



Received: 12/04/2012  
Accepted: 12/05/2012

## Photoluminescence of compounds of cerium aluminates and europium aluminates doped

P.C.Piña\*, R.L.D.González

División de Estudios de Posgrado, Facultad de Química, UNAM. 04510 D. F., (MEXICO)

E-mail: cppqic@unam.mx

### Abstract

Two ceramic aluminates luminescent doped: (M1)  $Ce_{0.93}Eu_{0.07}Al_{0.93}Cr_{0.07}O_3$  and (M2)  $Eu_{0.93}Ce_{0.07}Al_{0.93}Cr_{0.07}O_3$  have been synthesized via solid state. Results show that DRX are: fluorite structure  $CeO_2$  for M1 by due oxidation of  $Ce^{3+}$  at  $Ce^{4+}$  and perovskite structure  $AlEuO_3$  for M2. SEM shows in M1 isolated globules of approximately  $1.0\mu m$ , connected or with appearance of nanotubes and in the compound M2 globules agglomerated or geometric particles with edges rounded between  $1\mu m < 5\mu m$ . Analysis EDX indicates the purity of the samples. The photoluminescence spectra of the doped samples M1 and M2 is similar, the difference is the band at 725-800 present only in the M2 may that be influenced by the high concentration of europium oxide. Strong red emission centering at 613 nm is due at  $Eu^{3+}$  in both samples.

### Keywords

Cerium aluminates doped; Europium aluminates doped; Photoluminescence of  $Eu^{3+}$ .

Corresponding author's name and address

P.C.Piña

División de Estudios de Posgrado, Facultad de Química, UNAM. 04510 D. F., (MEXICO)

## INTRODUCTION

Today, there are many modern and more refined methods of synthesis, new structures, and new applications. Among these we have the development of new ceramic materials of lanthanide aluminates. The properties and uses of these lanthanides materials are investigated because recently it had been reported that these materials can be synthesized based on perovskite and fluorite structures<sup>[1,2]</sup>. These materials have a range in technological applications, especially optical as: photoluminescence, fluorescent lights, optical fibers, pigments, lasers etc<sup>[3,4]</sup>.

Another scientific studies show that europium and cerium trivalent ions have been extensively applied in technology because present photoluminescence red in the case of  $Eu^{3+}$  near 610 nm and blue at 450-500 nm in the case of  $Ce^{3+}$ <sup>[5]</sup>

In the chemical environment of the europium and cerium ions influences the light emission between this alumina is considered host material appropriate. On the other hand, there are many synthesis methods: sol-gel, spray, pyrolysis, sputtering, combustion<sup>[5,7,8]</sup> etc. In this work we synthesized by solid state technique two pigments doped aluminates luminescent: (M1) of  $Eu(III)$  and  $Cr(III)$  doped cerium aluminates  $Ce_{0.93}Eu_{0.07}Al_{0.93}Cr_{0.07}O_3$  and (M2)  $Ce(III)$  and  $Cr(III)$  doped europium aluminates  $Eu_{0.93}Ce_{0.07}Al_{0.93}Cr_{0.07}O_3$ .

## EXPERIMENTAL

### Synthesis

Samples were prepared using the solid state technique. The entire chemical reagent used as raw materials were:  $Ce(NO_3)_3 \cdot 6H_2O$ ,  $Al(NO_3)_3 \cdot 9H_2O$ ,  $Eu_2O_3$  and  $Cr_2O_3$  in stoichiometric relations agreed at M1,

$Ce_{0.93}Eu_{0.07}Al_{0.93}Cr_{0.07}O_3$ , and 5% of LiF as mineralize.

In the case of M2,  $Eu_{0.93}Ce_{0.07}Al_{0.93}Cr_{0.07}O_3$  the raw materials were:  $Eu_2O_3$ ,  $Al_2O_3$ ,  $CeSO_4 \cdot 4H_2O$  and  $Cr_2O_3$  in stoichiometric relations are in agreement with the formula and 5% of LiF as mineralize.

The chemical reagents were placed into platinum crucibles, water evaporation, nitrogen oxides and sulfur oxides elimination by thermal treatment. After the samples were calcined in an electrical furnace (Lindberg) at  $900^\circ C$  (24h), were mixed in an agate mortar and finally calcined at  $1000^\circ C$  (96h).

### Characterization

The characterization of the samples were carried out by X-ray diffraction powders in a Siemens D5000 diffractometer using Cu,  $K\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ) and a Ni filter in a  $20^\circ$  ( $2\theta$ )  $70^\circ$  range. The microstructure and morphology were done by a (SEM) scanning electron microscope JEOL model JSM-5900LV. Energy Dispersive X-ray Analysis (EDX) shows the microanalysis of the elements in the samples and the photoluminescence of the europium doped samples were realized at room temperature with an excitation He-Cd laser at the wavelength of 226 nm.

### RESULTS AND DISCUSSION

The examination of X-ray diffractogram of M1,  $Ce_{0.93}Eu_{0.07}Al_{0.93}Cr_{0.07}O_3$ , Figure 1 shows fluorite structure of  $CeO_2$  [PDF 34-0394] and traces of  $\gamma$ -alumina. In the case of M2,  $Eu_{0.93}Ce_{0.07}Al_{0.93}Cr_{0.07}O_3$  the X-ray diffraction corresponds at the perovskite structure  $AlEuO_3$  [PDF 30-0012] and traces of  $Eu_2O_3$  [PDF 43-1008]. Figure 2. The result in the case of M1 means oxidation of  $Ce^{3+}$  at  $Ce^{4+}$ .

The results from the observation of SEM micrographs, Figure 3, reveal that the morphology of the M1 compound, its isolated globules are observed of approximately  $1.0\ \mu m$ , connected or with appearance of nanotubes. In the compound M2, Figure 4, there are globules agglomerated or geometric particles with edges rounded between  $1\ \mu m < 5\ \mu m$ .

The microanalysis of Energy Dispersive X-ray Analysis (EDX) only shows the elemental chemical composition of the samples. Figures 5 and 6.

The photoluminescence of the doped samples M1 and M2 were realized at room temperature with an excitation He-Cd laser at the wavelength of 325 nm. By

excitation europium doped samples show red luminescence, Figure 7.

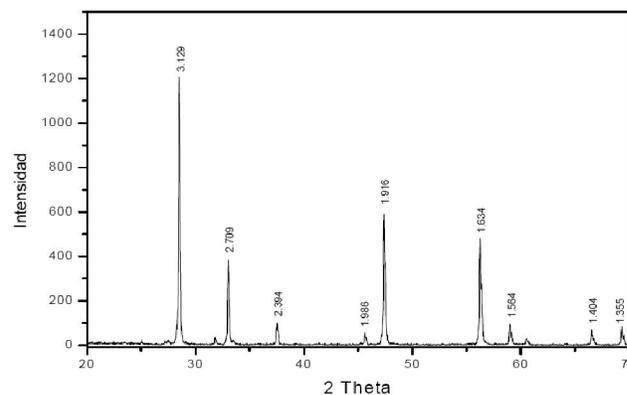


Figure 1 : XRD of M1  $Ce_{0.93}Eu_{0.07}Al_{0.93}Cr_{0.07}O_3$

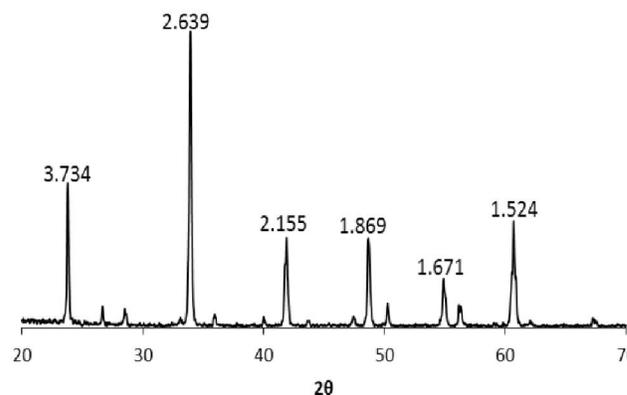


Figure 2 : XRD of M2  $Eu_{0.93}Ce_{0.07}Al_{0.93}Cr_{0.07}O_3$

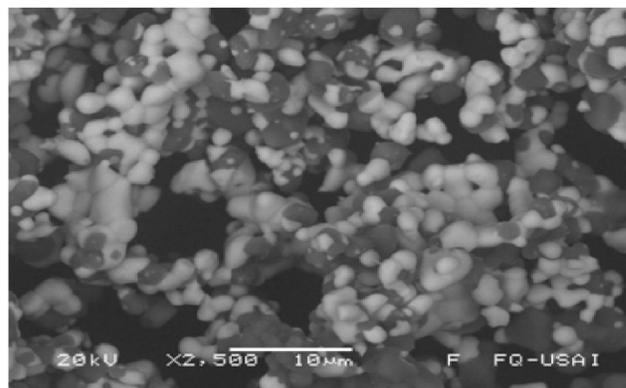


Figure 3 : SEM of M1  $Ce_{0.93}Eu_{0.07}Al_{0.93}Cr_{0.07}O_3$

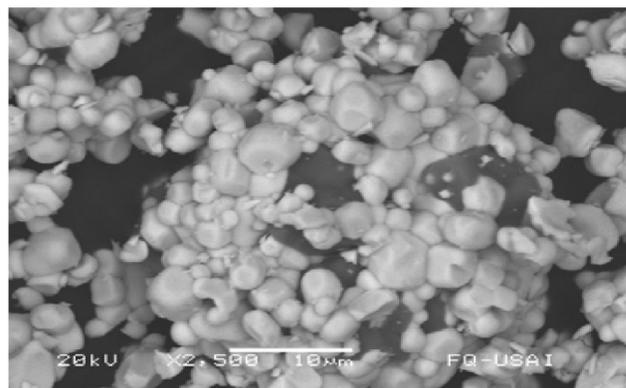


Figure 4 : SEM of M2  $Eu_{0.93}Ce_{0.07}Al_{0.93}Cr_{0.07}O_3$

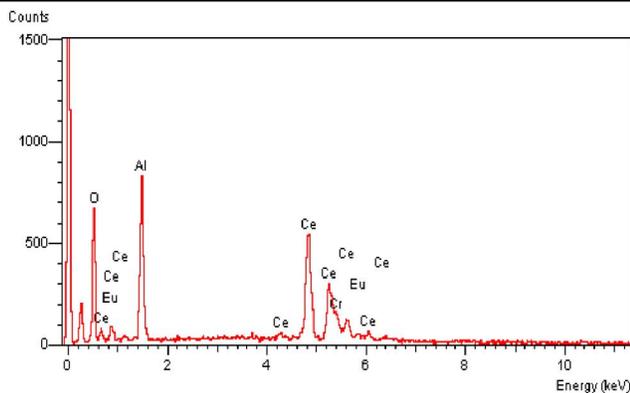


Figure 5 : EDX of M1  $\text{Ce}_{0.93}\text{Eu}_{0.07}\text{Al}_{0.93}\text{Cr}_{0.07}\text{O}_3$

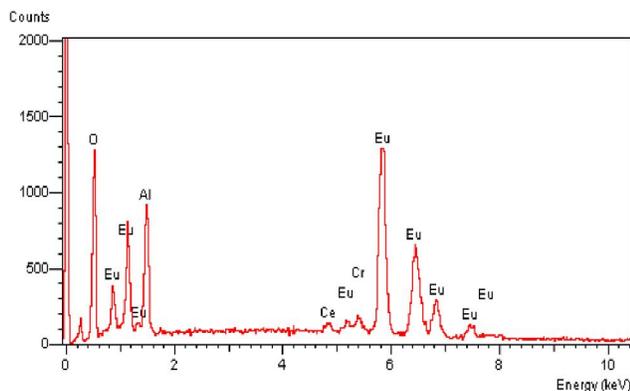


Figure 6 : EDX of M2  $\text{Eu}_{0.93}\text{Ce}_{0.07}\text{Al}_{0.93}\text{Cr}_{0.07}\text{O}_3$

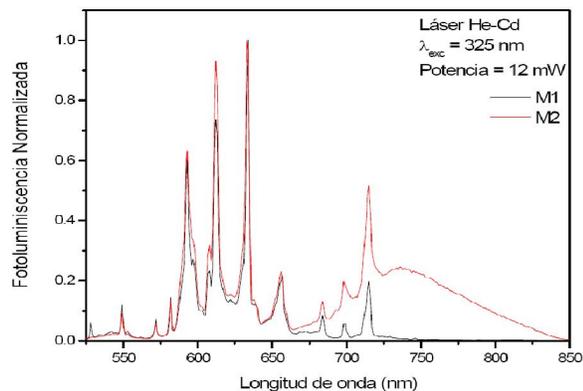


Figure 7 : Photoluminescence spectral of: M1  $\text{Ce}_{0.93}\text{Eu}_{0.07}\text{Al}_{0.93}\text{Cr}_{0.07}\text{O}_3$ , M2  $\text{Eu}_{0.93}\text{Ce}_{0.07}\text{Al}_{0.93}\text{Cr}_{0.07}\text{O}_3$ .

The emission bands are to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $j = 1, 2, 3, 4$ ) transitions of  $\text{Eu}^{3+}$  ions. In the emission band  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  at 580 nm its intensity is not influenced by the host environment, it does not occur at 612nm transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ , where around the europium ion its intensity depend on the symmetry of the crystal field. The observation of a fine splitting at 612nm transition revealed the low symmetry in europium ion doped these compounds. The photoluminescence of the compounds is red color, by UV excitation. Harkov opinion is it that can be due to energy transference between excited trivalent ions  $\text{Eu}^{3+}$  and Yuen reports that the synthesis by combustion of alumina europium

doped show photoluminescence red by UV excitation, which is due to  $ff$  dominant transition especially at 612nm. The emission bands at 656 nm and 715 nm are originated from  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  transitions respectively. The pick at 634 nm is the most intense and is assigned together with 715 nm at the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  transition<sup>[1,6-10]</sup>. The two samples show the same spectra, the difference is the band at 725-800 present only in the M2 may be influenced to the concentration of europium oxide.

At room temperature, the sample M1 shows violet color due to  $\text{Cr}^{3+}$  by substitution of  $\text{Al}^{3+}$  and it is possible that it can be used as ceramic luminescent pigment. In the case of the sample M2 shows beige color.

## CONCLUSIONS

Two ceramic doped aluminates luminescent: M1  $\text{Ce}_{0.93}\text{Eu}_{0.07}\text{Al}_{0.93}\text{Cr}_{0.07}\text{O}_3$  and M2  $\text{Eu}_{0.93}\text{Ce}_{0.07}\text{Al}_{0.93}\text{Cr}_{0.07}\text{O}_3$  were synthesized by solid state reaction in the present study.

The structural, form and size of particles, elemental analysis and luminescence of the compounds were investigated and the results can be summarized as follows:

1. M1, shows Fluorite structure  $\text{CeO}_2$  due to oxidation of  $\text{Ce}^{3+}$  at  $\text{Ce}^{4+}$ , are observed in isolated globules of approximately  $1.0\mu\text{m}$ , connected or with appearance of nanotubes, high purity elemental analysis and the photoluminescence spectra is red color, by UV excitation which is due to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  dominant transition especially at 613nm due to  $\text{Eu}^{3+}$  ions.
2. M2, Perovskite structure  $\text{AlEuO}_3$ , are observed in globules agglomerated or geometric particles with edges rounded between  $1\mu\text{m} < 5\mu\text{m}$ , high purity elemental analysis and similar red luminescence spectra by UV excitation. In this sample the band at 725-800 present may be due to the high concentration of europium.
3. This result shows that  $\text{Ce}^{3+}$  is a good sensitizer of  $\text{Eu}^{3+}$  in  $\text{Al}_2\text{O}_3$  doped with  $\text{Cr}^{3+}$ .
4. These systems illustrate the large potential for applications in luminescent devices.

## ACKNOWLEDGEMENTS

The authors express their thanks to Marel Monroy and Guillermo Santana for the luminescence determinations

---

**REFERENCES**

---

- [1] C.P.Piña; Perovskites Structure, Properties and Uses, in Maxim Borowsky Ed. PEROVSKITES Structure, Properties and Uses, Nova Science Publishers, Inc. New York, 539-557 (2010).
- [2] Nikifor Rakov, Dayanne F.Amaral, Renato B.Guimarães, Glauco S.Maciel; Jour.of Applied Physics, **108**, 073501 (2010).
- [3] R.Nikifor, Renato B.Guimarães, Glauco S.Maciel; Jour.of Luminescence, **131**, 342-344 (2011).
- [4] Yuen Yung Hui, Ching-Fuh Lin; Materials Letters, **61**, 3802-3804 (2007).
- [5] R.Chora-Corella, M.García-Hipólito, O.Álvarez-Fragoso, M.A.Álvarez-Pérez, C.Falcony; Revista Mexicana de Física, **55(3)**, 226-231 (2009).
- [6] L.S.Gomez, K.Marinkovic, M.I.Martin, I.Mena, O.Milosevic, M.E.Rabanal; Boletín de la Sociedad Española de Cerámica y Vidrio, 226-231 (2009).
- [7] Chung-Hsin Lu, Chung-Tao Chen; Jour.Sol-Gel Sci.Technol., **43**, 179-185 (2007).
- [8] G.A.Denisenko, V.A.Oleinikov, G.E.Malashkevich, A.P.Voitovich, A.G.Azylev, B.V.Mchedlishvili, V.Strenk; Journal of Applied Spectroscopy, **62(6)**, (1995).
- [9] Nikifor Rakov, Glauco S.Maciel, Whualkuer B.Lozano, Cid B.de Araújo; Applied Physics Letters, **88**, 081908 (2006).
- [10] Shengliang Zhong, Shijin Wang, Huaping Xu, Haoqing Hou, Zubiao Wen, Ping Li, Shangping Wang, Rong Xu; Jour.Mater Sci., **44**, 3687-3693 (2009).