

Luminescence Properties of Eu³⁺, Dy³⁺ Doped Sr₂CeO₄ Phosphor

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Abstract:

This paper reports, Photoluminescence (PL) properties of Sr_2CeO_4 micro phosphor doped with Eu and Dy synthesized by standard solid state reaction method. The phosphors were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). The photoluminescence (PL) and The Commission International de l'Eclairage co-ordinates (CIE-1931) are reported. XRD reveals that no other phase exists in the XRD spectra of Sr2CeO4 and was indexed to crystallize in the orthorhombic phase corresponding to ICDD No. 89-5546. SEM image of Sr2CeO4: Eu (0.5%): Dy (0.5%) shows uniform spherical shape and the morphology is looks like grains and agglomerated. Broad emission range of 350–650nm in PL emission spectrum of un-doped Sr2CeO4 phosphor is due to f \rightarrow t1g transition of Ce⁴⁺ ion. The PL emission spectra of Sr2CeO4 phosphor doped with Eu and Dy shows the intensity of red emission increases with an increase of Eu concentration from 0.01 to 1.0 mol%. The CIE co-ordinates were calculated by the Spectrophotometric method using the spectral energy distribution.

Keywords: Photoluminescence, Solid state reaction method, phosphor, CIE, SEM, XRD analysis.

1. INTRODUCTION

Recently various phosphor materials have been actively investigated to improve their luminescent properties and to meet the development of different display and luminescence devices. Inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators[1,2]. Danielson et al. have reported a novel blue phosphor Sr₂CeO₄ prepared via the combinatorial material synthesis technique [3]. Sr_2CeO_4 exhibiting the emission peak at ~480 nm upon the excitation at \sim 280 nm, is considered as a potential blue emitting phosphor. As a new blue luminescent material, Sr₂CeO₄ phosphor has been widely studied since it was found by combinatorial chemistry method [4]. Sr₂CeO₄ consists of infinite edge-sharing CeO₆ octahedral chains separated by Sr atoms. The luminescence originates from a ligand-to-metal Ce4+ charge transfer. The broad emission band is suitable for the doping of rare earth ions in pursuing new luminescent materials and some research work has been carried out by traditional solid-state reaction [5, 6]. This methodology is having so many advantages like less complexity in synthesis process. Subsequently, a control on structure, morphology of particles, and dispersion of different materials is also possible and it

is used to industrially important for preparing bulk material etc [7]. In this work, the spectroscopic study of Sr_2CeO_4 phosphor and co-doped Eu and Dy are reported.

2. EXPERIMENTAL

Analytical grade Strontium nitrate $[Sr(NO_3)_2]$, Cerium oxide (CeO₂), Europium oxide (Eu₂O₃) and Dysprosium oxide (Dy₂O₃) of assay 99.9% were used as starting materials. All the phosphor samples are prepared via solid state reaction method. Un-doped Sr₂CeO₄ phosphor prepared by weighing inorganic salts, Strontium nitrate $[Sr(NO_3)_2]$, Cerium oxide (CeO₂) in 2:1 molar ratio. Then mixing and ground into fine powder using agate mortar and pestle about an hour. The sample was fired at 1200 °C for 3 hours in a muffle furnace with a heating rate of 5°C/min by keeping in an alumina crucible closed with lid [**8-12**]. The phosphor samples doped with different concentrations (0.01, 0.5, and 1.0%) of Eu and Dy were prepared.

The structure and the particle size was determined by means of X-ray diffraction using SYNCHROTRON BEAM LINE-II, λ of beam line =0.895Å. The average crystallite size calculated by using Scherrer equation (t =K. λ / β cos θ) where 'k' the Scherrer constant (0.94), ' λ ' the wavelength of the X-ray (0.895 Å), ' β ' the full-width at half maxima

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(FWHM) and '0' the Bragg angle. A scanning electron microscope (PHILIPS XL 30 CP) was used to examine the morphology of the samples at 30kv. Photoluminescence spectra was measured at room temperature by SHIMADZU, RF-5301 PC model Spectrofluorophotometer (Xenon lamp as excitation source) with excitation and emission slit width=1.5mm.

3. RESULT'S AND DISCUSSION

The structure and the crystallite size were determined by means of X-ray diffraction technique. Figure-1 is the XRD pattern of undoped Sr₂CeO₄ phosphor and was indexed to crystallize in the orthorhombic phase corresponding to ICDD Card No. 89-5546, [13]. In addition, the refined crystallographic unit cell parameters were obtained and are listed in table- 1. These values are compared with Li et al. [14] and R. Seema et.al. [15]. The powder derived from the solid state reaction method was heated at 1200°C in air for 3hrs shows the starting materials disappeared completely and Sr₂CeO₄ was formed as the predominant product with a tiny amount of SrCeO₃. Except this, no other phase exists in the XRD spectra, indicating the formation of the final product [13]. The calculated average crystallite size of un-doped Sr₂CeO₄ is ~9nm, and Eu:Dy codoped is ~10nm. When compared with ICDD and other workers, the reduction in unit cell volume was observed and confirms the formation of nano crystallite phosphor, via solid state method.



Fig.1: XRD Pattern of un-doped Sr₂CeO₄

Figure-2 shows the SEM image of Sr_2CeO_4 : Eu (0.5%): Dy (0.5%). It is observed that uniform spherical shape with different size and shapes and the morphology is looks like grains and is



Fig.2: SEM image of Sr₂CeO₄: Eu (0.5%): Dy (0.5%)

agglomerated.Figure-3 shows PL emission spectrum of un-doped Sr₂CeO₄ phosphor with broad emission range 350 – 650nm for excitation of 250nm. The peak at 470nm attributed to the energy transfer between the molecular orbital of the ligand and charge transfer state of the Ce⁴⁺ ion. The emission band can be assigned to the f \rightarrow t_{1g} transitions of Ce⁴⁺ ions. Under 260nm excitation, the samples show same emission spectra with more intensity. However our results were compared with the previous workers [16-20].

Table.1

Crystal name	a (Å)	b (Å)	с (Å)	Cell volume (Å ³)
ICDD No. 89-5546 [13]	6.119	10.350	3.597	227.79
Our sample	5.964	8.279	4.472	220.81
Li et. al [14]	6.1153	10.3473	3.5957	227.52
R. Seema et. al[15]	6.07	10.32	3.62	226.76

Figure-4 shows the PL excitation and emission of Eu (0.01, 0.5, and 1.0%) at Dy (0.5%) codoped Sr₂CeO₄ phosphor under 250nm excitation, shows peaks at 468, 483, 537, 575, 587 and 617nm with good intensity. Under 260nm excitation, the samples show same emission spectra with slight increase in the intensity. The observed peaks at 468, 537, 587 and 617nm are from the transitions ${}^{5}D_{2} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{1} \rightarrow {}^{7}F_{1}$ and also from ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, 2, respectively. It is also observed that the intensity of peak at 617nm is increasing as the 'Eu' concentration increases while the intensity of peaks at 468, 537 and 587nm decreases. The peak around 610- 620nm is due to the electric dipole transition of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, which is induced by the lack of inversion symmetry at the Eu³⁺ sites. It is well known that the ${}^{5}D_{0} \rightarrow {}^{7}F_{2} / {}^{5}D_{0} \rightarrow {}^{7}F_{1}$ intensity ratio is a good measure of the site symmetry of rare-earth ions in a doped material.



Fig.3: Excitation and emission spectra of un-doped Sr₂CeO₄ phosphor

This is because the hypersensitive transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ tends to be much more intense at a site with no inversion symmetry, while the magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is constant, regardless of the environment. The visible spectra also consist of lines at around 483 and 575nm belongs to Dy3+ ion. These may be assigned to the transitions from ${}^{6}F_{9/2} \rightarrow {}^{6}H_{15/2}$. ${}^{6}F_{9/2} \rightarrow {}^{6}H_{13/2}$. The result indicated the presence of energy transfer is taking place from Ce to both Eu and Dy ions. It is concluded that may be at high concentrations of Eu(5-10mol%) by keeping Dy concentration at constant emit red colour emission. It may be at high concentrations of Dy(5-10mol%) by keeping Eu concentration at constant emit yellow colour emission. These unusual luminescent properties are due to low vibration energy of Sr₂CeO₄ and different energy transfer process from host to dopant. The high efficiency energy transfer allows us to expect that the Sr₂CeO₄ crystal structure could form the base for the creation of phosphors with different spectral emissions. Therefore this single host phosphor can be a good candidate in lamps and many display devices.

Figure-5 illustrates the CIE chromaticity diagram depicted on 1931 chart. The CIE co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution. The colour co-ordinates of un-doped Sr_2CeO_4 sample (A) are x = 0.208 and y = 0.28. The colour co-ordinates of Eu(0.01%): Dy(0.5%) co-doped Sr_2CeO_4 sample (B) are x=0.165 and y=0.250 and Eu(1%): Dy(0.5%) co-doped Sr_2CeO_4 sample (C) are x=0.260 and y=0.240. From figure-, it is observed that the emission varies from blue to cyan and then to red with increasing of the Eu concentration.



Fig.5 CIE -1931 Coordinates of A) Un-doped Sr_2CeO_4 B) Eu(0.01%): Dy(0.5%) Co-doped Sr_2CeO_4 C) Eu(1%): Dy(0.5%) co-doped Sr_2CeO_4

4. CONCLUSIONS

Sr₂CeO₄ and Eu^{3+,} Dy³⁺ co-doped phosphors were synthesized via solid state reaction method and measured their fluorescence spectra. XRD and SEM of the phosphors have shown that the average crystallite size of un-doped Sr₂CeO₄ is around~9nm, and Eu:Dy co-doped is ~10nm. The phosphors exhibit uniform spherical shape with different size and shapes, the morphology and the grains with agglomerated. From the optical properties it was found that the emission transition of ${}^{5}D_{0}$ - ${}^{7}F_{2}$ intensity was the strongest among the main lines and the emission from 5D1, 2 was observed due to the lowenergy vibration of the host lattice. Besides, the red emission 5D0-7F2 intensity was increased when the Eu³⁺ ion concentration was increased from 0.01 to 1.0 mol%. Furthermore, the characteristic emission lines of Dy3+ ion lines were well resolved at around 483(blue) and 575nm (vellow) was observed. Obviously there also exists low energy transfer process between Sr₂CeO₄ and Dy³⁺ transition of dysprosium in the yellow region. May be at high concentration of Dy (5-10mol %), high energy transfer takes place between host and Dy3+ ion in the vellow region makes it an important material for technological applications. Therefore these phosphors can be used as multicolor emitting fluorescence powder in many display devices.

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Fig.4: Excitation and emission spectra of Sr₂CeO₄ doped with Eu (0.01, 0.5, 1.0%) at 250nm excitation with Dy(0.5%) as constant