Nature of localized excitons in CsMgX₃ (X = Cl, Br, I) and their interactions with Eu²⁺ ions[†]

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[†] Electronic Supplementary Information available: X-ray powder diffraction patterns of the undoped halides CsMgX₃ (X = Cl, Br, I).

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In this paper, the luminescence properties of self-trapped excitons (STEs) of undoped and Eu²⁺ doped perovskite-type materials CsMgX₃ (X = Cl, Br, I) are presented. The three compounds crystallize isostructurally in a hexagonal crystal system that exhibits an intrinsic pseudo one-dimensionality. This feature has a highly stabilizing effect upon the localization of excitons. Similarities to the properties of STEs in alkali halides are drawn that are justified by band structure and density of states (DOS) calculations. The luminescence spectra of all three halides are characterized and interpreted despite of their high complexity with many emissive transitions. It is illustrated that both self-trapped excitons (STEs) and impurity-localized self-trapped excitons (IL-STEs) are responsible for the features in the spectra. The impurity localization of the STEs is proven by doping the hosts with Sr²⁺ ions instead of Eu²⁺ ions. The decay times in the μ s range indicate that emission predominantly occurs from a triplet state of the STEs with a prominent afterglow component for the IL-STEs that ideally suits a trapping model along the one-dimensional chains of the halides. Moreover, by thermal activation, the excitons tend to annihilate at the Eu²⁺ traps thereby inducing an energy transfer to the Eu²⁺ ions. Due to this action, an extreme increase of the intensity of the Eu²⁺-based 4f⁶5d-4f⁷ emission at room temperature could be observed, which might be a general explanation for unusual temperature-dependent emission intensities of Eu²⁺ ions. In general, an understanding of the basic optical properties of the STEs may give some new insights into the mechanism of currently used X-ray storage phosphors as well as scintillators.

1 Introduction

Many phosphors gain their luminescence properties by the intentional addition or even total composition of activators such as lanthanides, transition metals or s² ions. Their applications range from light-emitting diode (LED) phosphors over lasing materials to X-ray storage phosphors and scintillators [1]. Particularly for the last two applications, however, the optical properties of intrinsic defects that arise upon formation of excitons by incident ionizing radiation plays a major role in the mechanistic details of the luminescence process [2], [3]. Moreover, defects are generally created by doping if the size and/or the charge of the dopants and the substituted ion of the host does not coincide. In these cases, the defects influence the optical properties of the compounds usually remarkably due to quenching of the emissions of the activators or even due to intrinsic emission of defects stabilized by lattice distortions [2], [3]. One prominent example is the X-ray storage phosphor BaFBr:Eu²⁺, in which it was shown that point defects such as color centers are correlated to the local Eu²⁺ impurities thereby influencing its photostimulable luminescence (PSL) properties [4], [5]. Therefore, defects and excitons are of key importance concerning the luminescence properties and the efficiency of materials and are, thus, worth to be investigated in detail.

In ionic insulators such as alkali halides, a created hole shows a high tendency for self-localization due to the high strength of the coupling to longitudinal optical (LO) phonons in these compounds that supports the formation of a polaronic quasiparticle [6], [7], [8], [9]. Upon attraction of the electron, these self-trapped excitons (STEs) have a rich electronic structure that gives rise to complicated luminescence [10], [11], [12], [13], [14], [15] and electron paramagnetic resonance (EPR) spectra [16], [17], [18], [19]. The literature on the optical and magnetic properties of STEs in binary alkali halides is very exhaustive and a very broad overview over the different

properties is given in a review and a book by Song and Williams in the 1990s [20], [21]. Since then, however, no comparably detailed literature on the optical properties of self-trapped excitons in more complex halides has been published so far.

In binary halides it is now established that STEs can be well described by a “molecule in a lattice” configuration, in which the self-trapped hole forms a dimer anion X₂^{•-} (X = Cl, Br, I) and attracts the additional loosely bound electron without strong perturbation by the surrounding crystal field [16], [22], [23]. This (V_K + e) or on-centre configuration is highly unstable against adiabatic relaxation in the lighter halides, in which the electron first occupies an adjacent anion vacancy thus pushing the hole to the other anion vacancy [24], [25], [26]. A theoretical explanation for this phenomenon was first convincingly given by Toyozawa upon inclusion of a pseudo Jahn-Teller mixing between the excited |2p_z⟩- and |1s⟩-like states of the electron [27]. From this off-centre configuration, further separation of the electron and the hole gives rise to a separated F-H defect pair [25], [26], [28], [29], which has also been proven experimentally [30]. It has been moreover shown in detailed investigations that this configuration is basically determined by the geometry of the crystal lattice that is parametrized according to Rabin and Klick (see also section 3.2) [28], [31], [32].

Besides binary alkali halides, there are only few examples of more complex halides that were investigated regarding their intrinsic luminescence such as BaFX (X = Cl, Br, I) [33], [34], [35], [36], NH₄X (X = Cl, Br, I) [37], [38] or the fluoride-based perovskites AMgF₃ (A = K, Rb, Cs) [39], [40], [41], [42].

One special class of halides that are interesting in this context are representatives of the CsNiCl₃ crystal structure such as CsMnBr₃ and CsCdBr₃ [43], [44], [45]. It is well-known from these compounds that they show intrinsic luminescence ascribed to self-trapped excitons [46], [47], [48], [49], [50], [51], [52], [53]. Compounds of this structure type exhibit an

intrinsic pseudo one-dimensionality due to linear chains of face-sharing coordination octahedra that allows a spontaneous self-trapping of excitons by electron-phonon coupling without a potential barrier [54]. This phenomenon is already well investigated in the

Figure 1. (Color online) Schematic view on the crystal structure of the quasi one-dimensional halides CsMgX_3 ($X = \text{Cl}, \text{Br}, \text{I}$). The Cs^+ ions are twelve-fold coordinated and the Mg^{2+} ions are six-fold coordinated by the X^- ions.

related quasi one-dimensional solids $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{X}_2]\text{Y}_4$ with $\text{en} = \text{ethylenediamine}$ ($\text{C}_2\text{H}_8\text{N}_2$), $X = \text{Cl}, \text{Br}, \text{I}$ and Y as a complex anion such as ClO_4^- or PF_6^- , in which the exciton forms as a result of an intervalence charge transfer (IVCT) and becomes self-trapped along a Peierls-distorted one-dimensional chain [21], [55], [56].

The one-dimensionality also allows for a movement of the excitation energy through the lattice along the linear chains thus also enabling energy transfer processes [52], [53]. Thus, such systems are ideally suited for the investigation of the intrinsic electronic properties of STEs and their interaction with activators such as Eu^{2+} , which plays a tremendous role for the performance of novel scintillators or X-ray storage phosphors.

Out of the previous reasons, the intrinsic photoluminescence properties of STEs in the distorted perovskites CsMgX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) are presented in this paper, which also exhibit linear chains in their structure (see Figure 1). In CsMgCl_3 , an intrinsic luminescence has already been reported and also proven [57]. Moreover, this compound is known to show core-valence luminescence upon X-ray radiation [58], [59]. However, to the best of our knowledge, for CsMgBr_3 and CsMgI_3 no such studies have been reported yet. We therefore desire to present a systematic study about the varying optical properties of STEs as well as a comparison to binary alkali halides for these ternary compounds. Their chemical nature will be demonstrated with aid of band structure calculations. An efficient energy transfer to doped Eu^{2+} ions is illustrated, which makes these materials interesting for applications in the field of scintillators.

2 Experimental

2.1 Preparation

CsCl (Merck, 99.5%) and CsBr (Chempur, 99.9%) were pre-dried at 200 °C in a dynamic vacuum overnight. The starting materials $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (Riedel-de Haën, 99%) and $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (Sigma Aldrich, 99%) were carefully dehydrated by

sublimation under vacuum at 600 °C. All subsequent preparative steps were performed under dry Ar atmosphere in a glove box (Braun).

EuCl_2 was synthesized in liquefied NH_3 using Eu metal (smart-elements, 99.99%) and vacuum-dried NH_4Cl (Th. Geyer, 99.8%) [60], whereas EuBr_2 and EuI_2 were directly obtained upon thermal decomposition under vacuum of the ternary halides $(\text{NH}_4)_3\text{EuX}_6$ ($X = \text{Br}, \text{I}$) [61], [62], [63], [64]. The ternary halides were synthesized from a solution of Eu_2O_3 (smart-elements, 99.99%) and the desired ammonium halide NH_4Br (Acros Organics, 99%) or NH_4I (Riedel-de Haën, 99%) in the half-concentrated acids HBr (Alfa Aesar) and HI (Merck), respectively, upon evaporation of the solvent. The halides SrX_2 ($X = \text{Cl}, \text{Br}, \text{I}$) were also obtained upon drying of the respective hydrates $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$ (Riedel-de Haën, 99%), $\text{SrBr}_2 \cdot 6 \text{H}_2\text{O}$ (Alfa Aesar, 99%) and $\text{SrI}_2 \cdot x \text{H}_2\text{O}$ (Heraeus, 99.5%) at 200 °C under vacuum. Strontium iodide was pre-treated with diluted HI in order to remove traces of SrCO_3 that form upon standing on air.

The synthesis of the halides CsSrX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) doped with 0.1 mol% Eu^{2+} has already been described in literature in detail [65], [66], [67]. For the preparation of the Eu^{2+} and Sr^{2+} -co-doped compounds CsMgCl_3 and CsMgBr_3 , the corresponding anhydrous starting materials were fused together in stoichiometric amounts with small molar amounts of EuX_2 and/or SrX_2 ($X = \text{Cl}, \text{Br}$). Doped samples of CsMgI_3 were obtained by fusing CsI_3 (Alfa Aesar, 98%) with Mg metal (smart-elements, 99.8%) in stoichiometric amounts and doping the product with EuI_2 and/or SrI_2 . All mixtures were sealed in evacuated silica ampoules, respectively, and melted at temperatures higher than the corresponding melting points according to the binary phase diagrams for 36 h [68], [69], [70]. Afterwards, the mixtures were slowly (2 °C/h) cooled down to 100 °C below the melting point and finally to room temperature with a rate of 10 °C/h. The purity of all samples was verified by X-ray powder diffraction (Stoe Stadi P, Cu K_α radiation, see supplementary material).

2.2 Optical measurements

Clear and transparent pieces ($\sim 1 \text{ mm}^3$) of the products were sealed in evacuated thin silica ampoules for photoluminescence investigations. Emission and excitation spectra were detected with a Fluorolog3 (FL3-22) spectrofluorometer (Horiba Jobin Yvon) equipped with a 450 W Xe lamp and double Czerny-Turner monochromators that allow a resolution down to 0.05 nm. The signal was detected with a photomultiplier tube R928P (Hamamatsu) coupled with a photon counting system. Emission spectra were corrected for the photomultiplier sensitivity and excitation spectra for the lamp intensity. A He closed-cycle cryostat (Janis) allowed measurements between 10 K and room temperature. Decay times down to 5 μs were measured at 10 K using a 75 W Xe flash lamp that is attached to the same spectrometer. Diffuse reflectance measurements were performed with a Cary 5000 UV-VIS spectrometer (Agilent) that detects reflectance between 200 nm and 2500 nm. The reflectance spectra were corrected for the background with a Spectralon reference sample.

2.3 Band structure and density of states (DOS) calculations

Calculations of the band structures and the density of states (DOS) of the host compounds were performed with the Vienna *ab initio* simulation package (VASP) [71], [72], [73], [74], [75]. All calculations were carried out within the generalized gradient approximation (GGA) by a Perdew-Wang functional (PW91) to account for the exchange and correlation functionals [76], [77], [78]. The interaction between core and valence electrons was approximated in terms of the projected augmented wave (PAW)

Figure 2. (Color online) Diffuse reflectance spectra of the undoped halides CsMgCl₃, CsMgBr₃ and CsMgI₃ at room temperature.

method [79], [80]. Full geometry optimizations were performed with a cutoff energy of 550 eV and 10 *k* points in the Brillouin zone. The atomic positions were allowed to relax until the residual Hellmann-Feynman forces were smaller than 0.03 eV/Å. The band structure and density of states calculations were conducted with the relaxed structures and a plane-wave cutoff energy of 400 eV and 20 *k* points in each direction. Convergence was achieved for smaller energy variations than 10⁻⁶ eV.

3 Results and Discussion

3.1 Band structure and electronic density of states (DOS) calculations

Figure 2 depicts the reflectance spectra of the undoped halides CsMgCl₃, CsMgBr₃ and CsMgI₃. In the cases of CsMgBr₃ and CsMgI₃, strong absorption bands are detected at high energies, which are readily recognized as transition from the valence to the conduction band and allow a determination of the optical band gaps as given in Table 1. In particular, our experimentally determined value for the band gap of CsMgI₃ (4.57 eV) is in very good agreement with an earlier measurement by McPherson and Talluto (4.84 eV) [81]. In the case of CsMgCl₃, the band-band transition is energetically above the measurable range of the reflectance spectrometer. Additionally, several small absorption bands are present at lower energies than the actual band-band transition, which

can therefore be assigned to transitions into the different excitonic hydrogen-like states $|n\rangle$. Since all of the compounds crystallize in the same hexagonal crystal system with space group *P6₃/mmc* (no. 194) [45], [82], the band structures and DOS look accordingly similar (see Figure 2). All halides show a direct band gap at both the Γ and K point, which decreases for the heavier halides in agreement to expectations. Moreover, the calculated value for CsMgCl₃ of 5.24 eV agrees well with the recently reported value of 5.31 eV [83]. However, the theoretical values are lower than the experimentally determined band gaps (see Figure 2 and Table 1). This is a well-known fact from GGA-DFT calculations due to

Table 1. Calculated and experimental band gaps of CsMgX₃ (X = Cl, Br, I). For details on the calculations, see text.

Compound	$E_g(\text{theoretical})$ / eV	$E_g(\text{experimental})$ / eV
CsMgCl ₃	5.24	> 6 (8.50)*
CsMgBr ₃	4.16	5.95
CsMgI ₃	3.13	4.57

* References [58], [59].

the approximation in the electron exchange correlation functional [84], [85] and the energy derivative discontinuities that arise from the integer number of electrons [86], [87].

The low curvature of the valence band close to the Γ point in all three compounds indicates a high effective hole mass, whereas the effective electron mass is much lower according to the curvature of the lowest conduction band. This is a confirming aspect for the formation of STEs in the manner that is known from the binary alkali halides [16]. In particular, the direct band gap of all three compounds CsMgX₃ (X = Cl, Br, I) also suggests that the formation of excitons should be very efficient.

In general, several main groups of bands can be distinguished in all three compounds according to the DOS calculations (see Figure 3). The narrow core bands in the range between -15 to -10 eV have dominant *s* orbital contribution from the halide anions with very small mixing of Mg 2*s* and 2*p* character in all compounds. Additionally, at around -8 to -6 eV dominant 5*p* core bands from the Cs atoms are present in all cases, which shift to lower energies and become narrower for the heavier halides. This is reasonable since valence orbitals of the halides increase in energy with higher atomic number and lower electronegativity and therefore make the Cs core bands more non-bonding and hence, dispersionless. Since the gap between the upper edge of the valence bands and the core band, E_{vc} , increases for the heavier halides, only CsMgCl₃ is expected to show core-valence luminescence ($E_{vc} < E_g$), which agrees with reported observations [58], [59].

The calculations additionally show that the lowest valence bands are most dominantly composed of Mg 2*s* orbitals. For the uppermost valence bands, the *p* orbitals of the halide anions show by far the highest contribution, whereas also slight mixing of the Mg 2*p* and Cs 5*p* orbitals is obvious. Just below the Fermi level, however, only *p* bands from the halides are present. The lowest conduction bands are mainly

composed of Mg 3s orbitals. At higher energies (5 eV – 10 eV), conduction bands with mainly 5d contribution of the Cs ions and little mixing of Mg 2p orbitals as well as halogen s, p and d orbitals (for Br and I) are present (note the scales in Figure 3). Especially the projected DOS calculations indicate a striking similarity of the electronic properties of the compounds CsMgX₃

(X = Cl, Br, I) to the simple binary alkali halides [21], which is mainly related to the high ionicity in this compound. In fact, the sole contribution of the halogen p orbitals at the Fermi level and the Mg 3s orbitals at the bottom of the conduction bands confirms the previously stated argument that STEs in the presented compounds form in a similar way as known for the alkali halides. Moreover, the strong participation of Mg on the

Figure 3. (Color online) Calculated band structures and electronic total as well as projected density of states (DOS) of CsMgCl₃ ((a), (b)), CsMgBr₃ ((c), (d)) and CsMgI₃ ((e), (f)).

lowest conduction band allows the conclusion that the STEs are strongly confined along the linear chain of face-sharing [MgX₆]⁴⁻ octahedra in direction of the hexagonal *c* axis. This is in agreement to the reported luminescence properties of STEs

in isostructural compounds such as CsMnBr₃ or CsCdBr₃ [47], [51], [52], [53]. Due to the intrinsic one-dimensionality that is also exhibited in the compounds CsMgX₃ (X = Cl, Br, I), STE formation should be highly favoured [54].

Figure 4. (Color online) Photoluminescence emission (solid) and excitation spectra (dashed or dotted) of STEs in undoped (a) CsMgCl₃, (b) CsMgBr₃ and (c) CsMgI₃ at 10 K. The π and σ emissions are indicated in each case.

3.2 Photoluminescence of self-trapped excitons in CsMgX₃ (X = Cl, Br, I)

Figure 4 depicts that STEs are detectable in UV range, which are intrinsic to the hosts CsMgCl₃, CsMgBr₃ and CsMgI₃. Due to the dense packing of the perovskite-based structures of CsMgCl₃, CsMgBr₃ and CsMgI₃, STEs should predominantly orient along the hexagonal *c* axis at 10 K, as already suggested for CsMnBr₃ and (CH₃)₄NMnX₃ (X = Cl, Br) [88], [89]. The corresponding Rabin-Klick parameters for an orientation along the [011] direction are *S/D* = 0.1624, 0.1038 and 0.0286 for CsMgCl₃, CsMgBr₃ and CsMgI₃, respectively. Here, *S* denotes

the distance between two adjacent halide anions in the regarded direction minus the halide ionic diameter, whereas *D* is the diameter of the corresponding free halogen atom [28], [31], [32]. *S/D* is a measure for the tendency to separate the self-trapped hole from the electron thereby forming an F-H defect pair, in which both electron and hole occupy a single anion vacancy, respectively. The low values of *S/D* for the presented compounds compared to alkali halides indicate that the STEs in CsMgX₃ (X = Cl, Br, I) and accordingly in similar quasi one-dimensional compounds tend to be on-centered and can hence be well described within the (*V_K* + *e*) or type I

configuration according to the classification of Kan'no *et al.* [28], [29].

The low Rabin-Klick parameters imply that a singlet or σ emission should also be observed, which is characterized by low Stokes shifts [20], [21]. In fact, a UV emission band is observed at 340 nm (29410 cm^{-1}) in CsMgBr_3 (see Figure 4b) with a Stokes shift of 2680 cm^{-1} . Another lower energetic emission in at 406 nm (24610 cm^{-1}) is correspondingly assigned to a triplet or π emission. The respective excitation spectra are characterized by broad featureless bands in proximity to the conduction band, which additionally justifies the assignment.

For the other two halides, only one emission could be observed with similarly broad and featureless excitation bands (see Figure 4a & c). In CsMgCl_3 , it is located at 25700 cm^{-1} (389 nm), whereas in CsMgI_3 , the emission is peaking at 25520 cm^{-1} (392 nm) in perfect agreement to the reported value for the intrinsic emission in this iodide [81]. According to the decay times (see section 3.3), they are also assigned to π transitions.

All three π emissions are characterized by very large Stokes

Table 2. Characteristic values of optical properties of the STEs in CsMgX_3 (X = Cl, Br, I). All measured values were acquired at 10 K. For details, see text.

Compound	Rabin-Klick parameter S/D	E_{em} / cm^{-1}	FWHM $/ \text{cm}^{-1}$	Stokes shift $\Delta S /$ cm^{-1}	$\tau / \mu\text{s}$
CsMgCl_3	0.1624	25700 (π)	2110	11860 (π)	35 (π)
CsMgBr_3	0.1038	24610 (π)	2470	11600 (π)	57 (π)
		29410 (σ)	2240	2680 (σ)	< 10 (σ)
CsMgI_3	0.0286	25520 (π)	3240	13660 (π)	11 (π)

shifts (11860 cm^{-1} , 11600 cm^{-1} and 13660 cm^{-1} for CsMgCl_3 , CsMgBr_3 and CsMgI_3 , respectively) similar to the alkali halides [20], [21], which additionally justifies the assignment. Interestingly, the positions of all three π emission bands are very similar to each other. This may be assigned to a compensating effect between the expected redshift due to the higher degree of polarizability of the heavier halides and the stronger constraint of the surrounding lattice in formation of the STEs as indicated by the Rabin-Klick parameters S/D .

3.3 Decay times of self-trapped excitons in CsMgX_3 (X = Cl, Br, I)

The decay curves obtained upon detection of the emissions from the STEs and ITEs in CsMgCl_3 , CsMgBr_3 and CsMgI_3 show a multi-exponential behaviour with decay times in the μs range and an afterglow component in the range of tens of ms at 10 K (see supplementary material). This clearly identifies the transitions as triplet-like or π emissions in analogy to alkali halides [15], [20], [21]. Only the shortest components were interpreted due to the arbitrariness of the multi-exponential fitting function in order to crudely model the afterglow. In general, the decay time of the π emissions decreases with heavier halide due to the increasing impact of spin-orbit coupling that mixes singlet character into the excited state of the STE hence allowing the π emission at all. The decay time of the triplet state $^3\Sigma_u^+$ is given by [15], [29]

$$\tau_{\pi}^{-1} = C \cdot E_{\pi}^3 \cdot b^2 \cdot \left| \langle ^1\Pi_u | \vec{r} | ^1\Sigma_g^+ \rangle \right|^2 \quad (1)$$

where C is a constant, E_{π} is the π emission energy and b is the mixing coefficient indicating the amount of singlet-triplet mixing that is proportional to the spin-orbit coupling constant ζ of the free halogen atom. The radial integral accounts for the transition dipole moment between the excited and ground singlet state of the STE. Since the emission energies for the STEs do not vary significantly in the regarded isostructural compounds CsMgX_3 (X = Cl, Br, I), the main impact on the decay time arises from the mixing parameter b and hence, the spin-orbit coupling and the exchange splitting ΔE_{ex} between the singlet and triplet state. In the weak perturbation limit, it is [15], [29]

$$b = \frac{\zeta}{\Delta E_{ex}} \quad (2)$$

In the case of the presented halides, the shortest decay time components were assigned to the π emission and read 35 μs in CsMgCl_3 , 57 μs in CsMgBr_3 and 11 μs in CsMgI_3 at 10 K. Since the spin-orbit coupling constant ζ increases from the chloride to the iodide, the initial increase in decay time from the chloride to the bromide may be related to a compensating effect from the decrease in the π emission energy. The relatively low decay times in the μs range compared to values from some alkali halides in the ms range [15], [20], [21], [28], [29] is ascribed to the difference in Rabin-Klick parameters S/D and the corresponding amount of relaxation of the STEs. In CsMgX_3 , the S/D values are comparably low thereby leading to type I STEs with considerable singlet character of the excited states. In alkali halides, the more open structure allows for a higher degree of structural relaxation of the STEs also reflected in the larger S/D values [21]. This typically leads to the sole observation of a π emission and therefore larger decay times due to the larger triplet character.

A corresponding decay time for the singlet or σ emission was below the detectable limit of the employed flash lamp (< 10 μs) thereby justifying the assignment. Unfortunately, a corresponding measurement with a pulsed laser was not possible at the necessary cryogenic temperature.

3.4 Photoluminescence spectra of impurity-localized excitons in $\text{CsMgX}_3:\text{Eu}^{2+}$

The $4f^65d-4f^7$ luminescence of Eu^{2+} located at the Mg^{2+} sites in CsMgX_3 (X = Cl, Br, I) has already been discussed in detail in literature [66], [67], [90]. Only one redshifted emission band due to the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} ions is observed in each case. The occupation of the small Mg^{2+} sites has so far been proven by structure-luminescence relationships and theoretical considerations [66], [67], [91].

However, a second dominant emission is visible in the blue range in each of the halides (see Figure 5). Their maxima are located at 23360 cm^{-1} (428 nm), 22990 cm^{-1} (435 nm) and 22320 cm^{-1} (448 nm) for CsMgCl_3 , CsMgBr_3 and CsMgI_3 , respectively. Additionally, redshifted emission bands peaking at 21740 cm^{-1} (460 nm) in CsMgCl_3 and 21050 cm^{-1} (475 nm) in

CsMgBr₃ are detected upon excitation with UV light (see Figure 6 (a) & (c), upper spectra). The presence of these bands is not trivially understood since the crystal structure of the presented halides would intuitively only allow one additional emission band besides the one due to Eu²⁺ located on the Mg²⁺ sites that could formally be assigned to another 5*d*-4*f* emission of Eu²⁺ on the respective 12- fold coordinated Cs⁺ sites. Also the energetic positions of the blue emission bands would be reasonable for that assumption if compared to the emission energies of Eu²⁺ in CsCl ($E_{em} = 22730 \text{ cm}^{-1}$), CsBr ($E_{em} = 22680$

cm^{-1}) and CsI ($E_{em} = 22370 \text{ cm}^{-1}$) [92], [93], [94]. However, the mismatch both in charge and the Shannon ionic radii of Cs⁺ ($r(\text{Cs}^+) = 1.88 \text{ \AA}$) and Eu²⁺ ($r(\text{Eu}^{2+}) = 1.43 \text{ \AA}$) might imply that this situation is not highly probable [95]. Moreover, as indicated above, preliminary studies already excluded this interpretation for low concentrations (< 3 mol%) [66], [67], [91].

In order to elucidate the nature of the blue luminescence in the Eu²⁺-doped halides CsMgX₃, a concentration series with Eu²⁺ and Sr²⁺ was investigated (see Figure 5). With increasing Sr²⁺

Figure 5. (Color online) Emission spectra at 10 K of (a) CsMgCl₃: x% Eu²⁺, y% Sr²⁺, (b) CsMgBr₃: x% Eu²⁺, y% Sr²⁺ and (c) CsMgI₃: x% Eu²⁺, y% Sr²⁺. The total doping concentration was always (x) + (y)% = 1%.

concentration, the Eu²⁺-based 4*f*⁶5*d* → 4*f*⁷ emission band decreases in intensity in agreement to expectation, whereas the blue emission band retains its intensity. This indicates that the distortion caused by the ionic mismatch between Eu²⁺ or Sr²⁺, respectively, and Mg²⁺ is crucial for the origin of the blue luminescence bands [95].

The appearance of the photoluminescence excitation spectra (cf. Figure 6) upon detection of the corresponding blue emission

bands additionally show a striking similarity to the excitation spectra from CsSrX₃:Eu²⁺ (X = Cl, Br, I) both in energies and fine structure (see Figure 6, lower panels). The position of the higher energetic blue emission band agrees very well with the emission bands of Eu²⁺ in the previously mentioned Sr-based halides [66], [67]. Thus, the intense emission bands peaking at 23360 cm⁻¹ (428 nm), 22990 cm⁻¹ (435 nm) and 22320 cm⁻¹ (448 nm) for CsMgCl₃, CsMgBr₃ and CsMgI₃, respectively, are assigned to impurity-localized STEs (IL-STEs) at the Eu²⁺ ions. It

should be noted at this stage that this term is not to be confused with the also currently prominent impurity-trapped excitons (ITEs) in, e.g. Yb^{2+} -doped fluorides that contrarily stem from photoionization of the Yb^{2+} ions upon excitation of the electron into the conduction band [96], [97], [98], [99], [100], [101], [102], [103]. The IL-STEs regarded in this paper refer to mobile polaronic STEs along the linear chains in CsMgX_3 ($X = \text{Cl}, \text{Br}, \text{I}$), which become occasionally localized at impurities. A reasonable explanation for the assignment to IL-STEs is possible upon referring to the works on excitons in compounds with face-sharing octahedra such as CdX_2 ($X = \text{Cl}, \text{Br}, \text{I}$) or especially CsCdBr_3 [104], [105], [106]. Upon doping the halides

CsMgX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) with Eu^{2+} , their $5d$ orbitals are located in the band gap and can therefore interact with the np orbitals of the halide anions to form covalent bonds. Accordingly, the localized excitons in close proximity to the Eu^{2+} sites may be rather described in terms of a whole $[\text{EuX}_6]^{4-}$ octahedron ($X = \text{Cl}, \text{Br}, \text{I}$) within the linear chains along the hexagonal c axis instead of simple perturbed STEs. The similarity of the excitation spectra of the ITEs to the excitation spectra of isolated Eu^{2+} centres in CsSrX_3 [66], [67], [65] is a strong hint on this idea and arises from the fact that Eu^{2+} and Sr^{2+} have nearly similar ionic radii

Figure 6. (Color online) Photoluminescence emission spectra recorded at 10 K for (a) CsMgCl₃:Eu²⁺, (c) CsMgBr₃:Eu²⁺ and (e) CsMgI₃:Eu²⁺. Solid lines denote a doping concentration of 0.1 mol%, dashed lines a doping concentration of 1 mol% Eu²⁺. The assignments of the emissions arising from 4f⁶5d → 4f⁷ emissions of Eu²⁺ on Mg²⁺ sites are indicated. The lower spectra depict the 4f⁶5d-4f⁷ emissions of Eu²⁺ in CsSrX₃ (X = Cl, Br, I), respectively (cf. also refs. [65], [66], [67]). The corresponding photoluminescence excitation spectra upon detection of the IL-STE transitions are also given for (b) CsMgCl₃: 1% Eu²⁺, (d) CsMgBr₃: 1% Eu²⁺ and (f) CsMgI₃: 1% Eu²⁺ at 10 K. The dashed curves relate to the 4f⁶5d → 4f⁷ emission of Eu²⁺ on the Mg²⁺ sites. The corresponding excitation spectra.

($r(\text{Eu}^{2+}) = 1.17 \text{ \AA}$, $r(\text{Sr}^{2+}) = 1.18 \text{ \AA}$) and therefore characterize perfectly isolated [EuX₆]⁴⁻ octahedra [95]. Therefore, the actual excited states of the IL-STE are strongly localized on the Eu²⁺

ions, which may be interpreted in a decoupled scheme that treats the 4f⁶ core separately from the 5d orbital and has been discussed in detail by us earlier [66], [67]. The observation that

Figure 7. (Color online) Upper panels: Photoluminescence decay curves of (a) CsMgCl₃: 0.1% Eu²⁺ (λ_{ex} = 248 nm), (b) CsMgBr₃: 0.1% Eu²⁺ (λ_{ex} = 275 nm) and (c) CsMgI₃: 0.1% Eu²⁺ (λ_{ex} = 255 nm) for the π emissions of the STEs as well as the emissions of the IL-STE. Lower panels: Double-logarithmic plots of the decay curves of the IL-STE transitions indicating the tⁿ dependence of the afterglow components. Fitting curves are indicated as solid lines.

two blue emissions are observed in Eu^{2+} -activated CsMgCl_3 and CsMgBr_3 is explained by a perturbation from the local crystal field due to the ionic mismatch between Eu^{2+} and Mg^{2+} ions. In the iodide, the metal-ligand distances are, however, longer such that the local perturbation is assumed to be negligibly weak.

Alternatively, the incorporation of Eu^{2+} ions might also lead to stacking faults in the sense that the $[\text{EuBr}_6]^{4-}$ are tilted instead of face-sharing in the original structure of CsMgX_3 . Calculations or EPR measurements, which give further insight about the local structure of the IL-STEs, are planned.

3.5 Analysis of the afterglow of the luminescence of impurity-localized excitons

In the photoluminescence decay curves of the IL-STEs an additional afterglow component in the decay curve becomes more dominant (see Figure 7, lower panels), thus excluding a pure $4f^65d \rightarrow 4f^7$ emission of interstitial Eu^{2+} ions and justifying the attempted assignment. Contrarily, the decay times of the proposed $4f^65d \rightarrow 4f^7$ emission of Eu^{2+} at the Mg^{2+} sites are below 1 μs at room temperature and do not increase above 10 μs even at 10 K [66], [67]. The shortest components of the decay curves characteristic to the IL-STEs are very similar to the decay times obtained for the STEs (see Table 2), which indicates that they indeed are formed by localization of the

excitons at the Eu^{2+} impurities. It was shown that trapping of excitons at local impurities in an ideal one-dimensional chain should follow a $t^{-0.5}$ dependence in the decay curve, which was also experimentally confirmed [89], [107]. The afterglow components of the decay curves related to the IL-STEs in CsMgX_3 : 0.1% Eu^{2+} ($X = \text{Cl}, \text{Br}, \text{I}$) can be well fitted to a $t^{-0.4}$ to $t^{-0.7}$ decay instead. The deviation from the ideal case is interpreted to arise due to the possibility of interchain diffusion as the Cs^+ ions are not bulky enough to confine the exciton formation exclusively to the linear chains in the structure [89]. The decay kinetics therefore also justifies the picture of exciton trapping at present Eu^{2+} impurities.

3.6 Thermal annihilation of excitons at Eu^{2+} ions in CsMgX_3 ($X = \text{Cl}, \text{Br}, \text{I}$)

Both the π emissions of the STEs as well as the most intense IL-STE transition in all three halides (see Figure 4 and Figure 6) overlap with the excitation bands of Eu^{2+} thus fulfilling the resonance condition of an energy transfer from excitons to Eu^{2+} . Since the decay times of the excitonic transitions (see Table 2 and Figure 7) do not vary significantly with varying Eu^{2+} concentration within the range between 0.1 - 1 mol%, a classical resonance-type energy transfer according to Förster or Dexter

Figure 8. (Color online) Temperature-dependent emission spectra of (a) CsMgCl₃: 1% Eu²⁺, (b) CsMgBr₃: 1% Eu²⁺ and (c) CsMgI₃: 1% Eu²⁺. In all three cases, a UV excitation wavelength was used for the purpose of an efficient excitation into STE states.

may be excluded [108], [109]. Upon excitation in the UV range, the intensity of the Eu²⁺-based luminescence in the samples CsMgX₃: 1% Eu²⁺ increases with increasing temperatures (see Figure 8). This is especially pronounced for CsMgBr₃: Eu²⁺, where the highest intensity of the Eu²⁺ emission is detected at room temperature. This is an unusual observation if classical thermal quenching is taken into account and so far, only rarely reported [110]. Here, a thermally assisted energy transfer to the Eu²⁺ ions by the localized excitons must be indicated, most probably by thermal annihilation. A possible energy transfer mechanism that was thoroughly investigated in the class of quasi one-dimensional compounds relies on the possibility of exciton hopping within the linear chains along the hexagonal *c* axis [52], [53]. The hopping diffusion of the excitons is based on a “zig-zag”-like movement, in which the bonds of the V_K center X₂⁻ fold along the *c* axis. Hence, the activation energy for the hopping mechanism should correlate with the binding energy of the V_K center X₂⁻ (X = Cl, Br, I) [111]. This perfectly agrees with the decreasing activating temperature from CsMgCl₃ to CsMgI₃ required for an increase in luminescence intensity of the Eu²⁺-based 4f⁶5d → 4f⁷ emission. The presented results are particularly useful in the sense of applications as high-energy detecting materials, which strongly rely on an interaction of excitons or defects with an embedded activator. In that sense, these materials may provide a useful insight into the mechanistic details of exciton-activator interaction of halides.

Conclusions

In this paper, the optical properties of Eu²⁺-localized and self-trapped excitons in the quasi one-dimensional linear chain salts CsMgX₃ (X = Cl, Br, I) were investigated. The calculated DOS of the halides highly suggest that the excitons that form in these compounds are very similar to the well-investigated STEs in simple binary alkali halides and can hence be described as excitons of the form X₂⁻ + e⁻. The band structures justify this

idea due to the low curvature of the highest halide-based *p*-like valence band implying a high effective mass of the holes and, correspondingly, the high curvature of the lowest Mg-based *s*-like conduction band implying a low effective mass of the delocalized electron.

Self-trapped excitonic (STE) luminescence can be observed in the UV range in all three halides. The low Rabin-Klick parameters imposed by the densely packed crystal structure of the presented halides indicate a type I on-center or (V_K + e) configuration of the STEs. The decay times in the μs range of the excitonic transitions imply a triplet or π luminescence that is typical for STEs in halides. Both the emission energy and the increasing spin-orbit coupling play a role for the actual value of the decay time. In addition, impurity-localized self-trapped excitons (IL-STE) in Eu²⁺-doped CsMgX₃ show intense photoluminescence in the blue range at 10 K and can be readily identified by their excitation spectra, which are strikingly similar to the excitation spectra based on the 4f⁷ → 4f⁶5d transitions of the Eu²⁺-doped halides CsSrX₃, respectively. Their intrinsic nature has also been proven by doping with Sr²⁺ ions instead of Eu²⁺ ions. From the afterglow components of the decay curves of the IL-STE-based emissions, a *t*^{-0.4} to *t*^{-0.7} dependence was found that additionally indicates a trapping of the excitons at the Eu²⁺ impurities.

Finally, the interaction of the excitons with local Eu²⁺ impurities was investigated by means of temperature-dependent luminescence studies. An energy transfer from the excitons to the local Eu²⁺ impurities is evident that can be interpreted in terms of thermal annihilation of the excitons. In this context, it is very remarkable that the luminescence intensity of the Eu²⁺-based 4f⁶5d → 4f⁷ emission in CsMgBr₃:Eu²⁺ is much higher at room temperature than at low temperatures, which may be generally valid for an understanding of such observations. The activation energy for the energy transfer decreases from CsMgCl₃ to CsMgI₃, which is related to the decreasing bond strength of the self-trapped hole (X₂⁻) for heavier halides. This study gives valuable insights

into the mechanistic details of the non-radiative interaction between excitons and activators that may have relevance for the optimization of high energy detecting materials such as scintillators or storage phosphors.

Notes and references

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