



Optical Properties of Eu^{3+} doped CaSiO_3 Phosphors

Ch. Atchyutha Rao^{1*}, K.V.R. Murthy²

¹Department of Physics, GDC-CHINTAPALLI, ASR (DT), A.P, India

²Display Materials Laboratory, Applied Physics Department, M. S. University of Baroda, Vadodara, India

*Corresponding author: atchyuth@gmail.com

Received: 19-03-2024; Accepted: 21-04-2024; Published: 30-04-2024

© Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License

<https://doi.org/10.55218/JASR.2024150404>

ABSTRACT

Optical properties of Eu^{3+} doped CaSiO_3 phosphor were synthesized using the conventional solid-state reaction (SSR) technique. The morphology, size, and shape of the synthesized nano phosphorous powder were investigated using photoluminescence (PL), scanning electron microscopy (SEM), X-ray diffraction (XRD) and CIE color coordinates (1931-Chart) analysis. XRD profiles of samples sintered over 1200°C suggested a phase shift from amorphous powder grain to more ordered polycrystalline powder of triclinic type CaSiO_3 phosphor, with preferred crystal phase orientation of (112) and tetragonal type cristobalites of SiO_2 . The grain size, crystallinity, and chemical composition of the host matrix, activator and sensitizer strongly affected both these samples' absorption and emission bands. The amplitude of both the orange and red emission bands significantly increased with sintering temperature. The emission band is red-shifted with decreasing grain sizes.

Keywords: Polycrystalline phosphor; Photoluminescence; Eu^{3+} doped CaSiO_3 ; Solid state reaction method.

INTRODUCTION

The silicates of calcium are known for their thermal stability, high-temperature strength, low thermal expansion, creep resistance and chemical inertness. Silicate phosphors are used for a fluorescent, a cathode-ray tube, a luminous body, a vacuum ultraviolet excitation light emitting element etc. Specifically, for a vacuum ultraviolet excitation light emitting element such as PDP, an improvement of the brightness of the element has been highly desired, and therefore, an improvement of the brightness of the silicate phosphor has been required, hence are used in calcium silicate (CaSiO_3), otherwise known as wollastonite has a good matrix of luminescent material. Silicates of calcium phosphors have acquired a place of prominence in modern technology mainly on account of their ability to convert electromagnetic radiation into light.^[1] On account of their high-efficiency emission performance, rare earth ions are used as activators in different host matrices. In addition to the common properties of rare earth elements, Europium, a special element in the lanthanides, displays the property of valence fluctuation—with divalent or trivalent valence state. Europium also exhibits different luminescence characteristics due to different valences.^[2-4] The emission spectrum of Eu^{3+} ions (electronic configuration $4f_6$) show emission lines extending from visible region to the near-infrared. Eu^{3+} is an ideal element for the experimental probe of the crystalline structure due to its relatively simple energy level structure, with its $^5\text{D}_0 \rightarrow ^7\text{F}_j$ range facilitating ascertainment of microscopic symmetry around the site.^[5] Eu^{3+} ions are extensively used in electroluminescence panels (EL), plasma display panels (PDP), higher efficiency fluorescent lamps etc., since they are important emitters in the red region of the visible spectrum.

Calcium silicate acquires a higher luminous efficiency when it is doped with rare earth-activated ions. Very few research groups investigated the PL behavior of undoped CaSiO_3 . Several varied methods have been followed to prepare CaSiO_3 . The silicate is synthesized by sol-gel, hydrothermal, reverse micelles and colloidal methods. It is also prepared by colloidal emulsion method.^[6-7] Many researchers have followed the solid state reaction method to prepare undoped CaSiO_3 and calcium silicate doped with rare earth and transition metal. However, the focus has always been on increasing the luminescence properties of the CaSiO_3 . The different methods followed to synthesize CaSiO_3 have their own disadvantages. Sol-gel method requires expensive ingredients while the combustion propagates on its own without the need of any external heat. The silicate in a foamy form was obtained finally.^[8-10] In this research paper, we have studied the optical properties of Eu^{3+} doped calcium silicates phosphors prepared by the conventional solid-state reaction method calcined at 700, 950, 1100 and 1200°C for 3 hours. The prepared phosphors were characterized by being subjected to X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and CIE color coordinates (1931-Chart) analysis.

MATERIAL AND METHODS

The present paper reports on the Eu^{3+} doped CaSiO_3 phosphors were synthesized by conventional solid-state reaction method. The chemicals used for the preparation were of analytical grade and were not purified further. The compounds like calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), silica fumes (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 europium oxide (Eu_2O_3) chemicals were added to starting materials. The host material was taken in

stoichiometric proportions of Ca:Si as 2:1 and ground into a fine powder using an agate mortar and pestle about an hour. The grounded sample was placed in an alumina crucible and calcined at 700, 950, 1100, and 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 (Eu^{3+}) are doped at (0.5 mol%) concentration only.

We investigated the phase purity, morphology, photoluminescence excitation and emission and CIE color coordinates (1931-Chart). XRD analysis was carried out with a powder diffractometer (Rigaku-D/max 2500) using $\text{Cu K}\alpha$ radiation, microstructures/morphology of the samples were studied using scanning electron microscopy (Philips XL-CP-30), photoluminescence 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 1.5 nm. The spectrophotometric method calculated the Commission International de l'Eclairage (CIE-1931 Chromaticity diagram) color coordinates using the spectral energy distribution. The chromatic color coordinates (x, y) of prepared materials were calculated with color calculator version 2, software from Radiant Imaging.

RESULTS AND DISCUSSION

Powder X-ray Diffraction Analysis

Philips X-ray diffractometer with a $\text{Cu K}\alpha$ radiation ($\lambda=1.5405\text{\AA}$) was used to study the X-ray diffraction of the sample. The silicate formed and calcined at 700, 950, 1100 and 1200°C for 3 hours as shown in Fig. 1. The XRD pattern shows that the formed powder is amorphous but not formed the phase. When the sample was calcined at 700°C for 3 hours, the sample showed a smaller amount of crystallinity.^[11-13] As the temperature increased to 950°C for 3 hours, the sample indexed the β - CaSiO_3 and α phase at 1200°C for 3 hours. All the diffraction peaks are consistent with the standard PDF database (JCPDS file No. 27-0088). No prominent impurity peaks are detected. If the calcination temperature was 1100°C for 3 hours sample shows the mixed phase. 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, λ = X-ray wavelength of incident radiation [$\text{Cu K}\alpha$ ($\lambda=1.5405\text{\AA}$)], β = Full width at half maxima (FWHM), θ = Angle of the big peak. Based on Debye-Scherer's formula, the crystallite size is ~ 27 to 32 nm at calcined at 700, 950, 1100, and 1200°C for 3 hours. This may conclude that the formation of nanocrystallites in the phosphor.^[14-17] It is observed to be more in the 1200°C for 3 hours calcined sample when compared to 950°C for 3 hours calcined sample. This is because, the crystallinity increases particle size are also increases with heat treatment.

Scanning Electron Microscopy Analysis

Scanning electron microscopy (SEM) was used to study the morphology of the sample. The particle size of the phosphor plays an

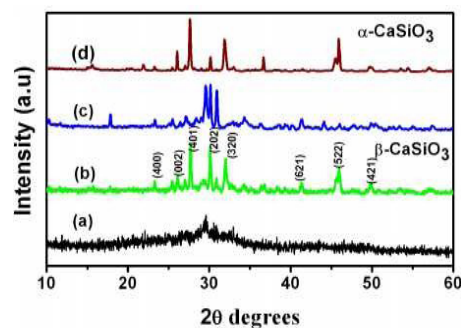


Fig. 1: XRD patterns of Eu^{3+} doped CaSiO_3 phosphors (a) as formed as calcined at 700°C for 3 hours (b) calcined at 950°C for 3 hours (c) calcined at 1100°C for 3 hours (d) calcined at 1200°C for 3 hours

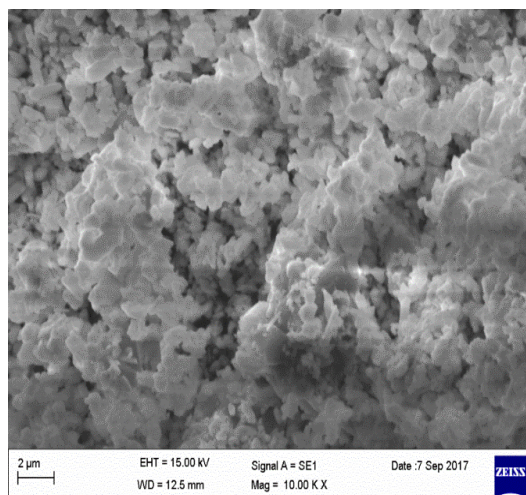


Fig. 2: SEM micrograph of Eu^{3+} doped CaSiO_3 phosphors (a) calcined at 950°C for 3 hours (b) calcined at 1200°C for 3 hours

important role in deciding the luminescence quality of the material. Uniform particle size distribution and fine particles ($< 5 \mu\text{m}$) is some of the requirements of good luminescent materials. Fig 2 (a, b) shows the SEM micrograph of Eu^{3+} doped CaSiO_3 phosphors (a) calcined at 950°C for 3 hours (b) calcined at 1200°C for 3 hours prepared by conventional solid-state reaction method. The entire sample exhibits grain-like morphology with different sizes and shape.^[18] At low magnification and high magnification (a) calcined at 950°C for 3 hours (b) calcined at 1200°C for 3 hours prepared by conventional solid-state reaction method, the particles 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. Average phosphor particles with less than $3 \mu\text{m}$ are a good sign of lamp phosphor for coating purposes^[19] also, which can be helpful for display device technological applications in LEDs.

Photoluminescence Spectra Analysis

Fig. 3 depicts the excitation and emission spectra of the Eu^{3+} doped CaSiO_3 phosphors that were calcined at 1200°C for 3 hours only. In this figure in the left shows two excitation spectra shown in the left (ultra-violet region), resolved at 220 and 223 nm. The excitation

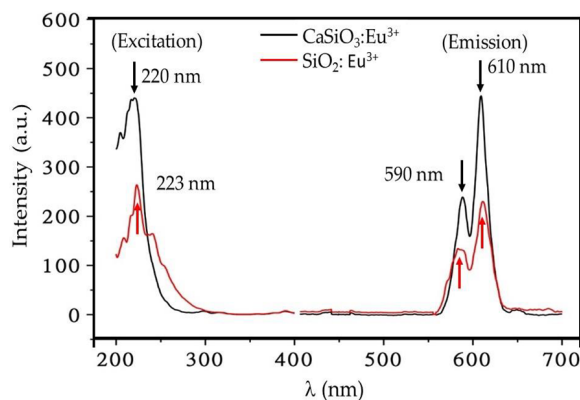


Fig. 3: Excitation (left) and emission (right) spectra of Eu^{3+} doped CaSiO_3 phosphors were calcined at 1200°C for 3 hours

spectra of Eu^{3+} doped CaSiO_3 phosphors is complicated to interpret as it depends largely on phase symmetry around the ion.^[20-22] In the present case, the excitation at around 220 and 223 nm is due to the Eu^{3+} - O_2 band charge transfer and is closely related to the degree of covalency of the Eu^{3+} -ligand bond, as explained by considering Eu^{3+} - O^{2-} - Ca^{2+} bonding structure. The broad adsorption band resolved at 220 nm is usually assigned to electronic shift involving the transfer of charge from O^{2-} ions to ligand to rare earth ion, whereas the excitation band at 390 nm is thought to be due to intra-ionic ${}^4\text{F}_6 \rightarrow {}^5\text{D}_1$ transition.^[23-25] Note these transitions are assigned based on lanthanide spectra. Since the Ca^{2+} ion is a cation with a smaller radius and larger electronegativity compared to the Eu^{3+} ion, the electron density clouding around O^{2-} ion decreases when it is bonded to the Ca^{2+} ion. In addition to the prominent excitation peaks, several weak shoulders are also observed due to the excitation from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ transitions ($j = 1, 2, 3, \dots$) here. The curve shows very small excitation near the $\lambda = 395$ nm.

Fig. 3 represents the right shows two emission spectra (visible region) at $\lambda = 590$ and 610 nm, corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (symmetry sites) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ((hypersensitive to local symmetry), electric and magnetic dipole transitions, respectively). The amplitude of the 610 nm is almost twice as large than the amplitude of 590 nm line. The emission around 650 nm. In addition, the emission spectra excited at 220 nm is sharper as compared to the emission spectra excited at 223 nm.^[26] Both of the prominent emission peaks excited at 220 and 223 nm are observed at around the same wavelengths of 590 and 610 nm, respectively. Based on our calculation, the quantum efficiency the ratio between number of photons created and the number of photons absorbed is estimated to be close to 100% .

CIE Color Coordinates Analysis

In order to further improve the CIE color coordinates and achieve good-quality white light emission, the attributed luminescence color 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 color location moves towards the center of the chromaticity diagram when the spectral bandwidth of a source gets broader. Hence, for red light emission, the coordinates are located near the center of the chromaticity diagram.^[27] Fig. 4 shows the CIE Coordinates of Eu^{3+} doped CaSiO_3 phosphors that were calcined at 1200°C for 3 hours presented in

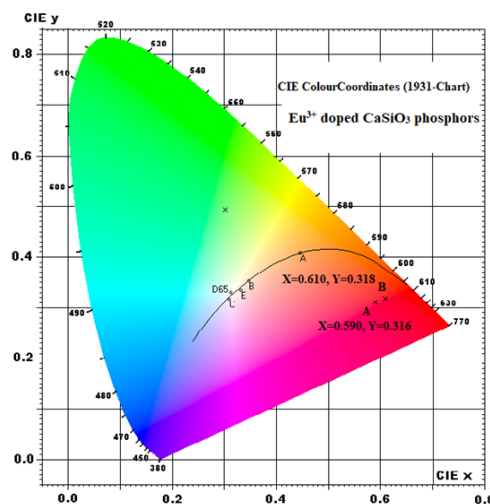


Fig. 4: CIE Coordinates of Eu^{3+} doped CaSiO_3 phosphors were calcined at 1200°C for 3 hours

the CIE-1931 chromaticity diagram. Fig. 4 shows that the CIE-1931 chromaticity diagram coordinates the emission spectrum of Eu^{3+} doped CaSiO_3 phosphors at points (A). $X = 0.590$ and $Y = 0.316$ ($\lambda_{\text{em}} = 590$ nm), (B). $X = 0.610$ and $Y = 0.318$ ($\lambda_{\text{em}} = 610$ nm), which indicates to complete red color region under 220 and 223 nm excitation wavelengths.

CONCLUSION

In conclusion, we successfully synthesized by conventional solid-state reaction method to prepare Eu^{3+} doped CaSiO_3 phosphors that were calcined at 700 , 950 , 1100 and 1200°C for 3 hours. The method followed has several benefits: low cost, energy efficiency, high production volume, no toxicity in nature, not requiring sophisticated equipment and an easy preparation method. Photoluminescence spectra (PL) of Eu^{3+} doped CaSiO_3 phosphors were calcined at 1200°C for 3 hours and was observed and analyzed. The excitation spectra of Eu^{3+} doped CaSiO_3 phosphors is complicated to interpret as it depends largely on phase symmetry around the ion. In the present case, the excitation at around 220 and 223 nm is due to the Eu^{3+} - O_2 band charge transfer and is closely related to the degree of covalency of the Eu^{3+} -ligand bond, as explained by considering Eu^{3+} - O^{2-} - Ca^{2+} bonding structure. Emission spectra (visible region) at $\lambda = 590$ and 610 nm, corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (symmetry sites) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ((hypersensitive to local symmetry), electric and magnetic dipole transitions, respectively). Based on Debye-Scherrer's formula, the crystallite size is ~ 27 to 32 nm at calcined at 700 , 950 , 1100 , and 1200°C for 3 hours. This may conclude that the formation of nanocrystallites in the phosphor. At low and high magnification, calcined at 950 and 1200°C for 3 hours prepared by conventional solid state reaction method, the particles appeared to be agglomerated and the nature of individual crystallites is evident. The CIE-1931 chromaticity diagram coordinates the emission spectrum of Eu^{3+} doped CaSiO_3 phosphors at points (A). $X = 0.590$ and $Y = 0.316$ ($\lambda_{\text{em}} = 590$ nm), (B). $X = 0.610$ and $Y = 0.318$ ($\lambda_{\text{em}} = 610$ nm), which indicates to complete red color region under 220 and 223 nm excitation wavelengths. Average phosphor particles with less than $3 \mu\text{m}$ are a good sign of lamp phosphor for coating. Also, which can

be helpful for display device 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

None declared.

SOURCE OF FUNDING

None declared.

REFERENCES

- Shionoya, S. Photoluminescence. In Luminescence of Solids; New York, NY, USA, 1998; pp. 95–133.
- Arunachalam Lakshmanan 2007 *Luminescence and display phosphors*: (NY, USA: Nova Publishers).
- Edgar, A., *Luminescent Materials, Handbook of Electronic & Photonic Materials-2017*, Springer. p.1-1.
- Yen, W.M. and H. Yamamoto, *Fundamentals of phosphors*, 2006: CRC press.
- Blasse, G. and B. Grabmaier, *A General Introduction to Luminescent Materials*, 1994, Springer. p. 1-9.
- Edgar, A., *L. Materials, Handbook of Electronic and Photonic Materials*2017, Springer. p. 1-1.
- Wang, L.; Zhang, H.; Zhou, X.; Liu, Y.; Lei, B. *RSC Adv.* 2016, 6, 98554–98562.
- P. Klug, L.E. Alexander, In: X-ray Diffraction Procedure, Wiley, New York, 1954.
- G.K. Williamson, W.H. Hall, *Acta Metall.* 1 (1953) 22–31.
- Leverenz, H.W.; Urbach, F. Introduction to the Luminescence of Solids. *Phys. Today* 2009, 3, 32–33.
- Singh, D.; Sheoran, S.; Tanwar, V. *Adv. Mater. Lett* 2017, 8, 656–672.
- Dhoble. S; Dhoble. N; Pode, R. *Bull. Mater. Sci.* 2003, 26, 377–382.
- Kumar, M.M.; Krishna, R.H.; et.al; *Acta Part A Mol. and Biomol. Spect.* 2015, 139, 124–129.
- Poort, S.H.M.; Reijnhoudt, H.M.; Van der Kuip, H.O.T.; Blasse, G. *J. Alloys Comp.* 1996, 241, 75–81.
- Murthy, K.V.R., *Recent Research in Science and Technology*, 2012. 4(8).
- Sunitha, D.; Nagabhushana, H.; Singh, F.; Nagabhushana, B.; *J. Luminescence* 2012, 132, 2065–2071.
- Sohal, S.; Zhang, X.; Kuryatkov, V.; Chaudhuri, J.; Holtz, M. *Mater. Lett.* 2013, 106, 381–384.
- Jiang Yong Dong, Fuli Zhang and Christopher Summers 1999 *J. Appl. Phys. Lett.* 74 1222.
- Zhang C X, Jiang W J and Yang X J 2009 *J. Alloys Compd.* 474 287.
- Rao, C., Babu, N., & Murthy, K. (2022). *Journal of Advanced Scientific Research*, 13(05), 137-145.
- Rao, C.A., Babu, N.B. & Murthy, K.V.R. (2023). *European J. of Theor. and Appl. Scie*, 1(4), 1288-1295.
- Q. Yanmin, Z. Xinbo, Y. Xiao, C. Yan, G. Hai, *J. Rare Earths*, 27 (2009) 323-326.
- Lei Zhou, Bing Yan, *J. Phys. Chem., Solids* 69 (2008) 2877–2882.
- J. Yang, Z. Quan, D. Kong, X. Liu, J. Lin, *Cryst. Growth and Des.*, 7 (2007) 730-735.
- K.C. Patil, S.T. Aruna, S. Ekambaram, *Curr. Opin. Solid State Mater. Sci.* 457 (1997) 158–165.
- Lei Zhou, Bing Yan, *J. Phys. Chem., Solids* 69 (2008) 2877–2882.
- Color Calculator, version 2, software from Radiant Imaging, Inc. 2007.

HOW TO CITE THIS ARTICLE: Rao CA, Murthy KVR. Optical Properties of Eu³⁺ doped CaSiO₃ Phosphors. *J Adv Sci Res.* 2024;15(4): 28-31 **DOI:** 10.55218/JASR.2024150404