Boron coordination change in alkali borate glasses and melts studied by neutron diffraction

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Neutron diffraction experiments were performed on alkali borate glasses, M_2O-$2B_2O_3$ with M=Li, Na and K, at room temperature and in the liquid state (1273 K), in order to investigate the structural modifications that occur between the glass and the melt. We have evidenced that the fraction of four-fold coordinated boron decreases with increasing temperature.

Introduction

Temperature-dependant structural changes are expected to have drastic consequences on the structure-related properties of glass-forming liquids, among them transport properties (viscous flow, cationic diffusivity), macroscopic thermodynamic properties (density, thermal expansivity) and mixing properties. Structural investigations have been mainly devoted to identify the changes in the short-range order due to the specific difficulties in determining the structure of amorphous systems.

Alkali borate melts are interesting because of their fragile behaviour[1] indicative of significant structural rearrangements with temperature. Their short-range structure is characterized by the coexistence of the two basic units corresponding to B in 3-fold (BO_3) or 4-fold coordination (BO_4^-). We present neutron diffraction data on M_2O-$2B_2O_3$ glasses, with M=Li, Na and K. These glasses exhibit the largest proportion of boron in four-fold coordination. The diffracted intensities were obtained at room temperature and up to the liquid state (1273 K). The ratio $^3B/^4B$ was carefully quantified in order to determine a coordination conversion between the glass and the liquid.

Experimental

Sample preparation

Glasses of composition M_2O-$2B_2O_3$ with M = Li, Na or K were prepared from dried reagent grade powders of boron oxide and alkali carbonate. In all the samples, boron was isotopically enriched in ^{11}B (99,62%) because of the high neutron absorption cross-section of ^{10}B nucleus. The Li_2O-$2B_2O_3$ composition was enriched in ^7Li (99,94%). These three glasses are named 7LB2, NB2 and KB2. Their composition measured by chemical analysis are reported in Table 1. The starting powders were decarbonated at 700°C and melted during 1 hour at 900°C, quenched by partial immersion of the bottom of the Pt crucible in water, then remelted for 15 minutes at 1050°C and quenched again, to ensure glass homogeneity. The 7LB2 glasses, whose melt temperature is higher (917°C), were decarbonated and melted for 20 minutes at 1020°C twice.

Neutron diffraction

The neutron diffraction experiments were performed at the Orphée reactor of the LLB (Saclay, France), on the 7C2 spectrometer which uses hot neutrons (λ=0.7186Å) allowing a wide Q range of 0.48 to 15.56 $Å^{-1}$. The powdered sample was poured in a cylindrical vanadium can (9.5 mm in diameter), mounted in the center of a cylindrical vanadium furnace. The neutron diffraction intensity was measured at room temperature and in the liquid state (Table 1) for each sample. After an equilibration time, the diffracted neutrons are collected during about 8 hours to obtain a good signal to noise ratio. The neutron intensities for the empty can in the furnace and the empty furnace were collected at 300 and 1273K. The data were corrected from the background, the furnace and the container and standard corrections from multiple scattering, attenuation and inelastic scattering were applied. A 9.5 mm diameter vanadium rod was measured for normalisation of the data. The notations for the normalized total scattering structure factor, S(Q), and the reduced total correlation function, D(r), are those explained in reference.[2]

	7LB2	NB2	KB2
%mol. M2O	37.1	35.8	34.8
%mol. B_2O_3	62.9	64.2	65.2
T_f (K)	1190	1015	1088
$T_{Mes.}$ (K)	RT,1273	RT,1100	RT,1200

Table 1: Molar compositions measured by chemical analysis, melt temperatures (Tf) of the M_2O-B_2O_3 compositions and temperatures of measurements (TMes).

Results

Results at room temperature

The normalized total structure factors S(Q) obtained at R.T. are shown in figure 1. For all the investigated glasses the oscillations in the high-Q range (Q > 5 $Å^{-1}$) are similar, indicating that the short-range order is little affected by the nature of the alkali cation. The oscillations in the low-Q region are dominated by correlations in the medium-range order (4-20 Å). Differences on this scale are obvious when comparing the three alkali cations and increase in the order Li < Na < K.

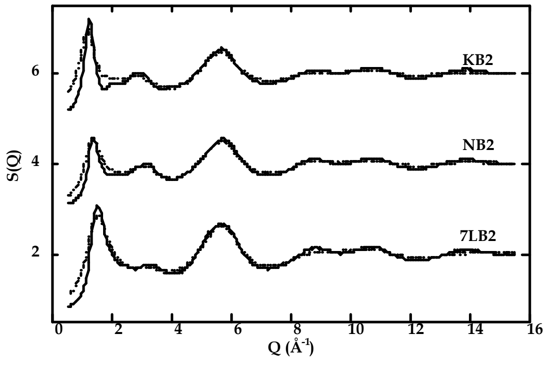

Figure 1: Total structure factors S(Q) obtained at R.T. (solid line) and at at high temperature (dashed line) for the three alkali glasses.

The Fourier transform of Q(S(Q)-1) multiplied by a Lorch modification function are shown in figure 2. The first peak at ~1.4 Å is attributed to the B-O correlation alone and has been adjusted with Gaussian functions (see below). The second peak at ~2.4 Å arises principally from O-O and Na-O or K-O correlations. The first Li-O correlation appears at about 2 Å with a negative contribution in the 7LB2 glass due to the negative neutron scattering length of ^{7}Li isotope. The third peak at ~3.6 Å arises from second B-O correlations.

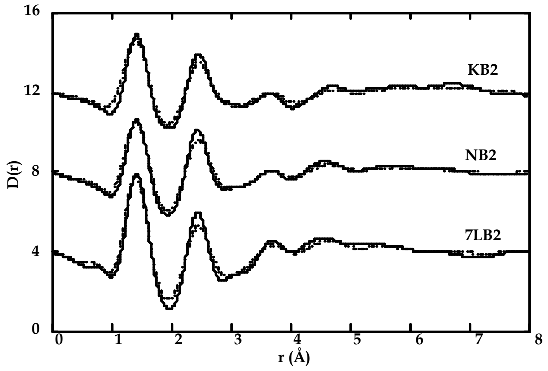

Figure 2: Reduced total correlation functions, D(r), obtained at R.T. (solid line) and at high-temperature (dashed line) for the three alkali borate glasses. These functions are the Fourier transform of Q(S(Q)-1)*M(Q), where M(Q) is the Lorch modification function.

Results at high temperature

The structure factors and correlation functions in the liquid are shown in figure 1 and figure 2, respectively (dashed curves). Oscillations are maintained on the high-Q range with a damping in amplitude due to static and thermal disorder. The intensities of the small oscillations around 3 Å^{-1} have markedly decreased so that the discrepancies between the alkalis are reduced. The relative positions of the first peak remain unchanged (1.55 Å^{-1}, 1.38 Å^{-1} and 1.21 Å^{-1} for 7LB2, NB2 and KB2, respectively). For the three alkalis, this peak has broadened due to the damping in amplitude of the corresponding real-space oscillations in the intermediate range order. A shift of this peak to the low-Q values is observed in the case of K, and may be related to the thermal expansion of both the forming and modifying networks.

The thermal broadening of the distributions occurring in the liquid state is also evidenced on the total correlation functions. The B-O peak has broadened and its position decreases from ~1.41 Å in the glass to ~1.39 Å in the liquid. This shift is attributed to a change of the BO_4^-/BO_3 ratio. The main differences between the correlation function for the glass and the liquid occur on the short-medium range order (2 to 5 Å). We observe a decrease of the intensity of the second peak (O-O and M-O correlations and small contribution from B-B correlations) and of the third (≈ 3.6 Å) and fourth (≈ 4.7 Å) peaks.

Local order around B

Figure 3 shows representative fits of the first peak of the total correlation functions. At room temperature, best fits were obtained using two Gaussian functions, each modelling one boron coordination state. In the liquid state, a two component fit was not needed because of the lower resolution due to the thermal broadening. Fitting results for the three compositions are listed in Table 2.

	Glassy state							Liquid state			
	R_1(Å)	N_1	σ_1 (Å)	R_2(Å)	N_2	σ_2 (Å)	N_4	R	N	σ	N_4
LB2	1.38	1.62	0.060	1.47	1.84	0.096	0.46	1.41	3.30	0.115	0.30
NB2	1.38	1.71	0.065	1.48	1.72	0.105	0.43	1.42	3.35	0.118	0.35
KB2	1.39	1.80	0.065	1.48	1.60	0.110	0.40	1.41	3.32	0.130	0.32

Table 2: Results of the Gaussian fits to the first peak in the total correlation functions. R is the distance and σ the width of the component. N_4 is the fraction of boron in fourfold coordinence, $N_1 = (1-N_4)*3$, $N_2=N_4*4$. The uncertainties on R and σ resulting from the fitting procedure are 0.01 Å. The uncertainty on the N_4 fraction is estimated to be 5 % and 10% in the glass and the liquid, respectively.

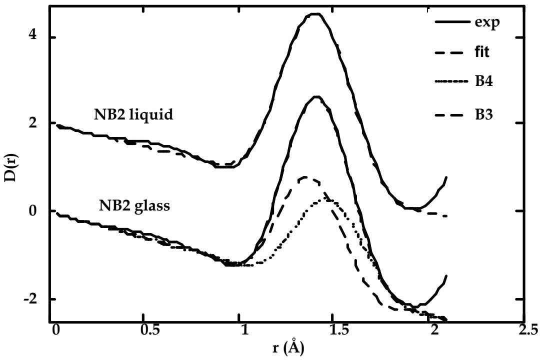

Figure 3: Representative Gaussian fit of the first B-O peak in the total reduced correlation function for the NB2 glass and liquid. B3 and B4 correspond to the contribution from boron in three and four-fold coordination, respectively.

Discussion

The diffraction neutron data suggest a decrease of the four-coordinated boron fraction N_4 from about 0.40 ± 0.03 in the glass to about 0.30 ± 0.05 in the melt. Concerning the NB2 composition, the results presented in Table 2 are in close agreement with thermodynamic calculations that predict a maximum decrease of N_4 from 0.45 at R.T. to 0.30 at 1473 K [3]. However, the N_4 fraction found by the present diffraction study is higher than the fraction determined from *in situ* high-temperature ^{11}B NMR experiments (N_4=0.1) [4]. This new diffraction study strengthen conclusions from X-ray diffraction measurements [5] but is in contradiction with previous neutron total diffraction data which did not reveal any boron coordination change with increasing temperature [6]. The use of a Pt cell on these latter data, instead of a V cell in our diffraction data, could be an explanation for this discrepancy since Pt Bragg peaks are difficult to remove.

The decrease of the proportion of BO_4^- tetrahedra in the melt results in a more depolymerized B-O network (greatest NBO proportion). Alkali are changing from a mainly compensating role in the glass to a mainly modifying role in the liquid. This boron coordination change has been modelized using the following reaction:

$$B\varnothing_4^- + (MO_n) \Leftrightarrow B\varnothing_3 + NBO + (MO_{n'})'$$

In this reaction, modifications in the short-range order are taken into account by mentioning alkali polyhedra changes from (MO_n) towards $(MO_{n'})'$ and the boron conversion from BO_4^- to BO_3. This reaction shifts to the right with increasing temperature. It has been suggested by far-IR studies and MD simulations that alkalis may occupy two kinds of sites: one formed mainly by bridging oxygens of $B\varnothing_4^-$ and $B\varnothing_3$ units (labelled b-site) and the other formed mainly by non-bridging oxygens (labelled nb-site). Furthermore, it was shown that alkalis prefer the nb-site rather than the b-sites due to the improved coulombic stabilisation in the more negatively charged nb-sites [7]. However at our compositions, the glass contains a small proportion of non-bridging oxygens, so that the majority of alkalis reside in b-sites. At high temperature, the kinetic energy allows alkalis to jump out of their initial b-site and migrate. This migration may unstabilize BO_4^- tetrahedra and explain the decrease of N_4. At room-temperature, the short and medium-range structure of alkali borate glasses is mainly controlled by the BO network, whereas, at higher temperatures, structure is controlled by both network and alkali stabilisation requirements.

Modifications beyond the short-range order are primarily observed in the second peak at about 2.4 Å, attributed to O-O and M-O correlations with a small contribution from B-B correlations. In the melts, this peak undergoes a high-r side shift of 0.01 Å and a decrease in intensity. The diminution of the O-O coordinence resulting from the BO_4^- to BO_3 conversion has been proposed to explain this decrease in intensity[1]. The high-r side shift may be related to an increase of the mean O-B-O angle and could thus indicate an opening of the superstructural rings. Indeed, *in situ* high temperature RAMAN measurements have shown a rearrangement of the borate groups above the glass transition temperature [8].

Conlusion

Neutron diffraction experiments were carried out on M_2O-$2B_2O_3$ glasses, with M=Li, Na and K, at room temperature and in the liquid state. The fraction of four-fold coordinated boron was determined. We evidenced a boron coordination change with increasing temperature from BO_4 terahedra towards BO_3 triangle, resulting in the depolymerisation of the network.

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