

Synthesis and Photoluminescence Study of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$, $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ doped with Ce, Eu and Tb containing Fluorine

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Abstract

Light emitting semiconductor diodes which in turn excite phosphors embodied in the matrix gives white light is the need of the day. The present paper reports photoluminescence studies and physical properties of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$, $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ compounds each co-doped with Ce, Eu and Tb with 10%, 5%, and 2.5% respectively. The samples were prepared using standard solid state reaction method and ground the starting materials with appropriate stoichiometry into a fine powder, and fired at 900°C, 1200°C with and with out Urea as flux for 2 hours in a muffle furnace. The entire photoluminescence spectra were recorded at room temperature.

Keywords: *photoluminescence; solid state reaction method; light emitting diodes; Phosphor; Fluorine; Calcium Silicates*

1. INTRODUCTION

Nowadays a great attention is paid to the research and development in the field of lighting technology in relation to the global problem of saving energy. One of the rapidly developing technologies is based on using very efficient light emitting diodes [LED] in light sources for general lighting. In the recent development, a new series of hosts, namely of fluorine containing alkali earth silicates are as potential phosphors for white LEDs. In the present paper describes, the Ce^{+3} , Eu^{3+} and Tb^{3+} doped fluorine containing alkali earth silicates were synthesized via high temperature solid state reaction method. The emission, excitation spectra and their solid state physical properties were examined.

2. MATERIALS AND METHOD

The compounds having crystal structure of Triclinic- $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$, Monoclinic- $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and Orthorhombic- $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ (as per the available literature) were synthesized using the conventional

solid state reaction method by doping Ce, Eu & Tb rare earth ions. The dopant concentration was varied within the 10%, 5% & 2.5 mol%. Calcium fluoride (CaF_2), Calcium carbonate (CaCO_3), Silicon dioxide (SiO_2), Cerium oxide (CeO_2), Europium oxide (Eu_2O_3), Terbium oxide (Tb_4O_7) and Urea ($\text{CH}_4\text{N}_2\text{O}$), were used as raw materials with purity over 99.9%. The materials were weighed and mixed in appropriate stoichiometry and ground into a fine powder using agate mortar and pestle, and fired at 900°C, 1200°C with out flux for 2 hours in a muffle furnace with a heating rate of 5°C/min. The same set of samples was also prepared by adding 10% of urea as flux and fired at 1200°C. The Photoluminescence (PL) emission and excitation spectra were measured by Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using Xenon lamp as excitation source. All the spectra were recorded at room temperature.

3. RESULTS AND DISCUSSION

3.1 Physical Properties

i) **After 1200°C without Urea as flux:** The compound $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ doped with Ce, Eu & Tb rare earth ions, appears as white colour, soft and crystalline was observed. Where as the compounds $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ appears as tablet like with brown colour and strong crystalline

ii) **After 1200°C with Urea as flux:** The compound $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ doped with Ce, Eu & Tb rare earth ions, appears as Cake like with Ash colour, and strong crystalline was observed. Where as the compounds $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ appears as tablet like with dark brown colour and strong crystalline

iii) **After 900°C without Urea as flux:** The compound $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ doped with Ce, Eu & Tb rare earth ions, appears as white colour, soft and crystalline was observed. Where as the compounds $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ appears as tablet like with brown colour and strong crystalline

In both the cases of 1200 and 900°C without urea as flux, the physical properties are same

3.2 Photoluminescence Spectra

i) **At 900°C without Urea as flux:**

Fig.1 shows the excitation and emission spectrum of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ doped with Ce, Eu and Tb. The excitation spectrum monitored at 400nm, shows broad peaks at 254 and 325nm respectively. Under the excitation of 254nm, the observed emission spectrum peaks are at 469, 544 and 611nm with high crystal field at 367nm. Interestingly it is observed that, when excited 325nm wavelength, the observed emission peaks (392, 469, 544, 576 and 617nm) are different than 254. A broad peak around 392nm wavelength, very low at 469, 544 and 617 but sharp and high at 576nm was observed may be due to less crystal field at 367nm

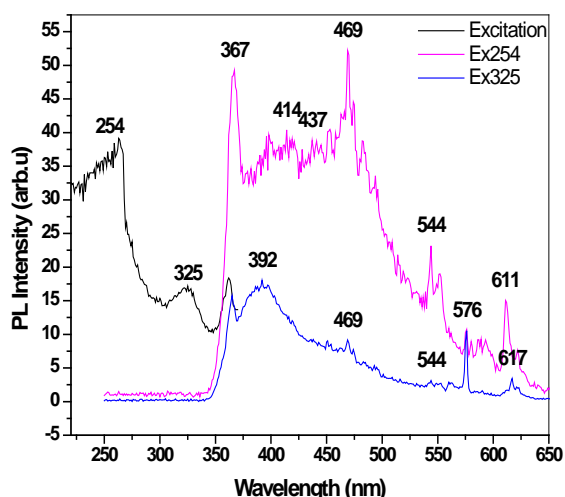


Fig.1: Excitation and Emission spectra of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ at 900°C

Fig.2 shows the excitation and emission spectra of $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$. The excitation spectra shows peak at 254nm monitored under 400nm wavelength. In both the compounds 325 peak is not present. Under the excitation of 254nm, the observed emission spectrum peaks are at 393, 422, 440, 469, 487, 543, 576, 595, 615 and 627nm. The excitation and emission spectra are same for both $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$, $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ samples and emission peaks are sharp & high at 543nm and sharp and low at other wavelengths. However $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ has higher intensity in comparison with $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$.

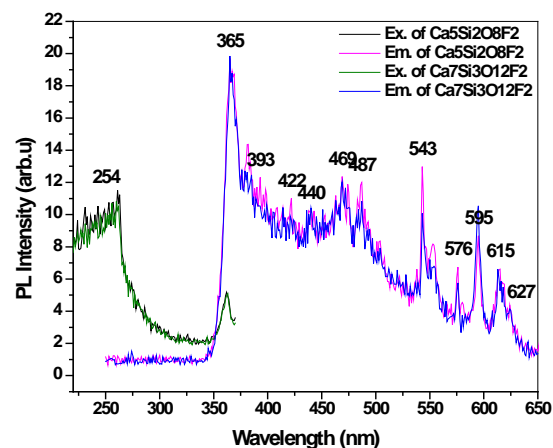


Fig.2: Excitation and Emission spectra of $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ & $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ at 900°C

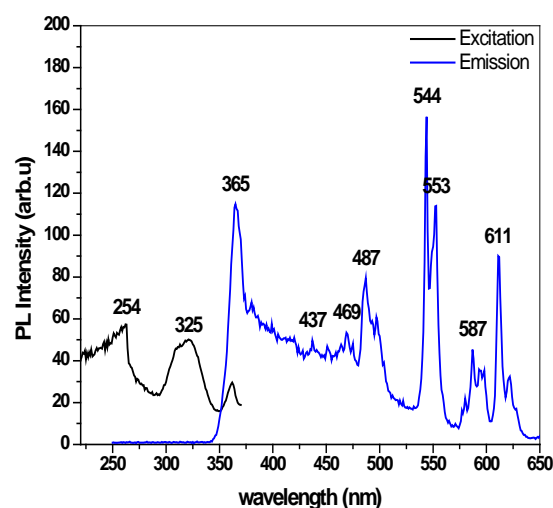


Fig.3: Excitation and Emission spectra of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ at 1200°C

ii) **At 1200°C without Urea as flux:** Fig.3 shows the excitation and emission spectrum of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ doped with Ce, Eu and Tb. The excitation spectrum monitored at 400nm, shows broad peaks at 254 and 325nm respectively. We observed that the excitation peak intensities are nearly equal to 900°C. Under the excitation of 254nm, the observed emission spectrum peaks are at 437, 469, 487, 544, 553, 587, 611 and

627nm. Interestingly it is observed that, a sharp and high intensity peaks around 487, 544, 553 and 611nm, sharp and low intensity peaks at other wavelengths was observed.

Fig.4 shows the excitation and emission spectrum of $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$. The excitation spectrum shows peak at 254nm monitored under 400nm wavelength. Under the excitation of 254nm, the observed emission spectrum peaks are at 380, 421, 438, 460, 489, 545, 590, 617 and 627nm. The excitation and emission spectra are same for both $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$, $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ the samples and emission peaks are sharp & high at 545nm and sharp and low at other wavelengths. However $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ has higher intensity in comparison with $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$.

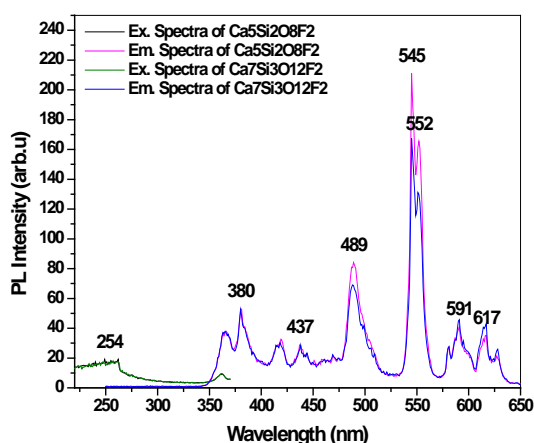


Fig. 4: Excitation and Emission spectra of $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ & $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ at 1200°C

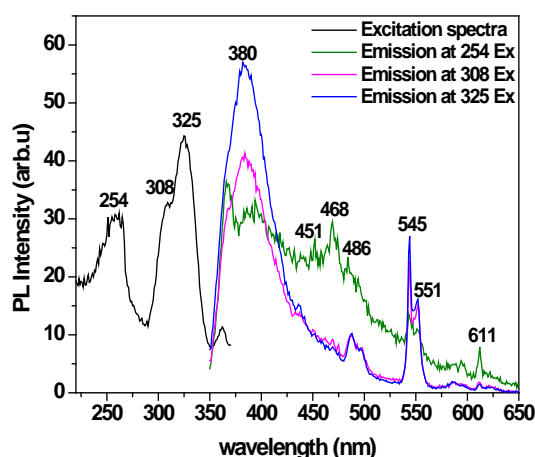


Fig.5: Excitation and Emission spectra of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ at 1200°C

iii) *At 1200°C with Urea as flux:* Fig.5 shows the excitation and emission spectrum of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ doped with Ce, Eu and Tb. The excitation spectrum monitored at 400nm, shows broad peaks at 254, 308 and 325nm respectively. We observed that an

additional peak at 308nm is observed apart from 254, 325 nm and also observed that the excitation peak intensities are reversed than at 900°C. Under the excitation of 254nm, the observed emission spectrum peaks are at 451, 468, 545 and 611nm. Interestingly it is observed that, when excited with 308 & 325nm wavelength, the observed emission peaks 380, 486, 545, 551 and 611nm are different than 254 nm. A broad and high intensity peak around 380nm wavelength, sharp and low at other wavelengths was observed.

Fig.6 shows the excitation and emission spectrum of $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$. The excitation spectrum shows peak at 254nm monitored under 400nm wavelength. Under the excitation of 254nm, the observed emission spectrum peaks are at 380, 421, 438, 460, 489, 545, 590, 617 and 627nm. The excitation and emission spectra are same for both $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$, $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ the samples and emission peaks are sharp & very high at 545nm and low at other wavelengths. However $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ has higher intensity in comparison with $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$.

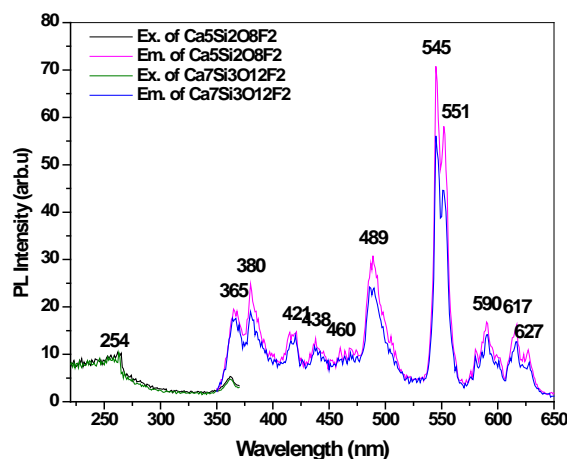


Fig.6: Excitation and Emission spectra of $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ & $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ at 1200°C

4. CONCLUSIONS

The Photoluminescence emission studies of $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$, $\text{Ca}_5\text{Si}_2\text{O}_8\text{F}_2$ and $\text{Ca}_7\text{Si}_3\text{O}_{12}\text{F}_2$ phosphors each co-doped with Ce, Eu and Tb with 10%, 5%, and 2.5% mol% respectively showed interesting results. It is important to note the final phosphor cake color, softness or hardness, appearance are different for all there phosphors before and after heat treatment. Interesting thing is the $\text{Ca}_3\text{Si}_3\text{O}_8\text{F}_2$ doped with Ce, Eu and Tb compound is different in all the above said aspects with other ones which displayed good PL as well as soft white powder in nature.

It is concluded the crystal field is affecting the PL emission intensity i.e the crystal field around 365nm

wavelength is inversely proportional to PL emission intensity.

Under the excitation of 254nm, the observed PL emission peaks are at 437, 469, 487, 544, 553, 587, 611 and 627nm with good intensity. Interestingly it is observed that, a sharp and high intensity peaks around 487, 544, 553 and 611nm, sharp and low intensity peaks at other wavelengths was observed.

From the PL studies, it is concluded this phosphor can act as a single host for producing white light, covering Blue, Green and Red regions with high intensity in all practical display devices.

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REFERENCES

- [1]. Pallavi Page, Rahul Ghildiyal., Murthy, K.V.R. Materials Research Bulletin, Vol.41, 10, (2006), 1854-1860.
- [2]. Pallavi Page and Murthy, K.V.R. Philosophical Magazine Letters, Vol. 90, No. 9, September 2010, 653–662.
- [3]. Blasse, G. and Grabmaier, B.C. Luminescent Materials, Springer-Verlag, Berlin (Germany) 1994.
- [4]. Yen, W.M. and Weber, M.J. Inorganic Phosphors (Composition, Preparation and Optical Properties), CRC Press. Boca Raton, FL (USA) 2004.
- [5]. Lakshmanan, A. R. Luminescence and Display Phosphors, Phenomenon and Applications, Nova Sci. Publishers, NY (USA) 2008.
- [6]. Rao, R.P. J. Electrochem. Soc. 143, 189, 1996.
- [7] Y. Narukawa, M. Ichikawa, D. Sanga, M. Sano, T. Mukai. J. Phys. D: Appl. Phys. 43, 354002 (6 pp) (2010)
- [8] L. Ottolini, F. Camara, S. Bigi, Am. Mineral. 85, 89-102 (2000)
- [9] K.H. Jang, E.S. Kim, L. Shi, N.M. Khaidukov, H.J. Seo. Luminescence properties of Eu^{3+} ions in K_2YF_5 crystals. Optical Materials 31, 1819–1821, 2009
- [10] N.A. Yamnova, K. Sarp, Y.K. Egorov-Tismenko, D.Y. Pushcharovskii.
- [11] E.V. Galuskin, V.M. Gazeev, B. Lazic, et al. Eur. J. Mineral. 21, 1045-1059 (2009)
- [12] I.O. Galuskina, B. Lazic, T. Armbruster, et al. Amer. Mineral. 94, 1361–1370 (2009)
- [13] W.B. Im, S. Brinkley, J. Hu, A. Mikhailovsky, S.P. DenBaars, R. Seshadri. Chem. Mater. 22, 2842 - 2849 (2010)
- [14] A.A. Setlur, E.V. Radkov, C.S. Henderson, J.-H. Her, A.M. Srivastava, N. Karkada, M.S. Kishore, N.P. Kumar, D. Aesram, A. Deshpande, B. Kolodin, L.S. Grigorov, U. Happek. Chem. Mater. 22, 4076–4082 (2010).
- [15] J. McKittrick, L.E. Shea, C.F. Bacalski, E.J. Bosze, Displays 19, 169 - 172 (1999)

[16] W.L. Suchanek, R. E. Riman. Advances in Science and Technology 45, 184-193 (2006)

[17] M. Mikami, H. Watanabe, K. Uheda, S. Shimooka, Y. Shimomura, T. Kurushima, N. Kijima. IOP Conf. Series: Materials Science and Engineering 1, 012002 (10 pp) (2009)

[18] G. Zimmerer. J. Lumin. 119-120, 1 - 7 (2006)

[19] V. Bachmann, T. Justel, A. Meijerink, C. Ronda, P. J. Schmidt. J. Lumin. 121, 441–449 (2006)

[20] G. Cheng, Q. Liu, et al. J. Rare Earths 28, 526-528, 2010

[21] Y. Chen, M. Gong, K W. Cheah. Mater. Sci. Eng. B 166, 24 – 27, 2010