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Synthesis, Characterization and Photoluminescence of Sr_2CeO_4: Dy^{3+}, La^{3+}) phosphor

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Abstract

In this work, pure Sr_2CeO_4 and Sr_2CeO_4: x=0.01, 0.1, 0.2, 0.5, 1.0mol% Dy^{3+}, 0.5mol% La^{3+} phosphors were synthesized by solid state reaction method. X-ray diffraction (XRD) patterns confirmed that the samples exhibited an orthorhombic crystal structure. Room temperature photoluminescence (PL) analysis indicated that the excitation peak at around 260 nm, and all the samples showed intense blue emission at 470nm. Scanning Electron Microscope (SEM) images showed that the sample fired at 1200^0C exhibits grain like morphology with different sizes and shape. Fourier Transform Infrared Spectroscopy (FTIR) revealed the chemical bonds in the molecule, while 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.*

PACS Code:

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, 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 1200^0C. 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 revealed that the emission colour varies from blue to pale yellow.

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 Dy^{3+} concentration in Sr_2CeO_4:Dy^{3+}, La^{3+} was 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 the 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 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 microstructures of the samples were studied using a scanning electron microscope (SEM) (XL 30 CP Philips). 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 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. The Commission International de l'Eclairage (CIE) co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution.

Results and discussion

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 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; this indicates that the prepared Dy^{3+},(La^{3+}) co-doped Sr_2CeO_4 phosphor is single phase.The crystallite size of the sample was determined from the XRD pattern parameters according to the Scherrer's equation $D_c=k\lambda/\beta\cos\theta$, 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 9 nm respectively. This confirms the formation of nano crystallite size phosphor.

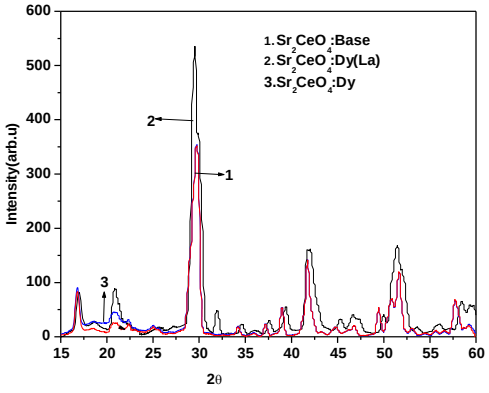


Figure.1 X-ray powder diffraction pattern of 1) Pure Sr_2CeO_4, 2) Sr_2CeO_4: (0.5 mol%) Dy^{3+} and 3) Sr_2CeO_4: 0.5mol% Dy^{3+}, 0.5mol% La^{3+} phosphor

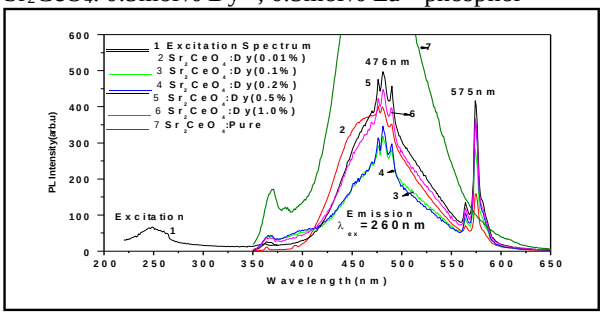
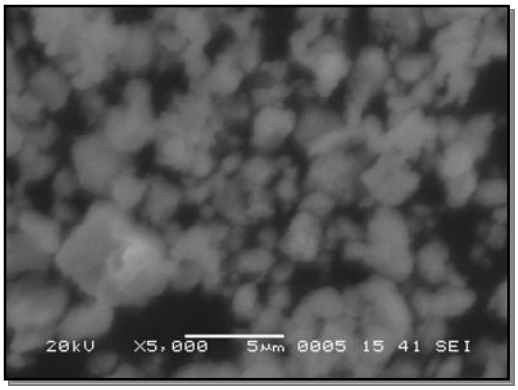


Figure.2 (b) Excitation and emission spectra of pure and Dy^{3+} doped Sr_2CeO_4 phosphor heated at 1200^0c [λ_{ex}=260nm]



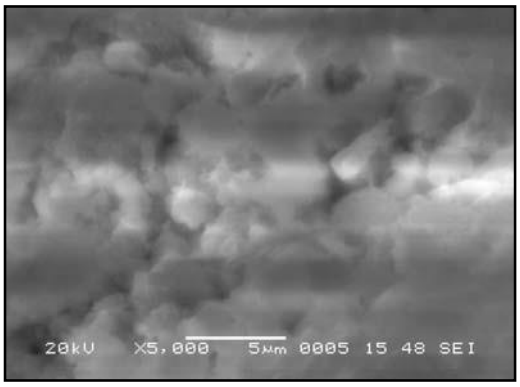


Figure.3 SEM micrographs of pure Sr_2CeO_4, Sr_2CeO_4: Dy^{3+} (0.5mol %) and Sr_2CeO_4: Dy^{3+} (0.5mol %) La^{3+} (0.5mol %) co-doped phosphor

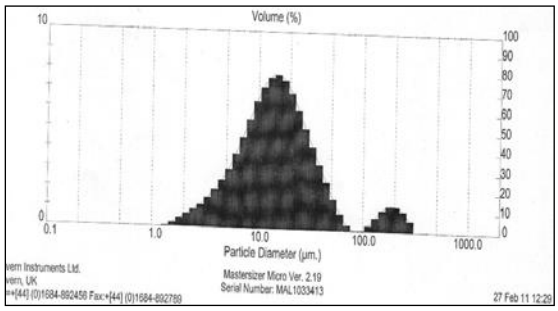


Figure.4. Particle size of Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor

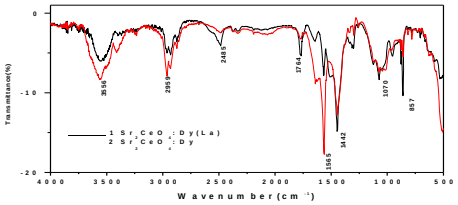


Figure.5 FTIR spectrum of Sr_2CeO_4: x mol% Dy^{3+} and Sr_2CeO_4: x mol% Dy^{3+}, 0.5mol% La^{3+} phosphor

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 results 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, but not influenced by Dy^{3+} concentration and excitation wavelengths.

Fig.3 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 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.

2.0 CONCLUSION

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 showed broad spectrum in the region 350–650nm with a peak around 470nm, which is can be assigned to f→ 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.

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