

Optical characteristics of the rare-earth-ions-doped calcium chlorapatite phosphors prepared by using the solid–state reaction method



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ABSTRACT

Rare-earth-ions-doped apatite-based phosphors for near ultra-violet excitation have been studied. $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{3+}$ and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Sm}^{3+}$ phosphors are synthesized by using the solid–state reaction method sintering at 1100 °C and 1300 °C, respectively. Optical properties of these phosphors are characterized by measuring the absorption, excitation, and emission spectra at room temperature. Strong red–orange emissions corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition of Eu^{3+} and the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ transition of Sm^{3+} from the near ultra-violet excitation are observed. $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{3+}$ and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Sm}^{3+}$ are red–orange emitting phosphors and the difference in emission intensity as varying the sintering temperatures is observed in both phosphors.

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1. Introduction

Rare-earth (RE)-ions-doped phosphors have been studied extensively for applications to backlights and other lighting systems; for examples, plasma display panels, field emission displays, and light-emitting diodes (LEDs) [1–3]. Among these applications, white LEDs have several advantages such as small size, low energy consumption, high power, and eco-friendly. Lots of researches on RE-ions-doped phosphors are in progress to apply for the white LEDs [4–6].

Apatite compounds attract lots of interests because of the applications to biocompatible ceramics, catalysts, ionic exchangers, oxide ion conductors, and fluorescent lightings [7–9]. Apatites are inorganic materials used in the production of phosphorus fertilizers and phosphor-organic compounds [10–12]. Among the apatites, calcium chlorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$] has several physical properties; for examples, a high elastic coefficient, a tolerance of abrasion and impact, non-toxic, and corrosion resistance. Thus, it can be utilized extensively as a host material for various phosphor materials.

Eu^{3+} and Sm^{3+} are important emitters in the red- and red–orange region of the visible spectra. Thus, Eu^{3+} and Sm^{3+} have

been used as local structure probes [13–16], and these ions exhibit higher efficiency for the operation with the near ultra-violet excitation [4,17]. The emission intensity of RE-doped phosphors is affected by the concentration of RE ions and the crystal structures [18]. The luminescent features of RE ions in apatites have been also studied [10,19–21]. However, the most results are based on the doped amount of the RE ions in apatites prepared with particular methods and/or temperatures. Thus, we would like to study the emission properties of the apatite powders prepared at different temperatures. We report the red–orange emissions in Eu^{3+} - and Sm^{3+} -doped $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ phosphors prepared by using the solid–state reaction method sintered at different temperatures. We study the optical properties by taking absorption, excitation, and emission spectra according to the concentrations of Eu^{3+} and Sm^{3+} at each sintered temperature. Ultimately, we show the correlation of the emission intensities with the concentrations of RE ions and crystal structures.

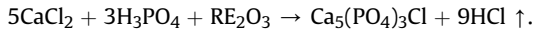
2. Experimental details

$\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{3+}$ and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{Sm}^{3+}$ phosphors are synthesized by using the solid–state reaction method. The starting materials are calcium chloride (CaCl_2 , Sigma–Aldrich, 99.9%), phosphoric acid (H_3PO_4 , Sigma–Aldrich, 85.0%), europium oxide

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(Eu₂O₃, Sigma–Aldrich, 99.9%), and samarium oxide (Sm₂O₃, Sigma–Aldrich, 99.9%). The compounds for this study are prepared according to the following scheme:



We convert the amount of H₃PO₄ carefully because the purity of the used H₃PO₄ is 85%. The concentrations of Eu³⁺ and Sm³⁺ are varied from 2 to 14 mol% and 3–6 mol%, respectively, but the mole ratio of CaCl₂ and H₃PO₄ is kept as 5:3 in all samples. The starting materials are mixed by using the ball-mill in deionized water for 24 h for homogeneous mixing, and then fully dried at 80 °C on the hot plate in the fume hood. After dried, they are crushed into a fine powder with a mortar and a pestle. Then, the materials are sintered at 1100 °C or 1300 °C for 6 h in atmosphere, and then grounded again. All samples are synthesized by using the identical process except for the concentrations of RE ions and the sintering temperatures.

The synthesized phosphors are characterized for structural properties by using an X-ray diffractometer (XRD, Philips X'Pert Pro) and a scanning electron microscope (SEM, Hitachi SU-70). The synthesized powders are pressed into a pellet of 1.3 cm diameter for the optical measurements by mixing potassium bromide (KBr, Pike Tech.). Optical properties of the phosphors are analyzed by taking absorption, excitation, and emission spectra. Absorption spectra are measured by using a UV–visible spectrometer (Varian Cary300). Excitation and emission spectra are measured by using the steady-state fluorescence system, where a 404 nm diode laser (PicoQuant LDH-P-C-400) and a 1000 W Xe-lamp (Muller Elektronik-Optik LAX-1000) are used as a light source for emission and excitation spectra, respectively. The fluorescence from the sample is collimated and focused into the emission monochromator (Dongwoo DM320i) with a 300 mm focal length. The signal is detected by using a photomultiplier tube (PMT, Hamamatsu R955) after passing the cut-off filter (Edmund OG 515) and is accumulated with a computer. All spectra are measured at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the Ca₅(PO₄)₃Cl phosphors: (a) and (b) are Eu³⁺- and Sm³⁺-doped Ca₅(PO₄)₃Cl powders sintered at

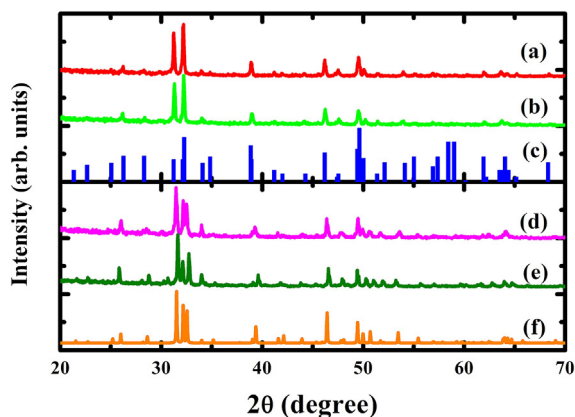


Fig. 1. XRD patterns of the Ca₅(PO₄)₃Cl phosphors: (a) and (b) are Eu³⁺- and Sm³⁺-doped Ca₅(PO₄)₃Cl powders sintered at 1100 °C, respectively, (c) is the XRD pattern of the hexagonal-structured Ca₅(PO₄)₃Cl powder from the JCPDS, (d) and (e) are Eu³⁺- and Sm³⁺-doped Ca₅(PO₄)₃Cl powders sintered at 1300 °C, respectively, and (f) is the XRD patterns of the monoclinic-structured Ca₅(PO₄)₃Cl powders from ICDD. The concentrations are 6 mol% in all phosphors.

1100 °C, respectively, (c) is the XRD pattern of the hexagonal-structured Ca₅(PO₄)₃Cl powder from the Joint Committee on Powder Diffraction Standards (JCPDS), (d) and (e) are Eu³⁺- and Sm³⁺-doped Ca₅(PO₄)₃Cl powders sintered at 1300 °C, respectively, and (f) is the XRD patterns of the monoclinic-structured Ca₅(PO₄)₃Cl powders from the International Center for Diffraction Data (ICDD). The concentrations of Eu³⁺ and Sm³⁺ shown in Fig. 1 are 6 mol%. All the prepared samples exhibit the same XRD patterns, and we show only one concentration in Fig. 1 for clarity. The Ca₅(PO₄)₃Cl powders sintered at 1100 °C form in hexagonal structure, while the ones sintered at 1300 °C form in monoclinic structure. We have discussed the details of the structural properties obtained by using XRD and SEM in the Ca₅(PO₄)₃Cl powders with different sintering temperatures in another paper [22].

Fig. 2 shows the UV–visible absorption spectra of the Ca₅(PO₄)₃Cl phosphors: (a) Eu³⁺- and (b) Sm³⁺-doped Ca₅(PO₄)₃Cl phosphors, respectively. The dopant concentrations are 6 mol% in both phosphors, and the sintering temperatures are 1300 °C (top) and 1100 °C (bottom) in both figures. In the absorption spectra of Eu³⁺-doped apatites shown in Fig. 2(a), strong absorption bands corresponding to the electronic transition ⁷F₀ → ⁵D₂ are observed at 458 nm and 467 nm in the Ca₅(PO₄)₃Cl phosphor, and the intensity of the band at 467 nm is stronger than that at 458 nm in the phosphor prepared at 1100 °C. The relative intensities of these bands are changed when the sintering temperature is increased to 1300 °C, because the crystal structures are changed from hexagonal phase to monoclinic phase [23]. Fig. 2(b) shows a strong absorption band at 407 nm due to the electronic transition ⁶H_{5/2} → ⁷F_{7/2} in Sm³⁺-doped Ca₅(PO₄)₃Cl phosphor. When the sintering temperature is increased to 1300 °C, another band originated from the ⁶H_{5/2} → ⁶P_{5/2} transition appears at 423 nm. In either case, the absorption bands are associated with the f–f transition of the Eu³⁺ and Sm³⁺ ions [24].

For the optical characteristics of the phosphors, we measure excitation and emission spectra of the prepared Ca₅(PO₄)₃Cl phosphors. Fig. 3 shows (a) the excitation and (b) the emission spectra of the 6 mol% Eu³⁺-doped Ca₅(PO₄)₃Cl phosphors, and the sintering temperatures are 1300 °C (top) and 1100 °C (bottom) in both figures. The excitation spectra are obtained by monitoring the fluorescence from the 572.0 nm emission corresponding to the ⁵D₀ → ⁷F₀ transition. We can observe a strong band originating from the ⁷F₀ → ⁵D₂ transition of Eu³⁺ in all prepared samples

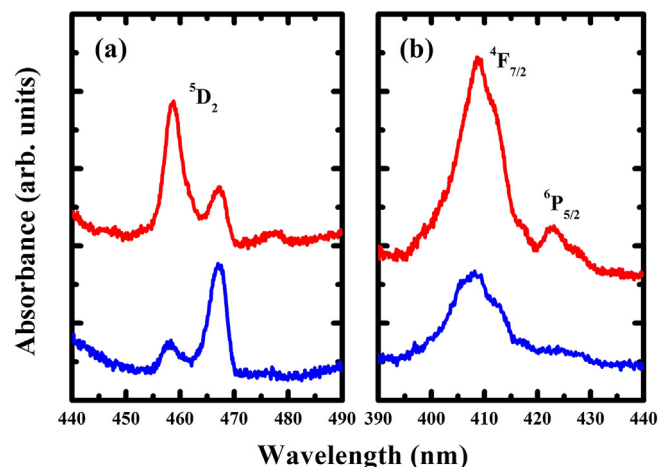


Fig. 2. Absorption spectra of the Ca₅(PO₄)₃Cl phosphors: (a) Eu³⁺- and (b) Sm³⁺-doped Ca₅(PO₄)₃Cl phosphors, respectively. The concentrations are 6 mol% in both phosphors. The sintering temperatures are 1300 °C (top) and 1100 °C (bottom) in both figures.

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