Low temperature solution combustion synthesis and luminescence properties of nanoparticle of $Sr_2SiO_4:Dy^{3+}$ phosphors

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ABSTRACT

In this paper Dy^{3+} activated Sr_2SiO_4 nanophosphors were prepared by low temperature solution combustion method using urea [CO $(NH_2)_2$] as a fuel. The obtained phosphor was well characterized by powder X-ray diffraction, scanning electron microscopy, and UV–visible spectroscopy. The average crystallite sizes were estimated by Debye–Scherer formula. Photoluminescence spectra consist of strong transition at 482nm (blue), 580nm (yellow) and weak transition at 674nm (red). Thermoluminescence study was carried out for the phosphor with UV irradiation show one glow peak .The trapping parameters associated with the prominent glow peak of $Sr_2SiO_4:Dy^{3+}$ are calculated by using Chen's glow curve method.

Keywords: Photoluminescence, Thermoluminescence, Combustion Method, X-ray Emission Spectra, Scanning Electron Microscopy, Nanocrystalline Materials.
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INTRODUCTION

Light-industry addresses special interest in rare earth phosphors. White light emitting diodes (LEDs) with their characteristics of high brightness , reliability, long life time, low environmental impact and energy efficiency [1,2] are expected to replace conventional Incan- descent and fluorescent lamp in the near future. Strontium orthosilicate exits in two crystallographic modification, viz. α'-Sr_2SiO_4 (orthorhombic) and β-Sr_2SiO_4 (monoclinic) [3]. .The transition occurs from low temperature β-phase to high temperature α-phase at 385^0K, and involves the rearrangement of tetrahedral SiO_4 without change in bonds [4-6].

With the development of materials science and technology, some soft-chemical synthesis methods, such as the sol-gel [7, 8], co-precipitation [9], spray pyrolysis and hydrothermal synthesis methods [10, 11] have been successfully applied in synthesizing phosphate-white LED phosphors. All of these methods use liquid components that can be accurately controlled and thoroughly mixed throughout. Combustion synthesis is characterized by its being a more complete reaction with increased reaction efficiency and its being a fast convenient reaction. The synthesis of phosphors by using the combustion method has been proven to be a facile route for the low-temperature preparation of various homogenous phosphors, including silicates and aluminates in a short time without the use of expensive high-temperature furnaces [12-14].

Thermoluminescence (TL) is the thermally stimulated emission of light following the previous absorption of energy from radiation. If TL emission is detected and plotted as a function of time during readout using a linear time-temperature heating profile, a curve is obtained named Glow Curve. The glow peak is analyzed by an empirical method in which a parameter called the order of kinetics is introduced. When the trapped electrons jump up to the conduction band by the thermal energy, they have two kinds of chances to jump down. One is the retrapping process returning to the same kind of traps and another is the recombination with the hole accompanied by the emission of TL light. When the probability of being retrapped is negligible, the glow curve has a narrow peak shape by a rapid recombination process explained by Randall and Wilkins [15]. Instead, if retrapping dominates, the recombination

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with the holes is suppressed and the curve has a wide peak explained by Garlick and Gibson [16]. These two descriptions are called the first order kinetics and the second order kinetics respectively.

In this paper, the $Sr_2SiO_4:Dy^{3+}$ phosphors were prepared by combustion synthesis and the effect of Dy^{3+} concentration on micro structural and luminescent characteristics of $Sr_2SiO_4:Dy^{3+}$ phosphors were investigated. The properties of $Sr_2SiO_4:Dy^{3+}$ powders were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence measurement (PL) and Thermoluminescence (TL).

MATERIALS AND METHODS

$Sr_2SiO_4:Dy^{3+}$ phosphors were synthesized adopting combustion method. Strontium nitrate $Sr (NO_3)_2$, silica gel, dysprosium oxide (Dy_2O_3) and urea $CO (NH_2)_2$ were used as the staring materials in stoichiometry weight. In which Dy_2O_3 is used as activators, which is dissolved in concentrated HNO_3 before pouring them to crucible. The small amount of ammonium chloride (NH_4Cl) is used as the flux while the urea $[CO (NH_2)_2]$ as a combustion fuel [17, 18]. The weighed quantities of each nitrates, flux and fuel were mixed into mortar for 15 min to convert into a thick paste. The prepared paste is then placed in vertical cylindrical muffle furnace maintained at 700°C. Then the prepared samples were annealed at 800 °C for 2 h under an air atmosphere.

The crystalline structure, size and phase composition of the sample are examined by PANanalytical using Cu-Kα radiation (λ=1.5406 Å), where X-ray are generated at 40kV/30mA voltage and current values respectively. The scanning electron microscopy (ZEISS EVO 18) was used to observe particle morphology of phosphors. Absorption spectra were recorded using (Shimadzu UV-1700 UV-Visible) spectrophotometer. The excitation and PL emission were recorded by Spectrofluorometer (PerkinElmer LS45). Thermo- luminescence was studied with PC based thermoluminescence analyzer (10091). The samples were irradiated with UV-rays source.

RESULTS AND DISCUSSION

Optical Absorption Spectra
Optical absorption is important to study the behavior of nano-crystals and a fundamental property is the band gap. Fig. 1 shows the optical absorption spectra of dysprosium doped Sr_2SiO_4 phosphors in the range of 200nm-500nm. It can be seen that no absorption occurs for wavelength λ>250 nm (visible), the absorption edges was found at λ= 225 nm, thus the band gap was found to be 5.5eV. This absorption edges may be originated from the charge transfer band (CTB) of dysprosium oxygen interaction.
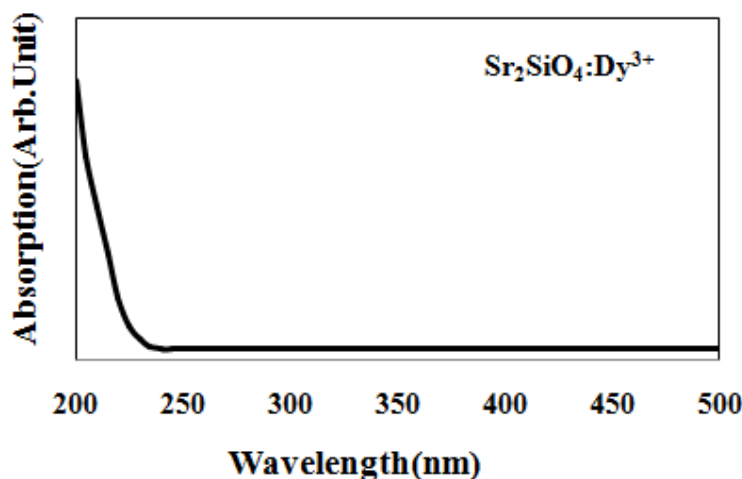

Fig.1. Absorption spectra of $Sr_2SiO_4:Dy^{3+}$phosphor

Structural analysis: X-ray Diffraction (XRD)
The analysis of XRD data of Sr_2SiO_4 phase is usually qualitative, just based on relative peak intensities. Strontium silicate exits in monoclinic (β- Sr_2SiO_4) phase at low temperatures and in orthorhombic (α'- Sr_2SiO_4) phase at high temperatures with a transition temperature of ~85^0C. It has been reported that the crystal structure of α'-Sr_2SiO_4 (orthorhombic), and β-Sr_2SiO_4 (monoclinic) are very similar [4, 5].

The typical X-ray diffraction patterns for combustion synthesized of the pure and $Sr_2SiO_4:Dy^{3+}$ phosphor powders are shown in fig. 2 from which it can be seen that all the diffraction peaks could be indexed to the monoclinic phase of β-Sr_2SiO_4 (Ref. code 98-003-6041). Incorporation of dysprosium has not changed the XRD pattern which

confirms that doping is proper has not distorted the structure of strontium silicate. Since no impurity peaks were observed, it is feasible to suggest that all samples are a single phase of β-Sr_2SiO_4.

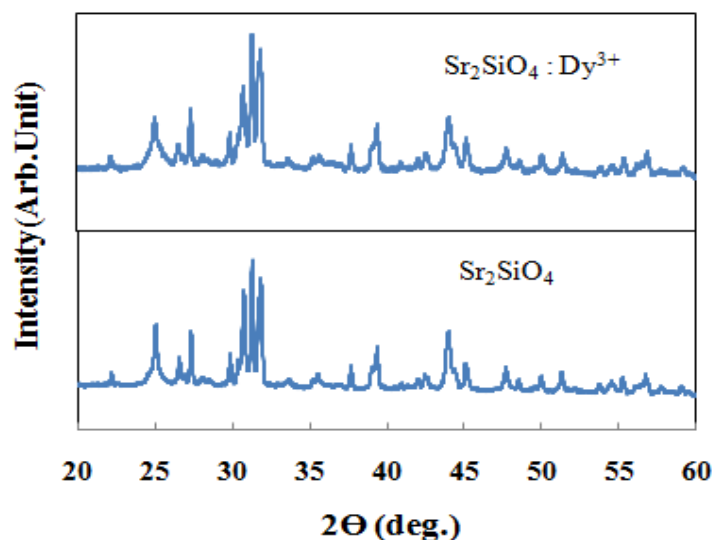**Fig.2. Power XRD pattern of Sr_2SiO_4:Dy^{3+} phosphor**

An estimation of average crystalline size for the sample is done using Scherer's formula [19, 20].

$$L = \frac{0.94\lambda}{\beta cos\theta}$$

Where L is the crystalline size, λ is the wavelength (for Cu Kα, λ=1.5406 A^0), β is the full width at half maximum (FWHM) and θ is the Bragg's angle. Table 1 shown calculation of XRD data Dy^{3+} doped Sr_2SiO_4 phosphor. The peaks in XRD patterns are attributed to Sr_2SiO_4 monoclinic phase. The calculated average crystalline size of Sr_2SiO_4:Dy^{3+} phosphor is 12 nm.

Table1: XRD data of Sr_2SiO_4:Dy^{3+} phosphor

2θ	$I/I_0(\%)$	FWHM(β)	Crystalline size(nm)	Lattice spacing (A^0)	hkl
25.0260	25.60	0.9984	8.14	3.5558	112
27.1930	13.25	0.7488	10.91	3.27671	113
30.8107	33.99	0.7488	11.0	2.89972	013
31.3317	100	0.5120	16.1	2.85211	102
31.6852	43.50	0.7488	11.02	2.82312	202
39.3196	26.77	0.6240	13.50	2.28959	031
44.0596	26.62	0.7488	11.44	2.05388	220

Morphological characterization: Scanning Electron Microscopy (SEM)
The luminescence properties of phosphor particles depend on the morphology of the particles, such as size, shape, defect and so on. Fig. 3 (a, b) shows the SEM images of the as prepared samples at different magnifications. SEM studies showed that the shape of the particles is irregular spherical from each other and the particles appear to be non-uniform and agglomerates composed of circular particles as can be seen from the higher magnification micrograph, The agglomerated particles, pores and voids were due to gases released during the combustion process.
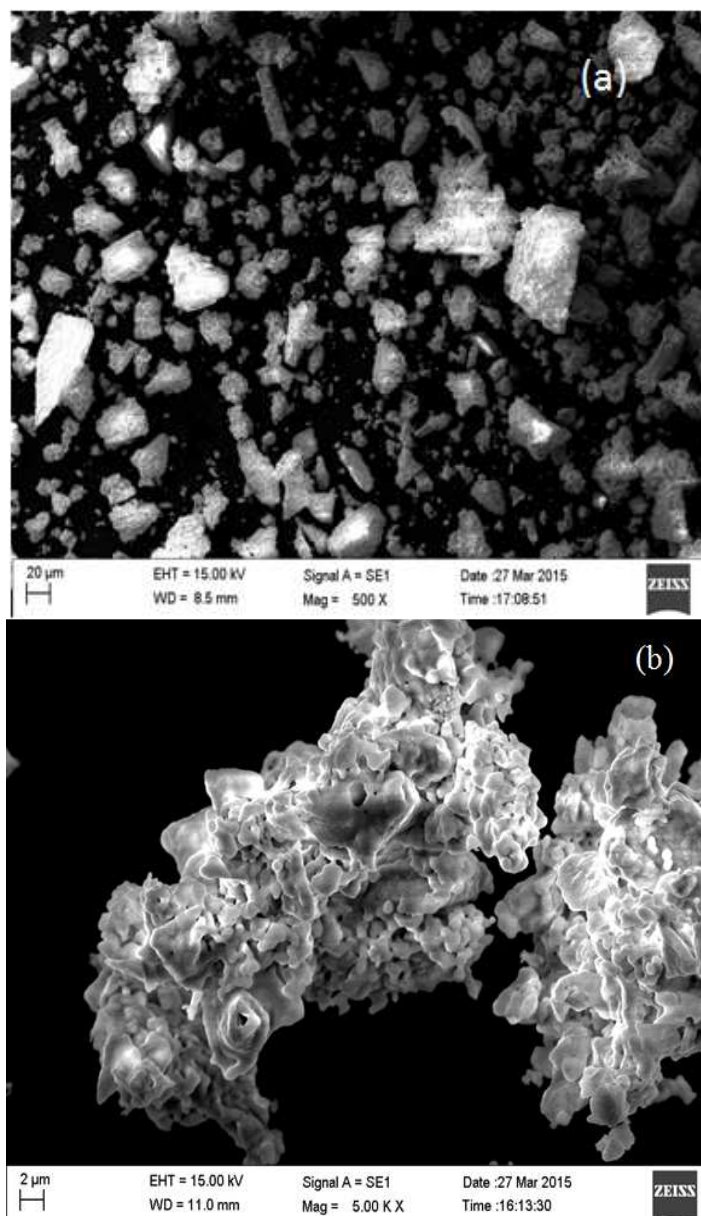
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Fig.3 (a, b). SEM micrograph of Sr_2SiO_4:Dy^{3+} phosphor at different magnifications (a) 500x, (b) 5000x

Photoluminescence Spectra

Fig.4a shows the excitation spectra of the Dy doped strontium silicate using combustion method, in the spectral region from 200 to 450 nm. The spectrum of Sr_2SiO_4:Dy^{3+} phosphors exhibit a broad band in the UV region centered at about 254 nm, and sharp lines between 300-450 nm. The board absorption band is called charge transfer band (CTB), which is caused by the electron transfer from filled 2p orbital of O^{2-} ions to vacant 4f orbital of Dy^{3+} ions [21]. The sharp excitation peaks located at 322, 356, 382, 402 and 427 nm were assigned to electronic transitions at of $^6H_{15/2} \rightarrow {}^6P_{3/2}$, $^6P_{7/2}$, $^4I_{11/2}$, $^4_{13/2}$ and $^4G_{11/2}$ respectively.

Fig.4b shows the emission spectra of Sr_2SiO_4:Dy^{3+} phosphors are excited with 356 nm wavelengths from a Xenon lamp. The emission spectrum is characterized by three bands located at 482, 580 and 674 nm corresponding to the transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (red) respectively. It is known that the Dy^{3+} emission around 480 nm corresponds to magnetic dipole (MD) and 580 nm belongs to electric dipole (ED) transition with the selection rule $\Delta J = \pm 2$ [22,23]. In Dy^{3+} doped Sr_2SiO_4 nano-phosphors, the intensity of the blue emission was lesser than that of the yellow emission. This is because the hypersensitive (forced electric dipole) transition was strongly influenced by the surrounding environment and the magnetic dipole transition was in sensitive to the crystal-field strength around the Dy^{3+} ions [24].

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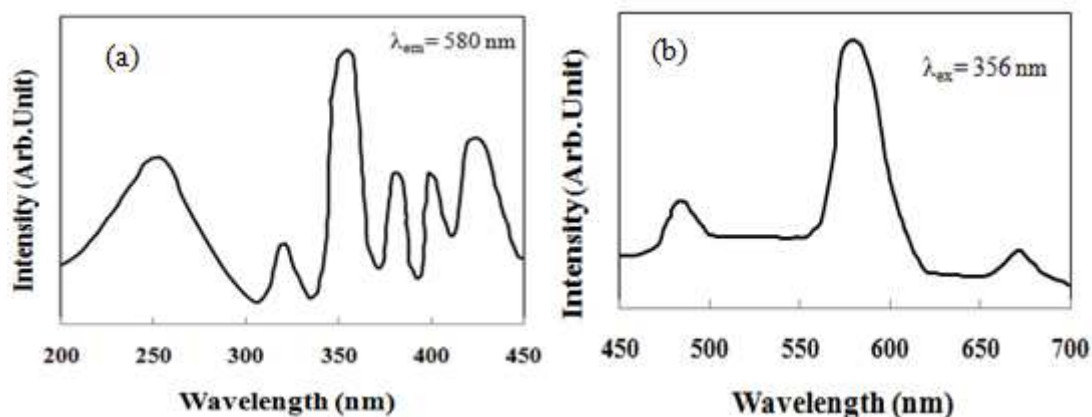

Fig.4. (a) Excitation spectrum and (b) Emission spectrum of the Sr$_2$SiO$_4$:Dy^{3+} phosphors

Thermoluminescence Studies

Thermoluminescence (TL) is an important tool for estimating the luminescent center in solids. Stimulated emission of light from an insulator or semiconductor after heating following the previous absorption of energy from ionizing radiation is known as TL. Using the Chen's peak shape method [25], the kinetic order can be related to the geometrical factor (μ_g) by the relation $\mu_g = \delta/\omega = T_2-T_m / T_2-T_1$ where T_1, T_m and T_2 represent the temperatures of half intensity at low temperature side peak temperature and high temperature side of TL peak. And $\delta = T_2-T_m$, $\tau = T_m-T_1$ and $\omega = T_2-T_1$ therefore E_δ , E_τ and E_ω are the corresponding activation energy. The activation energy (E) can be estimated from the thermal peak temperature with the following equation

$$E_\alpha = C_\alpha \left(\frac{kT_m^2}{\alpha}\right) - b_\alpha (2kT_m)$$

The frequency factor was calculated by

$$\frac{\beta E}{kT_m^2} = s\left[1 + (b-1)\frac{2kT_m}{E}\right] \exp(E/kT_m)$$

Fig. 5 shows TL glow curve of Sr$_2$SiO$_4$: Dy^{3+} phosphor, here sample is irradiate by UV source and only one peak is observed at around 510^0K due to one luminescence centre is formed The value of different parameters calculated from glow curves are presented in table 2. The value of trap depth, which resembles the activation energy, is calculated that is 0.76 eV. It is worth reporting that the shape factor, which is 0.48 and shows the second order kinetics that support the probability of retrapping released charge carriers before recombination [26].
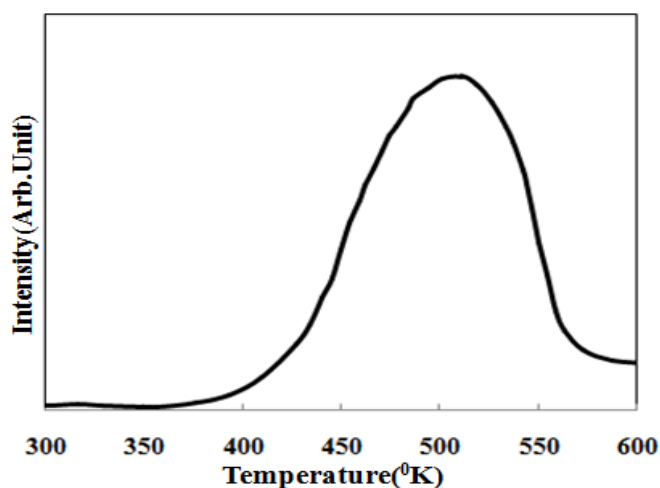

Fig.5. TL glow curve of Sr$_2$SiO$_4$:Dy^{3+} phosphor

Table 2: Values of different parameters calculated from TL glow curves

Heating Rate(Ks^{-1})	T$_1$(^{0}K)	T$_m$(^{0}K)	T$_2$(^{0}K)	τ	δ	$\mu=\delta/\omega$	Activation Energy (eV)	Frequency Factor c/s
5	465.1	510.50	552.5	45.09	42.0	0.48	0.76	2.3x10^8

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CONCLUSON

In this work Sr_2SiO_4:Dy^{3+} phosphor was prepared by combustion method which appears to be a more feasible method for production. The absorption spectra shows widened band gap because of quantum confinement effect. XRD studies confirmed the formation of a single phase compound. SEM studies have been shown the particles appear to be non-uniform and agglomerates composed of circular particles. PL spectra consist of three main groups of peaks in 460–500nm (blue), 555–610 nm (yellow) and 677 nm (red) respectively. These peaks were assigned to transition of $^4F_{9/2} \rightarrow ^6H_{15/2,\ 13/2,11/2}$ this PL intensity for application in white LEDs. Therefore, Dy^{3+} activated Sr_2SiO_4 was a promising single phased phosphor for WLED's. The TL glow curve for Sr_2SiO_4:Dy^{3+} expressed general order kinetics. Calculated trap depth of the phosphor indicates that obey second order kinetics and this phosphor is a quite good persistent luminescent material.

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