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Environment of Pr in fluorozirconate glasses: an XAFS and anomalous X-ray scattering study

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We present a combined X-ray Absorption and Anomalous X-ray Scattering (AXRS) study of the local atomic structure around Pr in fluorozirconate glasses. Exploiting the high flux available at high energy at third generation sources, Pr K-edge (≈ 42 keV) data was taken at the GILDA beamline of ESRF. We present data obtained with both techniques on a Pr-doped (10000 ppm), unmodified, fluorozirconate glass, which complement our recently published EXAFS investigation on modified glasses. The common conclusion is that the local Pr environment is independent from the doping precursor and that no first or second shell Pr-Pr correlations are present, even in samples having a Pr³⁺ concentration of 10000 ppm, i.e. one order of magnitude higher than the concentration quenching limit.

Keywords: Fluorozirconate glasses, Pr³⁺ dopant, anomalous scattering

1. Introduction

Pr doped optical fibres have been intensively studied in the last ten years because of the interest in signal amplification in telecommunication systems at the wavelength of 1.3 μm . Among them, Pr-doped ZBLAN (ZrF₄-BaF₂-LaF₃-AlF₃-NaF) fibres are considered very promising. The lifetime (τ) of the ¹G₄ level of Pr in ZBLAN glasses is only around 110 μs and is closely related to the concentration of Pr³⁺ in the glass. It is generally believed that, at low concentration, Pr³⁺ must be uniformly dispersed by non-bridging fluorine atoms in the glasses. When the concentration of Pr³⁺ reaches 1000 ppm τ significantly decreases; this is the so-called concentration quenching effect (Ohishi *et al.*, 1991), the structural origin of which is unclear at present. It has been suggested (Zhang *et al.*, 1997) that the lifetime of the metastable ¹G₄ level in Pr³⁺ could be increased by modifying the local structure in a high phonon energy host by incorporating other dopants or phases with low phonon energy; the structural implications of this suggestion are unclear. It therefore is of great interest to study the environment around Pr³⁺ in the glass host. We have recently published (Braglia *et al.*, 1998) an EXAFS study on a set of modified samples (named ZYSAN, see next section), demonstrating that the first shell environment of Pr is always very similar to that of PrF₃, independent of Pr concentration or

the nature of the dopant used. Here, we report new results on this issue, employing both EXAFS and AXRS to probe the local structure in unmodified ZBLAN samples. The EXAFS and AXRS techniques are largely complementary since the former probes with high accuracy the nearest neighbor distribution while AXRS gives more detailed information on medium range ordering.

2. Experimental

For the present EXAFS and AXRS investigation two ZBLAN (53ZrF₄-20BaF₂-4LaF₃-3AlF₃-20NaF, mol%) samples, one doped with PrF₃ (10 000 ppm), the other undoped, were prepared (Braglia *et al.*, 1996). In our previous investigation a series of ZYSAN samples (53ZrF₄-20SrF₂-4YF₃-3AlF₃-20NaF (mol%)) were *ad hoc* prepared for EXAFS measurements. This composition originated from the standard ZBLAN glass with the substitution of BaF₂ with SrF₂ and LaF₃ with YF₃ to eliminate the fluorescence of heavy atoms. Photoluminescence (PL) investigations (Braglia *et al.*, 1999) showed that ZYSAN and ZBLAN glasses have identical emission bands, supporting the underlying hypothesis that the environment of Pr is the same in the two sample types.

Pr K-edge EXAFS and AXRS spectra were recorded at room temperature at the "GILDA" BM8 CRG beamline (ESRF, Grenoble). The Si(511) monochromator was operated in a dynamically sagittal focussing mode (Pascarelli *et al.*, 1996). The EXAFS measurements were performed in the transmission mode for the PrF₃ model compound, and in the fluorescence mode for the ZBLAN sample. For the fluorescence measurements a plastic scintillator operated in the current mode was used; use of this previously unavailable detector made the measurements possible on the unmodified ZBLAN samples. Non-anomalous XRS measurements were performed on both doped and undoped ZBLAN samples at 30 keV using a NaI scintillation detector. AXRS measurements (Meneghini *et al.*, 1998) were performed on the doped ZBLAN sample at 41 and 41.995 keV using a Si(111) crystal analyzer on the diffracted beam to remove the background. XRS data were recorded in the q-range 0.1–23 \AA^{-1} . The data were treated using standard methods to subtract Compton scattering, to correct for volume and absorption effects and for data normalization (Magini *et al.*, 1988). More details can be found in the electronic archive of these proceedings.

3. Results and discussion

In Fig. 1 we show (dots) the raw, background subtracted, k-weighted EXAFS data for PrF₃ and for a 10 000 ppm Pr-doped ZBLAN sample. In order to perform a quantitative analysis, the first shell contribution was isolated by performing a Fourier transform in the range 2.3 to 10.3 or 14.2 \AA^{-1} for ZBLAN or PrF₃, respectively, and an inverse Fourier transform in the range 1.36 to 2.34 \AA . The first shell around Pr in crystalline PrF₃ is composed of 11 F atoms (Cheetham *et al.*, 1976) which can be grouped in four subshells (3 atoms at 2.38 \AA , 4 atoms at 2.44 \AA , 2 atoms at 2.59 \AA and 2 atoms at 2.95 \AA)[#]. The EXAFS

[#] A more accurate determination of the first shell interatomic distances than that reported in Braglia *et al.* (1998) has been performed, following Cheetham *et al.* (1976). Consequently, the values here reported are slightly different from the ones previously used; the difference between the values of the Debye-Waller factors here obtained (see Tab. 1) and the ones previously reported, also for PrF₃, is due to this improvement.

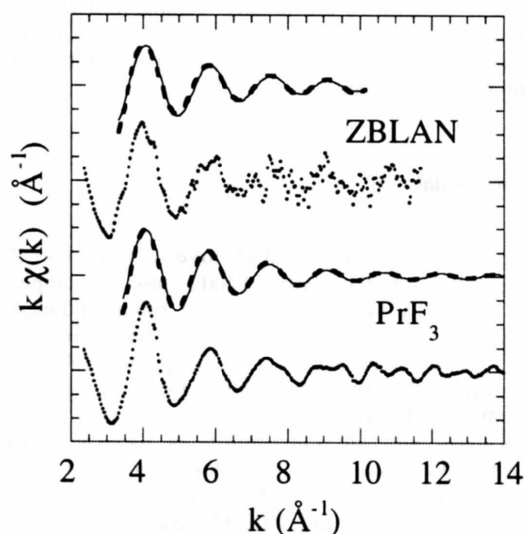


Figure 1

k-weighted EXAFS data for the PrF_3 model compound and for the Pr-doped ZBLAN sample: raw data (dots), first shell contribution (dashed line) and its fit (continuous line).

signal of PrF_3 was well reproduced by including theoretical contributions (McKale *et al.*, 1988) relative to these subshells (with fixed distances and coordination numbers), the only difference being that the subshell at 2.95 Å gave a negligible contribution; each subshell was taken to have a Gaussian pair distribution function. It was found that the signal from the Pr-doped ZBLAN sample could be fitted very well exactly in the same way, the only difference being in the values of the Debye-Waller factors which were used as free parameters (see Tab. 1); fits were performed with four free parameters (five for PrF_3) and are shown in Fig. 1 as the continuous line. The present data thus extend the previously obtained result: also in the unmodified ZBLAN glasses, at a concentration at which concentration quenching occurs, the Pr first shell closely resembles that of PrF_3 and there is no evidence of Pr-Pr bonds. XRS measurements were performed in order to obtain some information on shells more distant than the first. In Fig. 2 (top panel) we report the total pair correlation function, $G(r)$, of doped and undoped ZBLAN glasses obtained at 30 keV. In a first approximation, $G(r)$ can be expressed as a weighted sum of partial pair correlation functions $g_{\alpha\beta}(r)$: $G(r) = \sum_{\alpha\beta} W_{\alpha\beta} g_{\alpha\beta}(r)$ where α, β represent the atomic species present in the sample. From evaluation of the $W_{\alpha\beta}$ factors and structural considerations the main contributions to $G(r)$ are Zr-F at 2.1 Å, Ba-F at 2.6 Å and Zr-Ba, Zr-Zr and Ba-Ba at 4.1 Å, while for higher distances all correlations are smoothed out. In order to single out the partial $g_{\text{PrF}}(r)$ function from the total $G(r)$, we performed an anomalous XRS experiment on the Pr-doped ZBLAN sample; we chose the energies of 41.000 and 41.995 keV to maximize the anomalous effect for Pr while minimizing

Analysis of the ZYSAN samples with the present, correct, distances yields results which can be compared to those for ZBLAN. The use of different distances does not affect the conclusions of the previous work on ZYSAN.

the effect of all the other elements. The differential correlation function $\Delta G_{\text{Pr}}(r)$, calculated following the procedure described in Buffa *et al.* (1992), is reported in the lower panel of Fig. 2. The $\Delta G_{\text{Pr}}(r)$ shows two main contributions at ≈ 2.6 and 5 Å. The oscillations below 2 Å are due to truncation effects.

Table 1

EXAFS fitting results for the Pr-F first shell

	$\sigma_1 (10^{-2} \text{ \AA})$	$\sigma_2 (10^{-2} \text{ \AA})$	$\sigma_3 (10^{-2} \text{ \AA})$
	± 4	± 1	± 2
PrF_3	16	4	4
Pr-doped ZBLAN	23	6	8

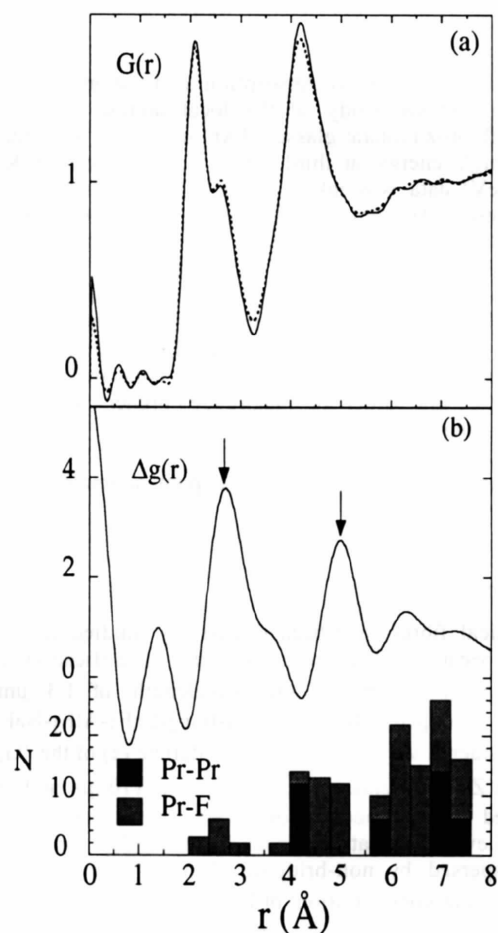


Figure 2

(a) Experimental $G(r)$ of undoped (full line) and Pr-doped ZBLAN samples (dashed line); (b) differential correlation function $\Delta G_{\text{Pr}}(r)$ of the doped glass (full line) and (histogram) the expected Pr-F and Pr-Pr correlations in PrF_3 .

The histograms reported in the lower part of Fig. 2 represent the Pr-Pr and Pr-F correlations calculated on the basis of the PrF₃ crystal structure. The peak at ≈ 2.6 Å is in fair agreement with the weighted average of the Pr-F correlations in PrF₃ at 2.54 Å. On the contrary, the peak at 5 Å does not correspond to the Pr-Pr second shell correlations in the model compound. The AXRS data thus confirm the EXAFS first shell results and provide us with the new information that no Pr-Pr clustering in the second shell, with a structure similar to that of PrF₃, occurs, even at 10 000 ppm Pr concentration.

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