

Synthesis and photoluminescence study of Sm³⁺ doped BaCa(SO₄)₂ phosphor.

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ABSTRACT

In this paper we report the photoluminescence (PL) characteristics of Sm³⁺ doped BaCa(SO₄)₂ phosphor prepared by solid state method. Prepared phosphor was characterized by X-ray powder diffraction (XRD) and photoluminescence (PL) properties. The XRD pattern indicates that the final product was formed in homogeneous form. The PL emission spectra showed green (564nm) and yellowish orange (597nm) and red (645nm) emission peaks when excited by 406nm wavelengths which are due to ⁴G_{5/2} → ⁶H_{5/2}, ⁶H_{7/2} and ⁶H_{9/2} transitions respectively within 4f₅ electronic configurations of Sm³⁺ ions. It can be concluded that BaCa(SO₄)₂ : Sm³⁺ phosphor was suitable as a white light emitting phosphor.

Keywords: solid state method, XRD, mixed sulphate, photoluminescence.

INTRODUCTION

Demand of new material with practical application is growing everyday in view of scientific and technological interest. If the material is phosphor, it receives much attention owing to their luminescence properties because of their wide range of application like solid state laser, multicolor emitting devices [1,2]. Trivalent rare earth ions doped phosphors possess unique nature of exhibiting sharp and distinct spectral lines of absorption and emission.

Samarium (Sm^{3+}) and europium (Eu^{3+}) have luminescence properties in visible region (orange to red) with potential applications in high dose measurements in medical radiation dosimetry and color displays.

Several mixed sulphates as host materials have been studied as luminescence materials e. g. The mixed sulphate $\text{K}_2\text{Ca}_2(\text{SO}_4)_3:\text{Eu}$ prepared by the conventional solid-state diffusion method is found to be a highly sensitive TLD phosphor [3]. Moreover, $\text{LiNaSO}_4:\text{Eu}$ in its nanocrystalline form has also been prepared and its thermoluminescence properties are studied [4]. Different researchers have studied on $\text{K}_3\text{Na}(\text{SO}_4)_2$ and $\text{K}_3\text{Na}(\text{SO}_4)_2:\text{Eu}$ [5-7]. Dhoble have shown that solid solution of KNaSO_4 and $\text{K}_3\text{Na}(\text{SO}_4)_2$ are highly sensitive phosphors [8]. Sahare explained that TL sensitivity of mixed alkaline earth sulphate, $\text{BaSr}(\text{SO}_4)_2:\text{Eu}$ is several times higher than that of Ba and Sr sulphates [9]. Work on Mixed sulphate $\text{Ba}_{0.12}\text{Sr}_{0.88}\text{SO}_4$ pure and doped with rare earth Eu has been reported [10]. S. P. Lochab worked on alkaline earth mixed sulphate, $\text{Ba}_{0.97}\text{Ca}_{0.03}\text{SO}_4$ doped with rare earth impurity Eu, and reported that to have a higher sensitivity than even the commercially available standard TLD phosphor, $\text{CaSO}_4:\text{Dy}$ (2.3 times of $\text{CaSO}_4:\text{Dy}$) when it irradiated by γ -ray. Mixed sulphates Phosphor had desired characteristics like a high temperature glow peak, linear response with gamma exposure, negligible fading and easy method of preparation. Therefore in this paper we are reporting the luminescence characteristics of samarium doped $\text{BaSr}(\text{SO}_4)_2$ phosphor.

METHODOLOGY

Mixed alkaline earth sulphate $\text{BaCa}(\text{SO}_4)_2$ was prepared by co-precipitation method. The sample $\text{BaCa}(\text{SO}_4)_2$ (pure) and $\text{BaCa}(\text{SO}_4)_2:\text{Sm}$ were prepared by co-precipitation method. All starting materials crush with additive solution with constant pH and filtered out and washed several times at constant temperature with activators. While preparing the samples the constituents BaSO_4 , CaSO_4 and the dopant samarium oxide (Sm_2O_3) were taken in a stoichiometric ratio and precipitated. Then ppt was kept in oven at 100°C for 12 hrs, The resultant polycrystalline mass was crushed to fine particles. Then this material was

heated at 800°C for 12 hrs in porcelain crucible, results the compound of $\text{BaCa}(\text{SO}_4)_2:\text{Sm}$ in powder form. The samples were then slowly cooled at room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible, this powder form was used in further study.

RESULTS AND DISCUSSION

XRD pattern of $\text{BaCa}(\text{SO}_4)_2$ host

Figure 1 shows the X-ray diffraction pattern of $\text{BaCa}(\text{SO}_4)_2$ material that matched with JCPDS file number 24-0093. The XRD pattern did not indicate the presence of the constituents BaSO_4 or CaSO_4 and other likely phases which is direct evidence for the formation of the desired compound. This result indicates that the final product was formed in homogeneous form. The prepared sample was characterized for their phase purity by X-ray powder diffraction using PAN-analytical diffractometer ($\text{Cu-K}\alpha$ radiation, $\lambda=1.5418 \text{ \AA}$).

Photoluminescence study of Sm^{3+} activated $\text{BaCa}(\text{SO}_4)_2$

Fig. 2 shows the excitation spectra of $\text{BaCa}(\text{SO}_4)_2$ Phosphor doped with samarium ions. The excitation spectrum was obtained by monitoring the emission wavelength at 597 nm which corresponds to ${}^4\text{G}_{5/2}$ to ${}^6\text{H}_{7/2}$ transition within Sm^{3+} . The excitation band wavelengths at 343,350,374,406,463 and 498nm correspond well to the electronic transition from ${}^6\text{H}_{5/2}$ to the upper state within Sm^{3+} . The most intense luminescence is observed by exciting the samples at 400-406nm. This is excitation to the ${}^6\text{P}_{3/2}$ level.

Fig.3 shows the emission spectra of $\text{BaCa}(\text{SO}_4)_2$ Phosphor doped with samarium ions. The emission spectra of $\text{BaCa}(\text{SO}_4)_2:\text{Sm}^{3+}$ was obtained by monitoring excitation wavelength at 406 nm wavelength, The emission spectrum consists of three peaks characteristic of Sm^{3+} ions, which are at 564 (green), 597 (orange) and 645 (red)nm. These three bands can be identified with the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$, ${}^6\text{H}_{7/2}$ and ${}^6\text{H}_{9/2}$ transitions respectively within ${}^4\text{f}_5$ electronics configuration of Sm^{3+} . Among the emission lines, the transitions at 564nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$) and 597nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$) are having the most similar intensity, which corresponds to green and near red emission of

Sm^{3+} : $\text{BaCa}(\text{SO}_4)_2$ phosphor. The emission at 597 due to ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ ($\Delta J = \pm 1$) is partly is magnetic dipole (MD) and partly electric dipole (ED) nature emission band [11]. The other transition at 564nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$) is purely MD nature and at 645nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$) is purely ED natured, which is sensitive to crystal fields. The intensity ratio of ED and MD transition has been used to measured the symmetry of the local environment of the trivalent 4f ions [12]. In $\text{BaCa}(\text{SO}_4)_2:\text{Sm}^{3+}$ we have found that the intensity of ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$ (MD) transition is more than the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ (ED) transition, indicating the symmetric nature of $\text{BaCa}(\text{SO}_4)_2$.

It is found that with the increase in the content of Sm^{3+} ion, emission intensity goes on increases and the maximum intensity was observed at 0.5mol% of Sm^{3+} ion concentration in $\text{BaCa}(\text{SO}_4)_2$ phosphor. The peak positions and the band-widths do not change up to 0.5 mol% dopant quantity, indicating that in this composition range the immediate surroundings of the emitting Sm^{3+} ions is independent on the concentration. In present case, luminescence was not quenched even at 0.5 mol% concentration of Sm^{3+} ion.

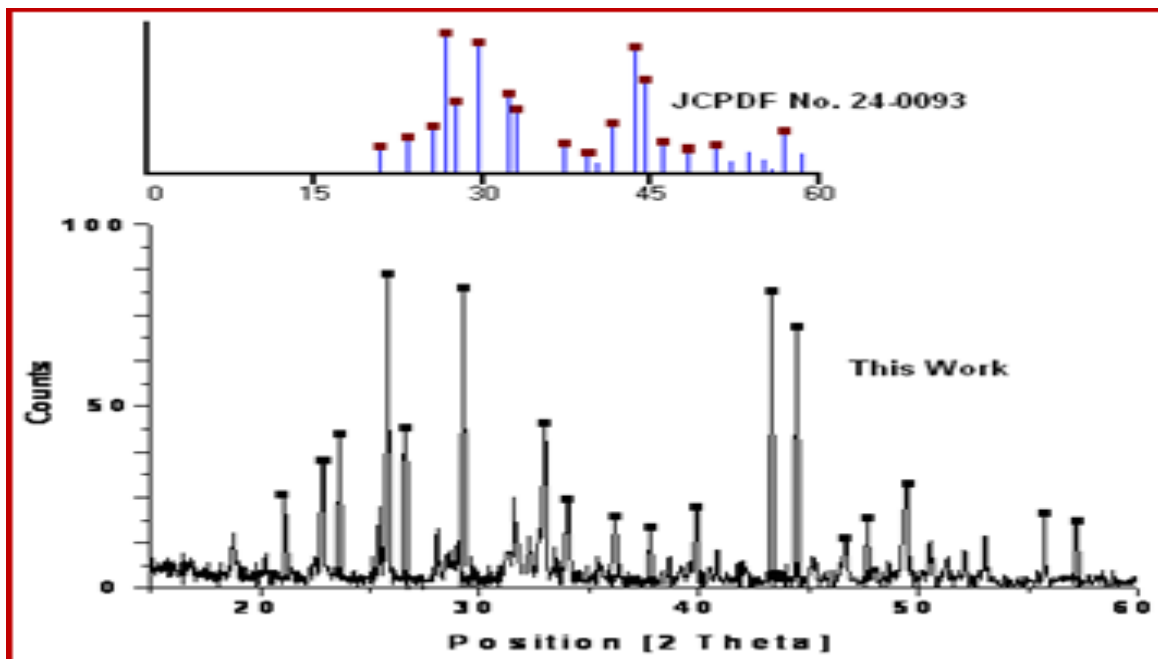


Fig.1 XRD pattern of $\text{BaCa}(\text{SO}_4)_2$ host prepared by solid state synthesis.

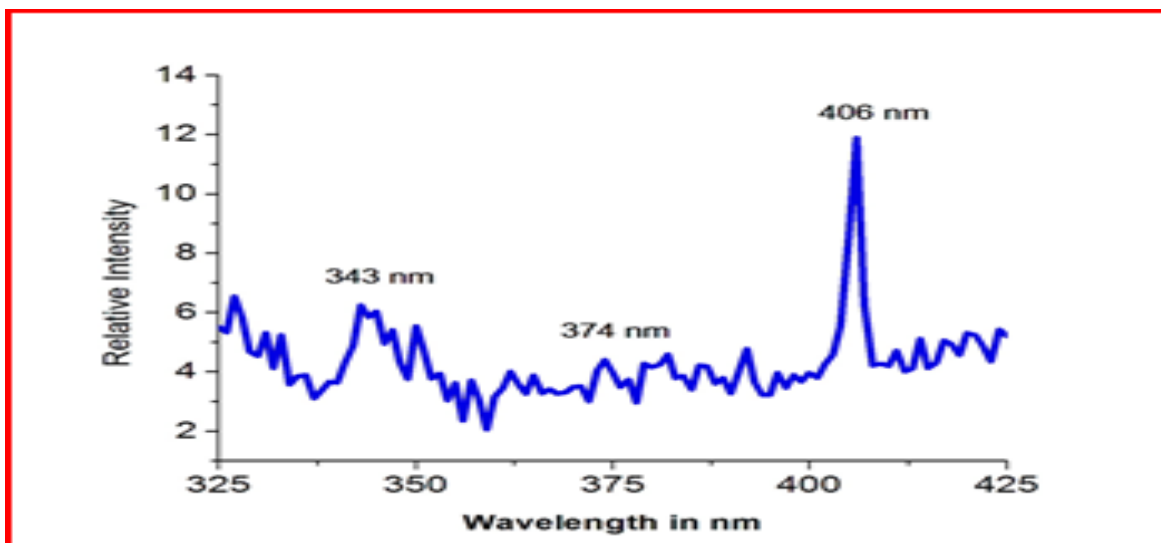
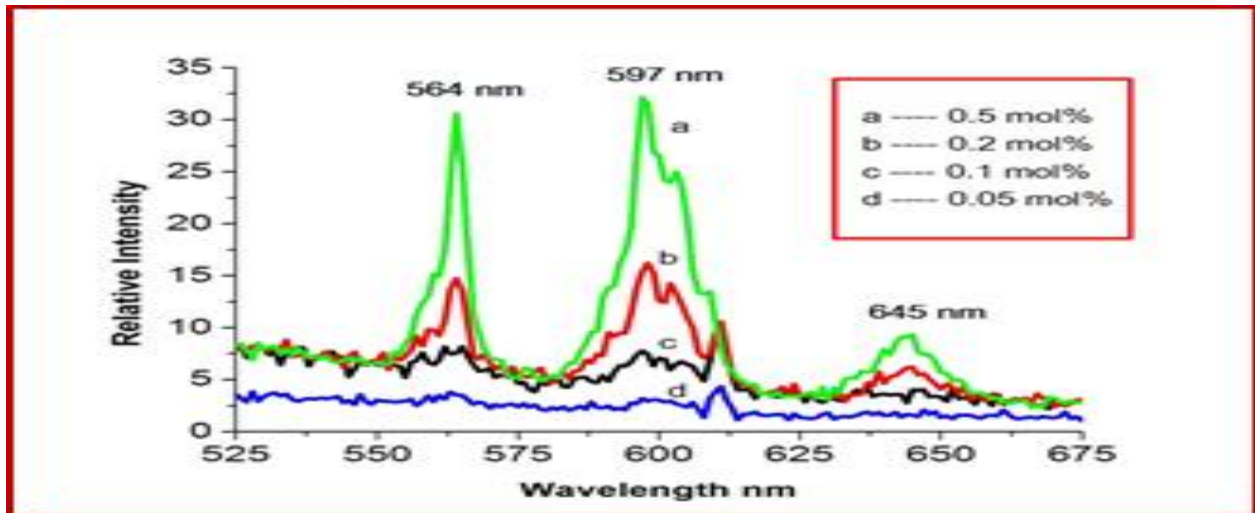


Fig. 2 Excitation spectra of BaCa(SO₄)₂:Sm³⁺ at λ_{em} = 597 nmFig.3 Emission spectra of BaCa(SO₄)₂:Sm³⁺ at λ_{ex}=406 nm.

CONCLUSION

Thus we have successfully showed a simple and cost effective solid state method to synthesize Sm³⁺ doped BaCa(SO₄)₂ phosphor. The phosphor was characterized by XRD. The PL emission spectra showed green (564nm) and yellowish orange (597nm) and red (645nm) emission peaks when excited by 406nm wavelengths which are due to ⁴G_{5/2}→⁶H_{5/2}, ⁶H_{7/2} and ⁶H_{9/2} transitions respectively within 4f₅ electronics configurations of Sm³⁺ ions. This shows that the BaCa(SO₄)₂: Sm phosphor can be used for NUV based white light emitting phosphor.

Conflicts of interest: The authors stated that no conflicts of interest.

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