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Photoluminescent Properties of Sr_2CeO_4 and Sr_2VO_4 Phosphors

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Abstract: *Sr_2CeO_4 and Sr_2VO_4 phosphors were synthesized by the solid-state reaction method. Photoluminescence (PL) and Thermoluminescence (TL) techniques were performed to characterize these samples. The excitation spectrum of Sr_2CeO_4 phosphor monitored under 470nm wavelength was characterized by a broad band ranging from 220-430nm. The emission spectra of Sr_2CeO_4 phosphor under excitations at 260, 280 and 350nm exhibited a strong, intense peak at 470nm (blue) with FWHM (full width at half maximum) of 87nm. The excitation spectrum of Sr_2VO_4 phosphor monitored under 510nm wavelength was characterized by a broad band ranging from 225-375nm. The emission spectrum of Sr_2VO_4 phosphor under excitations at 262nm exhibited emission peaks at 399nm (violet), 469nm (blue) and under 335nm excitation a strong, intense well resolved peak at 510nm (green) with FWHM (full width at half maximum) of 114nm is observed. Commission international de l'eclairage (CIE) co-ordinates of samples revealed that these phosphors emit blue and green colour and could be used for the generation of white light in display and lamp devices.*

Keywords: *Photoluminescence, Thermoluminescence, solid state reaction method, phosphor, CIE*

1. Introduction

In 1998, Danielson and co-workers reported unusual luminescence of the inorganic oxide compound Sr_2CeO_4 using combinatorial technique which exhibits the emission peak at 485 nm. In addition, it has been established that Sr_2CeO_4 exhibits photoluminescence under excitation with irradiation of ultraviolet rays.Sr_2CeO_4 phosphor has been widely studied because of its importance in the realization of a new generation of optoelectronic and displaying devices Subsequently, several studies of this luminescent material were conducted, and some different routes have been developed to prepare the Sr_2CeO_4 powders and films.

Sr_2CeO_4 exhibits photoluminescence due to the charge transfer (CT) mechanism. The luminescence was suggested to originate from a ligand-to-metal Ce^{4+} charge transfer. This phosphor exhibits blue luminescence efficiently under excitation with UV light, cathode ray or X-ray.

Strontium Vanadate, or Sr_2VO_4, is an interesting compound in the family of layered perovskites. A perovskite is a class of materials which generally form in a cubic structure and in most often contain oxygen as a major chemical component. Perovskite materials exhibit lot with V^0. The system, $SrO–V_2O_5$, forms a series of compounds.The structure of many of interesting and intriguing properties both from theoretical point of view as well as in its applications. Some of these are colossal magnetoresistance, charge ordering, spin dependent transport, interplay of structural, as well as magnetic and transport properties.These compounds are used as catalyst electrodes in certain types of fuel cells and are candidates for memory devices and spintronics applications. The metal, Sr_0, does not form any intermetallic compounds binary oxides can be predicted on the basis of the relative sizes of the metal and oxide ions and filling of holes in a close packed oxide lattice. Such predictions of structure are more difficult for ternary phases. The combination of two or more metals in an oxide generates a wealth of structural possibilities dependent on the relative sizes of the two metal ions and the oxide ion. In addition the stoichiometry of the ternary oxide may be changed by varying the proportions of the two component oxides and, for transition and lanthanide elements, the oxidation state. For example, at least twenty ternary oxide phases are formed between strontium and vanadium including $Sr_2V_2O_5$, (V-III) & (V-IV), $SrVO_3$ (V^{4+}), Sr_2VO_4 (V^{4+}) and SrV_2O_6 (V^{5+}).

In this article, we have studied on the synthesis, photoluminescence (PL) and thermoluminescence (TL) of Sr_2CeO_4 and Sr_2VO_4 phosphors prepared by the solid state reaction method in air at 1200^0C for 3 h. PL and CIE co-ordinates of Sr_2CeO_4 and Sr_2VO_4 phosphors reveals that the emission wavelengths 470nm(blue) and 510nm(green) could be used for the generation of white light for display and lamp devices

2. Experimental Methods

Sr_2CeO_4, and Sr_2VO_4 phosphors were synthesized by the conventional solid state reaction method.The starting materials, Strontium Carbonate ($SrCO_3$), Cerium Oxide (CeO_2) and Vanadium Oxide (VO_2) of purity (99.9%) were taken. For the production of Sr_2CeO_4 phosphor, the compounds Strontium Carbonate, Cerium Oxide were weighed with 2:1 stoichiometric ratio. The composite powders were grinded in an agate mortar and then placed in an alumina crucible with the lid closed. After the powders had been sintered at 1200°C for 3 hours in a muffle furnace and then cooled to room temperature. All the samples were again ground into fine powder using an agate mortar and pestle.

The V^{4+} containing compound Sr_2VO_4 was prepared in air of the appropriate mixture of Strontium Carbonate ($SrCO_3$) and Vanadium Oxide (VO_2) of purity (99.9%) sintered at 1200°C for 3 hr in a muffle furnace and then cooled to room temperature. The sample was grounded in an agate mortar with pestle. The resulting compound contains V^{4+} ions.

The chemical reaction for the production of Sr_2CeO_4 and Sr_2VO_4 are

$2SrCO_3 + CeO_2 \rightarrow Sr_2CeO_4 + 2CO_2{\uparrow}$

$2SrCO_3 + VO_2 \rightarrow Sr_2VO_4 + 2CO_2{\uparrow}$

The emission and the excitation spectra of the synthesized powders were characterized with a spectroflurophotometer (Shimadzu RF 5301 PC) with 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. Thermoluminescence of the phosphor powders were done by using Thermoluminescence Reader Type TL1009 (Nucleonix Systems) with a beta source as irradiation. 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 were calculated with colour calculator version 2, software from Radiant Imaging

3. Results and Discussions

3.1. Photoluminescence behaviour of Sr_2CeO_4 and Sr_2VO_4 phosphors

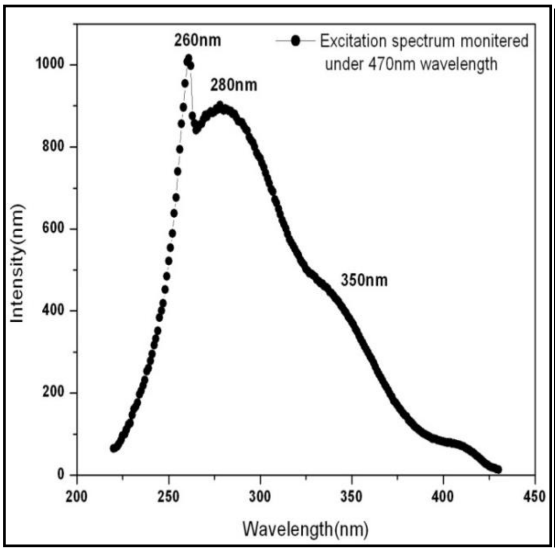
Fig.1 exhibits the PL excitation spectra of Sr_2CeO_4 phosphor. In the excitation spectrum monitored under 470nm wavelength, the broadband ranging from 225-370nm with peaks at 260, 280 and 350nm.This band could be assigned to the transition $t_{1g} \rightarrow f$, where f is the lowest excited charge transfer state of Ce^{4+} ion and t_{1g} is the molecular orbital of the surrounding ligand in six fold oxygen coordination.

Upon excitation at 260, 280 and 350nm, the emission spectrum of Sr_2CeO_4 phosphor emits a broad band range from 250-360nm with peak at 470nm (blue) with the full width at half maximum (87nm) as shown in fig.2. The peaks at 470nm(2.60 eV) is assigned to the $f \rightarrow t_{1g}$ transition. The shape of the emission spectra and emission wavelength is independent on the excitation wavelengths. This is mainly due to the charge transfer of the Ce^{4+}– O^{2-} ligand as described by Danielson et al. The Stokes shift is 210nm(2.131eV), determined from the difference between the first excitation maximum (260nm) and the emission maximum (470nm).

Fig.3 exhibits the PL excitation spectra of Sr_2VO_4 phosphor. In the excitation spectrum monitored under 510nm wavelength, the broadband ranging from 225-375nm with peaks at 262 and 335nm. Upon excitation at 262nm and 335nm, the emission spectrum of Sr_2VO_4 phosphor emits a broad band range from 350-650nm shown in fig.4. The shape of the emission spectra and emission peak wavelength is independent of the excitation wavelengths.

Table1. *Parameters of Sr_2CeO_4 and Sr_2VO_4 phosphors*

S.No.	Parameter	Sr_2CeO_4			Sr_2VO_4	
1	Excitation Wavelength (nm)	260	280	350	262	335
2	Emission Wavelength (nm)	470 (blue colour)			399, 469 (violet colour)	510 (cyan colour)
3	Stokes shift (eV)	2.131			2.302	
4	FWHM (nm)	87			114	
5	Ionic radius (Å)	Ce=1.01			V=0.92	
6	CIE co-ordinates	x=0.152, y=0.181			x=0.235, y=0.399	



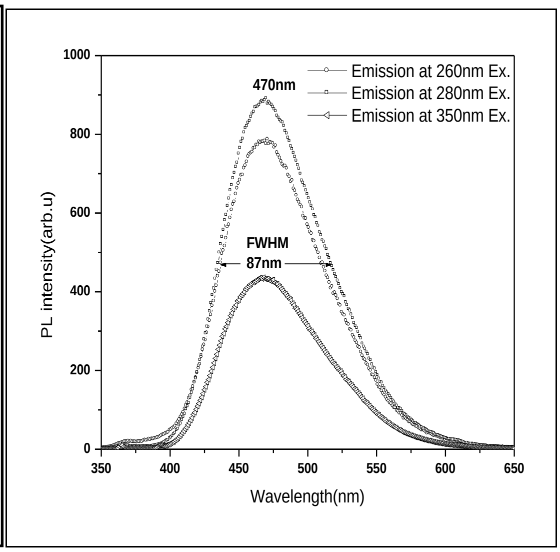
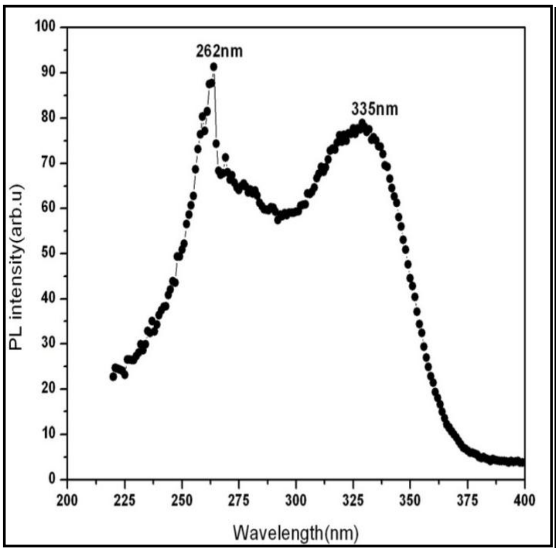


Fig1. *Excitation spectrum of Sr_2CeO_4* **Fig2.** *Emission spectrum of Sr2CeO4*



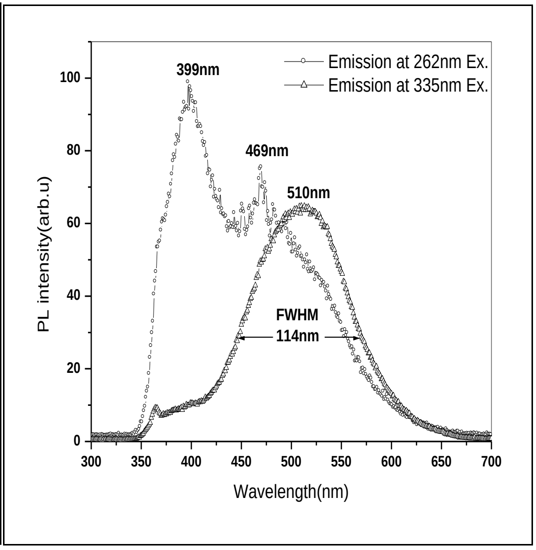


Fig3. *Excitation spectrum of Sr2VO4* **Fig4.** *Emission spectrum of Sr2VO4*

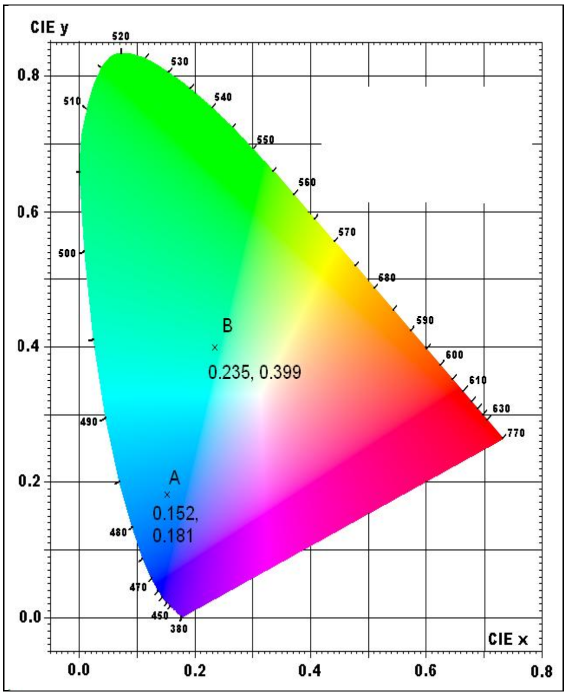


Fig5. *CIE colour co-ordinates depicted on 1931 chart (A) Sr_2CeO_4 (B) Sr_2VO_4 phosphor*

Upon excitation at 262nm, emission spectrum of Sr_2VO_4 phosphor emits two peaks at 399nm (3.1eV) (violet) and 469nm(2.6eV) (blue) respectively. Upon excitation at 335nm, emission spectrum of Sr_2VO_4 phosphor emit a peak at 510nm (2.4eV) (green) with the full width at half maximum (114nm). The Stokes shift is 248nm(2.3eV). Different parameters of Sr_2CeO_4 and Sr_2VO_4 phosphors are shown in Table 1.

From fig.2 and 4, It was observed that the shift of blue (470nm) to green(510nm) is due to the inception of smaller ion (ionic radius=0.92Å) of vanadium(V^{4+}) inplace of bigger ion (ionic radius=1.01Å) of cerium (Ce^{4+}), and the crystal field strength increases. As a result the emission shift to the longer wavelength side with increase of FWHM.

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 colour of the emission of each sample in the CIE diagrams 1931, and the colour of each sample is directly dependent on the presence of the carbonate species. Fig.5 shows the CIE coordinates depicted on the 1931 chart of Sr_2CeO_4 and Sr_2VO_4 phosphors. In the fig.4, the colour co-ordinates for Sr_2CeO_4 sample are x=0.152, y=0.181 indicates that blue colour(A) and Sr_2VO_4 sample are x=0.235, y=0.399 indicates green colour(B).

3.2. Thermoluminescence Behaviour of Sr2CeO4 and Sr2VO4 Phosphors

Thermoluminescence (TL) of pure Sr_2CeO_4 and Sr_2VO_4 phosphor powders was studied with β dose of 10Gy. No Thermoluminescence emission was observed from the irradiated powder phosphors due to formation of nano size paricles.

4. CONCLUSIONS

pure Sr_2CeO_4 and Sr_2VO_4 phosphor powders were successfully synthesized by the high temperature solid state reaction method. The prepared phosphor powders emit their characteristic lines. In a single host, Sr_2VO_4 phosphor has excellent colour tunability from violet to green under 262 and 335nm excitations. The Stoke shift and the FWHM of the emission of Sr_2CeO_4 were characteristic of a ligand-to-metal charge transfer(CT) emission. The Stoke shift of Sr_2VO_4 phosphor is more than Stoke shift of Sr_2CeO_4 and observed that the emission intensity is less. The Commission International de 1'Eclairage [CIE] co-ordinates of pure Sr_2CeO_4 phosphor exhibit excellent blue colour, where as Sr_2VO_4 phosphor reveals that the emission colour varies from violet to green. These phosphors could be used for the generation of white light for display and lamp devices.

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