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Synthesis and Luminescence behavior of SrS:EuCeX[X=La,Tb,Dy]Nano-sized phosphor fabricated through modified solid state reaction processes for white LED

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ABSTRACT - The new trivalent rare earth activated SrS: EuCe and SrS: EuCeX (where X=La, Tb and Dy) phosphors were prepared by modified solid state reaction method. The prepared phosphors are characterized by photoluminescence, XRD and SEM micrographs. The Excitation spectrum studied monitoring at 600 nm and the Emission spectrum studied under 450 nm Excitation visible light, the phosphors shows efficient yellow and orange mixture broad band emissions, which originates from the Eu^{2+} transitions. It is observed broad band which can be viewed as the typical emission of Eu^{2+} ascribed to the 4f–5d transitions. The emission spectrum of SrS: EuCeX was a broad band ranging from 550-675 nm with peaking at 600 nm and a full width at half-maximum (FWHM) of 60 nm at an excitation wavelengths of 450nm. Mainly the paper reports the variation of 600 nm peak intensity doped with X(X=La, Tb and Dy) in SrS: EuCe phosphor.

Keywords: Photoluminescence; phosphor rare-earth ions; XRD; solid state reaction technique, LED

I. 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. There is very much interesting in light emitting diodes (LEDs) with emission wavelengths in the ultraviolet-to-infrared range. LED technology has flourished for the past few decades. High efficiency, reliability, rugged construction, low power consumption and durability are among the key factors for the rapid development of the solid-state lighting based on high-brightness visible LEDs.[1] In this context, the search for stable, inorganic rare-earth-based phosphors with high absorption in the yellow and orange spectral region is an attractive research task. The white LEDs have several advantages over the conventional incandescent and fluorescent lamps due to its high power efficiency, long lifetime, non-pollution and flexibility in design process. This composition could be considered as an alternative approach due to advantages such as lower production cost, simpler manufacture procedure, non- hygroscopic and environmental-friendly characteristics [2,3]. The aim of the present work is synthesis and investigate luminescence properties of rare earth [La, Tb and Dy] doped SrS:EuCe phosphors for white LED, but we observed special and different behavior of the rare earth doped phosphor.

II. Experimental Details

A. Materials and Sample Preparation

All the inorganic chemical reagents were taken analytically pure (99.99%) and used without further purification. SrS:Eu,Ce and SrS:EuCeX[where X=La, Tb and Dy] doped phosphor samples were prepared by the conventional modified solid state reaction method. Strontium Carbonate ($SrCO_3$) and Sulphur(S) were taken as starting compounds in stoichiometric proportions is weighed and ground into a fine power using agate mortar and pestle to prepare SrS phosphor. The starting compounds along with the host phosphor, Europium oxide (Eu_2O_3), Cerium oxide (CeO_2), Lanthanum Oxide (La_2O_3), Terbium Oxide (Tb_4O_7) and Dysprosium Oxide (Dy_2O_3) were taken as dopents, these are taken into an agate mortar and pestle and they were mixed and grounded for one hour to make a fine powder with intermediate mixings and groundings. The obtained powder was taken into an alumina crucible and heated in a muffle furnace under reduced atmosphere at 900^0C for three hour.

B. Physical Characterization

All the prepared phosphor samples were characterized by X-ray diffraction using Synchrotron Beam Indus –II, the microstructures of the sample were studied using scanning electron microscopy (SEM) (XL 30 CP Philips) and the Photoluminescence (PL) emission and excitation spectra were measured by Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using Xenon lamp as excitation source at display research Lab, Department of Applied Physics, Faculty of Technology and Engg., M.S.University, Baroda. The emission and excitation slit were kept at 1.5 nm, recorded at room temperature.

III. RESULTS AND DISCUSSION

A. Photoluminescence Study

The excitation spectrum of the phosphor SrS:Eu(0.5 mol %), Ce(0.5 mol %),Dy(0.5 mol %) monitoring at 600nm is present in figure 1. From the figure it is found there are two excitation bands starting from 225 – 325 nm, peaking around 254 nm and second is from 400 – 570 nm. The first band is UV region and second band is perfect blue green visible region [10,11], there is also another small absorption band of 365 nm, the 365 nm band is due to charge transfer transition of Ce^{3+} from 4f to conduction band. The excitation bands at 254 nm and 460 nm can be assigned to the e_g to $2t_g$ 5d bands of Ce^{3+}. The broad excitation bands monitoring at 600 nm are found at 265 nm and 540 nm, which can be attributed to the ($4f^7$) e_g and $4f^6\ 5d^1(^t2_g)$ field splitting 5d bands of Eu^{2+} respectively.

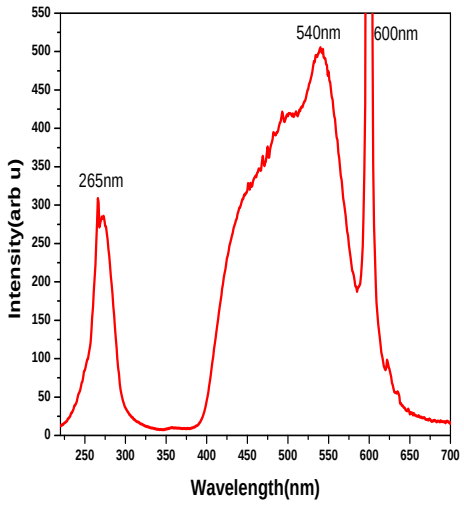

Figure 1 Excitation spectrum of SrS: EuCeDy Phosphor monitored at 600 nm

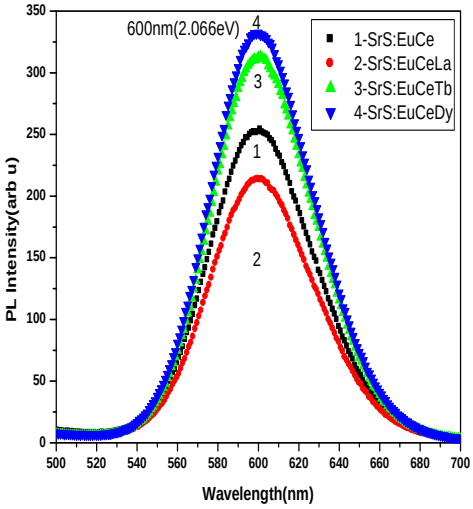

Figure 2
Emission spectrum of SrS:EuCeX[X=La,Tb and Dy] Phosphor under 450nm Excitation

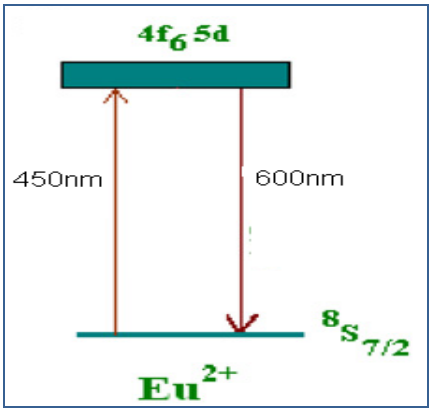

Figure 3 Energy level diagrams for all possible transitions of Eu^{2+} ions for Excitation and Emissions

Figure 2 is the emission spectrum of SrS:Eu(0.5 mol %), Ce(0.5 mol %) and X(0.5 mol %)[where X=La,Tb,Dy] phosphor, when excited with 450 nm, the emissions are found at 365 nm, 395 nm and 467 nm with less intensity(which are not shown in graph) along with a broad emission peaking at 600 nm. The rare earth element La is doped in the SrS:Eu,Ce phosphor the 600 nm peak Intensity is decreased by 20% when compared with

emission spectrum of the SrS:Eu,Ce phosphor, but Tb and Dy ions are doped in the SrS:Eu,Ce phosphor the intensity of 600 nm peak is raised by 30% and 50% respectively, this is due to dipole-dipole interaction and higher energy transition rate between Ce^{3+} to Eu^{2+}.

The 600 nm emission corresponding to the $4f^65d$-$4f^7$ transition, this broad luminescence band of Eu^{2+} ion, is an allowed electrostatic dipole transition of Eu^{2+}, which is broad emission range from 550-675 nm. From the emission spectrum it was observed the maximum emission intensity for 600 nm peak is found for Dy ion doped in the phosphor SrS:EuCe. The full width at half-maximum (FWHM) is around 60 nm. From figure it is concluded that the resonance energy transfer from Ce^{+3} to Eu^{+2} is more when Tb, Dy are doped in the SrS:Eu^{+2},Ce^{+3} in the excitation wavelengths 450 nm. From overall discussion SrS:Eu^{2+}, Ce^{3+},X^{3+} phosphor one can normally concluded that in the presence of Tb and Dy ions emission of PL intensity increase but these are not resolve any individual emission peaks. The preference of more than one phase but did not influence the PL emission peak shape of 600 nm. The higher energy transition rate between Ce^{3+} to Eu^{2+} is more when doped with Dy ion in SrS:EuCe phosphor, figure 3 is the energy level diagrams for all possible transitions of Eu^{2+} ions for Excitation and Emissions, figure 4 is the energy level diagrams for all possible transitions of Ce^{3+} and Eu^{3+} ions for Excitation and Emissions, and energy transfer mechanism.

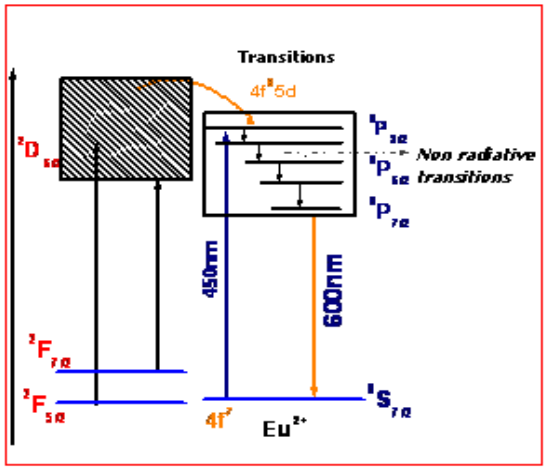

Figure 4 Energy level diagrams for all possible transitions of Ce^{3+} and Eu^{3+} ions for Excitation and Emissions, and energy transfer mechanism.

B. X-ray Diffraction (XRD)

The phase verification, structural parameters and crystalline structure of the SrS: Eu^{2+}, Ce^{3+} and SrS:Eu^{2+}, Ce^{3+}, X^{3+} phosphors were analyzed by X-ray powder diffraction studies (XRD) of powder samples, at room temperature in wide range of Bragg`s angle 2θ from 20 to 50. Figure 5 is the XRD pattern of SrS:Eu^{2+}, Ce^{3+} (0.5 mol %)X^{3+} (0.5 mol%) phosphor. The crystallite size is calculated using Scherrer's formula $d=K\lambda/\beta\cos\theta$, where 'K' is the Scherer's constant (0.94), 'λ' the wavelength of the X-ray (1.54060 Å), 'β' the full-width at half maxima (FWHM), 'θ' the Bragg angle, of the XRD big peak is found for all phosphors, shown in table-1, from table-1 it is clearly observed that all the samples are in nano size, the crystallite size of SrS:Eu^{2+},Ce^{3+},Dy^{3+} phosphor is around 63.426 nm.

SNo	Phosphor Name	Crystallite size(nm)
1	SrS:Eu^{2+},Ce^{3+}	70.266
2	SrS:Eu^{2+},Ce^{3+},La^{3+}	68.660
3	SrS:Eu^{2+},Ce^{3+},Tb^{3+}	76.393
4	SrS:Eu^{2+},Ce^{3+},Dy^{3+}	63.426

Table 1 Crystallite sizes of SrS:EuCe, SrS:EuCeX (X=La,Tb,Dy) phosphors.

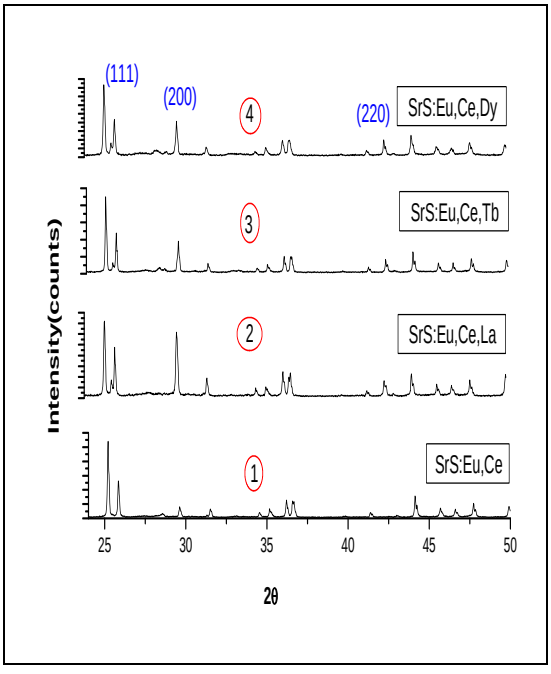

Figure 5 XRD pattren of SrS:Eu,Ce and SrS:Eu,Ce,X(X=La,Tb,Dy) phosphor

The XRD peaks of phosphors are well indexed based on the JCPDS No.75-0895. This reveals that the structure of doped (Eu,Ce and Eu,Ce,X) phosphor SrS is cubic and the arrangement of atoms are Face Centre Cubic system, and is agreement with previous workers[11]. From the XRD graphs in the presence of Dy the majority phosphor SrS:EuCe has single phase of the Bragg's angle $2\theta=25.207$, corresponding miller indices are (111), it is compared to other phosphors like SrS:EuCe and Co-doped with La,Tb, the phosphor Co-doped with Dy in SrS:EuCe, the energy transfer from Ce to Eu is more.

C. SEM Analysis

Characterizing particles of feature size for nano crystals and nano structures is done routinely using scanning electron microscope. The main advantages of SEM graphs are that they can be used to study the morphology of prepared nano particles and nano composites. Direct size measurements obtained from images are often used in conjunction with other measurements such powder, X-ray diffraction (XRD). Figure 6, figure 7, figure 8 and figure 9 are the SEM micrographs of the SrS:$Eu^{2+}Ce^{3+}$, SrS: $Eu^{2+}Ce^{3+}La^{3+}$, SrS: $Eu^{2+}Ce^{3+}Tb^{3+}$ and SrS: $Eu^{2+}Ce^{3+}Dy^{3+}$phosphors for different magnifications. From these graphs, it is observed that the particles look agglomerated and irregular shapes having size of 1 micron to 6 microns. From figure 7 the particles irregular shapes but all are having the nearly same size when compared to other due to this in the presence of Dy maximum amount of energy transfer from Ce to Eu in this host. This is same as reveal in the XRD graphs and photoluminescence behavior of the phosphor.

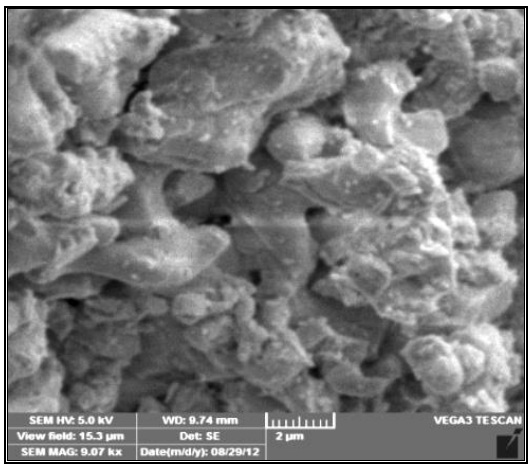

Figure 6 SEM image of SrS:Eu,Ce Phosphor

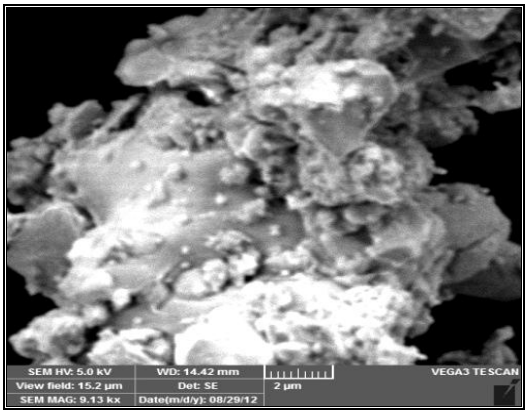

Figure 7 SEM image of SrS:Eu,Ce,La Phosphor

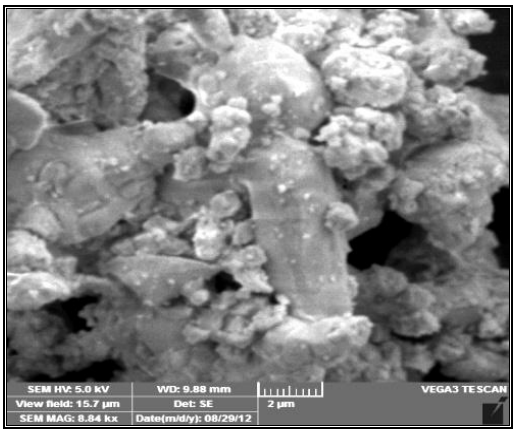

Figure 8 SEM image of SrS:Eu,Ce,Tb Phosphor

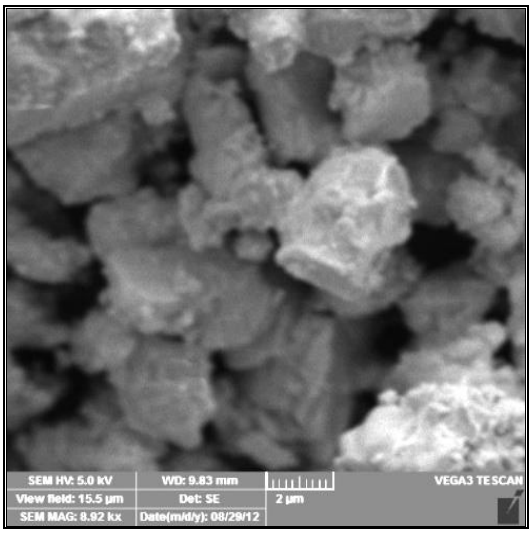

Figure 9 SEM image of SrS:Eu,Ce,Dy Phosphor

IV. CONCLUSION

Based on the results presented above, the following conclusions

1. SrS:EuCeX(X=La,Tb,Dy) doped phosphors were synthesized by modified solid state method.
2. The broad excitation bands of the 600 nm peak are attributed to the e_g and ^t2_g field splitting 5d bands of Eu^{2+}, respectively.
3. XRD examination of SrS:EuCeX phosphor revealed that the samples were crystalline in nature, with no evidence of any other phases and the phosphor is a single phase.
4. The electronic configuration of Eu^{2+} is $4f^7$. The lowest excited state of 4f levels is located at 28×10^3 cm^{-1} and is higher than the $4f^6$ $5d^l$ level in most of the crystals, so that Eu^{2+} usually gives broad band emission due to f-d transitions.
5. The 600 nm emission is corresponding to the transition of Eu^{2+}, is a broad emission range from 550-675 nm. From the emission spectrum it was observed that the sample shows 600 nm emission and the intensity is highest for Dy ion doped in the phosphor under 450 nm excitation wavelength, the phosphors shows efficient yellow and orange mixture broad band emissions,
6. Thus our reported result suggests that modified solid state reaction method is a promising technique for the preparation of rare earth doped SrS phosphors for field emission display and for the development of colour-LEDs, these phosphors meet the application requirements for blue LED chips because all of them have strong absorption in the blue region that is suitable to blue.

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