

Mechanisms of Radioluminescence of Rare Earths doped SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ Excited by X-Ray

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Abstract – In this work samples of pure and rare earths doped SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ were prepared via a sol-gel proteic methodology. Radioluminescence spectra indicate that X-ray irradiation induce the reduction of part of Eu³⁺ to Eu²⁺. The area of the sample that was irradiated became dark indicating the production of irradiation damage that can be connected to the reduction process of Eu ions. DXAS technique was used to monitor the kinetics of the reduction process of Eu ions during irradiation, in order to verify the connection between the generation of damage and the process of reduction.

SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ have been synthesized by sol-gel proteic methodology [1]. A study taking account calcination time and temperature was carried out to obtain the best preparation conditions. The crystalline phases and structural purity of all samples were routinely checked by X-ray powder diffraction measurements. Such methodology allowed producing of ceramic nanopowders with single crystalline phases.

The fluorescence spectra of rare earths doped SrAl₂O₄, excited at 265 nm, are shown in figure 1. Only Eu²⁺ and Eu²⁺, Dy³⁺ co-doped systems show a 520 nm emission. The sample which was not submitted to reducing treatment exhibit only the sharp f–f emissions of Eu³⁺ corresponding to the ⁵D₀–⁷F_J (J = 0,1,2,4) transitions. This permit stands that not all europium ions are reduced during synthesis. This can be confirmed in such results where it is possible to observe Eu³⁺ emissions around 625 nm in SrAl₂O₄: Eu²⁺ and SrAl₂O₄: Eu²⁺, Dy³⁺ samples. The differences in energies of the 4f transitions of Eu³⁺ ions in the three samples can be interpreted in terms of the presence of Eu²⁺ and Dy³⁺ at a Eu³⁺ neighbouring sites. Changes in crystalline field surround activator ions may cause differences in the transition energies. This fact indicates the interaction between Dy and Eu³⁺ ions, inducing the nephelauxetic effect (a red shift of transitions).

Radioluminescence spectra of rare earths doped SrAl₂O₄ excited by X-ray (fig. 2) indicate that irradiation induces the reduction of Eu ions, since the Eu³⁺ doped samples exhibit a broad 520 nm emission, which is associated with Eu²⁺ emission in SrAl₂O₄. This fact indicates a valence change of Eu species during the irradiation. Dispersive X-ray Absorption Spectroscopy (DXAS) of SrAl₂O₄: Eu³⁺ (fig. 3) was carried out to follow the kinetic of reduction process in samples during the irradiation. DXAS curves were obtained exciting both L2 and L3 edges of Sr ions in SrAl₂O₄ samples, K edge of Ca ions in Ca₁₂Al₁₄O₃₃ samples and L3 edge of Eu ions. These results do not show a stable change of valence, i.e. such event may occur in a very short time. An overall analysis of the results makes possible to build a mechanisms of radioluminescence of rare earths doped SrAl₂O₄ and Ca₁₂Al₁₄O₃₃ systems. (Work partially supported by CNPq, FINEP and CAPES. PJM is grateful to CNEN for the Dr grant)

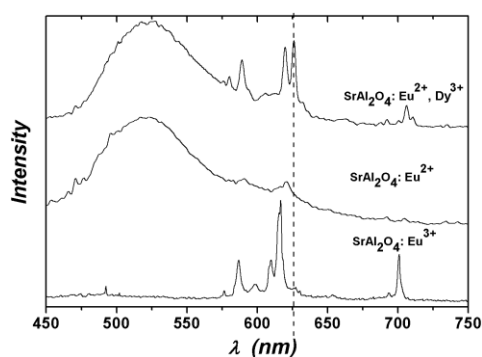


Figure 1: Fluorescence spectra of rare earths doped SrAl₂O₄, all excited at 265 nm.

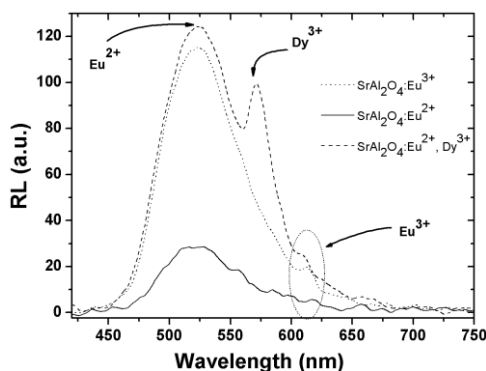


Figure 2: Radioluminescence spectra of rare earths doped SrAl₂O₄.

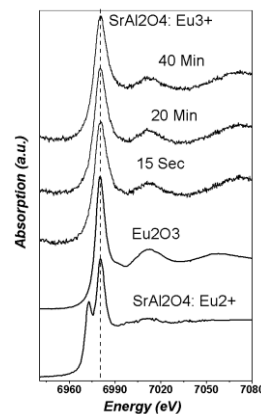


Figure 3: DXAS curves of SrAl₂O₄: Eu²⁺, Eu₂O₃ and SrAl₂O₄: Eu³⁺ in different times.

References

[1] P.J.R. Montes, M.E.G. Valerio and G.M. Azevedo. Nucl. Instrum. Meth. B, 266 (2008) 2923-2927.