^{3+} site in $\text{Cs}_2\text{AgInCl}_6$, as well as the nature of the HST associated with Eu^{3+} in $\text{Cs}_2\text{NaEuCl}_6$, have been investigated using PL, PLE, Raman and TL spectroscopy.

The results on $\text{Cs}_2\text{AgInCl}_6$ reveal the existence of up to six energetically different families of charge-trapping defects. Na^+ substitution modifies these defects in a non-systematic manner, with both the characteristic broadband luminescence and charge-trapping strongly suppressed upon complete replacement of Ag^+ by Na^+ . Bi^{3+} doping generally increases the depth of the charge-trapping defects and promotes the appearance of new, deeper trapping states, while simultaneously enhancing the broadband luminescence. Comparison with the Raman results indicates that these deeper traps are associated with Ag^+ vacancies formed near locally clustered BiCl_6 octahedra. The coexistence of deeper charge trapping and intense broadband luminescence is particularly important, as the deeper traps can retain charge carriers to higher temperatures while the strong broadband emission provides an efficient radiative pathway upon their release and recombination.

The results on $\text{Cs}_2\text{NaEuCl}_6$ revealed that the temperature-enhanced $^5\text{D}_0 \rightarrow ^7\text{F}_2$ HST is linked to increasing axial e_g distortions of the EuCl_6 octahedra, which relax the parity restriction of the transition. At higher temperatures, this enhancement competes with reverse energy transfer through a defect-related. Direct excitation of the Eu^{3+} $4f$ manifold bypasses this host-mediated pathway and gives a PLQY approaching 70%. These results show that both local lattice distortions and the excitation pathway are key factors controlling efficient Eu^{3+} luminescence in lanthanide-containing MHDPs.

Besides being of considerable fundamental interest, these new findings can be expected to be important for the rational design of new MHDPs, with a view toward their application in LEDs or other optoelectronic technologies.

Chapter 6

Outlook and future work

A continuation of the work presented in this thesis is to further investigate the effect of the type of B/B'-site cations on the local structure and luminescence of Cs-based MHDPs. In this context, $\text{Cs}_2\text{NaScCl}_6$ represents an interesting model system. The material typically exhibits blue emission centered around 445 nm upon UV excitation [86, 87]. However, measurements within our research group have revealed substantial variations in emission intensity and color between samples and even within individual crystals. Similar inconsistencies are found in the literature, where reported PLQYs vary between approximately 3% and 27% [86, 87].

To investigate this, simultaneous spatially resolved PL and XRD measurements will be performed at the Extreme Light Infrastructure (ELI) Beamlines in Prague, Czechia, on crystals with different emission properties. Variable-temperature measurements will correlate changes in luminescence with structural changes and thermal quenching, while time-resolved optical-pump/X-ray-probe measurements will determine whether transient lattice distortions accompany carrier localization and self-trapping. Similar photoinduced structural changes have been observed in CsPbBr_3 and $\text{Cs}_3\text{Bi}_2\text{Br}_9$ [88, 89]. Furthermore, the origin of the luminescence remains unresolved. While several studies attribute the broadband emission to intrinsic STEs [86, 87, 90, 91], impurity-related emission, for example from Sb^{3+} , has also been proposed [92]. Investigations of samples with varying concentrations of Sb^{3+} ions will help to shine light on this important aspect.

For $\text{Cs}_2\text{NaEuCl}_6$, further work will focus on the influence of moisture on the local structure and temperature-dependent luminescence. Previous TRPL studies have proposed that the excitation energy can migrate to defect Eu^{3+} sites associated with interstitial H_2O , where predominantly non-radiative relaxation occurs [67]. Infrared spectroscopy will be used to probe the presence and nature of H_2O impurities, while temperature-dependent TRPL measurements will be performed to provide further insight into the thermal quenching of the Eu^{3+} emission. Together, these measurements will help to determine whether moisture-related defect sites contribute to the observed thermal quenching of luminescence.

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