



AN EFFICIENT $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ PHOSPHOR FOR SOLID STATE LIGHTING

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ABSTRACT

A series of Tb^{3+} doped $\text{Li}_2\text{SrSiO}_4$ phosphors were prepared by high temperature solid state reaction. The structure and luminescent properties of $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ phosphor was characterized by X-ray diffraction and scanning electron microscopy (SEM), photoluminescence excitation (PLE) and emission (PL) spectra were utilized. From X-ray diffraction (XRD) patterns, it is indicated that the phosphor $\text{Li}_2\text{SrSiO}_4$ forms without impurity phase at 900°C . The photoluminescence (PL) excitation spectra indicate that the $\text{Li}_2\text{SrSiO}_4:\text{xTb}^{3+}$ phosphors can be effectively excited by ultraviolet (244 nm) light. The emission properties of $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ phosphors are strongly dependent on the concentration of Tb^{3+} . The stronger blue and green emission was presented here. The concentration quenching effect for Tb^{3+} was found at the optimum doping concentration of 0.5 mol%.

Keywords : Luminescence; Phosphor; $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$; Rare earth; Solid state lighting.

I. INTRODUCTION

Silicates are mostly occurs in the form of Si:O ratio in the nature, which are classified as ortho (1:4), meta (1:3), and pyro (2:7) silicates [1]. The study reveals that out of these three types, ortho silicate phosphor possesses wide excitation bands due to ultraviolet and blue light [2]. This kind of phosphor have more demands and attraction because of high chemical and physical stability, various crystal structure, excellent whether resistance [3], low price of high purity of raw SiO_2 and many

other advantages. Recent study adds that due to encouraging luminescent properties alkaline earth silicates material doped with rare earth have been increasing paid attention which makes them promising candidate for application in white light emitting diode [4-6], Display and solid-state lighting [7], multicolor phosphor [8], long lasting phosphor [9], high efficiency Si-solar cells [10]. The unique optical properties of rare earth (RE) ions are attributed to electronic transitions occurring within the partially filled 4f energy shell, which makes these ions a favourite activator for different host materials. Because of its high chemical and physical stability, wide band gap and excellent radiation conversion efficiency, the silicate-based compound has proven to be one of the best hosts for the incorporation of RE ions in a wide range of optical applications [11-15]. Recently, Wang et al. [16] synthesized the blue phosphor $\text{Na}_2\text{CaSiO}_4:\text{Eu}^{3+}$ by high temperature solid-state reaction and the white light could be generated by mixing it with the yellow phosphor $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$. Xie et al. [17] synthesized deep red-emitting phosphors $\text{Na}_{(2-x)}\text{Ca}_{(1-x)}\text{Eu}_x\text{SiO}_4$ with chromaticity coordinates (0.639, 0.359) by high temperature solid-state reaction.

Tb^{3+} doped silicates have been widely used because of higher luminescent intensity among rare-earth ions [18]. Some Tb doped phosphor like $(\text{Zn}_2\text{SiO}_4)$ [10], $(\alpha\text{-Si}_3\text{N}_4)$ [19], $(\text{Ca-}\alpha\text{-SiAlON})$ [20], $(\text{Mg}_2\text{SiO}_4)$ [21] have also many applications. Thus, the development of new phosphors for UV-LED applications is highly desirable. On the basis of latest investigation, few reports are present on the luminescence study of $\text{Li}_2\text{SrSiO}_4$ phosphor up to date. In this

paper Tb^{3+} doped $\text{Li}_2\text{SrSiO}_4$ phosphor are synthesized by Solid-State diffusion method and study the photoluminescence properties of said phosphor and we get more improved results. The aim of the present investigation is to examine ortho silicate based phosphors.

II. METHODS AND MATERIAL

The phosphors were prepared by solid state reaction. Stoichiometric amounts of starting materials, except for Li_2CO_3 , which was 2 mol% excess to compensate for the volatilization loss in Li_2O , is expected to be devoid of Li vacancies. SrCO_3 , SiO_2 (all A.R. grade) and Tb_2O_3 (99.99 purity) were ground well and preheated at 500 °C for 4h in order to avoid lithium volatilization. After the preheat treatment, the obtained product was ground well and placed in an silica crucible inside the furnace and heated to 900 °C for 5h under a reducing atmosphere of carbon. The samples were kept at this temperature for 5 h and then cooled to room temperature. The resultant powder was crushed to fine particles using an agate pestle and mortar. This powder was used as a phosphor in further study.

The phase composition and phase structure were measured by X-ray diffraction (XRD) pattern using a PAN-analytical diffractometer with Cu K α radiation ($\lambda=1.5405$ Å) operating at 40Kv, 30mA. The XRD data were collected in a 2θ range from 10 to 80°, with the continuous scan mode. The morphology and microstructure were characterized with JEOL, JSM-6360LV SEM environmental scanning electron microscope (SEM). The PL excitation and emission spectra were recorded using a RF-5301PC Spectrofluorophotometer fitted with a sensitive photomultiplier tube with a 150W 'xenon flash lamp' as an excitation source. This Spectrofluorophotometer was well intensity calibrated for the excitation and emission spectra. The excitation and emission spectra were recorded using a spectral slit width of 1.5nm with high sensitivity. All the measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

A. Phase identification and morphology

A series of phosphors, $\text{Li}_2\text{SrSiO}_4:\text{Tb}$, were synthesized by conventional solid-state reaction method. The X-ray diffraction pattern of

$\text{Li}_2\text{SrSiO}_4:\text{Tb}$ phosphor is shown in Fig.1. It can be seen from Fig.1 that all the XRD patterns are similar. All the reflections are indexed on the basis of a hexagonal unit cell of $\text{Li}_2\text{EuSiO}_4$ (JCPDS No. 47-0120) [13, 22], indicating that the doping of Tb^{3+} does not change the crystalline structure of $\text{Li}_2\text{SrSiO}_4$. It was reported that $\text{Li}_2\text{SrSiO}_4$ has a hexagonal crystal structure with the P3_121 space group, similar to $\text{Li}_2\text{EuSiO}_4$. This result also demonstrates that the Tb^{3+} ions are in the position of Sr^{2+} ions because the size of Tb^{3+} ($r = 0.092$ nm) ion near to Sr^{2+} ion ($r = 0.112$ nm).

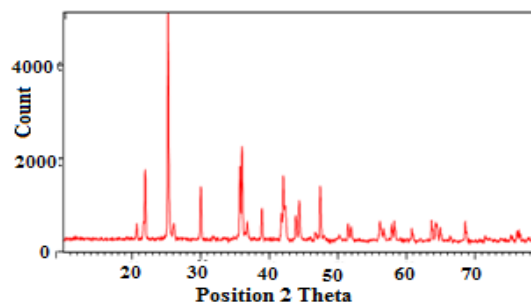


Fig.1 XRD powder pattern of $\text{Li}_2\text{SrSiO}_4$

Figure 2 displays the SEM photographs of $\text{Li}_2\text{SrSiO}_4:\text{xTb}^{3+}$ phosphors. Powder morphology was studied using SEM at STIC, Kochi, India (JEOL JSM-6390LV). Figure 2A shows inhomogeneous morphology and the relatively big grain size. The surface morphology of the powders is irregular, which shows a grain growth tendency and agglomeration at higher temperatures. The grain size distribution is broad and the average size is about 1 μm for the $\text{Li}_2\text{SrSiO}_4$ prepared by conventional solid-state reaction.

A. Photoluminescence studies

Figure 3 shows the PLE and PL spectrum of $\text{Li}_2\text{SrSiO}_4:0.005\text{Tb}^{3+}$ phosphor. The excitation spectrum consists of two absorption bands. One from 220-255nm with maximum at about 244nm and other from 255-350nm which is due to the spin-allowed $4\text{F}^8 \rightarrow 4\text{F}^75\text{d}^1$ transition of Tb^{3+} and the $4\text{f}-4\text{f}$ transition of Tb^{3+} respectively [23]. Upon 244nm excitation, the emission spectrum is composed of blue (383, 416, 421, 438, 459 nm) and bluish-green (471nm), green (493, 544, 553 nm). The blue and blue-green emission peaks at 383, 416, 421, 438, 459 and 471nm are originated from $^5\text{D}_3 \rightarrow ^7\text{F}_j$ ($J=3-6$) transitions and green emission peaks at 493, 544 and 553 nm are assigned to $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($J=3-6$) transition of Tb^{3+} respectively [19].

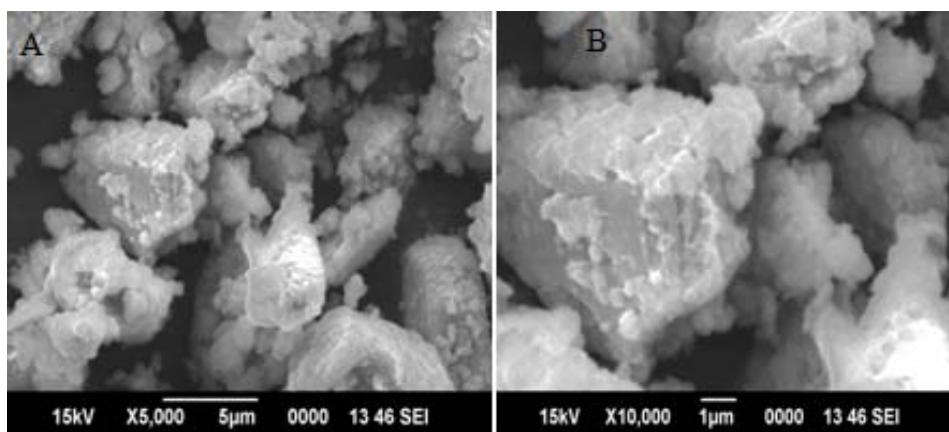


Fig.2 SEM images of $\text{Li}_2\text{SrSiO}_4$

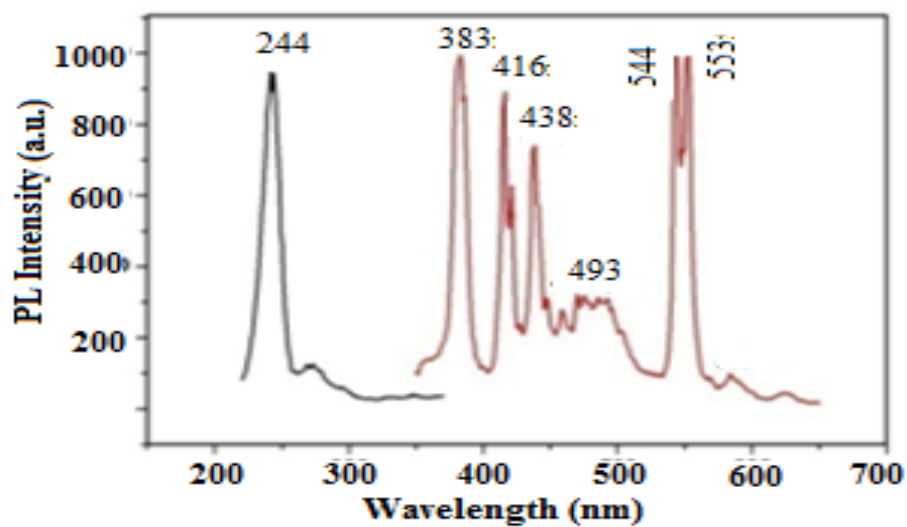


Fig3: PL emission spectrum of $\text{Li}_2\text{SrSiO}_4: 0.005\text{Tb}^{3+}$ phosphor monitored at 244nm excitation.

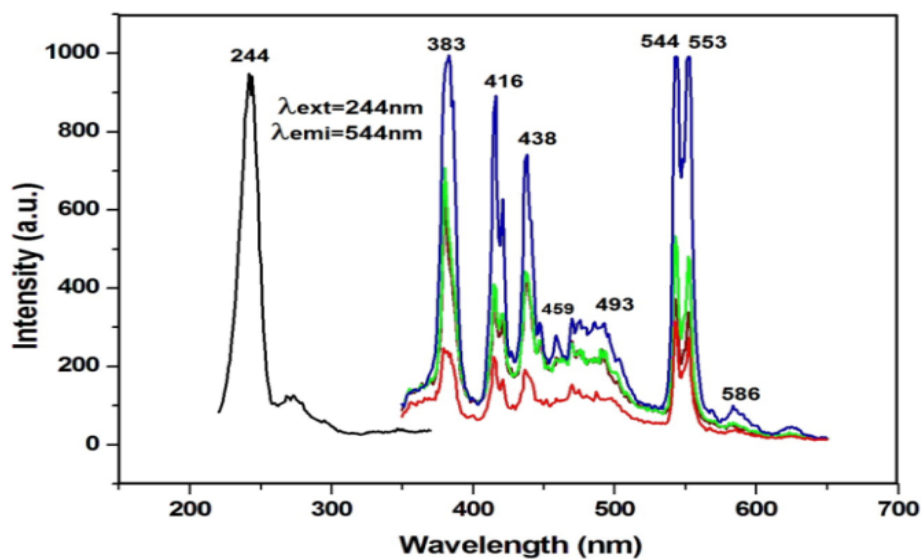


Fig4: PL emission spectra of $\text{Li}_2\text{SrSiO}_4: x\text{Tb}^{3+}$ phosphor monitored at 244nm excitation.

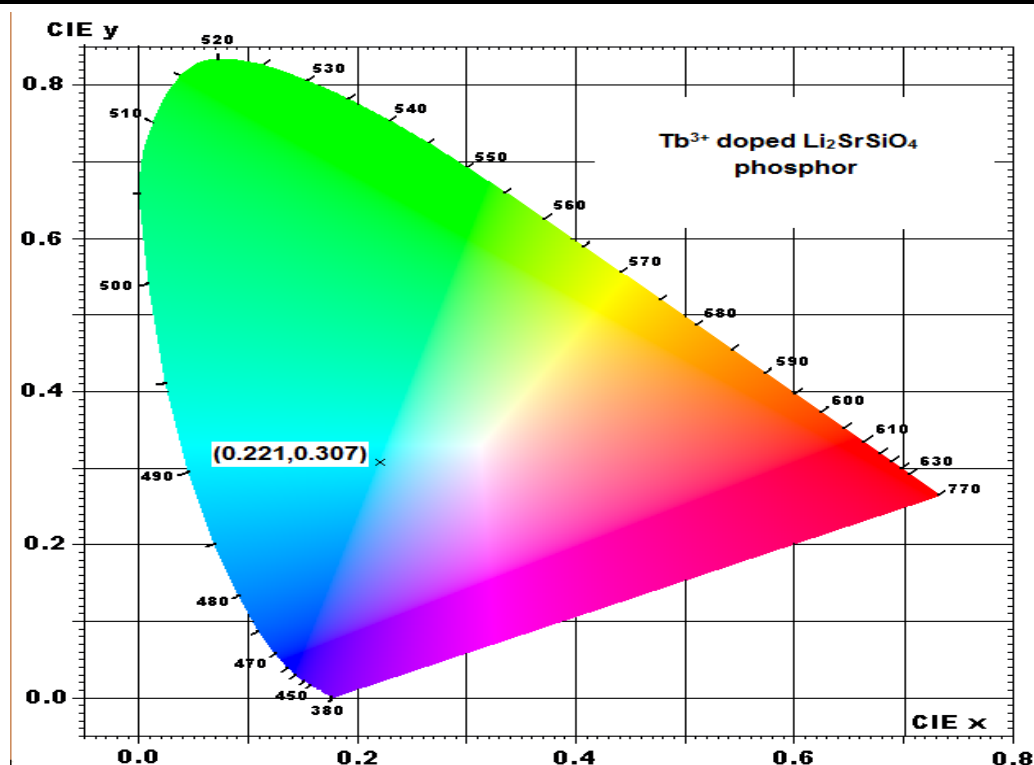


Fig.6 CIE color coordinates of $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ Phosphor.

The most intense peaks at 383 nm (blue) and 544, 553 nm (green) are due to $^5\text{D}_3 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition respectively. The green emission transition was split into two components centered at 544 and 553 nm. The splitting was identified as stark splitting and the results agree closely with results reported elsewhere [20] indicating that the Tb^{3+} emission features observed under VUV excitation are similar to those observed under UV excitation. The excitation and emission spectra consequences indicate that the $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ may act as a potential blue and green light-emitter for UV-LEDs.

Figure 4 shows the PL emission spectra of $\text{Li}_2\text{SrSiO}_4:\text{xTb}^{3+}$ for different concentration of Tb^{3+} ion. All the excitation or emission spectra show similar profile, however, their intensities are dependent on the x value. It can be seen from Fig.4 that the emission intensity at 383, 544 and 553nm (excited at 244 nm) increased with x value increasing from 0.1 to 0.5 mol% and then decreased with x value increasing from 0.5 to 1 mol%. The maximum of luminescent intensity lies at $x=0.5$ mol% indicating that the concentration quenching for the fluorescence of $\text{Li}_2\text{SrSiO}_4:\text{xTb}^{3+}$ occurs when value is higher than

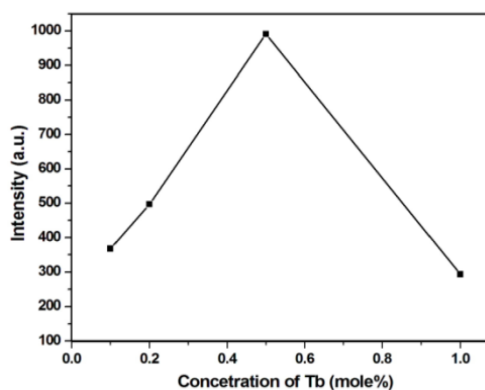


Fig. 5 Variation in PL intensity with the concentration of

Tb^{3+} ions in $\text{Li}_2\text{SrSiO}_4:\text{Tb}$

0.5 mol%. The quenching of the emission of the trivalent Tb^{3+} might be ascribed to cross-relaxation between pairs of Tb^{3+} ions. On the other hand, as the concentration of Tb^{3+} increases, distance between the activator is shortened and the energy transfer between adjacent Tb^{3+} ions in the host occurs with higher probability in the way of non-radiation transition, which makes the excitation energy consumed and results in the quenching of the emission of Tb^{3+} . Figure 5 shows the relationship between Tb^{3+} concentrations on relative luminescence intensity of the

$\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ phosphor and it is the maximum at 0.5mol%.

CIE (The Commission International de l'Eclairage) method is well defined to express the colors in color coordinates. This system recognizes that the human visual system uses three primary colors, red, green and blue. Every natural colors like red, green, and blue can be identified by (x, y) coordinates. The CIE coordinates of the $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ (x=0.221, y=0.307) are shown in the Fig.6. These color coordinates indicates that the prepared phosphor are close to the edge of CIE diagram [24].

IV. CONCLUSION

In the present work, the Tb^{3+} doped phosphor $\text{Li}_2\text{SrSiO}_4$ were synthesized by using solid-state diffusion method. The formation of this compound was confirmed by the XRD and SEM technique. The result revealed that the $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ would be a potential green phosphor. Upon the excitation with ultraviolet (UV) irradiation, the phosphors show a strong emission at around 383nm (blue) and 544nm (green) corresponding to the $^5\text{D}_3 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transitions of Tb^{3+} . Concentration quenching occurs, when the Tb^{3+} concentration is beyond 0.5 mol %. The Obtained CIE coordinates are suitable for fabrication of lighting device. $\text{Li}_2\text{SrSiO}_4:\text{Tb}^{3+}$ may act as a potential blue and green light-emitter for UV-LEDs.

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