

Optical properties of Eu^{3+} -doped CaAl_4O_7 synthesized by the Pechini method

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ABSTRACT

$\text{Ca}_{1-x}\text{Eu}_x\text{Al}_4\text{O}_7$ ($x = 0, 0.002, 0.01, 0.02, 0.05, 0.1$) and $\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{Al}_4\text{O}_7$ ($x = 0.002, 0.02, 0.05, 0.1$) crystalline phosphor powders have been synthesized by modified Pechini method and their spectroscopic properties at room and liquid nitrogen temperature were measured. Excitation spectra of synthesized materials contain broad band attributed to ligand to metal, $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$, charge transfer absorption and narrow lines related to ${}^7\text{F}_0 \rightarrow {}^5\text{D}_j$, ${}^5\text{H}_j$, ${}^5\text{L}_j$, ${}^5\text{G}_j$ transitions of europium ions. Upon excitation at 395 nm, the Eu^{3+} -doped calcium dialuminates exhibit red photoluminescence due to parity forbidden f–f intra-configurational transitions with the most intense component at 612 nm resulting from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ hypersensitive transition. The quantum efficiency of the powders emissions does not exceed 12%. The luminescence decay kinetics reveals that some quenching appears for higher concentrations. Site selective spectroscopy disclosed the presence of at least two well defined individual spectroscopic sites of Eu^{3+} and increasing disturbance of their local symmetries with raising concentration of the activator was observed. The increasing symmetry disorder led to a significant asymmetrical broadening of the luminescence lines at higher concentrations. Concentration dependence of the luminescence kinetics of the two diverse Eu^{3+} ions is different, as only one of them, with the characteristic luminescence at 579.5 nm, exhibits shortening of the decay time at higher Eu contents. The inexpensive $\text{CaAl}_4\text{O}_7:\text{Eu}$ powders are potentially good candidates for photonics applications. For Eu, Na co-doped powders the Eu^{3+} ions producing emission at 579.7 nm dominates strongly over those with luminescence at 577.2 nm.

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1. Introduction

The calcium aluminates continue receiving an interest in a variety of areas, such as materials of construction [1], luminescent materials [2–4], as well as model systems for the study of crystallization phenomena in amorphous precursors [5]. Various crystalline phases of calcium aluminates have been synthesized, including CaAl_2O_4 , CaAl_4O_7 , $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. All these compositions have been employed as host materials for RE-doped phosphors. Among them, (Eu^{2+} , $\text{Dy}^{3+}/\text{Nd}^{3+}$) co-doped CaAl_2O_4 is a well known, commercially offered persistent luminescence phosphor [6].

CaAl_4O_7 is an important ceramic material for high temperature refractory applications (melting point: 1765 ± 25 °C) [7]. It is also used as component of high-alumina cement and in steel industry as metallurgical slag. Calcium dialuminate, termed “grossite” in mineralogical field, is found in natural terrestrial rocks and meteorites [8]. Currently, this compound is of great interest because of its unique crystallographic features, particularly the existence of so-called “triclusters” consisting of an oxygen atom surrounded by three Al tetrahedra as well as a very low coefficient of thermal expansion [9,10]. CaAl_4O_7 is also an

attractive host for spectroscopic materials due to a high optical transparency from ultra-violet to near infrared spectral range, excellent mechanical properties and good chemical stability. Eu^{3+} ion has attracted significant attention as a dopant to design optical amplifiers, display phosphor, electroluminescence devices and optical storage phosphors [11]. Furthermore, Eu^{3+} ion is also known as a very sensitive site-symmetry probe.

Till now, only scant studies have been performed on RE-doped CaAl_4O_7 . The luminescence properties of CaAl_4O_7 powders activated with Pr^{3+} , Ce^{3+} , Tb^{3+} , (Ce^{3+} , Tb^{3+}) prepared by solid state reaction [3,12,13] and polycrystalline pellet containing 1% of Eu^{3+} and obtained by sintering have been reported [14]. All these phosphor materials were synthesized at high temperatures (above 1350 °C) using multistep procedures with intermediate grindings. This paper describes details of fabrication of Eu^{3+} -doped (0–10 mol%) CaAl_4O_7 crystalline powders with a modified Pechini method at much lower temperature (950 °C), and presents results of their structural (XRD) and spectroscopic (IR, photoluminescence) analysis.

2. Experimental

Calcium aluminates activated with Eu^{3+} ions, $\text{Ca}_{1-x}\text{Eu}_x\text{Al}_4\text{O}_7$ ($x = 0, 0.002, 0.01, 0.02, 0.05, 0.1$) and $\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{Al}_4\text{O}_7$

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($x = 0.002, 0.02, 0.05, 0.1$) were prepared via modified Pechini citrate process, similarly to the procedure described in [15] for undoped CaAl_4O_7 . The metal nitrates: $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, NaNO_3 , citric acid (CA) and ethylene glycol (EG) were used as starting materials. The molar ratio of CA, sum of metal cations (Al^{3+} , Eu^{3+} , Ca^{2+} , Na^+) and EG was 2:1:8. First, the required amount of CA was dissolved in EG, followed by the addition of stoichiometric amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The obtained solutions were heated to 80°C on a hot plate, under continuous stirring. Afterward, the solid resins were gradually heated on hot plate up to 600°C to obtain raw brownish powders (due to residual carbon). No vigorous combustion was observed. Finally, these materials were calcined in air atmosphere at 950°C in alumina crucibles for 3 h, resulting in fine, white powders.

All samples were checked by powder X-ray diffractometry (DRON-2 Diffractometer, Cu K_α radiation, $\lambda = 1.5418 \text{ \AA}$). The measurements were performed for 2θ ranging from 10° to 100° and with 0.1° step. The infrared absorption spectra were recorded with a Brüker FTIR IFS 113 V spectrophotometer using Nujol to disperse the powder.

Photoluminescence measurements were performed at room (298 K) and liquid nitrogen (77 K) temperatures using SpectraPro 750 1-meter monochromator, coupled to Hamamatsu R928 photomultiplier and equipped with a 1200 l/mm grating blazed at 500 nm. A 450 W xenon lamp was used as an excitation source. It was coupled to 275 mm excitation monochromator equipped with a 1800 l/mm grating blazed at 250 nm. Luminescence decay traces were recorded at 298 K and 77 K using a Tektronix TDS 3052B oscilloscope and Nd:YAG Lambda Physics pulsed laser with excitation line of 532 nm. Quantum efficiency of the powders were measured applying the procedure described in [16].

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the X-ray diffraction patterns of all the $\text{CaAl}_4\text{O}_7:\text{Eu}^{3+}$ ($x = 0, 0.002, 0.01, 0.02, 0.05, 0.1$) investigated samples. The spectra prove a single grossite monoclinic phase with a C2/c space group for all compositions (ICSD#14270) [9,17]. In the grossite structure, Ca^{2+} ion is placed in a sevenfold coordination sphere with C_2 (pseudo- C_{2v}) symmetry, whereas Al^{3+} ion is distributed over two symmetrically independent tetrahedral sites, which are distorted to some degree which leads to virtually C_1 site symmetry [9,17]. Because of similar ionic radii the Eu^{3+} ions ($r = 1.15 \text{ \AA}$) are

expected to substitute Ca^{2+} ($r = 1.20 \text{ \AA}$) rather than Al^{3+} ($r = 0.53 \text{ \AA}$). The replacement of one Ca^{2+} by one Eu^{3+} would cause accumulation of a positive net charge, compensation of which could be achieved creating Ca-vacancies or interstitial O^{2-} near the Eu^{3+} ions. Therefore, an appearance of more than just one Eu^{3+} site is anticipated and the symmetry of the coordination environment of the activator may further degrade enhancing especially the probability of the electric dipole hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition.

3.2. Photoluminescence study

Emission spectra of the Eu^{3+} doped calcium dialuminates as a function of the dopant content have been measured after excitation into ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition (395 nm) at 298 K and 77 K and the results are presented in Figs. 2 and 3, respectively. All samples yield red emission with the main component peaking around 612 nm and the spectra consist of characteristic lines due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ transitions. The luminescence arises exceptionally from the ${}^5\text{D}_0$ level; no transitions from the higher excited ${}^5\text{D}_1$ state are observed.

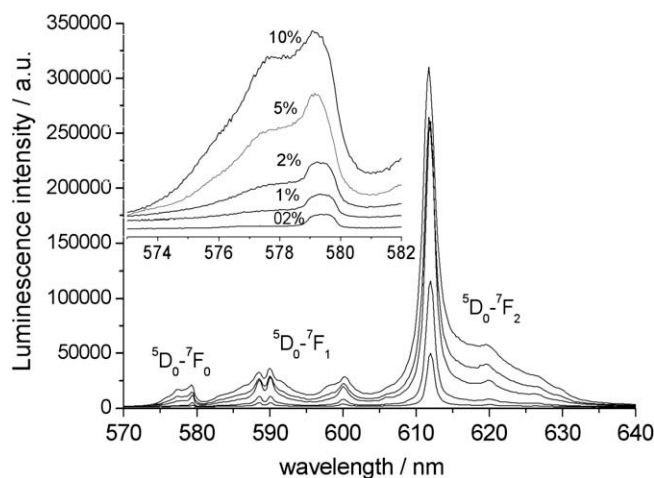


Fig. 2. Emission spectra of $\text{CaAl}_4\text{O}_7:\text{Eu}^{3+}$ samples under 395 nm excitation at 298 K. Under different excitation wavelengths in the 280–400 nm range no Eu^{2+} luminescence was observed.

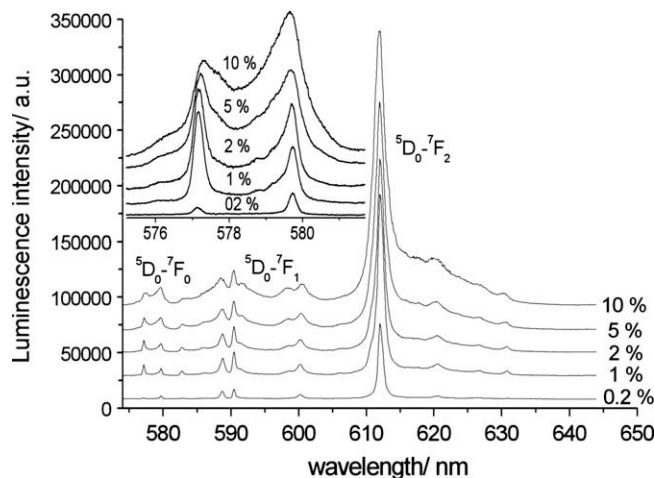


Fig. 3. Emission spectra of $\text{CaAl}_4\text{O}_7:\text{Eu}^{3+}$ samples under 395 nm excitation at 77 K. Under different excitation wavelengths in the 280–400 nm range no Eu^{2+} luminescence was observed.

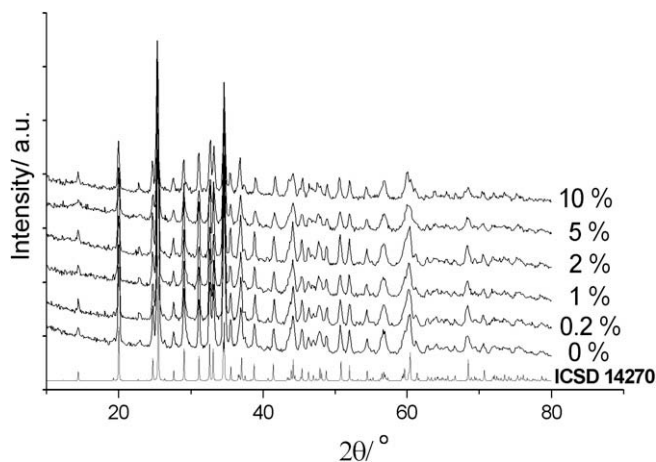


Fig. 1. XRD patterns of the undoped and $\text{CaAl}_4\text{O}_7:\text{Eu}^{3+}$ powder phosphor.

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