

Photoluminescence Properties of the Ce Doped Calcium Silicate

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Abstract: (1-7 mol %) Ce³⁺ doped CaSiO₃ nanophosphors have been prepared by combustion synthesis. The nano-phosphors have been characterized by PXRD, FESEM, FTIR and UV Visible spectroscopy. X-Ray diffraction pattern confirms monoclinic phase of CaSiO₃. The agglomerated and irregular shape of the particles is confirmed from FESEM micrographs. Energy band gap of the samples calculated from Kubelka-Munk method are found to be in the range of (3.3-3.4) eV. PL emission of the phosphors is observed at 483 nm concerned to transition 5d → 4f of the Ce³⁺ ions for excitation wavelength at 350 nm. CIE and CCT values are situated in the blue region suggesting the potential use of prepared phosphor in blue component of WLED's and solid-state display applications.

Keywords: Photoluminescence; Combustion synthesis; multipolar interaction; Display systems.

1. Introduction

Rare earth (RE) ions doped silicates are best known for their use in luminescence applications. Calcium silicate (CaSiO₃) is an inorganic compound which is capable of exhibiting luminescence that lasts for a long period, when substituted with different RE ions. CaSiO₃ crystallises in monoclinic crystal structure with P21/c (14) space group can be regarded as one dimensional chains of edge-sharing SiO₄ tetrahedron. Doping of other ions into the host lattice is done to create vacancies which acts as traps capable of storing excitation energy and emit light at room temperature (RT). Literature [1-4] reveals that reports on substitution of RE ions into CaSiO₃ via combustion synthesis are limited. Luminescent emission in Ce³⁺ ion is possible due to the unfilled 3d³ shell in which optical transitions occur. Luminescent properties of the Ce³⁺ ions are more sensitive to both static and dynamic environment of the host lattice and the optical spectra consists of both sharp and broad emission bands as 5d electrons are outside the ion core [5-8].

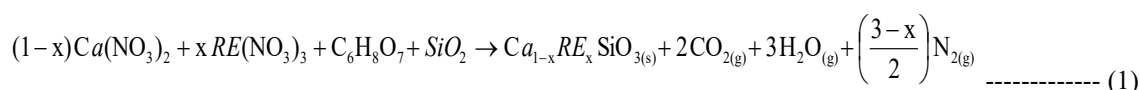
Reports on Luminescence indicate that CaSiO₃ is an excellent host for doping Ce³⁺ ions because it is highly compatible to Ce³⁺ ions and provides a crystal field strength, that is used for effective luminescence transitions. Ce³⁺ ions acts as an emitting center with a wide spread emission ranging from 700 nm to 1400 nm which includes a narrow band emission around 700 nm and a broadband emission around 483 nm due to 5d → 4f transition [9 – 13].

In the current work, CaSiO₃:Ce³⁺ (1-7 mol %) nano phosphor have been synthesized by self propagating combustion synthesis (CS) method. Combustion synthesis is found to be successful in synthesizing monoclinic CaSiO₃:Ce³⁺ at nano level. The morphological and structural details of the synthesized phosphor were obtained using X-ray diffraction pattern, micrographs of FESEM and FTIR spectra. The functional properties of CaSiO₃:Ce³⁺ nanophosphor were investigated by diffused reflectance spectra (DRS) of UV – Visible Spectrophotometer and photoluminescent (PL) studies.

2. Experimental Methodology

Preparation of CaSiO₃:Ce³⁺ nano phosphor:

Ce³⁺ (1-7 mol %) doped Calcium silicate nano powder has been synthesized by combustion technique using citric acid as fuel. [14]. Fig.1 shows the flow chart of the preparation of CaSiO₃:Ce³⁺ (1-7 mol %). The precursors used were, Calcium nitrate (Ca(NO₃)₂·4H₂O; Sigma Aldrich, 99.9 %), fumed silica (SiO₂, 99.9 %), Cerium nitrate Ce(NO₃)₃, 99.9 % and Citric acid (C₆H₈O₇). The stoichiometric amount of Ca(NO₃)₂·4H₂O, SiO₂ and C₆H₈O₇ (1:1: 0.6 in mole ratio) were dissolved in ~100 ml of deionized water and stirred well using a magnetic stirrer to get homogenized aqueous solution. The mixture was heated in a muffle furnace temperature at 500 ± 10 °C. The final product obtained was further calcined at 900 °C for 3 h for to obtain a crystalline sample. Equation (1) represents the chemical reaction of the synthesis process.



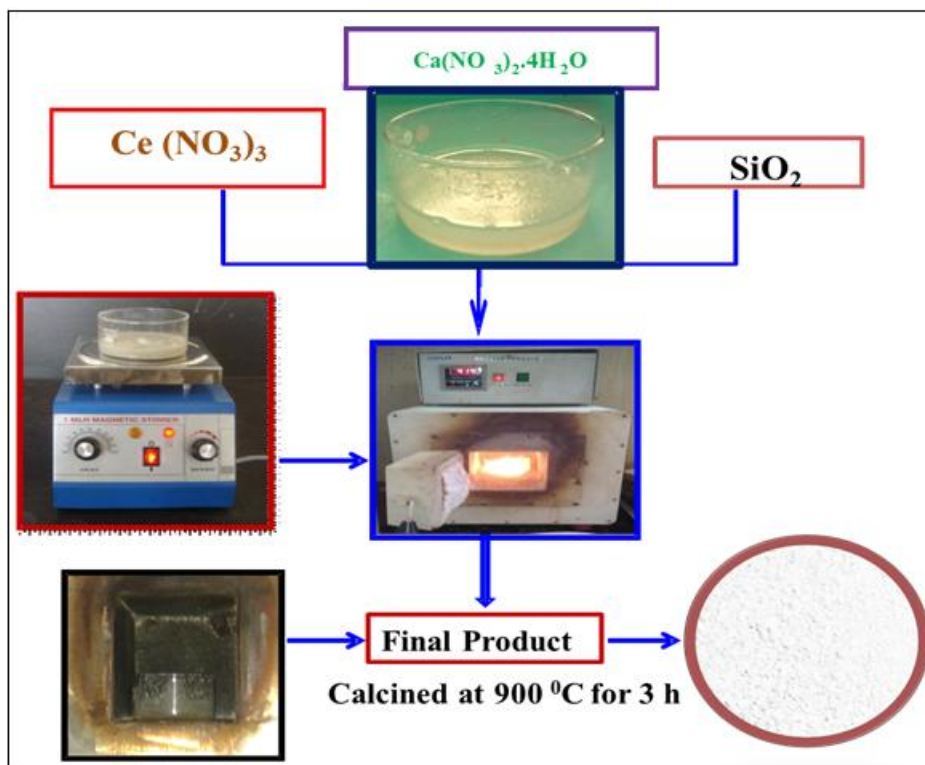


Figure 1: Flow chart of preparation of (1-7 mol%) Ce^{3+} substituted CaSiO_3 nanophosphor calcined at 900 °C for 3 h.

Characterizations Techniques

X-ray diffraction patterns were obtained from X'PERT Pro Philips analytical diffractometer which operates at 50 KV and 20 mA with $\text{CuK}\alpha$ (1.541Å) as a source radiation. Topographical morphology of the synthesized phosphors were analysed from the images obtained from FESEM (ULTRA55, FESEM (Carl Zeiss) with EDS). Absorption spectra has been recorded by Perkin Elmer spectrometer (Spectrum 1000) along with KBr pellets. The UV-Visible optical absorption study of the sample has been recorded in the range (200–800) nm using Perkin Elmer Lambda 19 to obtain diffused reflectance spectra (DRS). Photoluminescence (PL) studies has been done using emission spectra recorded from Agilent technologies, model Cary Eclipse, Spectrofluorimeter.

3. Results and Discussions

Fig. 2 displays XRD patterns of (1-7 mol %) of Ce^{3+} substituted calcium silicate calcined at 900 °C for 3 h. Peaks

were matched with JCPDS card No. 84-0655 [15]. Sharp peaks confirm crystalline nature of the samples, existing in single phase. The average crystallite size was estimated using the Scherrer's formula [16, 17] is found to vary between 34 - 40 nm. Lattice strain of the samples is determined from Williamson–Hall (W–H) plots [18, 19]. The particle size and lattice strain can be estimated from the extrapolation of the plot of $4\sin\theta$ versus $\beta\cos\theta$ as shown in Fig.3. The average crystallite size and lattice strain estimated from these methods of the linear fit are shown in the Table . The results confirms that synthesized powders are nano in size and matches well with the crystallite sizes as calculated by Scherrer's formula. Fig.4 (a-e) show FESEM and energy dispersive X-ray analysis (EDAX) of $\text{CaSiO}_3: \text{Ce}^{3+}$ (1-7 mol %) samples. The images suggest that the samples are highly porous, agglomerated containing voids and appears fluffy with polycrystalline nature. The pores and voids are due to the gases liberated during combustion. Elemental analysis shows that the formed nano powder is devoid of impurities .

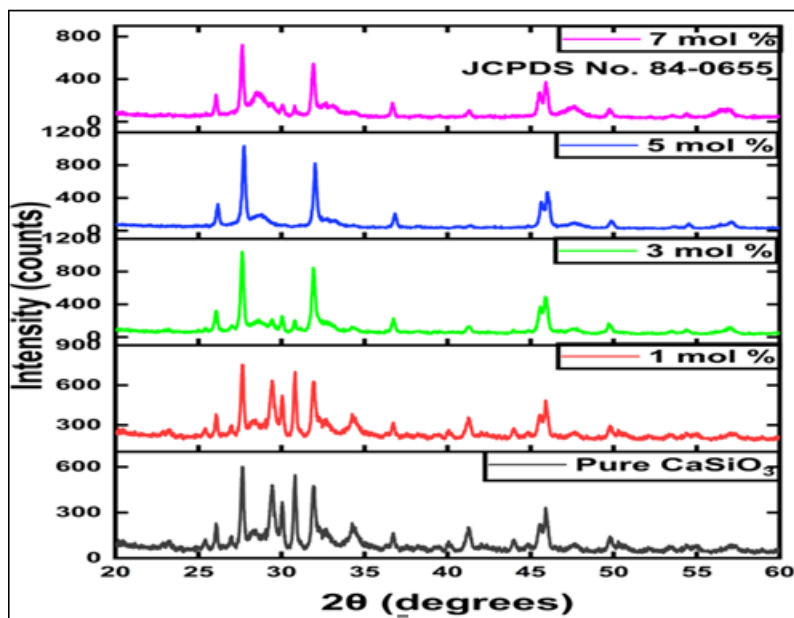


Figure 2: PXRD patterns of undoped and (1-7 mol%) Ce^{3+} substituted CaSiO_3 nanophosphor calcined at 900°C for 3 h.

Table 1: Estimated structural parameter values in undoped and (1-7 mol%) Ce^{3+} substituted CaSiO_3 nanophosphor.

S. No.	Mol%	Scherer's Equation in nm	W-H Plot in nm	Lattice Strain $\epsilon \times 10^{-3}$
1	Pure	38	40	0.24
2	1	35	42	0.46
3	3	34	39	0.43
4	5	36	39	0.29
5	7	40	42	0.22

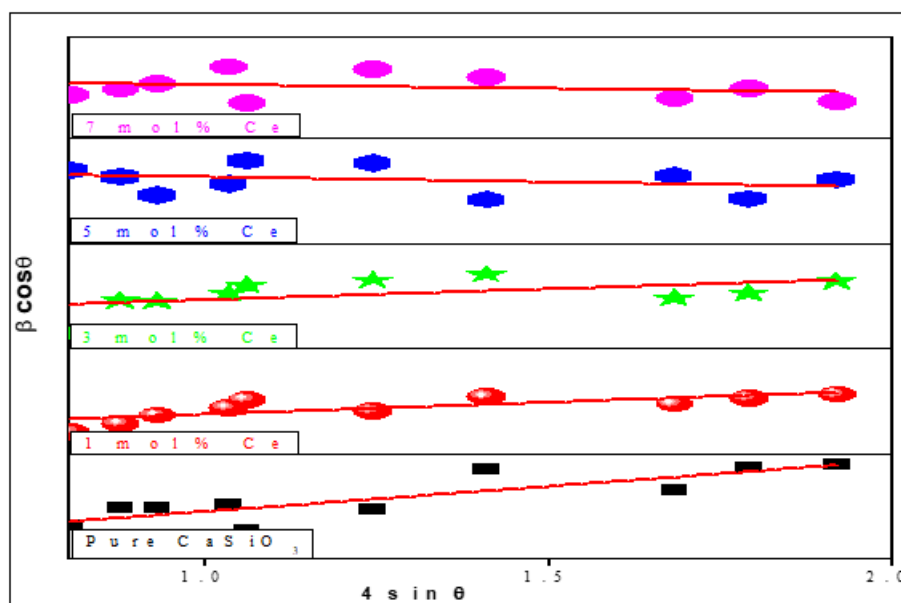


Figure 3: W-H plots of undoped and (1-7 mol%) Ce^{3+} substituted CaSiO_3 nanophosphor the lattice strain is extracted from the slope and the crystalline size are extracted from the y-intercept of the fit.

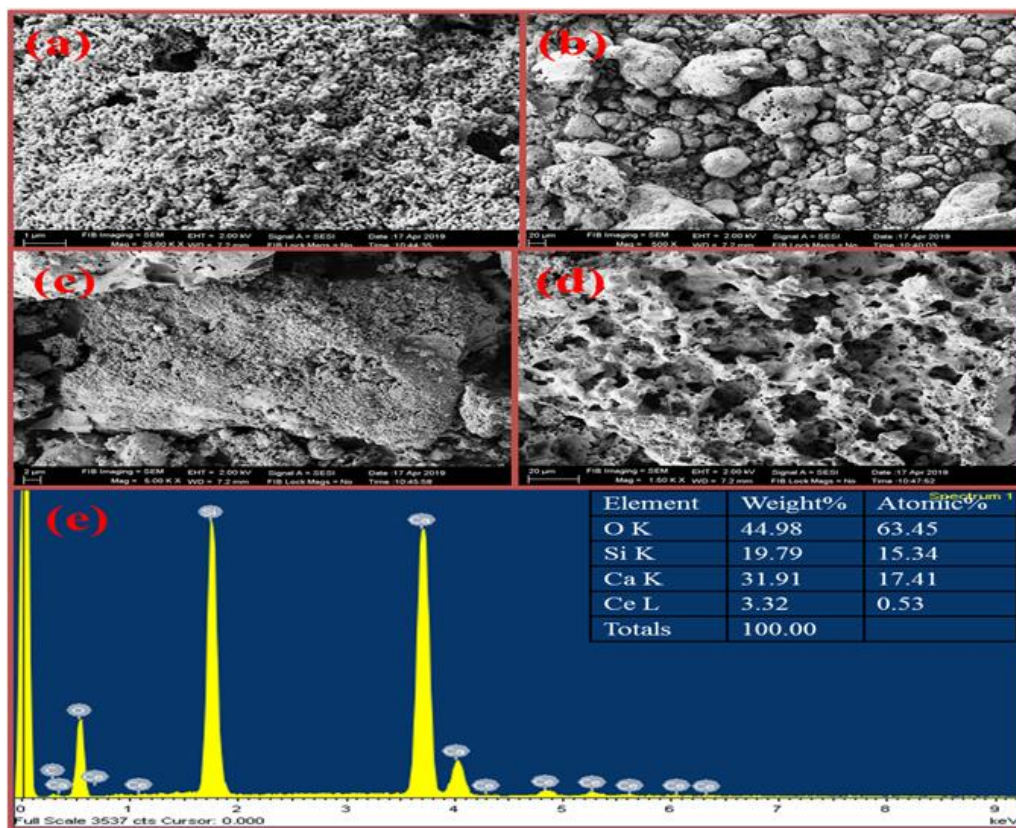


Figure 4: FESEM micrographs of (a) 1 mol% (b) 3 mol% (c) 5 mol% (d) 7 mol% and (f) EDAX (3 mol%) and the inset table shows elements with atomic weight % of Ce^{3+} substituted CaSiO_3 nanophosphor.

FTIR spectra, recorded in the range $4000\text{--}400\text{ cm}^{-1}$ is shown in (Fig.5). The region between 1000 cm^{-1} and 1500 cm^{-1} is characterized by overlapping Si–O bands. Different bands can be distinguished at 1009 , 1081 and 1483 cm^{-1} , which are assigned to various Si–O bonds. Sharp band at 888 cm^{-1} is due to asymmetric stretching vibration of Si–O–Si band and stretching vibrations of terminal Si–O bonds. The absorption

at 448 , 555 and 643 cm^{-1} are due to symmetric stretching vibrations Si–O–Si bridges [20]. The absorption peak at 2351 cm^{-1} indicates the presence of hydroxyl groups. For $\text{Ca}_{1-x}\text{RE}_x\text{SiO}_3$ samples it is observed that the intensity of transmittance varied with the variation in the dopant concentration as shown in Fig. 5.

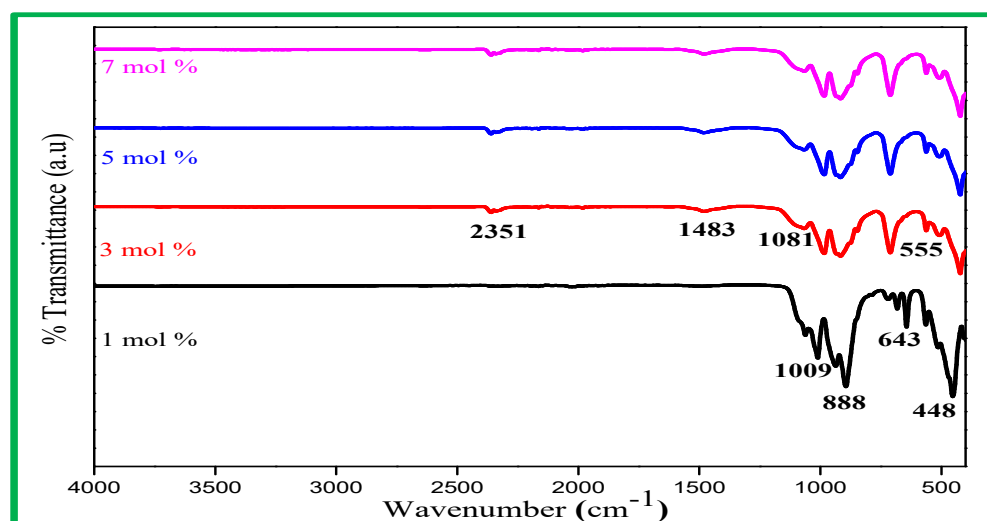


Figure 5: FTIR of (1-7 mol %) Ce^{3+} substituted CaSiO_3 nanophosphor.

Reflectance spectra of $\text{CaSiO}_3\text{:Ce}^{3+}$ (1-7 mol %) samples are shown in Fig. 6. The band gap energy (E_g) has been evaluated by Kubelka-Munk method. DRS of the material was converted to the U-V visible absorption spectra by using Kubelka – Munk function [22]. Fig.7. show the graph used for the determination of band gap energy (E_g) of the

material and is found to be in the range of (3.3 – 3.4) eV, confirming the semiconducting nature of the material. The band gap value decreases as the dopant concentration is increased. This is due to the occurrence of new inter band states between conduction and valence band.

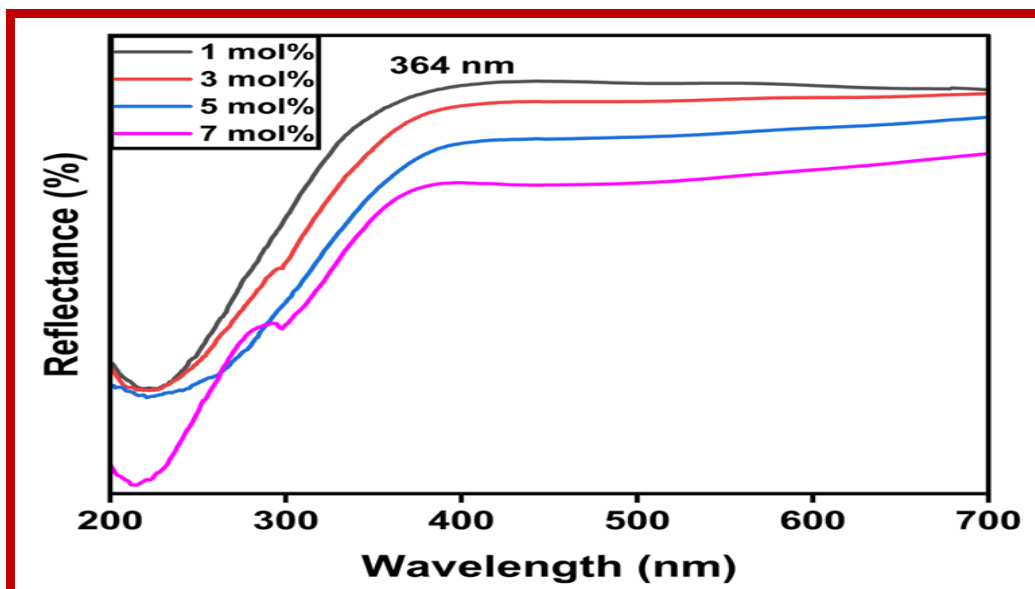


Figure 6: UV Visible DRS spectra of (1-7 mol %) Ce^{3+} substituted CaSiO_3 nanophosphor

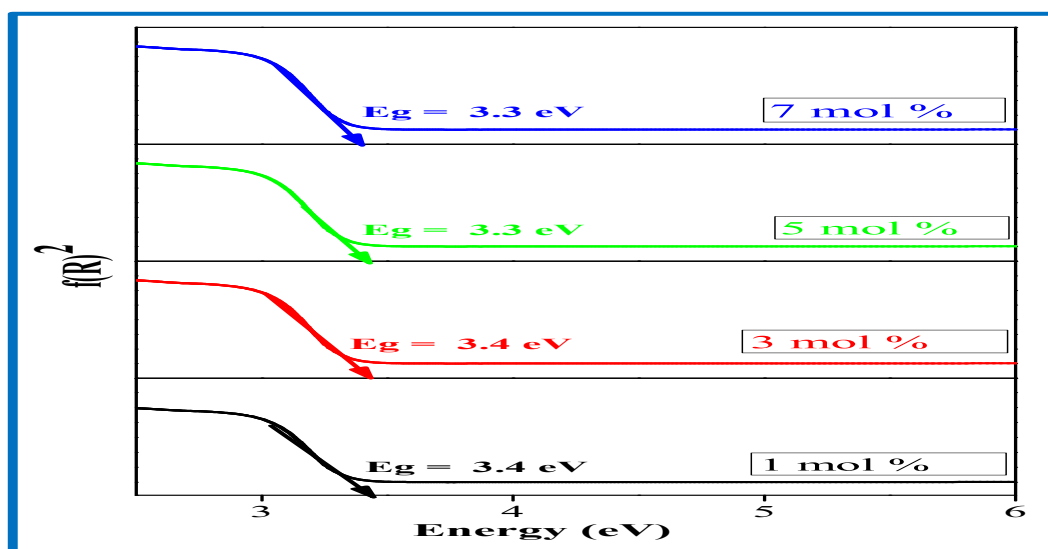


Figure 7: Energy band gap of (1-7 mol %) Ce^{3+} substituted CaSiO_3 nanophosphor.

Photoluminescence (PL) studies

Fig. 8. shows emission spectra of (1-7 mol %) $\text{CaSiO}_3:\text{Ce}^{3+}$ nanophosphor measured at 350 nm excitation. PL peaks at 440, 460, 483 and 544 nm, observed are due to Ce^{3+} ions [23-25]. The strongest emission peak at 483 nm is due to transition $5d \rightarrow 4f (2F_{5/2})$ of Ce^{3+} ions. Transition is a result of hypersensitive electric-dipole moment. Variation in the

PL intensity for various Ce^{3+} content has been studied and displayed in Fig. 9. Spectra shows that PL intensity rises with increase in Ce^{3+} content up to 3 mol% and thereafter it decreases with further increase in Ce^{3+} content. This is because of the concentration quenching and cross relaxation.

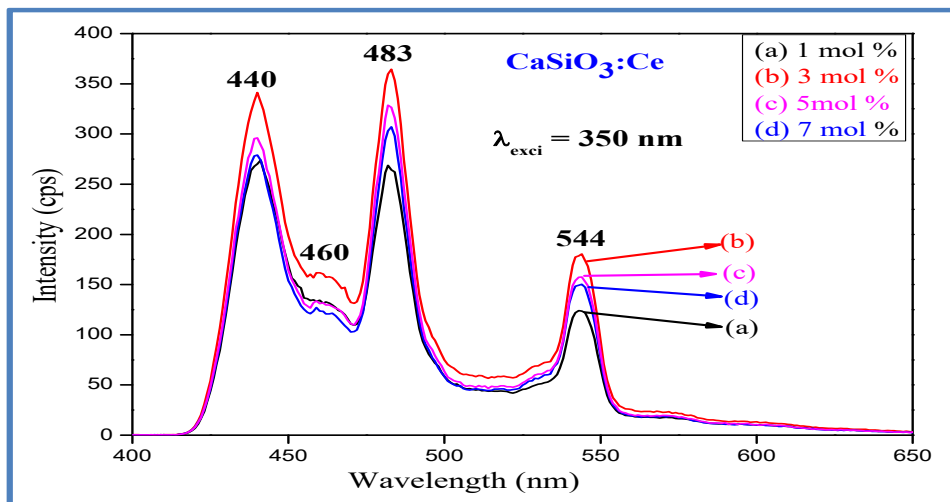


Figure 8: PL Emission spectra of (1-7 mol%) Ce^{3+} substituted CaSiO_3 nanophosphor excited at 350 nm

As per Blasse theory [26], non-radiative transitions in Ce^{3+} ions are due to multipole-multipole interaction. Multipolar interactions may be dipole-dipole (d-d) type, dipole-quadrupolar (d-q) type or quadrupole-quadrupole (q-q) type. Van Uitert's [27] equation is used to calculate the exact type of interaction for energy transfer in the material and the equation, (Assuming that $\beta(X)^{Q/3} \gg 1$) can be rewritten as

$$\log\left(\frac{I}{X}\right) = K' - \frac{Q}{3} \log X \quad \text{----- (2)}$$

$$(K' = \log K - \log \beta)$$

where 'I' is the integral intensity of emission peaks between 550-750 nm, 'X' is the activator concentration, (I/X) is emission intensity per activator, β and K are constants whose value depends on the host under same excitation condition. The equation gives the value of the multipolar character (Q) which can be obtained from the graph of $\log(I/X)$ versus $\log(X)$ as shown in Fig.10. The slope of the straight line is found to be - 0.94 and the intercept, 2.56. The value of Q, calculated using slope and intercept values, is found to be 6. As per Van Uitert's equation, Q value could be 6, 8 or 10 for d-d, d-q and q-q interactions respectively. Thus it can be concluded that the concentration quenching in the material is due to dipole-to-dipole interaction.

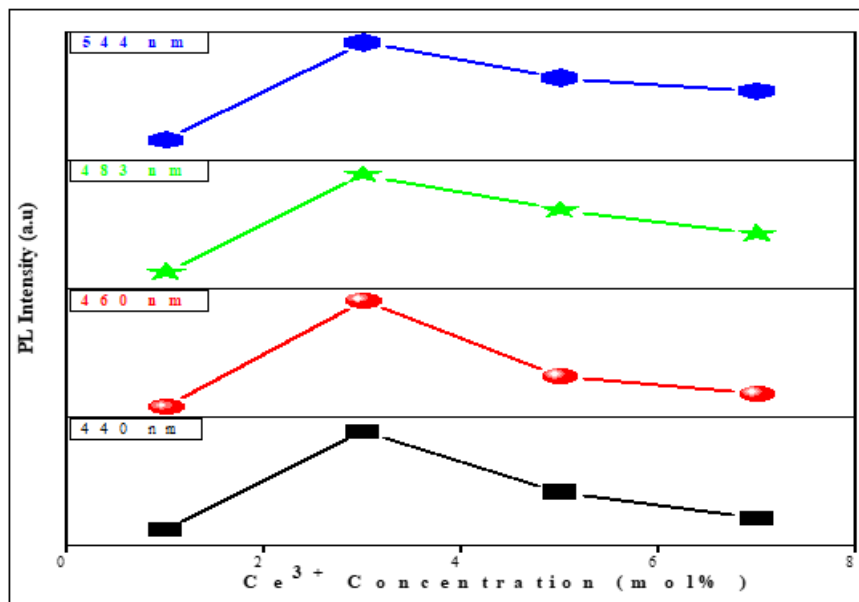


Figure 9: The variation of PL intensity with different Ce^{3+} concentration.

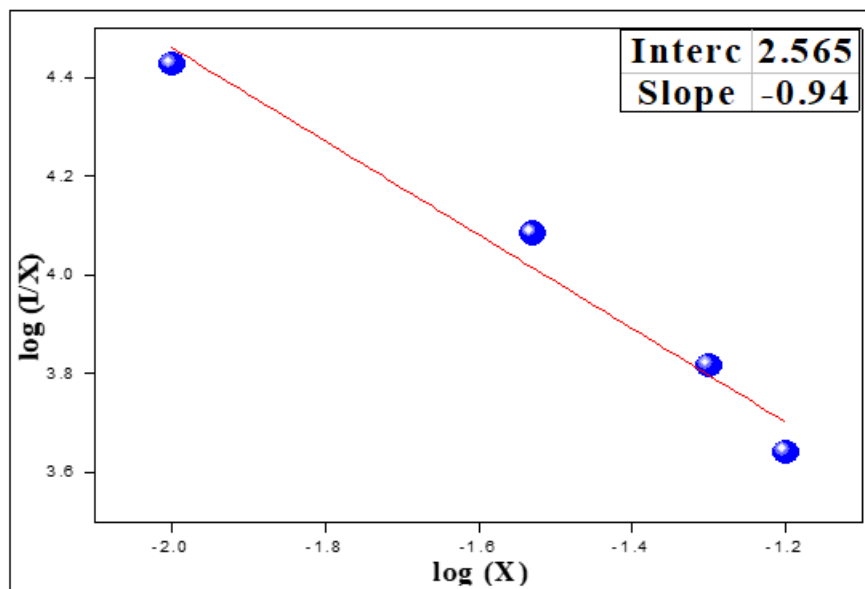


Figure 10: Relation between $\log(x)$ vs $\log(I/x)$ in $\text{CaSiO}_3:\text{Ce}^{3+}$ nanophosphor.

The Commission International De L'Eclairage (CIE) chromaticity coordinates for $\text{CaSiO}_3:\text{Ce}^{3+}$ (1-7 mol %) nanophosphors as a function of Ce^{3+} concentration for the luminous color were determined from the PL spectra. The CIE coordinates of blue emission of Ce^{3+} ions not only depend on the asymmetric ratio but also on the higher energy emission levels. Literature reports suggest that the effect of Ce^{3+} doping becomes efficient for crystalline materials resulting in an improved activation degree of Ce^{3+} .

X and Y co-ordinate values are shown in the table inset of Fig. 11.

The Co-ordinated Color Temperature (CCT) values are located in the blue region as shown in Fig. 12. The estimated Planckian locus defines the color temperature of light and using equations (3) and (4) the calculated values of u' , v' and CCT are in the table of Fig 12.

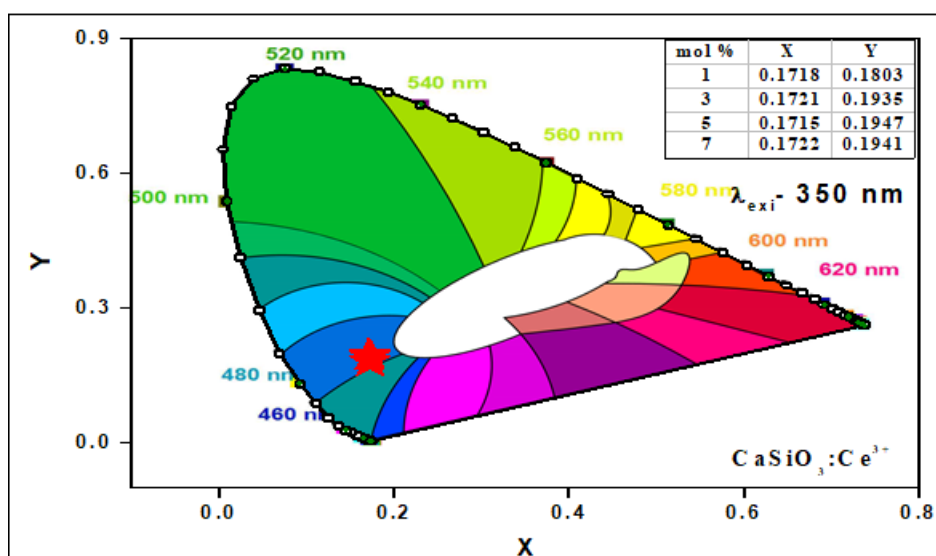


Figure 11: CIE chromaticity diagram of (1-7 mol%) Ce^{3+} substituted CaSiO_3 nanophosphor (Inst table: x and y values).

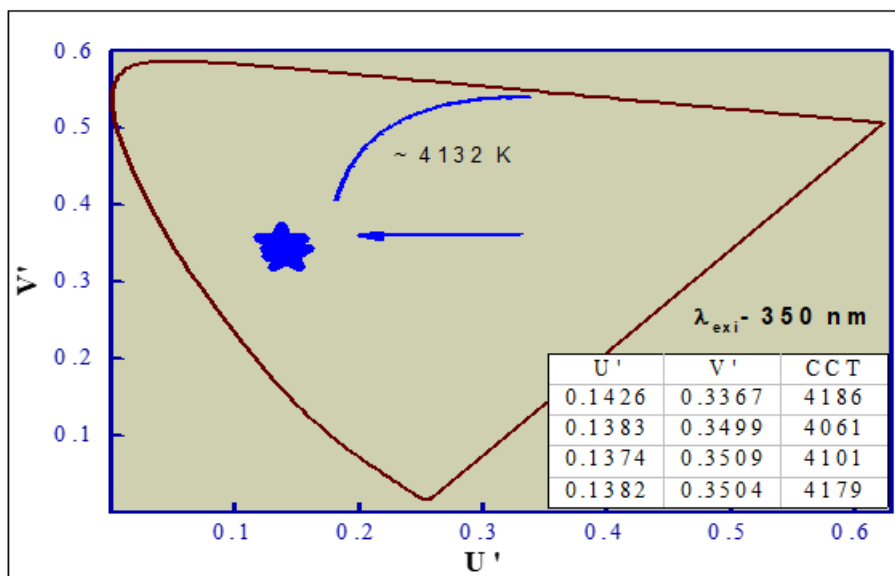


Figure 12: CCT of (1-7 mol%) Ce^{3+} substituted CaSiO_3 nanophosphor (Inst table: u' , v' and CCT values).

$$U' = \frac{4x}{-2x+12y+3} \quad (3)$$

$$V' = \frac{9y}{-2x+12y+3} \quad (4)$$

The average CCT value of prepared $\text{CaSiO}_3:\text{Ce}^{3+}$ nano phosphor is 4132 K which is very close to standard NTSC value [28]. This shows that strongest emission peak is for 3 mol % $\text{CaSiO}_3:\text{Ce}^{3+}$. Hence it can be concluded that nanophosphors are suitable material for the fabrication of blue component of WLEDs and may also be used for solid-state display applications.

4. Summary and Conclusions

$\text{CaSiO}_3:\text{Ce}^{3+}$ (1-7 mol %) nano phosphor were successfully prepared via combustion method. The average crystallite size was estimated from Scherer's and W-H plots. Emission spectra show that there is an increase in emission intensity with increase in Ce^{3+} concentration and beyond 3 mol% concentration, quenching is observed due to dipole-to-dipole interaction. The narrow blue emission peak observed at 483 nm in $\text{CaSiO}_3:\text{Ce}^{3+}$ is due to $5d \rightarrow 4f (2F_{5/2})$ transition from Ce^{3+} ions. The CIE chromaticity co-ordinates and CCT are situated in the blue region, hence $\text{CaSiO}_3:\text{Ce}^{3+}$ phosphor might be used in the blue component of WLEDs and display applications.

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