

# Studying the Short-Range Order of Lithium Borate Glasses

C. Tietz<sup>\*1</sup>, M. Ross<sup>1</sup> and B. Sepiol<sup>1</sup>

<sup>1</sup>Universität Wien, Fakultät für Physik, Strudlhofgasse 4, 1090 Wien, Austria  
\*christoph.tietz@univie.ac.at

## 1 Abstract

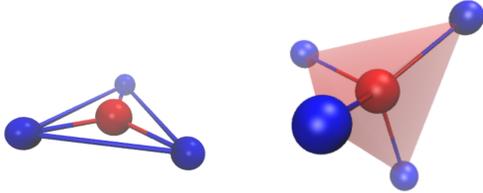
The short-range order of several lithium borate glasses with different fractions of lithium is studied via SAXS and WAXS. Accordingly diffuse regime including the first sharp diffraction peak is of particular interest. Supplementary Monte Carlo simulations are performed using a Born-Mayer-Huggins

type potential<sup>[1]</sup> used in previous eular dynamics simulations of alkali borate glasses. Thereof the partial structure factors and corresponding radial distribution functions describing correlations between two types of atoms can be calculated. Furthermore, the scattered intensity is obtained by the weighted

sum of the partial structure factors. Comparing with the experimental scattering data one can conclude about the most probable structure of the glass. This information will be necessary for the dynamics studies in the glass via atomic scale x-ray photon correlation spectroscopy<sup>[2]</sup> (aXPCS).

## 2 Theory

Borate glasses have a wide range of technical applications. The versatility of borate glasses derives from the flexibility of their atomic structure to accommodate glass modifiers like alkali atoms. This is due to the ambivalence of B atoms which can assume both three-fold and four-fold coordination forming BO<sub>3</sub> triangles and BO<sub>4</sub> tetrahedra.



When analysing aXPCS data the partial structure factor is essential to allow a comparison of correlation times from a model-dependent calculation of  $\tau_{inc}(\vec{q})$  with the experimental correlation times  $\tau(\vec{q})$ . Alkali diffusion in glasses is only weakly correlated with a static boron-oxide network<sup>[3]</sup>. Thus the connection between model and experiment is via eq.1, where

$S_{LiLi}(q)$  is a partial scattering function of lithium ions and  $c_{Li}$  the Li concentration.

$$\tau(\vec{q})^{-1} = \frac{\tau_{inc}(\vec{q})^{-1}}{1 + c_{Li}S_{LiLi}(q)} \quad (1)$$

$S_{LiLi}$  can be measured using contrast variation techniques. In order to extract the partial structure factor for the lithium-lithium-correlation one needs two measurements with different scattering lengths of lithium. Until these measurements are performed, computer simulations are used instead. The partial radial distribution functions are easily accessible quantities in the simulation

$$g_{\alpha\beta}(r) \xrightarrow{\text{Fourier}} S_{\alpha\beta}(q)$$

and give the partial structure factors through the Fourier transform. Finally one can calculate the scattered intensity

$$I(q) = N \sum_{\alpha, \beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} f_{\alpha} f_{\beta} S_{\alpha\beta}(q) \quad (2)$$

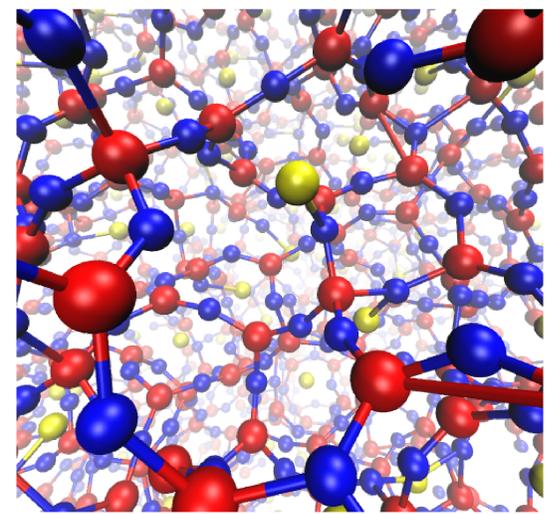


Figure 1: Glass network: oxygen (blue), boron (red) and lithium (yellow) atoms<sup>[4]</sup>

## 3 Some experimental results

SAXS spectra from borate oxide and alkali borate glasses over a wide range of reciprocal wave vectors are shown in Fig.2. In dispersed heterogeneous structures the scattering intensity is given by the Porod law

$$I(q) \propto q^{-p} \quad (3)$$

where  $p$  is the fractal dimension of the structures and their interfaces with the surrounding matrix. The scattering intensity decreases with  $q$  due to eq.3 falling to a minimum before Bragg scattering visible as the "first-sharp" diffraction peak at about  $20 \text{ \AA}^{-1}$  sets in. At the lowest  $q$ -values the SAXS profiles show different slopes. The slope

$p=4$  is an indication of scattering from three-dimensional smooth internal surfaces within the glass structure. As the dimensionality  $p$  diminishes, which means that the structure "depolymerize" or microsegregate - interfaces are no more smooth but fractal.

Three species with different alkali content were prepared: B<sub>2</sub>O<sub>3</sub>, 5(Li<sub>2</sub>O)95(B<sub>2</sub>O<sub>3</sub>) and 20(Li<sub>2</sub>O) 80 (B<sub>2</sub>O<sub>3</sub>) and measured at the SAXS facility at the Nanozentrum of the Faculty of Physics at the University of Vienna. Different detector-sample distances allowed measurement from  $2\theta \approx 0.1$  to 60 degrees.

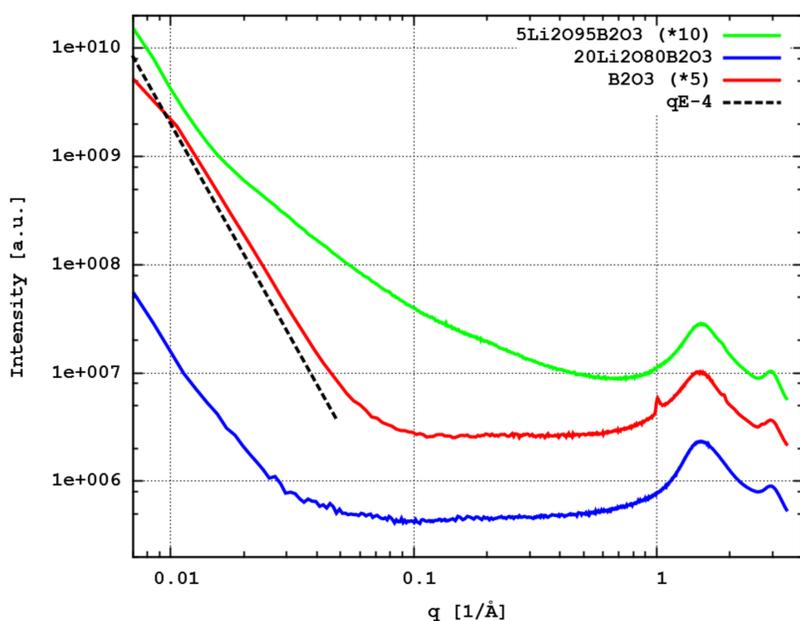


Figure 2: SAXS and WAXS intensities

## 4 Simulation

Performing Metropolis Monte Carlo with a BMH potential<sup>[1]</sup> comprised of a pair part

$$V_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho}\right) + \frac{z_i z_j e^2}{r_{ij}} \quad (4)$$

and a three-body part

$$V_{ijk} = \frac{1}{2} K_{ijk} (\theta - \theta_0)^2 \quad (5)$$

The strongest pair interaction B-O gives rise to the strongest peak in the B-O radial distribution function. Partial radial distribution functions from Monte Carlo simulations are shown for Li-Li at two concentrations of 5 mol% Li<sub>2</sub>O and 20 mol% Li<sub>2</sub>O

and for B-O on pure B<sub>2</sub>O<sub>3</sub> glass. One can see the homogeneous distribution of Li atoms in 5 mol% and 20 mol% glass with a typical distance between Li atoms of about 3.2 Å and 3.0 Å, respectively.

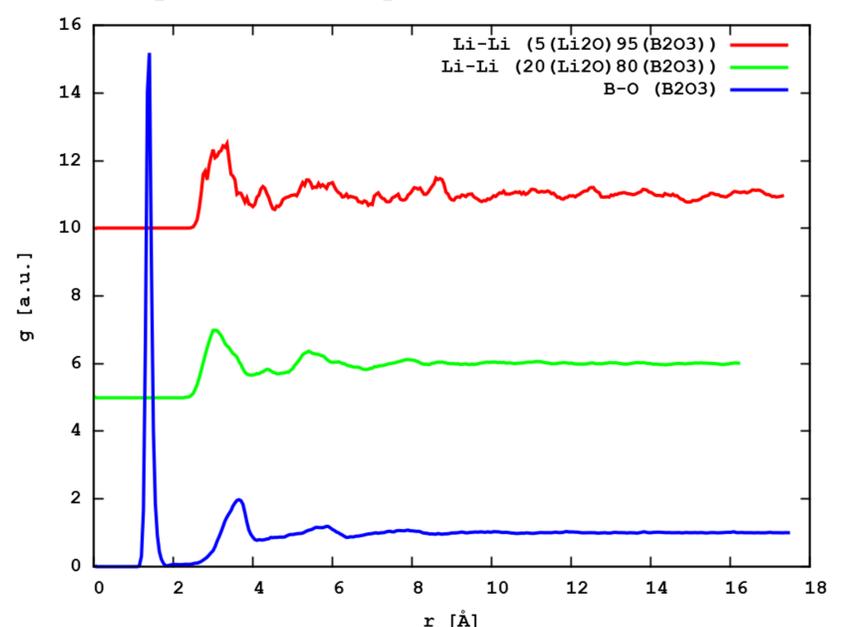
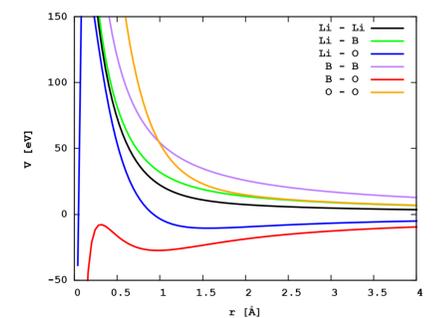


Figure 3: Selected radial distribution functions, shifted for better visibility

[1] A. H. Verhoef, H. W. Hartog, *Structure and dynamics of alkali borate glasses: a molecular dynamics study*, Journal of Non-Crystalline Solids, 182(3):235-247 (1995).  
[2] M. Ross, M. Stana, M. Leitner and B. Sepiol, *Direct observation of atomic network migration in glass*, New J. Phys. 16 (2014) 093042.

[3] G. N. Greaves and S. Sen, *Inorganic glasses, glass-forming liquids and amorphizing solids*, Advances in Physics, vol 56, no.1, pp. 1-166  
[4] W. Humphrey, A. Dalke and K. Schulten, *VMD: Visual molecular dynamics*, J Mol Graph. 1996 Feb;14(1):33-8, 27-8.