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

M. Ferrari, J. Rousset, A. Boukenter, A. Boyrivent, E. Duval, A. Monteil

► To cite this version:

M. Ferrari, J. Rousset, A. Boukenter, A. Boyrivent, E. Duval, et al.. STRUCTURE AND CRYSTALLIZATION OF FLUOROZIRCONATE GLASSES. STUDY BY THE FLUORESCENCE OF Pr^{3+} IONS. Journal de Physique Colloques, 1987, 48 (C7), pp.C7-463-C7-465. 10.1051/jphyscol:19877110 . jpa-00226927

HAL Id: jpa-00226927

<https://hal.science/jpa-00226927>

Submitted on 1 Jan 1987

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

M. FERRARI⁽¹⁾, J.L. ROUSSET, A. BOUKENTER, A. BOYRIVENT,
E. DUVAL and A. MONTEIL

*Laboratoire de Physico-Chimie des Matériaux Luminescents,
CNRS UA-442 et Université Claude Bernard, Lyon I,
43, Bd du 11 novembre 1918, F-69622 Villeurbanne Cedex,
France*

ABSTRACT

The $^1\text{D}_2 \rightarrow ^3\text{H}_4$ fluorescence in fluoro-zirconate 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 demixtion of the constituents appears. It was impossible to obtain transparent vitroceramics.

INTRODUCTION

Several different fluoro-zirconate 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 fluoro-zirconate 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

⁽¹⁾ Sponsored by European Economic Community

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 $^1\text{D}_2 \rightarrow ^3\text{H}_4$ emission from non heated sample is the envelope of the

Figure 1 - $^1\text{D}_2 \rightarrow ^3\text{H}_4$ fluorescence after excitation at $5827 \text{ \AA}$ 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 spectroscopy ³.

Decays obey perfectly the Inokuti-Hirayama ⁴ or rather Klafter-Blumen ⁵ 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 $^1\text{D}_2 \rightarrow ^3\text{H}_4$ 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 $310^\circ C$ (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 vitroceramics for laser application. The demixtion prior to crystallization makes impossible to obtain such transparent laser vitroceramics from fluorozirconate glasses.

REFERENCES

1. M. Eyal, E. Greenberg, R. Reisfeld and N. Spector, Chem. Phys. Lett. 177, 108 (1985).
2. J.L. Adam and W.A. Sibley, J. Non Cryst. Solids 76, 267 (1985).
3. J.L. Adam, V. Ponçon, J. Lucas and G. Boulon, J. Non Cryst. Solids 91, 191 (1987).
4. M. Inokuti and F. Hirayama, J. Chem. Phys. 43, 1978 (1965).
5. J. Klafter and A. Blumen, J. Chem. Phys. 80, 875 (1984).