

Blue-Light-Emitting Eu^{2+} Doped Lithium Calcium Silicate Phosphor for White-Light-Emitting-Diode

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Abstract: Eu^{2+} doped lithium calcium silicate $\text{Li}_2\text{CaSiO}_4$ phosphor was successfully prepared by traditional solid state reaction method at 800 °C. Morphology was studied by SEM demonstrated that the particle size was in the range of 2-10 μm , chemical composition was studied by EDAX and the exact phase was studied by XRD of the host sample. The excitation spectra is recorded in the range of 350 to 400nm considering solid state lighting application. The structure in the excitation spectrum is assigned to the crystal field splitting of the 5d level of Eu^{2+} ions. Upon 376nm excitation $\text{Li}_2\text{CaSiO}_4:0.01\text{Eu}^{2+}$ shows blue emission band with peak at 480 nm and a full width at half maximum (FWHM) of 31 nm. The optimum concentration of Eu^{2+} was 0.1 mole%. Concentration quenching is mainly caused by the nonradiative energy transfer among Eu^{2+} , which occurred as a result of multipole–multipole interaction. CIE colour coordinates were (x=0.108 and y=0.140), which clearly indicate that the phosphor $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ can be used as a potential blue phosphor candidate for the phosphor-converted blue LEDs as well as white LEDs under near-UV excitation.

KEYWORDS: Morphology, photoluminescence, optimum concentration, color coordinates.

1. INTRODUCTION

In the recent years, considerable amount of research has been devoted towards the development of White light emitting diodes (WLED). WLED is a potential source to replace the conventional fluorescence lamp. The advantages of LED, such as low power consumption, long lifetime and small size, made its application area and hence the world market to expand drastically [1-2]. Other importance of using LEDs is in reducing pollution in both the ways, by avoiding the use of highly poisonous Mercury and reducing carbon pollution in air by reducing number of power plants which consume coal as a fuel [3-4].

For blue-emitting phosphors excited by near UV-LEDs, $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ phosphor has been proved to be excellent phosphors because of their excellent luminescent properties, high thermal and chemistry stability, and relatively lower synthesized temperatures. Shi et al. reported $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ has high absorption from UV to NUV region and a strong emission around 480 nm with a narrow band width [6]. He et al. found that white light emission can be realized by mixing $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ and $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$ phosphors under UV excitation [7]. The optimal phosphor $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ has a very intense cyan-emission and with color coordinates (0.119, 0.203) under low voltage cathode ray excitation, which can enlarge the color gamut of field emission display (FEDs) [8]. Enhanced emission from $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ phosphors by doping with Y^{3+} is reported by J. Zhong et al. [9].

In the present work we have reported the synthesis of $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ by ball milling followed by conventional solid state reaction method at 800°C of temperature and explained the photoluminescence characteristics along with color coordinates.

2. EXPERIMENTAL

$\text{Li}_2\text{Ca}_{(1-x)}\text{SiO}_4:x\text{Eu}^{2+}$ (x=0.005,0.01,0.02) phosphors were synthesised through the traditional solid state reaction process. High purity of LiCO_3 (99.9%), CaCO_3 (99.9%), SiO_2 (99.9%) and Eu_2O_3 (99.9%), were used as starting materials. 8 mole % of H_3BO_3 was adopted as a flux. Stoichiometrical amount of starting materials and small quantity of ethanol were mixed thoroughly by ball milling for 2 hours. The mixture was first calcined at 800 °C for four hours in air. After intermediate grind the samples were heated in reducing atmosphere prepared from activated charcoal for four hours. The phosphor was allowed to cool slowly to room temperature by natural cooling.

The Crystal structure of the final product was determined by the conventional x-ray diffraction method. (XRD, XPERT PRO, Cu $\text{K}\alpha$, 40kV). High resolution XRD patterns were collected in the 2θ range from 20 to 70°. Energy dispersive x-ray analysis (EDAX) was done to analyze the chemical components of the phosphor. The morphology and the size of the obtained sample were observed with Scanning Electron microscopy, Quanta 200 with EDS (SEM). The excitation and emission spectra were measured by a Hitachi F-7000 fluorescence spectrofluorometer equipped with a 150W Xe lamp. All the experiments were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

Name and formula:

Reference code:	01-072-1729
ICSD name:	Lithium Calcium Silicate
Empirical formula:	$\text{CaLi}_2\text{O}_4\text{Si}$
Chemical formula:	$\text{Li}_2\text{CaSiO}_4$

Crystallographic parameters:

Crystal system:	Tetragonal
Space group:	I-42m
Space group number:	121
a (Å):	5.0470
b (Å):	5.0470
c (Å):	6.4860
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	90.0000
Calculated density (g/cm ³):	2.93
Measured density (g/cm ³):	3.03
Volume of cell (10 ⁶ pm ³):	165.21
Z:	2.00
RIR:	2.11

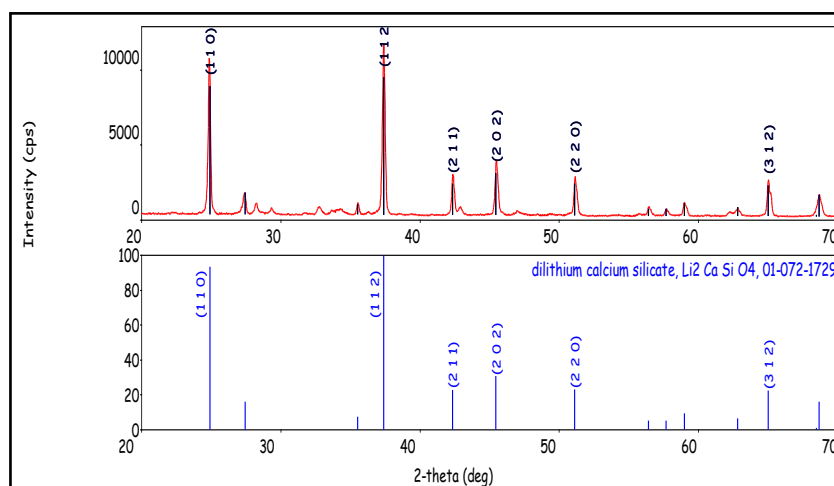


Figure 1: XRD pattern of $\text{Li}_2\text{CaSiO}_4\cdot\text{Eu}^{2+}$

The exact phase of $\text{Li}_2\text{CaSiO}_4$ is indicated by XRD pattern of the sample shown in Figure 1. The XRD pattern agrees well with ICSD card number 01-072-1729. $\text{Li}_2\text{CaSiO}_4$ has body centred tetragonal crystal structure with I-42m space group and the lattice constants are $a=5.047 \pm 0.005 \text{ \AA}$, $c=6.486 \pm 0.006 \text{ \AA}$, $c/a = 1.285$, V (cell volume) = 165.2 \AA^3 and $Z = 2$ [6]. Ca atom occupies 8-fold coordination distorted dodecahedral site, and Li atom locates at the centres of distorted $(\text{LiO}_4)^{7-}$ tetrahedral [9]. Eu^{2+} ions will occupy Ca^{2+} sites because of the similar ionic radius, which are about 0.125 nm and 0.09 nm, respectively. No Eu^{2+} ion is expected to occupy the site of Si^{4+} ($r=0.041 \text{ nm}$).

3.2. EDAX

Figure 2 indicates the Energy dispersive x-ray analysis (EDAX) graph of the as prepared sample. It is observed at magnification of 2000 and for 30 seconds of live period. The peaks in figure shows energy lines $\text{K}\alpha(3.69\text{eV})$ and $\text{L}\alpha(0.341\text{eV})$ corresponding to Calcium, $\text{K}\alpha(0.523\text{eV})$ corresponding to oxygen and $\text{K}\alpha(1.740\text{eV})$ corresponding to Silicon atoms. EDAX do not demonstrate Lithium as there are not enough electrons in Lithium atom to disperse the energy. One extra pick indicating Calcium may be corresponding to 0.01% impurity. This indicates the chemical composition of the sample $\text{Li}_2\text{CaSiO}_4$.

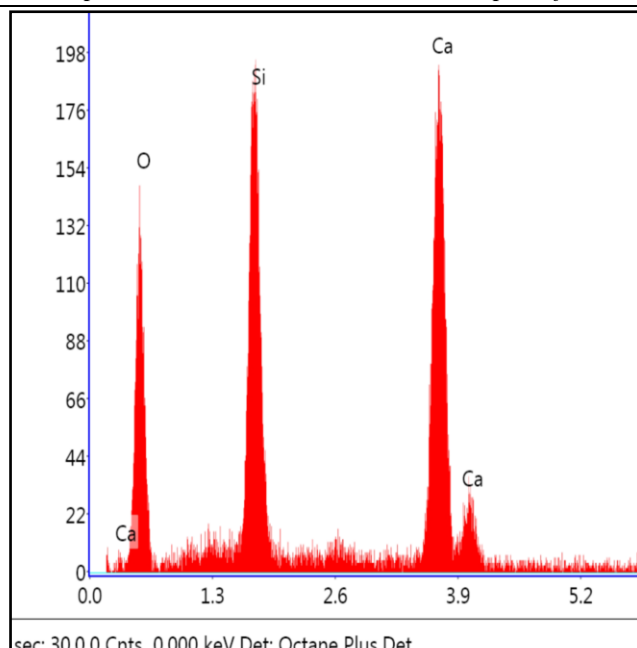


Figure 2: EDAX image of $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$

3.3. SEM-Micrograph

The morphology of $\text{Li}_2\text{CaSiO}_4$, synthesised by solid state reaction is indicated in Figure3. SEM is observed for as prepared sample without any further process. SEM micrographs show the agglomerated particles having nearly spherical shape with average diameter of 2-10 μm .

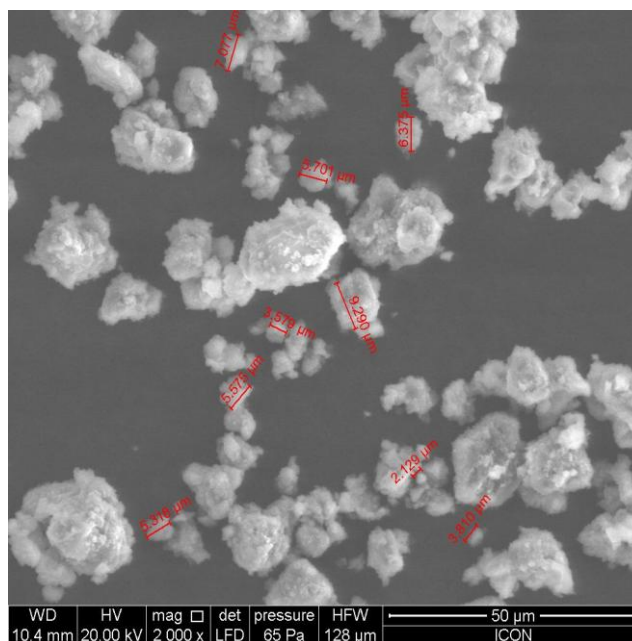


Figure 3: FE-SEM image of $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$

3.4. Photoluminescence Excitation

The photoluminescence excitation (PLE) spectrum of $\text{Li}_2\text{CaSiO}_4:\text{xEu}^{2+}$ ($\text{x}=0.005, 0.01$ and 0.02) is monitored at 480 nm, is shown in Figure 4. J. Liu et al. Reported the PLE spectrum ranging from 220 to 470 nm is composed of several bands, which are due to the parity allowed $4f^7(^8\text{S}_{7/2}) \rightarrow 4f^65d$ transitions of Eu^{2+} ions [6]. The subband with peak at 290 nm is due to the ground $^8\text{S}_{7/2}$ to the $e_g(4f^5d)$ state; the others at around 380, 400, 425 and 456 nm are attributed to the $t_{2g}(4f^5d)$ state. We have recorded the excitation spectra in the range of 350 to 400nm considering solid state lighting application. The structure in the excitation spectrum is assigned to the crystal field splitting of the 5d level of Eu^{2+} ions. The excited 5d levels are not shielded from the ligand field, giving rise to a marked splitting of the excited levels. The symmetry of the anion coordination polyhedron around the

emission centers determines the number of the splitting level. Dorenbos has made a clear correlation between the splitting and the coordination polyhedron, revealing that the crystal field splitting tends to be the largest for octahedral coordination followed by cubal, dodecahedral, and it is the smallest for tricapped trigonal prism (3ctp) and cuboctahedron (cubo) coordination [10]. In the crystal structure of Li₂CaSiO₄, the Ca atom occupies the 8-coordinated distorted dodecahedral site [11]. Since the doped Eu²⁺ ions occupy Ca sites and are exposed to strong crystal field, the excitation band of Eu²⁺ extends into visible region. According to the excitation spectrum, the crystal field splitting is estimated to be about 12260 cm⁻¹.

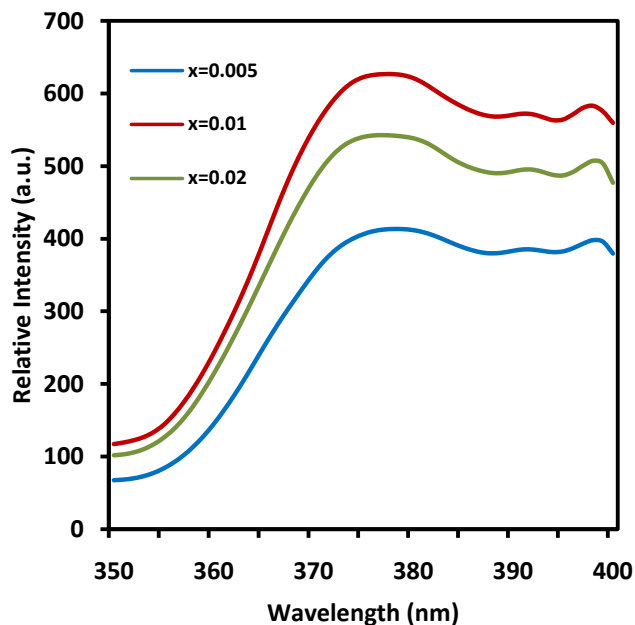


Figure 4: Excitation spectra of Li₂CaSiO₄:Eu²⁺ at 480nm emission

3.5. Photoluminescence Emission

Upon 376nm excitation Li₂CaSiO₄:0.01Eu²⁺ shows blue emission band with peak at 480 nm and a full width at half maximum (FWHM) of 31 nm. Compared with the common value of FWHM, 50–100 nm, of Eu²⁺ ions in most phosphor materials, this value is smaller in our case, which is indicative of weak interaction of Eu²⁺ ions with the host material, Li₂CaSiO₄. In lighting field, the smaller FWHM of emission band is helpful for high luminous output [12]. A rough estimate of the Stokes shift can be made by assuming that the excitation band is the mirror image of emission band. In this way, the Stokes shift of Li₂CaSiO₄:0.01Eu²⁺ is estimated to be about 1100 cm⁻¹, after considering the 480 nm emission band. In our case, the Stokes shift is comparatively smaller, which is attributed to the existence of numerous Li⁺ cations in the host material Li₂CaSiO₄. The reason is that the small cations which are behind the oxygen ions surrounding the emission centers will restrict the expansion of the emission centers, i.e. constrain the distortion of the excited state, which will lead to a small Stokes shift [13].

The effect of the Eu²⁺ concentration x on the emission intensity of Eu²⁺ doped Li₂CaSiO₄ ($\lambda_{ex}=376$ nm) is shown in Figure 5. The emission intensity under 376 nm excitation increases with increasing Eu²⁺ concentration, maximizing at about $x=0.01$. Concentration quenching occurs, when the Eu²⁺ concentration is beyond $x=0.01$. Concentration quenching is mainly caused by the nonradiative energy transfer among Eu²⁺, which usually occurs as a result of an exchange interaction, radiation reabsorption or a multipole–multipole interaction [14]. Since the fluorescent mechanism of Eu²⁺ in Li₂CaSiO₄:Eu²⁺ phosphor is the 4f–5d allowed electric-dipole transition, the process of energy transfer should be controlled by electric multipole–multipole interaction [15].

Blasse [16] has pointed out that if the activator is introduced solely on Z ion sites, where X_c is the critical concentration, N is the number of Z ions in the unit cell and V is the volume of the unit cell, then there is on the average one activator ion per $V/X_c N$. The critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with this volume. By taking the experimental and analytic values of V , N and X_c (namely 165.21 Å³, 2 and 0.01) into Eq. (1), the critical transfer distance of Eu²⁺ in Li₂CaSiO₄:Eu²⁺ phosphor is found to be about 17 Å.

$$R_C \approx 2 \left[\frac{3V}{4\pi X_C Z} \right]^{\frac{1}{3}} \text{-----(1)}$$

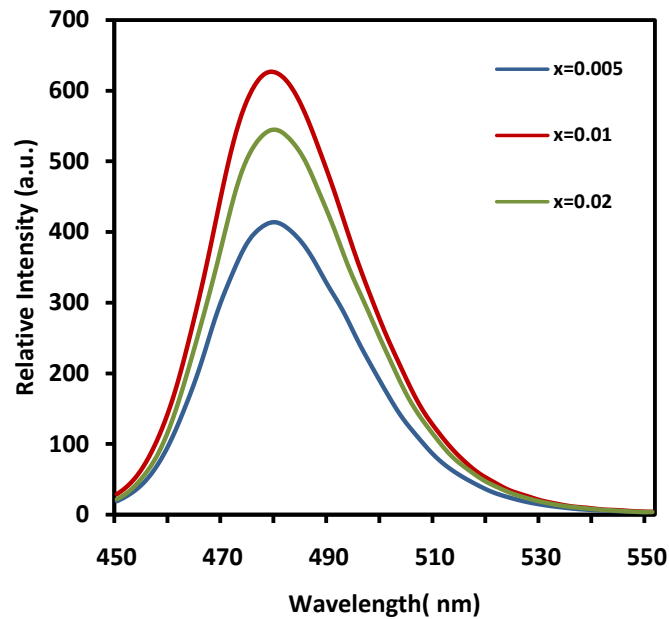


Figure 5: Emission spectra of $\text{Li}_2\text{CaSiO}_4:\text{Eu}^{2+}$ at 376nm excitation

3.6. Color Coordinates

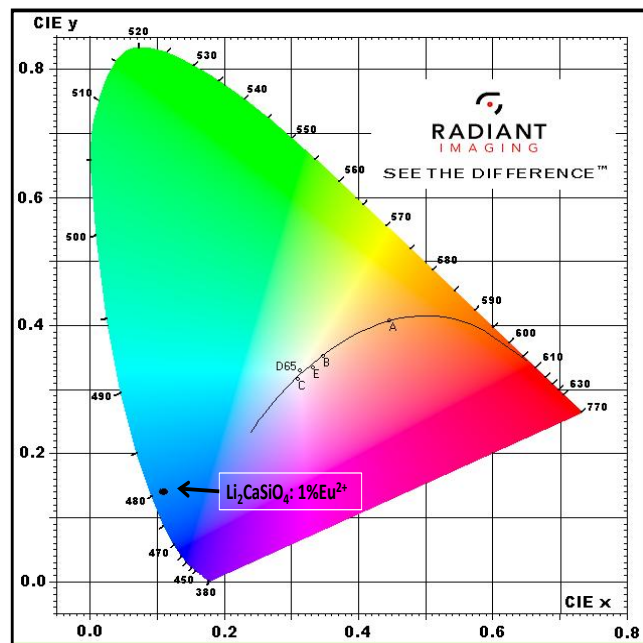


Figure 6: CIE color-coordinates of the $\text{Li}_2\text{CaSiO}_4:0.01\text{Eu}^{2+}$ phosphor

The Commission International de'Elclairage (CIE) chromaticity coordination of the $\text{Li}_2\text{Ca}_{0.99}\text{SiO}_4:0.01\text{Eu}^{2+}$ phosphor is shown in Figure 6. The chromaticity coordinates of $\text{Li}_2\text{Ca}_{0.99}\text{SiO}_4:0.01\text{Eu}^{2+}$ phosphor are $x=0.108$ and $y=0.140$ which corresponds to blue emission. For comparison, the chromaticity coordinates of $\text{Li}_2\text{CaSiO}_4:0.01\text{Eu}^{2+}$ as reported by J. Liu et al.[17] were $x=0.06$ and $y=0.44$ corresponding to blue green emission.

Blue-Light-Emitting Eu²⁺ Doped Lithium Calcium Silicate Phosphor for White-Light-Emitting-Diode

According to the excitation spectrum, Li₂Ca_{0.99}SiO₄:0.01Eu²⁺ phosphor can absorb the wavelength emitted by UV-LEDs (350–410 nm). It means the Li₂CaSiO₄:Eu²⁺ phosphor has more extensive application in solid state lighting. It is hence suggested that Li₂CaSiO₄:Eu²⁺ phosphor could be a good blue phosphor candidate for white LEDs.

4. CONCLUSIONS

Li₂CaSiO₄:Eu²⁺ phosphor is synthesized by conventional solid state reaction at 800°C. The particle size of the phosphor is found to be in the range of 2-10 μm. The chemical composition is verified by EDAX analysis. The exact phase formation is indicated by XRD analysis. Photoluminescence study indicates that the phosphor shows Blue emission for 376nm excitation wavelength with color coordinates (X=0.108, Y=0.140) for optimum doping concentration (0.1 mole %) which corresponds to blue light. Li₂CaSiO₄:Dy³⁺ can be a competitive blue phosphor candidate for white LEDs for UV excited white light emitting diode for solid state lighting application.

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