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STRUCTURE AND CRYSTALLIZATION OF FLUOROZIRCONATE GLASSES. STUDY BY THE FLUORESCENCE OF Pr^{3+} IONS

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ABSTRACT

The $^1\text{D}_2 \rightarrow ^3\text{H}_4$ fluorescence in fluorozirconate glasses has been studied in non-heated and heated samples. From spectra and decays, several informations were obtained. Two types of crystals grow in this glass. By thermal treatment at T_g a demixion of the constituents appears. It was impossible to obtain transparent vitroceraamics.

INTRODUCTION

Several different fluorozirconate glasses provided by the Laboratoire de Chimie Minérale D, University of Rennes, have been studied. We present here the results obtained with ZBA (58.5 %, ZrF_4 , 34.5 % BaF_2 , 7 % AlF_3) doped with Pr^{3+} ions (PrF_3 is substituted for AlF_3).

Several studies of Pr^{3+} fluorescence in fluorozirconate glasses have been published ^{1,2}. The study of $^1\text{D}_2 \rightarrow ^3\text{H}_4$ fluorescence is described in this communication.

EXPERIMENTAL RESULTS

The $^1\text{D}_2 \rightarrow ^3\text{H}_4$ fluorescence is detected after excitation at 5827 Å in the highest sublevels of the split $^1\text{D}_2$ level of Pr^{3+} ions. Due to the large inhomogeneous broadening the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ is very wide. In figure 1, the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ emission in non heated glass and heated 24h at 330°C are compared. The heated sample was crystallized and translucent. From this crystallized sample appeared four lines. The characteristics of the two higher lines (shape and decay) were identical, and it is assumed that

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they come from Pr^{3+} ions in same microcrystals and same sites. Some assumption is done for the two lower lines. It is concluded that two principal types grow in fluorozirconate glasses. The ${}^1D_2 \rightarrow {}^3H_4$ emission from non heated sample is the envelope of the

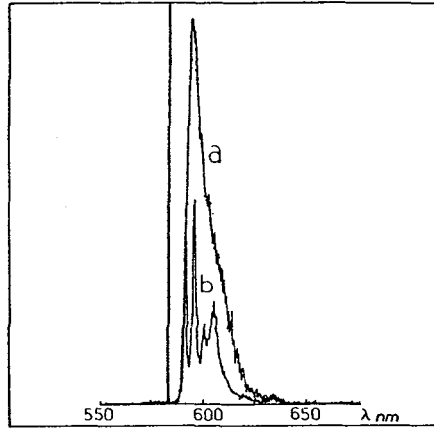


Figure 1 - ${}^1D_2 \rightarrow {}^3H_4$ fluorescence after excitation at 5827 \AA from ZBA.

Pr^{3+} 5 % at $T = 4\text{K}$. (a) non-heated glass; (b) heated 24h at 330°C under 10^{-3} torr, crystallized sample.

corresponding emission in crystallized samples. Consequently it is suggested that at the two types of microcrystals correspond two major types of sites for Pr^{3+} ions in glass. This confirms the conclusion from Eu^{3+} optical spectroscopy³.

Decays obey perfectly the Inokuti-Hirayama⁴ or rather Klafter-Blumen⁵ model :

$$\Phi(t) = \exp\left[-\frac{t}{\tau_0} - p \Gamma\left(1 - \frac{D}{s}\right) \left(\frac{t}{\tau_0}\right)^{D/s}\right]$$

Cross-relaxation between excited and non excited Pr^{3+} ions in pairs is induced by dipole-dipole interaction ($s=6$). For non heated samples the dimensionality D is found equal to 3 and p is proportional to the Pr^{3+} concentration, as expected.

After heat-treatments at the temperature T_g of glass transition, D was found smaller ($D \sim 2.75$) (Fig. 2). The change of dimensionality is explained by a spinodal demixtion of the glass constituents. The structure of one constituent in the other would be fractal, this fractal structure would be reflected on the Pr^{3+} ion distribution and on the ${}^1D_2 \rightarrow {}^3H_4$ fluorescence decay.

This demixtion without crystallization was confirmed by the elastic light scattering. Furthermore it appeared that demixtion is prior to crystallization. Consequently nucleation and very small microcrystals ($<500 \text{ \AA}$), were not observed. And it was impossible to obtain transparent vitroceramics.

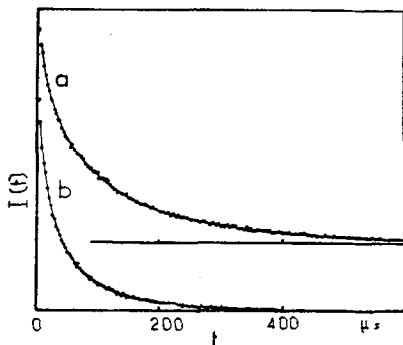


Figure 2 - Decays at room temperature of the ${}^1D_2 \rightarrow {}^3H_4$ fluorescence from non-heated ZBA glasses fitted by the Inokuti-Hirayama model. (a) ZBA 0.5%, $D=3.00$, $p=2.14$; (b) ZBA 1% $D=3.00$, $p=4.14$.

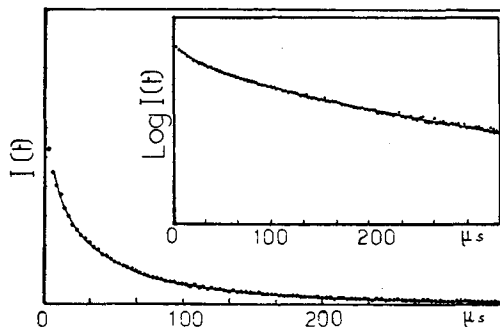


Figure 3 - Decay at room temperature of the ${}^1D_2 \rightarrow {}^3H_4$ fluorescence from ZBA Pr^{3+} 1% heated 24h at 310°C (T_g) under 10^{-3} torr, fitted by the Klafter-Blumen model : $D = 2.75$ $p = 4.30$.

CONCLUSION

The initial aim of this work was to observe small microcrystals in fluorozirconate glasses, and to obtain transparent vitroceraamics for laser application. The demixtion prior to crystallization makes impossible to obtain such transparent laser vitroceraamics from fluorozirconate glasses.

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