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Structure of single and mixed alkali Li–Rb borate glasses by neutron diffraction

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Abstract

We have compared the local structure of Li–, Rb– and Li–Rb diborate glasses using neutron diffraction and reverse Monte Carlo simulations. The fraction of tetrahedral boron decreases as the Rb content increases, but is similar in the single and mixed alkali glasses at diborate compositions. Rb borate glasses exhibit an extensive cation ordering with Rb–Rb correlations at 4.7 and 7 Å. The environment of alkalis is slightly modified between the single and mixed glasses while their relative distribution is essentially random. This indicates that the alkali environment is affected by the presence of a different alkali and this cation–cation interaction could be a fundamental mechanism, together with the site mismatch, to explain the mixed alkali effect.

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Keywords: Neutron diffraction/scattering; Mixed alkali effect; Monte Carlo simulations; Oxide glasses; Borates; Structure

1. Introduction

Properties related to ionic transport drastically drop when a fraction of the mobile ions is substituted by another type of mobile ions, giving rise to the so-called mixed alkali effect (MAE). [1,2]. An example of this effect is the deep minimum of the electrical dc conductivity when one type of alkali ion is progressively replaced by another, at constant overall cation content [3]. Many models have been proposed to explain MAE but a complete comprehensive view of this phenomenon is still lacking. The dynamic structure model (DSM) predicts that ions preferentially migrate via pathways formed by ion-specific sites [4–6]. Therefore, some conduction pathways are blocked in the mixed alkali glasses due to mismatch of different cation sites. This model is based on the assumption that the local environment of alkalis is unaffected by the presence of a second alkali. However, recent NMR data suggest that it may not be the case: in mixed alkali glasses, smaller and larger cations suffer site compression and expansion, respectively [7]. It was also proposed that MAE can be due to network modifications induced by alkali ions of different size and an energy distribution of sites with a preferential occupancy of the low energy sites by the smaller cations [8]. Some structural aspects are critical to improve the understanding of cation transport in glasses: local oxygen environment and spatial distribution of the mobile alkali metal ion, relative cation mixing in ternary glasses, influence of the network structure on cation mobility.

MAE has been recently widely studied in alkali borate glasses [9–16], for which the motion of alkali ions is appreciable already far below T_g. The dc conductivity of a Na-borate glass is larger by more than one order of magnitude than that of the corresponding Rb-borate glass, indicating that the smaller Na ions move faster than the larger Rb ions [16]. The diffusion of ions and the electrical

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conductivity operate through successive jumps from and toward the sites available within the essentially static borate network. Therefore the network structure may play a major control on long-range transport.

In pure B_2O_3, boron atoms are localized in BO_3 units forming a continuous random network (CRN). The incorporation of M_2O alkali oxide gives rise to BO_4 tetrahedral units, where the negative charge of the tetrahedron is charge-compensated by alkali ions. As the concentration of non-bridging oxygen atoms (NBO's) is negligible up to about 30 mol% alkali oxide content, the addition of alkali oxide to B_2O_3 improves the stability of the CRN by cross-linking BO_3 and BO_4 units [17]. Beyond this concentration, alkalis begin to depolymerize the network with the formation of a significant amount of NBO's.

In the present contribution, we present new data on the structure of single- and mixed alkali Li–Rb borate glasses, using neutron diffraction and Reverse Monte Carlo simulations. Li–Rb borate glasses were chosen because of the importance of MAE and the large difference in the ionic radius between the two alkalis. Single and mixed alkali diborate glasses exhibit a similar fraction of tetrahedral boron, but with a slightly modified environment of alkalis. As the alkali environment is affected by the presence of a different alkali, this cation–cation interaction could be a fundamental mechanism at the origin of the MAE.

2. Experimental

2.1. Glass preparation

Glasses were synthesized under dry conditions, using isotopically enriched $^{11}B_2O_3$ to avoid the high neutron absorption of ^{10}B nuclei, and reagent grade powders of $^7LiCO_3$ (99.94% ^7Li) and $RbCO_3$, according to the compositions in Table 1. The starting mixtures were decarbonated at 700 °C during 12 h, then melted in a covered Pt crucible at 1020 °C for 20 min. The melts were quenched by rapid immersion of the bottom of the crucible in water. This procedure was repeated twice to ensure good homogeneity. A previous chemical analysis of Li-diborate glasses prepared under the same conditions indicated only a weak deviation from the nominal composition [18]. Therefore, we used the nominal composition in the data analysis. Densities, measured by an Archimedes method with toluene as liquid reference, are reported in Table 1 and are in good agreement with those reported in the literature [16,19,20]. The samples were stored in a desiccator prior to experiments to avoid water absorption.

Table 1
Glass composition, density and glass transition temperature of the glasses

Composition	B_2O_3 (mol%)	Li_2O (mol%)	Rb_2O (mol%)	d (g cm^{-3})	T_g (K)
7LB2	66.66	33.34		2.23	780[a]
7LRbB2	66.66	16.67	16.67	2.64	697[a]
RbB2	66.66		33.34	2.92	707[a,b]
RbB3	75.00		25.00	2.74	720[b]
RbB4	80.00		20.00	2.54	707[b]

[a] Gao (2006).
[b] Berkemeier et al. (2005).

2.2. Neutron diffraction experiments and data analysis

The neutron diffraction experiments were performed on the 7C2 diffractometer (Orphée reactor, Laboratoire Léon Brillouin, France). This instrument uses hot neutrons of wavelength 0.697 Å, giving access to a Q-range of 0.5–16 Å^{-1}. Glasses were powdered just before the measurement in order to avoid hydration, and set in a cylindrical vanadium cell, at the center of a cylindrical vanadium furnace. The data were treated with standard procedures [21]. The inelastic scattering contribution in the structure factors was corrected using the MCGR code, which removes a quadratic background from the data [22].

The total structure factor $F(Q)$ is the distinct scattering term of the total neutron cross section and can be written in the Faber–Ziman formalism as

$$F_T(Q) = \sum_{\alpha,\beta}^{n,n} c_\alpha c_\beta b_\alpha b_\beta (A_{\alpha\beta}(Q) - 1), \tag{1}$$

where $A_{\alpha\beta}$ are the Faber–Ziman partial structure factors.

The Fourier transformation of $F(Q)$ gives the total radial distribution function $G(r)$, which is the neutron weighted sum of all the partial pair distribution functions $g_{\alpha\beta}(r)$.

$$G(r) = \sum_{\alpha,\beta}^{n,n} c_\alpha c_\beta b_\alpha b_\beta (g_{\alpha\beta}(r) - 1). \tag{2}$$

We define the total correlation function $T(r)$ as

$$T(r) = 4\pi\rho_0 r \left[G(r) + \left(\sum_i c_i b_i \right)^2 \right]. \tag{3}$$

2.3. RMC simulations

Reverse Monte Carlo (RMC) simulations have been carried out on the single Li and Rb diborate glasses and on the mixed Li–Rb glass using the neutron diffraction data. The RMC method consists in fitting the neutron diffraction data to obtain three-dimensional models that agree quantitatively with the experimental data (provided that the data do not contain significant systematic errors) and the physical constraints applied [23]. Starting with a hard-sphere Monte Carlo (HSMC) simulation results in a more disordered model than starting with molecular dynamics models [24]. However, in the present case, the advantage of a HSMC simulation is to be able to control the boron coordination. In the RMC simulations, 60% and 40% B atoms were constrained to be 3- and 4-coordinated. In this way, the fraction of BO_4 units corresponds to that estimated from a Gaussian fit of neutron diffraction data (see below)