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Spectroscopic investigation and crystallization study of rare earth metaborate glasses

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Abstract

Besides their interesting optical properties, Rare Earths (RE) can be found abundantly as fission products at the end of the nuclear fuel cycle. After reprocessing, they are stored by dissolution in a borosilicate glassy matrix. RE are also used to simulate actinides when studying nuclear waste immobilization. It is very important to understand the environment of RE in such complex glasses. Moreover, composition changes can strongly affect RE solubility in the glass melt and RE-rich phases (such as RE-silicate apatite) can crystallize during cooling. As boron oxide seems to play an important role on the solubility of RE by preventing the crystallization of RE-rich phases, we focused our study on a system containing only B₂O₃ and RE₂O₃ (with RE= La or Nd), and more precisely on the RE-metaborate composition RE₂O₃.3B₂O₃. As this glass, which has a congruent crystallization, is thought to have a structure similar to the corresponding crystalline phase REB₃O₆, we intended to go further in the understanding of its structure using ¹¹B MAS NMR, EXAFS at the Nd-L_{III} edge and optical absorption. The crystallization behavior of the glasses thermally treated was also studied using DTA, XRD and optical absorption.

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1. Introduction

Rare earths (RE) are interesting for their optical properties, for instance to create laser matrices or amplifying glass fibers (Clare, 1994), and also because they represent one of the most abundant families of fission products found in the waste at the end of the nuclear fuel cycle (Caurant et al., 2009). Such nuclear waste is then generally stored in complex borosilicate glassy matrices, where RE ions seem to interact more specifically with the boron (Majerus et al., 2011), B_2O_3 being used in these glasses as a flux agent and to decrease the melting temperature. Indeed, it has been observed that adding boron oxide tends to decrease the crystallization tendency of a RE-rich apatite phase in RE-bearing borosilicate glasses. Moreover, in those glasses, the Nd-L_{III} edge EXAFS spectra for higher boron concentrations (up to 27 mol %) resemble the one of RE-metaborate composition ($\text{RE}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$).

In order to investigate the environment of the RE inside such complex borosilicate glasses, and particularly the role played by boron on RE solubility, simplified glass systems were studied in this paper, starting with the binary system containing only RE_2O_3 and B_2O_3 . This system has a strong tendency to immiscibility in the liquid for boron-rich compositions, for almost all RE as shown by Levin (1961, 1966), although it has been recently shown that this tendency can be overcome by preparing the glasses under high pressure (Funabiki et al., 2013). Outside this immiscibility range, transparent glasses can be obtained close to the $\text{RE}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$ metaborate composition (Chakraborty et al. (1985), Shelby (1994), Vinogradova et al. (2003)). This paper is focused on RE metaborate glass ($\text{RE}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$ with RE= La or Nd). These glasses have a very good chemical durability (Chakraborty et al., (1984)) under ambient conditions and down to pH=3 in aqueous solution. According to infrared and Raman spectroscopic studies, these glasses were concluded to have a structure close to that of the REB_3O_6 crystalline phase of same composition (Chakraborty and Day (1985), Terashima et al. (1997)). The structure of this crystalline phase (Fig. 1) consists in ladder-type chains composed of BO_3 trigonal and BO_4 tetragonal units in a 2:1 ratio and are interconnected by RE^{3+} ions that are coordinated by ten oxygen atoms (Pakhomov et al. (1969), Ysker et al. (1970), Müller-Bunz et al. (2003)). In this structure, three types of oxygen atoms can be distinguished: two of them being bridging oxygen atoms (BO) connecting BO_3 and BO_4 units and the third one being a non-bridging oxygen atom (NBO), carried by the BO_3 units.

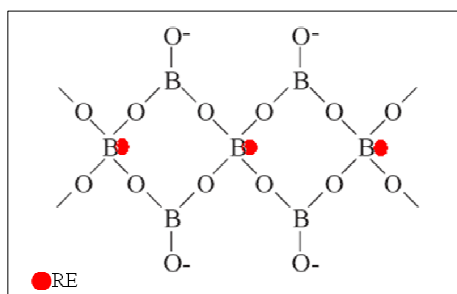


Figure 1. Schematic structure of RE crystalline metaborate showing only one ladder-type chain

In this paper, we intend to go further in the understanding of the RE metaborate glass structure using ^{11}B MAS NMR (RE= La), Nd-L_{III} edge EXAFS and optical absorption (RE= Nd). Its structure was compared with its crystalline counterpart REB_3O_6 . The crystallization behavior of these glasses was also studied using Differential Thermal Analysis (DTA) and X-Ray Diffraction (XRD).

2. Experimental techniques

Glasses were first prepared using a two-steps method, starting with mixing reagent-grade powders of RE_2O_3 (dried for 12 hours at 1000°C) and H_3BO_3 . The mixture ($m=30\text{g}$) was then placed in a platinum crucible, heated, under air, at 1250°C for 30 min and cooled directly in the crucible outside the furnace without casting. After crushing the glass obtained in an agate mortar, to ensure a better chemical homogeneity, the powder was melted again at 1250°C for 1h. The glass was left to cool under air in the crucible as in the first melting step. No crystallization occurred during the cooling step. The glasses compositions were checked by ICP-AES chemical analysis and a slight loss of boron during melting process was noticed (3 mol% B_2O_3). Crystalline LaB_3O_6 metaborate was prepared by heating LaB_3O_6 glass pieces at 850°C for a duration of 12 hours. Checking by XRD, the devitrified pieces contain metaborate crystals, and a minority of orthoborate crystals (LaBO_3 composition), consistently with the loss of boron noticed by ICP-AES. In order to prevent the loss of boron, glasses were then prepared using a single melting at 1250°C during 30 min, starting with B_2O_3 or H_3BO_3 along with RE_2O_3 , and left to cool outside the furnace in the crucible without casting. Chemical analysis performed on the sample used to prepare the crystalline phase for NMR experiment revealed that the glass prepared according to this one-step method was very close to the stoichiometric composition ($75.3\text{B}_2\text{O}_3, 24.7\text{La}_2\text{O}_3$). However, XRD performed on a NdB_3O_6 glass sample treated for 12h still showed a small proportion of orthoborate crystals. We suggest that some boron was lost during the recrystallization of this glass.

^{11}B MAS NMR experiments were performed on powdered samples of LaB_3O_6 (La^{3+} ion is not paramagnetic, as opposed to Nd^{3+} ion), using a Bruker Avance II spectrometer, operating at a magnetic field of 11.72T (Larmor frequency 160.14 MHz). Spectra were collected at a sample spinning frequency of 14 kHz using a commercial 4 mm (o.d.) CPMAS probe with a recycle delay of 2s. ^{11}B chemical shifts are reported in ppm relative to an external sample of 1 M aqueous boric acid at 19.6 ppm.

Optical absorption experiments ($^4\text{I}_{9/2} \rightarrow ^2\text{P}_{1/2}$ transition) were carried out on a double-beam CARY-5E spectrophotometer, in transmission mode through KBr pellet, of approximately 1mm thickness, at 10K, using a He-cryostat, so that only the lowest Stark level of the $^4\text{I}_{9/2}$ ground state was populated. X-ray absorption spectroscopy at the Nd L_{III} -edge (6212 eV in these glasses) has been carried out at the synchrotron ANKA (Karlsruhe, Germany). The spectrum was recorded in transmission mode at 15 K using a He-cryostat, in order to minimize thermal disorder. The EXAFS oscillations were extracted and fitted using the Athena-Artemis softwares (Rehr et al., (1991)). A linear pre-edge and a polynomial post-edge line were used to simulate the atomic absorption and normalize the edge. The background was simulated with a spline on the 0.2 to 11.2 \AA^{-1} range, using a low r cut-off of 1.4 \AA and a k-weight = 3 and removed from the spectra. Fourier transform of the $k^3\chi(k)$ function was computed on the $2.8 - 10.4 \text{ \AA}^{-1}$ range using a Hanning window with $dk = 2 \text{ \AA}^{-1}$. Only single scattering contributions were considered in the fit, because of the disorder. The Nd-O, Nd-B and Nd-Nd phase and amplitude functions were calculated using FEFF6 on the basis of the NdB_3O_6 structure. The Δe_0 and S_0^2 parameters were fixed at 4 eV and 1 respectively. These values were used to successfully fit glassy silicate and crystalline silicate reference spectra (sodium silicate glass and $\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_2\text{O}_2$) acquired and analysed in the same conditions. We assume they are also valid for Nd L_{III} -edge in the borate glass. The fits were performed in the r-space on the $1.4 - 4.8 \text{ \AA}$ range, using 4 single scattering paths (Nd-O, Nd-B, Nd-Nd1 and Nd-Nd2). Despite its weak amplitude, it was necessary to add a Nd-B contribution to fit the shoulder on the high r-side of the Nd-O peak. Thus, Nd-B, Nd-Nd1 and Nd-Nd2 considerably improved the fit, but only the structural parameters of the Nd-O distribution are considered truly reliable and are given in the paper. XRD powder measurements were carried out on an X'Pert PRO PANalytical instrument equipped with a high-speed PIXCel detector, using Cu-K α radiation ($\lambda=0.15406 \text{ nm}$) in Bragg-Brentano (θ - 2θ) geometry (U= 45 kV, I= 40 mA), at room temperature.

3. Results and discussion

3.1. Structure of rare-earth metaborate glasses- Comparison between crystalline and glassy phases.

3.1.1. Boron environment

Both glassy and crystalline LaB_3O_6 were studied by ^{11}B MAS NMR and their spectra (Fig. 2a and 2b) were

simulated considering a single contribution for both the BO_3 and BO_4 lines. NMR parameters and percentages of BO_4 and BO_3 units, deduced from the simulation using the method as described in Angeli et al. (2010), are shown in Table 1.

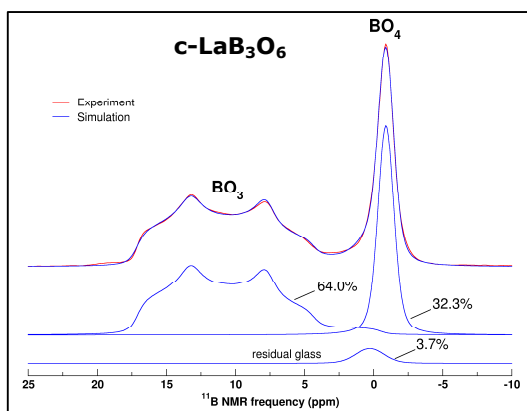


Figure 2.a. ^{11}B MAS NMR spectra of crystalline LaB_3O_6

showing experimental data (red line) and simulation (blue line)

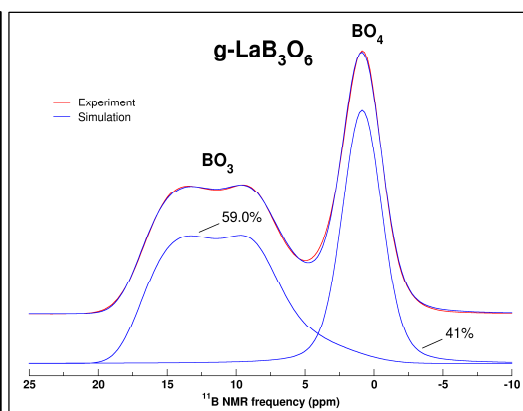


Figure 2.b. ^{11}B MAS NMR spectra of glassy LaB_3O_6 showing

experimental data (red line) and simulation (blue line)

	$\delta_{\text{iso}} (\pm 1.2 \text{ ppm})$	$C_q (\pm 0.1 \text{ MHz})$	$\eta_q (\pm 0.1)$	%
c BO_4	- 0.8	0.10	-	32
g BO_4	0.8	0.50	0.6	41
c BO_3	18.2	2.74	0.37	64
g BO_3	18.1	2.6	0.4	59

Table 1. NMR parameters and percentages of BO_4 and BO_3 units in La-metaborate glass (g) and crystalline phase (c). Standard deviation is indicated in brackets.

A difference between the ^{11}B chemical shifts in the glass and in the crystalline phase is observed for BO_4 units ($\Delta=1.6$ ppm), which could have several origins: a change in the B-O-B angle and/or in B-O distance, due probably to a higher tetrahedral distortion in the glass in accordance with the observed higher C_q value (Kroeker and Stebbins, 2001). This could be also explained by the presence of NBO on the BO_4 units in the glass, whereas in the crystal, all the NBO are borne by the BO_3 units. This evolution of δ_{iso} would be better understood by performing ^{17}O NMR experiment on RE metaborate glass. Concerning isotropic chemical shift for the BO_3 units, no significant difference is observed.

It is worth to note that the crystalline phase does have a ratio of 2:1 for BO_3 and BO_4 units, a value which is expected according to the crystalline structure (Fig.1). The glassy phase has more BO_4 units (41% instead of 33% for its crystalline counterpart). The greater proportion of BO_4 in the glass compared with the crystal put in evidence structural differences between these two states of the metaborate composition.

3.1.2. Environment of the rare earth inside the glass

Optical absorption spectra ($^4I_{9/2} \rightarrow ^2P_{1/2}$ transition) of the Nd-metaborate glass before and after crystallization at 754°C (onset of the crystallization peak, extracted from a DTA measurement) are shown in Fig.3a and 3f, respectively. A large peak (FWHM= 142 cm^{-1}) for the glass (Fig. 3a) is observed. This important bandwidth is consistent with a distribution of Nd^{3+} positions inside the glass. On the other hand, the peak related to the NdB_3O_6 crystalline phase (Fig. 3g) is thinner (FMWH= 13 cm^{-1}), showing a less distributed environment around Nd^{3+} ions,

and is displaced towards higher energies (23,332 cm^{-1} instead of 23,275 cm^{-1} for the glass). This latter observation can be related to a decrease of the covalence of the average Nd-O bond (nephelauxetic effect, Gatterer et al., (1998), Quintas et al., (2008), Majérus et al., (2011)) compared with the glass and thus to an increase of the distance between Nd^{3+} ions and oxygen atoms in the crystal.

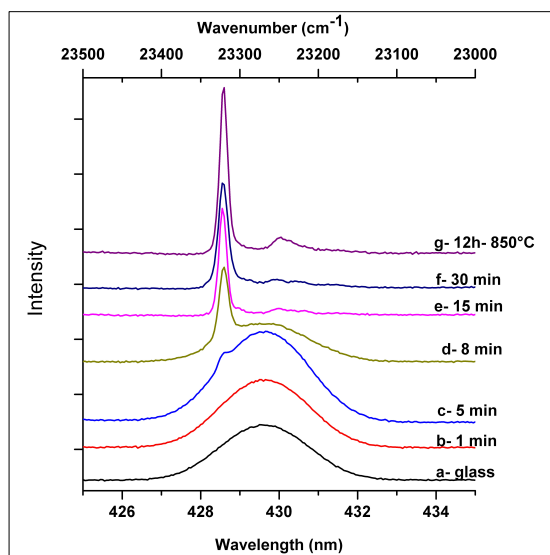


Figure 3. Optical absorption spectra ($^4I_{9/2} \rightarrow ^2P_{1/2}$ transition) performed at 10 K on thermally treated samples at 754°C (unless specified otherwise) for different durations

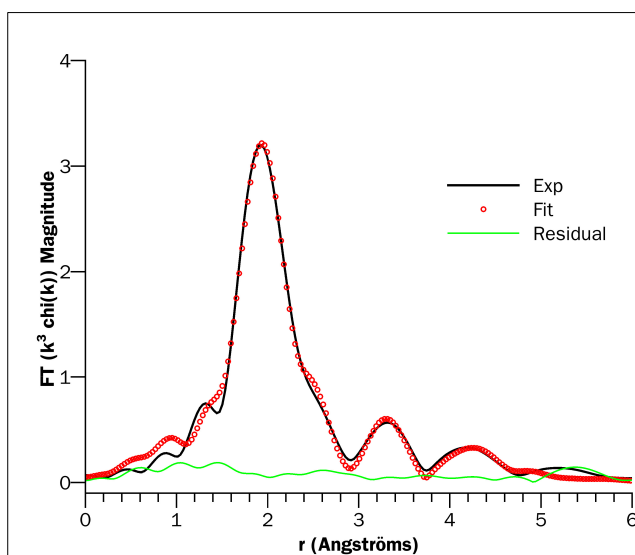


Figure 4. Magnitude of the Fourier Transform of the $k^3 \chi(k)$ EXAFS function extracted from the XAS spectrum at the Nd L_{III} -edge at 15 K of the Nd-metaborate glass

Considering EXAFS measurements performed on the Nd-metaborate glass, an average value of Nd-O distance was extracted: $d_{\text{Nd-O}} = 2.48 \text{ \AA} (\pm 0.02 \text{ \AA})$. It is to be compared with the Nd-O mean distance calculated from the crystalline structure of NdB_3O_6 (Pakhomov et al., 1969), $d_{\text{Nd-O}} = 2.52 \text{ \AA}$. The mean Nd-O distance in the glass is thus slightly smaller than the one in the crystal, which is in agreement with our results from optical absorption measurements.

3.2 Crystallization study

Thermal treatments of different durations between 1 and 30 min at 754°C were performed on powdered glass samples with controlled grain size (80-125 μm). The thermal treatment temperature was chosen at the onset of the crystallization peak as observed in a DTA measurement operated on a similar sample. Those samples, studied by optical absorption spectroscopy (Fig. 3), were also checked by XRD (Fig. 5) to witness the transformation from metaborate glass to crystalline NdB_3O_6 . The peak corresponding to metaborate crystal is observed as soon as crystallization begins on the optical absorption spectra, in accordance with the XRD patterns. The decrease of the contribution of the glass, particularly visible on the optical absorption spectra, is correlated with the growth of the crystal peak. From this, we conclude that there is no formation of an intermediary phase when crystallization occurs inside the glass.

On the other hand, when thermal treatment was performed on massive samples, it was noticed (Fig. 6) that the crystallization process started from the surface. These direct observations are in accordance with DTA measurements performed on samples with increasing grain sizes, which will be presented elsewhere, showing that the crystallization is highly heterogeneous. This observation suggests that the structure of the glass is different from the one of the crystal, in accordance with spectroscopic results above and similarly as other studies performed on alkali borate glasses (Chen et al. (2009), (2010)).

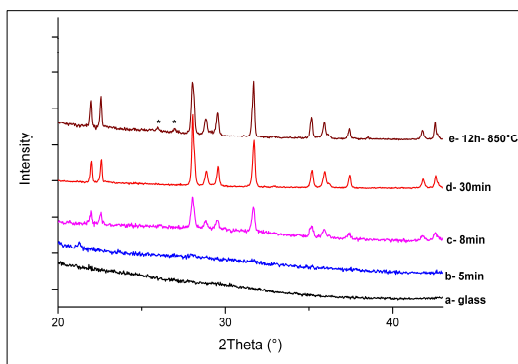


Figure 5. XRD patterns of Nd-metaborate glass samples thermally treated at 754°C (unless specified otherwise) for different durations. All the lines belong to NdB_3O_6 crystalline phase (reference file 00-013-1260 of the ICDD database) apart from the two belonging to orthoborate NdBO_3 indicated by this symbol * (reference file 00-012-0756)

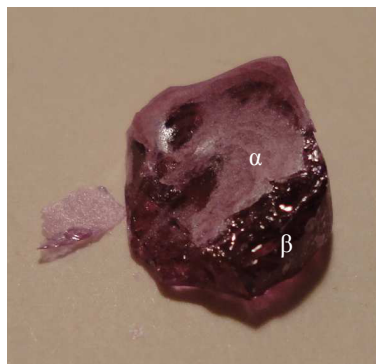


Figure 6. Thermally treated sample of Nd-metaborate glass at 754°C for 15 min showing that crystallization only starts from the surface (α : crystal layer; β : glass)

4. Conclusion

Several results tend to show that the local structure of the RE metaborate glass (with RE= La or Nd) is not similar to its crystalline counterpart REB_3O_6 , besides the structural disorder normally observed in a glass. Evidence are the smaller distance between RE and O, the isotropic ^{11}B chemical shift displacement of BO_4 units and the decrease of the BO_3/BO_4 ratio in the glass in comparison with the crystalline phase and the heterogeneous character of the crystallization. Others experiments are in progress in order to describe more accurately this structure, such as ^{17}O MAS NMR on ^{17}O enriched La-metaborate glass, neutron scattering and Wide-angle X-ray scattering (WAXS).

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