

Study of absorption, emission and EDS properties of Pr³⁺ incorporated in a SiO₂ matrix by sol-gel method

M Gómez-Miranda¹, C Velásquez Ordoñez² and R Sosa Fonseca¹

¹Physics Departement Universidad Autónoma Metropolitana- Iztapalapa, Distrito Federal, México PO BOX 55-532.

²Universidad de Guadalajara Centro Universitario de los Valles Centro de Investigación en Nanociencia y Nanotecnología de la Depto. de Ciencias Naturales y Exactas Ameca Jal. México

E-mail: marisol.gomez.miranda@gmail.com

Abstract

The optical response of the Pr³⁺ ions doped monolith of SiO₂ prepared by sol-gel method was investigated by absorption and emission spectra. The absorption spectrum shows some typical lines of Pr³⁺, with these data was made the diagram levels corresponding to SiO₂: Pr³⁺. The emission spectra were taken at 225 nm and 240 nm of wavelength of excitation was measured. In that there are reabsorption line at 423 of the Pr³⁺ ions in the emission host, that means that some kind of host-ion interactions exist. Red and NIR emission at 612 nm, 652 nm, 711 and 728 nm, respectively, from Pr³⁺ ions in SiO₂ was observed. The transition ¹S₀ → ³P₂ at 425 nm is observed because an effective radiative transfer between the silicate glasses host and the praseodymium ions is observed and discussed.

1. Introduction

Luminescent SiO₂ activated with trivalent rare earth are attractive due to their potential in technological applications. Narrow lines characterize the intra-4f emission spectra of rare earth ions due to the 4f electrons of rare earth ions are shielded by the outer 5s and 5p electrons from external forces, [1]. The positions of the 4f configuration energy levels are only slightly dependent on the host matrix, and are roughly the same as the free-ion levels. These unique properties are of interest in development of new materials with the capability to produce visible light with narrow lines for red, green, and blue phosphors. Trivalent praseodymium (Pr³⁺) has been used as an activator in various host matrices to prepare phosphors that can be used in different types of light emitting devices. Pr³⁺ ion has unique features, one of which is the ability to emit efficiently in the visible (VIS) to the infrared (IR) spectral regions depending on the host matrix and the ion concentration, [2,3]. Photoluminescence resulting from intra-4f-configurational transitions of rare earths ions embedded in inorganic glasses has been essential of a practical fibre amplifier, though some non-crystalline materials (including glass-ceramics sometimes) doped with transition metal ions or heavy metal ions are known to exhibit fluorescent emissions in the near-infrared wavelengths, [4]. On the other hand the sol-gel process had to be a good method to synthesize metallic oxides. In this were synthesized SiO₂ monoliths with praseodymium ions by sol gel technique. This material was optically characterized by absorption, emission and EDS measurements, which are presented and discussed here.



2. Experimental

All metal alkoxides, as well as, all solid reagents employed in this work, were acquired from Aldrich, while all solvents were purchased from Fluka. Sol-gel methods were used to produce monolithic silica xerogels doped with trivalent praseodymium ions. Continuous fluorescent spectra were obtained with a Perkin-Elmer model 650-10S spectrofluorometer equipped with a 150 W Xenon lamp, and the absorption was obtained from Cary 5 equip. The photoluminescence spectra emission and absorption of SiO₂: Pr³⁺ monoliths were analyzed in the range of 230 – 800 nm. And the Electron dispersion Scattering of X-Ray (EDS) measurements of the composition of the SiO₂: Pr³⁺ sample, was taken with a Scan Electron Microscope of high resolution HRSEM Jeol 7600F.

3. Results and Discussion

In figure 1(a), it is observed the absorption spectrum of SiO₂: Pr³⁺ from 400 nm to 800 nm, to RT. The inset shows details from 700 nm to 800 nm ranges. Absorption lines in 444nm, 449.5 nm, 468 nm, 481.5 nm and 589.5 nm are observed and they corresponding to ³P₂, ³P₁, ³P₀, ¹D₂ transitions, from ³H₄ level; and the ³F₄ → ³P₀ (at 732 nm) transition, respectively. With these data we make the diagram level and it appear in Figure 1(b). Radiative transitions (solid line) and no radiative transitions (dash line) observed in emission spectra are marked in figure 1b, too.

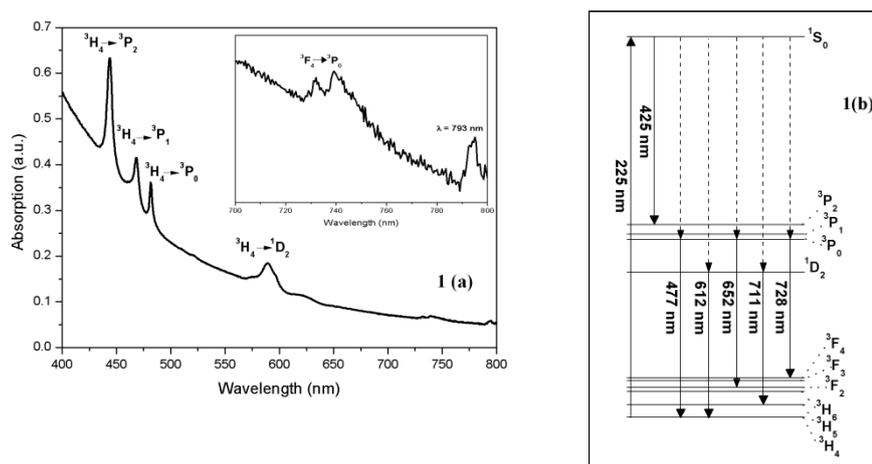


Figure 1. (a) Absorption spectrum of SiO₂: Pr³⁺ sol-gel monolith, (b) corresponding diagram levels.

Figure 2a, shows a characteristic RT emission spectrum of SiO₂:Pr³⁺ obtained to wavelength excitation at $\lambda_{exc} = 225$ nm and $\lambda_{exc} = 240$ nm, respectively. In the same figure the characteristic absorption spectrum of the same sample is shown. It consists of several sharp lines with transitions from the state ³H₄ to the excited state stark components of the 4f² configuration of the Pr³⁺ ion. The intensity of the spectra was adjusted in order to compare their shapes. In figure 2b, we present a comparison of both emission spectra and it is observe that there is a missing line at 425 nm; it is important to see that the wavelength excitation at 225 nm is a level energy corresponding to ¹S₀ → ³F₄ absorption transition from 4f5d configuration of Pr³⁺; whereas exciting at 240 we can observe a hole at the same wavelength. The reabsorption band in the intrinsic luminescence spectrum just appeared at the wavelengths where there is a transition of Pr³⁺, the ¹S₀ → ³P₂, at 425 nm proximately. It is observed because an effective radiative transfer between the silicates glasses host and the praseodymium ions occurred in our samples.

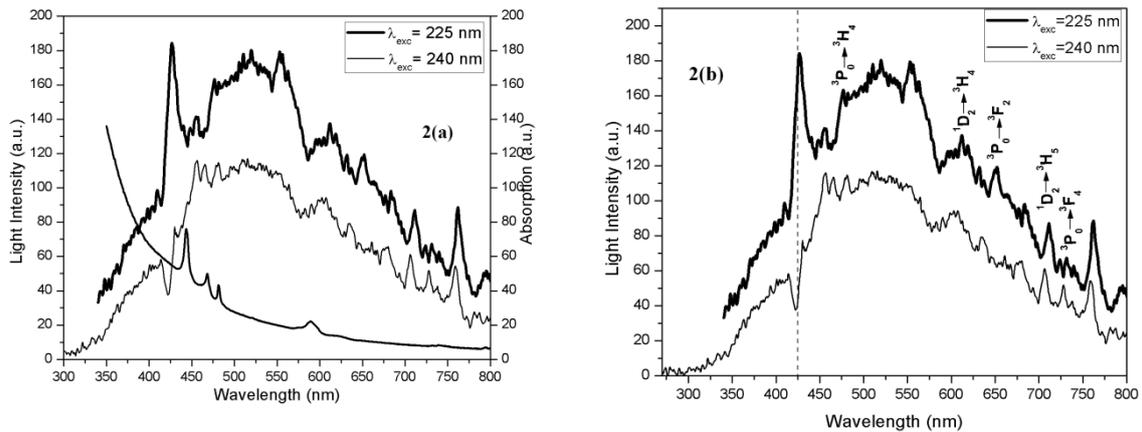


Figure 2. (a) Absorption and luminescence spectra measured to wavelength excitation 240 nm and 225 nm, respectively. (b) Identification of red and NIR transitions in the intrinsic emission of $\text{SiO}_2: \text{Pr}^{3+}$.

To account for the properties of the excited states it is applied a Gaussian fit deconvolution method to the optical absorption spectrum and it was evaluated the areas and the rate areas of each transition observed in absorption spectrum, see figure 3 and table 1. These were compared with reported data and it is observed that the $^3\text{H}_4 - ^3\text{P}_2$ transition is highest. Figure 4, shows the composition of our sample that consist of 16.11 ± 5.4 of C, 71.15 ± 3.6 of O, 12.49 ± 1.8 of Si, 0.20 ± 0.03 of Cl and $0.05\% \pm 0.02$ of Pr, all of them in atomic per cent. A homogeneous distribution of Pr ions in SiO_2 is presented in figure 5. It is relevant to know the dopant ions distribution to avoid the concentration quenching effect due to migration excitation energy among Pr^{3+} ions. Here we have enough low concentration of Pr^{3+} ions to consider it.

Table 1. Characteristics transitions of Pr^{3+} incorporated to SiO_2 glass with area under each absorption band, respectively.

| Transitions | Experimental Wavelength (nm) | Experimental Wave Number (cm^{-1}) | Reported Wavelength (nm) | Reported Wave Number (cm^{-1}) | Area | % Area |
|---|------------------------------|---|--------------------------|---|--------|--------|
| $^3\text{H}_4 \rightarrow ^3\text{P}_2$ | 444 | 22523 | 444 | 22520 | 737.05 | 28.30 |
| $^3\text{H}_4 \rightarrow ^1\text{I}_6$ | 449.5 | 22247 | 450 | 22211 | 126.43 | 4.85 |
| $^3\text{H}_4 \rightarrow ^3\text{P}_1$ | 468 | 21368 | 469.4 | 21330 | 211.13 | 8.11 |
| $^3\text{H}_4 \rightarrow ^3\text{P}_0$ | 481.5 | 20768 | 481.9 | 20750 | 109.78 | 4.21 |
| $^3\text{H}_4 \rightarrow ^1\text{D}_2$ | 589.5 | 16964 | 593.8 | 16840 | 211.01 | 8.10 |

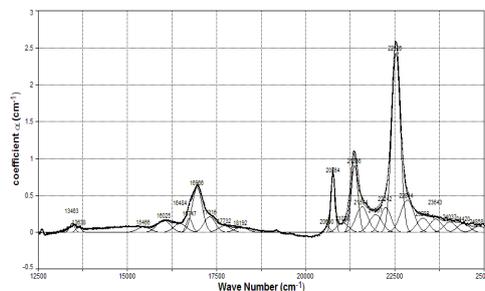


Figure 3. Gaussian fit of absorption spectra to account the individual intensity of optical transitions of the Pr^{3+} .

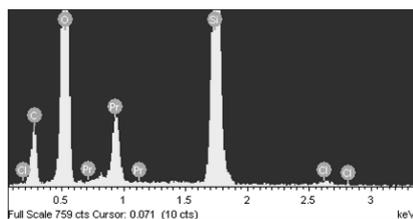


Figure 4. Electron by Dispersion Scattering X-Ray technique about the composition of $\text{SiO}_2:\text{Pr}^{3+}$ samples.

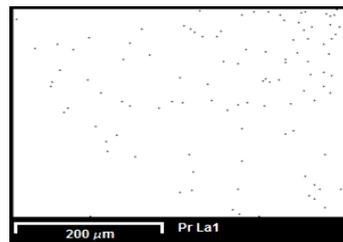


Figure 5. Photography of the Pr^{3+} ion distribution obtained by EDS spectroscopy.

4. Conclusions

Red and NIR emission at 612 nm, 652 nm, 711 and 728 nm, that corresponding to $^3\text{P}_0 - ^3\text{H}_4$, $^3\text{F}_2$ and $^3\text{F}_4$ and from $^1\text{D}_2 \rightarrow ^3\text{H}_4$, $^3\text{H}_5$, respectively, from Pr^{3+} ions in SiO_2 was analysed. Reabsorption line at 423 of the Pr^{3+} ions in the emission host is observed when we exciting at 240 nm but when $\lambda_{\text{exc}} = 225$ nm it is observed a peak at 425 nm, associated to the transition $^1\text{S}_0 \rightarrow ^3\text{P}_2$ at 425 nm. It is because an effective radiative transfer between the silicate glasses host and the praseodymium ions is observed and discussed. The possible mechanism of energy transfer from host SiO_2 to Pr^{3+} was discussed.

Acknowledgments

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References

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