Reddish-orange \( \text{Ca}_3-x\text{Al}_2\text{O}_6:x\text{Eu}^{3+} \) nanophosphors: Fast synthesis and photophysical properties

B.S. Barros \(^a\), R.S. de Oliveira \(^b\), J. Kulesza \(^c,\text{*}\), V.R.M. Melo \(^b\), D.M.A. Melo \(^b\), S. Alves Jr. \(^c\)

\(^a\) School of Science and Technology, Federal University of Rio Grande do Norte, Campus Universitário Lagôa Nova, 59078-970 Natal, RN, Brazil
\(^b\) Institute of Chemistry, Federal University of Rio Grande do Norte, Campus Universitário Lagôa Nova, 59072-970 Natal, RN, Brazil
\(^c\) Department of Fundamental Chemistry, Federal University of Pernambuco, Av. Prof. Moraes Rego, 1235 Cidade Universitária, 50670-901 Recife, PE, Brazil

**Abstract**

This paper focuses on the synthesis and the photoluminescent properties of \( \text{Ca}_3-x\text{Al}_2\text{O}_6:x\text{Eu}^{3+} \) \((0 \leq x \leq 0.1)\) nanophosphors prepared by microwave-assisted combustion method without any further heat treatment. X-ray diffraction, scanning electron microscopy and photoluminescence spectroscopy were used to characterize the produced samples. Nanosized particles smaller than 120 nm were obtained as confirmed by SEM. When exposed to UV light radiation at 254 nm, the europium-doped nanoparticles showed strong reddish-orange luminescence due to the characteristic transitions \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) (orange) and \( ^5\text{D}_0 \rightarrow ^7\text{F}_1 \) (red). The maximum emission intensity of the visible emission was obtained for \( x=0.05 \). It was also found that higher doping concentrations led to the luminescence quenching by a cross-relaxation mechanism between Eu\(^{3+}\) ions in the lattice.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Metal oxides doped with lanthanides have been received much attention for the last decades. Such materials usually show enhanced photoluminescent properties compared to the conventional sulfide phosphors. In general, suitable materials for phosphors must provide both, the high luminescence and chromatic resolution, what can be achieved by using ceramic-compounds doped with lanthanide ions. Beyond the recognized importance of these elements, due to unique features derived from the electronic configurations, the oxide host plays a fundamental role in the luminescent properties of such compounds [1,2].

The term “calcium aluminate” is a nomenclature used for a series of compounds with different Ca/Al ratios, just to give some examples: \( \text{CaAl}_2\text{O}_4 \), \( \text{Ca}_2\text{Al}_2\text{O}_6 \), \( \text{Ca}_3\text{Al}_2\text{O}_6 \), \( \text{Ca}_4\text{Al}_6\text{O}_{13} \) and \( \text{Ca}_5\text{Al}_6\text{O}_{14} \) [1]. Tricalcium aluminate (\( \text{Ca}_3\text{Al}_2\text{O}_6 \)) is one of the main components of Portland cement as well as an important refractory material. Recently, this oxide has been reported as a promising host for lanthanide ions [2–6]. As reported by Aitasalo et al. [5], the number of papers related to calcium aluminate doped with lanthanide ions has increased in recent years due to the fact that these compounds exhibit long-lasting persistent luminescence when compared to other existing luminescent materials. Typically, these compounds are prepared by solid state reactions between calcium oxide (CaO) or calcium carbonate (CaCO\(_3\)) and alumina (Al\(_2\)O\(_3\)), however, this process requires high temperatures and a long time of reaction [7,8]. Moreover, wet-chemical synthesis methods have been also applied to prepare mixed oxides such as calcium aluminates and others. Among the most used wet synthetic techniques, we can distinguish the hydrothermal [9], co-precipitation [10], Pechini [11] and sol–gel [7,12]. These methods provide high-quality ceramic powders with a high level of chemical homogeneity, high surface area and uniform particle size distribution. Nevertheless such methods are based on complicated procedures. On the other hand, microwave-assisted combustion method is a fast and simple synthetic route which can provide an alternative and interesting way to prepare high-quality oxide powders with the desired properties, without any intermediate step process.

The combustion process involves the exothermic chemical reaction of a solution containing metal salts, also known as oxidizing agents, and amino acids called fuels. Typically, the oxidizing agents are nitrates or acetates whereas urea, glycine and carbohydrazide are preferred as fuels [13,14]. When the oxidizing agents and the fuel begin to decompose, the gasses are released forming a high-temperature flame which promotes the crystallization of metal oxides. The flame temperature depends on the nature of both, the fuel and an oxidant. It is required that they decompose at the same time which can be reached using a mixture of fuels and/or by an instantaneous heating of the precursor solution via microwaves [14].
In this work, we demonstrate that tricalcium aluminate doped with lanthanide ions can be prepared by one-step process based on a fast self-combustion synthesis. The combination of a microwave heating together with a mixture of fuels was employed to obtain a fine powder with nanocrystalline characteristics. The photophysical properties of these samples were studied, and the optimum doping concentration was determined.

2. Experimental

2.1. Materials

Tricalcium aluminate doped with trivalent europium ions was synthesized by the microwave-assisted combustion method using a mixture of fuels. The samples with molar composition \( \text{Ca}_3 \cdot \text{Eu}_x \cdot \text{Al}_2 \cdot \text{O}_6 \) \( (0 \leq x \leq 0.1) \) were obtained without further thermal treatment. Both fuels, urea \((\text{CON}_2\text{H}_4)\) and glycine \((\text{C}_2\text{H}_5\text{NO}_2)\), as well as the metal nitrates \(\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}\) and \(\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}\) were purchased from VETEC. Because of the different total valencies of urea and glycine, a small amount of ammonium nitrate \((\text{NH}_4\text{NO}_3)\), purchased from CRQ, was used to balance the redox reaction. The europium nitrate was prepared from the corresponding oxide. A stoichiometric amount of europium oxide \((\text{Eu}_2\text{O}_3)\) was dissolved in an aqueous solution of nitric acid \((\text{HNO}_3)\), both purchased from VETEC and then the solution was kept under stirring at 90 °C until the complete evaporation.
2.2. Synthesis

All solid raw materials were used to form an aqueous precursor solution. The initial composition was determined based on the method introduced by Jain et al. [15]. The precursor solution was stirred in a beaker at room temperature until the formation of a viscous gel. Subsequently, the beaker with the precursor gel was placed in a conventional microwave-oven, Panasonic model NN-GT517WRUK, with a maximum output power of 800 W and frequency of 2.45 GHz, until the spontaneous ignition. During the synthesis, the power of the microwave-oven was adjusted to 70%.

2.3. Characterization

The crystal structure of the prepared samples was determined by powder x-ray diffraction analysis performed on a diffractometer SHIMADZU model XRD-6000, using Cu Kα radiation and operating at 40 kV and 30 mA. The powder diffraction patterns were recorded between 10° and 80° at steps of 0.02°. The morphological characteristics of the powders were analyzed by electron microscopy. The images were obtained on a Scanning Electron Microscope with Field Emission Gun (SEM-FEG) model JEOL 6700F. Photoluminescence (PL) excitation and emission spectra were collected at room temperature on a Fluorolog Horiba Jobin Yvon spectrofluorometer.

3. Results and discussion

X-ray diffraction analyzes were performed to study the crystalline composition of the prepared powders, and the respective diffraction patterns are shown in Fig. 1. All diffraction peaks were indexed to a single phase Ca₉Al₆O₁₈ matching well with the COD (Crystallography Open Database) cif file 1000039 [16]. According to this cif file, the calcium cycle-hexaluminate (Ca₉Al₆O₁₈ or Ca₃Al₂O₆) presents a cubic crystal structure with space group Pa₃ and a = 15.263 Å. The unit cell contains 24 asymmetric units, each one with three Ca²⁺, two Al³⁺ and six O²⁻ each. The structure consists of rings of six AlO₄ tetrahedra (Al₆O₁₈), eight per unit cell, surrounding holes of radius 1.47 Å. The tetrahedral AlO₄ rings are connected by Ca²⁺ ions.

As it can be observed in Fig. 2 (on the right), the coordination polyhedrons of calcium seem to be quite distorted, whereas the tetrahedra of aluminum do not show significant distortion. Fig. 2 (on the left) shows, four of the eight rings of six AlO₄ tetrahedra, the other four rings and the coordination polyhedrons of calcium are not shown for better clarity.

It is expected that Eu³⁺ ions (r=1.07 Å) will replace Ca²⁺ (r=1.12 Å) and not Al³⁺ (r=0.53 Å) cations, due to their similar ionic radii. As a result, at least six different coordination environments might be available for Eu³⁺ ions in the lattice. Even though this replacement will not have significant influence on the crystal structure, the luminescent properties of Eu³⁺ ions are greatly influenced by the environment. In Fig. 3 it can be seen that all calcium sites are significantly distorted with Ca1, Ca2, Ca3 and Ca6
coordinated by six, Ca4 coordinated by nine and Ca5 coordinated by eight oxygen atoms.

According to Wan and coworkers [17], the characteristic emissions of Eu3+ ions are also influenced by morphology of the host. Therefore, we have analyzed the obtained powders by scanning electron microscopy (SEM). It was found that powder morphology is little affected by europium addition. Fig. 4a and b show SEM micrographs of undoped and doped samples, respectively. In both cases, agglomerates of nanoparticles with size ranging from 62 to 110 nm can be observed.

Photoluminescence excitation spectra of the powders were obtained at room temperature by monitoring emissions at 612 and 702 nm related to the Eu3+ 5D0→7F2 and 5D0→7F4 transitions, respectively (Figs. 5 and 6).

Both spectra exhibit a broad band with a maximum at approximately 320, 361, 381, 394, 413 and 464 nm, ascribed to 7F0→5H6, 7F0→5D4, 7F0→5G2, 7F0→5L6, 7F0→5D3 and 7F0→5D2 transitions of Eu3+, respectively.

In both cases, the maximum emission intensity is achieved by excitation at 395 nm. It is noticed that the 5D0→7F2 transition is more sensitive to the excitation by charge-transfer state (CTS) than the 5D0→7F4 transition.

Fig. 7 shows a photograph of the produced powders under UV-light irradiation with 254 nm, corresponding to the excitation by CTS. All samples, except the undoped one (Fig. 7a), show a strong reddish-orange luminescence, characteristic for the 5D0→7F1 (orange) and 5D0→7F2 (red) emissions.

The photoluminescence emission spectra of the powders (Fig. 8) exhibit at least five characteristic transitions of the ion Eu3+ at approximately 578, 591, 612, 651 and 702 nm. These emission lines can be ascribed to the 5D0→7F0, 7F1, 7F2, 7F3 and 7F4 transitions, respectively. It is well established that the emission spectrum of trivalent europium ions is strongly influenced by its site symmetry. If Eu3+ ions are embedded at a site with inversion symmetry, only magnetic-dipole 5D0→7F1 transitions are allowed, but if they occupy sites with no inversion symmetry, the electric-dipole 5D0→7F2 transitions can be also observed. Moreover, the ratio of the emission intensities of these transitions, called as asymmetry ratio, gives a measure of the degree of distortion of the coordination sphere of Eu3+ ions in the host matrix [17,18].

As can be seen in Fig. 8, the band corresponding to the electric dipole transition at 612 nm is more intense than that ascribed to magnetic-dipole transition at 591 nm. Thus, the Eu3+ ions probably occupy sites without inversion symmetry. Since Eu3+ ions are bigger than Al3+ ions, it is expected that they will occupy Ca2+ sites in the host. As already mentioned, there are six different types of Ca2+ sites that could be occupied by Eu3+ ions. However, it is widely accepted that lanthanide ions have preference for sites with a high coordination number, typically from seven to twelve. This may suggest that Eu3+ ions occupy the Ca4 and Ca5 sites in the host, being coordinated by nine and eight oxygen atoms, respectively (see Fig. 3). It should be noted, however that Eu3+ ion has one extra positive charge compared to Ca2+ ion, and a direct replacement will entail the formation of an excess of positive charges in the matrix. In order to compensate such effect calcium
vancies must be formed as follows: $3\text{Ca}^{2+} \rightarrow 2\text{Eu}^{3+} + \square$ (defect) [8,19].

The optimum concentration of $\text{Eu}^{3+}$ ions was determined based on the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition ($x=0.05$). For $x<0.05$, few active centers are expected, whereas for $x>0.05$, the number of active centers increases substantially. Consequently, the average distance between those centers decreases leading to the luminescence quenching due to the cross-relaxation between $\text{Eu}^{3+}$ ions.

4. Conclusions

We have successfully prepared $\text{Ca}_3\text{Al}_2\text{O}_6:x\text{Eu}^{3+}$ nanoparticles using the self-Combustion method without necessity of any further calcination. SEM analysis revealed that the produced powders are formed of nanosized particles ranging from 62 to 110 nm. All doped samples showed strong reddish-orange luminescence due to the emissions $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (orange) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (red), typical for $\text{Eu}^{3+}$ ions. These emissions occurred to be more sensitive to the charge-transfer state than direct excitation in the f-f levels at 395 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_6$ transitions). The maximum luminescence intensity was observed when $x=0.05$. For $x<0.05$ a small number of active centers ($\text{Eu}^{3+}$) is expected, while for $x>0.05$, the number of active centers increases substantially decreasing the average distance between the ions and leading to the quenching effect. The results indicate that calcium cycle-hexaluminate nanoparticles are promising hosts for lanthanide ions. In addition, this nanosized material was easily produced by a simple, fast and cheap synthetic route.

Acknowledgements

The authors gratefully acknowledge the Brazilian agencies CAPES and CNPq for financial support.

References