

Optimization and Improvement in Photoluminescence of Rare earth activated Willemite salt ($\text{CaSO}_4: \text{Eu}^{2+}$) Prepared by Co-precipitation Method.

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ABSTRACT: Polycrystalline $\text{CaSO}_4: \text{Eu}^{2+}$ phosphor has been prepared by co-precipitation method for its optimization and improvement in the photoluminescence (PL) characteristics. And also find applications in photoluminescence liquid crystal display (PLLCD). Photoluminescence measurements suggest that there is direct conversion of Eu^{3+} to Eu^{2+} on 273 nm irradiation which is corresponding to charge transfer band of Eu^{3+} ions and reduction of Eu^{2+} ions with 384 nm illuminations representing $f \rightarrow d$ transitions of Eu^{2+} ions.

Keywords - Photoluminescence, PLLCD, $\text{CaSO}_4: \text{Eu}$, Emission spectra, Excitation spectra.

I. INTRODUCTION

The Eu doped solid state material usually shows strong broad band luminescence with a short decay time of the order of some tens of nanoseconds. The luminescence is strongly dependent on the host lattice and can occur from the UV to the red region of the electromagnetic spectrum. The Eu^{2+} emission is intense enough to find important application in the various devices like the tricolor low-pressure mercury fluorescence lamps. The most common types of transition in Eu emission are due to $4f_6^5d_1 \rightarrow 4f_6$ ($^8S_{7/2}$). As the position of band corresponding to $4f_6^5d_1$ configuration is strongly influenced by the host, the emission can be anywhere from 365 nm to (BaSO_4) 650 nm (CaS) Blasse [1] has listed the Eu^{2+} can be vary in a broad range from UV to Red. Since the $4f \rightarrow 5d$ transition is an allowed electrostatic dipole transition. The absorption and emission of Eu^{2+} is very efficient in many hosts, which makes the Eu^{2+} doped phosphors for practical importance. The Efficient Eu^{2+} emission has been obtained in many compounds [2, 3, 4], many of such phosphors have found applications in sulphate based compounds [5, 6]. The UV emitting phosphors are useful in erythema and photocopying lamps. RPL in $\text{CaSO}_4: \text{Eu}^{3+}$ and $\text{CaSO}_4: \text{Sm}^{3+}$ phosphors were studied by Calvert and Danby (1984). They also demonstrated the application for dosimetry. Later Moharil and co-workers gave recipe for preparing $\text{CaSO}_4: \text{Eu}$ phosphors with Eu in predominantly $2+$ or $3+$ form and used these phosphors for establishing the mechanism of TL in $\text{CaSO}_4: \text{RE}$ systems have also presented the work on these aspects. They also reported cathodoluminescence in $\text{CaSO}_4: \text{Eu}$. The Narrow PL emission located near the UV-Visible border in $\text{CaSO}_4: \text{Eu}^{2+}$ phosphor was found to be suitable for applications in PLLCD. In this paper, we described the synthesis of $\text{CaSO}_4: \text{Eu}^{2+}$ phosphor for PLLCD with the view of optimization and improvement in Photoluminescence.

II. EXPERIMENTAL METHOD

$\text{CaSO}_4: \text{Eu}^{2+}$ phosphor has been synthesized by co-precipitation method. Eu_2O_3 was dissolved in dilute HNO_3 then slowly evaporated to get Europium nitrate. This fresh prepared Europium nitrate and calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) were dissolved on double distilled water. This solution gives precipitate by concentrated H_2SO_4 . Then after repeatedly washed and dried obtained precipitate at 100 °C for 1 hour in an oven. The dried sample was annealed in air at 920 °C for 1 hour and quenched on thin aluminum block at room temperature. The photoluminescence of various samples were studied on a Hitachi F-7000 fluorescence spectrometer. The emission and excitation spectra were recorded using a spectral slit of 1.5 nm. The XRD data of prepared $\text{CaSO}_4: \text{Eu}^{2+}$ phosphor matched well with standard data of JCPDS (ICDD file No- 00-037-1496).

RESULT AND DISCUSSION

The XRD pattern of the polycrystalline powder samples of the phosphor $\text{CaSO}_4: \text{Eu}^{2+}$ have been analyzed for the structural confirmation. The powder XRD pattern of the phosphors $\text{CaSO}_4: \text{Eu}^{2+}$ was compared with the standard JCPDS files and found to be good agreement with the ICDD file No.: 00-037-1496 as shown in fig.1

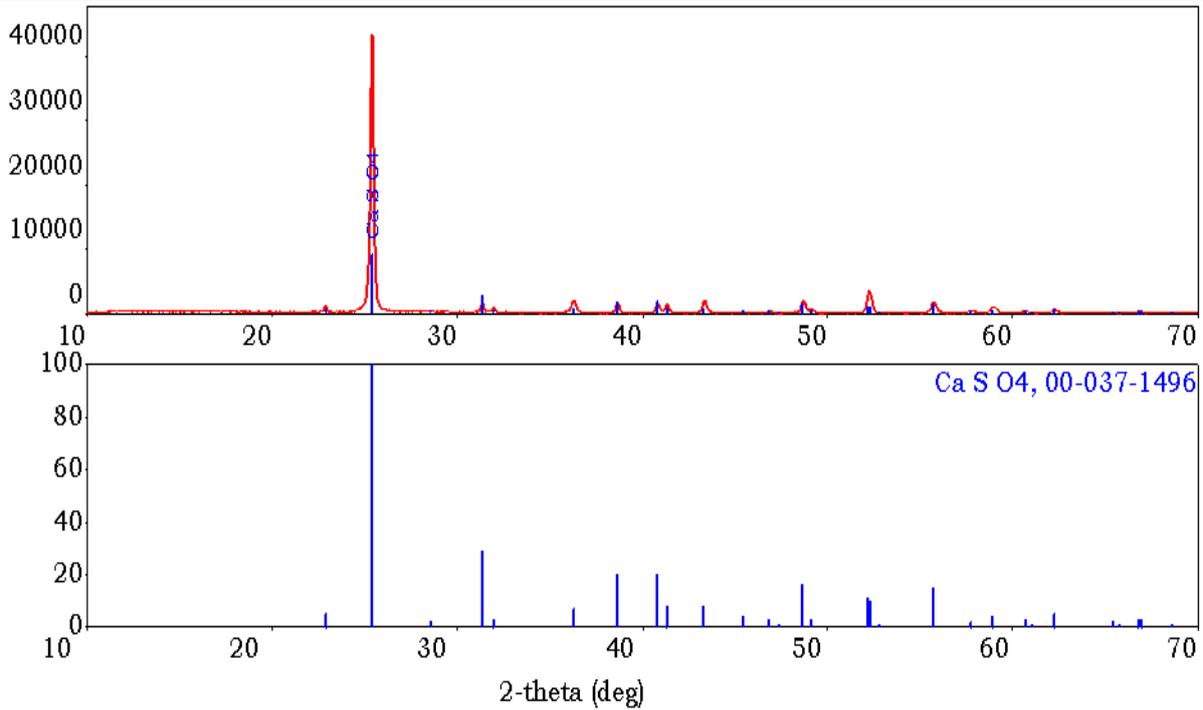


Fig. 1: XRD pattern of CaSO₄ host lattice.

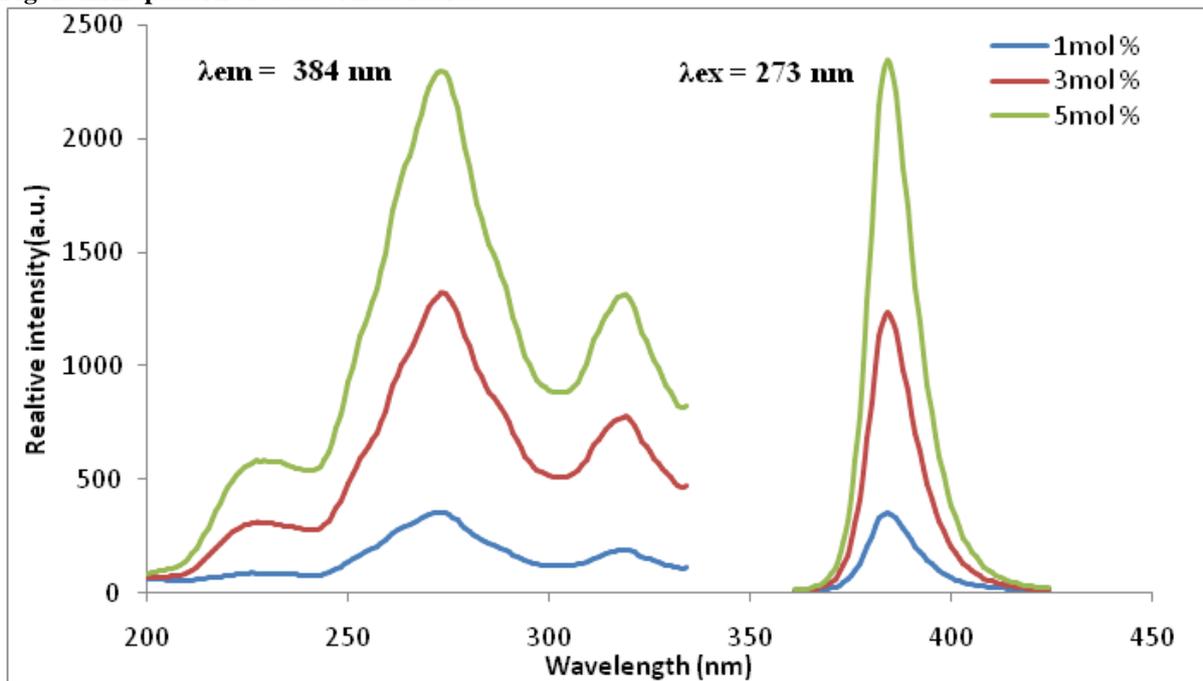


Fig. 2: Typical PL spectra of CaSO₄: Eu²⁺ phosphor. (a) Excitation spectrum for 384 nm Eu²⁺ emission and (b) Eu²⁺ emission spectrum for 273 nm excitation.

PL Study In CaSO₄:eu²⁺

The Eu²⁺ ions have very complex energy levels which in turn are modified by the host matrices. The first excited state ⁴f₆→⁵d₁ configuration lies close to the excited ⁴f₇ levels. Further more because of the large spatial extension of the 5d wave function, optical spectra due to the f-d transitions are usually broadened and depend on the surrounding of the Eu²⁺ ions. Thus the choice of host is a critical parameter for determining the optical properties of Eu²⁺ ions. Eu²⁺ ions in the CaSO₄ host are a favorable photo luminescent material. The PL excitation spectra of CaSO₄: Eu²⁺ phosphor monitored for 384 nm emission shows double humped peaking at 273 nm and 319 nm. The former is due to the splitting of first excited ⁴f₆→⁵d₁ levels closed to ⁴f₇ levels, while

later is due to complex splitting of Eu^{2+} level in to several levels due to surrounding environment of strong crystal field which leads to an cross relaxation from various levels give broad excitation. Thus the selection of host lattice surrounding field of host will responsible for the optical properties and favorable photoluminescence of Eu^{2+} ions. The emission spectra recorded for 273 nm of excitation shows narrow sharp band peaking at 384 nm which corresponds to the transition of Eu^{2+} ions from level $4f_6 \rightarrow 5d_1$ configuration to ground state $8S_{7/2}$ configuration state.

CaSO₄: Eu²⁺ Phosphor for photoluminescence liquid crystal display (PLLCD)

Liquid crystal display is most widely used as flat panel screens. They require very small current. However, these are passive type of displays; they are not emissive. Voltage applied to the display elements modifies the optical transmission. A light source is needed to convert these modifications into visible display. The conventional full colour LCD have restricted viewing angle. The contrast and brightness and colour of such display vary considerably with the viewing angle. A novel PLLCD architecture that gives a display with the same contrast, brightness and colour at all angles has been describe by Vechet et al.(1998). The display consists of a narrow band, collimated, near UV, backlight, a liquid crystal modulator and photo luminescent phosphor screen. The near UV light that passes through the liquid crystal cell causes visible emissions from the phosphor screen. Each pixel on the PL screen is made up of red, green and blue (RGB) dot, which enable generation of full colours. The phosphors are isotropic emitters and hence a full viewing angle like CR tubes is provided. As a backlight a narrow band near UV emitting source is required with a peak emission wavelength close to, but not extending into, the visible region. Any visible emission is undesirable since it will change the screen colours. A phosphor with narrow emission band around 390 nm is desirable, since at this wavelength the transmission of standard glass, polarizing plastic, other coating and LCD material is at acceptable level. This is not the case at the shorter wavelength, e.g. transmission of the standard liquid crystals at 390 nm is 94% while at 365 nm it falls to 87%. $\text{CaSO}_4:\text{Eu}^{2+}$ has a peak emission wavelength of 384nm, FWHM of 13 nm and quantum efficiency of 87% under 273 nm excitation. It is an ideal phosphor.

In $\text{CaSO}_4:\text{Eu}^{2+}$ phosphor strong Eu^{2+} emission is observed in all the phosphors annealed at and quenched from 1193K. It is remarkable that mere thermal treatment in air is sufficient to reduce Eu^{3+} to Eu^{2+} . Also in $\text{CaSO}_4:\text{Eu}^{2+}$ PL intensity is increases for concentration exceeding 1mol%. The sharp rise in intensity for Eu concentration above 1 mol% can be explained by postulating the presence of Eu^{2+} dimmers or even a micro-dispersed phase like $\text{CaEu}(\text{SO}_4)_2$ and further postulating that the luminescence efficiency of these are higher than that of isolated Eu^{2+} ion. This is quite contrasting to the behavior of Dy^{3+} . Survey of literature shows that Dy^{3+} luminescence is quenched for quite low concentration. This difference may be related to the forbidden nature of highly localized f-f transitions of Dy^{3+} .

III. CONCLUSION

- i) CaSO_4 : RE Phosphor are mostly prepared by the precipitation method.
- ii) The preparation method of phosphors and thermal treatments affects the properties of CaSO_4 : RE phosphor.
- iii) $\text{CaSO}_4:\text{Eu}^{2+}$ phosphors for PLLCD applications can be obtained using precipitation.

IV. ACKNOWLEDGEMENTS

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