

# Luminescence properties of Praseodymium ions doped $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3$ Cl Phosphor.

<sup>1</sup>Nahida Baig, <sup>2</sup>Vaibhav Kawthe, and <sup>3</sup>Dhoble SJ

<sup>1</sup>Department of Physics, Janata Mahavidyalaya Chandrapur India

<sup>2</sup>Department of Physics, Janata Mahavidyalaya Chandrapur India

<sup>3</sup>Department of Physics, RTM Nagpur University, Nagpur-440033, India

Email: [nahidaejaz@gmail.com](mailto:nahidaejaz@gmail.com), [sjdhoble@gmail.com](mailto:sjdhoble@gmail.com)

## Manuscript Details

Available online on <http://www.irjse.in>  
 ISSN: 2322-0015

## Cite this article as:

Baig Nahida, Vaibhav Kawthe, and Dhoble SJ. Luminescence properties of Praseodymium ions doped  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3$  Cl Phosphor, *Int. Res. Journal of Science & Engineering*, February, 2020, Special Issue A7 : 331-337.

© The Author(s). 2020 Open Access

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License

(<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## ABSTRACT

$\text{Pr}^{3+}$  doped  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3$  Cl were synthesized by wet synthesis method. The samples were characterized by photoluminescent excitation and emission spectra. The Photoluminescent excitation spectra show that the synthesized phosphor samples have narrow blue excitation bands lying between 440 to 500 nm, which lies in the emission wavelength range of blue light emitting diode chips. When excited with 449 nm wavelengths light, emission lines peaking in the range between 480 to 680 nm centered at 487nm (blue), 527nm (green), 600nm (red) and 669nm are observed. The emission of Red, Green and Blue emission makes it useful in the white LEDs.  $\text{Pr}^{3+}$  doped  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3$  Cl phosphor may possibly be used for applications such as solid state lighting devices.

**Keywords:** Praseodymium, wet synthesis method, solid state lighting

## INTRODUCTION

The phosphate compound  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3$  Cl known as phosphohedyphane having IMA approved status has been studied for its photoluminescence properties with rare earth ion activators like Tb, Sm, Dy and Eu [1,2]. Rare earth activated inorganic luminescence materials have multi applications such as for devices like X-ray imaging, radiation dosimetry, solid state lighting etc. [3-8].

They have been used as activators for a variety of host materials. Among these, Praseodymium  $\text{Pr}^{3+}$  ions have been known widespread for their possible applications as red emitter in luminescence and laser action. Research suggests that the energy levels of  $\text{Pr}^{3+}$  ions contain several metastable multiplets such as  $^3\text{P}_{0,1,2}$ ,  $^1\text{D}_2$  and  $^1\text{G}_4$  [9, 10] which generate several possibilities for pumping and laser action.

It is also studied that the emission color of rare earth ions in general and  $\text{Pr}^{3+}$  ions in particular strongly depend on the type of substrate, concentration of dopants, and the pumping condition [11]. The emission of  $\text{Pr}^{3+}$  ions is found to be similar to that of trivalent Europium ions which have been known as efficient red phosphor.

Dengfeng Peng et al reported novel red emission centered at 621nm, useful for white LEDs, in  $\text{CaBi}_2\text{Ta}_2\text{O}_9:\text{Pr}^{3+}$  phosphor when excited by blue light [12]. Diallo et al, suggested that  $\text{CaTiO}_3:\text{Pr}^{3+}$  was excitable in a wide range of UV light and exhibited a unique red emission from  $^1\text{D}_2$  level of  $\text{Pr}^{3+}$  [13]. Thus the  $\text{Pr}^{3+}$  ions are known for their fast and efficient UV d-f emission and are full of f-f energy structures which lead to various mutual interactions resulting in the phenomenon of up- and down conversions.

Although we find several luminescence studies of  $\text{Pr}^{3+}$  activated phosphors in the recent past, but to the best of our knowledge, the luminescent studies of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$  has not been reported so far. In this research paper we are presenting our investigations on emission and excitation spectra of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$  synthesized by combustion method and their chromatic characterization.

## METHODOLOGY

### Synthesis of $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$

Pure and rare earth ions (Pr) doped  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$  phosphors were synthesized by wet chemical method. All the starting materials of AR grade quality, taken in stoichiometric proportion are individually dissolved in distilled water and stirred till a clear solution is obtained. These solutions are then mixed together to obtain a resultant phosphor solution. The dopant is mixed in their nitrate forms. The concentration of

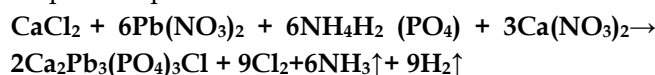
dopants is varied from 0.05-1mol%. Complete procedure is depicted schematically in Fig. 1.

The solution form of the resultant phosphor is dried in an oven at about  $80^\circ\text{C}$  for 10-12 hours. The dried polycrystalline mass is cooled to room temperature and then crushed to fine powder using Mortar and Pestle. These powders are used for further study.

### Starting materials:

Lead Nitrate ( $\text{Pb}(\text{NO}_3)_2$ )  
 Calcium chloride ( $\text{CaCl}_2$ )  
 Calcium Nitrate ( $\text{Ca}(\text{NO}_3)_2$ )  
 ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2(\text{PO}_4)\cdot\text{H}_2\text{O}$ )  
 Praseodymium Oxide ( $\text{Pr}_3\text{O}_7$ )

### Required Equation:



The photoluminescence (PL) emission spectra of the sample were recorded using fluorescence spectrometer (RF -5301). The same amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral slit width of 1.5.

## Characterization

### a) X-ray diffraction

The formation of crystalline phases in the samples was confirmed by powder XRD characterization. Fig. 1 shows the XRD pattern of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$  phosphor. XRD pattern did not show the presence of the starting materials and other likely phases which is indirect evidence for the formation of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$  phosphor. It matches well with card database-code-amcsd 0004255 given by Kampf et al [17]. This result indicates that the final product was formed in homogeneous form. This XRD structure is typical of apatite group.

### b) Scanning Electron Microscopy/SEM

#### Characterization

Fig. 3 shows SEM images of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$  phosphor with different magnifications. The images show that the phosphor consists of micro particles. The particle size ranges from  $2\mu\text{m}$  to  $10\mu\text{m}$ .

## RESULTS AND DISCUSSION

### Photoluminescence study of $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$

Fig. 4 shows PL excitation spectra of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$ , monitored at 487 nm emission. These phosphors show strong excitation peaks in the long wavelength 430-530 nm region corresponding to the f-f transition absorption of  $\text{Pr}^{3+}$  whereas lower wavelength excitation peaks are not visible. There are three sharp excitation peaks in the range from 430 to 500 nm peaking at  $\sim 449$  nm,  $\sim 472$  nm,  $\sim 481/493$  nm, which are assigned to  $^3\text{H}_4 \rightarrow ^3\text{P}_2$ ,  $^3\text{H}_4 \rightarrow ^3\text{P}_1$ ,  $^3\text{H}_4 \rightarrow ^3\text{P}_0$  transitions of  $\text{Pr}^{3+}$ , respectively [15,18,19].

The excitation characteristics of the phosphor in the region around 449 nm make it suitable for blue LED chips [14, 16, 19].

The  $\text{Pr}^{3+}$  concentration dependent PL emission spectra for of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$  is shown in Fig.5 which were measured under 449 nm excitation. A blue color attributed to an f-f transition of praseodymium (III) was observed. In general the photoluminescent properties of five samples of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$  with different concentration do not differ greatly from one

another and no obvious red or blue shift was observed.

Two prominent emission peaks located at around 487 nm, and 527 which are assigned to the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$ ,  $^3\text{P}_1 \rightarrow ^3\text{H}_5$ , transitions of  $\text{Pr}^{3+}$ , respectively [18]. The appearance of multiple emission peaks is due to the splitting of 4f energy level of  $\text{Pr}^{3+}$ . But in this case we find that blue, green and red emission exists and strong red emission which is characteristics of  $\text{Pr}^{3+}$  is not found in PL emission spectra of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$ . The strongest emission is at around 487 nm, blue emission, and we also have green and red emissions, all this leading to white color.

The PL emission spectra also consist of red emission peaks at 600 nm and 669 nm attributed to  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  and  $^3\text{P}_0 \rightarrow ^3\text{F}_2$ , transitions of  $\text{Pr}^{3+}$ . As compared to the broad band feature of  $\text{Pr}^{3+}$  in some hosts, the fluorescence emission spectra of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$  shows line feature.

From the emission spectra we find that maximum intensity is obtained for 0.5 mol% concentration of dopant  $\text{Pr}^{3+}$  ions. This indicates that  $\text{Pr}^{3+}$  ions produce results at low concentrations.

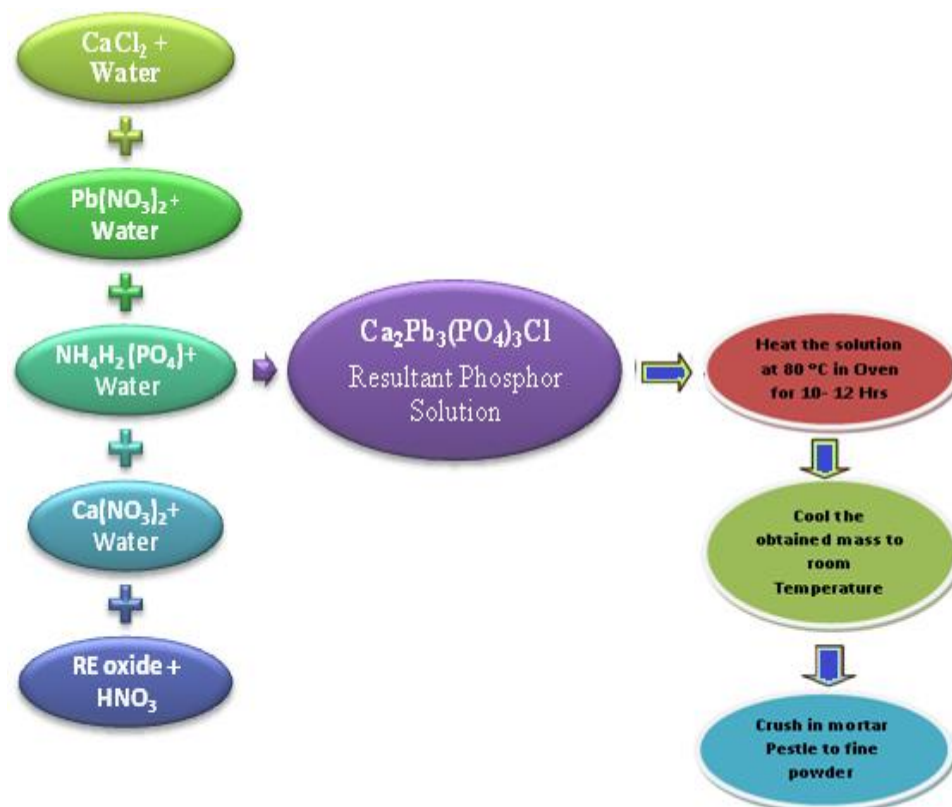


Fig.1: Schematic diagram of synthesis of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{RE}^{3+}$  phosphor

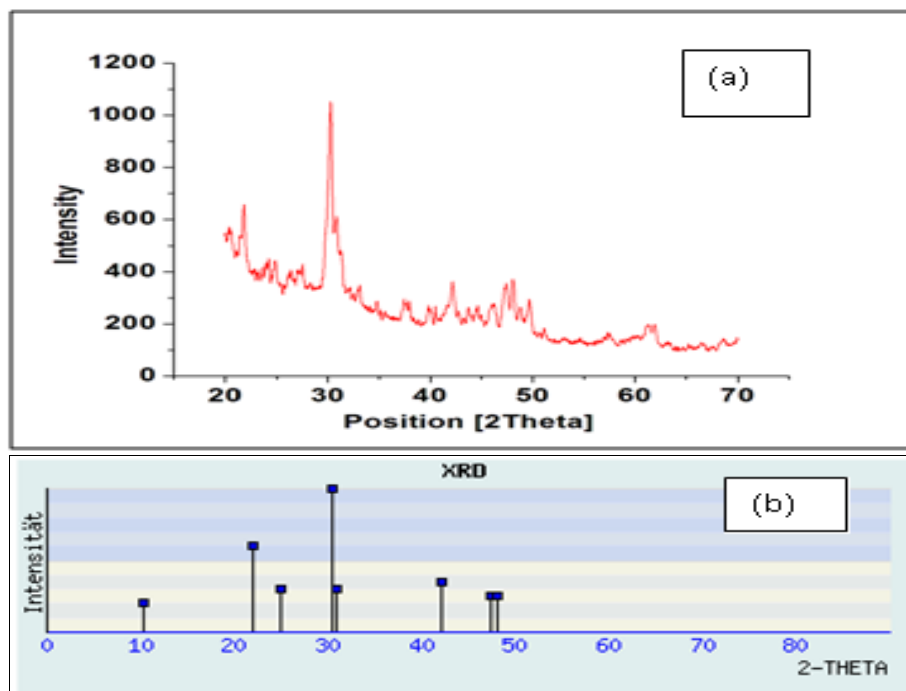


Fig. 2 XRD pattern of (a)  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$  synthesized here (b) as given in card database-code-amcsd 0004255 given by Kampf et.al.

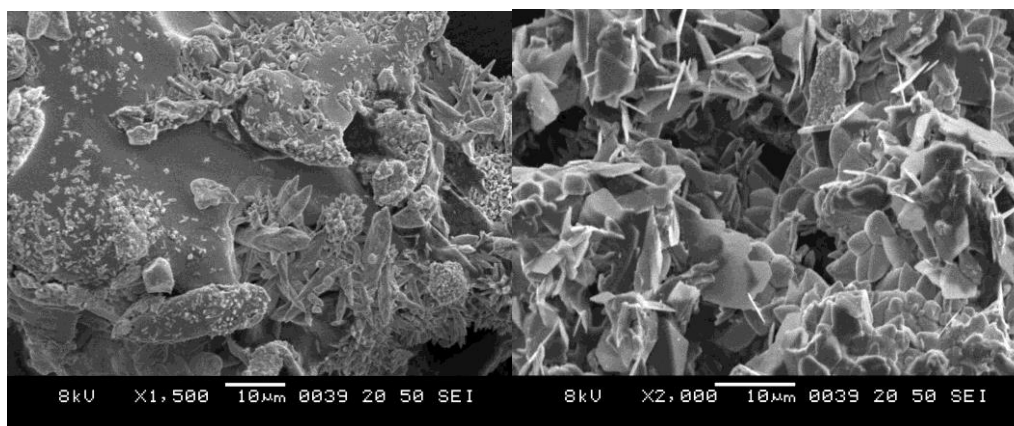


Fig.3: SEM images of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$  phosphor

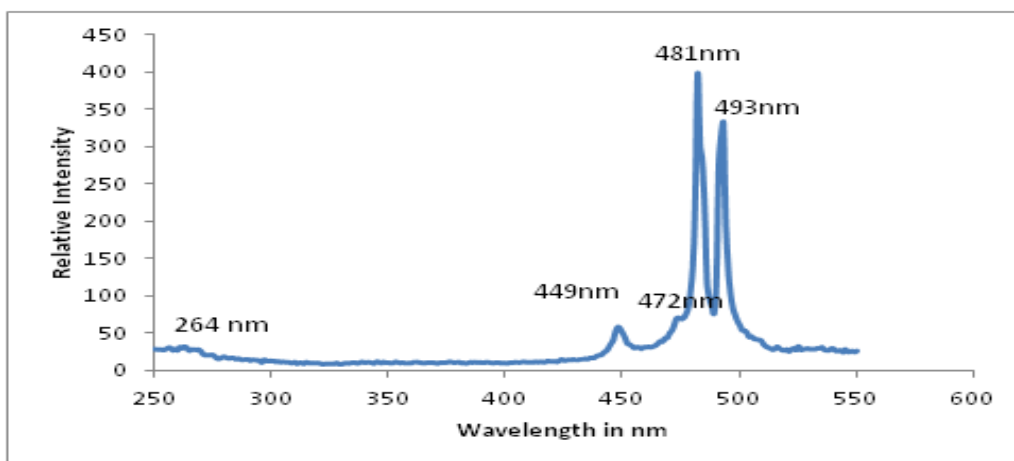


Fig. 4 PL Excitation spectra of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$  monitored at emission wavelength of 487 nm.

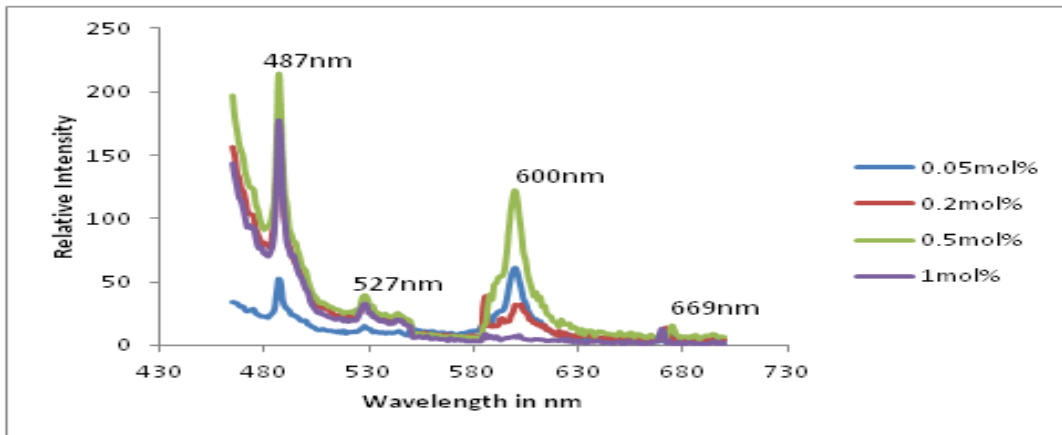


Fig.5 PL Emission spectra of  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}$  at 449 nm wavelength

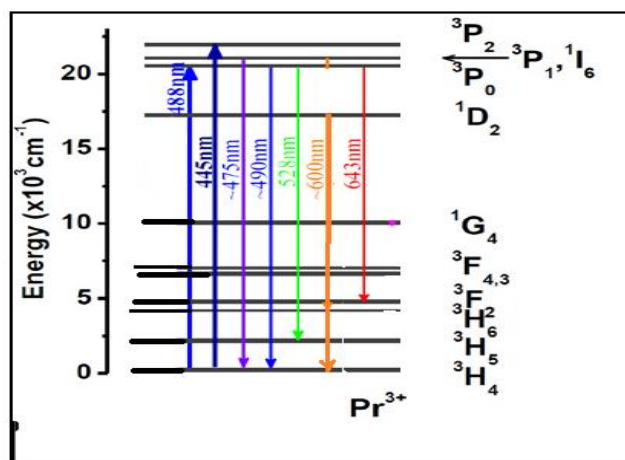


Fig. 6 Energy level diagram of  $\text{Pr}^{3+}$  ions in  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}:\text{Pr}^{3+}$

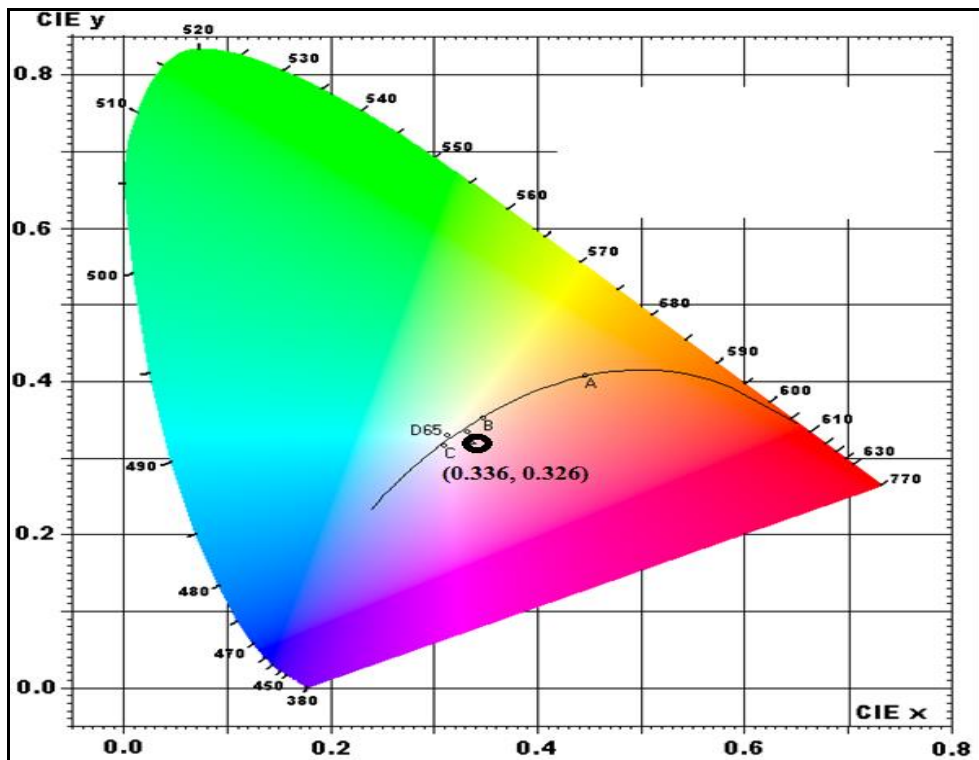


Fig. 7 CIE Chromaticity diagram for emission  $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl} :0.5\%\text{Pr}^{3+}$  under 449 nm excitation



### Chromatic properties of Pr<sup>3+</sup> -doped Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl phosphor:

CIE method is the well known method to express the colors in terms of color coordinates. The Commission Internationale de l'Éclairage (CIE) system recognizes that the human visual system uses three primary colours, red, green and blue. Every natural color like red, green and blue can be identified by (x, y) coordinates. The CIE chromaticity coordinates of Pr<sup>3+</sup> doped Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl phosphor as shown in Fig 7.

Considering the fact that the emission peaks of Praseodymium doped phosphors has three different colors blue, green and red, and the peak intensities for 487 nm and 527 nm and 600 nm are as shown in fig. 5. in Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Pr<sup>3+</sup> phosphor, we have calculated the CIE chromaticity coordinates for 0.5% Pr<sup>3+</sup> doped Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl from the spectral distribution, which are obtained as (0.336,0.326). Fig. 7 shows the CIE chromaticity coordinates (value of x and y) calculated from the emission spectra of 0.5%Pr<sup>3+</sup> doped Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl phosphor. The chromaticity coordinates for standard white light are (0.33, 0.33). The chromaticity coordinates obtained in this case lie close to the standard value. This indicates the phosphor compositions of Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Pr<sup>3+</sup> can generate white light emission and may be used for solid state lighting purpose.

### CONCLUSION

A series of chloride based Pr<sup>3+</sup> activated halophosphor material Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl were synthesized by wet chemical method and characterized by Powder diffraction pattern and Photoluminescence. The formation of crystalline phases in the samples prepared by the wet chemical method was confirmed by powder XRD measurements. XRD pattern did not show the presence of the starting materials and other likely phases which is indirect evidence for the formation of Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl phosphor.

The morphological characterization by SEM images of Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl phosphor show that the phosphor consists of micro particles. The particle size ranges from 2µm to 10 µm.

The PL excitation spectra monitored at 487 nm emission wavelength produces several excitation peaks specific of Pr<sup>3+</sup> ions. And the PL emission spectra monitored at 449 nm shows different colors blue, green and red, with peak intensities at 487 nm, 527 nm and 600 nm and 669nm in the visible region of electromagnetic spectrum attributed to f-f transitions of Pr<sup>3+</sup> ions.

The CIE chromaticity coordinates for 0.5mol % Pr<sup>3+</sup> doped Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl from the spectral distribution are obtained as (0.336,0.326) which lies in the white light region of chromaticity diagram.

This indicates the phosphor compositions of Ca<sub>2</sub>Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl:Pr<sup>3+</sup> can generate white light emission and may be used for solid state lighting purpose.

**Conflicts of interest:** The authors stated that no conflicts of interest.

### REFERENCES

1. Nahida Baig, R.S.Yadav, N.S.Dhoble, Vijay L.Barai, S.J.Dhoble; Journal of Luminescence 215 (2019) 116645
2. A.R.Kampf, I.M.Steele, R.A. Jenkins, Am. Minerals, 91(2006)1909
3. Nahida Baig, N.S.Dhoble, A.N.Yerpude, Vijay Singh, S.J.Dhoble; Optik 127(2016) 6574-6582
4. B.Suneetha, S.Sailaja, S.J.Dhoble, B.SudhakarReddy, Optik 155(2018)216-224
5. Arti Durugkar, Sumedha Tamboli, N.S.Dhoble, S.J.Dhoble, Materials Research Bulletin 97(2018)466-472
6. N. Jaba, H. Ben Mansour, A. Kanoun, A. Brenier, B. Champagnon, Spectral broadening and luminescence quenching of 1.53 µm emission in Er<sup>3+</sup>-doped zinc tellurite glass, J. Lumin. 129 (2009) 270-276.
7. P. Nandi, G. Jose, Spectroscopic properties of Er<sup>3+</sup> doped phospho-tellurite glasses, Physica. B 381 (2006) 66-72.
8. D. Atul Sontakke, K. Kaushik Biswas, Annapurna, Concentration - dependent luminescence of Tb<sup>3+</sup> ions in high calcium aluminosilicate glasses, J.Lumin. 129 (2009) 1347-1355.

9. F.S.Kao and Teng-Ming Chen; Journal of Solid state Chemistry 155, 441-446 (2000)
10. G.Blasse and B.C.Grabmaier, "Luminescent Materials," p.26 Springer-Verlag, Berlin, 1994.
11. R. Balda, J.Fernandez, I.S.deOcariz, M.Voda, A.J.Garcia and N. Khaidukov, Phys.Rev.B59, 9972(1999)
12. Dengfeng Peng, Haiqin Sun, Xusheng Wang\*, Juncheng Zhang, Mianmian Tang, Xi Yao; Journal of Alloys and Compounds 511 (2012) 159– 162
13. P. T. Diallo, P. Boutinaud, R. Mahiou, and J. C. Cousseins, Phys. Stat.Sol. (a) 160, 255 (1997).
14. E. Cavalli, P. Boutinaud, M. Bettinelli, P. Dorenbos, J. Solid State Chem. 181 (2008)1025–1031.
15. F.B. Xiong, H.F. Lin, Z. Ma, Y.P. Wang, H.Y. Lin, X.G. Meng, H.X. Shen, W.Z. Zhu, Opt. Mater. 66 (2017) 474–479.
16. S.Y. Xin, G. Zhu, B. Wang, Z.F. Shao, J. Lumin. 181 (2017) 455–458.
17. Y.Q. Zhou, J. Liu, X.Y. Yang, X.B. Yu, J. Zhuang, J. Electrochem. Soc. 157 (2010)H278–H280.
18. A.K. Soni, V.K. Rai, Dalton Trans. 43 (2014) 13563–13570.
19. I.E. Seferis, K. Fiaczyk, D. Spassky, E. Feldbach, I. Romet, M. Kirm, E. Zych, J.Lumin. 189 (2017) 148–152.