

# Synthesis and Characterization of Nanocrystalline Eu<sup>3+</sup>-doped Gd<sub>2</sub>O<sub>3</sub>

S. Jáuregui-Rosas<sup>1,2</sup>, O. Perales-Pérez<sup>3\*</sup>, M. Tomar<sup>1</sup>, W. Jia<sup>1</sup>, O. Vásquez<sup>1</sup> and E. Fachini<sup>4</sup>

<sup>1</sup>Department of Physics, University of Puerto Rico-Mayagüez Campus, Mayagüez, PR 00681

<sup>2</sup>Department of Physics, Universidad Nacional de Trujillo, Trujillo - Perú

<sup>3</sup>Department of Engineering Science & Materials, University of Puerto Rico-Mayagüez Campus, Mayagüez, PR 00681. \*ojuan@uprm.edu

<sup>4</sup>Chemistry Department, University of Puerto Rico-Rio Piedras Campus, San Juan, PR 00931

## ABSTRACT

In the present work, nanocrystalline Gd<sub>2-x</sub>Eu<sub>x</sub>O<sub>3</sub> phosphors have been synthesized by sol-gel method. The effect of Eu<sup>3+</sup> concentration and annealing temperature on structural and luminescence properties of nanocrystalline powders were investigated. X-ray diffraction analyses showed that cubic Eu-doped Gd<sub>2</sub>O<sub>3</sub> was formed and exhibited an average crystallite size ranging from 29nm to 41nm when the annealing temperature varied from 750 to 950°C, respectively. Photoluminescence (PL) measurements verified the presence of all transitions of Eu<sup>3+</sup> dopant, being the <sup>5</sup>D<sub>0</sub> to <sup>7</sup>F<sub>2</sub> transition the most intense. It was also found that, on a common weight basis, the PL intensity was strongly dependent on both the annealing temperature and dopant concentration. The highest PL intensity was observed for 'x'=0.15. The observed quenching in luminescence would result from exchange interactions. Preliminary results on the PL characterization of nanocrystalline Gd<sub>2-x</sub>Eu<sub>x</sub>O<sub>3</sub> thin films are also presented.

**Keywords:** Sol-Gel, Eu<sup>3+</sup>-doped Gd<sub>2</sub>O<sub>3</sub>, nanocrystalline materials, luminescence, quenching.

## 1 INTRODUCTION

Nanosize materials are the focus of attention due to their novel and interesting size-dependent functional properties [1]. In particular, nanosize rare earth (RE)-doped phosphors have become one of the most promising materials because of their fundamental and potential applications including solid state lasers, lighting and immunoassays systems [2,3]. The luminescence in phosphor materials is strongly dependent on both, the type of host and the nature of the dopant species. Then, any effort on the synthesis of RE sesquioxides (RE<sub>2</sub>O<sub>3</sub>), which are considered excellent host lattices for trivalent ions, is justified. One of these oxides, Gd<sub>2</sub>O<sub>3</sub>, is an inorganic insulator with a band gap of 5.4eV [4] and exhibits cubic structure at room temperature. The fact that Gd<sup>3+</sup> is a well known contrast agent for magnetic resonance imaging, (MRI), increases the attractiveness of using RE-doped Gd<sub>2</sub>O<sub>3</sub> nanophosphor as fluorescence and MRI labels [5]. In turn, Europium (Eu<sup>3+</sup>) ions produce a red luminescence characterized by sharp PL peaks associated to

the intra-4f shell transitions <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>J</sub>. This feature enables nanosize Eu<sup>3+</sup>-doped Gd<sub>2</sub>O<sub>3</sub> phosphors to be considered a promising biomarker material. Despite of this fact, there is a lack of systematic studies focused on the synthesis and characterization of this type of nanocrystalline material. Among the various synthesis approaches for nanocrystalline RE-oxides, the sol-gel technique exhibits the advantage of allowing a precise compositional control and homogeneity under moderately low-temperature conditions. Typical sol-gel methods involve the use of chelating agents that may greatly influence the final properties of the materials [6].

Under the above premises, the present work investigated the effects of the annealing temperature and atomic fraction of Eu<sup>3+</sup> ions ('x') on the structural and luminescence properties of nanocrystalline Eu<sup>3+</sup>-doped Gd<sub>2</sub>O<sub>3</sub>. This phosphor was synthesized by using a simple sol-gel method that did not require the use of any chelating agent.

## 2 EXPERIMENTAL

### 2.1 Materials

Required weights of the hydrate acetate salts of Gadolinium and Europium (99%, Alfa Aesar) were dissolved in 2-ethylhexanoic acid (98%, Alfa-Aesar). All reagents were used without further purification. Unlike other related reports, no chelating agent was used in our case.

### 2.2 Synthesis of Nanocrystalline Powders

A modified sol-gel method and subsequent annealing were used to prepare crystalline Gd<sub>2-x</sub>Eu<sub>x</sub>O<sub>3</sub> nanophosphor, with 'x' ranging from 0.01 to 0.30. Suitable amounts of Gd(III) and Eu(III) acetates were dissolved in 2-ethylhexanoic acid. A solid intermediate was obtained after evaporating the solvent at 200°C for 72h. In order to develop the desired structure, the solid intermediate was annealed at different temperatures (750, 850 y 950°C) for 2h and cooled down in air. The annealing temperatures were selected based on previous TG-DTA analyses of the precursor salts [7]. Annealed solids were grounded and submitted to characterization.

### 2.3 Characterization Techniques

Structural characterization of the solids were carried out in a Siemens D500 x-ray diffractometer (XRD) using the Cu-K $\alpha$  radiation. Fourier Transform Infrared (FTIR) measurements were undertaken in a MIRacle TM ATR FTS 1000 spectrometer in the transmittance mode. Photoluminescence spectra were collected using a Spectrofluorometer FluoroMax-2 with a 150mW continuous ozone-free Xe lamp as the excitation source.

## 3 RESULTS AND DISCUSSION

### 3.1 XRD Analyses

Figure 1 shows the XRD patterns of the intermediate before and after annealing at different temperatures. The solids were prepared for a Eu atomic fraction, 'x', of 0.05. Only very sharp peaks corresponding to cubic Gd<sub>2</sub>O<sub>3</sub> phase (JCPDS 12-0797) were identified in the annealed samples. Similar results were observed at different 'x' values [7].

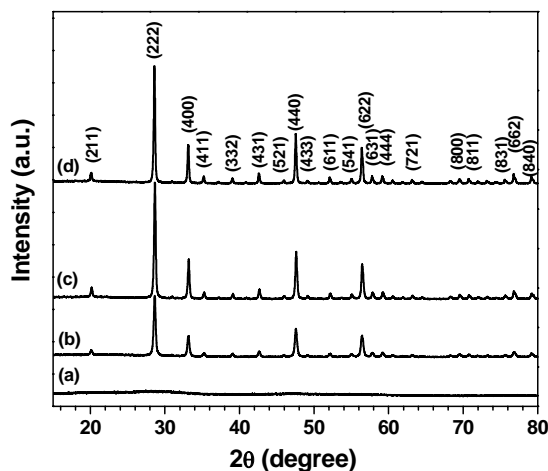


Figure 1: XRD patterns of Gd<sub>2-x</sub>Eu<sub>x</sub>O<sub>3</sub> (x=0.05) solids before (a) and after annealing at 750°C (b), 850°C (c) and 950°C (d). All peaks correspond to cubic Gd<sub>2</sub>O<sub>3</sub>.

The enhancement in the peak sharpness by increasing the annealing temperature would suggest the enlargement of the crystal size in the oxide.

As figure 2 shows, the average crystallite size - estimated by using the Scherrer's equation- were 29nm, 36nm and 41nm when the solids were annealed at 750°C, 850°C and 950°C, respectively. This enlargement in crystallite size with annealing temperature can be explained by the improvement of the inter-grain diffusional processes, involved with grain growth, at higher temperatures. Figure 2 also suggest the negligible influence of Eu<sup>3+</sup> ion content on the crystallite size. This observation agrees with the results reported by Pires, *et al.* [8] in Eu-Gd<sub>2</sub>O<sub>3</sub> synthesized by precipitation.

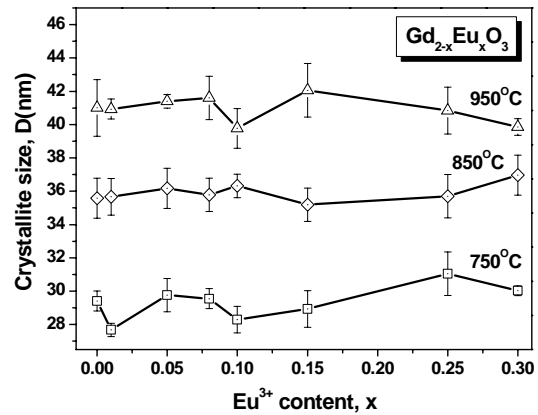


Figure 2: Effect of annealing temperature and Eu<sup>3+</sup> content, 'x', on the average crystallite size of Gd<sub>2-x</sub>Eu<sub>x</sub>O<sub>3</sub> nanocrystalline powders.

x	a (Å)		
	750°C	850°C	950°C
0.00	10.816±0.002	10.817±0.001	10.813±0.001
0.05	10.809±0.004	10.799±0.006	10.816±0.001
0.10	10.818±0.002	10.816±0.001	10.806±0.005
0.15	10.827±0.002	10.822±0.001	10.821±0.001
0.30	10.826±0.002	10.830±0.001	10.825±0.001

Table 1. Variation of lattice parameter of Eu<sup>3+</sup>-doped Gd<sub>2</sub>O<sub>3</sub> powders annealed at different temperatures.

Table 1 shows the negligible variation of the lattice parameter 'a' with the annealing temperature of the oxide produced at different 'x' values. Nevertheless, a small but noticeable increment on the lattice parameter was observed when the 'x' value varied from 0.05 to 0.30. This variation of the lattice parameter can be attributed to the actual substitution of Gd ions (0.94Å, ionic radii) by Eu ions (0.95Å) in the Gd<sub>2</sub>O<sub>3</sub> lattice. The lattice parameter for pure Gd oxide (x = 0.00) is in good agreement with the bulk value (10.813Å).

### 3.2 FT-IR Measurements

The F-IR spectra of the solids produced at different annealing temperatures and x = 0.08 are presented in figure 5. The intense bands centered at 1535cm<sup>-1</sup> and 1419cm<sup>-1</sup> can be assigned to symmetric and asymmetric C=O stretching vibration modes in acetate species, respectively, contained in the intermediate. The spectra of the annealed powders only showed a sharp band at 540cm<sup>-1</sup> that is assigned to the vibration of the Gd-O bond in the Gd<sub>2</sub>O<sub>3</sub> structure. Furthermore, the absence of the acetate bands in the annealed samples suggests the complete thermal decomposition of the intermediate into the oxide structure. Similar spectra were obtained in other doped samples.

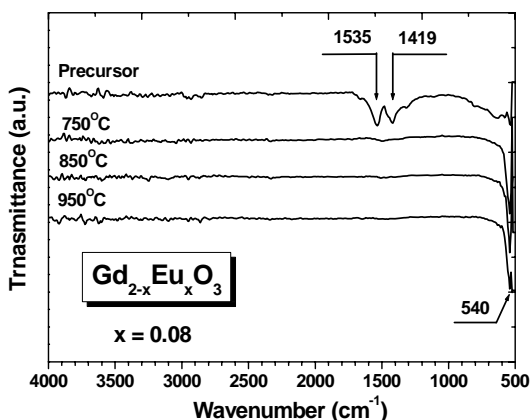


Figure 3: FT-IR spectra of  $\text{Eu}^{3+}$ -doped  $\text{Gd}_2\text{O}_3$  ( $x=0.08$ ) before (precursor) and after annealing at different temperatures.

### 3.3 Photoluminescence Measurements

Figure 4 shows the room temperature (RT) excitation spectra for  $\text{Eu}$ -doped  $\text{Gd}_2\text{O}_3$  ( $x=0.15$ ) annealed at different temperatures. The large band around 250nm corresponds to the  $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$  charge transfer band (CTB). Other weak bands at 274nm and 312nm are related to  $\text{Gd}^{3+}$  transitions promoted by the  $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$  energy transfer process. The weak narrow bands above 330nm are assigned to transitions of  $\text{Eu}^{3+}$  [9]. The rise of the CTB intensity by increasing the annealing temperature is attributed to the enhancement on crystallinity of the solids, as suggested by XRD. Figure 5 shows the RT emission spectra of the solids synthesized at different 'x' values obtained using the CTB (250nm) as the excitation wavelength. Figure 6 summarizes the variation of the relative luminescence intensity at 611nm with 'x' on a common sample-weight basis. As seen, the maximum intensity was obtained at  $x=0.15$ . This 'x' value is smaller than that reported in powders with similar crystallite size (41nm) but synthesized by liquid-phase reaction ( $x=0.20$ ) [10]. Quenching became evident for ' $x$ '>0.15.

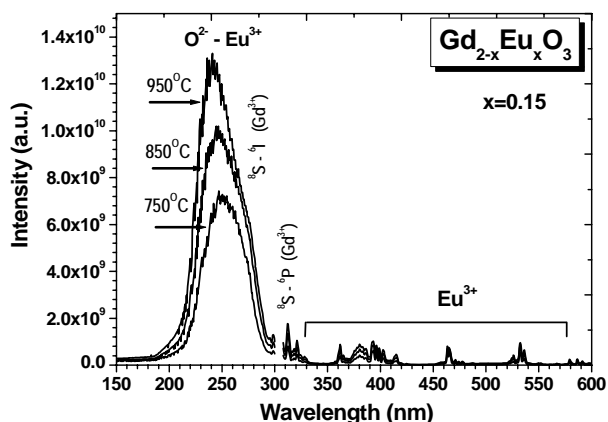


Figure 4: Effect of annealing temperature on excitation spectra of  $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$  powders. The 611nm line was used for monitoring.

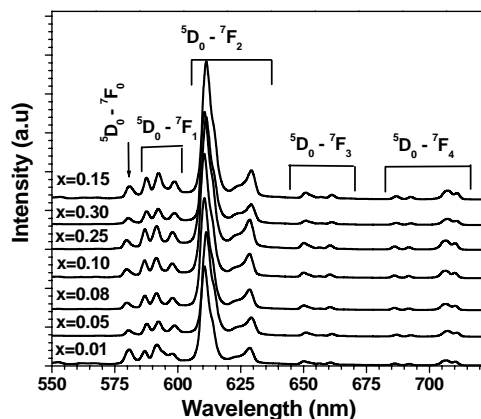


Figure 5: RT-Emission spectra  $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$  powders synthesized at different 'x' values. The samples were annealed at 750°C for 2 hours.

In order to analyze the type of interactions involved with the observed quenching of luminescence, the mutual interactions constant, 's', was determined from the following relationship between the relative emission intensity (I) and the atomic fraction of the dopant species, 'x' [11]:

$$I \propto x^{(1-s/3)} \quad (1)$$

Figure 7 shows the linearized plot of equation (1). The corresponding 's' value was estimated at of 3. This value is in excellent agreement with the one reported by Li and Hong [11]. The same authors proposed that the electric multipole resonant transfer between nearby  $\text{Eu}^{3+}$  ions and exchange interactions should be involved with the observed quenching phenomena.

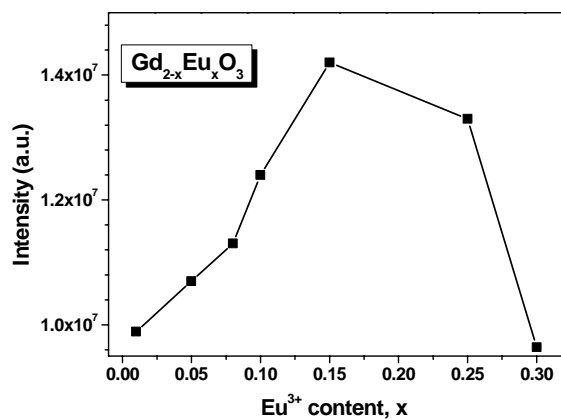


Figure 6: Relation between  $\text{Eu}^{3+}$  atomic fraction, 'x', and luminescence intensity at 611nm under excitation with 250nm radiation. The intensity values were measured from annealed samples on a common weight basis. The quenching phenomenon is evidenced by the drop in the luminescence intensity for ' $x$ '>0.15.

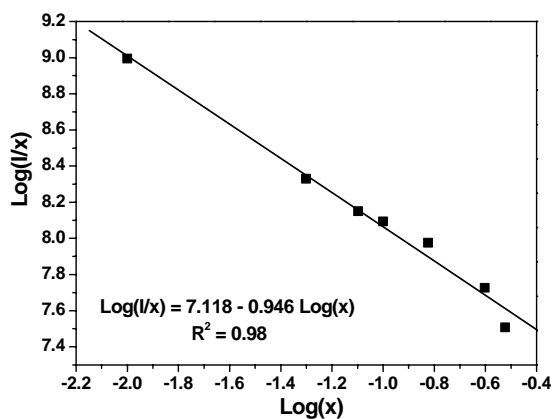


Figure 7: Log(I/x)-Log(x) plot for  $Gd_{2-x}Eu_xO_3$  nanocrystalline powders synthesized at 750°C.

### 3.4 Characterization of Thin Films.

Based on the above preliminary results, the deposition of thin films of  $Gd_{2-x}Eu_xO_3$  ( $x=0.08$ ) onto fused quartz was attempted. The details of the experimental procedure will be published elsewhere [12]. The film exhibited the preferential growth of the (400) crystallographic plane (figure 8). The corresponding average crystallite size and lattice parameter were 22nm and 10.775Å, respectively. Figure 9 shows the RT PL-emission spectra obtained under different wavelength excitation. All emission bands correspond to typical intra shell  $^5D_0-^7F_J$  transitions of  $Eu^{3+}$  ions. The spectra also suggest that the  $Gd_2O_3$  absorption band excitation (229nm) produces the strongest and brightest red emission compared with the conventional direct excitation wavelength (393nm). The inset shows the excitation spectrum of the thin film produced after thermal treatment at 750°C for 1h. Again, the CTB from  $O^{2-}$  to  $Eu^{3+}$ , the weak bands at 274nm and 312nm (related to internal  $Gd^{3+}$  transitions) and those weak bands representing the direct absorption of  $Eu^{3+}$  were observed. However, unlike nanocrystalline powders, a strong band at 229nm was detected. This band can be consequence of the absorption by  $Gd_2O_3$  host [12].

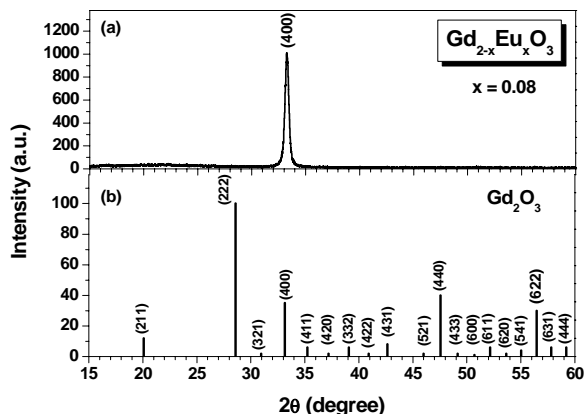


Figure 8: (a) XRD pattern of Eu-doped Gd oxide ( $x=0.08$ ) thin film; (b) standard pattern for  $Gd_2O_3$  cubic phase.

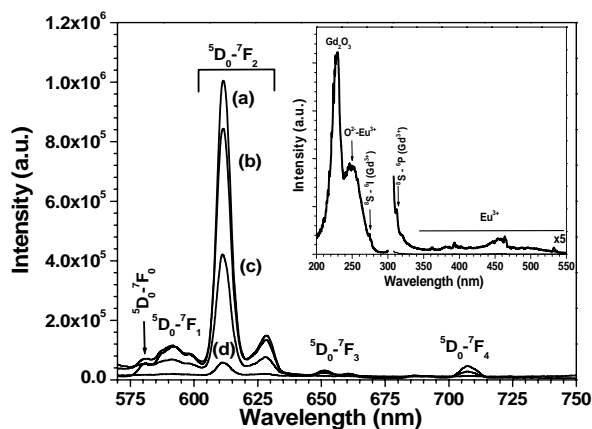


Figure 9: RT Emission spectra of  $Gd_{2-x}Eu_xO_3$  ( $x=0.08$ ) thin film, annealed at 750°C for 1h. The spectra were collected under different excitation wavelengths: (a) 229nm, (b) 248nm, (c) 274nm and (d) 393nm. The inset shows the excitation spectra obtained when the 611 nm line was used.

## 4 CONCLUDING REMARKS

Powders and films of  $Eu^{3+}$ -doped  $Gd_2O_3$  have been successfully synthesized by sol-gel method without the use of any chelating agent. The average particle size varied from 29nm to 41nm when the intermediate was annealed in the temperature range between 750°C and 950°C. PL characterization evidenced the formation of luminescent centers that facilitated the energy transfer from host Gd to Eu ions. The subsequent quenching of the luminescence for ' $x$ '>0.15 was attributed to exchange interactions. PL analyses of the films suggested that excitation by the  $Gd_2O_3$  absorption band would be more effective than direct excitation to obtain red luminescence.

## 5 ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 0351449.

## REFERENCES

- [1] L. Brus, J. Phys. Chem., 90, 2555, 1986.
- [2] G. Blasse, Chem. Mat., 1, 294, 1989; Chem. Mat., 6, 1465, 1994.
- [3] M. Nichkova, et al., Anal. Biochem. 369, 34, 2007.
- [4] H. Guo, et al., Appl. Surf. Sci., 230, 215, 2004.
- [5] D. Dosev, et al., Appl. Phys. Lett. 88, 011906, 2006.
- [6] C. Louis, et al., J. Solid State Chem., 173, 335, 2003.
- [7] S. Jáuregui-Rosas, O. Perales-Perez, W. Jia, M. S. Tomar et al., Presented at MRS Spring Meeting, 2008.
- [8] A.M. Pires, et al., J. Alloys Comp., 344, 276, 2002.
- [9] M. Buijs, et al., J. Lumin. 37, 9, 1987.
- [10] C.-S. Park, et al., J. Lumin. 118, 199, 2006.
- [11] Y. Li and G. Hong, J. Lumin. 124, 297, 2007.
- [12] S. Jáuregui-Rosas, O. Perales-Perez, W. Jia, M. S. Tomar et al., In preparation.