

# Effects of ZnO and Ce<sup>3+</sup> incorporation on the photoluminescence and cathodoluminescence intensity of Pr<sup>3+</sup> doped SiO<sub>2</sub>.

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**Abstract.** The successful incorporation of ZnO nanoparticles and Ce<sup>3+</sup> ions in Pr<sup>3+</sup> doped SiO<sub>2</sub> using a sol-gel process is reported. SiO<sub>2</sub>:Pr<sup>3+</sup> gels, with or without ZnO and Ce<sup>3+</sup>, were dried at room temperature and annealed at 600 °C. The Field Emission Scanning Electron Microscopy indicated clustered SiO<sub>2</sub> nanoparticles with particle size diameter ranging from 20 to 120 nm while the energy dispersive x-ray spectroscopy (EDS) revealed the presence of Zn, Ce, and Pr clusters enveloped in the SiO<sub>2</sub> matrix. The emission intensity from SiO<sub>2</sub>:Pr<sup>3+</sup>-Ce<sup>3+</sup> at 494 nm was slightly enhanced compared to Ce<sup>3+</sup> singly doped SiO<sub>2</sub>. The red emission of Pr<sup>3+</sup> was enhanced when ZnO nanoparticles were incorporated in SiO<sub>2</sub> suggesting that energy was transferred from ZnO to Pr<sup>3+</sup>. Possible energy transfer mechanisms between Pr<sup>3+</sup> and Ce<sup>3+</sup> and between ZnO and Pr<sup>3+</sup> are discussed in detail.

## 1. Introduction

Among rare earths, trivalent praseodymium (Pr<sup>3+</sup>) has been used as an activator in various host matrices to prepare phosphors [1-4] that can be used in different types of light emitting devices. The possibility of enhancing luminescence efficiency via energy transfer between activator ions (i.e. the sensitizer and the acceptor) was predicted by Dexter [5] in the 1960s. Studies of energy transfer process between Pr<sup>3+</sup> and other ions co-doped in the same host matrix have been reported [6,7]. Interest has also been focused on nanocrystalline semiconducting quantum dots as they are considered as another good choice of sensitizing centres for radiative relaxation of activator ions since their excitation cross sections are very high due to the efficient band-to-band absorptions. Rare earth ions doped glass matrices containing nanocrystal semiconducting quantum dots prepared by the sol-gel

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method have been reported [8,9]. In such cases, the enhanced luminescence from rare earth ions can be achieved by efficient energy transfer from the quantum dots to rare earth ions. In the present work, we report the enhanced emission of  $\text{Pr}^{3+}$  induced by energy transfer from ZnO nanoparticles incorporated in situ in sol-gel silica under VUV and electron beam excitation. Energy transfer between  $\text{Pr}^{3+}$ - $\text{Ce}^{3+}$  co-doped in  $\text{SiO}_2$  was also studied under electron beam excitation.

## 2. Experimental

### 2.1. Preparation of $\text{SiO}_2\text{:Ce}^{3+}\text{-Pr}^{3+}$ and $\text{ZnO:SiO}_2\text{:Pr}^{3+}$

$\text{SiO}_2\text{:Pr}^{3+}$  co-doped with different concentrations of  $\text{Ce}^{3+}$  phosphor samples were prepared by mixing 0.05 mol of tetraethylorthosilicate (TEOS), 0.1 mol of  $\text{H}_2\text{O}$ , 0.1 mol of ethanol, and 0.145 mol of dilute nitric acid. The mixture was stirred at room temperature for 1 hour. The resulting transparent sol was mixed with a desired amount of  $\text{Pr}(\text{NO})_3\cdot 6\text{H}_2\text{O}$  dissolved in 5 ml of ethanol and was stirred for 30 minutes. A desired amount of  $\text{Ce}(\text{NO})_3\cdot 6\text{H}_2\text{O}$  dissolved in 5 ml of ethanol was also added to the solution and stirred further for 30 minutes until a gel formed. The gel was then dried at room temperature for 3-8 days. The dried gel was ground and annealed in air at 600 °C for 2 hrs. The  $\text{ZnO:SiO}_2\text{:Pr}^{3+}$  nanocomposite phosphor was prepared by mixing the  $\text{SiO}_2\text{:Pr}^{3+}$  sol with ZnO nanoparticles suspended in ethanol. The detailed preparation of ZnO nanoparticles has been reported [8].

The particle morphology was analyzed by JEOL 2100 High Resolution Transmission Electron Microscopy (HRTEM) and JEOL JSM-7500F, Field Emission Scanning Electron Microscope (FESEM). The cathodoluminescence (CL) data of the phosphor samples were recorded using an Ocean Optics S2000 spectrometer coupled with an ultra high vacuum chamber of the Physical Electronics PHI 549 Auger electron spectrometer. The photoluminescence (PL) data was recorded at the Deutsche Elektronen Synchrotron (DESY) using the setup at SUPERLUMI experimental station of HASYLAB in Hamburg. The emission spectrum of ZnO was obtained using a LS 55, Fluorescence spectrometer.

## 3. Results and discussion

### 3.1. Particle morphology, size, and phase structure

The FE-SEM image in figures 1 illustrates the morphologies of the  $\text{SiO}_2$  nanoparticles calcined at 600 °C for 2 hrs. The image exhibits the agglomeration of mostly spherical  $\text{SiO}_2$  particles with an average particle size in the range of ~20 to 120 nm in diameter. Similar morphology was observed for  $\text{ZnO:SiO}_2\text{:Pr}^{3+}$  and  $\text{SiO}_2\text{:Pr}^{3+}\text{-Ce}^{3+}$  samples. Figure 2 (a) and (b) show the XRD patterns of  $\text{SiO}_2$  nanoparticles and ZnO nanoparticles, respectively. The XRD patterns of the ZnO nanoparticles presented in figure 2 (b) are consistent with a hexagonal phase of ZnO referenced in JCPDS file No. 80-0075. The broadening of the ZnO diffraction peaks is attributed to the smaller particle sizes. The average crystallite size of the ZnO nanoparticles estimated using Scherer's equation was ~ 4 nm. Figure 2 (a) shows only one broad diffraction peak of amorphous  $\text{SiO}_2$  at 22°. The diffraction peaks of  $\text{SiO}_2\text{:Ce}^{3+}\text{-Pr}^{3+}$  and  $\text{ZnO:SiO}_2\text{:Pr}^{3+}$  samples resembled that of pure  $\text{SiO}_2$  probably due to the relatively low concentration of  $\text{Pr}^{3+}$  and the ZnO nanoparticles and/or high amorphous scattering background from the  $\text{SiO}_2$  matrix [8]. The presence of the  $\text{Pr}^{3+}$ ,  $\text{Ce}^{3+}$  ions and ZnO nanoparticles in the phosphor powders (not shown) was confirmed by Electron Dispersive Spectroscopy (EDS).

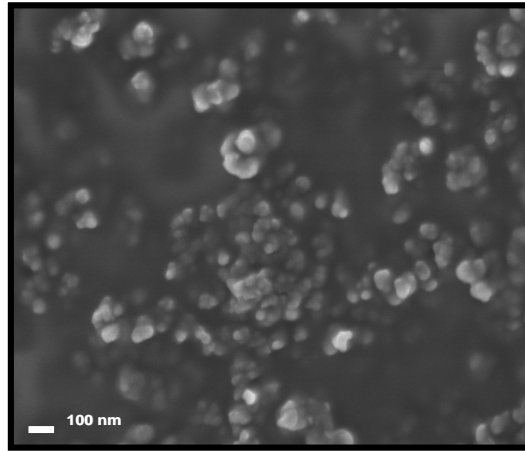


Fig. 1 FE-SEM image of SiO<sub>2</sub>.

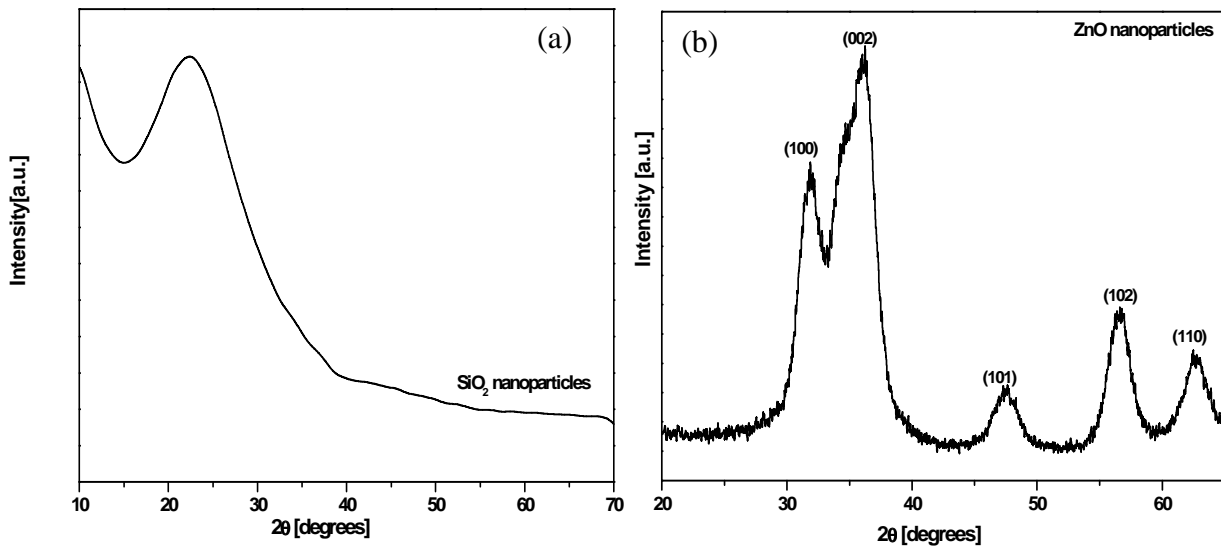


Fig.2 XRD patterns of the (a) SiO<sub>2</sub> nanoparticles after calcination at 600 °C and (b) ZnO nanoparticles dried at 90 °C.

### 3.2. PL and CL properties of ZnO:SiO<sub>2</sub>:Pr<sup>3+</sup>.

CL spectra of the SiO<sub>2</sub>, SiO<sub>2</sub>:0.2 mol% Pr<sup>3+</sup> and ZnO:SiO<sub>2</sub>:0.2 mol% Pr<sup>3+</sup> nanophosphor powders excited by 2 keV electrons, at 20 μA beam current in a high vacuum chamber at a base pressure of  $\sim 1.6 \times 10^{-8}$  Torr are shown in figure 3. The CL spectrum of SiO<sub>2</sub> showed the emission peak at 445 nm which can be assigned to structural defects in the SiO<sub>2</sub> network or charge transfer between O and Si atoms [8]. The characteristic emission peaks with maximum emission at 614 nm that can be associated with transitions in Pr<sup>3+</sup> were observed from both SiO<sub>2</sub>:Pr<sup>3+</sup> and ZnO:SiO<sub>2</sub>:Pr<sup>3+</sup> samples. This emission can be assigned to the transitions originating from the <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> energy levels to the <sup>3</sup>H<sub>(J=6, 5, 4)</sub> and <sup>3</sup>F<sub>(J=2, 3, 4)</sub> energy levels all localized in the 4f<sup>2</sup> intra-configuration of the Pr<sup>3+</sup> ions with a dominant emission at 614 nm corresponding to the <sup>3</sup>P<sub>0</sub>→<sup>3</sup>H<sub>6</sub> transition. It was also noticed that there was no emission from ZnO nanoparticles (usually at  $\sim 370$  and 560 nm), instead the red emission of Pr<sup>3+</sup> was enhanced when ZnO nanoparticles were incorporated. Lack of emission from ZnO nanoparticles and the subsequent enhancement of the red emission of Pr<sup>3+</sup> demonstrate sensitization of Pr<sup>3+</sup> emission centres by ZnO nanoparticles. That is, energy was transferred non-radiatively from ZnO to Pr<sup>3+</sup>. The transfer was most probably by phonon mediated processes as previously reported [8-10].

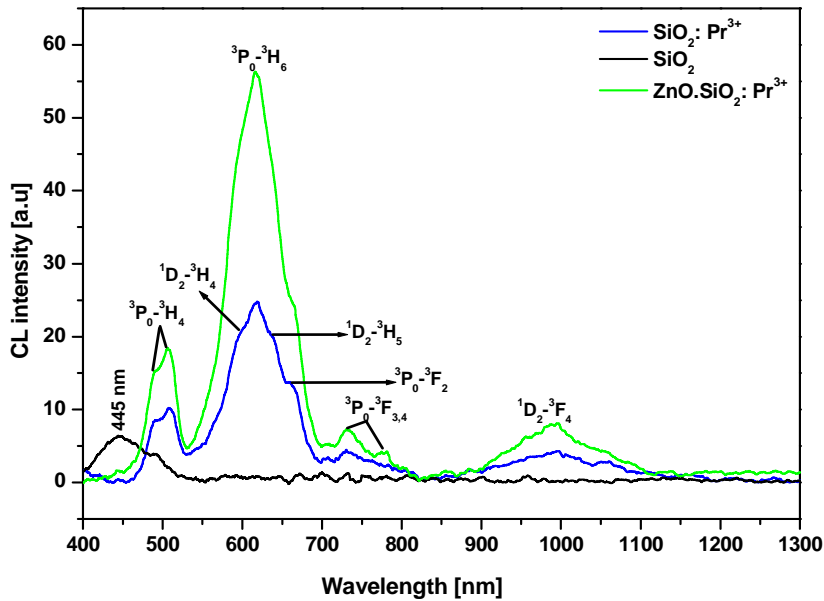


Fig.3 CL spectra  $\text{SiO}_2$ ,  $\text{SiO}_2:0.2 \text{ mol\% Pr}^{3+}$  and  $\text{ZnO.SiO}_2:0.2 \text{ mol\% Pr}^{3+}$  irradiated with 2 keV, 20  $\mu\text{A}$  beam of electrons in a high vacuum chamber containing  $1.6 \times 10^{-8}$  Torr.

Figure 4 presents the PL emission spectra of  $\text{SiO}_2:0.2 \text{ mol\% Pr}^{3+}$  and  $\text{ZnO.SiO}_2:0.2 \text{ mol\% Pr}^{3+}$  phosphors under excitation at 90 nm using synchrotron radiation. Also, only characteristic emissions from  $\text{Pr}^{3+}$  ion with the main red emission centred at 614 nm were detected from both  $\text{SiO}_2:\text{Pr}^{3+}$  and  $\text{ZnO.SiO}_2:\text{Pr}^{3+}$  phosphors. The PL intensity of  $\text{ZnO.SiO}_2:\text{Pr}^{3+}$  was enhanced with ZnO incorporation indicating energy transfer from ZnO to  $\text{Pr}^{3+}$  ions.

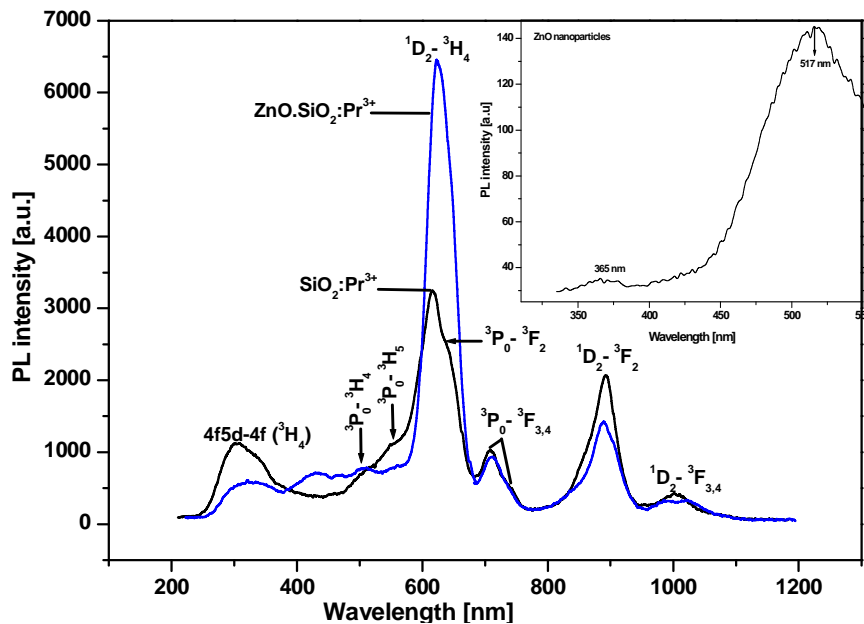


Fig. 4 PL emission spectra of  $\text{SiO}_2:0.2 \text{ mol\% Pr}^{3+}$  and  $\text{ZnO.SiO}_2:0.2 \text{ mol\% Pr}^{3+}$  after VUV excitation at 90 nm using synchrotron radiation. The inset shows the PL emission spectrum of ZnO nanoparticles after excitation at 325 nm.

Note that the emission spectrum from ZnO could not be measured due to charging when exciting using synchrotron radiation. However the spectra was recorded when a monochromatized xenon lamp ( $\lambda_{\text{exc}} = 325 \text{ nm}$ ) was used as shown in the inset in figure 4. The direct band gap emission and green emission from the ZnO nanoparticles was measured at 365 nm and 517 nm, respectively. Based on these results it was then concluded that the energy transfer from ZnO could be due to bandgap absorption and relaxation to the defects states of ZnO [9].

### 3.3. CL properties of $\text{SiO}_2\text{:Ce}^{3+}\text{-Pr}^{3+}$ .

Figure 5 shows the CL emission spectra of  $\text{SiO}_2\text{:1 mol\% Ce}^{3+}$  phosphor powder under irradiation with 2 keV electrons, 8.5  $\mu\text{A}$  beam current in a high vacuum chamber at a base pressure of  $1.2 \times 10^{-8}$  Torr. The CL emission spectrum from  $\text{SiO}_2\text{:Ce}^{3+}$  consists of two blue bands located at 452 nm (shoulder) and 494 nm (strong). The two bands at 452 nm and 494 nm can be associated with  ${}^2\text{D}_{3/2}\text{-}{}^2\text{F}_{7/2}$  and  ${}^2\text{D}_{3/2}\text{-}{}^2\text{F}_{5/2}$  of  $\text{Ce}^{3+}$ , respectively [7].

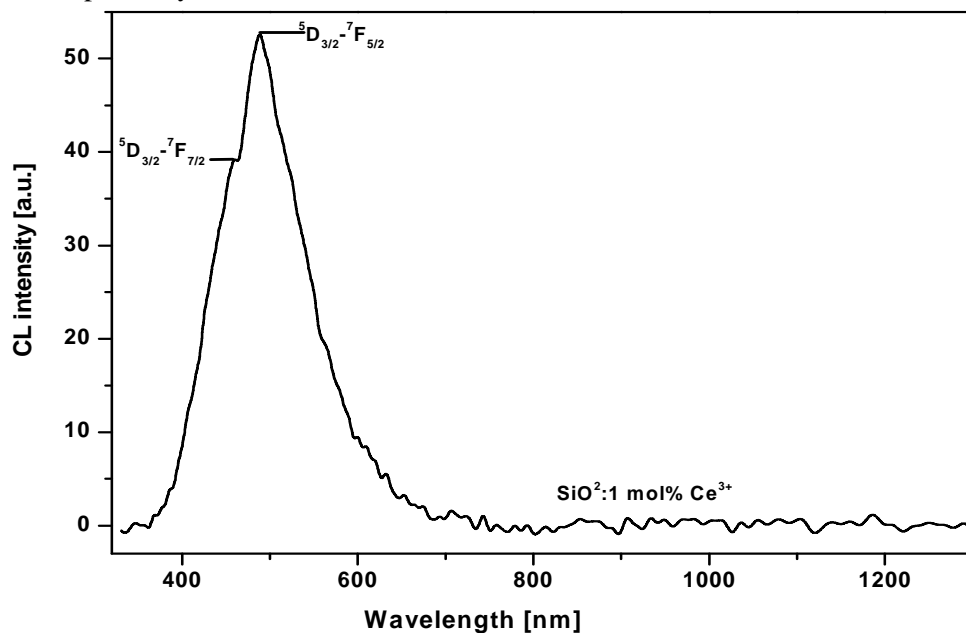


Fig. 5 CL emission spectra of  $\text{SiO}_2\text{:Ce}^{3+}$  (1mol %) irradiated with 2 keV, 8.5  $\mu\text{A}$  beam of electrons in a high vacuum chamber containing a base pressure of  $1.2 \times 10^{-8}$  Torr.

The CL emission spectra of the  $\text{SiO}_2\text{:Pr}^{3+}$ ,  $\text{SiO}_2\text{:Ce}^{3+}$ , and  $\text{SiO}_2\text{:Pr}^{3+}\text{:Ce}^{3+}$  (with different  $\text{Ce}^{3+}$  concentrations) phosphor powders under irradiation with 2 keV electrons, 8.5  $\mu\text{A}$  beam current in a high vacuum chamber at a base pressure of  $1.2 \times 10^{-8}$  Torr are shown in figure 6. The CL emission spectra of  $\text{SiO}_2\text{:Ce}^{3+}\text{-Pr}^{3+}$  showed both bands from  $\text{Ce}^{3+}$  in the blue spectral region and a small shoulder from  $\text{Pr}^{3+}$  in the red spectral region when the amount of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  were both 0.2 mol%. The small shoulder from  $\text{Pr}^{3+}$  was slowly quenched with increasing  $\text{Ce}^{3+}$  concentration and only blue emission from  $\text{Ce}^{3+}$  could be observed. Blue emission from  $\text{Ce}^{3+}$  was slightly enhanced with addition of 1 mol%  $\text{Ce}^{3+}$  into 0.2 mol%  $\text{Pr}^{3+}$  compared to singly doped  $\text{SiO}_2\text{:Ce}^{3+}$ . These results suggest the energy transfer from  $\text{Pr}^{3+}$  ions to its nearest neighbouring  $\text{Ce}^{3+}$  ions. In addition, it appears that at 1 mol% of  $\text{Ce}^{3+}$ , the  $\text{Ce}^{3+}$  neighbouring ions are close enough to each other for energy transfer from  $\text{Pr}^{3+}$  to  $\text{Ce}^{3+}$  to take place. An increase in  $\text{Ce}^{3+}$  concentration led to the shortening of the distance between its neighbouring ions as a result of non-radiative loss of excitation energy between  $\text{Ce}^{3+}$  ions favoring quenching effect thus decreasing luminescence intensity. The quenching of the CL intensity of  $\text{SiO}_2\text{:Pr}^{3+}\text{:Ce}^{3+}$  with increasing  $\text{Ce}^{3+}$  concentration is demonstrated in the inset of figure 6.

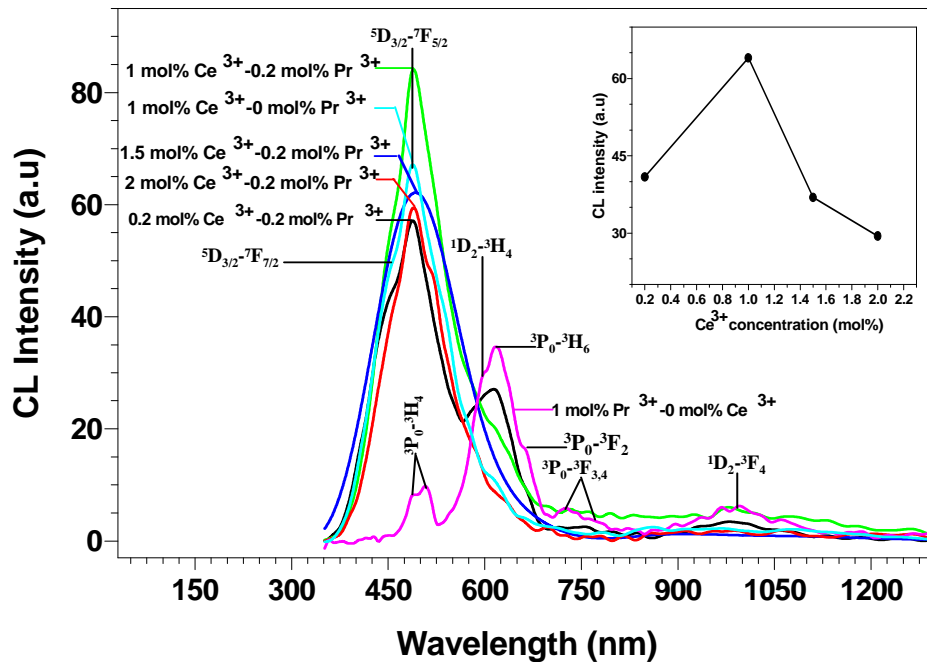


Fig. 6 CL emission spectra of the  $\text{SiO}_2:\text{Pr}^{3+}$  (1mol %),  $\text{SiO}_2:\text{Ce}^{3+}$  (1mol %), and  $\text{SiO}_2:\text{Pr}^{3+}$  (0.2mol %) -  $\text{Ce}^{3+}$  (0.2, 1, 1.5, 2mol %) irradiated with 2 keV, 8.5  $\mu\text{A}$  beam of electrons in a high vacuum chamber containing a base pressure of  $1.2 \times 10^{-8}$  Torr. The insert shows the CL intensity as a function of different  $\text{Ce}^{3+}$  concentrations.

#### 4. Conclusion

Enhanced red and blue emissions from  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  due to energy transfer from ZnO and  $\text{Pr}^{3+}$  respectively were demonstrated. The luminescence enhancement of  $\text{Pr}^{3+}$  due to energy transfer from ZnO to  $\text{Pr}^{3+}$  in  $\text{ZnO}:\text{SiO}_2:\text{Pr}^{3+}$  was confirmed by both PL and CL analysis. Addition of 1 mol%  $\text{Ce}^{3+}$  to 0.2 mol%  $\text{Pr}^{3+}$  led to quenching of  $\text{Pr}^{3+}$  emission while the blue emission from  $\text{Ce}^{3+}$  was slightly enhanced as compared to  $\text{SiO}_2:\text{Ce}^{3+}$  indicating an energy transfer from  $\text{Pr}^{3+}$  to  $\text{Ce}^{3+}$ . The excitation energy was most probably transferred by phonon mediated processes.

#### 5. Acknowledgements

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#### 6. References

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