ORIGINAL RESEARCH PAPER

Volume-7 | Issue-4 | April-2018 | PRINT ISSN No 2277 - 8179

INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

Synthesis, Characterization and Photoluminescence of Sr_2CeO_4: x=0.01, 0.1, 0.2, 0.5, 1.0 mol % Dy3+ (0.5 mol% La_{3+}) phosphor

Chemistry

Savali Ravi Kumar Department of Physics, SKRBR Junior College, Narasarao pet, A.P., India,

Ch. Atchyutha Rao* Department of Physics, Bapatla College of Arts & Sciences, Bapatla– 522101, A.P., India*Corresponding Author

K.V.R.Murthy Display Materials Laboratory, Applied Physics Department, M.S University of Baroda, Vadodara – 390 001, India

ABSTRACT

In this article, pure Sr2CeO4 and Sr2CeO4: x=0.01, 0.1, 0.2, 0.5, 1.0mol% Dy3+, 0.5mol% La3+ phosphors were synthesized by solid state reaction method. X-ray diffraction (XRD) patterns disclosed that the samples exhibited an orthorhombic crystal structure. Room temperature photoluminescence (PL) analysis indicated that the excitation peaking at around 260 nm, and all the samples showed intensely blue emission at 470nm.Scannimg Electron Microscope (SEM) images showed that the sample fired at 12000C exhibits grain like morphology with different sizes and shape. Fourier Transform Infrared Spectroscopy (FTIR) determined the chemical bonds in a molecule and the particle size distribution histogram indicated the mean diameter of sample.Commission international de l'eclairage (CIE) co-ordinates of samples revealed that the emission varies from blue to pale yellow with increasing of dysprosium concentration.

KEYWORDS

Sr_2CeO_4; Solid state reaction method; blue emission; pale yellow emission; particle size distribution histogram.

1. Introduction

In the recent years, much attention has been focused on oxide-based luminescent materials due to their commercial applications in color television, fluorescent tube, X-ray phosphors, and scintillators [1, 2]. 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 [3]. There is growing interest in the development of new full colour emitting phosphor materials that combine thermal and chemical stability in air with high emission quantum yield at room-temperature.

In 1998, a blue phosphor compound, Sr_2CeO_4, possessing one-dimensional chain of edge-sharing CeO_6 octahedra, was identified by Danielson and his co-workers with combinatorial chemistry [4]. It exhibited a blue–white emission band that peaks at 485 nm under 254 nm excitation. The luminescence was suggested to originate from a ligand-to-metal Ce^{4+} charge transfer. In addition, it has been established that Sr_2CeO_4 exhibits photoluminescence under excitation with irradiation of ultra violet rays [5, 6]. Sr_2CeO_4 phosphor has been widely studied because of its importance in the realization of a new generation of optoelectronic and displaying devices. Recently, some groups began using all kinds of methods to fabricate this promising material and research its luminescent properties [7-10].

In this research article, we have studied on the synthesis, size, morphology and to get yellow emission photoluminescence properties of Sr_2CeO_4: x mol % $Dy^{3+}$and Sr_2CeO_4: x mol % Dy^{3+}, 0.5mol % La^{3+} phosphors prepared by solid state reaction method in air at 1200^{0}C. The prepared materials were characterized by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), particle size distribution histograms and photoluminescence techniques. PL studies and CIE co-ordinates of Sr_2CeO_4: x=0.01,0.1,0.2,0.5,1.0 mol % Dy^{3+}, 0.5mol % La^{3+} phosphors reveals that the emission colour varies from blue to pale yellow.

2. Experimental methods

Sr_2CeO_4: x mol % Dy^{3+} and Sr_2CeO_4: x mol % Dy^{3+}, 0.5mol % La^{3+} phosphors were synthesized by the conventional solid state reaction method. The dopant concentration in Sr_2CeO_4:Dy^{3+} varied from 0.01-1.0 mol% range.Strontium Nitrate $Sr(NO_3)_2$ assay(99.995%) Sigma-Aldrich Chemie Inc,Germany, Cerium oxide (CeO_2) assay (99.5%), Dysprosium oxide (Dy_2O_3) assay (99.9%), Lanthanum Oxide(La_2O_3) assay (99.9%), National Chemicals, Nutan Gujarat Industrial Estate, Vadodara, India, were used as starting materials to prepare Sr_2CeO_4: x mol % Dy^{3+} and Sr_2CeO_4:x=0.01, 0.1, 0.2, 0.5, 1.0 mol% Dy^{3+},0.5mol % La^{3+} phosphors. The stoichiometric mixture (Sr^{2+}/Ce^{4+}, 2:1) of these staring materials were thoroughly homogenized in an agate mortar and pestle for 1hr and then put into an alumina crucible. Different samples were obtained after subsequent thermal treatment at 1200°C for 3h in muffle furnace in air with a heating rate of 5°C/min. Finally the samples were allowed to cool down to room temperature for about 20h. All the samples were again ground into fine powder using agate mortar and pestle about an hour.

To identify the crystal phase, X-ray diffraction (XRD) analysis was carried out with a powder X-ray diffractometer (Angle Dispersive X-ray diffraction Indus beam line-II, (ADXRD BL-12), Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. The electron source size at this port is approximately 0.5mm (H) x 0.5 mm (v). The beam acceptance of the beam line is 2mrad (H) x 0.2mrad (V). The microstructures of the samples were studied using a scanning electron microscope (SEM) (XL 30 CP Philips). The scanning continues time is 10s, and 2θ range is from 15 to 60°. The Fourier Transform Infrared (FTIR) spectra were recorded in an FTIR spectrometer (IRAffinity-1) in the range from 500 to 4000 cm^{-1}. The particle size analyses of the phosphors were in solid state method obtained at a laser based particle size analyzer (Malvern Instrument Ltd (U.K). The photoluminescence (PL) emission and excitation spectra were recorded with a spectrofluorophotometer (SHIMADZU, RF-5301 PC) equipped with a Xenon lamp as excitation source. All the spectra were recorded at room temperature. Emission and excitation spectra were recorded using a spectral slit width of 1.5nm. The Commission International de l'Eclairage(CIE) co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution. The chromatic coordinates (*x*, *y*) of prepared materials was calculated with colour calculator version 2, software from Radiant Imaging [11].

3. Results and discussion

3.1 Crystal structure of pure and Dy^{3+} doped Sr_2CeO_4

The crystalline structure of the powders was analyzed by X-ray powder diffraction (XRD). The present XRD phosphors were done on (Angle Dispersive X-ray diffraction (ADXRD BL-12), Raja Raman Centre for Advanced Technology (RRCAT), at Indore, India. The typical X-ray diffraction (XRD) pattern of Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor shown in fig.1 and all the diffraction peaks were well indexed on the basis of International Centre for Diffraction Data (ICDD) database. 89-5546. No other phase observed in XRD spectra, it indicates that the prepared Dy^{3+}, (La^{3+}) co-doped Sr_2CeO_4 phosphor is single phase and a tiny amount of $SrCO_3$. The crystallite size of the sample was determined from the XRD pattern parameters according to the Scherrer's equation D_c=kλ/ βcosθ, where D_c is the average crystallite size, k is the Scherrer's constant equal to 0.94, λ is the wavelength of the X-ray (0.8592 Å), β is the full-width at half maxima (FWHM) and θ is the Bragg angle (diffraction angle) of the XRD peak, [6-10]. The calculated average crystallite size of Sr_2CeO_4: x mol% Dy^{3+} and Sr_2CeO_4: x=0.01, 0.1, 0.2, 0.5, 1.0 mol% Dy^{3+}, 0.5mol% La^{3+} phosphor are 7.4nm and 9nm respectively. This confirms the formation of nano crystallite size phosphor, via solid state reaction method.

3.2 PL behaviour of Sr_2CeO_4: x mol % Dy^{3+} and Sr_2CeO_4: x=0.01, 0.1, 0.2, 0.5, 1.0 mol % Dy^{3+}, 0.5mol % La^{3+} phosphor

PL excitation spectra of pure and Sr_2CeO_4: 0.5 mol % Dy^{3+} phosphors as shown in fig.2a. The excitation spectrum of pure Sr_2CeO_4 was characterized by a broad band ranging from 220-375nm with peaks at 260nm. This band could be assigned to the transition t_{1g}→f, where f is the lowest excited charge transfer state of Ce^{4+} ion and t_{1g} is the molecular orbital of the surrounding ligand in six fold oxygen coordination [6, 12, 13]. The Dy doped Sr_2CeO_4 phosphor shows excitation spectra similar to the pure Sr_2CeO_4 phosphor with slight variation in intensity.

When excited with the radiation of wavelength 260nm, pure Sr_2CeO_4 phosphor emits a broad band in the blue region which extends from 350-650nm with a peak at 470nm as shown in fig.2b. The emission band can be assigned to f→t_1g transitions of Ce^{4+} ions. The shape of the emission spectra and emission peak wavelength is independent of the excitation wavelengths. This is mainly due to the charge transfer of the Ce^{4+} – O^{2-} ligand as described by Danielson et al [14].

In PL emission spectra of Sr_2CeO_4: x mol% Dy^{3+} phosphor with different concentrations (0.01, 0.1, 0.2, 0.5, 1.0mol %) under 260nm excitation (Fig.2b), one peak is centered at 476nm (blue) and other peak is at 575nm (yellow). They are assigned to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions in Dy^{3+} respectively. The result indicate the presence of energy transfer from the triplet excited state of the metal to ligand charge transfer (MLCT) state for Sr_2CeO_4 (sensitizer) to Dy^{3+} (activator). This is shown clearly in the fig.2c. The position of the emission peaks of Dy^{3+} doped Sr_2CeO_4 phosphor is well resolved and but not influenced by Dy^{3+} concentration and excitation wavelengths.

A series of Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor with various Dy^{3+} concentrations (0.01, 0.1, 0.2, 0.5, and 1.0mol %) were prepared and the effect of Dy^{3+} concentration on the emission intensity was investigated. PL excitation and emission spectra of Sr_2CeO_4: x mol % Dy^{3+}, 0.5mol % La^{3+} phosphor with different concentrations under 260nm excitation was shown in fig.3. The excitation spectra of Sr_2CeO_4: x=0.01, 0.1, 0.2, 0.5, 1.0 mol % Dy^{3+} and Sr_2CeO_4: x =0.01, 0.1, 0.2, 0.5, 1.0 mol % Dy^{3+}, 0.5mol % La^{3+} phosphors were monitored at the emission wavelength of 400nm, have similar features. It consists of a broad band in the range 220 - 370nm with peak at 260nm. Under the excitation of the wavelength 260nm, the corresponding emission spectra of Sr_2CeO_4: x=0.01, 0.1, 0.2, 0.5, 1.0 mol% Dy^{3+}, 0.5mol% La^{3+} phosphor was measured. As shown in fig.3, the emission spectra of Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor consists of the characteristic lines of Dy^{3+} corresponding to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions located at 476nm (blue) and 575nm (yellow) respectively. From the fig.3, it was observed that main emission of pure Sr_2CeO_4 is intact at 470nm but the overall intensity reduced to 15%. The co-doping of Dy^{3+}, La^{3+} reduced the PL intensity of the Sr_2CeO_4:Dy^{3+} phosphor system and also the intensity of the characteristic peak of Dy^{3+} at 476nm is reduced by 20% and at 575nm is reduced by 10%. PL emission peaks of Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} under 260nm excitation shown in Table-1.

3.3 Morphology and size of pure and Dy^{3+} doped Sr_2CeO_4

Fig.4 shows the SEM micrograph of Sr_2CeO_4: x=0.01, 0.1, 0.2, 0.5, 1.0 mol% Dy^{3+}, 0.5mol% La^{3+} phosphor at different resolutions. The sample exhibits grain like morphology with different sizes and shape. At low magnification the particles appear agglomerated and at high enough magnification, the nature of individual crystallites is clearly evident. The samples prepared by solid state reaction method were granular and their diameters were less than 1.25μm.

The Particle size distribution histogram of the Sr_2CeO_4: x=0.01, 0.1, 0.2, 0.5, 1.0 mol% Dy^{3+}, 0.5mol% La^{3+} phosphor particles synthesized using solid state reaction method is illustrated in fig.5. The prepared phosphor sample particle size was measured by using laser based system Malvern Instrument U.K. The mean diameter of the particle of Sr_2CeO_4: x mol% Dy^{3+} and Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor are 32 μm and 28μm respectively. As such many molecular particles agglomerated and form as a crystallite and many crystallites together become a particle. In the present case approximately 2000 crystallites (9nm) in (0.5650 specific surface area/gm), together forms a particle with a mean diameter of 28μm in Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor system.

FTIR analysis was carried out to determine the chemical bonds in a molecule. Fig.6 shows the FTIR spectrum of Dy^{3+} doped Sr_2CeO_4 phosphor and Dy^{3+} (0.5%), La^{3+} (0.5%) co- doped Sr_2CeO_4 phosphor heated at 1200°C. From FTIR spectrum, it was observed that almost all peaks of Dy^{3+} doped Sr_2CeO_4 phosphor and Dy^{3+} (0.5%), La^{3+} (0.5%) co-doped Sr_2CeO_4 are same, with variation in intensity. The peak at 3556cm^{-1} is assigned to H-O-H stretching vibration of crystal water or lattice water with medium intensity. The sample might have absorbed moisture from the atmosphere. Some times the presence of H-O-H bond may be degrading the phosphor luminescence. The peak at 2959cm^{-1} and 2485cm^{-1} is the stretching band with medium intensity. The peaks at 1764cm^{-1}, 1565, 1442cm^{-1}, 1070cm^{-1}, 857cm^{-1} are assigned to stretching characteristics of $SrCO_3$. The peak at 578cm^{-1} is assigned to lattice water band with medium intensity. No peaks in the range 350-50 cm^{-1} shows no existence of SrO_2. And it is observed that there are no peaks in the range 470-90 cm^{-1}, it indicates no presence of CeO [11-13].

The CIE co-ordinates of (chart -1931) were calculated by the Spectrophotometric method using the spectral energy distribution. Based on the emission spectra, it was possible to see the color of the emission of each sample in the CIE diagrams 1931, and the color of each sample is directly dependent on the presence of the carbonate species [15-18]. Fig.7 shows the CIE coordinates depicted on 1931 chart of pure Sr_2CeO_4 and Dy^{3+}, (La^{3+}) co-doped Sr_2CeO_4 phosphor.

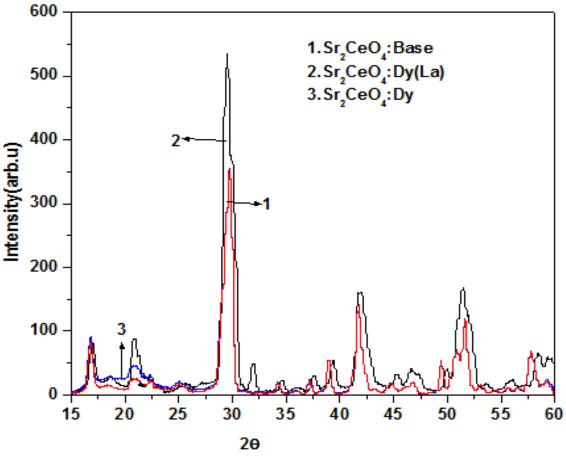

Figure.1 X-ray powder diffraction pattern of 1) Pure Sr_2CeO_4 2) Sr_2CeO_4: (0.5 mol%) Dy^{3+} and 3) Sr_2CeO_4: 0.5mol% Dy^{3+}, 0.5mol% La^{3+} phosphor

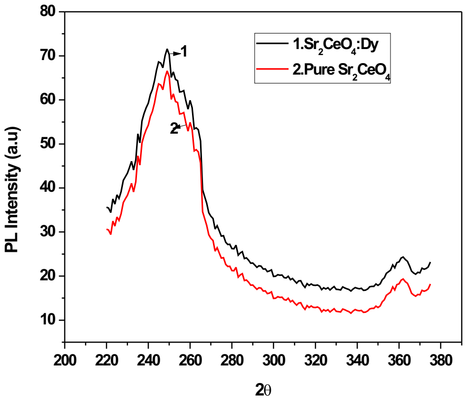

Figure.2 (a) Excitation spectra of pure and Dy^{3+} doped Sr_2CeO_4 phosphor

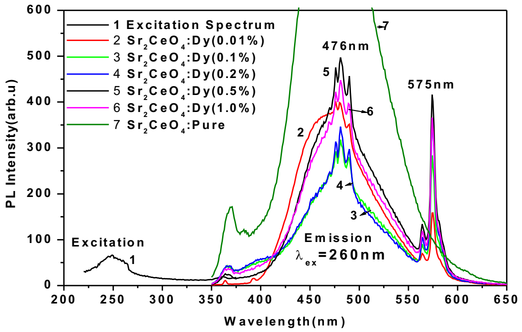

Figure.2 (b) Excitation and emission spectra of pure and Dy^{3+} doped Sr_2CeO_4 phosphor heated at 1200^oc [λ_{ex}=260nm]

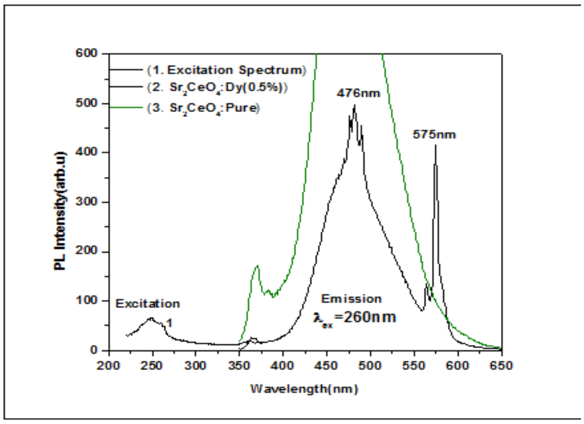

Figure.2(c) Excitation and emission spectra of pure and Dy^{3+} doped Sr_2CeO_4 phosphor heated at 1200^oc [λ_{ex}=260nm]

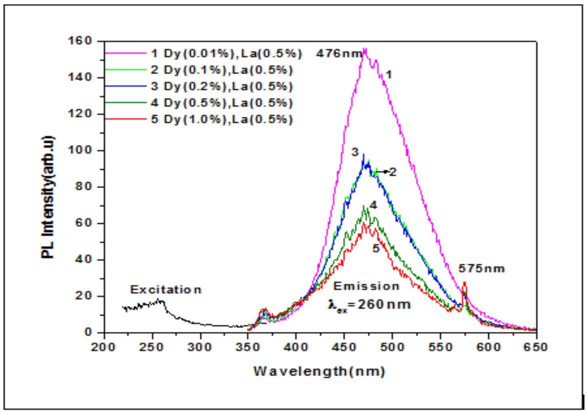

Figure.3 Excitation and emission spectra of Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} heated at 1200^oC[λ_{ex}=260nm]

Table.1 PL emission peaks of Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} under 260nm excitation

Concentration (mol %)	λemi (nm)		Intensity under 260nm Ex			
			Sr2CeO4:Dy3+		Sr2CeO4:Dy3+ :La3+	
(0.01% Dy):(0.5%La)	476	575	558	247	166	-
(0.1% Dy):(0.5% La)	476	575	277	218	97	22
(0.2% Dy):(0.5% La)	476	575	336	267	95	24
(0.5% Dy):(0.5% La)	476	575	364	319	69	26
(1.0% Dy):(0.5% La)	476	575	362	309	60	28

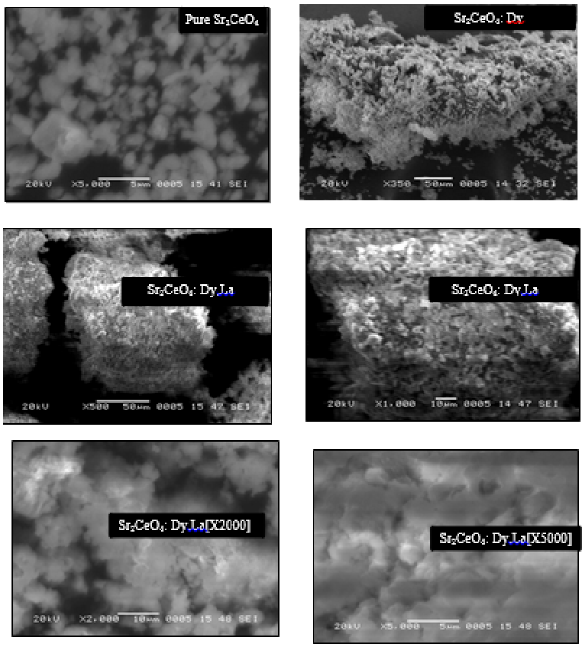

Figure.4 SEM micrographs of pure Sr_2CeO_4, Sr_2CeO_4: Dy^{3+} (0.5mol %) and Sr_2CeO_4: Dy_3+ (0.5mol %) La3+ (0.5mol %) co-doped phosphor

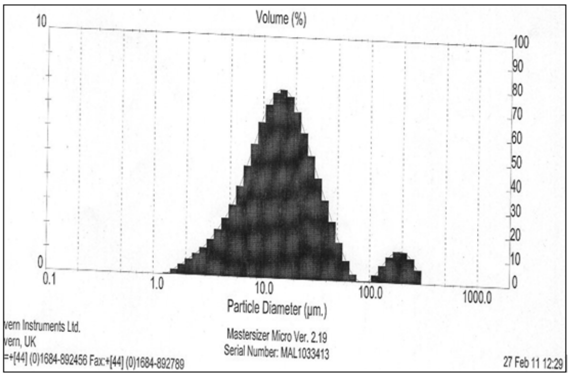

Figure.5. Particle size of Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor

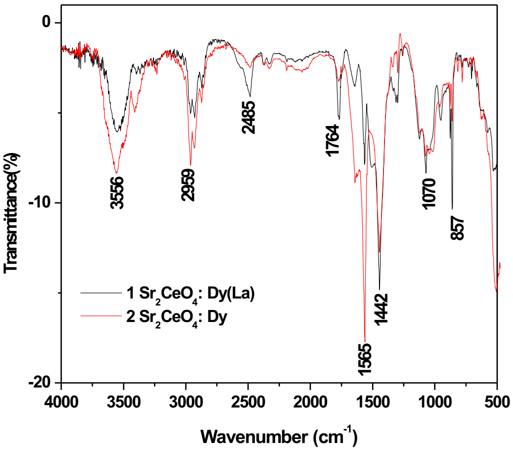

Figure.6 FTIR spectrum of Sr_2CeO_4: x mol% Dy^{3+} and Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor

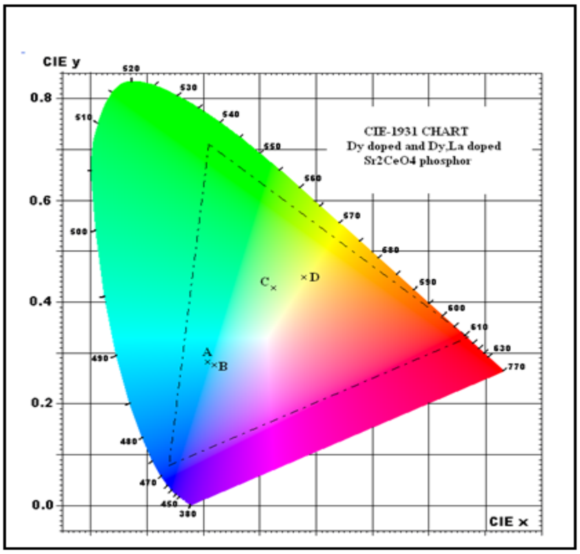

Figure.7 CIE coordinates depicted on 1931 chart where (A) Pure Sr_2CeO_4, (B) Sr_2CeO_4: x mol% Dy^{3+}, (C) Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} (D) (0.5mol %) Dy^{3+} doped Sr_2CeO_4 phosphor

In the fig.7, the color co-ordinates for pure Sr_2CeO_4 sample (A) are x = 0.208 and y = 0.28, Sr_2CeO_4: x mol% Dy^{3+} phosphor sample (B) are x = 0.428 and y = 0.496, Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor sample (C) are x = 0.464 and y = 0.512, and (0.5mol%) Dy^{3+} doped Sr_2CeO_4 sample (D) are x = 0.479 and y = 0.520. From the fig.7, it was observed that the emission varies from blue to pale yellow with increasing of the dysprosium concentration [19-22].

4. Conclusions

Pure Sr_2CeO_4, Sr_2CeO_4: x mol% Dy^{3+} and Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor have been synthesized by the high temperature solid state reaction method and characterized by powder XRD, FTIR, particle size analysis and SEM studies.

The excitation spectrum recorded for Sr_2CeO_4 displays a broad band ranging from 220-375nm with peaking at 260nm.This band could be assigned to the transition $t_{1g} \rightarrow f$, where f is the lowest excited charge transfer state of Ce^{4+} ion and t_{1g} is the molecular orbital of the surrounding ligand in six fold oxygen coordination. In Sr_2CeO_4, two kinds of Ce^{4+} ions exist, that is, there are two different bond lengths of Ce^{4+}- O^{2-} in the lattice.

The emission spectra of Sr_2CeO_4 under 260nm excitation showed broad spectrum in the region 350–650nm with a peak around 470nm. The emission band can be assigned to $f \rightarrow t_1g$ transitions of Ce^{4+} ions.
PL emission spectra of Dy^{3+} doped Sr_2CeO_4 with different concentrations (0.01, 0.1, 0.2, 0.5,

1.0mol %) showed two emission peaks, one is at 476nm (blue) and other is at 575nm (yellow). They are assigned to the Dy^{3+} electronic transitions of ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ energy levels respectively. The position of the emission peaks of Dy^{3+} doped Sr_2CeO_4 phosphor is well resolved and but not influenced by Dy^{3+} concentration and excitation wavelengths.

In Dy^{3+}, La^{3+} co-doped Sr_2CeO_4 phosphor the PL intensity of the characteristic peak of Dy^{3+} at 476nm is reduced by 20% and at 575nm is reduced by 10%.

The Commission International de 1'Eclairage [CIE] co-ordinates of pure Sr_2CeO_4 phosphor exhibit the excellent colour tunability of blue, Dy^{3+} doped Sr_2CeO_4 phosphor reveals that the emission varies from blue to yellow and then to orange with increasing of the dysprosium concentration and Dy^{3+}, La^{3+} co-doped Sr_2CeO_4 phosphor shows the emission varies from blue to pale yellow with increasing of the dysprosium concentration.

Acknowledgement

The author (Ch. Atchyutha Rao) is gratefully thanking University Grant Commission (UGC), New Delhi, India for financial assistance under Minor Research Project (MRP) XII Plan.

References

[1]. Blasse,G.,Grabmaier,B.C.,Luminescent Materials,Springer,Berlin,(1994)
[2]. Ju¨stel,T.,Nikol,H.,Ronda,C.R.,Angew.Chem.Int.Ed.37,3084,(1998)
[3]. Wang,Y H.,Wang,Z Y.,Zhang,P Y.,Hong,Z L.,Fan,X P.,Qian,G D., Mater. Lett., 58: 3308,(2004)
[4]. Danielson,E.,Devenney,M.,Giaquinta,D.M.,Golden,J.H.,Haushalter,R.C.,Mcfarland, E.W., Poojary,D.M.,Reaves,C.M.,Weinberg,W.H.,Wu,X.D.,Science,279,837,(1998)
[5]. Van Pieterson,L.,Soverna,S.,Meijerink,A., J. Electrochem. Soc,147,4688,(2000)
[6]. Sankar,R.,Subba Rao,G.V., J. Electrochem. Soc.,147,2773,(2000)
[7]. Jiang,Y.D.,Zhang,F.,Summers,C.J., Appl. Phys. Lett.,74,1677,(1999).
[8]. Serra,O.A.,Severino,V.P.,Calefi,P.S.,Cicillini,S.A.,J. Alloys Compd.,323–324,667,(2001)
[9]. Khollam,Y.B.,Deshpande,S.B.,Khanna,P.K.,Joy,P.A., Potdar,H.S.,Mater. Lett.,58,2521, (2004)
[10]. Tang,Y.K.,Guo,H.P.,Qin,Q.Z.,Solid State Commun.,121,351,(2002)
[11]. Color Calculator version 2, software from Radiant Imaging, Inc, 2007, http://radiant-imaging-color-calculator.software.informer.com/2.0/
[12]. Toshiyuki Masui, Takanobu Chiga, Nobuhito Imanaka, Gin-ya Adachi, Material Reseach Bulletin,38,17-24,(2003).
[13]. Li, L., Zhou, S.H., Zhang, S.Y., Chem. Phys. Lett. 453,283, (2008).
[14].Danielson,E., Devenney, M., Giaquinta, D.M., Golden, J.H., Haushalter, R.C.,McFarland, E.W., Poojary, D.M., Reaves, C.M., Weinberg, W.H., Wu, X.D., Science, 279,837, (1998).
[15]. Dorenbos, P., J. Lumin. 111,89, ,(2005).
[16]. Dorenbos, P., J. Phys.: Condens. Matter,15,8417, (2003).
[17]. Van Pieterson, L., Meijerink, A., J. Alloys Compd. 300,426, (2000).
[18] Li,L.,Zhou,S.H.,Zhang,S.Y., Chem. Phys. Lett.,453,283,(2008)
[19]. Klug,H.P,Alexander,L.E.,X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials M I., New York: Wiley, 637, (1997)
[21]. Nikifor Rakov, Renato B.Guimaraes, Glauco S.Maciel, Journal of Luminescence, 131, 342-346, (2011).
[22]. Nakamoto,K.,Infrared and Raman spectra of Inorganic and Coordination Compounds,Wiley, New York,(1986)