Effects of ZnO and Ce$^{3+}$ incorporation on the photoluminescence and cathodoluminescence intensity of Pr$^{3+}$ doped SiO$_2$.

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Abstract. The successful incorporation of ZnO nanoparticles and Ce$^{3+}$ ions in Pr$^{3+}$ doped SiO$_2$ using a sol-gel process is reported. SiO$_2$:Pr$^{3+}$ gels, with or without ZnO and Ce$^{3+}$, were dried at room temperature and annealed at 600 °C. The Field Emission Scanning Electron Microscopy indicated clustered SiO$_2$ 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$_2$ matrix. The emission intensity from SiO$_2$:Pr$^{3+}$-Ce$^{3+}$ at 494 nm was slightly enhanced compared to Ce$^{3+}$ singly doped SiO$_2$. The red emission of Pr$^{3+}$ was enhanced when ZnO nanoparticles were incorporated in SiO$_2$ suggesting that energy was transferred from ZnO to Pr$^{3+}$. Possible energy transfer mechanisms between Pr$^{3+}$ and Ce$^{3+}$ and between ZnO and Pr$^{3+}$ are discussed in detail.

1. Introduction

Among rare earths, trivalent praseodymium (Pr$^{3+}$) 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$^{3+}$ 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...
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 Pr³⁺ induced by energy transfer from ZnO nanoparticles incorporated in situ in sol-gel silica under VUV and electron beam excitation. Energy transfer between Pr³⁺-Ce³⁺ co-doped in SiO₂ was also studied under electron beam excitation.

2. Experimental

2.1. Preparation of SiO₂:Ce³⁺-Pr³⁺ and ZnO:SiO₂:Pr³⁺

SiO₂:Pr³⁺ co-doped with different concentrations of Ce³⁺ phosphor samples were prepared by mixing 0.05 mol of tetraethylorthosilicate (TEOS), 0.1 mol of H₂O, 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)₃·6H₂O dissolved in 5 ml of ethanol and was stirred for 30 minutes. A desired amount of Ce(NO)₃·6H₂O 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 ZnO:SiO₂:Pr³⁺ nanocomposite phosphor was prepared by mixing the SiO₂:Pr³⁺ 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 SiO₂ nanoparticles calcined at 600 °C for 2 hrs. The image exhibits the agglomeration of mostly spherical SiO₂ particles with an average particle size in the range of ~20 to 120 nm in diameter. Similar morphology was observed for ZnO:SiO₂:Pr³⁺ and SiO₂:Pr³⁺-Ce³⁺ samples. Figure 2 (a) and (b) show the XRD patterns of SiO₂ 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 SiO₂ at 22°. The diffraction peaks of SiO₂:Ce³⁺-Pr³⁺ and ZnO:SiO₂:Pr³⁺ samples resembled that of pure SiO₂ probably due to the relatively low concentration of Pr³⁺ and the ZnO nanoparticles and/or high amorphous scattering background from the SiO₂ matrix [8]. The presence of the Pr³⁺,Ce³⁺ ions and ZnO nanoparticles in the phosphor powders (not shown) was confirmed by Electron Dispersive Spectroscopy (EDS).
3.2. PL and CL properties of ZnO-SiO$_2$:Pr$^{3+}$.

CL spectra of the SiO$_2$, SiO$_2$:0.2 mol% Pr$^{3+}$ and ZnO-SiO$_2$:0.2 mol% Pr$^{3+}$ nanophosphor powders excited by 2 keV electrons, at 20 µA beam current in a high vacuum chamber at a base pressure of ~1.6 x 10$^{-8}$ Torr are shown in figure 3. The CL spectrum of SiO$_2$ showed the emission peak at 445 nm which can be assigned to structural defects in the SiO$_2$ 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$^{3+}$ were observed from both SiO$_2$:Pr$^{3+}$ and ZnO-SiO$_2$:Pr$^{3+}$ samples. This emission can be assigned to the transitions originating from the $^3$P$_0$ and $^1$D$_2$ energy levels to the $^3$H$_{6,J=6,5,4}$ and $^3$F$_{J=2,3,4}$ energy levels all localized in the 4$f^2$ intra-configuration of the Pr$^{3+}$ ions with a dominant emission at 614 nm corresponding to the $^3$P$_0$$\rightarrow$$^3$H$_6$ transition. It was also noticed that there was no emission from ZnO nanoparticles (usually at ~370 and 560 nm), instead the red emission of Pr$^{3+}$ was enhanced when ZnO nanoparticles were incorporated. Lack of emission from ZnO nanoparticles and the subsequent enhancement of the red emission of Pr$^{3+}$ demonstrate sensitization of Pr$^{3+}$ emission centres by ZnO nanoparticles. That is, energy was transferred non-radiatively from ZnO to Pr$^{3+}$. The transfer was most probably by phonon mediated processes as previously reported [8-10].
Fig. 3 CL spectra SiO$_2$, SiO$_2$:0.2 mol% Pr$^{3+}$ and ZnO:SiO$_2$:0.2 mol% Pr$^{3+}$ irradiated with 2 keV, 20 µA beam of electrons in a high vacuum chamber containing 1.6 x 10$^{-8}$ Torr.

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

![Fig. 4 PL emission spectra of SiO$_2$:0.2 mol% Pr$^{3+}$ and ZnO:SiO$_2$:0.2 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.](image)
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 defect states of ZnO [9].

3.3. CL properties of SiO\(_2\) Ce\(^{3+}\)-Pr\(^{3+}\).
Figure 5 shows the CL emission spectra of SiO\(_2\): 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 \( 1.2 \times 10^{-8} \text{ Torr} \). The CL emission spectrum from SiO\(_2\):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 \( ^2\text{D}_{3/2} - ^2\text{F}_{7/2} \) and \( ^2\text{D}_{3/2} - ^2\text{F}_{5/2} \) of Ce\(^{3+}\), respectively [7].

![CL emission spectra of SiO\(_2\):Ce\(^{3+}\) (1 mol\%)](image)

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

The CL emission spectra of the SiO\(_2\):Pr\(^{3+}\), SiO\(_2\):Ce\(^{3+}\), and SiO\(_2\):Pr\(^{3+}\).Ce\(^{3+}\) (with different 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 \( 1.2 \times 10^{-8} \text{ Torr} \) are shown in figure 6. The CL emission spectra of SiO\(_2\):Ce\(^{3+}\)-Pr\(^{3+}\) showed both bands from Ce\(^{3+}\) in the blue spectral region and a small shoulder from Pr\(^{3+}\) in the red spectral region when the amount of Pr\(^{3+}\) and Ce\(^{3+}\) were both 0.2 mol\%. The small shoulder from Pr\(^{3+}\) was slowly quenched with increasing Ce\(^{3+}\) concentration and only blue emission from Ce\(^{3+}\) could be observed. Blue emission from Ce\(^{3+}\) was slightly enhanced with addition of 1 mol\% Ce\(^{3+}\) into 0.2 mol\% Pr\(^{3+}\) compared to singly doped SiO\(_2\):Ce\(^{3+}\). These results suggest the energy transfer from Pr\(^{3+}\) ions to its nearest neighbouring Ce\(^{3+}\) ions. In addition, it appears that at 1 mol\% of Ce\(^{3+}\), the Ce\(^{3+}\) neighbouring ions are close enough to each other for energy transfer from Pr\(^{3+}\) to Ce\(^{3+}\) to take place. An increase in 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 Ce\(^{3+}\) ions favoring quenching effect thus decreasing luminescence intensity. The quenching of the CL intensity of SiO\(_2\):Pr\(^{3+}\).Ce\(^{3+}\) with increasing Ce\(^{3+}\) concentration is demonstrated in the inset of figure 6.
Enhanced red and blue emissions from Pr$^{3+}$ in ZnO to Pr$^{3+}$ respectively were demonstrated. The luminescence enhancement of Pr$^{3+}$ due to energy transfer from ZnO to Pr$^{3+}$ in ZnO:SiO$_2$:Pr$^{3+}$ was confirmed by both PL and CL analysis. Addition of 1 mol% Ce$^{3+}$ to 0.2 mol% Pr$^{3+}$ led to quenching of Pr$^{3+}$ emission while the blue emission from Ce$^{3+}$ was slightly enhanced as compared to SiO$_2$:Ce$^{3+}$ indicating an energy transfer from Pr$^{3+}$ to Ce$^{3+}$. The excitation energy was most probably transferred by phonon mediated processes.

5. Acknowledgements
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6. References

Fig. 6 CL emission spectra of the SiO$_2$:Pr$^{3+}$ (1mol %), SiO$_2$:Ce$^{3+}$ (1mol %), and SiO$_2$:Pr$^{3+}$ (0.2mol %) - Ce$^{3+}$ (0.2, 1, 1.5, 2mol %) irradiated with 2 keV, 8.5 µA beam of electrons in a high vacuum chamber containing a base pressure of 1.2 x10$^{-8}$ Torr. The insert shows the CL intensity as a function of different Ce$^{3+}$ concentrations.