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Introduction

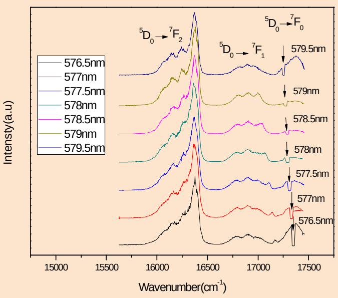
Silicophosphates (SiO_2-P_2O_5) glasses doped with Eu^{3+} ions have been synthesized by the sol–gel process with different Si/P/Eu molar ratios. Optical properties of these glasses were investigated by means of emission spectra and lifetime measurements. The fluorescence line narrowing (FLN) technique has been used in order to explore the local structure around the Eu^{3+} ions in this host and to understand the role of phosphate as a codopant. As it is the case for aluminum **[1],** the ability of phosphate to avoid the rare-earth clustering can be explained by its propensity to modify the local order around the rare-earth ion through a structuring effect. The analysis of our FLN and decay measurements is consistent with this interpretation.

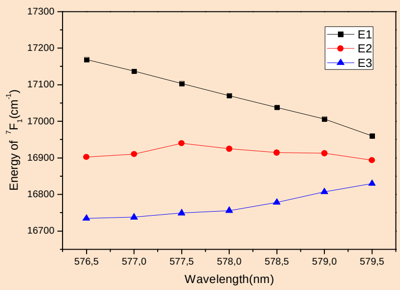
Synthesis of studied structures by sol-gel method

The sol-gel process, having the advantage of using a mixture of liquid precursors of high purity, uniform and stable at the molecular level, is particularly well suited to the insertion of molecular species in transparent matrices. In the present work, silicophosphates gels were prepared via hydrolysis and condensation of tetraethoxysilane (TEOS), triethylphosphate (TEP), ethanol (C_2H_5-OH) and distilled water (H_20), in presence of hydrochloric acid (HCl). Europium was introduced in the initial stage of the process, by dissolving hydrated europium nitrate Eu $(NO_3)_3.5H_20$ in the mixture of HCl and water **[2]**.

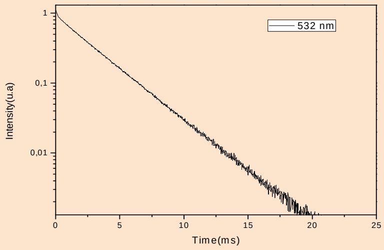
Results

The fluorescence line-narrowing spectra of 1mol% Eu^{3+} doped sample of sol-gel silicophosphate with Si/P/Eu=1/0.1/0.01 molar ratio densified at 900°C was investigated. The spectra were obtained by selective excitation within the inhomogeneously broadened $^7F_0 \rightarrow {}^5D_0$ absorption band. Intensities are normalized to the most intense $^5D_0 \rightarrow {}^7F_1$ peak.

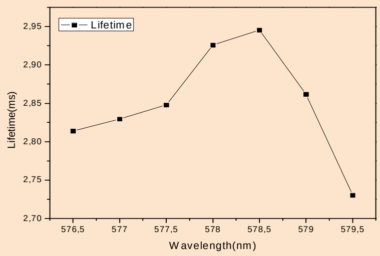




The average peak position energies of the three $^7F_1$ bands of Eu^{3+} in silicophosphate glass are plotted as a function of the excitation wavelength within the $^7F_0 \rightarrow {}^5D_0$ excitation band.



The lifetimes of 1mol% Eu^{3+} doped sample was measured at green excitation (532 nm) and at different excitation wavelengths along the $^7F_0 \rightarrow {}^5D_0$ absorption band. The luminescence was collected at 612 nm within the $^5D_0 \rightarrow {}^7F_2$ band and measurements were performed at 77K. The results show a two-step behavior as excitation wavelength increases which supports the existence of at least two broad varieties of Eu^{3+} sites.



The crystal field strength parameter decreases with the increase of the excitation wavelength but with a change in the slope. That is consistent with the results obtained by the decay measurements.

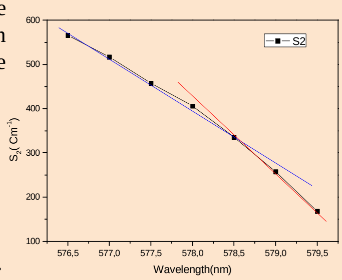
$$S_2 = \sqrt{\frac{1}{5}\left(B^2{}_{20} + 2B^2{}_{22}\right)}$$

$$B_{22} = \frac{5}{\sqrt{6}}\,(E_3 - E_1)$$

$$B_{20} = -5/3(E_3 + E_1 - 2E_2)$$

B_{22} , B_{20} : Crystal field's parameters.

E_1 , E_2, E_3 : Energies of the three $^7F_1$ bands of Eu^{3+} .



The strong decrease of the average crystal parameter S_2 suggests a large variation in the local environment for the Eu^{3+} ions in this glass.

It's shows an intermediate behavior between a pure phosphate and a pure silicate. This combination of properties can be understood by taking into account the mixed nearest-neighbor coordination, as the influence of the local environment in the Eu^{3+} spectra not only depends on the geometrical changes of coordination but also on the nature of the coordinating species.**[3]**

Conclusion

The effect of phosphate codoping in europium-doped silica glasses was investigated using both FLN technique and decay times at different excitation wavelengths.

The wavelength dependence of lifetimes shows a two-step behavior as excitation wavelength increases which supports the existence of at least two broad varieties of Eu^{3+} sites. This result is also confirmed by the crystal parameter S_2 analysis.

The study of other concentrations is in progress.

References

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