New fluorophosphate glasses doped with Eu^{3+} - Structural and spectroscopic properties

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In recent years, rare earth containing glasses have attracted much attention for their applications in lighting, laser systems and optical communication devices. Particular attention has been given to oxyfluoride glasses and glass ceramics with the potential to combine the characteristic advantages of low phonon energy fluorides and the higher chemical stability and mechanical strength of the oxides. In this work, glasses with nominal composition $25BaF_2$-$25SrF_2$-(30- x)$Al(PO_3)_3$-$xAlF_3$-(20-z)YF_3:$zEuF_3$ with x = 25, 20, 15 or 10, Eu = 0.25, 2, 3, 4, 5 mol% were prepared by conventional melt quenching techniques in Pt crucibles. Homogeneous mixtures of reagent grade precursors were melted at 1100 °C for 5 min, quenched between copper plates and heat treated for 8 h at 400 °C. The dopant ion Eu^{3+} was chosen due to its importance as a structural probe. The hypersensitive electric dipole $^5D_0 \rightarrow {}^7F_2$ transition at around 612 nm is highly dependent on the chemical environment of Eu^{3+}, whereas the intensity of the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition at 590 nm does not depend on the local ligand field. Because of that one can see that, in the photoluminescence spectra of Eu^{3+}-doped samples, the intensity ratio I_{612}/ I_{590}, the normalized phonon sideband intensities in the excitation spectra, and the excited state $^5D_0$ lifetime values are systematically dependent on the fluoride content in oxyfluoride based glasses. Altogether, the results in this work indicate that the rare-earth ions are found in a mixed fluoride/phosphate environment, to which the fluoride ions make the dominant contribution. Nevertheless, even at the highest fluoride levels (x = 25), the data suggest residual rare-earth−phosphate coordination. In order to study the environment of the dopant ion pulsed EPR spectroscopy of the Yb^{3+} spin probe (S = 1/2) was employed, revealing composition-dependent echo-detected lineshapes and strong hyperfine coupling with ^{19}F nuclei in hyperfine sublevel correlation (HYSCORE) spectra consistent with the formation of Yb^{3+}−F bonds. Lifetime and quantum yields were measured for all doped glasses and we obtained similar results using two analysis methods.