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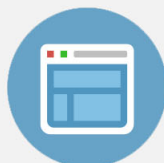
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The effect of the host composition on the lifetime decay properties of barium/strontium aluminates compounds

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This paper reports the influence of the structural change on the luminescence of Eu-doped barium/strontium aluminates when excited with monochromatic X-rays (also known as X-ray excited optical luminescence—XEOL). $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4$ samples, with $0 < x < 1$, were produced via proteic sol-gel route and it was observed that the XEOL emission spectra are composed by the Eu^{2+} and Eu^{3+} transitions, although no Eu^{2+} was observed in the X-ray absorption spectra. The XEOL intensities while the sample is under irradiation decreased as a function of the irradiation time, indicating the buildup of radiation damage. The saturation level of the XEOL is directly correlated to the amount of damages induced by the irradiation and the sample composition. The Ba-rich samples are the ones with higher XEOL yield. X-ray induced long lasting phosphorescence (LLP) was also observed for all samples and it was found that the duration of the phosphorescence emission also depends on the sample composition. In Sr-rich samples, the LLP has a slower decay time constant than in Ba-rich samples. A model of the radiation induced luminescence is presented and all these features are discussed in terms of the energetic costs and the type of defects generated in the sample. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4868470>]

I. INTRODUCTION

The main scientific and technological interest in the alkaline earth aluminates doped with Eu^{2+} and Dy^{3+} ($\text{MAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} ; $\text{M} = \text{Ca, Sr, Ba}$) is the long lasting phosphorescence (LLP) that in these compounds were found to have higher brightness and longer persistency than previous LLP materials like ZnS.^{1–3} In addition, all these aluminates have much better chemical stability^{1–3} allowing the use of them in wider range of devices, such as, luminous paint on highways, airports, buildings, and ceramic products, phosphorescence pigments on textiles, warning signs, escape routes, and instruments.^{4–8}

The phosphorescence of Eu^{2+} ions, in the alkaline earth aluminates, is due to the transition between the ground ($^8\text{S}_{7/2}(4f^7)$) and the excited ($4f^65d^1$) configurations.⁹ The emission is strongly dependent on the host lattice, i.e., are sensitive to the change of the crystal field and can occur from the ultraviolet to the red region of the electro-magnetic spectrum. This happens because the 5d excited states are strongly affected by local environment and the symmetry of crystalline field. The 4f electronic states of all lanthanide ions, however, are just slightly affected by the crystalline field due to the electronic shielding given by the 5s and 5p filled orbitals. Although the influence of the local environment in the 4f levels is not as strong as in the 5d, some Eu^{3+} emissions dependent on the host lattice like the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ one. The characteristic lifetime constant of the Eu^{2+} and Eu^{3+} emissions is also dependent on the host lattice.¹⁰

Alkaline earth aluminates showed a diversity of crystalline structures. SrAl_2O_4 , at room temperature, has a monoclinic

structure changing to the hexagonal phase above 650 °C.¹¹

BaAl_2O_4 has hexagonal structure but was found to be ferroelectric at room temperature. Above 123 °C, it has a phase transition to a higher symmetric hexagonal phase and become paraelectric.¹² Eu ions were found to substitute at the M^{2+} sites in all this structures and due to the different environments both emission peak positions and lifetime of the Eu^{2+} or Eu^{3+} ions are different.¹³ For example, in SrAl_2O_4 lattice Eu^{2+} ions show an intense emission peaking at 530 nm.¹⁴ This emission peak shifts to 500 nm in the BaAl_2O_4 lattice.¹⁵

Long afterglow in correlated systems has been associated to the probability of charge transfer between the conduction band and the defect center, including also the emitting Eu^{2+} center.¹⁶ The probability is dependent on the concentration of defects already present in the material and also on the radiation-induced defects. Some experimental works have reported the effect of the host composition on the afterglow and phosphorescence decay properties of strontium-barium aluminates co-activated with Eu and Dy, when the concentration ratio between barium and strontium were changed.^{17,18}

In this paper, we report the systematic investigation of optical properties of a series of $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4$ materials with the Sr molar fraction x varying from 0 up to 100%. The main aim is to study the effect of changing the crystal field interaction with the luminescent Eu^{3+} ion on the luminescence of these systems. The X-ray Excited Optical Luminescence (XEOL) decay time was measured using synchrotron radiation. The excitations were given by monochromatic X-rays tuned at the Eu L_{III} -edge. The XEOL emission spectra were also measured for all range of Sr substitution, and long lifetime of the luminescence was carried out to correlate the substitution effect.

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II. EXPERIMENTAL

The proteic sol-gel route¹⁹ was used to produce a series of nanopowder samples with composition $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4:\text{Eu}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$). This synthesis route uses coconut water (*Cocos nucifera*) as the starting solvent for the metal salts. The organic compounds usually found in the coconut water are responsible for the anchoring of the metallic ions during the sol step and also lead to a natural formation of the gel. The samples were prepared by mixtures of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ to coconut water in the desired proportion according to the stoichiometric balance. The mixtures were dried at 100°C for 24 h, forming xerogels. The xerogels were calcined at 1100°C for 2 h in open air atmosphere. This methodology was applied successfully previously to produce pure and doped SrAl_2O_4 (Ref. 20) and BaAl_2O_4 .²¹

Powder X-ray diffraction (XRD) measurements were carried out in a Rigaku 2000/PC in order to determine the crystalline phases present in the samples. The measurements were done at room temperature using $\text{CuK}\alpha_{1,2}$ radiation, in step scan mode, from 10 to 80° in 2θ , with steps of 0.02° . The X-ray tube operating conditions were 40 kV and 4 mA and the detection system is equipped with a pyrolytic graphite monochromator. The XRD data reduction was done comparing the experimental powder pattern to the available structural information in the literature, using Rietveld refinement method embodied in the ReX code.²²

XEOL experiments were performed in the Brazilian Synchrotron Light Laboratory—LNLS source in Campinas, São Paulo, Brazil, around the Eu L_{III} -edges at the X-ray absorption fine structure (D08B-XAFS-2) beamline (proposal No. 13512/12/XAFS). The usual X-ray absorption measurements were done in fluorescence mode monitoring the area under the $L\alpha_1$ and $L\alpha_2$ (5849.5 and 5818.4 eV, respectively) X-ray fluorescence lines of the Eu dopants. The XEOL was measured simultaneously with the X-ray fluorescence using a Hamatsu R 928A PMT and an Ocean Optics HR2000 spectrometer. A bifurcated optical fibre collected the light generated during the XEOL measurements sending it to the PMT and the spectrometer. The incident beam intensity was monitored using an ionization chamber with appropriate gas mixture and pressure, and the number of counts for each incident photon energy was used to normalize the X-ray fluorescence signal, giving the absorption curve, the total XEOL yield, and XEOL emission spectra. The same experimental setup has been used successfully in other ternary oxides and fluorides compounds, such as $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$,²³ CdWO_4 ,²⁴ BaY_2F_8 ,^{25,26} giving quite interesting results. All measurements were performed at room temperature.

III. RESULTS

XRD results obtained for the $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4:\text{Eu}^{3+}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) samples are shown in Figure 1(a). The XRD patterns were compared to the monoclinic (space group $P2_1$) and hexagonal (space group $P6_322$) SrAl_2O_4 (Refs. 27 and 28) and hexagonal (space group $P6_3$) BaAl_2O_4 (Ref. 12) standard diffraction patterns. All diffraction peaks in Figure 1(a) for $x = 0$ up to $x = 0.6$ were visually

indexed to the BaAl_2O_4 structure, and no additional peaks belonging to other phases were observed. With the increase even further of the Sr content, some new peaks were observed in the XRD patterns that can be related to both monoclinic and hexagonal SrAl_2O_4 crystalline phases. XRD pattern for sample with $x = 1$ (Ba ions fully exchanged by Sr ions) showed some additional peaks, which are identified as cubic $\text{Sr}_3\text{Al}_2\text{O}_6$.²⁹ The formation of the $\text{Sr}_3\text{Al}_2\text{O}_6$ byproduct during the synthesis of SrAl_2O_4 has already been observed in previous work.³⁰ This byproduct contribute to the formation of strontium vacancies (V_{Sr}), and hence oxygen vacancies (V_{O}), needed for charge neutrality. Oxygen vacancies (V_{O}) were supposed to be the main electron traps, and strontium vacancies (V_{Sr}) were identified as hole traps in the phosphorescence mechanism originally proposed by Clabau *et al.*¹¹

Since other phases were formed as the Sr content increased, the diffractograms of all samples were quantitatively analyzed using Rietveld refinement method. An example of such procedure can be seen in Figure 1(b), and Table I summarizes all the results obtained after the refinement. It is

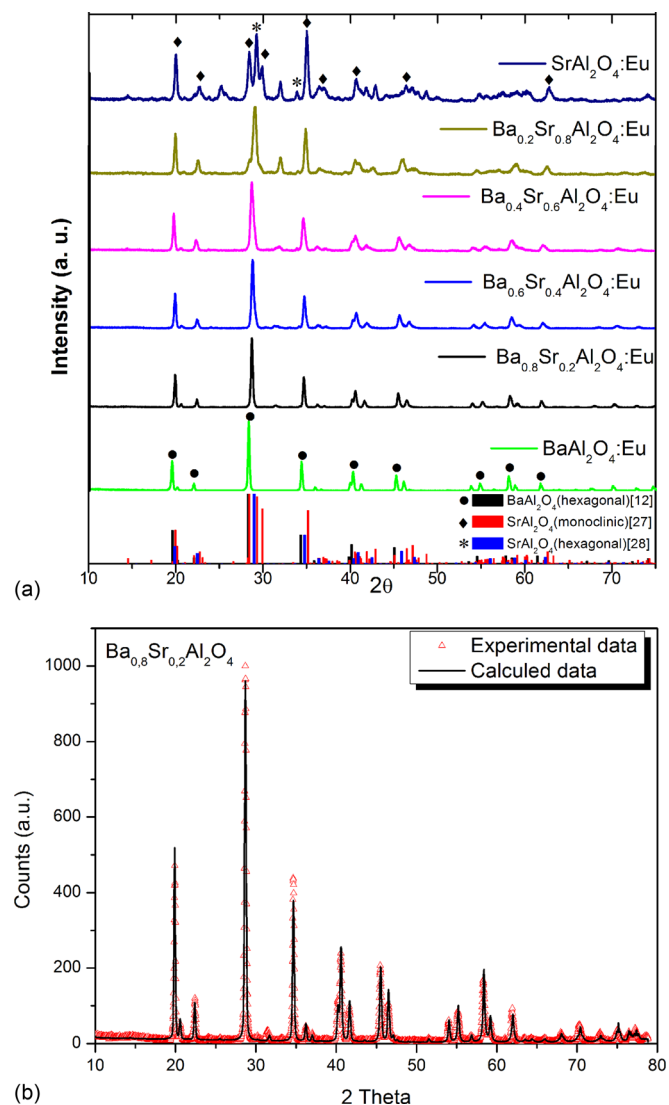


FIG. 1. (a) X-ray powder diffraction patterns of $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4:\text{Eu}^{3+}$, ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) samples. (b) Rietveld refinement result for sample with $x = 0.2$.

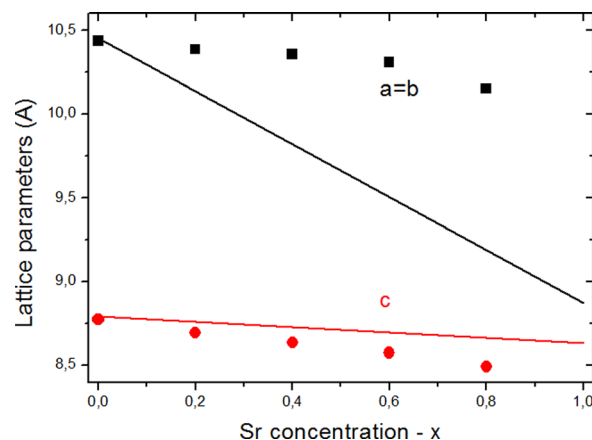
TABLE I. Phase concentrations and lattice parameters obtained via Rietveld refinement as a function of Sr/Ba substitution (x).

Phases	Composition ($\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4$)					
	x = 0	x = 0.2	x = 0.4	x = 0.6	x = 0.8	x = 1
BaAl_2O_4						
a (Å)	10.4343	10.3855	10.3552	10.3072	10.1511	...
b (Å)	10.4343	10.3855	10.3552	10.3072	10.1511	...
c (Å)	8.7720	8.6950	8.6351	8.5736	8.4932	...
Conc. (%)	100	99	98	98	48	...
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$						
a (Å)	...	24.8109	24.5121	24.4973	...	...
b (Å)	...	8.5139	8.5302	8.3012	...	...
c (Å)	...	4.7894	4.7826	4.6946	...	...
Conc. (%)	...	1	2	2	...	...
SrAl_2O_4 (Mono)						
a (Å)	...	...	...	...	8.6141	8.4409
b (Å)	...	...	...	...	8.9653	8.8428
c (Å)	...	...	...	...	5.1041	5.1543
Conc. (%)	...	...	...	...	52	79
SrAl_2O_4 (Hexa)						
a (Å)	...	...	...	...	...	8.8734
b (Å)	...	...	...	...	...	8.8734
c (Å)	...	...	...	...	...	8.6325
Conc. (%)	...	...	...	...	...	17
$\text{Sr}_3\text{Al}_2\text{O}_6$						
a (Å)	...	...	...	...	...	15.8199
b (Å)	...	...	...	...	...	15.8199
c (Å)	...	...	...	...	...	15.8199
Conc. (%)	...	...	...	...	...	4

possible to see that except from sample with $x = 0$ all other samples have extra crystalline phases, although the amount of these extra phase are very small for sample with $x = 0.2$ (1%), $x = 0.4$ (2%), and $x = 0.6$ (2%). In all these three samples, the additional phase formed is the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ one, a phase rich in Al and O, that was responsible for the segregation of part of the Sr added to the samples. Since the amount of Ba^{2+} and Sr^{2+} starting reactants were added to keep the stoichiometry of the system, i.e., 1:2:4 for [M], [Al], and [O], respectively, the appearance of this additional phase is an indication that the amount of cationic and anionic vacancies were increased.

It is also interesting to notice that only for x as high as 0.8, the SrAl_2O_4 is being formed. Sample with $x = 0.8$ has 52% of the monoclinic SrAl_2O_4 phase and 48% of BaAl_2O_4 phase, a proportion that did not correspond to the total amount of Sr added to the mixture. This means that some of the Sr ions are still dissolved inside the hexagonal BaAl_2O_4 matrix. As expected, the sample with $x = 1.0$ has only the Sr aluminates, as both hexagonal and monoclinic phases, and a small amount of the $\text{Sr}_3\text{Al}_2\text{O}_6$ phase.

The refined hexagonal lattice parameters (a and c) of $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4\cdot\text{Eu}^{3+}$ samples were plotted as a function of x (Sr concentration) in Fig. 2. It can be seen that the lattice although the lattice parameters decreased, they do not follow the Vegard's law³¹ represented by the continuous lines in the figure. One should not expect that the hexagonal lattice

FIG. 2. Evolution of the refined lattice parameters (a = b and c) of the hexagonal $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4\cdot\text{Eu}$ structures as a function of the Sr concentration, x . Solid lines indicate the predictions according to the Vegard's law.

parameters would follow the Vegard's law³¹ since the Ba and Sr aluminates are not isostructural at room temperature and that was clearly showed in the results of the Rietveld refinement. Nevertheless, the results indicate that Sr^{2+} is substituting for the Ba^{2+} ions and infinite solid solutions have been formed. The BaAl_2O_4 lattice contraction is due to the replacement of larger ion, Ba^{2+} with ionic radii of 1.47 Å,³² by the smaller one, Sr^{2+} , with ionic radii equal to 1.31 Å.³²

Figure 3(a) shows the XEOL spectra of all $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4$ samples with different composition ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) when excited with photon energy of 6985 eV, above the Eu L_{III} -edges. All spectra exhibit the same general feature with a broad emission band around 500–540 nm due to the $5d^{14}f^6 \rightarrow 4f^7$ electronic transition of Eu^{2+} , and a group of narrower peaks at about 595–620 nm due to the $^5D_0 \rightarrow ^7F_J$ of Eu^{3+} ions. Figure 3(b) shows the X-ray absorption spectra (XAS) of all samples close to the Eu L_{III} -edge, as compared to the absorption of the standard Eu_2O_3 compound, also measured in the same experimental setup. It is possible to see that in all samples the Eu absorption is typical of the trivalent species showing no sign of the divalent one. In previous works,³³ it was shown that, after choosing the right atmosphere during the calcination step, it is possible to stabilize Eu^{2+} ions inside the SrAl_2O_4 , although not all Eu ions were converted to the divalent state. In these works, the Eu valence was followed by monitoring the XAS absorption edge and the valence change from 3+ to 2+ was accompanied by absorption edge shift to lower energies.

Results presented in Figures 3(a) and 3(b) seem to be conflicting since, on one hand, they gave evidences of having both divalent and trivalent Eu ions during the XEOL emission but, on the other hand, no divalent species were seen during the absorption step. These results can only be reconciled if the Eu^{2+} ions were generated during the X-ray absorption step and they return back to the trivalent ionic charge state soon after the emission in the visible range.

The processes taking place can be schematically represented in Figure 4. The first step is the X-ray absorption that promoted electrons from the L_{III} shell of Eu^{3+} ions to the conduction band. As a consequence, holes were created in the core level inside the crystalline matrix and this core holes

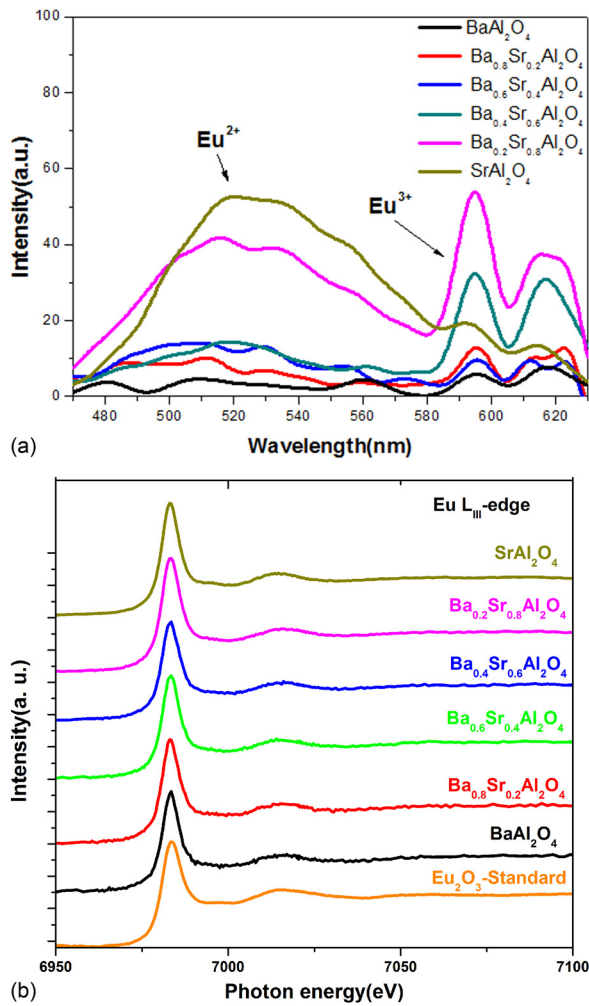


FIG. 3. (a) XEOL spectra of the $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4:\text{Eu}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) samples excited with 6985 eV X-ray photons, above the Eu L_{III} -edge. (b) XAS measured around the Eu L_{III} -edge for all samples as compared to the XAS curve of the Eu_2O_3 , where Eu ions are in trivalent charge state.

were moved up in the conduction band mainly by two dominant processes: (1) the X-ray fluorescence mechanism, that involves the decay of an upper core electron to the empty L_{III}

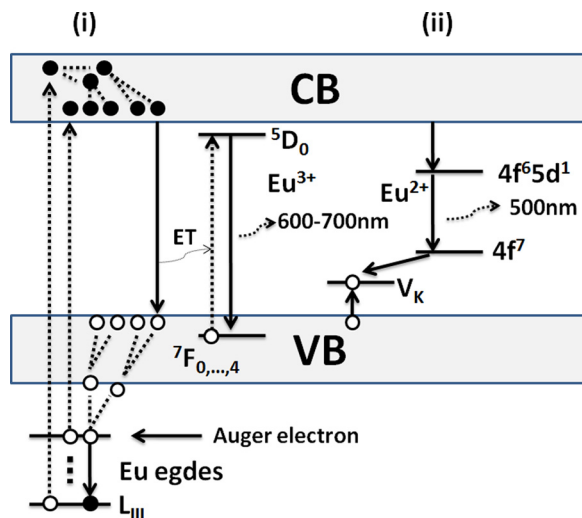


FIG. 4. Representation of the excitation and emission processes involved in XEOL spectra of Eu -doped $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4:\text{Eu}$.

level emitting the typical X-ray fluorescence lines or (2) Auger electrons, that involves the decay of a upper core electron to the empty L_{III} level and the energy is used to promote another electron from one of the filled core levels to the conduction band. These two processes can happen a few times until the holes get to the top of the valence band. The electrons that were promoted to the conduction band will lose their kinetic energy (if any) by non-elastic scattering with valence electrons or with the phonons of the lattice until they decay to the bottom of the conduction band. The Auger electrons and the scattered electrons also follow similar paths and these two extra processes will contribute to increase the number of free carriers (electrons and holes) in the lattice. At this point, the Eu^{3+} ions that lost an electron becoming Eu^{4+} that is very unstable and will capture a free electron returning back to Eu^{3+} but in an excited state. This excited Eu^{3+} will decay to the ground state emitting the typical Eu^{3+} spectra. But not all Eu^{3+} in the lattice absorbs the incident photons since the absorption process is a statistical phenomenon. The remaining Eu^{3+} can follow two possible routes: (1) they can be excited by the photon emitted due to the direct interband electron-hole recombination and then relax back to the ground state emitting the typical Eu^{3+} spectra or (2) they can trap a free electron from the conduction band forming the Eu^{2+} species in an excited state that will relax to the ground state emitting the characteristic broad band peaking around 500–540 nm.

The local environment of the original Eu^{3+} ions is not expected to be the same as the local symmetry of the Eu^{2+} ion. First of all, the Eu^{3+} ions were dissolved in the matrix substituting at the Ba or Sr site during the synthesis. Since this is an aliovalent substitution, it will produce charge compensating defects. That is not the case for the Eu^{2+} ions because they were produced due to the irradiation in a crystalline environment that was suitable for the Eu^{3+} ions. Previous computer modelling results^{34,35} revealed that the main charge compensating defect in this matrix is given by oxygen interstitial ions, O_i'' , in Kroger-Vink notation,³⁶ located nearby the Eu^{3+} . Since oxygen interstitial ions, O_i'' , have an effective charge of -2 , each O_i'' compensates for two Eu^{3+} substituting at the Ba or Sr site. So, the process that takes place in the material that reduces part of the Eu^{3+} to Eu^{2+} under X-ray irradiation must also neutralise the O_i'' accompanying defects. One possibility is that the holes produced in the valence band after the absorption of the X-rays generate V_k -type centres, i.e., O_2^{3-} molecule formed by a regular O^{2-} lattice anion and the O_i'' trapping a hole.

When the Eu^{2+} decays to the ground state, the “extra” electron can recombine with the hole trapped in the V_k centre via tunnelling process. This will bring the Eu back to its trivalent state and, at the same time, reform the O_i'' and the original configuration of the matrix is recovered. The electron (or hole) tunnelling process is only possible because the O_i'' were found to be located very close to the Eu ions.^{34,35} All these steps are expected to be quite fast and almost no Eu^{2+} is available to absorb the incident X-ray photons. That is the reason why in the XAS spectra no indication of the presence of Eu^{2+} is seen and, as a consequence, no edge shift is observed.

The intense XEOL emission band due to the Eu^{2+} observed in Figure 3(a) around 500–540 nm is consistent with

the band at 500 nm reported by Katsumata *et al.*,¹⁵ the 496 nm band reported by Lin *et al.*,³⁷ and the 505 nm band found by Palilla *et al.*³⁸ and Blasse *et al.*³⁹ in BaAl_2O_4 . Peng and Hong⁴⁰ also report two intense peaks around 500 nm in BaAl_2O_4 , the first one at 495 nm and the second one, at 530 nm. In the SrAl_2O_4 , an intense peak around 520 nm is found by Katsumata *et al.*⁴¹ and Aitasalo *et al.*⁴² Kamiyanagi *et al.*⁴³ reported one intense peak around 530 nm and Lü *et al.*¹⁴ observed a peak around 506 nm in the same system.

Results on Figure 3(a) also showed that, for Ba-rich samples, the emission due to the Eu^{3+} ions is higher than the emission related to Eu^{2+} ions. For the Sr-rich samples, the opposite trend is observed. These results can be explained based on the difference on the host matrix structure. The changes in the structure could affect the local environment around of the Eu^{2+} and Eu^{3+} ions and, therefore, can influence both the wavelength shift and intensity of emission. The changes in the relativity intensity of both activator ions (Eu^{3+} and Eu^{2+}) also can be related to the relative amount of both activator species. During irradiation, the amount of Eu^{2+} that is generated can be different for each host structure and this can be due to the different energetic cost involved in the reduction process of the Eu^{3+} to Eu^{2+} . In the energetic cost, it should be also included the energy needed to create the compensation defect associated to the Eu^{3+} incorporation in the matrix. In previous works,^{34,35} computer modelling results revealed that Eu^{3+} the energy cost involved in the incorporation of the Eu^{3+} ions in BaAl_2O_4 matrix is 2.01 eV and the incorporation of the Eu^{3+} ions in SrAl_2O_4 is 1.01 eV. In both systems, the main defect is formed by two Eu^{3+} at the M^{2+} site compensated by one O^{1-} . Since the energetic cost to form Eu^{3+} defect in the Sr-based lattice is lower than in the Ba-based matrix, the cost to partially destroy this defect upon $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction is also lower and this can explain why the Eu^{3+} emission would be higher in Ba rich samples than is Sr rich ones.

The fact that the Eu^{2+} emission is broad, between 470 and 580 nm, can be related to additional defects attributed to the presence of other crystalline phases, mainly in the $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4$ samples for $x = 0.8$ and 1 (Sr-rich ones). This extra phase, rich in Sr ions, contributes to former of strontium and oxygen vacancies. These additional intrinsic defects will cause extra distortions in the $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4$ matrix. When these vacancies are located close to Eu^{2+} or Eu^{3+} ions, the distortions will influence the crystal field at the Eu sites and this, in turn, will affect the XEOL emission.

The X-ray induced phosphorescence was followed using a three step procedure. First, all samples are exposed to the X-ray beam tuned in the energy of the Eu L_{III}-edge (6977 eV) during 160 s and, simultaneously, the XEOL light yield was measured. In the second stage, the X-ray shutter was turned off and the XEOL light yield was recorded for 640 s, enough time to observe that the phosphorescence practically vanished. In the third stage, the sample is again exposed to the X-ray beam with the same photon energy used in the first step for 450 s. This time interval was enough to observe saturation in the XEOL emission intensity due to radiation damage.

Fig. 5 shows the total XEOL light yield for all samples measured in the first step. It is important to streets that all

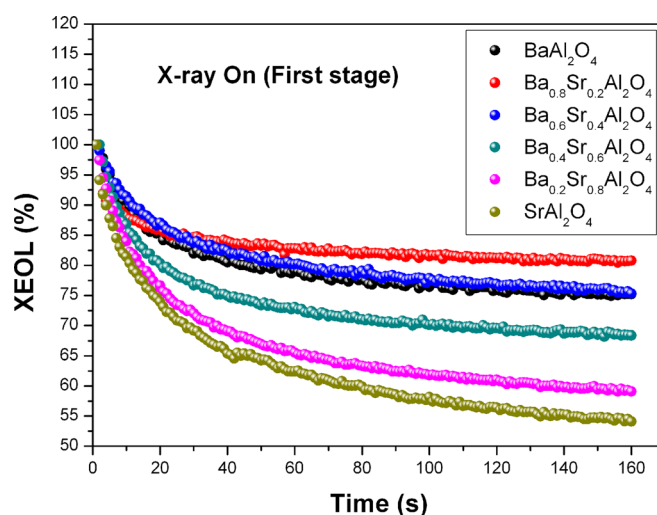


FIG. 5. Relative intensity of XEOL emission as a function of the time duration of the exposure to the X-ray photons of energy 6985 eV (first stage).

samples were not exposed to the X-ray beam beforehand and that the XEOL intensities were normalized to intensity at $t = 0$ s. The total XEOL yield includes emissions from both Eu species so it will depend on the total number of electron-hole recombination processes independently on whether it happens via intraband recombination exciting the Eu^{3+} ions directly, or if it happens via generating Eu^{2+} and V_k centres, as explained above. So, the decrease of the XEOL intensity, as the irradiation time increased, that was observed for all samples can be interpreted considering the presence of meta-stable trapping centers. Electrons and holes cannot recombine to produce the excitation of Eu ion, generating radiation damage, thereby, decreasing the intensity of the light emission. The fact that the decrease in the XEOL yield is higher for the Sr-rich samples is related to the presence of higher amounts of defects (Sr/Ba vacancies and O vacancies) due to the presence of extra Sr-rich phases, as discussed before. It was also observed that after the irradiation the exposed area became dark due to radiation damage processes. The dark area is stable at room temperature for a long period. This is an indication that the defects generated by the irradiation are competing with the luminescent center, thus reducing the scintillation efficiency of the all aluminates compounds.

In the other experimental works, it is also observed that the radiation damage could be also related to dopant and the oxidation state of the dopant. Montes *et al.*¹⁰ reported that $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ presented larger stability than $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ samples when excited by $\text{CuK}\alpha$ X-rays. They reported that saturation level were about 59%, 64%, and 65% of the initial intensity for Eu^{2+} , Dy^{3+} and Eu^{3+} emission peaks, respectively.

Fig. 6 shows the X-ray induced phosphorescence decay all samples (step 2). The results indicate that, when the X-ray was switched off, all samples have a short time decay component and at least one long time persistent component. As already seem before, phosphorescence decay curves depend on the compositions of the sample. The results indicate that for Sr-rich samples phosphorescence persistence is longer than for Ba-rich samples. This behavior could be

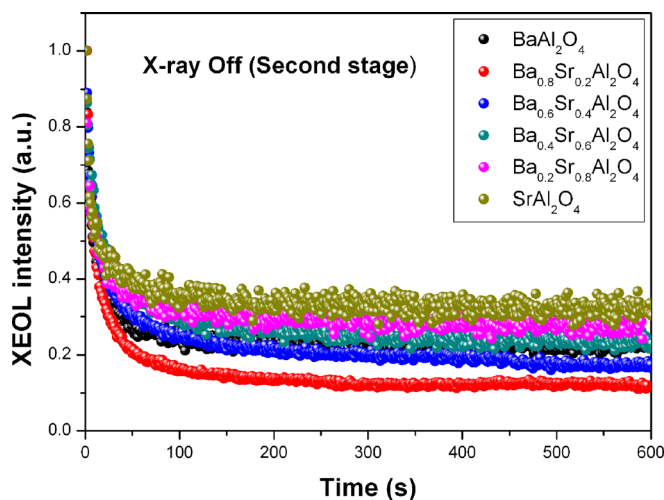


FIG. 6. Relative intensity of XEOL emission as a function of time length after switching off the irradiation (second stage).

related to the local distortion and total structural changes generated by the inclusion of the Sr ions in the BaAl_2O_4 that may affect the trap depth¹³ and, as a consequence, the probability of the charge release from the traps. In addition, it was stated before that the Sr-rich sample is likely to have higher amounts of vacancies that will act as electrons and hole traps. If the Sr ion incorporation contributed to create deep traps in the forbidden gap of the host material, this, in combination with the higher amounts of trapping centers, could explain the longer decay component for the Sr-rich samples. These results suggest that the trap densities and the trap depth in Sr-rich crystal are different from those in Ba-rich compounds. In another experimental work,¹⁰ the authors observed that the long persistency was due to the co-doping rare earth ions (Dy^{3+} ions). A well-known behavior of Dy^{3+} ions in these matrix is that they act as hole traps. The phosphorescence decay depends on the depth of Dy^{3+} traps. In this case, Dy^{3+} ion incorporation creates deeper traps in the forbidden gap of the host material which leads to the longer persistence.

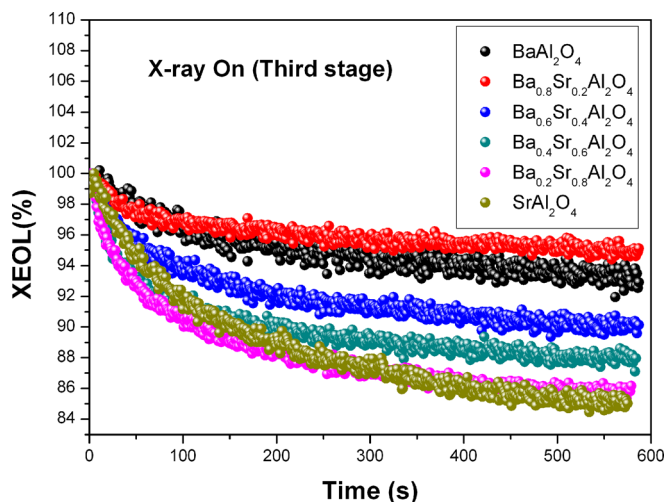


FIG. 7. Relative intensity of XEOL emission as a function of the time duration of the exposure to the X-ray photons of energy 6985 eV (third stage).

Fig. 7 (third stage) shows the total XEOL yield when the sample were again exposed to the X-ray beam with the same energy during the 450 s, enough time to see a saturation of the luminescence. The results showed that the total XEOL emissions decreased for all samples as the radiation time increased. It can be seen that, as observed in the first stage, the XEOL yield of the Ba-rich samples saturated at higher intensities than the Sr-rich ones. These results also indicate that the Ba-rich samples presented larger stability and this is again consistent with the fact that the Ba-rich samples have lower amount of defects than the Sr-rich ones. In the third stage, all samples saturated at higher levels than the ones observed in the first step. This behavior could be related to the radiation damage generated during the first irradiation stage, since that is stable at room temperature for a long period of time.

IV. CONCLUSION

X-ray induced optical luminescence (XEOL), stimulated with monochromatic X-rays from synchrotron source, was studied in $\text{Ba}_x\text{Sr}_{1-x}\text{Al}_2\text{O}_4: \text{Eu}^{3+}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) samples produced via sol-gel route. The XEOL emission spectra of all samples exhibited the usual Eu^{2+} and Eu^{3+} transitions, when the X-ray photons were tuned at the Eu L_{III} -edge and the relative intensities of the Eu^{2+} to Eu^{3+} emissions depend on x , the amount of Sr concentration in the samples. However, no Eu^{2+} was found when the usual X-ray absorption spectra were recorded around the Eu L_{III} -edge. This results were interpreted in terms of the processes that lead to reduction of Eu^{3+} to Eu^{2+} during irradiation and the energetic costs to stabilize both Eu^{3+} and Eu^{2+} related defects in the $\text{Ba}(\text{Sr})\text{Al}_2\text{O}_4$ lattices. XEOL emission decreased as a function of the irradiation time indicating the buildup of radiation damage in the compounds. The XEOL time decay constants and the saturation levels were found to depend on the Sr content added to the samples, the Ba-rich samples being the ones that showed the longer decay constant and the higher saturation level. These results are compatible with the interpretation of the available defects in the lattice. LLP was also observed for all samples, after switching off the X-ray beam, and both the saturation level and the decay constant were found to be dependent on the sample composition. In Sr-rich samples, the LLP lasted for longer times than the B-rich ones.

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