

Thermoluminescence and synchrotron radiation studies on the persistent luminescence of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$

L.C.V. Rodrigues^{(1,2)*}, R. Stefani⁽¹⁾, H.F. Brito⁽¹⁾, M.C.F.C. Felinto⁽³⁾,
J. Hölsä⁽²⁾, M. Lastusaari⁽²⁾, T. Laamanen^(2,4)

- (1) Universidade de São Paulo, Instituto de Química, Departamento de Química Fundamental, Av. Prof. Lineu Prestes, 748, CEP 05508-900, São Paulo-SP, Brazil, email: lucascvr@iq.usp.br
 - (2) University of Turku, Department of Chemistry, FI-20014 Turku, Finland
 - (3) Instituto de Pesquisas Energéticas e Nucleares, Centro de Química e Meio Ambiente, Av. Prof. Lineu Prestes, 2242, CEP 05508-000, São Paulo-SP, Brazil
 - (4) Graduate School of Materials Research, Turku, Finland
- * Corresponding author.

Abstract – Barium aluminates doped with Eu^{2+} and Dy^{3+} ($\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$) were prepared with the combustion synthesis at temperatures between 400 and 600 °C as well as with the solid state reaction at 1500 °C. The concentrations of $\text{Eu}^{2+}/\text{Dy}^{3+}$ (in mole% of the Ba amount) ranged from 0.1/0.1 to 1.0/3.0. The electronic and defect energy level structures were studied with thermoluminescence (TL) and different synchrotron radiation spectroscopies: UV-VUV excitation and emission, XANES and EXAFS. Theoretical calculations using the Density Functional Theory (DFT) were carried out in order to compare with the experimental data.

The alkaline earth aluminates doped with Eu^{2+} and R^{3+} ($\text{MAl}_2\text{O}_4:\text{Eu}^{2+},\text{R}^{3+}$; M: Ca, Sr, Ba) [1] were the first modern persistent luminescence phosphors to show significantly long and strong emission to be used in several commercial applications. Among these phosphors, $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ showed a special property that europium could be reduced without the use of a reducing atmosphere [2]. Despite the advances in producing highly persistent luminescence materials, the mechanism of this phenomenon is still uncertain. To a better understanding of this phenomenon, a systematic study of these materials is necessary [3].

The thermoluminescence glow curves for the solid state phosphors showed in general two broad bands centered at ca. 70 and 200 °C (Fig. 1). The bands were deconvoluted using the program TLanal v1.0.3 [4]. The trap energy increased less than 0.1 eV with increasing total dopant and co-dopant concentration. The TL glow curves for the combustion prepared materials presented only one band centered at ca. 75 °C. The trap energy decreased 0.1 eV with the increase of the temperature from 400 to 600 °C. The TL band at 70 °C presented smaller FWHM values for the solid state than for the combustion prepared materials. The increase in the FWHM value can be attributed to the smaller particle size. With smaller particles, the heat transfer within the sample is weaker, broadening the band. The average crystallite sizes confirmed that the combustion method produced significantly smaller particles than the solid state synthesis. The larger particle size of the solid state materials is due to sintering at high temperatures.

The synchrotron radiation excitation spectrum of Eu^{2+} (Fig. 2) reveals broad bands from ca. 210 to 334 nm (the experimental limit) due to the $\text{Eu}^{2+} 4f^7 \rightarrow 4f^6 5d^1$ transitions. One can also observe a sharp edge at ca. 190 nm (6.5 eV) for both the doped and nondoped BaAl_2O_4 . The edge is the excitation from the top of the valence to the bottom of the conduction band, *i.e.* the band gap energy E_g . In contrast to SrAl_2O_4 [3], the experimental E_g value differed from 5.3 eV obtained by the DFT calculations. This is probably due to the higher covalent character in barium aluminate. The analysis of the results proved useful to increase the understanding of the persistent luminescence mechanisms.

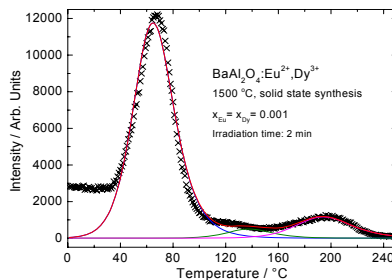


Figure 1: Thermoluminescence glow curve of solid state prepared $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$

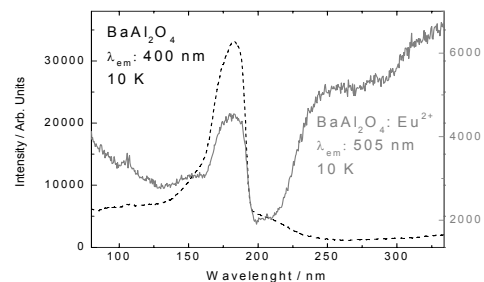


Figure 2: Synchrotron radiation excitation spectra of BaAl_2O_4 and $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$

- [1] T. Matsuzawa, Y. Aoki, N. Takeuchi and Y. Murayama, J. Electrochem. Soc., 143 (1996) 2670
- [2] R. Stefani, L.C.V. Rodrigues, C.A.A. Carvalho, M.C.F.C. Felinto, H.F. Brito, M. Lastusaari and J. Hölsä, Opt. Mater. (2009), in press
- [3] J. Hölsä, T. Laamanen, M. Lastusaari, M. Malkamäki and P. Novák, J. Lumin. (2009), in press
- [4] K.S. Chung, H.S. Choe, J.I. Lee, J.L. Kim and S.Y. Chang, Radiat. Prot. Dosim., 115 (2005) 345