

Ce³⁺ emission in hexagonal and orthorhombic phases of CaSO₄

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Abstract

CaSO₄ exists in several phases. The most common phase of CaSO₄ is orthorhombic and reported Ce³⁺ emission corresponds to this phase. However, significant change in the emission of Ce³⁺ is observed when CaSO₄ crystallizes in hexagonal phases. The emission is observed at 354 nm as compared to the split band at 305 and 326 nm for the orthorhombic phase. The preparation procedure and photoluminescence spectra for orthorhombic and hexagonal phases are described in this paper.

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1. Introduction

Rare earth-doped alkaline earth sulfates received attention for applications in various areas [1,2]. Of the several sulfates, rare earth-doped CaSO₄ is studied extensively for the possible application as phosphor for photoluminescence crystal liquid display (PLLCD), optical storage material and cathodoluminescent material [3–7]. Several studies have been made with regard to control of particle size and morphology of CaSO₄ [8,9]. Rare earth-doped CaSO₄ is also used in radiation dosimetry. As early as 1955, Sm-doped CaSO₄ was shown to have useful properties for applications in thermoluminescence (TL) dosimetry of ionizing radiations [10,11]. Yamashita et al. reported CaSO₄:Dy phosphor having high TL sensitivity [12]. Due to high sensitivity and ease of preparation in large batches, it is used for environmental radiation measurements and personnel monitoring. Yamashita et al. reported other CaSO₄:RE phosphors also. CaSO₄:Tm, in particular, was found to be as good as CaSO₄:Dy [13]. Radio-photoluminescence (RPL) in CaSO₄:Eu³⁺ and CaSO₄:Sm³⁺ phosphors was studied by Calvert and Danby. They also demonstrated the application for dosimetry [14]. CaSO₄:Pr system is studied by several workers for the possible

application in quantum cutting, and information on levels of Ce³⁺ is also well documented [15]. Ce³⁺-doped CaSO₄ is also studied for the applications in thermoluminescence dosimetry [16]. The control of crystal growth and the morphology of CaSO₄ are very important in several contemporary technologies. Over the past decades, in order to inhibit the crystallization process and to modify the morphology of the crystalline product, a number of important studies on the formation of calcium sulfates have been made [9].

The above discussion on CaSO₄ reveals that most of the work is done on controlling morphology for the possible applications. Relatively less work is done on controlling phase of CaSO₄ which may be a factor in certain applications, particularly in luminescence. CaSO₄ exists in two phases, the most common phase is orthorhombic. However hexagonal phase can be obtained at room temperature which has significant effect on the emission and excitation of Ce³⁺ ion. The procedure for obtaining hexagonal phase and the data on photoluminescence (PL) of Ce³⁺ in this phase are presented in this paper.

2. Experimental

The alcoholic solution of calcium acetate (0.1 M) was made to which CeCl₃ solution was added so as to give doping concentration 0.1 mol%. Alcoholic solution of

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(NH₄)₂SO₄ was made and added dropwise to the calcium acetate solution with constant stirring. The white precipitate formed is then centrifuged, washed several times and dried under IR lamp. The drop rate and the concentration play very important roles in deciding the phase of the powder. The drop rate in the present case is 30 drops a min. The drop is formed from a capillary of size 0.1 mm. CaSO₄ powder doped with Ce using fast precipitation was also made for comparison. This sample is labeled as S₁ while sample with controlled precipitation is labeled as S₂. XRD measurements were carried out on Philips machine with copper target in the range $\theta = 0-90^\circ$. TGA-DTA measurements were carried out on Shimadzu DTG 60.

PL spectra of various samples were studied on a Hitachi F-4000 fluorescence spectrophotometer. The same amount

of sample was used every time. Emissions and excitation spectra were recorded using a spectral slit of 1.5 nm. Particle size measurements were carried out on Cilas 1180 particle size analyzer. Particle size of samples S₂ ranged from 500 to 7000 nm while particles for sample S₁ were about 10 times bigger.

3. Results and discussions

Fig. 1 shows the PL spectra of S₁ sample. The emission for sample S₁ is observed at 305 and 326 nm (Fig. 1a). The double humped emission spectrum is characteristic of Ce³⁺ and could be attributed to 5d → 4f (²F_{5/2}, ²F_{7/2}) transitions. The excitation to this band is observed around 253 and 295 nm (Fig. 1b). This is similar to what is observed and reported in literature [15,17]. However, the sample S₂ shows a very different emission as well as excitation. The emission is observed at 354 nm (Fig. 2a), longer to what is observed for S₁. The excitation band to this emission is also different and is observed at 308 nm with small peaks at 253 and 270 nm (Fig. 2b). To test genuinity of this changed emission, the sample S₂ is heated at 400 °C for 1 h, and then PL was taken. It was observed that emission shifts back to 305 and 326 nm, same as that observed for sample S₁. The excitation also becomes similar to that of sample S₁. This confirms that different emission in sample S₂ is genuine Ce³⁺ emission and not spurious one. Moreover, undoped CaSO₄ samples prepared by either method did not show

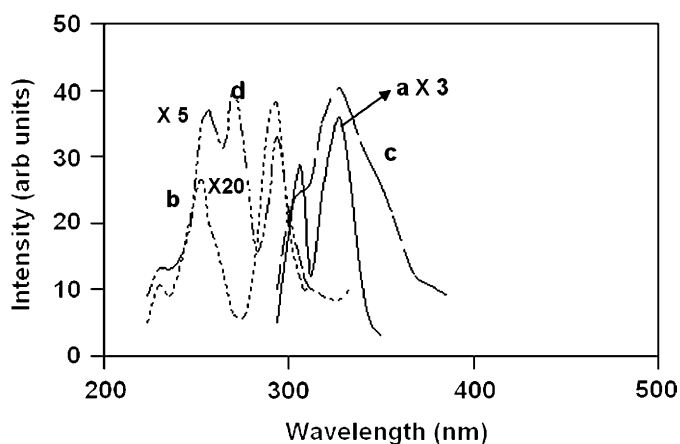


Fig. 1. Photoluminescence of Ce³⁺ in sample S₁. (a) Emission at 305 and 326 nm for $\lambda_{exc} = 254$ nm. (b) Excitation at 254 and 290 nm for $\lambda_{em} = 326$ nm. Spectra for the sample S₂ heated at 200 °C for 10 h are also shown. (c) Emission at 305, 326 and 354 nm for $\lambda_{exc} = 254$ nm. (d) Excitation at 260, 276 and 295 nm for $\lambda_{em} = 326$ nm. Numbers on the curves are the multipliers of the ordinate for obtaining the relative intensities.

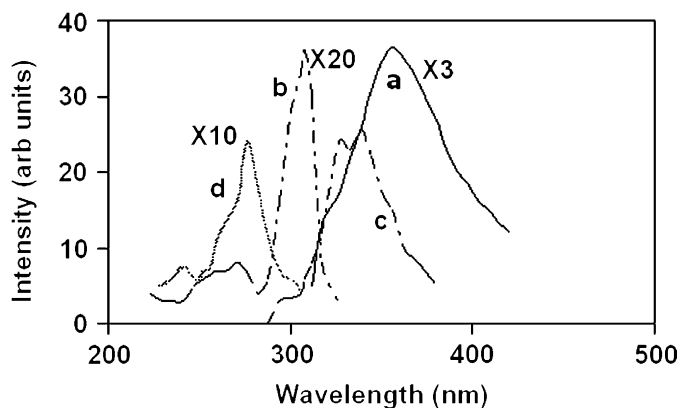


Fig. 2. Photoluminescence of Ce³⁺ in sample S₂. (a) Emission at 354 nm for $\lambda_{exc} = 308$ nm. (b) Excitation at 308 nm for $\lambda_{em} = 354$ nm. (c) Emission at 338 and 326 nm for S₂ heated at 200 °C for 1 h for $\lambda_{exc} = 276$ nm. (d) Excitation at 276 and 258 nm for $\lambda_{em} = 326$ nm. Numbers on the curves are the multipliers of the ordinate for obtaining the relative intensities.

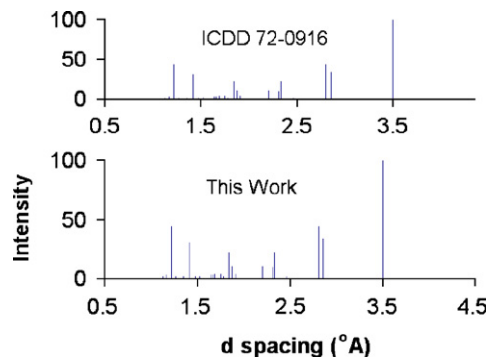


Fig. 3. XRD pattern for sample S₁. Major diffraction lines are compared with the data file ICDD 72-0916.

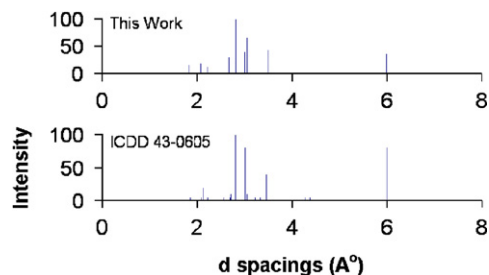


Fig. 4. XRD pattern for sample S₂. A good match is observed with CaSO₄ · 0.6H₂O (data file ICDD 43-0605).

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