

Rare Earth Ion (Dy^{3+}) Photoluminescence Behaviour in Sr_2CeO_4 Phosphor

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Abstract:- Solid state reaction method was used to prepare rare earth's powder samples of strontium cerium oxide (Sr_2CeO_4) that are doped with (Dy^{3+}) ion. Laser diffraction particle size analysis, Fourier Transform Infrared spectrometer (FTIR) technique, photoluminescence (PL) technique, scanning electron microscope (SEM), and X-ray diffraction (XRD) techniques were used to characterize these samples that are fired at $1200^{\circ}C$ for 3h. Also, it has been disclosed by the XRD patterns that an orthorhombic crystal structure is exhibited by the $Sr_2CeO_4:Dy^{3+}$ phosphor. According to the room temperature photoluminescence (PL) analysis there exists three excitation peaks that are situated at 250, 260 and 270nm as well as an intense blue emission is showed by samples at 470nm and yellow emission at 575nm. Also, it has been shown by the SEM images that samples fired at $1200^{\circ}C$ were highly agglomerated with multi layered structure. Sample's mean diameter is indicated by particle size distribution histogram and molecule's chemical bonds are determined by FTIR. It was also revealed by $Sr_2CeO_4:Dy^{3+}$ CIE (Commission international de l'eclairage) that there is a variation in emission from blue to yellow and finally to orange when dysprosium concentration is increased.

Keywords:- Particle size distribution histogram; Yellow emission; Blue emission; Solid state reaction method; Sr_2CeO_4 .

I. INTRODUCTION

In the recent years, the phosphors development for three prime colours has attracted significant interest of researchers because of their possibility in technological applications like, high-resolution display devices and high-performance fluorescent lights [1-3]. Recently, research related to the phosphors utilised for white LEDs has gained lot maturity and became a hot topic. During the excited phase, absorbed energy is converted into electromagnetic radiation by the oxide-based phosphors in infrared, visible, ultraviolet regions as well as phosphors based on the rare earth's luminescence allows the trichromatic luminescence lighting development. Danielson and his co-workers along with the combinatorial chemistry identified a blue phosphor compound, Sr_2CeO_4 , which possesses 1-dimensionaledge-sharing CeO_6 octahedron's chain in 1998 [4]. Furthermore, a blue-white emission band is exhibited by it which has excitation under 254 nm and peak at 485 nm. A ligand-to-metal Ce^{4+} charge transfer originates the suggested

luminescence. Additionally, it is also determined thatwith ultra violet rays irradiation and under excitation photoluminescence is exhibited by the Sr_2CeO_4 [5, 6]. Due to the vast significance of Sr_2CeO_4 phosphor in displaying devices and optoelectronics' new generation realization, it has been studied widely. In recent times, there are few groups that started every technique for fabricating such potential material as well as research its luminescent properties has been also researched [7-10].

The particular research article focuses on the morphology, size, synthesis and photoluminescence properties of pure and Dy^{3+} ion doped Sr_2CeO_4 phosphors made by solid state reaction technique in air at $1200^{\circ}C$. Various techniques such as photoluminescence, particle size distribution histograms, SEM, and XRD techniques were used for characterization of prepared material. It has been revealed by Dy^{3+} (0.5mol %) doped Sr_2CeO_4 phosphor's. CIE co-ordinates and PL studies that has a variation in emission colour is noticed from blue to yellow. Also, for the technological applications a good potential has been showed by this phosphors.

II. EXPERIMENTAL METHODS

Conventional solid state reaction method was used for synthesizing pure and dysprosium ion doped Sr_2CeO_4 . $Sr_2CeO_4:Dy^{3+}$ contains a varied dopants concentration having range from 0.01-1.0 mol%. Pure and Dy^{3+} doped Sr_2CeO_4 phosphors are prepared with the help of Nutan Gujarat Industrial Estate, Vadodara, India, National Chemicals, Dysprosium oxide (Dy_2O_3) assay (99.9%), Cerium oxide (CeO_2) assay (99.5%), and Strontium Nitrate $Sr(NO_3)_2$ assay (99.995%) in Sigma-Aldrich chemicals Inc Germany. An agate mortar and pestle is used for 1 hour for homogenizing the starting material's stoichiometric mixture (Sr /Ce, 2:1) and after that an alumina crucible is used to store them. After the succeeding thermal treatment with a heating rate of $5^{\circ}C/min$ in muffle furnace for 3 hours $1200^{\circ}C$, various samples were obtained. After that for next 20 hours at room temperature these samples are allowed to cool down. Furthermore, agate mortar and pestle is used for an hour so that these samples are tuned into fine powder.

Powder X-ray diffractometer (Indus beam line-II (ADXRD BL-12), RRCAT, Indore, India) is used in the X-ray diffraction (XRD) analysis for identifying the crystal phase. At this port, the size of electron source is nearly of 0.5mm (H) x 0.5 mm (V). Also, beam line's beam

acceptance is 2mrad (H) x 0.2mrad (V). SEM (Scanning Electron Microscope) (XL 30 CP Philips) is used for studying the samples' microstructures. Furthermore, scanning 2 θ range is from 15 to 60 $^\circ$ and continues time is 10s. FTIR spectrometer (IRAffinity-1) is used for recording FTIR spectra that has range from 500 to 4000 cm $^{-1}$. Phosphors' particle size analysis is obtained in solid state method at a laser based particle size analyzer (Malvern Instrument Ltd (U.K). A spectrofluorophotometer (SHIMADZU, RF-5301 PC) is used for recording the excitation spectra and photoluminescence (PL) emission. This spectrofluorophotometer is equipped with a Xenon lamp as excitation source. All the spectra were recorded at room temperature. A spectral slit having 1.5 mm width is used for recording excitation as well as emission spectra. The spectrophotometric method which uses spectral energy distribution is used for calculating the CIE (Commission International de l'Eclairage) co-ordinates. Software from Radiant Imaging, colour calculator version 2 was used or calculating the prepared materials' chromatic coordinates (x, y) [11].

III. RESULTS AND DISCUSSION

A. PL behaviors of pure and Dy $^{3+}$ (0.5 mol %) doped Sr $_2$ CeO $_4$ phosphor

Figure 1 shows the pure and Dy $^{3+}$ doped Sr $_2$ CeO $_4$ phosphor's emission spectra and PL excitation. The excitation spectrum of pure Sr $_2$ CeO $_4$ was described by a broad band that ranges from 220-390nm with peaks at 250nm, 260 and 370nm. Transition $t_{1g} \rightarrow f$ is allocated with this band, where t_{1g} represents the surrounding ligand's molecular orbital in six fold oxygen coordination and f represents the Ce $^{4+}$ ion's slowest excited charge transfer state [6,12,13]. In Sr $_2$ CeO $_4$, the Ce $^{4+}$ ion is in the oxidation state and the 4f shell is empty. In Sr $_2$ CeO $_4$, two kinds of Ce $^{4+}$ ions exist, that is, there are two different bond lengths of Ce $^{4+}$ - O $^{2-}$ in the lattice [14]. From the axial O $^{2-}$ to the $^2F_{5/2}$ of the Ce $^{4+}$ ions the charge transfer are allocated with the strong excitation band at 260nm by considering the edge shared octahedral (CeO $_6$) structure, however, at 370nm shoulder is assigned for CT from the equatorial O $^{2-}$ to the Ce $^{4+}$ ion's same energy level. Particle's luminescent characteristics are dependent on the particle size and its other properties which include doped activator ions' valence state, defects and crystallization degree.

When excited with the radiation of wavelength 260nm, pure Sr $_2$ CeO $_4$ phosphor emits a broad band in the blue region which extends from 350-650nm with a peak at 470nm with the full width at half maximum (FWHM) value of 80nm. The emission band can be assigned to $f \rightarrow t_{1g}$ transitions of Ce $^{4+}$ ions. The Stokes shift is 8936cm $^{-1}$ determined from the difference between the first excitation maximum (250nm) and the emission maximum (470nm). It has been concluded from the literature that a typical Stokes shift for a charge transfer (CT) transition on a rare earth ion ranges from 4000 cm $^{-1}$ (0.5 eV) up to 17000 cm $^{-1}$ (2.1 eV) [15,16]. The FWHM of the charge transfer (CT) emission is typically between 3000 cm $^{-1}$ (0.37 eV) and 6000 cm $^{-1}$ (0.74 eV) [17]. In our experiment, the Stokes shift and the

FWHM fall within the range expected for charge transfer (CT) transitions in which the Ce $^{4+}$ ions are involved. The excitation wavelength does not have any effect on the emission peak wavelength and emission spectra shape. The main reason is considered as Ce $^{4+}$ - O $^{2-}$ ligand's charge transfer as explained by Danielson et al [14].

A series of Sr $_2$ CeO $_4$:Dy $^{3+}$ phosphors with various Dy $^{3+}$ concentrations (0.01, 0.1, 0.2, 0.5, and 1.0mol %) were prepared as well as Dy $^{3+}$ concentration effect on emission intensity was examined. Fig.1 represents Dy $^{3+}$ doped Sr $_2$ CeO $_4$ emission spectra and PL excitation with various concentrations under 260nm excitation. The excitation spectrum of Dy $^{3+}$ doped Sr $_2$ CeO $_4$ was also characterized by a broad band ranging from 220 to 390nm with peaks at 250nm, 260nm and 270nm. Two emission peaks were shown by the samples. These peaks are situated at 476nm (blue) and 575nm (yellow). Furthermore, Dy $^{3+}$ $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions are allocated by these respectively. The results shows the energy transfer presence for Sr $_2$ CeO $_4$ (sensitizer) to Dy $^{3+}$ (activator) from metal's triplet excited state to charge transfer (MLCT) state. Also, Dy $^{3+}$ doped Sr $_2$ CeO $_4$ phosphor's emission peaks position is resolved efficiently but excitation wavelengths and Dy $^{3+}$ concentration does not effect it. As Dy $^{3+}$ concentration increases it results in increase in emission intensity and results at about 0.5mol% concentration is maximum. When Dy $^{3+}$ concentration goes beyond 0.5mol% it results in quenching. There is no UV excitation at 260nm excitation peak as well as thus, in the lamp industry it is utilized for solid state lighting. The excitation spectrum of 220-390nm range involves the Dy $^{3+}$ ion's $f \rightarrow f$ transition. $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ Dy $^{3+}$ electronic transitions around 476nm and 575nm are due to magnetic dipole origin and electric dipole origin.

B. Crystal structure, morphology and size of pure and Dy $^{3+}$ doped Sr $_2$ CeO $_4$

Figure 2 presented the pure and Dy $^{3+}$ doped Sr $_2$ CeO $_4$ Phosphors' crystal structure. Edge-sharing CeO $_6$ octahedron's 1-dimensional chain structure is possessed by the compound. There are two molecules per unit cell. Every cerium atom has corresponding six oxygen atoms. These octahedrons show 2 trans-terminal Ce-O1 perpendiculars to the plane described by 4 equatorial O $_2$ atoms, whereas, in comparison to Ce-O2 bonds, Ce-O1 bonds are nearly 0.1 Å shorter [18]. The phosphor's luminescent mechanism is depends on ligand-to-metal, charge-transfer (CT) transition, from O $^{2-}$ to Ce $^{4+}$ and does not raises from Ce $^{3+}$ defect centres. This charge transfer is caused in the lower coordination number terminal O atoms related with the low-dimensional structure in combination with an adjacent Ce $^{4+}$ centre. In Sr $_2$ CeO $_4$, in the lattice two distinct bond lengths Ce $^{4+}$ - O $^{2-}$ are present. Furthermore, solid state Sr $_2$ CeO $_4$ structure matches with these results.

Figure 3 presents pure and Dy $^{3+}$ ion doped Sr $_2$ CeO $_4$ phosphors' typical XRD patterns. ICDD (International Centre for Diffraction Data) database card numbers 50-0115,89-5546 is used for indexing the diffraction peaks. In the XRD spectra, there was no other

phase which indicates that the prepared samples are orthorhombic structure's single phase as well as well-crystallized [4, 6]. Lattice parameters were calculated with the help of XRDA 3.1 software. The crystallographic unit cell parameters of pure Sr₂CeO₄ phosphor listed in Table-1. The calculated lattice parameter of sample is less when compared with cell constants of standard values. Furthermore, unit cell volume has been observed to reduce which shows the lattice's distortion in pure Sr₂CeO₄.

The XRD pattern parameters with the help of Scherrer's equation is used to determine crystallite size of the pure and Dy³⁺(0.5mol%) doped Sr₂CeO₄ phosphor [19], $D_c = k\lambda / \beta \cos\theta$, where θ represents the Bragg angle (diffraction angle), β represents the full-width at half maxima (FWHM), λ represents the X-ray wavelength (0.8592 Å), k represents the Scherrer's constant equal to 0.94, and D_c represents the average crystallite size of the XRD peak. The calculated average crystallite size of pure Sr₂CeO₄ and Sr₂CeO₄: Dy³⁺(0.5mol %) are 9nm and 7.4nm respectively. It results in nano crystallite phosphors confirmed formation through solid state reaction method.

SEM images of the solid-state derived pure and Dy³⁺(0.5mol %) doped Sr₂CeO₄ phosphor heated at 1200°C.

From fig.4 it is clearly shows that good dispersion and small particle size varying from 609nm to 1.70µm for Sr₂CeO₄ phosphor and 875nm to 1.75µm for Dy³⁺(0.5 mol %) doped Sr₂CeO₄ phosphor.

Figure 5 illustrates the particle size distribution histograms of Sr₂CeO₄:Dy³⁺phosphor which were synthesized with the help of solid state reaction method. Pure Sr₂CeO₄ phosphor's particles' mean diameter is 26µm and for Sr₂CeO₄:Dy³⁺ is 32µm.

FTIR analysis was carried out to determine the chemical bonds in a molecule. Fig.6 shows the FTIR spectrum of pure and Dy³⁺(0.5mol %) doped Sr₂CeO₄phosphor heated at 1200^o c. From FTIR spectrum, it was observed that almost all peaks of pure and Dy³⁺ doped Sr₂CeO₄ phosphor are same, with variation in intensity. The peak at 3558cm⁻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. The peak at 2969cm⁻¹ is the stretching band of the molecules of lattice water with medium intensity. The peaks at 1562cm⁻¹, 1444cm⁻¹, 1070cm⁻¹, 860cm⁻¹ are assigned to stretching characteristics of SrCO₃.

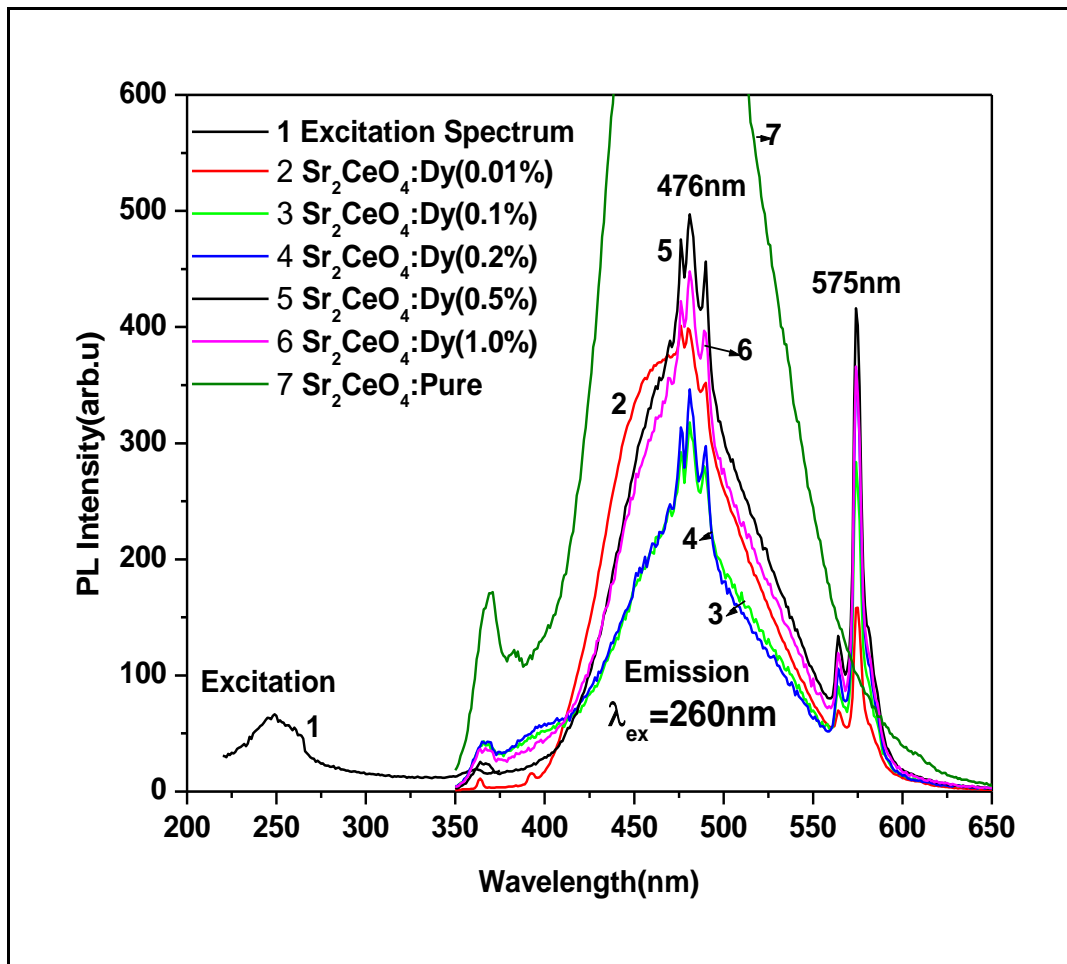


Fig 1:- Excitation and emission spectra of pure and Dy³⁺ doped Sr₂CeO₄phosphor heated at 1200^oc [λ_{ex} =260nm]

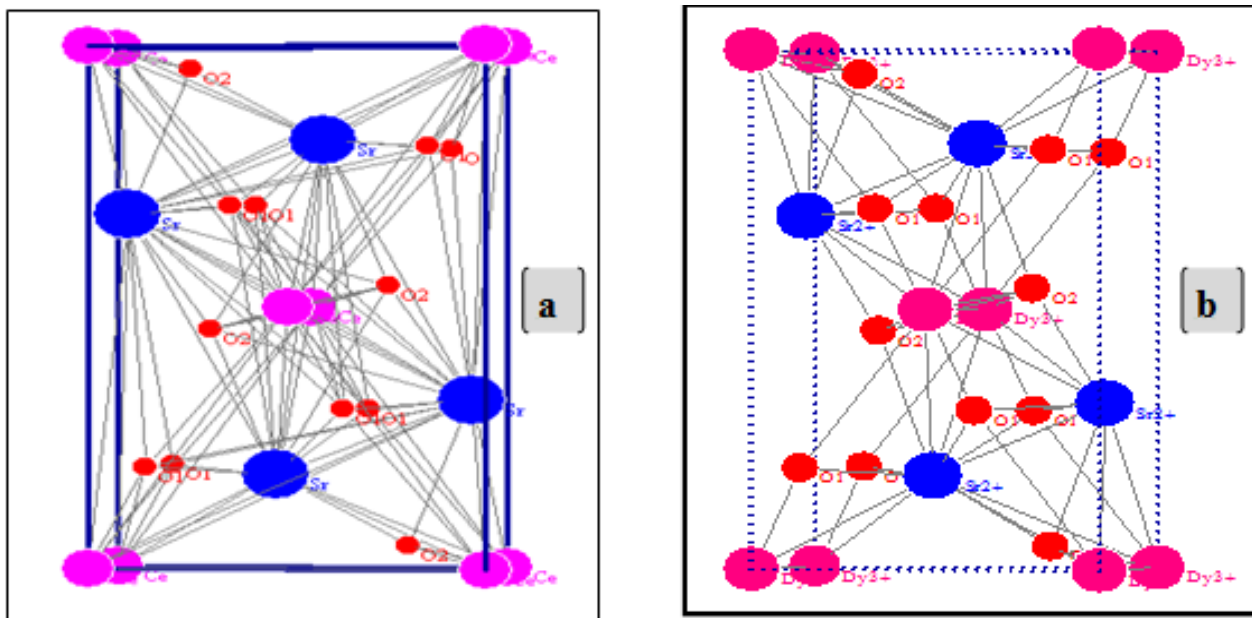


Fig 2:- The crystal structure of pure Sr_2CeO_4 (a) and Dy^{3+} (0.5mol %) doped Sr_2CeO_4 phosphor(b)

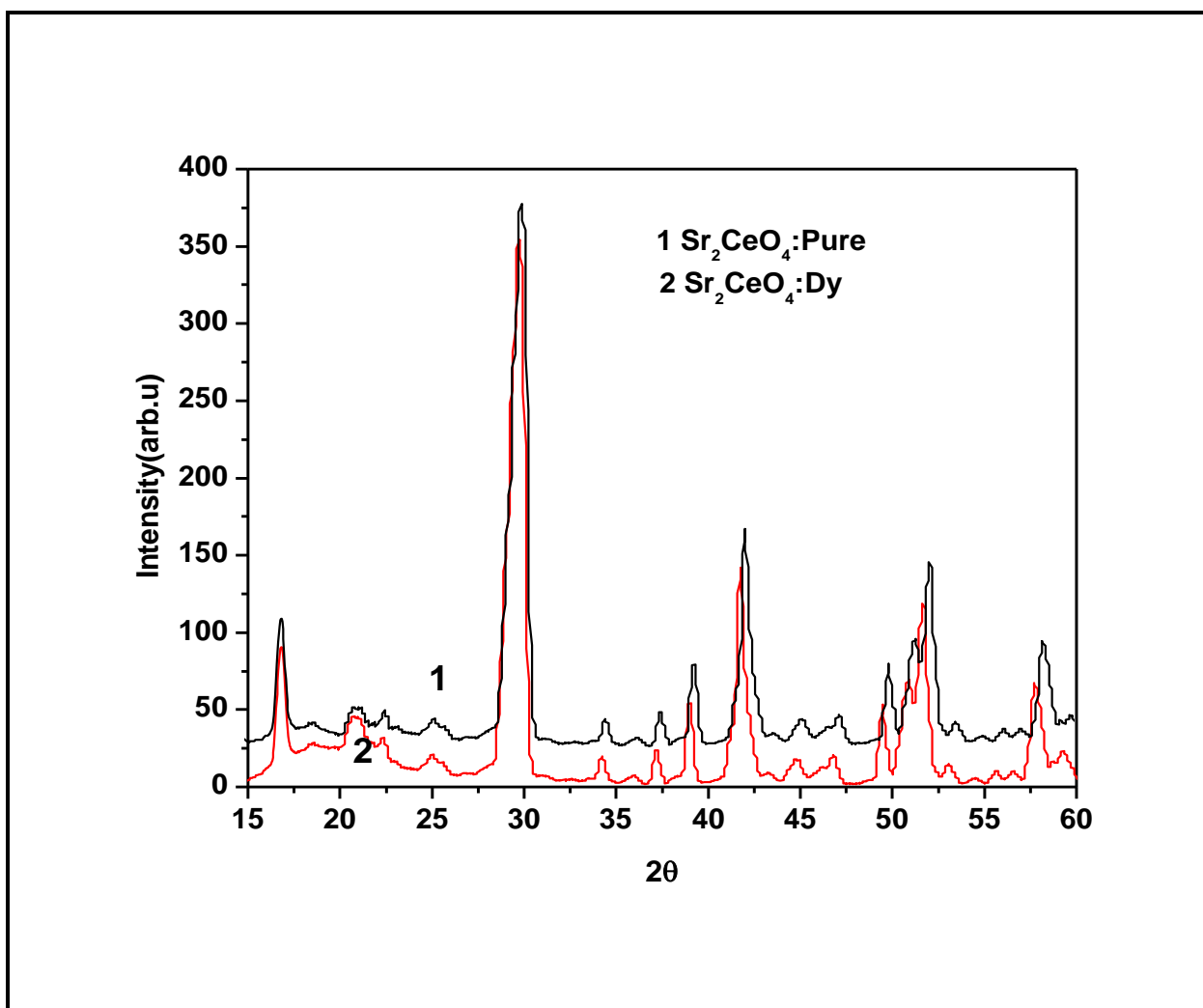


Fig 3:- X-ray powder diffraction pattern of pure and Dy^{3+} (0.5mol %) doped Sr_2CeO_4 phosphor

Different workers and standards	a (Å)	b (Å)	c (Å)	Cell volume (Å ³)
ICDD No. 50-0115	6.119	10.350	3.597	227.79
ICDD No. 89-5546	6.115	10.342	3.595	227.79
Prepared Pure Sr ₂ CeO ₄ phosphor	5.964	8.279	4.472	220.81
L. Li et.al.[12]	6.115	10.3473	3.5957	227.52
R. Seema et.al.[20]	6.07	10.32	3.62	226.76
Danielson et.al.[21]	6.12	10.357	3.597	227.79
NikiforRakov et.al.[22]	6.115	10.342	3.5954	227.38

Table 1:- Crystallographic unit cell parameters of pure Sr₂CeO₄phosphors

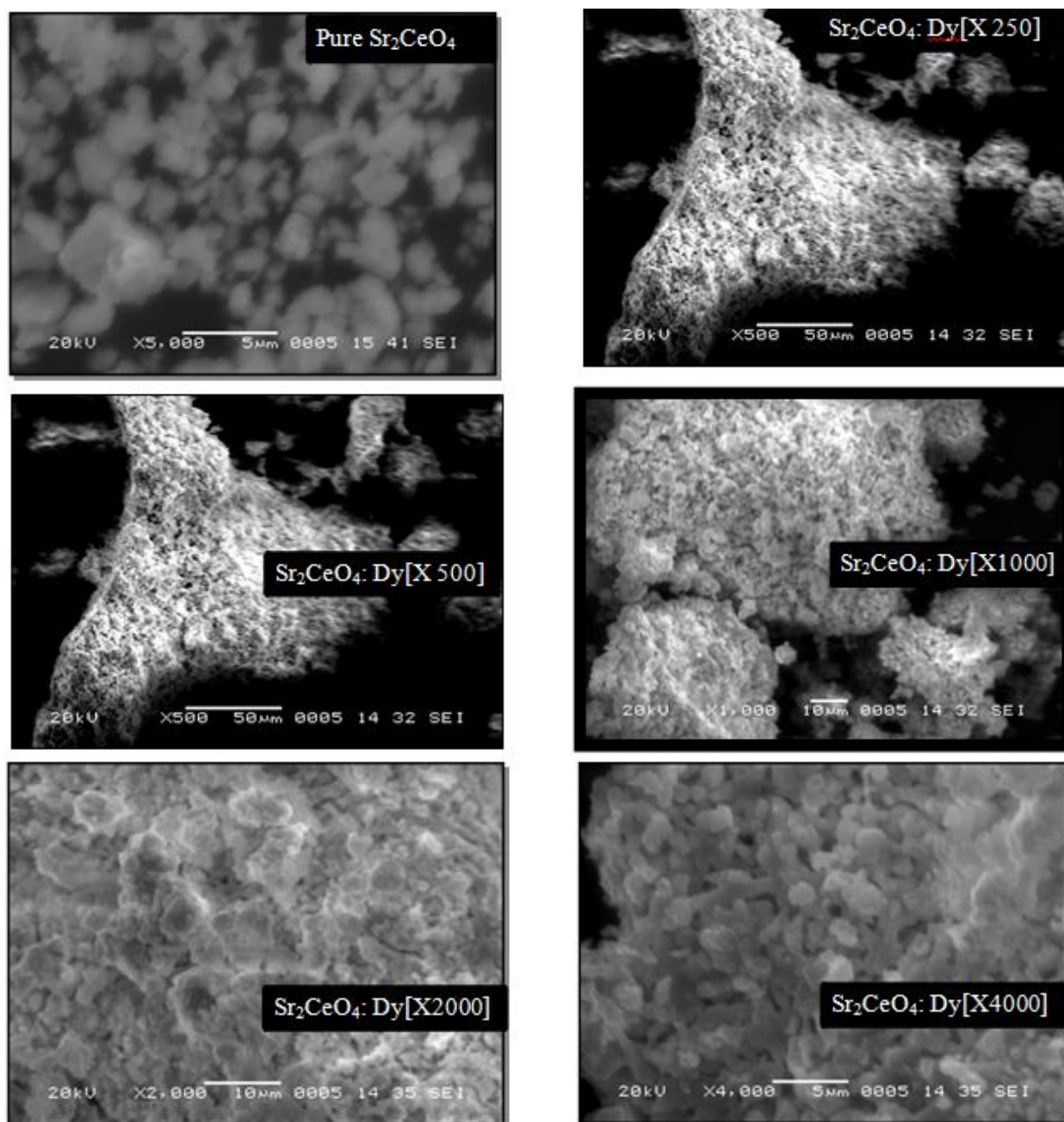


Fig 4:- The SEM images of pure and Sr₂CeO₄: Dy(0.5mol %) phosphor

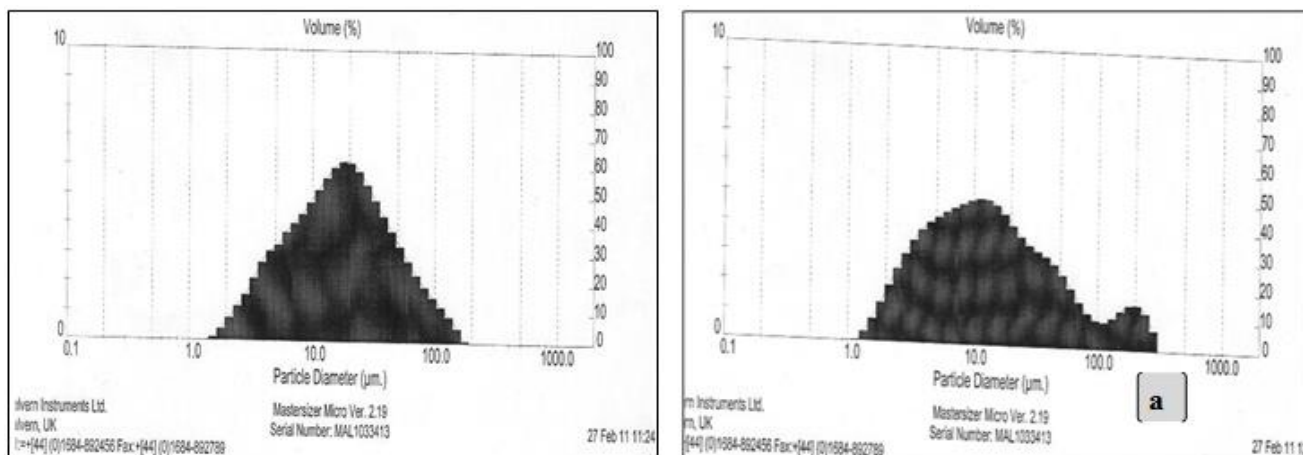


Fig 5:- Particle size of pure and Sr₂CeO₄ phosphor (a) and Sr₂CeO₄: Dy phosphor (b)

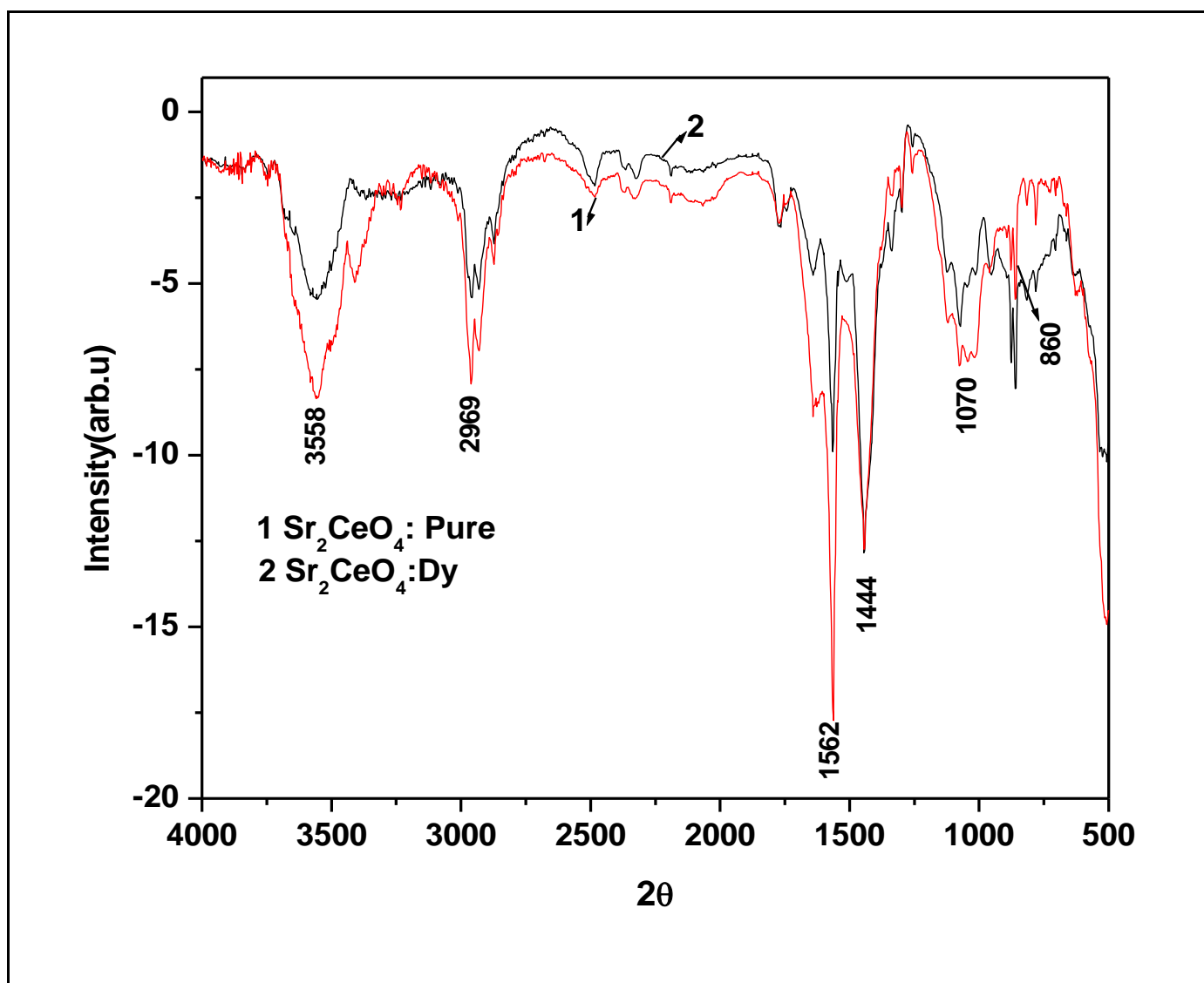


Fig 6:- FTIR Spectrum of pure and Dy³⁺(0.5mol %) doped Sr₂CeO₄ phosphor

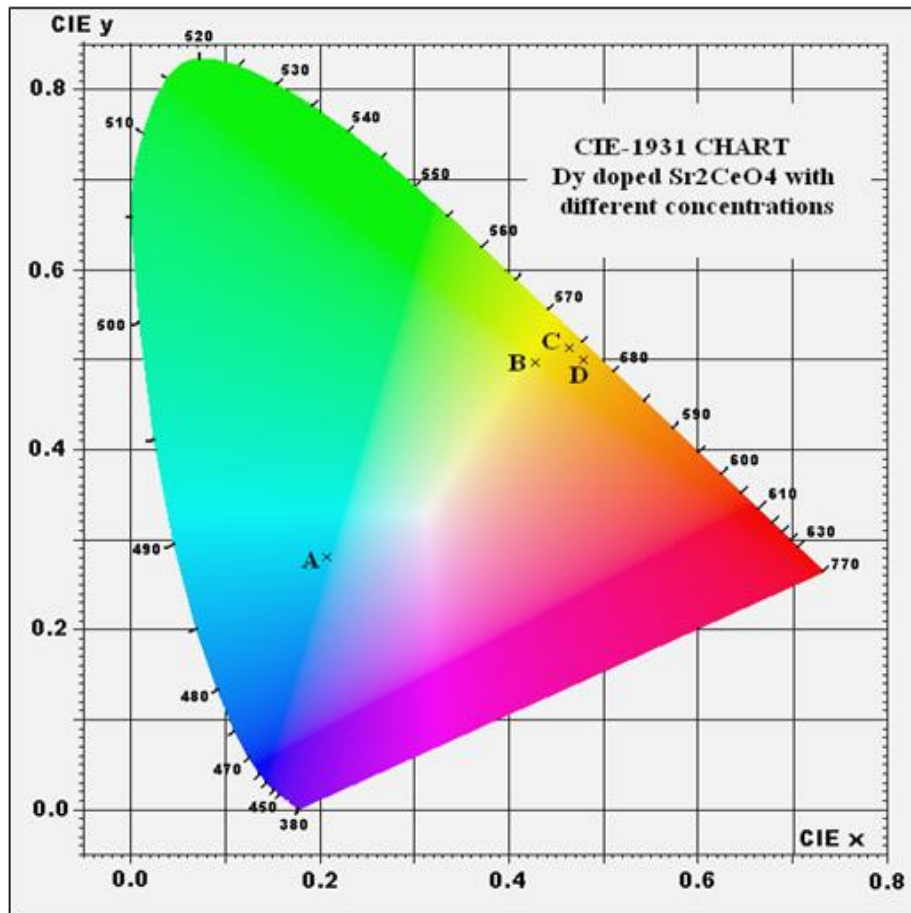


Fig 7:- CIE co-ordinates of A) Pure Sr_2CeO_4 , B) Dy doped Sr_2CeO_4 (0.01%), C) Dy doped Sr_2CeO_4 (0.2%) and D) Dy doped Sr_2CeO_4 (0.5%) depicted on 1931 chart

Figure 7 presented that (Chart -1931)'s CIE co-ordinates were calculated with the help of Spectrophotometric method where of pure Sr_2CeO_4 and Dy^{3+} doped Sr_2CeO_4 phosphor's spectral energy distribution is used at different concentrations (0.01, 0.2, and 0.5mol %). The color co-ordinates for sample (A) pure Sr_2CeO_4 are $x = 0.208$ and $y = 0.28$, sample (B) Dy^{3+} doped Sr_2CeO_4 (0.01%) are $x = 0.428$ and $y = 0.496$, sample (C) Dy^{3+} doped Sr_2CeO_4 (0.2%) are $x = 0.464$ and $y = 0.512$, sample (D) Dy^{3+} doped Sr_2CeO_4 (0.5%) are $x = 0.479$ and $y = 0.520$. It has been concluded from figure 7 that there is a variation in emission from blue to yellow and finally to orange when dysprosium concentration is increased [25-27].

IV. CONCLUSIONS

High temperature solid state reaction method is used for synthesizing pure Sr_2CeO_4 and Dy^{3+} doped Sr_2CeO_4 (0.01, 0.1, 0.2, 0.5 and 1.0mol %) compounds as well as SEM analysis, particle size analysis, FTIR, and powder XRD studies are used for its characterization. A broad band is displayed by Sr_2CeO_4 recorded excitation spectrum which has range from 220-390nm with peaks at 250nm, 260 and 370nm. Transition $t_{1g} \rightarrow f$ uses this band, where t_{1g} represents the surrounding ligand's molecular orbital in six fold oxygen coordination, and f represents the Ce^{4+} ion's lowest excited charge transfer state. Two types of Ce^{4+} ions are

presented in Sr_2CeO_4 , which means in the lattice $\text{Ce}^{4+} - \text{O}^{2-}$ is having two different bond lengths.

Under 260nm excitation broad spectrum is displayed by the emission spectra of Sr_2CeO_4 along with 470nm peak with the full width at half maximum (80nm). The Ce^{4+} ions' $f \rightarrow t_{1g}$ transitions is allocated by these emission band.

Ligand's-to-metal charge transfer (CT) emission characteristic includes Stokes shift and the FWHM. The excitation wavelength does not have any effect on the shape of emission peak wavelength and emission spectra. This results because of the $\text{Ce}^{4+} - \text{O}^{2-}$ ligand's charge transfer.

Rare earth ions' doping can be suitably performed with broad emission band for developing new luminescent materials. For advanced display devices, the pure Sr_2CeO_4 phosphor can be considered as a good candidate who has strong blue emitting.

Dy^{3+} doped Sr_2CeO_4 ion's PL emission spectra having various concentrations showed 2 emission peaks that are at 575nm (yellow) and at 476nm (blue). Furthermore, they are allocated to the energy levels ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ for Dy^{3+} electronic transitions respectively. Also, Dy^{3+} doped Sr_2CeO_4 phosphor's emission peaks position is

well resolved but Dy^{3+} excitation wavelengths as well as concentration does not influence it.

On doping dysprosium (Dy^{3+}), predominant yellow visible emissions from the crystallites were due to ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, positioned as 575nm. Thus, for the technological applications dysprosium is considered as an important material because of its visible transition in the yellow region.

Furthermore, a blue colour tenability is exhibited by pure Sr_2CeO_4 phosphor's CIE [Commission International de l'Eclairage] co-ordinates as well as it was also revealed by the Dy^{3+} doped Sr_2CeO_4 phosphor that there is a variation in emission from blue to yellow and finally to orange when dysprosium concentration is increased. Also, process of energy transfer is existed among Dy^{3+} and Sr_2CeO_4 through which a novel phosphor can be found that emits blue-yellow luminescence in a single host.

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