

SYNTHESIS AND PHOTOLUMINESCENCE PROPERTIES OF  $\text{CaSiO}_3:\text{Dy}^{3+}$  Phosphor\*Ch. Atchyutha Rao, <sup>1</sup>Bujji Babu, N., <sup>2</sup>Srinivasa Rao, K. and <sup>3</sup>Murthy, K.V.R.<sup>\*</sup>Department of Physics, GDC-Nakkapalli-531081, Anakapalli(DT), A.P, India<sup>1</sup>Department of Chemistry, PR Govt Degree College (A), Kakinada- 533001, A.P, India<sup>2</sup>Department of Physics, MRR, GDC-Udayagiri-524226, NELLORE (DT). A. P, India<sup>3</sup>Display Materials Laboratory, Applied Physics Department, Faculty of Technology and Engineering, M. S. University of Baroda, Vadodara-390001, IndiaReceived 27<sup>th</sup> March 2024; Accepted 25<sup>th</sup> April 2024; Published online 30<sup>th</sup> May 2024

## Abstract

The present paper reports the Synthesis and photoluminescence properties of rare-earth ion ( $\text{RE}^{3+}$ ) doped Calcium Silicate Phosphors. The Dysprosium Oxide ( $\text{Dy}^{3+}$ ) was used as rare-earth ion-doped. The phosphor is prepared by using the Conventional Solid-state reaction method were heated at 1200°C for 3 hrs. The received cakes are grounded for 30 minutes each. The phosphors are prepared and the received powder is subjected to Powder X-ray diffraction (PXRD) patterns revealed that the phosphors are crystalline and can be indexed to a monoclinic phase. Scanning electron micrographs (SEM) exhibited faceted plates and angular crystals of different sizes with a porous nature. Photoluminescence properties (PL) of the  $\text{Dy}^{3+}$ -doped  $\text{CaSiO}_3$  phosphors were synthesized and analyzed. The photoluminescence emission spectra were peaks at 483,573 and 610nm corresponding to  $\text{Dy}^{3+}$  were assigned as  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ ,  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  and  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$  transitions respectively, and dominated by the  $\text{Dy}^{3+} {}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  hyperfine transition. Experimental results revealed that the luminescence intensity was affected by both heat treatment and the concentration of  $\text{Dy}^{3+}$  (1–5 mol%) in the  $\text{CaSiO}_3$  as a single host. The CIE (1931-Chart) colour coordinates blue and yellow light emission were analyzed. The following section discusses and the experimental results are mentioned in these phosphors. The present Phosphor can act as a host for blue light emission in many display devices and technological applications.

**Keywords:** Calcium Silicates Phosphors, Rare earth ion, Conventional Solid state reaction method, Photoluminescence, Colour coordinates (CIE-1931 Chart)

## INTRODUCTION

The novel luminescent properties of nanophosphors particularly those with three-dimensional (3D) micro fabrication has triggered extensive research on the synthesis and characterization of nanophosphors in recent years. Of these, the synthesis and characterization of nanophosphors doped with rare earth (RE) elements is of particular interest, the focus being on its luminescence properties and their variation with reduced dimensionality [1-3]. The energy efficiency, greater radiation stability, colour rendering index and improved lumen output render RE ions effective luminescent centers in host lattices.  $\text{Dy}^{3+}$  ions have been investigated extensively since they give out two typical emission bands in the blue (480 nm) and yellow (575 nm) regions, the quintessential requirement for full colour displays. Moreover, the crystal field and radial integral of 4f and 5d electrons greatly influence the emission probability of electric-dipole transitions. Thus, the study of luminescence properties of  $\text{Dy}^{3+}$  ion in different host lattices proves itself to be an interesting investigation [4-8]. Silicates are considered one of the best host materials for luminescent centers due to their excellent chemical and thermal stability. When mixed with RE ions or transition metal ions, silicates become phosphor powders that produce excellent luminescence in the blue, green and red regions of the spectrum. Furthermore, considerable attention has been paid to silicate hosts because of their stable crystal structure, high physical and chemical stability, good formability, long persistence time, relatively easy preparation, multicolor phosphorescence and resistance to acid, alkali and oxygen.

Phosphors are generally prepared by the traditional method involving solid-state reaction. The product can contain several impurity phases on account of insufficient mixing and low reactivity of raw materials [9-12]. Moreover, the size of phosphor particles synthesized by solid-state reaction is large, usually in the micrometer range. Combustion synthesis has several advantages over solid-state reaction method. Simple experimental set-up, quick synthesis with very short time between the preparation of reactants and availability of the product, low cost and energy conservation are some of the several merits of combustion method. A study of the literature discloses that there are no earlier reports of preparation of  $\text{Dy}^{3+}$  activated  $\text{CaSiO}_3$  nanophosphors through conventional solid state reaction method route. The presents paper reports on a study of Synthesis and Photoluminescence properties of  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors of different compositions prepared by the conventional solid state reaction method process.

## MATERIALS AND METHODS

The present paper reports on the  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors were synthesized by conventional solid state reaction method. The chemicals used for the preparation were of analytical grade and are not purified further. The compounds like Calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , silica fumes ( $\text{SiO}_2$ ), (Sigma-Aldrich Chemie. Inc., Germany) in the oxide form of high purity of analytical grade exceeding (99.9% assay) and for the preparation of doped sample known amount of impurity Dysprosium oxide ( $\text{Dy}_2\text{O}_3$ ) chemicals were added to starting materials. The host material taken in stoichiometric proportions of Ca: Si as 2:1 and ground into a fine powder using agate mortar and pestle about an hour. The grounded sample was placed in an alumina crucible and calcined at

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1200°C for 3 hours in a muffle furnace with a heating rate of 5°C/min. The sample is allowed cool to room temperature in the same furnace for about 20 hours. In the same way rare earth (RE) ions ( $\text{Dy}^{3+}$ ) are doped at (1-5mol%) concentration only [13-15]. We investigated the phase purity, morphology, Photoluminescence excitation and emission and CIE colour coordinates (1931-Chart). Powder X-Ray Diffraction (PXRD) analysis was carried out with a powder diffractometer (Rigaku-D/max 2500) using Cu  $K\alpha$  radiation, microstructures/morphology of the samples were studied using a Scanning Electron Microscopy (SEM) (Philips XL-CP-30), Photoluminescence (PL) emission and excitation spectra were measured by Spectro fluorophotometer (SHIMADZU, RF5301 PC) using 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. The Commission International de l'Eclairage (CIE-1931 Chromaticity diagram) colour co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution. The chromatic colour coordinates (x, y) of prepared materials were calculated with colour calculator version 2, software from Radiant Imaging.

## RESULTS AND DISCUSSION

### Powder X-ray diffraction Analysis

To determine the crystal structure and phase purity of the phosphors, XRD analysis was carried out. The crystal structure of the prepared silicate phosphor was determined by using X-ray diffraction analysis. The powder X-ray diffraction (PXRD) profiles of  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  (1-5 mol%) phosphors, calcined at 1200°C for 3h are shown in figure.1. The patterns for 1-4 mol %  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors samples readily index to the  $\beta$ - $\text{CaSiO}_3$  phase. The peak positions conform to the literature values. However, when doped with 5mol%  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors samples exhibited  $\gamma$ - $\text{CaSiO}_3$  phase (JCPDF-310297) along with small traces of the orthorhombic  $\text{CaSiO}_3$  phase. All the diffraction peaks tallied well the standard values from the joint committee on powder diffraction standards (JCPDF card No. 84-0655) and indexed to the monoclinic phase. No prominent impurity peaks are detected. If the calcination temperature was 1200°C for 3hours sample shows the pure phase [16]. The high intensity characteristic peaks indicate the good crystalline nature of the product. The average crystallite size was calculated from the XRD pattern using Debye Scherer's formula is nano form. Debye Scherer's formula is  $D = K \lambda / \beta \cos \theta$ , Where  $D$  = crystallite size for the (hkl),  $K$  = constant,  $\lambda$  = X-ray wavelength of incident radiation [Cu  $K\alpha$  ( $\lambda=1.5405\text{\AA}$ )],  $\beta$  = Full width at half maxima (FWHM),  $\theta$  = Angle of the big peak. Based on the Debye-Scherer's formula, the crystallite size is calculated at calcined at 1200°C for 3hours. The average crystallite size was calculated at different  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors samples (1-5mol%) were shows in the table.1. This may conclude that the formation of nano crystallites in the phosphors calcined at 1200°C for 3hours are more sufficient in good heating treatment.

### Scanning electron microscopy Analysis (SEM)

Scanning electron microscopy (SEM) was used to study the morphology of the sample. Particle size of phosphor plays an important role in deciding the luminescence quality of the material. Figure. 2.(a-f) shows the SEM micrograph of  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors calcined at 1200°C for 3hours prepared by conventional solid state reaction method.

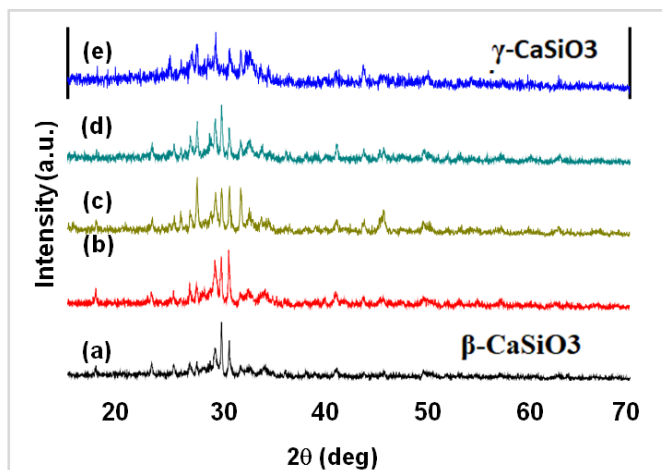


Fig. 1 XRD patterns of  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors (a) 1mol% (b) 2mol% (c) 3mol% (d) 4mol% (e) 5mol% calcined at 1200°C for 3 hours.

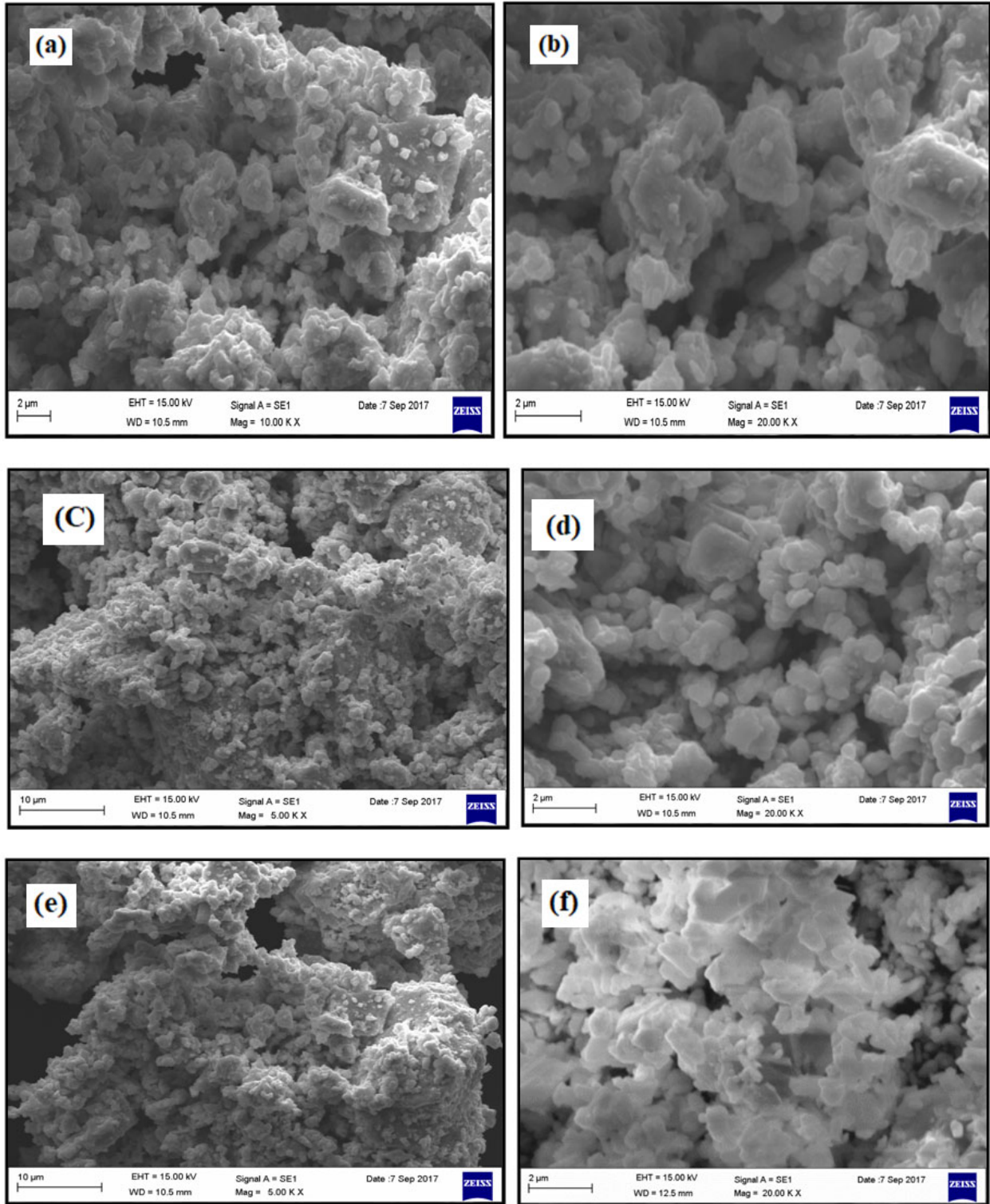
Table.1 shows  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors (1-5 mol%) with Crystallite sizes

S. No	Samples (Calcined at 1200°C for 3hours)	Crystallite size (nm) (Debye Scherer's formula)
1.	$\text{Dy}^{3+}\text{CaSiO}_3$ (1-mol%)	20
2.	$\text{Dy}^{3+}\text{CaSiO}_3$ (2-mol%)	28
3.	$\text{Dy}^{3+}\text{CaSiO}_3$ (3-mol%)	25.8
4.	$\text{Dy}^{3+}\text{CaSiO}_3$ (4-mol%)	17.5
5.	$\text{Dy}^{3+}\text{CaSiO}_3$ (5-mol%)	24.5

The entire sample exhibits grain like morphology with different sizes and shape. At high magnification calcined at 1200°C for 3hours prepared by conventional solid state reaction method, the particles were appeared to be agglomerated and the nature of individual crystallites is evident. Particle size is estimated through this analysis as uniformity of the particle shape and size affects the luminescence efficiency of phosphor materials [17-19]. The powders also show a porous structure. The system undergoes violent combustion since the redox reaction mixture with nitrate salts is strongly exothermic. The pores formed are sparse and irregular owing to the uncontrolled dynamics of the process. However, the porous structure is distributed non-uniformly in the matrix. Average particles of phosphor with less than 3  $\mu\text{m}$  are a good sign of lamp phosphor for coating purpose. Also, which can be helpful for display device technological applications in LEDs.

### Photoluminescence studies Analysis (PL)

PL spectroscopy study is an important tool to understand the optical properties of the  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors material. Figure 3. shows excitation spectrum (in the range 200-400 nm) of 2 mol % of  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors, measured with the emission wavelength of fixed at 575 nm corresponding to the electronic transition  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ . The spectrum is characterized by sharp and broad excitation bands at 258 nm, assigned to the host absorption band (HAB). It also displays broad excitation bands at 270-380 nm regions. Clearly, the later arise from f-f transitions of  $\text{Dy}^{3+}$  within its  $4f_9$  configuration, which are assigned to the electronic transitions ( $^6\text{H}_{15/2} \rightarrow ^5\text{P}_{3/2}$ ) at 320 nm, ( $^6\text{H}_{15/2} \rightarrow ^5\text{P}_{7/2}$ ) at 351 nm, ( $^6\text{H}_{15/2} \rightarrow ^5\text{P}_{3/2}$ ) at 366 nm, ( $^6\text{H}_{15/2} \rightarrow ^4\text{I}_{13/2}$ ) at 378 nm. Figure.4 shows the concentration effect (1-5 mol%) on the emission of  $\text{Dy}^{3+}$  doped  $\text{CaSiO}_3$  phosphors excited at 351nm [20-22].



**Fig.2 (a-f) SEM micrographs of (a) Undoped and Dy<sup>3+</sup>-doped CaSiO<sub>3</sub> phosphors (b) 1 mol % (c) 2 mol % (d) 3 mol % (e) 4 mol % (f) 5 mol % calcined at 1200°C for 3hour**

The photoluminescence (PL) spectra were comprising three main groups of lines in the blue (460-500 nm) and yellow (555-610 nm) regions. Apart from this, some weak lines are observed in red (677nm) region. The blue, yellow and red emissions are attributed to the electronic transitions  ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ ,  ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$  and  ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$  respectively. The blue emission ( ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ ) pertains to magnetic dipole transition while yellow ( ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ ) emission represents hypersensitive (forced electric dipole) transition with the selection rule  $\Delta J = 2$ . The transitions of excitation and emission spectra have been assigned based on the earlier results of Carnall et al [23].

The crystal-field splitting components of Dy<sup>3+</sup> correlate well with the Kramer's doublets,  $(2J+1)/2$ , where J is the angular momentum of the electrons. The correlation indicates that Dy<sup>3+</sup> ions are well substituted into Ca<sup>3+</sup> sites, since the ionic radius of Dy<sup>3+</sup> (0.103nm) is less than Ca<sup>3+</sup> (0.106 nm). The intensity of yellow emission is greater than that of the blue emission in the case of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors. The hypersensitive (forced electric dipole) transition is known to be strongly influenced by the external environment whereas the magnetic dipole transition is not sensitive to the crystal field strength around Dy<sup>3+</sup> ions [24-26].

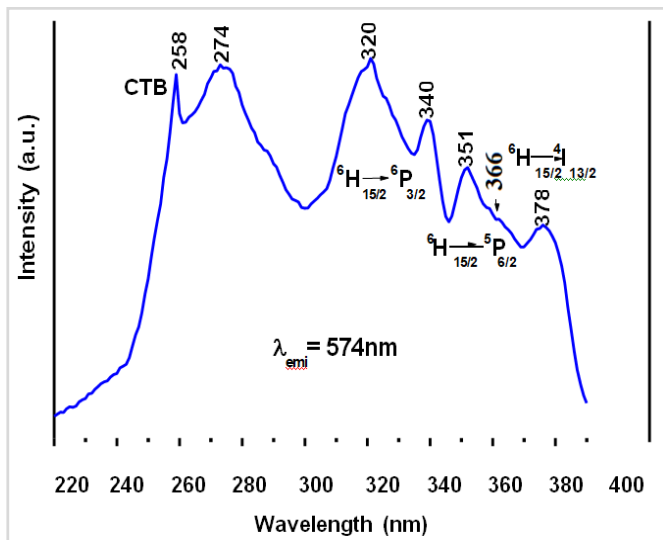


Fig 3. Excitation spectrum of the Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors (2mol%) calcined at 1200°C for 3 hours

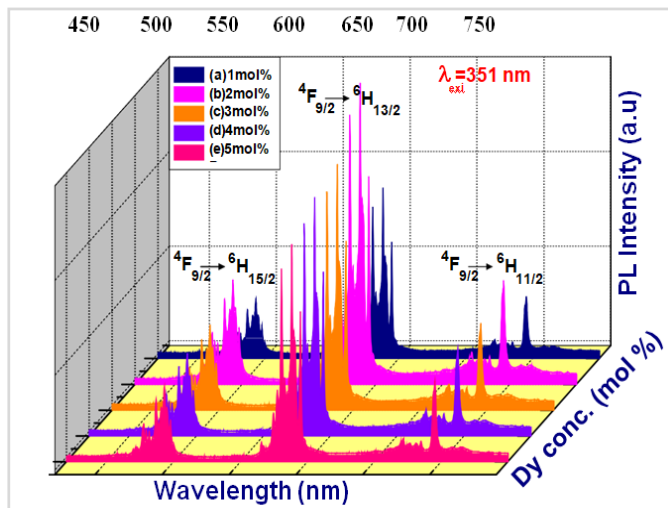


Fig 4. PL emission spectra of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors (a) 1 mol % (b) 2 mol % (c) 3 mol % (d) 4 mol % (e) 5 mol % calcined at 1200°C for 3 hours

The yellow emission is often dominant in the emission spectrum when Dy<sup>3+</sup> is located at a low-symmetry local site (without inversion symmetry). The blue emission is dominant in the emission spectrum and stronger than the yellow emission when Dy<sup>3+</sup> is at a high-symmetry local site (with inversion symmetry). The PL intensity goes up to 2 mol % of Dy<sup>3+</sup> and later the intensity of the emission decreases with further increase of Dy<sup>3+</sup> dopant concentration. The behavior can be explained by concentration quenching. Two factors enhance the concentration quenching-(i) the excitation migration due to resonance between the activators enhances with the increase in doping concentration, and thus the excitation energy reaches quenching centers, and (ii) the activators are paired or coagulated and changed to quenching center [27-30]. In addition, it is found that the yellow to blue (Y/B) ratio depends on the concentration of Dy<sup>3+</sup> ions. Thus, the ratio increases when the concentration increases to 2 mol%, and Y/B decreases as the concentration increases above 2 mol%. The phenomena can be understood if one considers the  $\Delta J = 2$  transition probability changes with polarity of the neighboring ions.

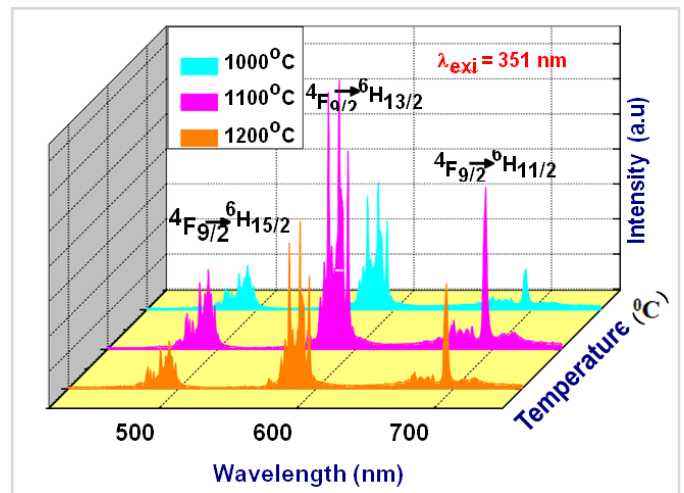


Fig 5. PL emission spectra of calcined at 1000 °C, 1100°C, 1200°C for 3 hours (2mol%) of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors

The study of photoluminescence emission spectra intensity of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors (2 mol %) with respect to annealing with different temperatures were depicted in figure 5. The intensity of the yellow emission (575nm) ( ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ ) goes up as the temperature rises from 1000-1200°C. The behavior could be explained as the improved crystallization of the products which reduces defect concentration and a more uniform distribution of Dy<sup>3+</sup> in host lattices. The energy level scheme adopted to explain the mechanisms involved in the emission processes of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors (2mol%) is shown in figure 6.

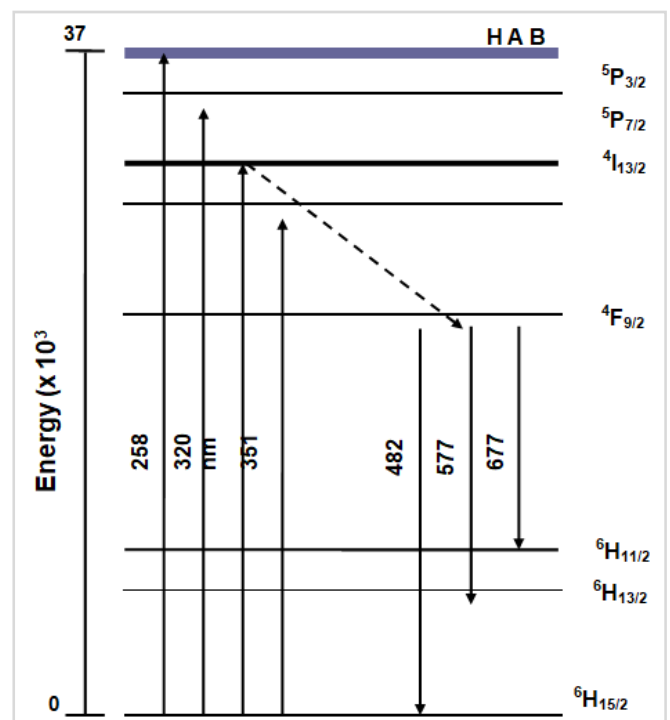


Fig 6. The energy level scheme of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors calcined at 1200°C for 3 hours

In order to further improve the CIE Colour Co-ordinates and achieve good quality blue and yellow light emission, the attributed luminescence colour of the sample has been characterized by the CIE-1931 chromaticity diagram. Generally, monochromatic sources ( $\Delta\lambda=0$ ) are located on the perimeter of the chromaticity diagram. The colour location

moves towards the center of the chromaticity diagram, when the spectral bandwidth of a source gets broader. Figure. 7 shows the CIE Coordinates of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors were calcined at 1200°C for 3hours presented in CIE-1931 chromaticity diagram [31, 32]. From the figure. 7 it is observed that the CIE-1931 chart chromaticity diagram of colour coordinates in photoluminescence emission spectrum of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors at points (A).X=0.143 and Y=0.156 (Blue emission  $\lambda_{em}$  =480nm), (B).X=0.448 and Y=0.497 (Yellow emission  $\lambda_{em}$  =575nm), which indicates to complete blue and yellow colour region under 351nm excitation wavelengths. This particular colours are especially decorated lightings and display devices.

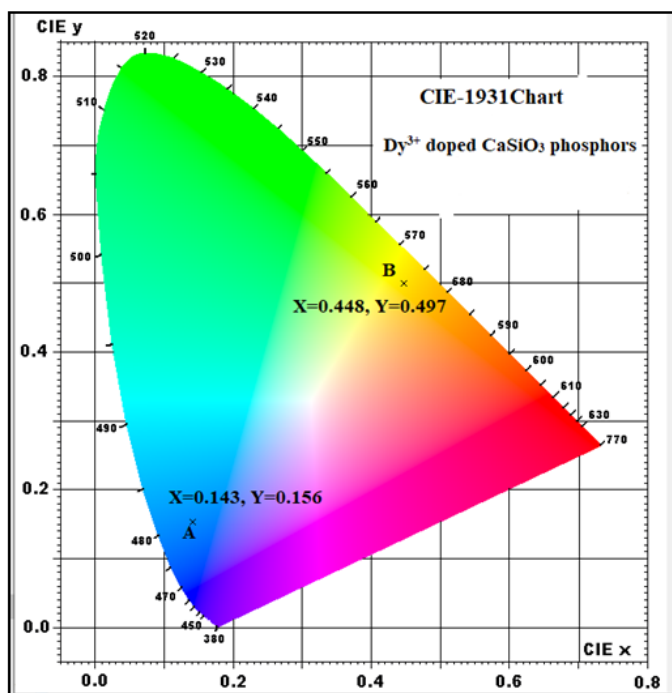


Fig.7 CIE Co-ordinates of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors were calcined at 1200°C for 3hours.

## CONCLUSION

- In conclusion, we successfully synthesized by conventional solid state reaction method has been followed for the first time to prepared 1-5mol% Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors were calcined at 1200°C for 3hours. In this process, the reaction temperature for the formation of CaSiO<sub>3</sub> is found to be lower compared to other methods and this is one of the important results of the present work.
- The method followed has several benefits such as low cost, energy efficiency, high production volume, no toxic in nature, do not require sophisticated equipment's and above all, easy method of preparation. The PL of the Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphor has been observed and analyzed. The emission peaks at 483, 573 and 610 nm corresponds to emission of Dy<sup>3+</sup> and can be attributed to the transitions of  $^4F_{9/2} \rightarrow ^6H_{15/2}$ ,  $^4F_{9/2} \rightarrow ^6H_{13/2}$  and  $^4F_{9/2} \rightarrow ^6H_{11/2}$  respectively and dominated by the Dy<sup>3+</sup>  $^4F_{9/2} \rightarrow ^6H_{13/2}$  hyperfine transition. The emission pattern has been explained in terms of an energy level scheme. The results disclose that heat treatment and concentration of Dy<sup>3+</sup> in the CaSiO<sub>3</sub> host may affect the luminescence intensity. Optimum luminescence conditions can be obtained with 2 mol% concentration of Dy<sup>3+</sup>. The optical energy band gap of

undoped phosphor is found to be lower than that of the Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors.

- Based on the Debye-Scherrer's formula, the crystallite size is calculated at calcined at 1200°C for 3hours, it may be concluded that the formation of crystallites size is nano in this phosphor.
- The SEM micrograph of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors calcined at 1200°C for 3hours prepared by conventional solid state reaction method. The entire sample exhibits grain like morphology with different sizes and shape. At high magnification calcined at 1200°C for 3hours prepared by conventional solid state reaction method, the particles were appeared to be agglomerated and the nature of individual crystallites is evident. Particle size is estimated through this analysis as uniformity of the particle shape and size affects the luminescence efficiency of phosphor materials. The powders also show a porous structure.
- CIE-1931Chart chromaticity diagram of colour coordinates in photoluminescence emission spectrum of Dy<sup>3+</sup> doped CaSiO<sub>3</sub> phosphors at points (A).X=0.143 and Y=0.156 (Blue  $\lambda_{em}$  =480nm), (B).X=0.448 and Y=0.497 (Yellow  $\lambda_{em}$  =575nm), which indicates to complete blue and yellow colour region under 351nm excitation wavelengths. This particular colours are especially decorated lightings, display devices and technological applications in LEDs.

**Acknowledgment:** One of the authors (Dr.CH. Atchyutha Rao) is grateful for the financial support from the University Grant Commission (UGC), New Delhi, India, under Minor Research Project (MRP No: 4687/14-SERO/UGC), and the author expresses their sincere thanks to Prof. K. V. R. Murthy Garu to provide 'Display Materials Laboratory Lab' facility in M.S. University, Baroda. Also, very much thankful to the Principal GDC-NAKKAPALLI, ANAKAPALLE (Dt).

**Conflict of interest:** The author declares that there is no conflict of interest regarding the publication of this scientific article.

**Source of funding:** None declared

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