



Substantial approach for energy transfer model and tunable emission for white light diodes (w-LEDs)

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Abstract

Rare earth Dy³⁺/Sm³⁺ activated polycrystalline CaSO₄ phosphors were prepared by co-precipitation method. Powder XRD pattern confirmed their structure and phase formation while FE-SEM investigation reflected the particle morphology. Optical absorption and emission spectroscopic analysis were carried out to find energy transfer within co-doped phosphors; a possible energy transfer mechanism was discussed. The Dy³⁺/Sm³⁺ ions co-doped phosphors exhibited a classic yellowish green and red emission due to efficient energy transfer from Dy³⁺ to Sm³⁺ ions under 363nm excitation. By adding a series of Sm³⁺ ions to the Dy³⁺/Sm³⁺ ions co-doped CaSO₄ phosphors, a pleasant white light emission was obtained. The multicolor emission from this material suggests sustainable approach towards possibility of obtaining white light emission.

Keywords

Phosphors, Co-precipitation, Energy Transfer, Tunable emission, FED, W-LED

1. Introduction

In recent years, optical properties of rare-earth (RE) doped inorganic material are extensively studied for their potential and diversified applications in the fields of lasers, fluorescent lighting, display devices, optical detectors, wave guides and fibre amplifiers [1–4], due the advantages of their luminous efficiency, energy-saving, reliability, safety, fast response, environmental-friendly and so on [5-7]. However, several drawbacks appear in their practical application, especially due to low luminous efficiency and poor color-rendering index [8, 9].

At present, more attention has been paid towards multi-doped phosphor for producing white light emission with the possibility for tuning wavelength.

CaSO₄ is potential and well known anhydrite salt; the luminescent studies of these compounds, doped with several RE (rare earth) ion are of interest, because of their high effective atomic number, low cost or easy to prepare and easy handling process.

Dysprosium (Dy³⁺) ions exhibit characteristic emission bands in the blue and yellow regions arising from the (⁴F_{9/2}→⁶H_{15/2}) and (⁴F_{9/2}→⁶H_{13/2}) transitions, respectively [10]. Among the RE³⁺ ions, Sm³⁺ ions are excellent activators to produce intense orange or red emissions due to the (⁴G_{5/2}→⁶H_{7/2,9/2,11/2}) transitions [11]. So far, the details luminescence properties of Dy³⁺-Sm³⁺ co-doped CaSO₄ phosphors have been reported by few [12-17]. The energy transfer from a donor to an acceptor is an important phenomenon that governs their luminescence.

In this study, we explore the luminescent emission properties of Dy³⁺/Sm³⁺ doped CaSO₄ phosphors with justified energy transfer mechanism for brighter luminescence and possible tuning of emission.

2. Experimental

Multi-doped powder samples of CaSO₄: RE³⁺ (RE= Dy³⁺, Sm³⁺) were prepared by simple route of chemical co-precipitation method. In this method analytical reagent grade (AR) Calcium nitrate was dissolved in de ionized double distilled water along with rare earth oxide (RE₂O₃) then concentrated sulphuric acid was added drop wise until formation of precipitation was completed, while adding sulphuric acid the mixture was stirred by a magnetic stirrer. The precipitate was collected and washed repeatedly by distilled water until water in the beaker became neutral. Then the precipitated was dried in an oven at 100⁰C for 1h. The resultant dried crystalline samples were crushed to fine powder in a crucible. Then it was annealed in a quartz crucible at 900⁰C for 1hr.

The excitation and emission photoluminescence spectra of various sample s were recorded using Hitachi F-7000 fluorescence spectrometer .The photoluminescence data were collected from the range of 200-650nm. The emission and excitation spectra were recorded at room temperature. For the confirmation of desired product, the crystal structure and phase identification of the sample was analyzed by powder XRD technique. The structural data of prepared CaSO₄ phosphor well matched with standard data of JCPDs (ICDD file No-00-037-1496) shown in Fig.1. The particle morphology was studied by Hitachi type2 FE-SEM, which is

shown in Fig.2. SEM micrograph clearly indicates the formation of spherically dense and agglomerated particles.

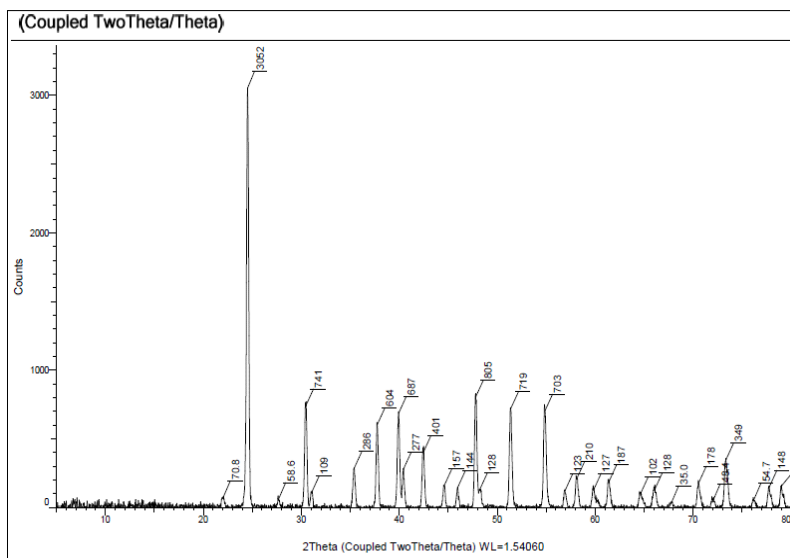


Fig.1 Indexed XRD Pattern of Host lattice CaSO₄

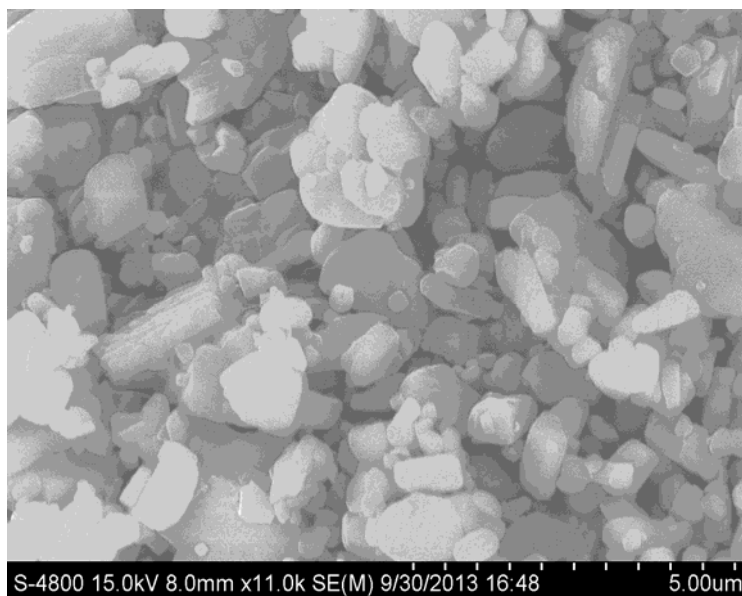


Fig.2 FE-SEM Micrograph CaSO₄: Dy-Sm

3. Results and Discussion

3.1 PL of CaSO₄: Dy³⁺-Sm³⁺

The PL and PLE of $\text{CaSO}_4:\text{Dy}^{3+}$ depicted in Fig.3. Emission monitored at 363nm excitation shows emission bands at 486 nm (blue region) and 574 nm (yellow region), assigned to the electronic transitions ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) and ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$) of Dy^{3+} ions respectively and excitation monitored at 574 nm shows broad host absorption (HAB) and characteristic peak at 363nm. Whereas double-doped RE ions $\text{CaSO}_4 \text{Dy}^{3+}, x\text{Sm}^{3+}$ ($x = 0.05, 0.5, 1$ mol%), polycrystalline phosphors as a function of Sm^{3+} ion concentration by monitoring with the excitation wavelength at 363 nm are shown in Fig.4, the spectra display co-doped RE ions (Dy^{3+} and Sm^{3+}) shows the emission bands at 565 nm (green region) and 603 nm (orange region), weak band 651nm, which are assigned to the ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$) and ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$) transitions of Sm^{3+} ions respectively, these emission bands, suggest the availability of co-doped ions in the host lattice.

By varying the concentration of Sm^{3+} ion from 0.05 to 1 mol %, while the Dy^{3+} ion concentrations were fixed at 1 mol%, the emission peak intensity corresponding to the ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$) transition of Sm^{3+} ions increased, at the excitation wavelength 363nm of Dy^{3+} . This is due to the possibility of energy transfer from $^4\text{F}_{9/2}$ level of Dy^{3+} to the $^4\text{G}_{5/2}$ level of Sm^{3+} ions, because the $^4\text{G}_{5/2}$ level of Sm^{3+} ions lies lower than the $^4\text{F}_{9/2}$ levels of Dy^{3+} ions, there is an opportunity of energy transfer from the Dy^{3+} ions to the Sm^{3+} ions. In the present case, the emission band at 565 nm corresponding to the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ transition of Sm^{3+} ions is almost overlapped with the Dy^{3+} emission band at 573 nm and so the intensity of these emission bands is not remarkably reduced whereas the intensity of blue emission band decreases. Therefore, from the above results, we presume that the energy transfer occurred from blue emission band of Dy^{3+} ions to Sm^{3+} ions. The possible ways of energy transfer from Dy^{3+} ions to Sm^{3+} ions are shown in Fig. 5.

It is observed that the co-doped phosphor (Dy-Sm) is efficiently excited by the 363nm (near ultraviolet) and emission is obtained in green to red region (CIE chromatic coordinate of optimized composition was found to be (0.38, 0.37), (0.39, 0.40) and (0.40, 0.38) in warm white region are close to that of white light (0.33, 0.33) [17] shown in fig.6.

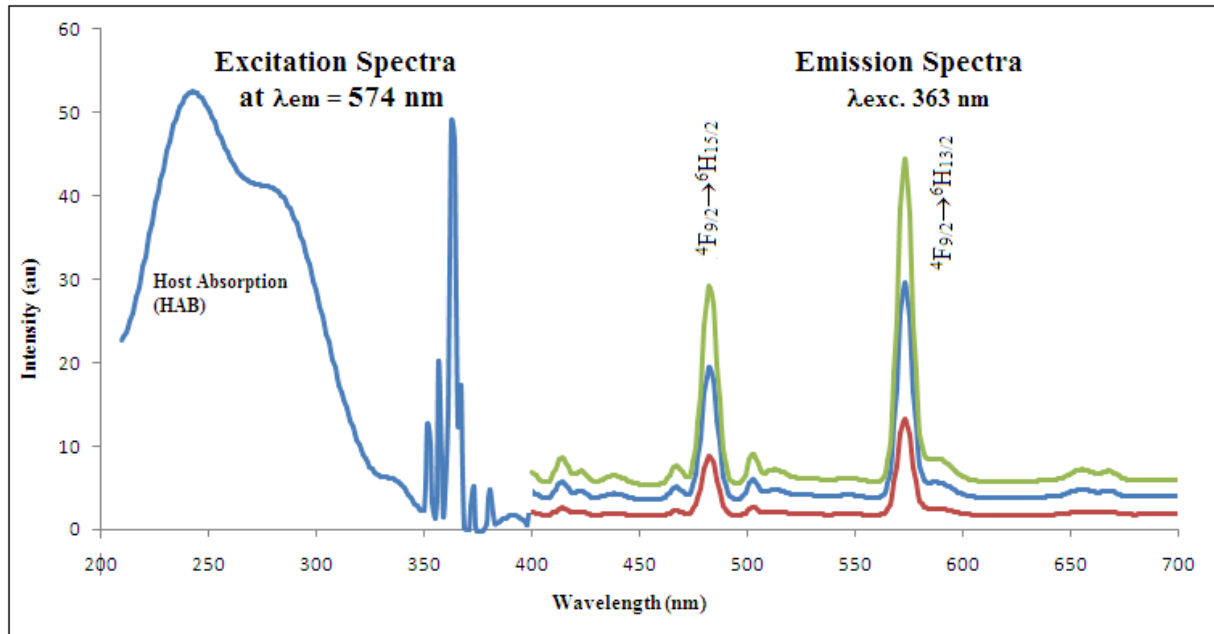


Fig.3 PL Excitation at λ_{em} 574 nm and Emission spectra at λ_{exc} 363 nm of $\text{CaSO}_4:\text{Dy}$

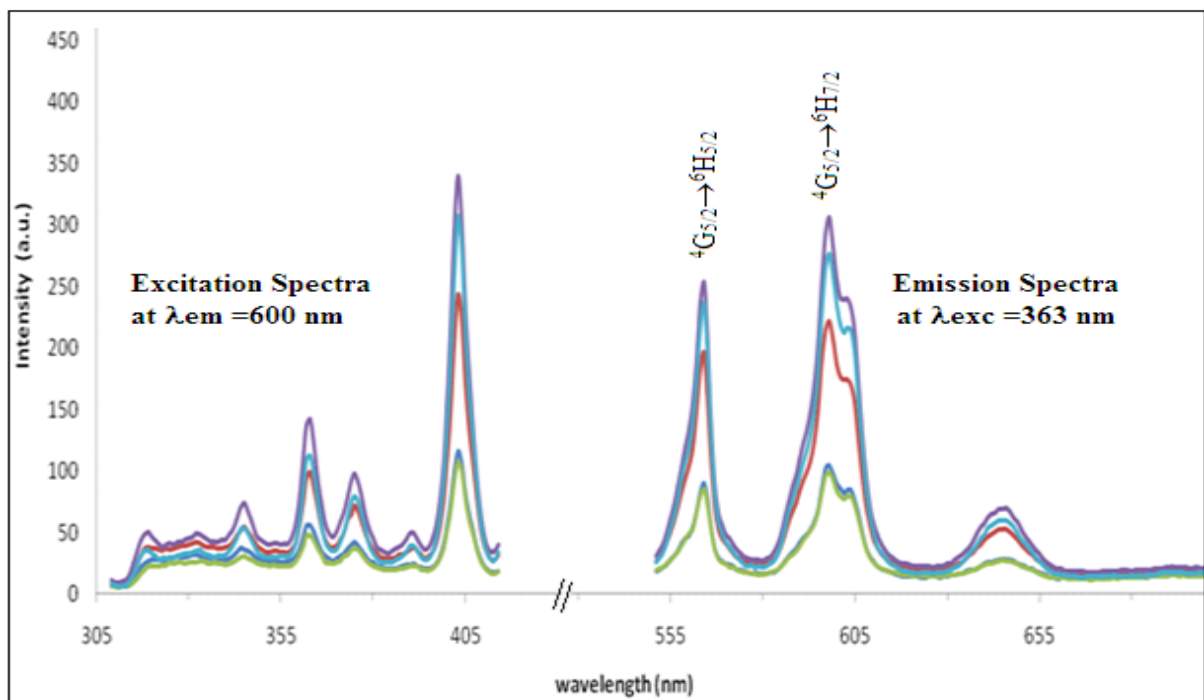


Fig.4 PL Emission at λ_{exc} =363 nm and PL Excitation at λ_{em} =603 nm spectra of $\text{CaSO}_4:\text{Dy}$, Sm Phosphor with variation in Sm Concentration

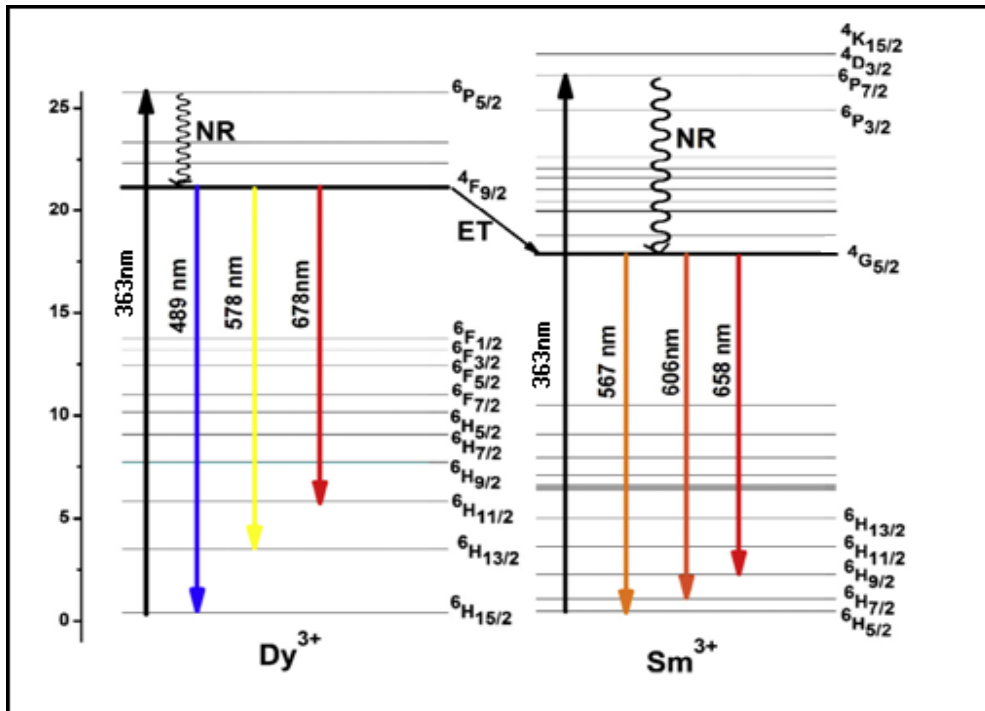


Fig.5 Energy transfer scheme Dy → Sm in CaSO₄: Dy-Sm Phosphor

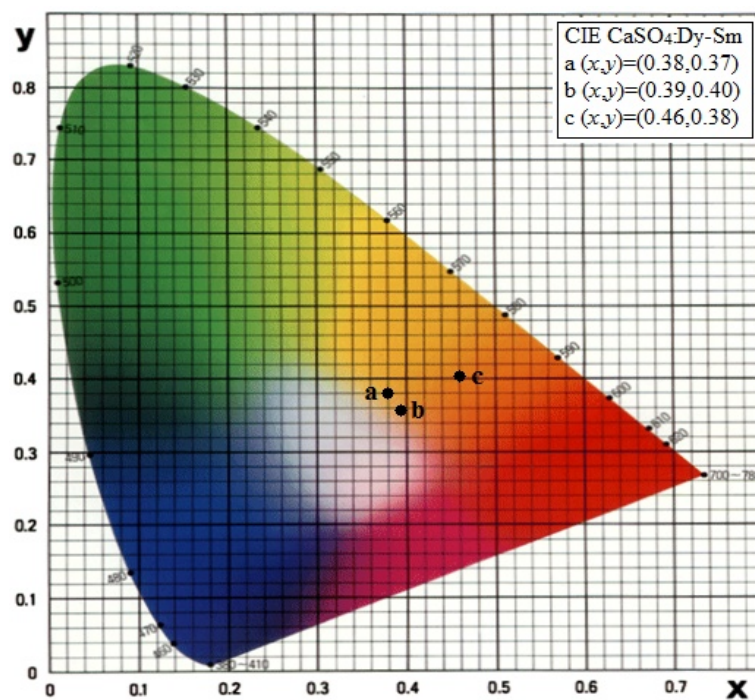


Fig.6 CIE Co-ordinates [a, b, c] of CaSO₄:Dy³⁺/Sm³⁺

4. Conclusion

Dy³⁺ and Sm³⁺ ions co-activated CaSO₄ polycrystalline phosphors were synthesized by simple route of co-precipitation method. The orthorhombic pure phase was obtained after annealed at 900⁰C and morphology of particles formed well defined obliquely spherically dense with packed nature. Dy³⁺ single ions doped CaSO₄ were effectively excited by 363 nm radiation and obtained green to red emission while, Dy³⁺/Sm³⁺ double doped phosphor upon excitation with 363 nm radiation, yields Sm³⁺ emission suppressing Dy³⁺ due to energy transfer and exhibit white light emission.

5. References

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