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Effect of crystalline ordering on the luminescent properties of Eu³⁺-doped aluminum oxide nanophosphors



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ABSTRACT

 $Al_2O_3:Eu^{3+}$ nanophosphors were synthesized by the microwave assisted solvothermal technique. The structural and photoluminescence characteristics of alumina powders doped with 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% Eu, calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C for 3 h, were investigated by X-ray diffraction, and reflectance, photoluminescent and X-ray fluorescence spectroscopies. The effects of the calcination temperature on the structure and, in turn of it on the photoluminescence properties are investigated. Luminescent decays curves were measured for the emission ascribed to the ${}^{5}D_{0}$ - ${}^{7}F_{2}$ transition in all the samples and a non-exponential behavior is observed. An increase in the average lifetime correlates well with the formation of the EuAlO₃ perovskite phase as the calcination temperature increases. Judd-Ofelt analyses were performed and

some additional quantities were derived from them such as the radiative and nonradiative transition rates and the emission quantum efficiency. The decrease in the Ω_2 parameter value as the calcination temperature increases is compatible with a higher symmetry around the Eu³⁺ site as well as with a reduction in the Eu³⁺ covalence bonding within this ion into EuAlO₃ perovskite.

1. Introduction

Lanthanide ions are commonly used as activators in several host lattices for their excellent luminescent properties. There is a huge number of applications in which they are used; for example, phosphors for lighting, displays, lasers, scintillators, biosensors, etc. [1–4]. Among lanthanides, the europium has been one of the most extensively used because as trivalent ion (Eu^{3+}) exhibits a strong red emission ascribed to its ${}^{5}D_{0}{}^{-7}F_{2}$ transition. Derived from this feature Eu^{3+} -doped materials have been recognized as efficient luminophores possessing a high potential in some optical fields such as electroluminescence devices, optical amplifiers, polychromatic displays and mercury-free lamps [5–8].

The emission of Eu³⁺ ion is routinely used as a probe of the local structure in host lattices for the following reasons: (1) The Eu³⁺-ground state (⁷F₀) is non-degenerate, and (2) the electronic transitions among ⁵D_J and ⁷F_J -whose energy values are well separated are found in the

spectral region suitable for an optical spectroscopic characterization. Thus, if the ${}^{5}D_{0}{}^{-7}F_{1}$ transition is dominant it is implied that Eu^{3+} ion is in a site with inversion symmetry; this transition shows three emission peaks if Eu^{3+} occupies a site with C₁, C_{2h}, and D_{2h}, point group symmetries. When the Eu^{3+} ion occupies sites with C₄, D_{4h}, D_{3d}, C_{6h} and D_{6h} point group symmetries two emission peaks are observed and only one peak for higher point group symmetries [9–11].

On the other hand, alumina is an important material in many technological developments due to its excellent chemical and physical properties. It is well known for its high hardness, high melting point and good chemical stability [12,13]. Furthermore, alumina has been used as a host matrix for several trivalent lanthanide ions because it has a wide band gap and consequently an optical transparency ranging from the ultraviolet to near infrared region [14].

Regarding the synthesis methods, the microwave assisted solvothermal technique, unlike other techniques as sol gel, combustion, and

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the conventional solvothermal, has the advantage of being a technique with a rapid synthesis rate due to the energy transfer is over localized. This characteristic results in a synthesis time reduction, and also an homogeneous heating is achieved over the entire solution. This technique has other advantages such as its easy scalability, high reproducibility, and good control of the particle size [15].

This work is focused in the investigation of the photoluminescent properties dependence on the crystalline structure of nanosized $Al_2O_3:Eu^{3+}$ powders obtained by the microwave assisted solvothermal technique and their further annealing. In these nanophosphors, Eu^{3+} shows important changes in its photoluminescence features when it is incorporated into amorphous and different alumina crystal structures or in EuAlO₃. Also, the luminescence behavior as a function of the Eu^{3+} content is investigated. High Eu content and high temperatures in the thermal treatments give rise to the EuAlO₃ crystallization, which possesses a perovskite-like structure. In the ABO₃ general chemical formula for like-perovskite compound, the A-larger cation, i.e. the Eu^{3+} , possesses a C_s point symmetry [16].

The dependence of the photoluminescence properties was studied as a function of the annealing temperature and the Eu content, too. Annealing temperatures range from 900 °C to 1200 °C, following incremental steps of 100 °C. Since, so far there is no detailed information in the literature about the luminescent dynamical measurements and their dependence with the crystalline structure of the alumina, especially for the chemical form EuAlO₃. For that reason, in this paper the structural and photoluminescence properties that includes the decay times are also reported. As additional information the radiative properties also were studied by the Judd-Ofelt theory (JO) which was used to predict different parameters such as oscillator strengths, luminescence branching ratios, excited state radiative lifetimes and quantum efficiencies. JOES, an application software was used to analyses the $Al_2O_3Eu^{3+}$ emission spectra in order to obtain the JO intensity parameters and derived quantities [17].

In addition to photoluminescence spectroscopy, and photoluminescence decay measurements the Al_2O_3 :Eu³⁺ powders were characterized by X-ray diffraction, including the quantification of the phases by the rietveld method and reflectance diffuse spectroscopy.

2. Experimental details

2.1. Synthesis

The Al_2O_3 : Eu³⁺ powders were synthetized by the microwave assisted solvothermal technique. The solution was prepared with Al(NO₃)₃.9H₂O (98%, Sigma-Aldrich, USA) and EuCl₃.6H₂O (99.9%, Sigma-Aldrich, USA). Both precursors were dissolved in ethanol (ACS reagent, J.T. Baker, USA) for 10 min until a homogeneous solution was reached. Four different concentrations of europium, namely 0.012 mol/L, 0.015 mol/L, 0.018 mol/L and 0.03 mol/L but maintaining a total (Eu + Al) concentration of 0.150 mol/L were used. Accordingly, the samples were prepared using a total volume of 30 mL and the following Al(NO₃)₃.9H₂O/ EuCl₃.6H₂O mass relations: 1.5532 g/0.1319 g, 1.5193g/0.1649 g, 1.4855 g/0.1978 g and 1.3505 g/0.3298 g, respectively. Each one of the mixed solutions were placed into a borosilicate vial, which was tightly closed and placed into a microwave reactor. For the synthesis, the solution was kept at 160 °C for 20 min. The as-synthesized product obtained after the solvothermal-microwave assisted procedure took place was a gel, subsequently separated by centrifugation and dried at 200 °C for 2 h. Finally, the solid material was grinded and calcined for 3 h at 900 °C, 1000 °C, 1100 °C and 1200 °C.

2.2. Characterization

The crystal structure of Al_2O_3 :Eu³⁺ powders was established by X-ray diffraction performed in a Bruker D-8 Advance diffractometer fitted with a CuK α tube and a one-dimensional position-sensitive silicon strip

detector (Bruker, Lynxeye) [18]. The diffraction patterns were measured between 15° and 108° , with a 2θ step of 0.020° and a counting time of 115.20 s per point, and subsequently refined by the Rietveld method, implemented in the TOPAS software, version 4.2 [19] using the fundamental parameter approach [20]. In order to parametrize the whole pattern fittings, a Lorentzian profile for modeling the average crystallite size, lattice parameters, crystal symmetry, and ion positions into the crystal cell, among others, were used.

The emission and excitation spectra, and the luminescent decay curves were recorded with an Edinburgh Instruments FSP920 spectrofluorometer based on the method of single photon counting which combines steady state and phosphorescence lifetime measurements. In the latter, the electronics operate in multichannel scaling mode. The spectrofluorometer is equipped with a 450 W xenon lamp as a CW light source and an R928P PMT as a detector. In order to avoid the light dispersion, a double monochromator (two coupled 0.3 m) was employed to excite the samples. The emission was detected using a 0.3 m monochromator. All the excitation and emission spectra were corrected for the wavelength dependent responses of the Xe lamp and the detector, respectively. For the measurements of the luminescence decay curves, the excitation photons were provided by a 60 W µF920H pulsed Xe flash lamp with a pulse width of \sim 1.5 µs and a repetition rate of 100 Hz. The absorption spectra were obtained by using the diffuse reflectance technique. The measurements were performed in a Cary 5 spectrophotometer equipped with a Praying Mantis accessory (Harrick Scientific Products, Inc.) for diffuse reflection spectroscopy. The spectra were recorded in the wavelength range from 200 nm to 800 nm. The morphology of the samples was characterized by spherical aberration-corrected scanning transmission electron microscopy (ARM200F, JEOL). For these studies, the powder was ultrasonically dispersed in isopropanol and a drop of the suspension was deposited on a carbon-coated copper grid.

3. Experimental results and discussion

3.1. Crystalline structure

The X-ray diffraction patterns of Al₂O₃:Eu³⁺ powders doped at 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% Eu and calcined at 900 °C, 1000 °C, 1100 $^\circ C$ and 1200 $^\circ C$ are shown in Fig. 1. Figs. 1a and b depict the XRD patterns of alumina powders doped with the lower contents of europium (6.4 at.% and 7.5 at.% Eu) which have similar characteristics when calcined at 900 °C. In both samples a mix of amorphous and γ -Al₂O₃ phases is found. The first crystalline phase to appear is y-Al₂O₃ (JCPDS file No. 01-074-4629). By increasing the temperature of the thermal treatment at 1000 °C, a second crystalline phase (EuAlO₃) begins to be formed, but a poor signal associated with this phase is observed. However, at 1100 °C it is evident the formation of EuAlO₃, the narrower peaks assigned to this phase become more pronounced and defined at this temperature, being a clear evidence that the quantity of EuAlO₃ increases with the temperature. When the powders are calcined at 1200 °C the wt% fraction of amorphous component decreases substantially, conversely to what happens to the EuAlO3 phase. For these samples a mix of amorphous, y-Al₂O₃ and EuAlO₃ phases is observed.

Fig. 1c and d shows the XRD patterns obtained from powders with 9.5 at% and 13 at.% Eu after being subjected to thermal treatments at 900 °C, 1000 °C, 1100 °C, and 1200 °C. In these figures, it may be observed the changes in the crystalline structure produced when the temperature rises. For these samples, with a higher Eu content and annealed at the lowest temperature (900 °C), a γ -Al₂O₃ –delayed or absent formation is observed, which is more evident for the sample with 13 at.% Eu. In this case, only an amorphous structure is observed. The same powders calcined at 1000 °C have peaks centered at about 45.5° and 66.6°, in 20, corresponding to the tetragonal γ -Al₂O₃ phase, also at this temperature peaks become more clearly defined when both, the annealing temperature and the europium content increase. Powders with 9.5 at.% Eu



Fig. 1. X-ray diffraction patterns from a) 6.4 at.%, b) 7.5 at.%, c) 9.5 at.% and d) 13 at.% Eu-doped alumina nanophosphors annealed at 900 °C, 1000 °C, 1100 °C and 1200 °C.

calcined at 1100 $^\circ C$ have a very small signal associated with the amorphous phase. The amorphous component decreases as the annealing temperature increases until at 1200 $^\circ C$ it finally seems to disappear.

Due to the presence of more than one amorphous or crystalline phase in the powders, Rietveld analyses were performed in order to determine the concentration of the phases, but also these analyses allow for quantifying the average crystallite size and the cell parameters of all the samples. Once each phase, crystalline or amorphous was identified, they were described as follows. The γ -Al₂O₃ unit cell was modeled assuming a tetragonal symmetry according to the space group *I*41/*amd* [21]; the EuAlO₃ unit cell was modeled with an orthorhombic symmetry described by the *Pbnm* space group (# 62), and a basis containing one Eu³⁺ at (*x*, *y*, ¹/₄), one Al³⁺ at ($\frac{1}{2}$, 0, 0) and two O²⁻ at (*x*_{OI}, *y*_{OI}, ¹/₄) and at (*x*_{O2}, *y*_{O2}, *z*_{O2}). Initial values for the cell parameters and variable coordinates were those ones reported in Ref. [22]. Quantifying amorphous components by whole XRD pattern fitting procedures represents a challenge because the factor structure which is necessary to weight the concentration of a phase, and straightforwardly obtained when a crystalline unit cell is known, is, for all practical purposes unavailable for amorphous phases. Different approaches to overcome such difficulty have been proposed,

but most of them require the use of internal or external standards [23]. In order to avoid the use of those standards, we opted to model the contribution to the XRD pattern of the amorphous phase from an Al₂O₃ crystalline phase. The β-Al₂O₃ one was the best to describe that contribution, and "amorphization" was given by reducing the crystallite size through the refinement procedure until a reasonable agreement between experimental and calculated X-ray diffraction intensities was reached. So that, the β -Al₂O₃ unit cell was modeled with a monoclinic structure symmetry described by the C2/m space group (# 12) and a basis containing two Al³⁺ at (x_{Al1} , 0, z_{Al1}) and at (x_{Al2} , 0, z_{Al2}) and tree O²⁻ at (x_{O1} , $(0, z_{01}), (x_{02}, 0, z_{02})$ and at $(x_{03}, 0, z_{03}), (\text{JCPDS file No. 04-002-2602})$ [24]. Parameters such as the unit cell dimensions, atomic positions and the size-crystallite-related were refined in order to achieve the best fit to the observed pattern associated with the amorphous component. However, only the wt% fraction obtained from the Rietveld refinement for this component was taken into account. The results about the phases quantification and unit cell parameters are reported in Tables 1 and 2, respectively.

The results obtained from the Reitveld analyses on the weight percentages of the different phases, given in Table 2, allows a direct comparison with the qualitative observations. On one hand, EuAlO₃ phase markedly increases as the annealing temperature and europium content increase, on the other hand, the γ -Al₂O₃ concentration phase has a reduction for powders calcined at 1100 °C. When the annealing temperature rises at 1200 °C the amorphous and γ -Al₂O₃ phases are reduced for powders with Eu contents of 6.4 at.% and 7.5 at.%, and particularly the amorphous phase suffers a drastic reduction in their weight percentages finally disappearing in the cases of samples with 9.5 at.% and 13 at. % Eu. Fig. 2 shows representative plots from among all resulting refinement analyses corresponding to Al₂O₃ powders doped with 9.5 at.% Eu, calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C, a good agreement between experimental and calculated data is observed.

3.2. STEM

STEM observations of the annealed samples revealed that the powders consist of agglomerates of nanoparticles, with individual sizes less than 50 nm, several micrographs were obtained for a small set of samples and their detailed characteristics were reported in a previous work [25]. However, annular dark-field imaging also was obtained by scanning transmission electron microscopy (STEM) with high spatial resolution. For illustrative purposes only two micrographs corresponding to $Al_2O_3:Eu^{3+}$ powders doped with 7.5 at.% Eu calcined at 900 °C and 1200 °C are shown (Fig. 3). The morphology is similar between them (Fig. 3a

Table 1

Quantification of crystalline phases in powders with 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% of Eu annealed at 900 °C, 1000 °C, 1100 °C and 1200 °C.

at.%			Phase qua	vt. %)		
Eu	Annealing Temperature (°C)	Phases found	Amorphous Al ₂ O ₃	γ -Al ₂ O ₃	●EuAlO ₃	
6.4	900	$A + \gamma$	90.9	9.1	0	
	1000	$A{+}\gamma + \bullet$	80.4	18.9	0.7	
	1100	$A\!\!+\!\gamma + \bullet$	76.9	21.7	1.4	
	1200	$A{+}\gamma + {\textcircled{\bullet}}$	64.9	33.6	1.5	
7.5	900	$A + \gamma$	88.6	11.4	0	
	1000	$A{+}\gamma + {\textcircled{\bullet}}$	71.6	26.8	1.5	
	1100	$A{+}\gamma + {\textcircled{\bullet}}$	56.4	41.8	1.8	
	1200	$A{+}\gamma + {\textcircled{\bullet}}$	56.1	35.3	8.6	
9.5	900	Α	100	0	0	
	1000	$A{+}\gamma + {\textcircled{\bullet}}$	86.7	11.0	1.3	
	1100	$A{+}\gamma + {\textcircled{\bullet}}$	80.9	14.8	3.7	
	1200	$\gamma + ullet$	0	88.5	11.5	
	900	Α	100	0	0	
13	1000	$A\!\!+\!\gamma + \bullet$	88.9	10.0	1.1	
	1100	$A{+}\gamma + {\textcircled{\bullet}}$	50.15	40.3	9.6	
	1200	$\gamma + ullet$	0	73.0	27.0	

Table 2

Unit cell parameters and average crystallite size (nm) calculated for the crystalline phases in alumina powders with 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% of Eu annealed at 900 °C, 1000 °C, 1100 °C and 1200 °C. The different space groups (s.p.) are indicated.

at.%	Annealing	Latt	Crystallite				
Eu	Temperature		Size (nm)				
	(°C)						
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~							
64	900	5 503(42)	5 50(42)	7 95(12)	23		
0.1	1000	5 568(11)	5 568(11)	7 977(31)	44		
	1100	5 568(19)	5 568(19)	7 928(30)	55		
	1200	5 539(4)	5 539(4)	7 936(5)	38		
	1200	EnAl	$O_2$ (s.p. Phnn	) )	50		
	900	<b>EUAIO</b> ₃ ( <b>5.p.</b> <i>Poluli</i> )					
	1000	4 939	4 939(68)	7 43(11)	5		
	1000	(68)	1.555(66)	7.10(11)	0		
	1100	5 274(4)	5.274(4)	7 464(5)	5		
	1200	5 290(2)	5 290(2)	7.462(3)	5		
75	1200	ν-Al ₂ O	(s.n. 141/a)	nd)	0		
7.0	900	5 573(17)	5 573(17)	8 150(44)	33.0		
	1000	5 556(7)	5 556(7)	8.056(16)	34.6		
	1100	5 558(8)	5 558(8)	7 98(15)	42.1		
	1200	5 5 9 1 (49)	5 581(48)	7.90(13)	70.8		
	1200	5.501(40) F11A1	$O_{\alpha}$ (s n Phnn	3.381(48) 7.90(14)			
	900	-		-	_		
	1000	5 250(9)	7 517(17)	5 298(15)	10.5		
	1100	5 203(3)	7 442(7)	5 263(3)	42.4		
	1200	5.293(3) 5.281(2)	7.442(7) 7.468(8)	5.203(3) 5.281(1)	66.6		
95	1200	1200 $3.201(2)$ $7.400(8)$ $3.201(1)$					
5.5	900	γ-A1 ₂ O ₃ (s.p. 141/ <i>uniu</i> )					
	1000	5 570(10)	5 570(10)	7 976(21)	70 1		
	1100	5 569(9)	5 569(9)	7 934(23)	92.2		
	1200	5.60(23)	5.60(23)	7.93(50)	24.0		
	1200	5.00(25) F11A1	24.0				
	900				_		
	1000	5 286(2)	7 468(2)	5 268(2)	38.8		
	1100	5.570(10)	7.465(8)	5.200(2) 5.272(1)	41.8		
	1200	5 2020(4)	7 4580(5)	5 2762(2)	52.7		
13	1200		(sn I41/a)	nd)	55.7		
10	900	7 1120		_	_		
	1000	5 66(35)	5 66(35)	7 97(96)	28.0		
	1100	5 549(2)	5 549(2)	8 024(6)	47.8		
	1200	5 549(2)	5.549(2)	8.024(6)	30.7		
	1200	E11A1	$O_2$ (s.n. Phnn	)	00.7		
	900	-	- -	_	_		
	1000	5 282(3)	7 468(4)	5 261(5)	33.1		
	1100	5 293(4)	7 461(7)	5 272(4)	67.3		
	1200	5.2942(4)	7,4561(5)	5.2769(3)	46.7		
	1200	2.22.20(1)					

and c) but by Z-contrast images (Fig. 3b and d), the distribution of the europium ion can be distinguished in both images. In powders calcined at 900 °C, the Eu element is localized in an homogeneous way although in an amorphous structure, unlike the sample calcined at 1200 °C where saturated areas of europium are observed in a crystalline structure, this characteristic is responsible of the concentration quenching in the emission intensity and probably also corresponds to areas where  $\rm Eu^{3+}$  is in the EuAlO₃ phase.

#### 3.3. UV-vis DR spectra

The UV–vis absorbance spectra of the Eu³⁺ doped Al₂O₃ powders calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C were obtained by the diffuse reflectance technique and they are shown in Fig. 4. BaSO₄ was used as a reference standard material for measuring the absorbance spectra. All the samples exhibit a broadband centered at 260 nm corresponding to the charge transfer from the, either the ligand-metal (O²⁻Eu³⁺) of the oxygen 2*p* orbital to the Europium 4*f* orbital or due to an 4*f*⁶ to 4*f*⁷ O^{1–} transition. From these spectra it is also possible to observe a set of sharp peaks in the 350 nm–600 nm range ascribed to the Eu³⁺ 4*f*-4*f* transitions. The absorption peaks may be assigned to the electric dipolar transitions: ⁷F₀ → ⁵D₄ at 362 nm, ⁷F₀ → ⁵G₂ at 377 nm, ⁷F₁ → ⁵L₆ at 394



Fig. 2. Rietveld refinement plots of Al₂O₃ powders doped with 9.5 at.% Eu, calcined at a) 900 °C, b) 1000 °C, c) 1100 °C and d) 1200 °C.

nm,  ${}^7F_1 \rightarrow {}^5D_3$  at 415 nm,  ${}^7F_0 \rightarrow {}^5D_2$  at 465 nm,  ${}^7F_0 \rightarrow {}^5D_1$  at 526 nm this is a magnetic dipolar transitions and  ${}^7F_1 \rightarrow {}^5D_1$  at 535 nm.

#### 3.4. Photoluminescence properties

The photoluminescence response of the alumina nanophosphors doped with 6.4 at. %, 7.5 at. %, 9.5 at. % and 13 at. % of Eu calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C were investigated through emission and excitation spectra and luminescence decay curves. Fig. 5 shows the emission spectra for all concentrations and annealing temperatures upon excitation wavelength at 393 nm. Spectra are grouped depending on their features; hence, those ones having similarities are plotted together. The first group (Fig. 5(a)) includes emission spectra of samples doped at all at.% Eu and calcined at 900 °C and 1000 °C, i.e., at the lower annealing temperatures. All the emission spectra of this group exhibit the splitting of the maximum band, ascribed to the  ${}^{5}D_{0}-{}^{7}F_{2}$ transition, in two peaks at 613 nm and 616 nm, and in most cases the 613 nm emission peak is slightly higher. When these powders are calcined at 900 °C, the highest emission intensity is observed for the sample with the larger amount of europium (13 at.% Eu). However, the emission intensity in this sample is reduced when microstructural changes in the material are induced by increasing the annealing temperature as we have explained previously.

The reduction in the emission intensity may be associated with two factors; the first of them is related to the well-known concentration quenching effect, given by the actual Eu concentration (mass Eu/total mass compound) increase into the samples, while the second one is related to the changes in the crystalline structure induced by the temperature increasing of the heat treatments. Actually, the latter phenomenon has already been reported in a previous work but in powders calcined at 1000  $^{\circ}$ C [25].

Unlike Fig. 5(a), in Fig. 5(c) the emission spectra of alumina nanophosphors doped with 6.4 at. %, 7.5 at. % calcined at 1200 °C and 9.5 at.% Eu and 13 at.% Eu calcined at 1100 °C are included, from this figure it is possible to recognize a splitting into four peaks of the  ${}^{5}D_{0}{}^{-7}F_{2}$  transition, this behavior is the result of the change in the Eu³⁺ ion local environment. In Fig. 5(d) it is possible to observe the emission spectra of two samples that have the maximum Eu content (9.5 at.% and 13 at.%) calcined at 1200 °C. In these samples, EuAlO₃ is the dominant phase and this fact is reflected in the emission spectra shape through the well-defined peaks at 613 nm and 617 nm. Since the strongest emission of the powders is mainly due to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition, Eu³⁺ should be occupying non-centrosymmetric sites.

Fig. 6 shows the excitation spectra for alumina powders doped at 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% Eu calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C. All the excitation spectra were measured monitoring at 616 nm. They exhibit several sharp peaks associated with the following transitions between the different electronic energy levels of the Eu³⁺:  $^{7}F_{0} \rightarrow ^{5}H_{6}$  (319 nm),  $^{7}F_{0} \rightarrow ^{5}D_{4}$  (362 nm),  $^{7}F_{0} \rightarrow ^{5}G_{3}$  (381 nm),  $^{7}F_{1} \rightarrow ^{5}L_{6}$  (395 nm),  $^{7}F_{1} \rightarrow ^{5}D_{3}$  (413 nm),  $^{7}F_{0} \rightarrow ^{5}D_{1}$  (464 nm) and  $^{7}F_{0} \rightarrow ^{5}D_{0}$  (526 nm) dipolar magnetic and  $^{7}F_{1} \rightarrow ^{5}D_{1}$  at 535 nm. The excitation spectra were also grouped in four different sets. In Fig. 6(a) are depicted the spectra that have a broad peak centered at around 270 nm, which is ascribed to an Eu³⁺-O₂- charge transfer (CT) state. This excitation band diminishes for higher temperatures and Eu³⁺ concentration. In Fig. 6(b) it is observed a shoulder in the charge transfer band around 300 nm, which is more pronounced for the excitation spectra in Fig. 6(c). Since surprisingly there is no report in which unambiguously the luminescent



Fig. 3. Annular dark-field imaging by scanning transmission electron microscopy (STEM) for Al₂O₃:Eu³⁺ powders doped with 7.5 at.% Eu calcined at a) 900 °C and b) 1200 °C.

properties of  $Eu^{3+}$  are presented in a single phase  $EuAlO_3$  compound (see Fig. 6 d), in our opinion this band should be associated with an  $O_2^{-}-Eu^{3+}$ -CT state in  $EuAlO_3$ . Despite this band has been observed in other reports where the  $EuAlO_3$  phase is formed, it was not associated with an  $O^{2-}$  $Eu^{3+}$  charge transfer process. Yuya et al. have showed excitation spectra for  $EuAlO_3$  phosphor where a broad band centered at around 295 nm is present [26]. Analogous results have been reported by Yue Hu et al. in  $Al_2O_3$ : $Eu^{3+}$  system where a strong broadband in the wavelength range from 255 nm to 320 nm is also present; however, they assume that the change in this band from 255 nm to lower energies is related to the  $Eu^{3+}$ - $O_{2-}$  bond length reduction [27].

#### 3.4.1. Phtotoluminescence decay

The luminescence decay curves were obtained for alumina powders doped at all at.% Eu concentrations, and annealing temperatures. Fig. 7 illustrates the behavior of the normalized luminescence decay curves for all samples. The experimental decay curves show a strong dependence on the Eu³⁺ doping content and calcination temperature, but all of them can be fitted by two single exponential decays. In this figure are shown the photoluminescence decays plots ln I vs t. It is possible to observe essentially four groups of decay times. Fig. 7(a) includes the powders with 6.4 at.%, 7.5 at.% and 13 at.% Eu calcined at 900 °C and 1000 °C, as well as powders with 9.5 at.% Eu calcined at 900 °C. In this first group, it is seen the quenching concentration effect. This behavior has been associated with an energy migration increase among Eu³⁺ ions, as the europium content increases since the Eu³⁺-Eu³⁺ inter-ionic distance is reduced. This phenomenon has been reported in a previous work [25]. In Fig. 7(b) the decay times have almost the same behavior, the description of the luminescence dynamics through a bi-exponential decay model is compatible with the presence of at least two different chemical environments around the  $Eu^{3+}$ . Intriguingly the XRD patterns of these samples exhibit a mix of amorphous, gamma and EuAlO₃ phases. This group have similar characteristics to those depicted in Fig. 7(c), however the non-exponential behavior is more pronounced for these samples.

The experimental decay data are analyzed by fitting the experimental data using the expression [28]:

$$I(t) = \sum_{i} a_{i} \exp\left(-\frac{t}{\tau_{i}}\right) \tag{1}$$

with

$$\sum a_i = 1 \tag{2}$$

When the decay curve is not a single exponential, an average lifetime can be calculated from the following equation:

$$\tau_{av} = \frac{\sum_{i} a_i \tau_i^2}{\sum_{i} a_i \tau_i} \tag{3}$$

The average lifetime  $(\tau_{av})$  values are included in Table 3. From these results, it can be observed a reduction in the average decay times for powders calcined at 900 °C and 1000 °C (Fig. 8(a)) as the Eu³⁺ concentration increases. This behavior, attributed to an increase in the non-radiative decay rate, and further supported by the decrease in the luminescence emission intensity, also when Eu³⁺ concentration increases, is well-correlated with a concentration quenching effect (Fig. 9). On the



Fig. 4. Absorption spectra of  $Al_2O_3$ : Eu³⁺ powders doped with a) 6.4 at.%, b) 7.5 at.%, c) 9.5 at.% and d) 13 at.% of Eu calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C.



Fig. 5. Emission spectra for Eu³⁺-doped alumina nanophosphors with 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% of Eu calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C.

other hand, powders calcined at 1100 °C and 1200 °C show a different behavior, in these cases the decay time become slower (Fig. 8(b)) and there is a tendency to a linear behavior decay related to the predominance of the EuAlO₃.

# 3.4.2. Judd-Ofelt parameters

The Judd–Ofelt (JO) analysis is a useful tool for assessing the luminescence performance in lanthanides -doped materials [29,30]. The JO intensity parameters are the conspicuous information derived from the



Fig. 6. Excitation spectra for Eu³⁺-doped alumina nanophosphors with 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% of Eu calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C.

analysis that give relevant information about the local structure and bonding around the lanthanide ions [31].

The emission spectra of a lanthanide ion produced by the radiative relaxation from an excited state  $\Psi J$  to several lower lying states  $\Psi 'J'$  give place to the different bands in such spectra. From the JO theory the spontaneous emission probability A of the transition  $\Psi J \rightarrow \Psi'J'$  can be expressed by the equation:

$$A(\Psi J, \Psi' J') = \frac{64\pi^4 \tilde{v}^3}{3h(2J+1)} \left[ \frac{n(n^2+2)}{9} D_{ED} + n^3 D_{MD} \right]$$
(4)

Where *h* is the Planck's constant,  $\tilde{v}$  is the average transition energy in cm⁻¹, 2J + 1 is the degeneracy of the initial state, *n* is the medium's refractive index, and D_{ED} and D_{MD} are the electric and magnetic dipole strengths, respectively. As pointed above, the luminescence of Eu³⁺ is mainly the result of transitions from the ⁵D₀ excited electronic state to the lower ⁷F_j levels. The transitions from ⁵D₀ to ⁷F_{0,3,5} are strictly forbidden by the Laporte's rule, which implies that D_{ED} and D_{MD} should be zero. However, this selection rule is relaxed for lanthanides embedded in a host, due to the transitions can be partly allowed by some phenomena such as vibronic coupling, the non-centrosimetric distortion of the lanthanide site ocupation, of via mixing of higher configurations into the 4f wavefunctions by the crystal-field effect [32].

The transition  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  is the only magnetic dipole transition that has no electric dipole contribution, this transition is independent of the local ion environment and its value is  $D_{MD} = 9.6 \times 10^{-42} esu^{2} cm^{2}$  [33]. The  ${}^{5}D_{0} \rightarrow {}^{7}F_{2,4,6}$  transitions are forced electric dipole allowed and the strength of all induced dipole transitions is determined by the following equation:

$$D_{ED} = e^2 \sum_{\lambda=2, 4,6} \Omega_{\lambda} |\Psi J| |U^{(\lambda)}| |\Psi' J'|^2$$
(5)

where  $\Omega_{\lambda}$  are the JO parameters, e is the elementary charge and  $|\Psi J||U^{(\lambda)}||\Psi'J'|^2$  are the squared reduced matrix elements. In the case of Eu^{3+} most of the matrix elements are zero, except for the transitions  ${}^5D_0 \rightarrow {}^7F_2$ ,  ${}^5D_0 \rightarrow {}^7F_4$  and  ${}^5D_0 \rightarrow {}^7F_6$  for which those element are  $U^{(2)} = 0.0032$ ,  $U^{(4)} = 0.023$  and  $U^{(6)} = 0.0002$ , respectively.

JOES software allows the implementation of JO analysis in a very simple way from emission spectra of Eu³⁺-doped compounds, thus it is possible to obtain important data related to the luminescent properties of our compounds, such as the radiative lifetime, branching ratios, stimulated emission cross section, luminescence quantum efficiency and optical gain [17], some of these parameters obtained from the Judd-Ofelt analyses are listed in Table 3. Since, the  ${}^{5}D_{0}{}^{-7}F_{6}$  transition was not observed in the present case, its J–O associated parameters could not be evaluated.

The observed lifetime obtained experimentally, takes into account both radiative  $(A_r)$  and non-radiative  $(A_{nr})$  rates and it is mathematically expressed as:

$$\tau = \frac{1}{A_{nr} + A_r} \tag{6}$$

Theoretical radiative lifetime is obtained directly from the emission spectrum and it is given by the following equation:

$$\tau_{rad}^{th} = \frac{n_1^{-3} J_1}{14.65 J_{tot}}$$
(7)



**Fig. 7.** Photoluminescence decay curves for Al₂O₃:Eu³⁺ powders calcined at different temperatures divided in four groups according to their behavior. (a) 6.4 at.%, 7.5 at.%, 9.5 at.%, 13 at.% of Eu calcined at 900 °C (b) 6.4 at.%, 7.5 at.% of Eu calcined at 1100 °C and 9.5 at.% Eu calcined at 1000 °C, (c) 6.4 at.% and 7.5 at.% of Eu calcined at 1200 °C, 9.5 at.% and 13 at.% of Eu calcined at 1100 °C. (d) 9.5 at.% and 13 at.% of Eu calcined at 1200 °C.

Fable 3
JOES output data for alumina nanophosphors doped with 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% Eu ³⁺ calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C.

	6.4 at.% Eu3+			7.5 at.% Eu3+				
Temperature (°C)	900	1000	1100	1200	900	1000	1100	1200
$\Omega_2 \ [10^{-20} \ { m cm}^2]$	7.208	7.200	6.984	6.598	7.364	7.050	7.0129	6.483
$\Omega_4 \ [10^{-20} \ \mathrm{cm}^2]$	4.773	4.654	5.053	4.840	4.885	4.815	4.960	5.026
$\beta_{exp}({}^{5}D_{0} \rightarrow {}^{7}F_{1})$	0.132	0.133	0.134	0.137	0.130	0.134	0.134	0.137
$\beta_{exp}$ ( ⁵ D ₀ $\rightarrow$ ⁷ F ₂ )	0.592	0.592	0.578	0.138	0.594	0.584	0.580	0.549
$\tau_{th}$ [ms]	1.912	1.916	1.930	1.978	1.878	1.930	1.929	1.980
$\tau_{av}$ [ms]	2.111	2.123	2.128	2.226	2.072	2.137	2.133	2.231
A _R	473.783	470.960	469.865	449.204	482.659	468.004	468.840	448.147
A _{NR}	284.464	485.465	350.627	679.668	268.966	783.090	1040.549	562.515
η x 100 (%)	69	54	63	45	71	41	34	50
Asymmetric ratio	4.985	4.985	4.933	4.869	4.968	4.944	4.931	4.899
	9.5 at.% Eu3+	-			13 at.% Eu3+			
Temperature [°C]	900	1000	1100	1200	900	1000	1100	1200
$\Omega_2 \ [10^{-20} \ {\rm cm}^2]$	7.277	7.097	6.751	6.764	7.148	7.137	6.936	6.670
$\Omega_4 \ [10^{-20} \ \mathrm{cm}^2]$	4.863	4.952	4.760	3.824	4.640	5.013	5.215	4.394
$\beta_{exp}({}^{5}D_{0} \rightarrow {}^{7}F_{1})$	0.131	0.132	0.137	0.139	0.134	0.131	0.132	0.140
$\beta_{exp}$ ( ⁵ D ₀ $\rightarrow$ ⁷ F ₂ )	0.592	0.582	0.572	0.582	0.596	0.581	0.567	0.577
$\tau_{\rm th}$ [ms]	1.896	1.910	1.980	2.006	1.941	1.898	1.909	2.016
$\tau_{av}$ [ms]	2.090	2.116	2.204	2.247	2.136	2.105	2.123	2.258
A _R	478.449	472.463	453.574	445.016	468.145	475.107	470.944	442.915
A _{NR}	764.497	978.179	815.541	381.997	411.920	1204.380	280.664	411.465
η x 100 (%)	42	36	40	60	59	31	70	58
Asymmetric ratio	4.917	4.917	4.9	4.885	4.897	4.902	4.899	4.886

Where n is the refractive index, and  $J_k = \int I_K (\tilde{\nu}) d\tilde{\nu}$  is the integrated intensity of the  ${}^5D_0 \rightarrow {}^7F_{\kappa}$ , transition, where  $\kappa = 1, 2, 4, 6$ .

The Judd-Ofelt parameters provide information on the chemical

bonding and the chemical environment of the ion. The  $\Omega_2$ , for example, is a structure-sensitive parameter and depends on the covalence of the Eu³⁺ site [33]; an increase in the value of  $\Omega_2$  indicates a high covalence



Fig. 8. Behavior of the average time decay constants (listed in Table 3) as a function of the europium content in the nanophosphors calcined at (a) 900 °C and 1000 °C (b) 1100 and 1200 °C.



Fig. 9. Integrated emission intensity from all the nanophosphors calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C.

between the Eu³⁺ ion and the surrounding O²⁻ as well as low symmetry at the Eu³⁺ site [34]. On one hand, a variation in  $\Omega_2$  is an indicator of the change in the local environment; on the other hand,  $\Omega_4$  and  $\Omega_6$  are related to the viscosity and rigidity of the host matrix in which the ions are located. The structural changes in the vicinity of the Eu³⁺ ion in a short and long range are related to  $\Omega_2$  and  $\Omega_4$ , respectively. In Fig. 10 ((a) and (b)) is illustrated the variation of the  $\Omega_{2,4}$  parameters as a function of the annealing temperature. The changes on  $\Omega_2$  (Fig. 10 (a)) from high to low values as calcination temperature increases show that the system shifts from low to high symmetry, and that the chemical covalence is reduced.

Branching ratios, also shown in Fig. 10 ((c) and (d)), may be used to predict the relative intensities of all emission lines originating from a given excited state [15]. The theoretical branching ratio is obtained from the JO theory according to the equation:

$$\beta_k^{th} = \frac{A_k}{\sum A_k} \tag{8}$$

These parameters also can be calculated from the emission spectra because they are ratios of the integrated intensities,

$$\beta_k^{exp} = \frac{J_k}{J_{tot}} \tag{9}$$

Experimental branching ratios were obtained directly from the emission spectra since these parameters are the fraction of the total photon flux from an upper to a lower level [35] In this case, theoretical and experimental  $\beta$  for  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions are plotted (Fig. 10 (c) and (d)). For the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition the branching ratio

increases with the calcination temperature, nevertheless the branching values are lower than 0.5, indicating a slow emission radiation. The highest branching ratios are reported for the  ${}^5D_0 \rightarrow {}^7F_2$  transition, all of them are higher than 0.5, meaning a strong emission radiation. In general, high values for branching ratios implies the potential application in laser creation [36].  $\beta \, {}^5D_0 \rightarrow {}^7F_2$  values are reduced when the annealing temperatures increase. We speculate this behavior is related with the EuAlO₃ perovskite phase formation and its fast emission radiation due to the Eu $^{3+}$  concentration quenching.

Luminescence quantum efficiency (or intrinsic quantum yield),  $\eta$ , is, by definition, the ratio of the number of photons emitted to the number of photons absorbed. For lanthanide ions it is also equal to the ratio of the observed lifetime to the radiative lifetime [37].

$$\eta = \frac{\tau_{obs}}{\tau_{out}} \tag{10}$$

The  $\eta$  quantum yield (QY) values calculated using eq. (10) from the  $\tau_{rad}$  obtained through the JOES software and the lifetimes measured ( $\tau_{obs}$ ) are presented in Table 3. These values are an approximation that allows to assess which one among the nanophosphor synthesized is the most efficient. It corresponds to the sample doped at 7.5 at. % Eu calcined at 900 °C (QY = 71%). At this temperature, the quantum yield for powders doped at 6.4 at. % Eu (QY = 69%) is closer to 71%. This result confirms that the maximum radiative efficiency of the Eu^{3+} ion corresponds to the sample possessing the lower symmetry around the Eu^{3+} ion, i.e., the samples calcined at 900 °C. On the other hand, the QY for powders calcined at higher temperatures (1100 and 1200 °C) undergoes a reduction, which is probably related with the formation of the crystalline phases.

Equations for radiative transition probability in the simplest form are:

$$A_{\lambda} = 8.034X10^9 \,\tilde{v}_{\lambda}^3 n_{\lambda} \left(n_{\lambda}^2 + 2\right)^2 \Omega_{\lambda} U^{\lambda} \tag{11}$$

The asymmetric ratios also were obtained through the JOES software and they are shown in Fig. 11. The trend is like that observed in Fig. 10 (a), that is because  $\Omega_2$  and the hypersensitive ratio have similar physical significance regarding the symmetry and the covalent or ionic nature of the bonding between Eu³⁺ and the surrounding ligands [34].

# 4. Conclusions

Eu³⁺-doped aluminum oxide nanophosphors were synthetized by the microwave assisted solvothermal technique. The effect of the calcination temperature and the concentration of Eu on the photoluminescent properties were analyzed. Both the increment in the temperature and the concentration of Eu give place to the formation of the crystalline  $\gamma$ -Al₂O₃ and EuAlO₃ phases. The effect of the crystalline ordering on the luminescent properties were investigated by means of XRD diffraction and Rietveld refinement analyses. They show that at high temperatures EuAlO₃ becomes the dominant phase. However, photoluminescent



**Fig. 10.** Judd-Ofelt parameters for alumina nanophosphors doped with 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% Eu³⁺ calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C, a)  $\Omega_2$  and b)  $\Omega_4$ , c)  $\beta$  for  ${}^5D_0 \rightarrow {}^7F_1$  and d)  ${}^5D_0 \rightarrow {}^7F_2$  transitions.



Fig. 11. Asymmetric ratio for alumina nanophosphors doped with 6.4 at.%, 7.5 at.%, 9.5 at.% and 13 at.% Eu³⁺ calcined at 900 °C, 1000 °C, 1100 °C and 1200 °C.

results show that the emission intensity of the  $\rm Eu^{3+}$  in  $\rm EuAlO_3$  phase is reduced even when the order has been increased in the structure. Nevertheless, a new excitation band appears at around 303 nm,

associated plausibly with the charge transfer band of EuAlO₃ contrary to the band at 250 nm, which is associated with the  $\mathrm{O}^{2}\mbox{-}\mathrm{Eu}^{3+}$  charge transfer in Al₂O₃ diminishes considerably as the annealing temperature increases. Interestingly, the nanophosphor exhibiting the highest emission intensity corresponds to the sample with 13 at. %  $\mathrm{Eu}^{3+}$  and calcined at 900 °C, which is completely amorphous. The decay time shows a strong dependence on the Eu³⁺ doping content and calcination temperature and it was fitted by two single exponential decays in all cases, which is associated with the presence of at least two different chemical environments around the  $Eu^{3+}$  ion, a result that is supported by the XRD analysis. The parameters obtained by the J-O theory, such as  $\Omega_2$  and the asymmetric ratio show that the system shifts from low to high symmetry, and that the chemical covalence is reduced with the increase in calcination temperature, a result that is compatible with the increase in symmetry around the site of the Eu³⁺ with the formation of the EuAlO₃ phase. However, the question about what are the Eu³⁺ luminescent properties only in the EuAlO₃ phase remains open.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# CRediT authorship contribution statement

I. Padilla-Rosales: Formal analysis, Investigation, Writing - original draft, Visualization. C. Falcony: Methodology, Resources, Writing -

review & editing. **R. Sosa:** Validation. **M. Aguilar-Frutis:** Resources. **G. Alarcón-Flores:** Resources, Writing - review & editing. **F. González:** Conceptualization, Methodology, Resources, Writing - original draft, Visualization.

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#### References

- [1] G. Blasse, B.C. Gramaier, Luminescent Materials, Springer, Berlin, 1994.
- [2] Cees Ronda, Luminescence, from Theory to Applications, Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim, 2008.
  [3] G. Blasse, Luinescent materials: is there still news? J. Alloys Compd. 225 (1995)
- [4] S. Basavarajappa Patil, et al., Enhanced photocatalytic activity and biosensing of
- [4] S. Basavarajappa rati, et al., Emanded photocatarytic activity and prosensing of gadolinium substituted BiFeO₃ nanoparticles, Chemistry 3 (2018) 9025–9033.
- [5] G. Hirata, N. Perea, M. Tejeda, J.A. Gonzalez-Ortega, J. McKittrick, Luminescence study in Eu-doped aluminum oxide phosphors, Opt. Mater. 27 (2005) 1311–1315.
- [6] S. Kumar, R. Prakash, V. Kumar, G.M. Bhalerao, R.J. Choudhary, D.M. Phase, Surface and spectral studies of Eu³⁺ doped α-Al₂O₃ synthesized via solution combustion synthesis, Adv. Powder Technol. 26 (2015) 1263–1268.
- [7] M. Nogami, T. Hayakawa, T. Ishikawa, Room- temperature photochemical hole burning in Eu³⁺ - doped Al₂O₃ -SiO₂ glass, Appl. Phys. Lett. 75 (1999) 3072–3074.
   [8] H. Mack, R. Reisfeld, D. Avnir, Fluorescence of rare earth ions adsorbed on porous
- yycor glass, Chem. Phys. Lett. 99 (1983) 238–239.
  J. Zhou, L. Xie, J. Zhong, H. Liang, J. Zhang, M. Wu, Site occupancy and
- [9] J. Zhou, L. Xie, J. Zhong, H. Lang, J. Zhang, M. Wu, She occupancy and luminescence properties of Eu3+ in double salt silicate Na3LuSi3O9, Opt. Mater. Express 8 (2018) 736–743.
- [10] J.C.G. Bünzli, G.R. Choppin, in: Lanthanide Probes in Life, Chemical and Earth Sciences, Theory and Practice, Elsevier, Amsterdam, 1989, p. 219.
- [11] C. Görller-Walrand and K. Binnemans, in: Handbook on the Physics and Chemistry of Rare Earths, Rationalization of Crystal Field Parametrization, eds. K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam), to be published.
- [12] E. Dörre, H. Hübner, B. Ilschner, N.J. Grand, Alumina: Processing, Properties and Applications, Springer, Berlin, 1984.
- [13] Y. Kim, S.M. Lee, C.S. Park, S.L. Lee, M.Y. Lee, Substrate dependence on the optical properties of Al₂O₃ films grown by atomic layer deposition, Appl. Phys. Lett. 71 (1997) 3604–3606.
- [14] E.P. Gusev, M. Copel, E. Cartier, I.J.R. Baumvol, C. Krug, M.A. Gribelyuk, High reolution depth profiling in ultrathin Al₂O₃ films on Si, Appl. Phys. Lett. 76 (2000) 176–178.
- [15] I. Bilecka, M. Niederberger, Microwave chemistry for inorganic nanomaterials synthesis, Nanoscale 2 (2010) 1358–1374.

- [16] C.E. Rodríguez-García, N. Perea-López, G.A. Hirata, Near UV-Blue Excitable Green-Emitting Nanocrystalline Oxide, Advances in Materials Science and Engineering 2011 (2011), 790517.
- [17] A. Ćirić, S. Stojadinović, M. Sekulić, M.D. Dramićanin, JOES: An application software for Judd-Ofelt analysis from Eu³⁺ emission spectra, J. Lumin. 205 (2019) 351–356.
- [18] W. Dabrowski, P. Grybos, P. Hottowy, K. Swientek, P. Wiacek, Integrated readout of silicon strip detectors for position sensitive measurement of X-rays, Nucl. Instrum. Methods Phys. Res., Sect. A 512 (2003) 213–219.
- [19] A. Coelho, TOPAS and TOPAS-Academic: an optimization program integrating computer algebra and crystallographic objects written in C++, J. Appl. Crystallogr. 51 (2018) 210–218.
- [20] R. Cheary, A. Coelho, A fundamental parameters approach to X-ray line profile fitting, J. Appl. Crystallogr. 25 (1992) 109–121.
- [21] C.M. Gómez, G. Del Angel, E. Ramos-Ramírez, I. Rangel-Vázquez, F. González, A. Arrieta, A. Vázquez-Zavala, A. Bonilla-Sánchez, M. Sánchez-Cantú, Alumina coating with TiO₂ and its effect on catalytic photodegradation of phenol and pcresol, J. Chem. Technol. Biotechnol. 91 (2016) 2211–2220.
- [22] P.J. Saines, M.M. Elcombe, B.J. Kennedy, Lanthanide distribution in some doped alkaline earth aluminates and gallates, J. Solid State Chem. 179 (2006) 613–622.
- [23] N.V.Y. Scarlett, I.C. Madsen, Quantification of phases with partial or no Known crystal structures, Powder Diffr. 21 (4) (2006), 278–274.
- [24] L.M. Foster, G.V. Chandrashekhar, J.E. Scardefield, R.B. Bradford, Phase diagram of the system Na₂O-Ga₂O₃-Ga₂O₃ and its relation to the system Na₂O-Al₂O₃-Al₂O₃, J. Am. Ceram. Soc. 63 (1980) 509–512.
- [25] I. Padilla-Rosales, J.G. Cabañas-Moreno, G.L. Jimenez, M.A. Frutis, G. Alarcon-Flores, C. Falcony, Near UV excitable Eu-doped alumina nanophosphors synthesized by the microwave assisted solvothermal technique, Mater. Res. Express 4 (2017) 125007.
- [26] Y. Onishi, T. Nakamura, S. Adachi, Solubility limit and luminescence properties of Eu³⁺ ions in Al₂O₃ powder, J. Lumin. 176 (2016) 266–271.
- [27] Y. Hu, Q. Liu, G. Liu, Z. Zhou, Al₂O₃:Eu³⁺ spherical red-emitting phosphor: Synthesis by hydrothermal technique and luminescence characteristics, J. Alloys Compd. 724 (2017) 969–974.
- [28] M.H.V. Werts, R.T.F. Jukes, J.W. Verhoeven, The emission spectrum and the radiative lifetime of Eu³⁺ in luminescent lanthanide complexes, Phys. Chem. Chem. Phys. 4 (2002) 1542–1548.
- [29] B.R. Judd, Optical Absorption Intensities of Rare-Earth Ions, Phys. Rev. 127 (1962) 750–761.
- [30] G.S. Ofelt, Intensities of Crystal Spectra of Rare-Earth Ions, J. Chem. Phys. 37 (1962) 511–520.
- [31] Mithlesh Kumar, T.K. Seshagiri, S.V. Godbole, Fluorescence lifetime and Judd–Ofelt parameters of Eu doped SrBPO₅, Physica B 410 (2013) 141–146.
- [32] K. Binnemans, Interpretation of europium (III) spectra, Coord. Chem. Rev. 295 (2015) 1–45.
- [33] Lj Dacanin, S.R. Lukić, D.M. Petrović, M. Nikolić, M.D. Dramićanin, Judd–Ofelt analysis of luminescence emission from Zn₂SiO₄:Eu³⁺ nanoparticles obtained by a polymer-assisted sol-gel method, Physica B 406 (2011) 2319–2322.
- [34] M. Ferhi, C. Bouzidi, K. Horchani-Naifer, H. Elhouichet, M. Ferid, Judd-Ofelt analysis of spectroscopic properties of Eu³⁺ doped KLa(PO₃)₄, J. Lumin. 157 (2015) 21–27.
- [35] B. Di Bartolo and O. Forte, Advances in Spectroscopy for Lasers and Sensing Chapter: 21 Publisher: Springer Netherlands.
- [36] M.J.F. Digonnet, in: Marcel Dekker (Ed.), Rare-Earth-Doped Fiber Lasers and Amplifiers, 2 edn, 2001. New York.
- [37] C.K. Jørgensen, R. Reisfeld, Judd-Ofelt parameters and chemical bonding, J. Less Common Met. 93 (1983) 107–112.