



Thermal quenching mechanisms of the Eu^{3+} luminescence in $\text{Ca}_9\text{Al}(\text{PO}_4)_7$ obtained by citric route

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ABSTRACT

The citric route was employed for synthesis of the pure phase $\text{Ca}_9\text{Al}(\text{PO}_4)_7:\text{Eu}^{3+}$ (CAIP:Eu³⁺) powders as an attractive alternative to the solid state reaction (no need of multistep and long thermal treatment). Structural properties of the final product were studied by means of X-ray diffraction as well as Rietveld refinement was conducted in order to calculate the cell parameters. The thermal behavior of the emission was studied using excitation line well matched with the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$ absorption band covering broad range of temperature. Activation energy was estimated to be equal to $10,550 \text{ cm}^{-1}$. The thermal behavior of the Eu^{3+} luminescence in CAIP crystal lattice shown that the almost 80% of intensity is kept up to 430 K.

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1. Introduction

Constantly growing interest in development and engineering of new phosphor materials for modern, environmentally friendly and energy saving light sources and other optical applications demands more and more detailed analysis of the luminescence properties extended to the identification of the mechanisms leading to the thermal quenching of the luminescence. Why is this issue extremely important? The answer on this question is fairly straightforward, indeed, in many devices containing phosphors (e.g. LEDs technology, lamps, projection television tubes, etc.), the operating temperature exceeds room temperature [1]. Unfortunately majority of the published scientific articles devoted to the new materials do not contain any information on the luminescence stability of phosphors at elevated temperatures being a critical parameter. Additionally extended studies could provide more facts facilitating the understanding of the emission quenching processes.

Among of variety of the phosphors based on the mixed metal oxides serving as a host-lattice for *d* and *f* metal cations phosphates of different types are nowadays attracting increased attention due

to their excellent thermal and chemical stability as well as excellent luminescence performances [2]. They are interesting candidates for mercury-free lamps due to high absorption and transfer efficacies of the VUV radiation to the emitting RE^{3+} dopant. In view of the EU communication concerning the usage of mercury in the lightning industry, findings of new phosphors for VUV lamps is of great importance [3]. According to our knowledge there is only one article published on the solid-state synthesis and luminescence characteristics of $\text{Ca}_9\text{Al}(\text{PO}_4)_7$ (hereafter CAIP) [4], but authors did not raise the problem of thermal quenching of luminescence at all. In this paper, we report on the synthesis, structural properties and the effect of temperature on the luminescence performance of the Eu^{3+} emission in CAIP powders.

2. Experimental details

2.1. Instruments

The X-ray diffraction (XRD) patterns were collected in a 2θ range of $5\text{--}100^\circ$ with X'Pert Pro PANalytical X-ray diffractometer (Cu, $K_{\alpha 1}$: 1.54060 \AA). Raman spectra were acquired using a LabRam HR 800 Horiba Jobin Yvon equipped with a 9 mW HeNe laser emitting 632.8 nm line. The microstructure and morphology of CAIP particles were investigated by high resolution transmission electron microscopy (HRTEM) using a Philips CM-20 Super Twin microscope, operated at 200 kV. Samples for HRTEM measurements were

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prepared by dispersing the powders in methanol and depositing a droplet of the suspension on a copper microscope grid covered with perforated carbon. Elemental analysis was carried out using a scanning electron microscope FEI Nova NanoSEM 230 equipped with EDS spectrometer (EDAX PegasusXM4). Up to 10 measurements were made from different random areas for each sample. The excitation spectra were recorded using a McPherson spectrometer equipped with a 150 W xenon lamp as the excitation source and a Hamamatsu R928 photomultiplier as the detector. The emission spectra and decay profiles were collected in the temperature range 77–693 K using a Jobin-Yvon/Horiba TRIAX 550 monochromator. The nitrogen-cooled CCD camera for detecting the emission or a R928 Hamamatsu photomultiplier connected with a 400 MHz LeCroy digital oscilloscope (input impedance 50 Ω) for acquiring the decay curves were used. For the 77 K measurements, the samples were conditioned in quartz tubes and immersed in liquid nitrogen using a home-made cryostat. The high temperature measurements were done using a home-made copper holder heated by a thermocoax wire connected to a temperature controller. A ND 60 dye laser pumped by a frequency doubled YAG:Nd laser was used for site selective and time resolved spectroscopy. The dye laser was equipped with rhodamine 590 and its output (when required) was up-shifted by 4155 cm^{-1} using a Raman cell filled with 30 atm H_2 .

2.2. Synthesis of $\text{Ca}_9\text{Al}(\text{PO}_4)_7:\text{Eu}^{3+}$ powders

The 1 mol% of Eu^{3+} -doped CAIP powders were prepared by mixing 1.9991 g (8.46 mmol) of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.98% Alfa Aesar), 0.0015 g (0.042 mmol) of Eu_2O_3 (99.99% Alfa Aesar), 0.8845 g (6.65 mmol) of $(\text{NH}_4)_2\text{HPO}_4$ (99.99% Alfa Aesar), 0.3564 g (0.95 mmol) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 15.5168 g (80.76 mmol) of anhydrous citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (99.5% Alfa Aesar). Eu_2O_3 was digested in HNO_3 and the europium nitrate was recrystallized three times. Then, all the nitrates, dibasic ammonium phosphate and citric acid were dissolved in water. The addition of citric acid, resulted in a transparent and viscous solution that was transferred into a plastic container and dried at 90 $^\circ\text{C}$ for 2 days until the formation of a stiff resin. The final step involved thermal treatment in the temperature range 700–1000 $^\circ\text{C}$ for 8 h.

3. Results

3.1. Structural data

The X-ray diffraction (XRD) pattern of Eu^{3+} -doped CAIP sample heated at 900 $^\circ\text{C}$ is shown in Fig. 1. The patterns matched the ICSD card no. 43-136 for CAIP [5]. No extra reflection was observed,

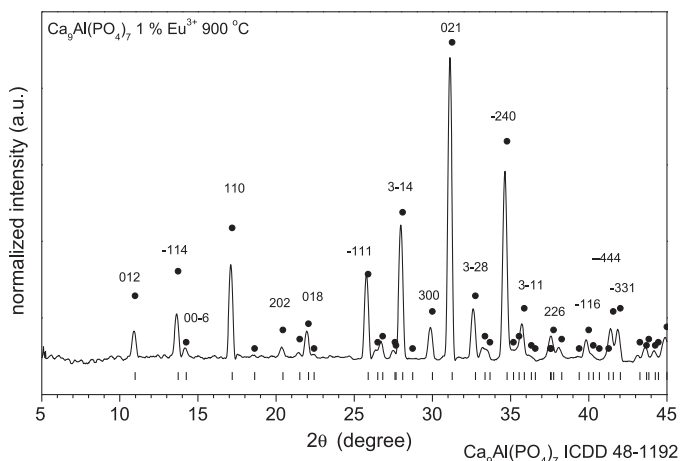


Fig. 1. XRD patterns of $\text{Ca}_9\text{Al}(\text{PO}_4)_7:\text{Eu}^{3+}$.

confirming the formation of single phased compound. Only the most intense reflections were indexed for better clarity.

Representations of the unit cell, supercell and coordination polyhedra for the cation sites in CAIP are shown in Figs. 2 and 3 (the size of oxygen atoms was adjusted for clarity). CAIP crystallizes in the trigonal $R3c$ space group [4]. Its structure consists of isolated $[\text{PO}_4]^{3-}$ units separated by $[\text{CaO}_8]^{14-}$ or $[\text{CaO}_7]^{12-}$ polyhedra. The sites Ca(1) and Ca(2) are 7-fold coordinated while the site Ca(3) is 8-fold coordinated. For all of them, the point symmetry is C_1 . Considering the ionic radii and charge balance, it is concluded that the Eu^{3+} ions will replace the Ca^{2+} sites in CAIP [6].

The unit cell parameters were calculated after Rietveld refinement [7] using the isotropic approach [8] implemented in X'pert High Score software. The results are compared to the reference data of un-doped single crystal of CAIP [5] in Table 1.

In this phosphate, the site occupancy is the same for the three calcium sites. The ionic radius of Ca^{2+} ranges from 1.06 Å (CN 7) to 1.12 Å (CN 8) while that of Eu^{3+} varies from 1.01 Å (CN 7) to 1.066 Å (CN 8). Owing to this criterion, no great change in cell parameters has to be expected. Du et al. [4] noticed a contraction of only 0.8% of the unit cell lattice of 5 mol% Eu^{3+} -doped CAIP compared to the single undoped crystal. Strangely, we observe an expansion of 0.8% of the unit cell volume in our sample. On one hand such small deviation might be caused by the error during the fitting procedure or lays in difference between preparation routes as well. In fact the latter case is well known since cell parameters of materials could differ depending on the synthetic approach [9]. On the other it has to be stress out that the Eu^{3+} content in our report is five times lower than in Du studies. Thus expected effect of the Eu^{3+} doping is less pronounced here.

Representative result of the TEM analysis is presented in Fig. 4. The samples heated at 900 $^\circ\text{C}$ contain irregular and agglomerated particles with primary size in the range of 70–220 nm (average 160 nm) for the $\text{CAIP}:\text{Eu}^{3+}$. The mean particle size was estimated only basing on the TEM results since the samples are characterized by the relatively broad size distribution with the predominance of large submicron particles. No Scherrer based size calculations were performed since the upper limit of its applicability is estimated to be 100 nm [10,11]. Occurrence of relatively broad diffraction peaks were ascribed to the presence of significant size distribution or microstrain in CAIP induced by the charge compensation mechanism due to the substitution of Ca^{2+} by Eu^{3+} . The Eu^{3+} content in the samples was checked by energy dispersive spectroscopy (EDS). The average content of Eu^{3+} 1.1–1.2 mol% was found. Obtained values are within standard error margin for this technique. The SAED analysis revealed the presence of sharp and individual spots corresponding to the trigonal $R3c$ group for CAIP.

The Raman spectra $\text{CAIP}:\text{Eu}^{3+}$ is very complex and was not assigned in the present study. However the maximum phonon

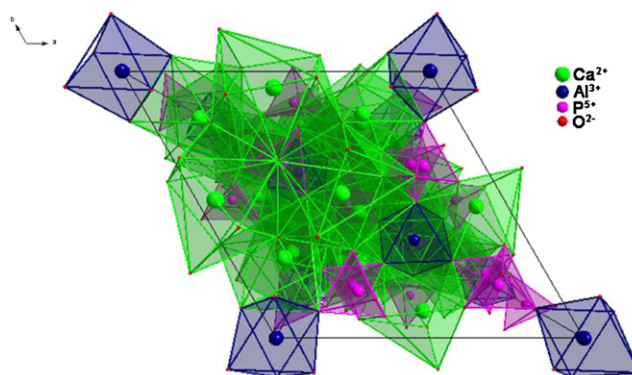


Fig. 2. Projection of the $\text{Ca}_9\text{Al}(\text{PO}_4)_7$ unit cell.

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