

DFT and synchrotron radiation study of Eu²⁺ doped BaAl₂O₄

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Abstract: The structural distortions resulting from the size mismatch between the Eu²⁺ luminescent centre and the host Ba²⁺ cation as well as the electronic structure of BaAl₂O₄:Eu²⁺(Dy³⁺) were studied using density functional theory (DFT) calculations and synchrotron radiation (SR) luminescence spectroscopy. The modified interionic distances as well as differences in the total energies indicate that Eu²⁺ prefers the smaller of the two possible Ba sites in the BaAl₂O₄ host. The calculated Eu²⁺ 4f⁷ and 4f⁶5d¹ ground level energies confirm that the excited electrons can reach easily the conduction band for subsequent trapping. In addition to the green luminescence, a weak blue emission band was observed in BaAl₂O₄:Eu²⁺,Dy³⁺ probably due to the creation of a new Ba²⁺ site due to the effect of water exposure on the host.

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1. Introduction

Persistent luminescence materials can store energy from solar radiation or artificial lighting and release it over a period of several hours without a continuous excitation source. These materials are widely used to improve human safety in emergency and traffic signalization [1]. They can also be utilized in novel applications including *e.g.* structural damage sensors [2] and medical diagnostics [3].

The alkaline earth aluminates doped with Eu²⁺ and R³⁺ (MAl₂O₄:Eu²⁺, R³⁺; M: Ca/Sr/Ba; R: *e.g.* Nd/Dy [4,5]) are amongst the most efficient persistent luminescence materials. As for the aluminate phosphors, the BaAl₂O₄:Eu²⁺, R³⁺ materials have a special feature that europium can be obtained in the divalent form without the use of a reducing atmosphere [6,7]. Despite now possessing the same formal valence, the effect of structural distortions resulting from the size mismatch between the Eu²⁺ luminescent centre and Ba²⁺ (Eu²⁺ being statistically 12 % smaller [8]) is not known. In addition, details of the energy level systems – including the structure of the valence (VB) and conduction band (CB) and the energy gap between them, the 4f^{*n*} and 4f^{*n*-1}5d¹ level energies of Eu²⁺ as well as other R^{2+/3+} ions – remain largely unknown preventing a systematic tailoring of the defect chemistry of these materials.

The goal of this work was to clarify the mechanism of the persistent luminescence in BaAl₂O₄:Eu²⁺ by employing a systematic approach combining the *ab initio* density functional theory (DFT) calculations with experimental synchrotron radiation (SR) spectroscopy. The BaAl₂O₄:Eu²⁺(Dy³⁺) materials were prepared with a combustion reaction. The modifications in the host crystal structure due to the introduction of Eu²⁺ were explored using DFT. The structure of the valence and conduction bands as well as the band gap energy of the non-doped and Eu²⁺ doped BaAl₂O₄ was studied. The 4f^{*n*} and 4f^{*n*-1}5d¹ ground level energies of Eu²⁺ in the host band structure were determined, too. Eventually, the excitation and emission were studied using the SR UV-VUV spectroscopy. The energy transfer and storage processes are discussed based on these theoretical and experimental results.

2. Materials and methods

2.1 Materials preparation

The $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}(\text{Dy}^{3+})$ materials were prepared employing the combustion synthesis. Metal nitrates ($\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$ and $\text{Dy}(\text{NO}_3)_3$) and urea were used as reactants and fuel, respectively. The hydrated europium and dysprosium nitrates were obtained from the respective oxides with a reaction with concentrated nitric acid. The precursors were suspended into the smallest possible amount of distilled water. A silica capsule filled with the homogeneous solution was inserted into a furnace pre-heated to 500 °C. The reaction began *ca.* 5 minutes afterwards when the mixture was self-ignited with a white flame producing a white powder. In this chemical reaction, H_2O , NH_3 , CO_2 , O_2 and N_2 gases are released though the reactions are complex and not known in detail. After the completion of the reaction, the furnace was turned off and was let to cool freely. The products were removed from the furnace when the temperature had lowered to *ca.* 25 °C. The nominal concentrations of Eu^{2+} and Dy^{3+} (of the Ba^{2+} amount) were 1.0 and 2.0 mole-%, respectively. The formation of Eu^{2+} using Eu^{3+} as a source without the use of reductive atmosphere has been explained by the evaporation of interstitial oxygen at high temperatures [9].

2.2 Synchrotron radiation UV–VUV spectroscopy

The SR excitation and emission spectra of the $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}(\text{Dy}^{3+})$ materials were measured between 80 and 330 as well as 360 and 640 nm, respectively, by using the UV–VUV synchrotron radiation beamline SUPERLUMI of HASYLAB at DESY (Hamburg, Germany) [10]. The samples were mounted on the cold finger of a liquid He flow cryostat and the spectra were recorded at selected temperatures between 20 and 298 K. The setup consisted of a 2-m McPherson type primary monochromator with a resolution up to 0.02 nm (excitation) and an ARC SpectraPro-308i monochromator equipped with a Hamamatsu R6358P photomultiplier and a SSL CCD detector (emission). The UV–VUV excitation spectra were corrected for the variation in the incident flux of the excitation beam using the excitation spectrum of sodium salicylate as a standard.

2.3 Calculation method

The electronic structures of the non-doped and Eu^{2+} doped BaAl_2O_4 materials were calculated employing the density functional theory with the WIEN2k package [11]. WIEN2k is based on the full potential linearized augmented plane wave method (LAPW), an approach which is among the most precise and reliable ways to calculate the electronic structure of solids. The semi-local spin density generalized gradient approximation (GGA) method was applied to the non-doped material. In order to describe better the strongly correlated 4f electrons of the Eu^{2+} doped BaAl_2O_4 , the GGA+*U* method (“Fully Localized Limit” version) [12] was used without the spin-orbit coupling.

The GGA+*U* method requires as the input the Coulomb repulsion strength (Hubbard parameter *U*) and the exchange parameter *J* (magnetic coupling constant), which are related to the Slater integrals [13]. *U* increases with the increasing nuclear charge and oxidation state, whereas *J* is almost independent of the number of nd (nf) electrons. The *U* and *J* values 7.62 and 0.68 eV, respectively, have been found to reproduce the experimentally observed splitting between the majority and minority spin states of the Gd^{3+} ion [14]. Since both Gd^{3+} and Eu^{2+} have the rather similar 4f⁷ electron configuration, the dependence of the Eu^{2+} doped system on the Hubbard parameter was calculated using selected values between 4.35 and 7.62 eV, while the exchange parameter was fixed at 0.68 eV.

Every eighth of the Ba^{2+} ions (either at the Ba1 or Ba2 site) in the normal unit cell of BaAl_2O_4 (Z: 8 [15], 56 atoms) was replaced with Eu^{2+} corresponding to the defect concentration of 12.5 %. A detailed description of the BaAl_2O_4 structure is given in section 3.1.1. The local defect concentration is high due to the use of a single unit cell in the DFT calculations. However, even with the used concentration, the shortest Eu–Eu distance is 8.8 Å (the shortest M–M distance in the lattice is 4.4 Å) and the Eu^{2+} ion can be considered isolated.

The local changes in the electronic structure induced by Eu^{2+} may thus be probed. Larger lattices with lower concentrations need to be studied further, however, this requires a very high computational effort. The reliable calculation of the electronic structure requires the optimization of the crystal structure including the Eu^{2+} ion. This was achieved by relaxing the positions of all atoms in the unit cell, while the lattice parameters were not changed. The equilibrium position of each atom was calculated using the GGA method.

In the DFT calculations, the single particle Kohn-Sham equations can be solved on a grid of sampling points (k -points) in the symmetry irreducible wedge of the Brillouin zone [16]. The number of the k -points in the irreducible part of the Brillouin zone of BaAl_2O_4 was 4. The number of basis functions used was *ca.* 4000 and 6000 for the non-doped and Eu^{2+} containing normal cell of BaAl_2O_4 , respectively.

3. Results and discussion

3.1 Structure optimization

3.1.1 Crystal structure

The BaAl_2O_4 materials studied possess the hexagonal structure (space group: $P6_3$, no. 173, Z: 8, a: 10.470, c: 8.819 Å [15]). The structure consists of Ba^{2+} ions situated within channels formed by six interconnected AlO_4 tetrahedra (Fig. 1) with two Ba, four Al and six O sites. The Eu^{2+} ion is expected to substitute for Ba^{2+} in both nine coordinated sites (Ba1 (2a) and Ba2 (6c), with C_3 and C_1 site symmetries, respectively) since the Ba-O distances (average: 2.894 and 2.971 Å for Ba1 and Ba2, respectively) are rather similar. However, the Eu^{2+} ion probably prefers the 0.077 Å smaller Ba1 site because of being statistically 12 % smaller than Ba^{2+} . Structural distortions can also be expected due to the size difference between Eu^{2+} (CN: 9, 1.30 Å) and Ba^{2+} (1.47 Å) [8]. An off-centre position for Eu^{2+} can also be possible. To simplify things, Eu^{2+} does not fit at all into the four coordinated Al^{3+} site (0.39 Å) which is much too small also for Eu^{3+} (CN: 9, 1.12; CN: 6, 0.95 Å; Al^{3+} with CN 6: 0.54 Å).

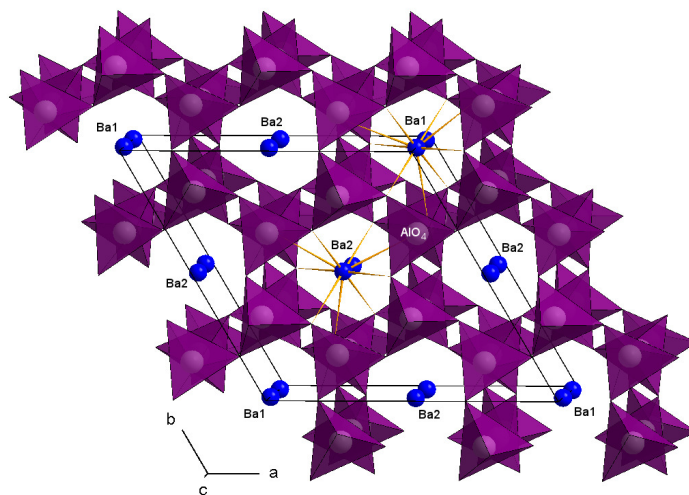


Fig. 1. The hexagonal structure (space group $P6_3$) of BaAl_2O_4 consisting of Ba^{2+} ions situated within channels of AlO_4 tetrahedra.

The stoichiometric BaAl_2O_4 system is known to show complex polymorphism as a function of temperature [17,18], though the X-ray powder diffraction [9] confirmed that the materials studied were of the hexagonal form. In addition to the desired form, a small amount of $\text{BaAl}_{12}\text{O}_{19}$ not exceeding 5 % of the total material was observed as an impurity phase.

3.1.2 Structural modifications due to Eu^{2+} doping

The distortions due to the introduction of europium in BaAl_2O_4 were probed by structure optimization using DFT. The Eu^{2+} ion at the Ba1 site shifts towards the nearest Ba^{2+} ion (Ba1b in Table 1) along the unit cell c axis in the channel formed by the interconnected AlO_4 tetrahedra. This corresponds to a shift (x: 0.010, y: 0.010, z: 0.162 Å) to an off-centre position when compared to the barycentre of the nearest O^{2-} ions (optimized positions). The Ba^{2+} ion also shifts slightly towards the Eu^{2+} ion along this channel (Table 1). As a result of these modifications, the Eu-Ba1 distance decreases by 0.154 Å (from 4.410 to 4.256 Å) due to the structure optimization. Movement of Eu^{2+} and Ba^{2+} within this channel can be expected since empty space exists in the structure in this direction.

Table 1. Atomic Positions in the Original and Optimized Crystal Structure of BaAl_2O_4 with Eu^{2+} at Ba1 or Ba2 Site (Space Group in Calculation: P1, no. 1)

Atom	Original structure			Optimized			Total shift / Å
	x	y	z	x	y	z	
Eu at Ba1a	0.0000	0.0000	0.0000	0.0011	0.0013	0.0157	0.139
Ba1b	0.0000	0.0000	0.5000	0.9994	0.9991	0.4983	0.017
Ba2a	0.5041	0.0020	0.5091	0.5094	0.0110	0.5095	0.082
Ba2b	0.9980	0.5021	0.5091	0.9898	0.4976	0.5097	0.075
Ba2c	0.4979	0.4959	0.5091	0.5028	0.4914	0.5100	0.086
Ba2d	0.4959	0.9980	0.0091	0.4929	0.9899	0.0066	0.078
Ba2e	0.0020	0.4979	0.0091	0.0094	0.5042	0.0070	0.075
Ba2f	0.5021	0.5041	0.0091	0.4953	0.5060	0.0069	0.085
Ba1a	0.0000	0.0000	0.0000	0.9995	0.0007	0.9971	0.035
Ba1b	0.0000	0.0000	0.5000	0.9991	0.9993	0.4962	0.028
Eu at Ba2a	0.5041	0.0020	0.5091	0.5130	0.0176	0.5046	0.147
Ba2b	0.9980	0.5021	0.5091	0.9877	0.4966	0.5078	0.094
Ba2c	0.4979	0.4959	0.5091	0.5023	0.4923	0.5081	0.073
Ba2d	0.4959	0.9980	0.0091	0.4888	0.9908	0.0078	0.076
Ba2e	0.0020	0.4979	0.0091	0.0106	0.5031	0.0052	0.086
Ba2f	0.5021	0.5041	0.0091	0.4989	0.5083	0.0076	0.069

The environment of Eu^{2+} and Ba^{2+} was probed using the Eu-O and Ba-O distances which are equal in the non-optimized structure. Due to the structure optimization of Eu^{2+} at the Ba1 site, the shortest Eu-O distances (below 3.1 Å) were decreased (Table 2), whereas the longer ones increased relative to the original values [15]. The Eu-O1 distance changed the most significantly whereas the Eu-O5 distances remained almost unchanged. The direction of these modifications is in agreement with the shift of Eu^{2+} along the unit cell c axis (Fig. 2). Such a modification in the local structure of Eu^{2+} is possible since the M-O bonds are less rigid than the Al-O bonds in the interconnected AlO_4 tetrahedra preventing significant shifts in the Al^{3+} and O^{2-} positions. However, even larger modifications might be expected because of the difference of 0.17 Å in the statistical ionic radii of Eu^{2+} and Ba^{2+} [8]. This is an indication of some rigidity of the structure. Only slight modifications near Ba^{2+} were found at the Ba1 site and the average Ba1-O distance did not change (Table 2).

A slightly more significant shift for the Eu^{2+} ion was found when it was introduced in the larger Ba2 site (Table 2). This corresponds to a shift (x: 0.073, y: 0.176, z: 0.023 Å) to an off-centre position. In this site, Eu^{2+} moves mostly in the ab plane of the unit cell instead of the channel along its c axis. The distances to the nearest Ba^{2+} ions (Ba2) in this plane are thus decreased: Eu-Ba2b and Eu-Ba2c by 0.211 and 0.177 Å, respectively. Empty space between the AlO_4 tetrahedra exists also in the ab plane and the movement of Eu^{2+} is significantly different in the two Ba sites.

Table 2. Distances Between Ba²⁺ (Eu²⁺) and the Nearest O²⁻ Ions in the Original and Optimized Structure of BaAl₂O₄:Eu²⁺

Ba-O distance / Å		Difference ^a / Å		Eu-O distance / Å		Difference ^a / Å	
Original		Optimized					
Ba1-O1 (3x)	2.748	Ba1a-O1a	2.701	-0.047	Eu-O1a ^b	2.569	-0.178
		-O1b	2.723	-0.024			
		-O1c	2.730	-0.018			
-O5 (3x)	2.919	-O5a	2.917	-0.001	-O5a	2.835	-0.084
		-O5b	2.940	0.022			
		-O5c	2.950	0.031			
-O1' (3x)	3.017	-O1a'	3.006	-0.011	-O1a'	3.119	0.101
		-O1b'	3.030	0.013			
		-O1c'	3.066	0.048			
Average	2.894		2.896	0.024 ^c		2.869	0.122 ^c
Ba2-O2	2.622	Ba2b-O2	2.670	0.048	Eu-O2 ^b	2.553	-0.069
-O5	2.761	-O5	2.691	-0.070	-O5	2.557	-0.205
-O3	2.796	-O3	2.835	0.038	-O3	2.792	-0.004
-O4	2.826	-O4	2.798	-0.028	-O4	2.688	-0.138
-O3'	2.973	-O3'	2.990	0.017	-O3'	2.942	-0.032
-O4'	3.003	-O4'	3.029	0.026	-O4'	3.014	0.011
-O6	3.007	-O6	2.968	-0.040	-O6	2.776	-0.231
-O2'	3.283	-O2'	3.248	-0.035	-O2'	3.344	0.061
-O5'	3.466	-O5'	3.691	0.225	-O5'	3.682	0.216
Average	2.971		2.991	0.059 ^c		2.927	0.107 ^c

^a Difference to the distance in the original (non-optimized) structure.

^b One of the eight Ba²⁺ in the unit cell is replaced with Eu²⁺.

^c Average of the absolute difference values.

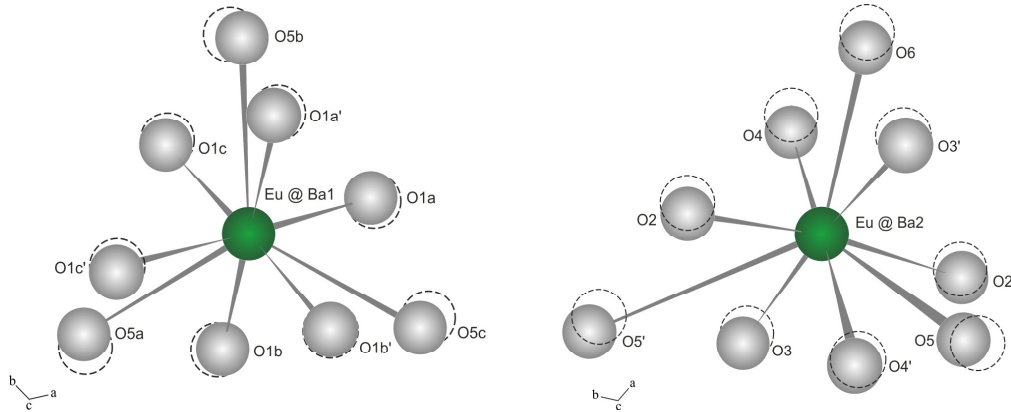


Fig. 2. Environment of Eu²⁺ at the Ba1 (left) and Ba2 (right) site of the structure optimized BaAl₂O₄:Eu²⁺. The non-optimized ion positions are marked with dashed spheres.

The shortest Eu-O distances (below 3.1 Å) were decreased and the longer Eu-O distances were mostly increased at the Ba2 site (Table 2). The Eu-O5 distances changed the most significantly. The average Eu-O distance was decreased by 0.043 Å relative to the original value. A nearly two-fold decrease in this distance for the Ba2 site when compared to Ba1 (0.026 Å) was thus found. However, the average of the absolute changes in the Eu-O distances describes the modification of the local environment of Eu²⁺ better though this value was almost the same for both sites (Eu²⁺ at Ba1 and Ba2: 0.122 and 0.107 Å, respectively). More significant modification was found near the Ba²⁺ ion at the Ba2 than Ba1 site with structure optimization (Table 2).

For the Eu^{2+} ion at the Ba1 and Ba2 sites, two types of ion movement – changes in both the O-Eu-O angles and the Eu-O distances – results from optimization (Fig. 2). The differences between the non-optimized and optimized crystal structure are relatively small and more significant changes might have been expected due to the size mismatch of Eu^{2+} and Ba^{2+} . Since the tabulated ionic radii are statistical, the actual inter-atomic distances may differ in the individual materials, however.

The difference in the total energies (39 eV lower for Eu^{2+} at the Ba1 site) calculated by DFT suggests that Eu^{2+} prefers the Ba1 site which may result in only one emission band, at least at low (*e.g.* 1 mole-%) doping levels. As a result of the structure optimization, the distortion of the environment of Eu^{2+} at the Ba1 site lowers the site symmetry from C_3 to C_1 . This can be considered unlikely since a luminescent centre has been found more frequently than not to possess the same site symmetry as the host cation as easily indicated by the sharp line emission of the R^{3+} ions. The site symmetry of the luminescent centre needs to be probed in more detail *e.g.* by studying the Sm^{2+} luminescence. This ion exhibits easily identified line emission to be used as a luminescence probe due to the quite similar $4f^6$ electron configuration with Eu^{3+} . The interatomic distances, off-centre position of Eu^{2+} as well as the nature of the neighboring atoms should be studied employing the extended X-ray absorption fine structure (EXAFS) method.

Significant structural modifications are expected with high Eu^{2+} concentrations since EuAl_2O_4 possesses the same monoclinic structure as SrAl_2O_4 (space group: $P2_1$, no. 4 [19,20]), whereas BaAl_2O_4 is hexagonal. Two seven coordinated Eu sites (Eu1 and Eu2, C_1 site symmetry for both) exist in EuAl_2O_4 with shorter Eu-O distances (average: 2.69 and 2.67 Å for Eu1 and Eu2, respectively) than in BaAl_2O_4 (Table 2). These sites may, however, also be considered nine coordinated with an average Eu-O distance of 2.88 and 2.84 Å, respectively, which suggests less significant modifications. Preliminary EXAFS data indicates that the shortest Eu-O distance in EuAl_2O_4 is *ca.* 2.35 Å [21] which is clearly shorter than the M-O distances in BaAl_2O_4 (Table 2). However, the DFT results suggest that only minor modifications in the local structure are induced by the isolated Eu^{2+} ions.

3.2 Electronic structure

3.2.1 Host band structure

The band gap energy (E_g) provides the basic data for the determination of the electronic structure. The DFT calculations did not provide an absolute measure for E_g due to the presence of scattered non-zero density of states (DOS) 4-5 eV above the top of VB (Fig. 3). This may indicate the presence of intrinsic shallow electron traps which exist even without the introduction of any defects in this material. A significant increase in the DOS appears at 5.3 eV which may be used as a more reliable measure for E_g than the scattered DOS at lower energy. Slightly better agreement between the experimental and calculated (5.7 eV) E_g values was found with the optimized crystal structure. Only fair agreement between the experimental (6.5 eV) and calculated values was thus found probably due to the covalent character in BaAl_2O_4 . The experimental value corresponds to the optical band gap in the synchrotron radiation excitation spectrum of $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}$ (Fig. 3). However, the difference of 1.2 eV is in agreement with the discrepancy of more than 1 eV generally found using DFT [22]. The valence band of BaAl_2O_4 has mainly the O 2p character (Fig. 3) whilst the conduction band consists mostly of the Ba (5.3 to 13 eV) and Al (13+ eV) levels.

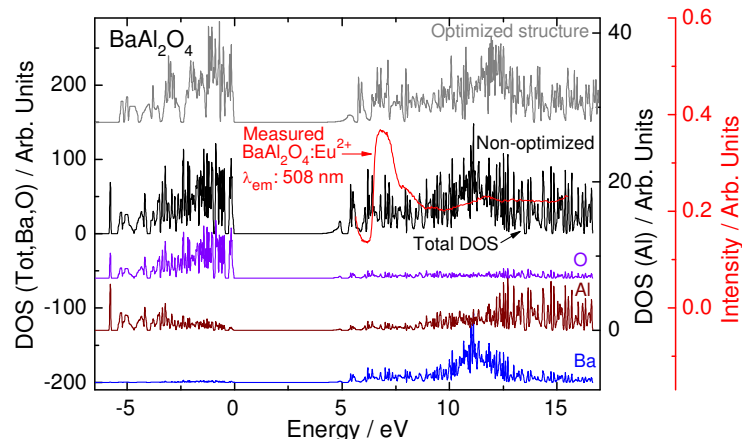


Fig. 3. Calculated (GGA method) density of states and the SR UV-VUV excitation spectrum (at 50 K, λ_{em} : 508 nm) of the non-doped and Eu^{2+} doped BaAl_2O_4 , respectively (modified from [9]).

3.2.2 Eu^{2+} doped material

The structure of the valence and conduction bands as well as the E_g value did not change from the non-doped to the Eu^{2+} doped BaAl_2O_4 . In addition, E_g did not change if Eu^{2+} was introduced either at the Ba1 or Ba2 site in BaAl_2O_4 . A local maximum of DOS is found at *ca.* 5 eV above the top of VB also with Eu^{2+} doping (*cf.* previous section) which may correspond to a shallow electron trap. The relatively minor structural distortions caused by the Eu^{2+} doping (see section 3.1.2) are expected to create traps which have only low energy (*i.e.* shallow traps).

The knowledge of the $\text{Eu}^{2+} 4f^7 {}^8S_{7/2}$ ground level energy is essential for the persistent luminescence processes since it is involved in both the $4f^7 \rightarrow 4f^6 5d^1$ photoexcitation and $4f^6 5d^1 \rightarrow 4f^7$ photoemission of Eu^{2+} . This energy can be experimentally determined when the Eu^{3+} charge transfer (CT) energy – which is approximately the same as the energy difference between the top of VB and the $4f^7$ ground level of the Eu^{2+} ion [23] – is known. A CT energy of 4.1 eV has been observed for the $\text{BaAl}_2\text{O}_4:\text{Eu}^{3+}$ material [24] locating the level in the energy gap. However, there always remains an uncertainty of *ca.* 0.5 eV due to the broad band nature of the CT absorption.

The calculated $\text{Eu}^{2+} 4f^7$ ground level is located in the energy gap of BaAl_2O_4 irrespective of the value of the Hubbard parameter U (Fig. 4). The dependence of the $4f^7$ ground level energy on U is linear for Eu^{2+} at both the Ba1 and Ba2 site, with this level located close to the valence band for the high U values. The calculated energy difference between the top of VB and the $4f^7$ ground level of Eu^{2+} is 1.5–2.8 eV for both Ba sites. The $4f^7$ ground level energies thus are underestimated by *ca.* 2 eV when compared to the experimental CT values and an agreement could be found by decreasing the U value to 1.0 eV. A decrease in the Hubbard parameter from the value obtained for Gd^{3+} (7.62 eV, *cf.* section 2.3) can be expected for Eu^{2+} due to its lower nuclear charge and oxidation state. In addition, Eu^{2+} replaces the larger Ba^{2+} ion in BaAl_2O_4 with significant covalent bonding character which is expected to decrease the electron repulsion and thus also the Hubbard parameter. However, a U value of 1.0 eV may be considered unrealistically low. The experimental CT energy may also overestimate the $4f^7$ position due to its relaxation after the CT absorption.

Important theoretical evidence on the $\text{Eu}^{2+} 4f^6 5d^1$ ground level energy can be obtained using the DFT calculations. The 2D level should be split into five components by the crystal field of low symmetry (C_3 or C_1 in BaAl_2O_4) [25]. The total energy span of the $4f^6 5d^1$ levels may be close to 25 000 cm^{-1} (3.1 eV) in oxides as in BaAl_2O_4 . Therefore, at least some of these levels are located within CB.

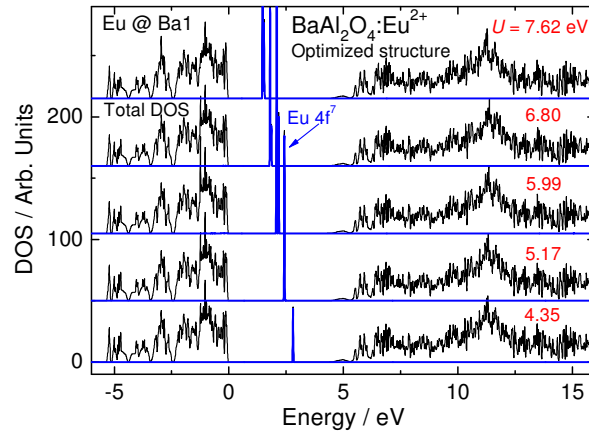


Fig. 4. Dependence of the calculated (GGA+ U method, U : 4.35-7.62 eV) density of states of the non-optimized $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ (Eu^{2+} at the Ba1 site) on the Coulomb repulsion strength.

The calculated states within and close to the bottom of CB of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ possess significant Eu^{2+} 5d character which was used to estimate the $4f^65d^1$ energies (Fig. 5, inset). The lowest state with distinct Eu^{2+} 5d character is located at 0.8 (Eu^{2+} at Ba1) or 0.7 eV (Ba2) below CB. The $4f^65d^1$ ground level energy can be considered independent of the Hubbard parameter U since an upward shift of only 0.01 eV in the 5d energy was found for Eu^{2+} at the Ba1 site when U was increased from 4.35 to 7.62 eV. No shift was found for Eu^{2+} at the Ba2 site. These results provide theoretical verification for the empirical model of persistent luminescence [24] since they confirm that the $4f^65d^1$ levels are located mainly in CB and the excited electron can reach CB easily from these levels for subsequent trapping to charge the persistent luminescence.

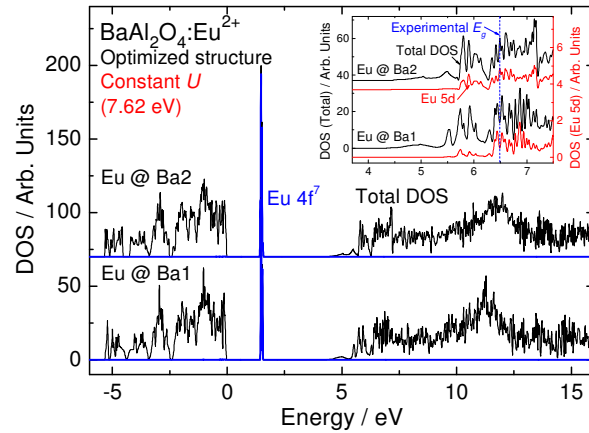


Fig. 5. Calculated (GGA+ U method, U : 7.62 eV) density of states of the optimized BaAl_2O_4 with Eu^{2+} at the Ba1 or Ba2 sites. Inset: Calculated density of the Eu^{2+} $4f^65d^1$ states.

The energy difference between the $4f^7$ and the $4f^65d^1$ ground levels can be approximately deduced from experiments when the energy of the luminescence band due to the $4f^65d^1(^2D) \rightarrow 4f^7(^8S_{7/2})$ transition of the Eu^{2+} ion is known. Such a luminescence band in the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ material is observed at 505 nm (2.46 eV, *cf.* section 3.3). The corresponding calculated $4f^65d^1-4f^7$ energy difference was 4.2 (U : 7.62 eV) for the Ba1 and 4.3 eV for Ba2 site after the optimization of the crystal structure (Fig. 5). These results suggest that the emission energy is almost the same irrespective of the Ba site occupied by Eu^{2+} . The energy difference is, however, overestimated by the too high Hubbard U value and its reliable

determination for Eu^{2+} would be necessary. An agreement between the calculated and experimental values could be found by using a quite low value of 3.0 eV for this parameter.

The calculated $4f^65d^1-4f^7$ energy difference should be considered only as an approximated value since the fixing of the 5d occupation was not feasible with the DFT calculations. In addition, the experimental value underestimates the energy difference due to the relaxation of $4f^7$ after the emission which, when taken into account, results in a better agreement. The exact amount of especially the 4f relaxation energy depends on the appropriate host lattice and cannot be calculated or obtained from the present experimental data but can be estimated to less than $5\,000\text{ cm}^{-1}$ (0.62 eV).

3.3 SR excited luminescence

The luminescence spectra of the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ materials excited to the conduction band by synchrotron radiation (λ_{exc} : 92 nm (13.5 eV)) at selected temperatures between 20 and 300 K are characterized by a strong green and a weak blue band centered at *ca.* 505 and 440 nm (2.46 and 2.82 eV), respectively (Fig. 6). An additional low energy emission band due to the $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions of Dy^{3+} was found centered at 580 nm (2.14 eV). Deconvolution of this emission is not feasible since even for only one Dy^{3+} site there may be up to 35 lines. Only the deconvoluted Eu^{2+} spectra have thus been included in Fig. 6. These two bands at higher energy may be due to the $4f^65d^1(^2D) \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} at both Ba sites. However, the energy difference of 0.36 eV between the bands is not directly indicated by the electronic structure since the same $4f^65d^1$ and $4f^7$ energies were found for these sites.

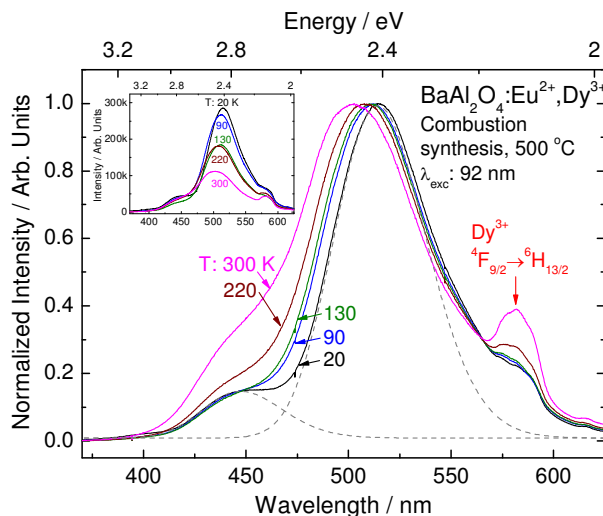


Fig. 6. The synchrotron radiation excited (λ_{exc} : 92 nm) emission spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ at selected temperatures between 20 and 300 K (SUPERLUMI, HASYLAB). Deconvoluted spectra at 20 K are indicated by dashed curves.

No band in blue was observed for $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ prepared with a high temperature solid state synthesis [9]. This band was found also with conventional UV excitation (λ_{exc} : 320 nm) which confirms that it is not uniquely related to the high energy excitation. These results indicate that the weak band may originate from the creation of a new Ba^{2+} site due to the effect of water exposure on this material. This effect is probably most pronounced on the surface of the material since the surface Ba/Eu sites are first attacked by humidity. The system is very complex and dynamic since the energy and intensity of the blue band depend on the time of exposure to humidity, too. The formation of new compounds has also been indicated by X-ray powder diffraction [9]. Further studies are required to study the exact effect of water exposure on the local environment of the luminescent centre.

A stronger temperature quenching was found for the Eu^{2+} bands than for Dy^{3+} (Fig. 6). Both Eu^{2+} luminescence bands were shifted by 0.05 eV to higher energy due to the effect of the crystal field when the temperature increased from 20 to 300 K (Fig. 7). The crystal field decreases due to the expansion of the lattice with increasing temperature. The crystal field splitting of the Eu^{2+} $4f^65d^1$ levels becomes thus less pronounced and the $4f^65d^1$ ground level shifts to higher energy with respect to the $4f^7$ ground level. This increases the band energy at high temperatures.

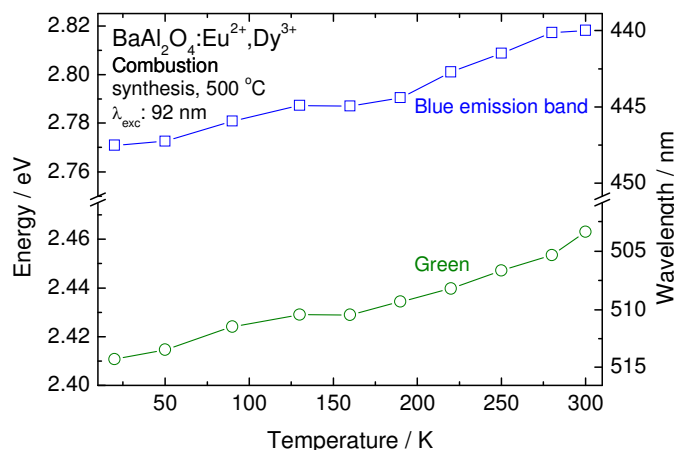


Fig. 7. Energy of the green and blue emission bands of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ at selected temperatures between 20 and 300 K obtained from the deconvoluted emission spectra (λ_{exc} : 92 nm, SUPERLUMI, HASYLAB).

3.4 Persistent luminescence mechanism

The Eu^{2+} $4f^7$ and $4f^65d^1$ ground level energies close to the conduction band confirm that the electrons act as the charge carriers responsible for persistent luminescence in the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{R}^{3+}$ materials. This process commences with the $4f^7 \rightarrow 4f^65d^1$ photoexcitation of Eu^{2+} which is induced by blue light or UV radiation (Fig. 8). The excited electron can escape directly to CB from a $4f^65d^1$ level located within CB. It can also escape from a $4f^65d^1$ level below CB with the aid of thermal energy ensuring a broad excitation of persistent luminescence. The Eu^{2+} ion becomes thus either an excited (Eu^{3+})* species or – more likely – an excited ($\text{Eu}^{2+}-h^+$)* pair. The electron moving quite freely in CB is then captured by traps close to the bottom of CB. The probable origin of the electron traps is *e.g.* the R^{3+} co-doping (ion), a vacancy or even defect aggregates [26]. The R^{3+} co-dopant may trap an electron from the conduction band thus creating the R^{2+} species or an $\text{R}^{3+}-e^-$ pair. In addition, efficient trapping of electrons by the oxygen vacancies is expected. The calculation of the vacancy energy levels is out of scope of the current study and this will be a subject of a further work. The temperature controlled gradual transfer of the trapped electrons back to CB is followed by their migration (or retrapping) to the luminescent centre through CB or by direct tunneling for the recombination and emission of visible light.

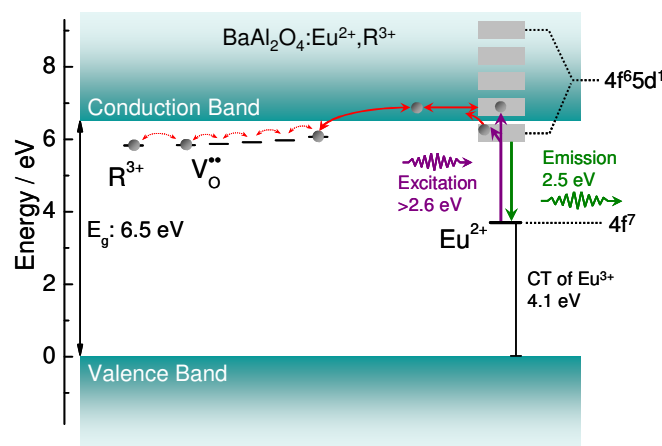


Fig. 8. Persistent luminescence mechanism of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$.

4. Conclusions

Modifications in the crystal structure due to the introduction of the Eu^{2+} luminescent centre were found using the DFT calculations. The changes in the interionic distances as well as differences in the total energies show that Eu^{2+} prefers the Ba1 site, though Ba2 is also possible. A reasonable agreement between the calculated and experimental band gap was obtained. The calculated $\text{Eu}^{2+} 4f^7$ ground level was located in the energy gap but its energy above the valence band was underestimated when compared to the experimental CT values. This is probably due to the less accurate description of BaAl_2O_4 with significant covalent character than of the more ionic hosts. Important theoretical evidence on the $\text{Eu}^{2+} 4f^65d^1$ level energies relative to the conduction band was obtained. The results confirm that the excited electrons can reach the conduction band easily from these levels followed by trapping in the persistent luminescence process. An additional blue emission band apart from the green luminescence of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ was observed using synchrotron radiation excitation. The former is probably due to the creation of a new Ba^{2+} site due to the effect of water exposure on the host.

The current approach combining DFT calculations and synchrotron radiation luminescence spectroscopy is an excellent tool to probe the crystal and electronic structure of the Eu^{2+} doped materials especially when the properties are difficult or impossible to study only experimentally. Trap levels induced by the isolated defects and defect aggregates present in the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$ materials should still be studied in detail since they are expected to have a crucial effect on the persistent luminescence efficiency of these materials.

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