The influence of Pr^{3+} co-doping on the photoluminescence and cathodoluminescence properties of $SiO_2:Eu^{3+}/Tb^{3+}$.

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Abstract. Tb^{3+}- Pr^{3+}, and Eu^{3+}- Pr^{3+} ion pairs co-doped in a SiO_2 matrix were prepared by a sol-gel method. Red and green photoluminescence associated with $^5D_0\rightarrow{}^7F_2$ $^5D_4\rightarrow{}^7F_5$ transitions of Eu^{3+} and Tb^{3+} singly doped in SiO_2 were observed at 614 and 543 nm respectively. Co-doping of Eu^{3+} and Tb^{3+} ions with Pr^{3+} in SiO_2 resulted in the quenching of Eu^{3+} and Tb^{3+} emissions with increasing Pr^{3+}concentrations. The quenching was also confirmed by cathodoluminescence measurements recorded from the same powders. The quenching effects are discussed.

1. Introduction

Enhanced luminescence induced by energy transfer between trivalent rare earth co-activators in host matrices has been demonstrated in nanophosphors. The enhanced luminescence is investigated in a variety of studies for potential application in different types of light emitting devices. Such studies have provided information about the interaction between the activators and the host matrix, as well as an insight in regard to the long-range interactions and energy transfer between the activator ions. For example, Mahato et al [1] studied energy transfer between Pr^{3+} and Tb^{3+} and observed that increasing the Pr^{3+} concentration reduced the emission intensity of Tb^{3+} while that of Pr^{3+} was enhanced indicating the energy transfer from the $^5D_4$ level of Tb^{3+} to the $^3P_0$ level of Pr^{3+}. Wang et al [2] observed the energy transfer from both $^1S_0$ and $^3P_0$ states of Pr^{3+} ions to Er^{3+} ions co-doped in $CaAl_{12}O_{19}$. In some cases, co-activators quench the luminescence intensity instead of enhancing it. For example, Meijerink et al [3] observed quenched luminescence of Pr^{3+} when Eu^{3+} and Pr^{3+} were co-doped in YF_3.

In the present paper, we have synthesized Pr^{3+} co-activated $SiO_2:Eu^{3+}/Tb^{3+}$ using the sol-gel method. The effect of Pr^{3+} co-doping in the luminescence properties under excitation of ultraviolet (UV) light and an electron beam was demonstrated. Fluorescence quenching effects due to Pr^{3+} co-doping are discussed.

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2. Experimental

SiO_2 phosphors co-doped with different concentrations of Pr^{3+}-Tb^{3+} ion pairs were prepared by mixing 0.05 mol of tetraethylorthosilicate (TEOS), 0.1 mol of H_2O, 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 $Pr(NO)_3.6H_2O$ dissolved in 5 ml of ethanol and was stirred for 30 minutes. A desired amount of $Tb(NO)_3.6H_2O$ 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. A similar procedure was used to prepare SiO_2:Pr^{3+}-Eu^{3+}phosphors with different concentrations of $Eu^{3+}$and Pr^{3+}.

The cathodoluminescence (CL) data of the samples were recorded using an Ocean Optics S2000 Spectrometer. The photoluminescence (PL) data were recorded using a DongWoo Optron Co. setup equipped with a Xe Arc lamp DL180-Xe. The particle morphology was analyzed using a JEOL 2100 High Resolution Transmission Electron Microscopy (HRTEM) while the chemical composition was analyzed by Energy Dispersive Spectrometer (EDS).

3. Results and discussion

3.1. HRTEM, particle morphology and size

Fig. 1 (a), (b), and (c) show the HRTEM images of SiO_2:Tb^{3+}-Pr^{3+}, SiO_2:Eu^{3+}-Pr^{3+}, and pure SiO_2, respectively. As indicated in Fig. 1 (c), pure SiO_2 was amorphous while fig. 1 (a) and (b) revealed the presence of smaller spherical particles enveloped in amorphous SiO_2. As confirmed by EDS data (not shown) these particles were composed of Pr, Eu, and Tb.

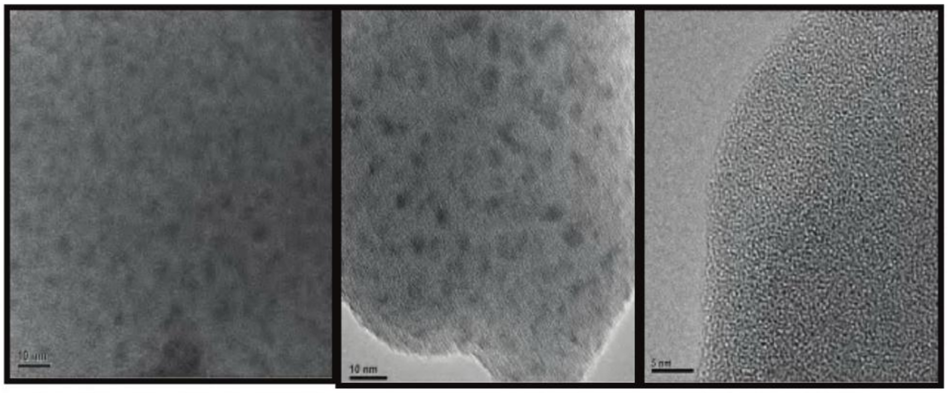

Fig. 1. HRTEM images of (a) SiO_2:Tb^{3+}-Pr^{3+}, (b) SiO_2:Eu^{3+}-Pr^{3+}, and (c) pure SiO_2.

3.2. Photoluminescence (PL) properties of SiO_2:Eu^{3+}-Pr^{3+} and SiO_2:Tb^{3+}-Pr^{3+}

In order to evaluate the effect of Pr^{3+} co-doping in SiO_2:Eu^{3+}, the PL properties were investigated. In fig. 2, the PL emission spectra of SiO_2:1 mol% Eu^{3+} and SiO_2:1 mol% Eu^{3+}-0.2 mol% Pr^{3+} obtained after excitation at 395 nm using a Xenon lamp are compared. It can be seen from the spectra that the emission associated with the $^5D_0 \rightarrow {}^7F_{J\ (J=0,1,2,3,4)}$ transitions of Eu^{3+} with the intense red emission at 614 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition was observed. The assignment of these emission peaks is in accordance with the previous work reported by Changqing et al [5] and Wang et al [6] for SiO_2:Eu^{3+} phosphors. It can be noticed from the spectra that the Eu^{3+} emission is well pronounced even after Pr^{3+}

co-doping and no emission from Pr^{3+} was observed, which indicates no contribution from Pr^{3+}. Also, the relative intensities of SiO_2:Eu^{3+} and SiO_2:Eu^{3+}-Pr^{3+} show that the luminescence from Eu^{3+} ion is strongly quenched due to addition of 0.2 mol% of Pr^{3+}. These results confirm the observation of Kandpal et al [7] for Pr^{3+}-Eu^{3+} ion pairs co-doped in a dimethylsulphoxide (DMSO) system.

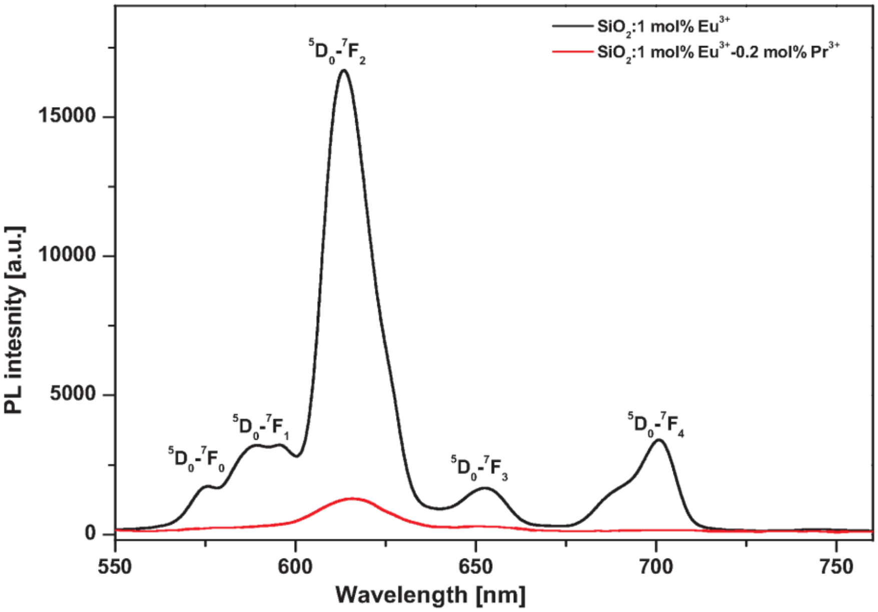

Fig. 2. Emission spectra of SiO_2:1 mol% Eu^{3+} and SiO_2:1 mol% Eu^{3+}-0.2 mol% Pr^{3+} obtained during excitation at 395 nm at room temperature.

The emission spectra of SiO_2:1 mol% Tb^{3+} and SiO_2:1 mol% Tb^{3+}-0.2 mol% Pr^{3+} are compared and shown in figure 3. These spectra were collected during excitation at 371 nm at room temperature. Both spectra exhibit green emission at 543 nm which can be attributed to the $^5D_4 \rightarrow {}^7F_5$ transition and the minor emission peaks associated with $^5D_4 \rightarrow {}^7F_{J\ (J\ =\ 0,1,2,3,4)}$ transitions of Tb^{3+} were also observed at 489, 543, 549, 584, 622 nm, respectively. These results agrees well with results reported elsewhere [1,8-10]. Again, when adding Pr^{3+} the luminescence intensity from Tb^{3+} was significantly quenched but to a lesser extent when compared to the data in Figure 2.

The strong quenching of the PL intensity is apparent from all Pr^{3+} co-doped SiO_2:Eu$^{3+/}$Tb^{3+} phosphor powders. There are two possible reasons which may cause this. First, the aggregation of Pr^{3+} ions or pairing of Pr^{3+} ions with Eu^{3+}/Tb^{3+} ions. Such a process leads to migration of excitation energy from one activator ion to its nearest ion by nonradiative transitions and via a large number of transfer steps, before the energy is released. During the transfer process, the energy can be transferred to defects which act as energy sinks within a transfer chain thus leading to a significant decrease in the PL intensity. In this case, it is most likely to happen that the energy may be exhausted by killer or/and defects during the energy transfer process among one kind of Pr^{3+} ions prior to the other kind of Tb^{3+}/Eu^{3+} ion. Secondly, it is also possible that the interaction between Pr^{3+}-Eu^{3+} and Pr^{3+}-Tb^{3+} ion pairs is through a Pr^{4+}-Eu^{2+} and Pr^{4+}-Tb^{2+} metal-to-metal charge transfer state and this energetically overlaps the Tb^{3+} ($^5D_4$) level or Eu^{3+} ($^5D_0$) level hence the strong quenching [3].

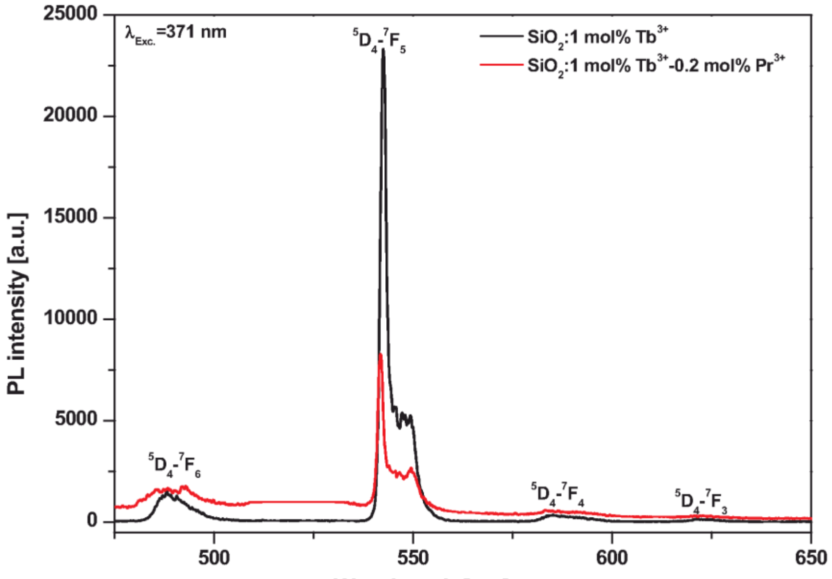

Fig. 3. Emission spectra of SiO_2:1 mol% Tb^{3+} and SiO_2:1 mol%Tb^{3+}-0.2 mol% Pr^{3+} obtained after excitation at 371 nm at room temperature.

3.3. CL properties of SiO_2: Eu^{3+}-Pr^{3+} and SiO_2: Tb^{3+}-Pr^{3+}

The CL properties of Pr^{3+} co-doped in SiO_2:Eu^{3+}/Tb^{3+} phosphor powders were also investigated under electron beam bombardment. In Fig. 4, the CL spectra of SiO_2:1 mol% Tb^{3+}, SiO_2:1 mol% Tb^{3+}-0.2 mol% Pr^{3+} phosphor powders obtained under irradiation with a 2 keV beam of electrons and 20 µA beam current in a high vacuum chamber at a base pressure of ~ 1.6 x 10^{-8} Torr are compared. It was realized that under electron beam excitation, both SiO_2:Tb^{3+} and SiO_2:Tb^{3+}-Pr^{3+} phosphor powders exhibited typical emission lines of Tb^{3+} and a significant decrease in Tb^{3+} emission with addition Pr^{3+} concentration was also observed. However, in comparison with the SiO_2:Tb^{3+}, SiO_2:Tb^{3+}-Pr^{3+} phosphor powders excited by UV light, extra emission peaks associated with the $^5D_3 \rightarrow {}^7F_{3,4}$ transitions of Tb^{3+} in the blue region can be obviously observed for identical samples in the CL spectrum in fig. 4. The insert in fig. 4 shows the CL intensity behavior of the phosphor powders when the concentration of Tb^{3+} is kept constant at 1 mol% while that of Pr^{3+} is varied from 0.2, 0.5, and 1 mol%. The Tb^{3+} emission was shown to significantly decrease with increasing Pr^{3+} concentration.

Fig. 5 presents the CL spectra of SiO_2:1 mol% Eu^{3+}, SiO_2:1 mol% Eu^{3+}-0.2 mol% Pr^{3+} phosphor powders under irradiation with a 2 keV, 20 µA electron beam in a high vacuum chamber containing a base pressure of ~ 1.6 x 10^{-8} Torr. Under electron beam irradiation, the addition of 0.2 mol% of Pr^{3+} into SiO_2:1 mol% of Eu^{3+} completely suppressed the Eu^{3+} emission and only emission from Pr^{3+} associated with *f-f* transitions from $^3P_0 \rightarrow {}^3H_4$, $^3H_6$, $^3F_2$, $^3F_{3,4}$ and $^1D_2 \rightarrow {}^3H_4$, $^3H_5$, $^3F_4$ with the main red emission at 614 nm assigned to $^3P_0 \rightarrow {}^3H_6$ was observed. It was realized that the CL intensity of SiO_2: Eu^{3+}-Pr^{3+} kept on dropping with increasing concentrations of Pr^{3+} (0.5 and 1 mol%) as shown in an insert in fig. 5. Such results confirm the observations of Zachau et al [11].

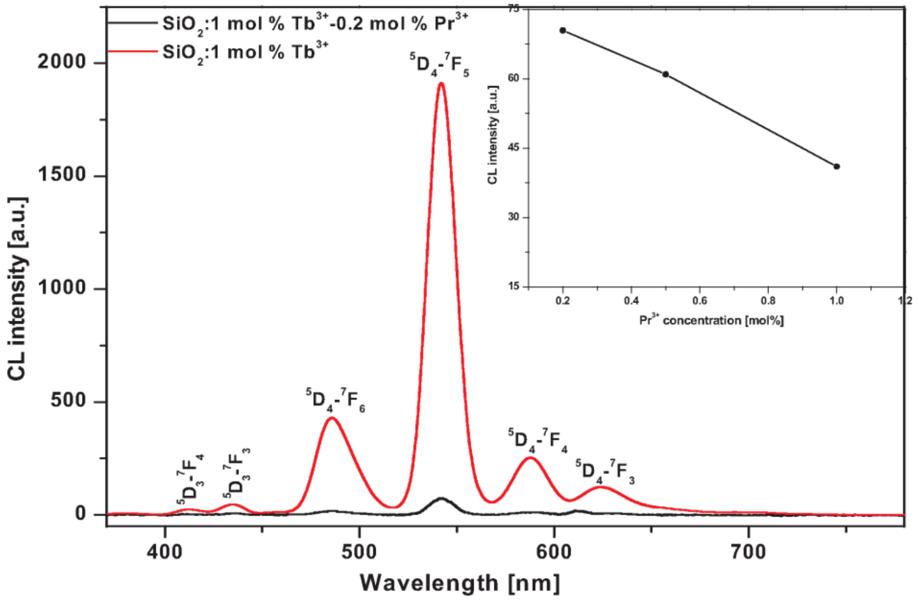

Fig. 4. CL intensities of SiO$_2$1 mol% Tb^{3+} and SiO$_2$:1 mol% Tb^{3+}-0.2 mol% Pr^{3+} at 2 keV, 20 µA in a high vacuum pressure of 1.6 x10^{-8} Torr. The inset shows the CL intensity from SiO$_2$:Pr^{3+}-Tb^{3+} as a function of 0.2, 0.5, and 1 mol% Pr^{3+} concentrations.

The CL analysis also revealed the strong quenching with Pr^{3+} addition of the luminescence from both SiO$_2$: Eu^{3+}-Pr^{3+} and SiO$_2$: Tb^{3+}-Pr^{3+} phosphor powders. However, we observed an obvious difference between the CL and PL spectra. Such difference between the CL and PL spectra obtained from phosphor samples may be attributed to two possible factors. First, the differences of the excitation mechanisms involved during the PL and CL. During the PL process, the photons used for excitation have energy less than the bandgap of the host matrix so that no electron-hole pairs are generated. While in the case of CL, the generation of charge carriers (electrons and holes) under irradiation by energetic electrons occurs through impact ionization. As a result, the accelerated electrons create a multiplicity of charge carriers and the excitation energy is transferred by excitons to luminescent centres. Secondly, in comparison with the UV excitation, the excitation intensity and excitation density of luminescence centres are very high under electron beam bombardment. For example, in the case of Tb^{3+} doped samples, the cross relaxation $^5D_3+^7F_6 \rightarrow ^5D_4+^7F_0$ may be depressed to some extent, hence, the appearance of the $^5D_3$ emission with electron beam irradiation.

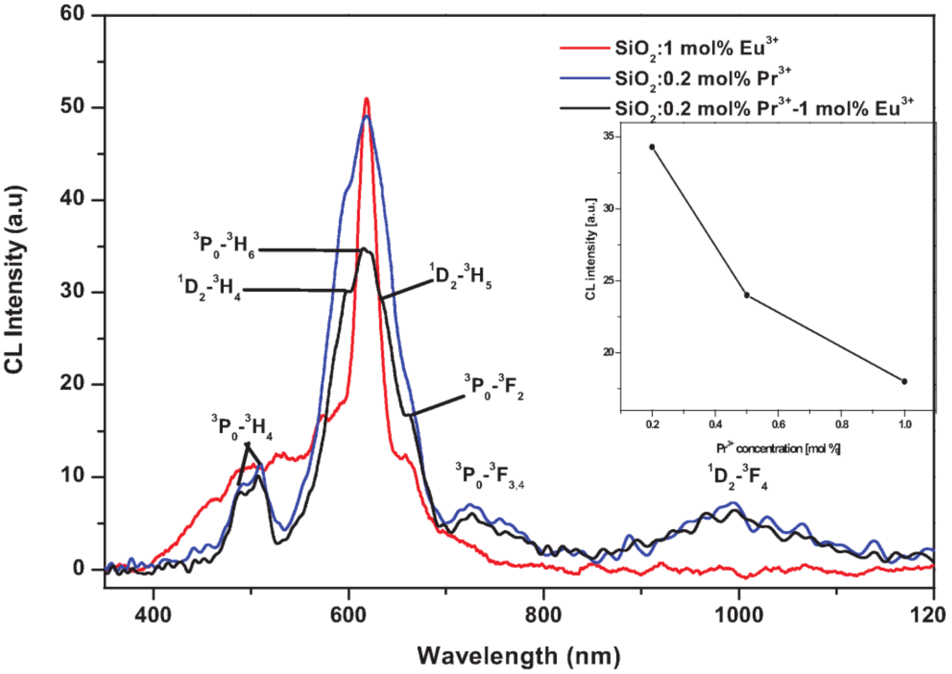

Fig. 5. CL intensities of SiO$_2$:1 mol% Eu^{3+}, SiO$_2$:0.2 mol% Pr^{3+}, and SiO$_2$:1 mol% Eu^{3+}-0.2 mol% Pr^{3+} at 2 keV, 20 µA in a high vacuum pressure of 1.6 x10^{-8} Torr. The inset shows the CL intensity from SiO$_2$:Pr^{3+}-Eu^{3+} as a function of 0.2, 0.5, and 1 mol% Pr^{3+} concentrations.

4. Conclusion

The CL and PL properties of SiO$_2$:Tb^{3+}/Eu^{3+} co-doped with Pr^{3+} derived from sol gel method were studied by varying the concentration of Pr^{3+}. The strong fluorescence quenching with increasing Pr^{3+} concentration was observed from both SiO$_2$:Tb^{3+}/Eu^{3+} co-doped with Pr^{3+} phosphor powders and no sign of Pr^{3+} emission was observed. The possible reasons which might have been the main cause of this quenching are discussed in detail.

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6. References

[1] Mahato K K, Rai S B, 2000 *Spectrochim. Acta Part A* **56** 2333-2340

[2] Wang X–J, Huang S, Lu L, Yen W M, Srivastava A M, Setlur A A, 2001 *Optics Comm.* **195** 405-410

[3] Meijerink A, Wegh R, Vergeer P, Vlugt T, 2006 *Opt. Mater.* **28** 575-581

[4] Mhlongo G H, Ntwaeaborwa O M, Dhlamini M S, Swart H C, Hillie K T, 2011 *J. Alloys Compd.* **509** 2986-2992

[5] Changqing H, Ting S, Weijian T, Baoping Z, 2006 *J. Rare Earths* **24** 134-137

[6] Wang R Y, 2004 *J. Lumin.* **106** 211-217

[7] Kandpal H C, Tripathi H B, 1979 *Solid State Comm.* **29** 139-142

[8] Liu X, Pang R., Li Q, Lin J, 2007 *J. Solid State Chem.* **180** 1421-1430

[9] Silversmith A J, Boye D M, Brewer K S, Gillespie C E, Lu Y, Campbell D L, 2006 *J. Lumin.* **121** 14-20

[10] Wakefield G, Keron H A, Dobson P J, Hutchison J L, 1999 *J. Phys. Chem. Sol.* **60** 503-508

[11] Zachau M, Zwaschka F, Kummer F, 1998 Proccedings- *Electrochem. Soc.* **97**(29) 314–324