



# Structural, electronic and photoluminescence properties of Eu<sup>3+</sup>-doped CaYAlO<sub>4</sub> obtained by using citric acid complexes as precursors



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## ABSTRACT

The search for new materials that meet the current technological demands for photonic applications, make the Rare Earth ions embedded in inorganic oxides as excellent candidates for several technological devices. This work presents the synthesis of Eu<sup>3+</sup>-doped CaYAlO<sub>4</sub> using citric acid as ligand to form a complex precursor. The methodology used has big draw due to its easy handling and low cost of the materials. The thermal analysis of viscous solutions was evaluated and the obtained compounds show the formation of a polycrystalline tetragonal phase. Rietveld refinement was used to understand the structural and the cell parameters of the crystalline phase as a function of temperature of heat-treatment. Crystallite size and microstrain were determined and were shown to have a direct relationship with the temperature of the heat-treatment. The band-gap of the CaYAlO<sub>4</sub> doped with 1 and 10 mol % of Eu<sup>3+</sup> showed values close to 4.30 eV, resulting in their transparency in the visible region between 330 and 750 nm. Besides the intense photoluminescence from Eu<sup>3+</sup>, a study was conducted to evaluate the possible position of the Eu<sup>3+</sup> in the CaYAlO<sub>4</sub> as host lattice. Lifetime of the emission decay from Eu<sup>3+</sup> excited state <sup>5</sup>D<sub>0</sub> show that CaYAlO<sub>4</sub> is a good host to rare earth ions, once it can avoid clustering of these ions in concentration as high as 10 mol%. The predictions of the sublevels of the <sup>7</sup>F<sub>1</sub> crystal field level are discussed through the method of equivalent nearest neighbours (MENN). The intensity parameters (Ω<sub>λ</sub>, λ = 2 and 4) are reproduced with physically reasonable values of average polarizabilities. The set of charge factors used in both calculations are in good agreement with the charge of the europium ion described by the Batista-Longo improved model (BLIM). The quantum efficiencies of the materials were calculated based on Judd-Ofelt theory. Based on the results obtained in this work, the materials have potential use in photonic devices such as lasers and solid state imaging devices in the red region of electromagnetic spectrum.

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## 1. Introduction

Materials doped with Rare Earth ions (RE<sup>3+</sup> and RE<sup>2+</sup>) have received special attention due to their unique photoluminescent

properties, which have potential application in several technological sectors [1–9]. In recent years, the use of materials doped specifically with RE<sup>3+</sup> in emitting devices, such as Light Emitting Diodes (LEDs) and Organic Light Emitting Diodes (OLEDs), has grown tremendously [10–12]. The advantage of using these type of devices in comparison to fluorescent lamps, is that they are free of mercury vapor, that even in small amounts, is highly toxic for the environment and humans [12,13]. In particular, LEDs have advantages due their high efficiency, low energy consumption, low operating voltage and longer lifespan when compared to

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fluorescent lamps [12].

Recently, inorganic oxides doped with  $\text{RE}^{3+}$  have been used for the development of White Light Emitting Diodes (WLEDs) [13–16]. Usually, WLEDs are composed by a junction of a blue LED chip emitting at 465 nm with a yellow light phosphor emitter ( $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ) [13,14]. However, due to lack of red light emitters, this combination shows a poor color reproduction, limiting their application for electronic devices [15]. Another approach used for manufacturing of WLEDs is combining LEDs, with different intensities of blue, green and red emissions excited by a near ultraviolet InGaN chip, which gives rise to the sense of white color [13–15,17]. Nevertheless, the red light emitting phosphor currently used,  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ , exhibit low chemical and physical stability [13].

An alternative way of solving the problem of chemical and physical instability of the  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  is to use aluminates as host matrices for  $\text{Eu}^{3+}$ . Aluminates are more stable than sulphides and fluorides, and have higher mechanical strength and thermal conductivity [18]. Particularly, the  $\text{CaYAlO}_4$  has received much attention in recent years [18–20]. It presents a structure similar to  $\text{K}_2\text{NiF}_4$ , with space group of  $I4/mmm$  [18]. It belongs to the family of compounds with general formula  $\text{ABCO}_4$ , wherein A is a cation from alkaline-earth metals group, B is  $\text{Y}^{3+}$ ,  $\text{Sc}^{3+}$ , or  $\text{RE}^{3+}$  and C is a trivalent ion like  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  or transition metal ion. This crystal structure is composed by perovskite type structures, where  $\text{Al}^{3+}$  ions occupy sites of octahedral symmetries, while divalent A and trivalent cations B are randomly distributed in sites of  $\text{C}_{4v}$  symmetry.

In the literature, there are many methods of synthesis reported, like sol–gel process [21], Czochralski crystal growth [22], the chemical solution technique [23] and the uses of cation complexation with citric acid ligands, also known as amorphous citrate process [24–26]. Citric acid is well known for its easy forming of complexes, due to the molecules to form highly stable rings, especially with transition metal cations [27]. Furthermore, this technique has several advantages, such as pH control, homogeneity of the precursor solution, low cost and obtaining metal aluminate solution at low temperatures, when compared with other synthesis routes, such as solid state synthesis [25].

By using the local structure of the luminescent site, crystal field calculations were performed using the method of equivalent nearest neighbours (MENN) [28], in order to discuss the sublevels of the  ${}^7\text{F}_1$  level. Intensity parameters ( $\Omega_\lambda$ ,  $\lambda = 2$  and 4), related to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{2,4}$  transitions, were also predicted through the dynamics coupling mechanism described earlier [29]. Also, the Batista-Longo improved model (BLIM) [30] is used to compare the set of charge factors which enter in the MENN.

Based on that, this work presents the synthesis of  $\text{CaYAlO}_4$  containing  $\text{Eu}^{3+}$  in different concentrations, based on the use of citric acid to form complexes precursors. The study of the photoluminescence, electronic and structural properties of these materials were performed and related to the concentration of  $\text{Eu}^{3+}$  and to the different heat-treatment temperatures.

## 2. Experimental procedure

$\text{CaYAlO}_4$  containing 1, 3, 5, 7 and 10 mol% of  $\text{Eu}^{3+}$  in powder form were synthesized by use citric acid (Synth-99.5%) to form complexes precursors. This experimental procedure was based on our previous work reported in literature [1] with slight modifications. Stoichiometric amounts of  $\text{Y}_2\text{O}_3$  (Aldrich – 99.999%),  $\text{CaCO}_3$  (Dynamic – 99%),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Synth – 99%) and  $\text{Eu}_2\text{O}_3$  (Aldrich – 99.999%) were dissolved in acidic aqueous solution. The solutions were standardized based on complexometric titration with EDTA  $0.01 \text{ mol L}^{-1}$  as titrant. The defined volumes of the solution

containing  $\text{Eu}^{3+}$  were pipetted into some beakers, to obtain materials doped with different amounts of  $\text{Eu}^{3+}$ . The follow, a mass corresponding to 5 times the citric acid as a function of number of moles of the metals were dissolved in deionized water and transferred to a beaker containing  $\text{Ca}^{2+}$ ,  $\text{Y}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Eu}^{3+}$  to obtain the homogenous solution precursor. The complexes solutions were kept under magnetic stirring at  $70^\circ\text{C}$  by 6 h, which leads to an increasing in the solutions viscosities. For each concentration of  $\text{Eu}^{3+}$ , viscous solutions were obtained. The viscous solutions containing 1, 5 and 10 mol% of  $\text{Eu}^{3+}$  were submitted to thermogravimetric analysis (TG) and differential thermal analysis (DTA) by using a thermobalance Shimadzu model DTG – 60H, from room temperature up to  $1100^\circ\text{C}$ , with heating rate of  $10^\circ\text{C}/\text{min}$ , under air atmosphere. All viscous solutions were dried in an oven at  $120^\circ\text{C}$  for 24 h and then, heat-treated at 900, 1000 and  $1100^\circ\text{C}$  for 5 h. The morphology of the materials obtained after the heat-treatment were analyzed by Scanning Electron Microscopy, SEM (Hitachi TM-3000). The crystalline structure was evaluated by X-ray diffraction (XRD) by a Shimadzu XRD 6000 diffractometer with  $\text{Cr K}\alpha$  radiation ( $\lambda = 2.2897 \text{ \AA}$ ) in the range  $2\theta$  between  $30^\circ$  and  $120^\circ$ . The microstrain and average crystallite sizes were determined based on diffractograms obtained. The Rietveld refinements [31] were performed using the General Structure Analysis System (GSAS) software with an EXPGUI interface [32]. Parameters of crystallites structure were based on the reference of ICSD 72104 ( $\text{CaYAlO}_4$ ), ICSD 63650 ( $\text{Al}_2\text{Y}_4\text{O}_9$ ) and ICSD 86815 ( $\text{Y}_2\text{O}_3$ ). The Fourier Transform Infrared Spectroscopy (FTIR) analyses were carried out operating the spectrophotometer Perkin Elmer Spectrum GX. The samples were prepared in the form of transparent pellets diluted into KBr and kept under pressure of around 10 tons during 1 min. The spectra were collected in the region between 4000 and  $400 \text{ cm}^{-1}$  with  $4 \text{ cm}^{-1}$  of spectral resolution. The diffuse reflectance spectra were carried out operating the Varian spectrophotometer Cary model 5000 between 250 and 750 nm with 0.2 nm of spectral resolution. Based on diffuse reflectance spectra, electronic structural properties were evaluated. The photoluminescence measurements were performed at room temperature using a spectrofluorometer Shimadzu, Model RF – 5301 PC equipped with a xenon lamp of 150 W. The emission spectra were obtained at 300 K within the range of 550–750 nm under excitation fixed at 394 nm, which corresponds to the electronic transition  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  of  $\text{Eu}^{3+}$  [33]. The excitation and emission slits were fixed at 5 and 2 nm, respectively. The measurements of the lifetime of the  ${}^5\text{D}_0$  excited state of the  $\text{Eu}^{3+}$  were performed at 300 K using the spectrofluorometer SPEX Fluorolog F2121 equipped with phosphorimeter and pulsed lamp, with excitation at 394 nm and emission at 620 nm, with excitation and emission slits of 5 and 2 nm, respectively.

## 3. Results and discussion

The studies of the thermal behavior of the viscous solutions obtained in this work were carried out for samples containing 1, 5 and 10 mol% of  $\text{Eu}^{3+}$ . The Fig. 1 shows the TG and DTA curves of the viscous solutions. The first thermal event occurs approximately at  $107^\circ\text{C}$  and can be attributed to the dehydration of the solution and also to the loss of uncomplexed citric acid [34]. The loss of mass occurs continuously up to approximately  $600^\circ\text{C}$  followed by an exothermic event above  $400^\circ\text{C}$ , which can be related to decomposition of organic matter in the form of  $\text{CO}_{(\text{g})}$  and  $\text{CO}_{2(\text{g})}$ . The mass loss continuously indicates that the thermal decomposition is of Type I, in accordance to Courty, et al. [24]. It is known that compounds prepared using citric acid as the complexing agent may present two Types of thermal decomposition, labeled Type I and Type II. The thermal decomposition of Type I is characterized by a

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