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Mechanisms of radioluminescence of rare earths doped $SrAl_2O_4$ and $Ca_{12}Al_{14}O_{33}$ excited by X-ray



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ABSTRACT

Pure and rare earth doped SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ have been synthesized by a new sol–gel proteic methodology. Photoluminescence (PL) and radioluminescence (RL) spectra show different behavior when excited with either UV light or X-ray radiation. Such behavior may be connected to the X-ray absorption/reduction of Eu ions process in samples. X-ray absorption spectroscopy (XAS) was carried out simultaneously with X-ray excited optical luminescence (XEOL) and the analysis indicates that are depends on the energy of excitation and the kind of excited species. Dispersive X-ray absorption spectroscopy (DXAS) was carried out to follow the kinetic of reduction process in the samples during the irradiation. The reduction process does not produce stable Eu²⁺ species. An overall analysis of the results makes possible to build the mechanisms of radioluminescence of rare earths doped SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ systems.

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1. Introduction

The scintillators are luminescent materials that absorb ionizing radiation and convert it into light within the region of the visible/IR [1]. The main experimental technique that measures the scintillation properties is named radioluminescence (RL). The emission mechanism of a typical scintillation is modeled in three parts, (i) the conversion process in which the energy of the incoming radiation or energetic particles is converted into a large number of electron-hole pairs, (ii) the transfer process in which the recombination energy of an electron-hole pair is transferred to the luminescent ion involved, and (iii) the emission process in which the ground state [2]. A mechanism that takes into account excitation by X-ray and its initial interaction with the scintillator material had not been proposed up to now for SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ systems.

The SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ systems present a long lasting phosphorescence (LLP) property when doped with rare earths ions [3–7] making possible a large number of practical applications in the areas of safety improvement and energy saving (e.g., traffic signs, emergency signs, safety clothes, and advertising). A long lasting phosphor (LLP) is a material that shows bright light emission after the exposure to ionizing or UV radiation. The LLP elements,

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which emit photons for a long period after stopping the irradiation without any external excitation, are a promising candidate as simple and easy-to-use radiation detection elements, especially for digital radiography [8].

Ca₁₂Al₁₄O₃₃ is commonly known as the mineral mayenita and it is a minority constituent of cements of calcium aluminates. The mayenita crystallizes in space group $I\overline{4}3d$ (2 2 0) with lattice parameters a = 11.989 Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 1723.3 Å³, Z = 2 [9]. Recently it was discovered that the Ca₁₂Al₁₄O₃₃, due to its unique crystalline structure, provides new unusual properties that make it an attractive material for applications in electronics, optics and chemistry [10].

Strontium aluminate SrAl₂O₄ exists in two crystallographic forms and a reversible transition between the two occurs at 650 °C [11]. The low-temperature phase have a monoclinic structure, space group $P2_1$ (a = 8.447 Å, b = 8.816 Å, c = 5.163 Å, β = 93.42°) and it is well established [12], but the high-temperature phase (hexagonal, space group $P6_322$, a = 5.140 Å, c = 8.462 Å) is not [11]. SrAl₂O₄: Eu²⁺, Dy³⁺ shows a high quantum efficiency, long afterglow lifetime, and good chemical stability, which make them potential persistent luminescence materials to replace the traditional ZnSbased phosphors [4].

In recent work it has been found that X-ray irradiation induced the reduction of part of Eu^{3+} to Eu^{2+} in the excited state originating a broad band emission at 520 nm in Eu^{3+} doped $SrAl_2O_4$ whilst studying RL emission [13]. Since those materials present a potential application as radiation detectors, a deeper investigation about the radioluminescence mechanisms is of great importance.

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The aim of this work is to introduce a mechanism for the radioluminescence of rare earths doped Ca₁₂Al₁₂O₃₃ and SrAl₂O₄ taking into account the X-ray absorption and reduction of Eu ions in the samples.

2. Experimental techniques

The nanopowders of $Ca_{12}Al_{14}O_{33}$, $Ca_{11.9}Eu_{0.1}Al_{14}O_{33}$ and $Ca_{11.8}Eu_{0.1}Nd_{0.1}Al_{14}O_{33}$ as well as $SrAl_2O_4$, $Sr_{0.97}Eu_{0.03}Al_2O_4$ and $Sr_{0.97}Eu_{0.02}Dy_{0.01}Al_2O_4$ were produced via a new sol-gel route [14]. Details of sample preparation methodology were presented in previous work [13].

Calcium aluminates were produced calcining the xerogels at 800 °C for 4 h and the strontium aluminates ones were produced at 1100 °C for 4 h. A reducing atmosphere of N₂ + 5%H₂ was used to produce Eu²⁺ doped samples. The crystalline phases and structural purity of all samples were routinely checked by X-ray powder diffraction (XRPD) measurements using CuK α radiation on Rigaku Ultima+ RINT 2000/PC diffractometer in the Bragg–Brentano geometry, operating at 40 kV/40 mA. The XRPD analyses are also shown in previous work [13] and all samples exhibited single crystalline phases.

The photoluminescence (PL) spectroscopy was carried out at room temperature using ISS PC1 Spectrofluorometer. The RL measurements were obtained exciting the samples with a Cu X-ray tube source and light collection was done using an Ocean Optics HR2000 spectrometer equipped with an optical fiber. The X-ray absorption spectroscopy (XAS) measurements were performed around the Sr L₂ and L₃ edges in total electron yield mode (TEY) at the soft X-ray spectroscopy beamline (D03B-SXS) and in fluorescence mode at the Eu L₃ edge at the X-ray absorption fine structure beamline (D08B-XAFS-2), both at LNLS (Brazilian Synchrotron Light Laboratory, Campinas, Brazil, proposals XAFS1 #6738/07 and SXS #4850/05). The Dispersive X-ray absorption spectroscopy (DXAS) measurements were performed around the Eu L₃ edge as a function of exposure time to the X-ray beam at the D06A-DXAS beamline at LNLS (project number DXAS #7311/08). The luminescence of the sample (XEOL - X-ray excited optical luminescence) [15-17] due to the absorption of the X-rays was measured simultaneously with the XAS and DXAS spectra using an Ocean Optics HR2000 spectrometer equipped with an optical fiber.

3. Results and discussion

The photoluminescence (PL) and radioluminescence (RL) spectra of rare earths doped Ca₁₂Al₁₄O₃₃ and SrAl₂O₄ are shown in Figs. 1 and 2, respectively. In Fig. 1 the PL peaks correspond to typical emissions due to the 4f-4f transitions, ${}^{5}D_{0} \rightarrow {}^{4}F_{1-4}$ of Eu³⁺ [18]. The UV excitation wavelength was 245 nm (5.06 eV) and it may be associated with the optical absorption edge of intrinsic Ca₁₂Al₁₄O₃₃ [19]. Wang et al. have found for Ca₁₂Al₁₄O₃₃ samples with different concentrations of Er³⁺ ions that the absorption bands at 214 nm (5.79 eV) and 244 nm (5.08 eV) appeared which were associated with the host and the defect level [20]. In other words, stimulation by photons of λ = 245 nm excites Eu³⁺ ion to the interconfigurational charge-transfer state (CTS) from the ground state. This excited state relaxes through nonradiative steps to the ⁵D emitting levels followed by radiative transition to the ⁷F₁ levels.

A similar result was obtained for SrAl₂O₄: Eu³⁺ samples which the PL spectrum, shown in Fig. 2, was taken with excitation at 265 nm. The emission peaks also correspond to typical emissions of Eu³⁺. The excitation wavelength, on the other hand, corresponds to the 4f–5d transitions or a charge transfer excitation, via the conduction band of the matrix, i.e. stimulation by photons of λ = 265 nm excites Eu³⁺ ion to the charge-transfer state (CTS) from the ground

Eu³⁺ Intensity (a. u.) RL Exc - X-ray Eu²⁺ 8046 eV PL Exc - UV 245 nm 700 800 300 400 500 600 900 1000 Wavelength (nm)

Fig. 1. Typical emission spectra obtained during the irradiation, i.e. the radioluminescence (RL) and photoluminescence (PL) spectra of $Ca_{12}Al_{14}O_{33}$: Eu³⁺.

state and after a relaxation by nonradiative decay to the ⁵D levels that decays to the ⁷F_J levels originating the observed emissions peaks. The excited transition results in the charge transfer from the p orbitals of oxygen ligands to the f orbitals of Eu³⁺. The charge-transfer transition frequency of Eu³⁺ ion lies in high-energy region of the spectrum because of the low polarizability of the oxygen of the host lattice in the (Al₂O₄)^{2–} groups [21].

When irradiated with X-rays, the $Ca_{12}Al_{14}O_{33}$: Eu^{3+} , $SrAl_2O_4$: Eu^{3+} and $SrAl_2O_4$: Eu^{2+} , Dy^{3+} samples scintillates emitting visible light. Typical emission spectra obtained during the irradiation, i.e. the radioluminescence (RL) emission spectra are also shown in Figs. 1 and 2.

Some of the rare earth elements can be found inside a host matrix as divalent or trivalent or both charged states and this feature is quite common for Sm, Eu and Yb. It was found that small amounts of such trivalent rare earths ions in CaF₂ can be converted into divalent ones by irradiation with gamma, X-rays or even ultraviolet radiation [22]. Wang et al. have observed no broad Eu²⁺ emission band but only Eu³⁺ emission in the 12CaO-7Al₂O₃: Eu glass synthesized in air, revealing that the doped Eu³⁺ ions cannot be reduced to Eu²⁺ in this glass [18].

RL emissions bands around 450 nm (Fig. 1) and 520 nm (Fig. 2) are shown for rare earths doped calcium and strontium aluminates, respectively. Those emissions are associated to the $4f^{6}5d^{1} \rightarrow 4f^{7}$



Fig. 2. RL and PL spectra of Sr₂Al₂O₄ doped with rare earths.

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Fig. 3. XAS spectrum of SrAl₂O₄: Eu³⁺ and luminescence efficiencies of SrAl₂O₄: Eu³⁺ SrAl₂O₄: Eu²⁺, Dy³⁺ nanopowders.

transitions of Eu²⁺ [3,6] and indicate the presence of reduced europium in the samples. The emission around 615 nm, in both samples, is associated to Eu³⁺. These results indicate that in both matrix the X-ray irradiation induced the reduction of part of Eu³⁺ to Eu²⁺ in the excited state originating a broad band emission at 450 nm or 520 nm. In previous work [13] similar phenomenon was observed for the RL emission on SrAl₂O₄ host matrix doped with rare earths. Wu et al. [23], when studying SrAl₂O₄ based green phosphor for white LED's, also obtained both emissions in Sr_{0.95}Al₂O₄: (Eu²⁺)_{0.05} system. In the case of the SrAl₂O₄:Eu,Dy samples, the extra emission peak at 570 nm (Fig. 2) can be associated to the emission of the Dy³⁺ ions that were directly excitated the L₃ absorption edge of Dy (7790 eV) that is very close in energy to the CuK α or K β lines.

The RL measurements shown in Figs. 1 and 2 were obtained using a CuK α ($E_{\alpha 1}$ = 8046 eV, $E_{\alpha 2}$ = 8026 eV) X-ray tube source. The K α line of Cu is almost resonant with the Eu L₁ absorption edge at 8052 eV. So, one should expect that most of the incident photons were absorbed by the Eu ions.

The X-ray absorption spectroscopy (XAS) measurements performed in total electron yield mode (TEY) around the Sr L_2 and L_3 edges and in fluorescence mode at the Eu L_3 edge were carried out simultaneously to the XEOL spectra of rare earths doped samples. These results are shown in Figs. 3–5. The shape of XEOL curves (shown in Fig. 6) did not change within the energy range X-rays used in the measurements (6800–7500 eV or 1900–2100 eV), but



Fig. 4. Luminescence efficiency and XAS spectrum of $Ca_{12}Al_{14}O_{33}\colon Eu^{3+}$ nanopowders.



Fig. 5. XAS spectrum around of L3 and L2 Sr edges and luminescence efficiency of $\rm SrAl_2O_4\colon Eu^{3*}.$

the luminescence efficiency (area under the XEOL curves) had a different behavior depending on range of energy of the incident X-rays. In contrast to some of the previous measurements [16], in the present work the XEOL measurement was not used as an alternative detection mode for the XANES/XAFS but as a technique to study the recombination of charge carriers and production of luminescence in the samples. The reason why the XEOL spectra did not clearly show the typical X-ray absorption profile is due to the poor signal-to-noise ratio probably caused by rather low dopant concentrations used in both aluminates.

When the sample was excited with X-ray photons in the 6800-7500 eV range (see Figs. 3 and 4) the X-ray fluorescence of the Eu ions, used to evaluate the absorption coefficient (continuous line in the figures), follows the well known absorption due to the L₃ edge of Eu, showing the white line absorption and all features of a regular X-ray absorption measurements. At the same time, the area under the XEOL curves increased as the energy of the photons increased.

In Fig. 5 the samples of $SrAl_2O_4$: Eu^{3+} was excited in the X-ray photon energies range of the L_2 and L_3 Sr edges. The typical X-ray absorption profile is obtained, using the total electron yield (TEY) mode. In this case, the area under the XEOL spectra decreased as the photon energy increased. This means that the luminescence



Fig. 6. XEOL Spectra of $Ca_{12}Al_{14}O_{33}$: Eu^{3+} . $Ca_{12}Al_{14}O_{33}$: Eu^{2+} , Nd^{3+} and $SrAl_2O_4$: Eu^3 . All of them were taken at 7000 eV.

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Fig. 7. DXAS spectra as a function of time obtained during the irradiation of Ca₁₂Al₁₄O₃₃: Eu²⁺, Nd³⁺, the energy is represented by the position of Pixel CCD detector (a), DXAS spectra of Ca₁₂Al₁₄O₃₃: Eu³⁺ compared to Eu₂O₃ reference (b).

conversion efficiency decreased as the absorption of the Sr ions increased.

The XEOL spectrum of Ca₁₂Al₁₄O₃₃: Eu²⁺, Nd³⁺ (Fig. 6) is composed by two intense peaks around 450 nm and 615 nm followed by a weaker emission peaking around 900 nm. The first two emissions are associated to Eu²⁺ and Eu³⁺ emissions, respectively, and the last one is associated with ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transition of Nd ions.

Since the reduction process occurs during irradiation of the samples, one may argue if such process is stable or not and if any net amount of Eu^{2+} will be left in the sample after irradiation, as a consequence of the radiation damage.

Dispersive X-ray absorption spectroscopy (DXAS) is a technique which uses dispersive optics that allows acquiring measurements of a range of energies of an X-ray absorption spectrum simultaneously. Thereby other parameters can be incorporated in analysis like time, temperature, pressure, etc. Analysis of the reduction dynamics of the Eu³⁺ to Eu²⁺ can give information about radiation damage process in the samples and DXAS technique can be used to follow it. The changes in the light emission due to X-ray absorption can be accompanying simultaneously through XEOL spectra.

Figs. 7 and 8 show DXAS spectra of rare earths doped Ca₁₂Al₁₄O₃₃ and SrAl₂O₄ as a function of time during the irradiation with X-rays. Since the average dose rate is approximately constant during the elapsed time of each DXAS experiment, the time is actually a measure of the amount of radiation deposited in the sample. Typical time interval between each DXAS spectrum is about 100 ms to 1 s. The energy range of the DXAS beamline was set around the L₃ europium absorption edge (6977 eV). The experiment was carried out to follow the kinetic of reduction process in samples during the irradiation. In the results of Fig. 7b, the comparison with DXAS profile of Eu₂O₃ standard sample showed that the peak associated with Eu³⁺ absorption does not change with time, and thus with the radiation dose. This means that no stable Eu²⁺ was actually generated during irradiation. But the irradiation does produce Eu²⁺ since its emission is present in the XEOL measurements, taken at the same time as the DXAS kinetic measurements (see Fig. 6).

DXAS spectra of SrAl₂O₄:Eu²⁺ (Fig. 8b) showed a splitting of the Eu L₃ absorption edge. The presence of a second absorption edge at lower energies than the Eu³⁺ one is consistent with the reduction process Eu³⁺ \rightarrow Eu²⁺. In the SrAl₂O₄:Eu²⁺ sample, the Eu²⁺ ions

was obtained during a sample annealing, since trivalent europium oxide, Eu_2O_3 , is usually the starting material used for doping. In this case, the phosphors were prepared using a reducing atmosphere of $N_2 + 5\%H_2$ during annealing. Fig. 8b shows that the absorption edge due to the Eu^{3+} does not disappear completely, suggesting that not all of Eu^{3+} ions are reduced to Eu^{2+} when the reducing atmosphere are used during annealing.

One possible interpretation to these results are that the Eu²⁺ generated is a kind of transient state and the light emission is just part of the recovering back of the sample to the Eu³⁺ charge state. Since X-ray absorption is an average measurements and the time interval between measurements is not enough to catch the Eu²⁺ in the transient state and virtually all incident X-ray photons were absorbed by the Eu³⁺ ions giving rise to a typical absorption edge of the trivalent charge state of Eu.

The same result occurred for the $SrAl_2O_4$: Eu^{3+} , as shown in Fig. 8b. DXAS peak associated with Eu^{3+} absorption does not change with time, indicating again that no stable Eu^{2+} is generated.

The area of XEOL curves increased with the X-ray photon energy when the samples were excited around the L_3 absorption edge of Europium and decreased when excited close to the L_2 and L_3 Strontium edges.

One possible explanation for this behavior is the following:

- i) Sr ions absorb the X-ray from the incident beam and decays mainly via X-ray fluorescence emission;
- ii) the two main fluorescence lines of Sr are the $L_{\alpha 1}$ (1804 eV) and $L_{\beta 1}$ (1871 eV) that can excite the absorption of the Al K edge ions (1559 eV);
- iii) as the energy of the X-ray increases and becomes higher than the L_3 and L_2 absorption edges of Sr, the absorption due to Sr increases and thus the number of Al that are excited via the X-ray fluorescence of the Sr ions also increase;
- iv) this process directly competes to the non-resonant energy transfer to the Eu ions causing a decrease in the luminescence associated with both species Eu²⁺ and Eu³⁺.

When the sample is now excited with X-ray photons in the 6800-7200 eV range (see Figs. 2 and 3) the X-ray fluorescence of the Eu ions follows the well known absorption due to the L₃ edge

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Fig. 8. DXAS spectra as a function of time obtained during the irradiation of SrAl₂O₄: Eu²⁺,Dy³⁺, the energy are represented by the position of Pixel CCD detector (a), DXAS spectra of SrAl₂O₄: Eu³⁺ compared to Eu₂O₃ reference (b).



Fig. 9. Possible mechanisms of radioluminescence of rare earths doped $SrAl_2O_4$ (or $Ca_{12}Al_{14}O_{33}$) taking into account the X-ray absorption/reduction of Eu ions process in samples. (a) Photons absorptions by the matrix elements and (b) emission of both the Eu^{2+} and the Eu^{3+} ions.

of Eu and the area of XEOL curves increased as the energy of the photons increased. This result can also be interpreted in terms of the model described above. When exciting the Eu via the L₃ edge, the main decay process is via the X-ray fluorescence emission at 5850 (L_{\alpha1}) and 5814 (L_{β1}) eV [24] and these values are far from any absorption lines due to the ions in the crystalline matrix. It means that most of the remaining excited species will be either Eu²⁺ or Eu³⁺ and the decay of that to the ground states will produce the typical XEOL spectra shown in Fig. 6. According to this model, the luminescence efficiency should increase as the X-ray absorption of the Eu ions increases, as shown in Figs. 3 and 4.

Considering now DXAS/XEOL results the above explanation can be reinforced and complemented:

- i) X-ray absorption by material creates photoelectrons: the measurements shown in Figs. 7 and 8 were obtained around L₃ europium absorption edge, so, one should expect that most of the incident photons were absorbed by the Eu ions and the free electrons generated in the matrix were coming from the L shell of the Eu ions;
- ii) The hole left in that shell is quickly filled by the decay of outer Eu electrons in a cascade process, moving the hole to the most outer shell of Eu.

- iii) The recombination of the free electrons with these holes thus produce both the Eu²⁺ and the Eu³⁺ in the excited states: photoelectrons are captured by Eu ions inducing the reduction and excitation;
- iv) Returning back to the ground state through 4f⁶5d¹ → 4f⁷ transition of Eu ions give rise to the typical 520 nm/455 nm emissions;
- v) All process occurs in a very short time and the X-ray photons induce the $Eu^{3+} \rightarrow Eu^{2+}$ reduction that is not a stable process.

Fig. 9 pictures the proposed mechanisms of radioluminescence of rare earths doped $SrAl_2O_4$ and $Ca_{12}Al_{14}O_{33}$. X-ray and its initial interaction with the scintillator material are showed in the figure. In Fig. 9(a), photons absorption and transitions to the continuum from Sr (or Ca) ions and self absorption by Al ions are showed. In Fig. 9(b), decay of outer Eu electrons in a cascade process producing both the Eu²⁺ and the Eu³⁺ in the excited states that emit the light returning back to the ground state are showed.

4. Conclusion

PL and RL spectra showed different behavior when excited with either UV light or X-ray radiation and such behavior was connected to the X-ray absorption/reduction of Eu ions process in samples. RL/XEOL spectra of powders indicated that X-ray P.J.R. Montes et al. / Journal of Electron Spectroscopy and Related Phenomena 189 (2013) 39-44

irradiation induced the reduction of part of Eu³⁺ to Eu²⁺ in the excited state originating a weak peak at 520 nm (450 nm) presented by Eu³⁺ doped SrAl₂O₄ (Ca₁₂Al₁₄O₃₃). XAS/XEOL measurements suggested a possible energy transfer, via X-ray fluorescence, from strontium to aluminum in the X-ray photon energy range of the L₃ and L₂ absorption edge energies of strontium. DXAS/XEOL results showed that the Eu³⁺ \rightarrow Eu²⁺ reduction is not stable during irradiation, indicating that reduction/recover process must be very quick. An overall analysis of the results made possible to build a mechanism of radioluminescence of rare earths doped SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ systems.

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