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**Evaluation of the diffuse X-Ray scattering on Alkali-Borate
Glasses**

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Abstract

Ion-conducting materials have been noted for their potential use in electrochemical devices, thus a comprehensive investigation into their structure is necessary. Within this thesis the results of a series of total scattering experiments, conducted on alkali-borate glasses, is examined and evaluated in order to give insight into the amorphous structure of the samples.

Being the main focus of this work, Borate glasses doped with various concentrations of alkali-oxides, from lithium to caesium, are examined, though additionally the scattered spectra of specific vanadium-phosphate and lead-silicate glasses are also presented.

Within the first chapter the theoretical background of amorphous structures is explained, as well as the X-ray diffraction theory essential to understand these structures.

The complete experimental set-up and measurement process is explained in the second chapter, as well as the sample and data preparation, evaluation and data-processing necessary for further analysis. Finally the results are shown in the third chapter and are compared to Monte-Carlo computer simulations of the respective samples. In the end alternative approaches for the data-analysis that may lead to possible improvements are qualitatively examined as well.

Zusammenfassung

Ionenleitende Materialien haben durch ihren potentiellen Nutzen in elektrochemischen Geräten Interesse erregt, was detaillierte Erforschung ihrer Struktur erforderlich macht. Innerhalb dieser Arbeit werden die Erkenntnisse, gewonnen aus einer Serie von Gesamtstreuungsexperimenten, an mit Alkali-Oxiden modifizierten Boroxid Gläsern, untersucht und ausgewertet, um Einsicht in die amorphe Struktur dieser Materialien zu gewinnen.

Der Fokus dieses Werks sind Boroxid Gläser, dotiert mit verschiedenen Konzentrationen von Alkali-Oxiden, in der Spanne von Lithium bis Cäsium. Zusätzlich werden jedoch die gemessenen Streuspektren von spezifischen Vanadium-Phosphat und Blei-Silikat Gläsern präsentiert.

Das erste Kapitel befasst sich mit dem theoretischen Hintergrund für die Beschreibung von amorphen Strukturen und mit der notwendigen Röntgen-Streutheorie um diese Strukturen zu verstehen.

Der vollständige experimentelle Aufbau, Messprozess, einschließlich der Proben- und Datenvorbereitung, sowie schließlich die Auswertung und Datenbearbeitung für die weitere Analyse, wird im zweiten Kapitel erläutert. Letztendlich werden die Resultate der einzelnen Proben im dritten Kapitel präsentiert und mit Monte Carlo Computersimulationen verglichen. Am Ende werden alternative Ansätze im Bereich der Datenanalyse, welche die Ergebnisse verbessern könnten, qualitativ untersucht.

1 Introduction

The Introduction section covers all theoretical methods used to evaluate the experimental results of this work. Starting with a short description of the known structure of the respective glasses, then explaining the method of total scattering and PDF analysis to characterize the samples and finally the Laue-monotonic-scattering term shall be discussed.

1.1 Structure of Alkali-Borate Glasses

In order to understand the ionic transport in alkali-borate glasses, a thorough understanding of their structure is needed. Glasses in general are not perfectly randomly ordered materials. While they lack long range order, they do inhibit short-range and intermediate-range order. It is just on these scales where the physical properties of interest manifest themselves. The introduction to alkali-borate glasses will start at a generic look at glass structures, then progress to B_2O_3 glass, and finally the case of B_2O_3 modified with alkali-oxides will be considered.

1.1.1 Hierarchical structure of glass and network model

The common property of all glasses is the absence of long range order, a property that is fundamental to the description of crystal-structures. In order to relate the physical properties of a glass to its structure, another viewpoint must be taken, namely the local atomic environment of the material. Consider for example the case of SiO_2 , where one silicon atom is coordinated by four oxygen atoms [13]. From this point onwards a hierarchy of structural ranges can be constructed, to give insight into mechanisms that inform the macroscopic properties of the material.

The **short-range order** is the primary structure unit of glass and consists mainly of the nearest neighbours in the first coordination shell. When investigating the ionic transport for example, nuclear magnetic resonance can be used to separate the structure units in the glass and determine the ratio of them. Then the relation between the ionic transport properties and the local structure can be discussed [4].

The second or higher coordination shells, such as ring structures and clusters lie in the category of the **intermediate range order** [4]. The typical range of these structures is around one to ten nanometres and can be determined by small-angle X-ray scattering (SAXS).

Depending on the dimension scale of investigation a glass can exhibit properties in various hierarchical structures. It may be homogeneous on the millimetre scale, show inhomogeneities on the nanometre scale and have some ordered structure on the Angstrom scale, as shown in figure 1.

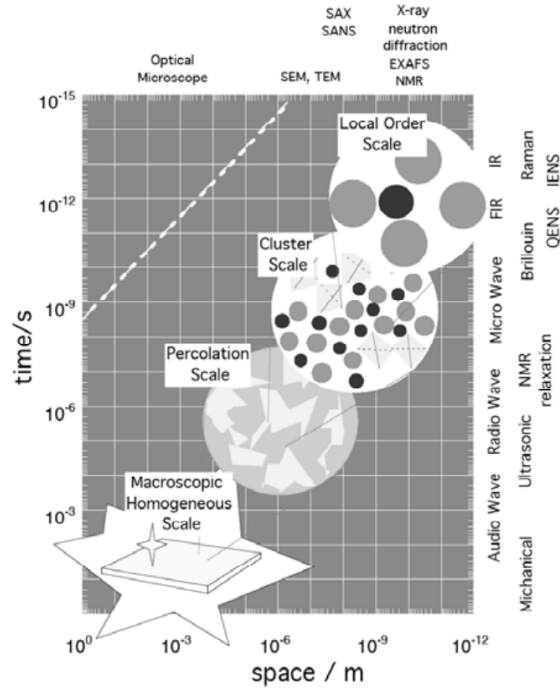


Figure 1: Space-Time Structure Hierarchy of glasses showing experimental techniques within their respective domains. [4]

The short range order structural units, formed by a metal atom at the centre and oxygens at the corners, such as SiO_4 tetrahedrons for example, share amongst one another their corner oxygen atoms to form three-dimensional **networks** [4]. These oxygen atoms are called bridging oxygens (BO) and connect the network-forming oxides into clusters, and are responsible for fluctuations of the average density at the intermediate range scale.

1.1.2 Borate-Glass

Nuclear magnetic resonance spectroscopy has given insight into the structure of B_2O_3 glass [8]. B atoms in the short range structural units can assume both three-fold and four-fold coordinations, i.e BO_3 triangles and BO_4 tetrahedra, leading to the adaptability of the network structure, with oxygen atoms adopting both bridging (BO) and non-bridging oxygen (NBO) configurations. This causes a greater variety of configurations in network and modifier atoms than silicates. [8].

Investigations of the B_2O_3 glass structure by Raman- and neutron scattering, as well as by nuclear magnetic resonance, indicate the structure consisting of planar B_3O_6 boroxol rings, which are constructed by three corner-sharing BO_3 triangles. These rings are furthermore connected to adjacent rings by a small population of BO_3 not included in rings themselves [8]. The fraction of B atoms belonging to boroxol rings is approximately 75 - 80% in pure B_2O_3 , implying a substantial intermediate range order. A representation of B_2O_3 glass structure is depicted in figure 2.

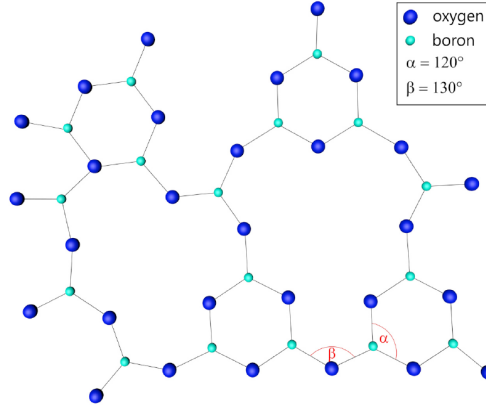


Figure 2: Two dimensional representation of the B_2O_3 network model [10].

1.1.3 Transition to Alkali-Borate Glass

Modifier alkali ions added to B_2O_3 initially results in the conversion of BO_3 to BO_4 structural units, without the forming of NBOs. The molar ratio of alkali-oxide in B_2O_3 is written as $R = \frac{x}{1-x}$, with x being the concentration of alkali ions. The concentration of BO_4 units increases with increasing x until a maximum is reached at $R \approx 0.5$ [8]. As R grows further, the BO_4 population decreases, with formation of BO_3 units and appearance of NBOs according to [8]:



The variation of BO_4 and BO_3 units with rising alkali concentration changes the physical properties in alkali-borate glasses, such as the glass-transition temperature following the BO_4 concentration [8]. A diagram showing the change in structure after inserting Na_2O can be seen in figure 3.

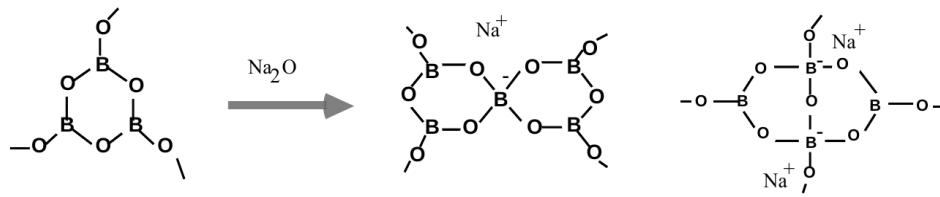


Figure 3: B_2O_3 doped with Na_2O , small addition of the alkali-oxide increases the BO_4 concentration, above $30\text{mol}\%$ added Na_2O causes its decrease and the appearance of non bridging oxygens. [4]

1.2 X-Ray Scattering on amorphous materials

In comparison to common structure determination of crystalline samples, X-ray scattering on amorphous materials, such as glasses, represent a more complex situation. Glasses exhibit no periodicity found in the elementary cells in crystals, however their atomic structure is not fully random. In fact near- and intermediate range order is found these materials. In order to understand the properties of these materials an examination of the structure is important, but knowing every atomic position explicitly is unnecessary [1].

Since the properties themselves are not determined by the absolute positions of each atom, but rather their relative positions, in which some interaction can occur, focusing on the local atomic environment is enough to understand our amorphous materials.

The aim of this chapter is to introduce methods and definitions used for the examination of the glass samples, specifically the **Pair Distribution Function** (PDF) and the **total scattering method**, as well as their derivations.

1.2.1 Pair-Distribution Function

We have already proposed that our prime interest lies in the local atomic environment, such that a method for describing the inter-atomic space correlations is required. If the system is isotropic, as is our case, this can be achieved by a set of inter-atomic distances $r_{\nu\mu}$, where the indices refer to individual atoms, respectively. In the first step we consider an atom situated at $\vec{r}_0 = \vec{0}$ and another at $\vec{r}$. If one imagines the distance between the two to span a sphere with the first atom at the origin, it would be simple to count every other atom centre that intersects with the sphere's shell. This is the **number density** $n(\vec{r})$ [2]. Clearly taking the average of this function would be equal to dividing the total number of atoms by the sample volume:

$$n_0 = \langle n(\vec{r}) \rangle = \frac{N}{V} \quad (2)$$

The function $n(\vec{r})$ outputs the absolute number of atomic centres within sphere's shell. It can be used to define the **Pair Distribution Function**, which describes the probability to find an atom at $\vec{r}_\mu$ if at the origin $\vec{r}_\nu$ there already exists an atom:

$$g(\vec{r}_\nu, \vec{r}_\mu) = \frac{1}{n_0^2} \langle n(\vec{r}_\nu) n(\vec{r}_\mu) \rangle \quad (3)$$

Since we are only interested in the isotropic case, we can continue to the definition of the **atomic PDF** by only using the scalar difference in distance $r_{\mu\nu} = |\vec{r}_\mu - \vec{r}_\nu|$, as the direction is not relevant:

$$G(r) = n_0 g(r) = \frac{1}{4\pi N r^2} \sum_{\nu} \sum_{\mu} \delta(r - r_{\nu\mu}) \quad (4)$$

To avoid confusion $g(r)$ will be called the pair distribution function and $G(r)$ the atomic PDF. $G(r)$ will show pronounced peaks at inter-atomic distances $r_{\nu\mu} = |r_\nu - r_\mu|$, it is a one dimensional function giving the probability to find an atom at r_μ , when previously an atom was at r_ν . The resulting histogram shows all atom-atom distances in the sample. By plotting $G(r)$ we can extract information about the local environment, specifically the number of nearest neighbours, by examining the first peak, as well as the distance to them. Various oscillations following the first represent short-range order. An example of an amorphous Pd-Ni-P alloy is shown in figure 4.

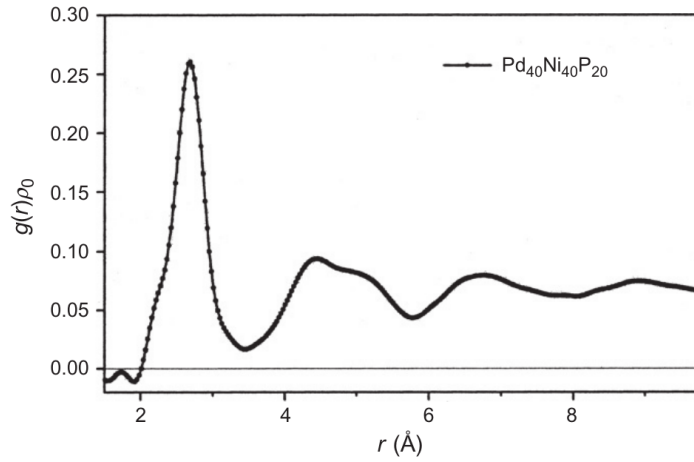


Figure 4: Atomic PDF measured from Pd₄₀Ni₄₀P₂₀. The oscillations after the first peak denote deviations from average density and therefore atomic correlations. At longer distances $G(r)$ leads towards unity thus returning to the average density within the sample.[1]

Later we will find that the atomic PDF can be obtained by reverse Fourier transforming a quantity related to scattering intensity. This makes it possible to simulate a specific structure of the sample in question, calculate its atomic PDF and compare the experimental and simulated results. By using this method an accurate understanding of the structure can be gained.

1.2.2 Total scattering method and PDF analysis

We now venture into the domain of diffraction methods, specifically in our case to X-ray scattering. In crystalline materials only certain discrete directions will contribute to the scattered intensity due to the translational symmetry of the lattice planes, whereas in our amorphous context they naturally don't exist. The sample will scatter incoming radiation into all scattering angles. The intensity itself, however, will be modulated as a function of scattering angle [2].

As in conventional diffraction methods, the total scattering method measures diffracted intensity as a function of momentum transfer $\vec{q} = \vec{k}_{init} - \vec{k}_{final}$. As such, our prime measured quantity is related to reciprocal space, whereas the atomic PDF is a function relating to real space. It will turn out that the reciprocal space equivalent of $G(r)$ is the total scattering function $S(\vec{q})$ [1]. Total scattering means measuring over a wide range of $\vec{q}$ and the gathered intensity contains Bragg peaks, elastic diffuse scattering and inelastic diffuse scattering, with the aim of collecting all coherent scattered intensity. The relation between the scattered intensity and the atomic PDF will now be derived [1] [3].

The scattering amplitude for a series of atoms is:

$$\Psi(\vec{q}) = \sum_i f_i(\vec{q}) e^{i\vec{q} \cdot \vec{r}_i} \quad (5)$$

Where the f_i are the atomic scattering factors. The intensity is the modulus squared of this amplitude, at multiple scattering centres waves may combine coherently or incoherently. For the incoherent case we get:

$$I_{inc} = \sum_i f_i^* f_i \quad (6)$$

The $\vec{Q}$ -Dependence is omitted from this point onwards for brevity. At this point all information on the location of individual atoms is lost, I_{inc} can thus be written as a sum over the various atomic species α in the sample:

$$I_{inc} = \sum_{\alpha} N_{\alpha} f_{\alpha}^* f_{\alpha} = N \sum_{\alpha} c_{\alpha} f_{\alpha}^* f_{\alpha} = N \langle f^2 \rangle \quad (7)$$

With $c_{\alpha} = \frac{N_{\alpha}}{N}$ being the atomic species fraction, and $\langle f \rangle = \sum_{\alpha} c_{\alpha} f_{\alpha}$ the sample average scattering power.

For the square of $\langle f \rangle$ we get:

$$\langle f \rangle^2 = \frac{1}{N^2} \sum_{i,j} f_j f_i = \sum_{i,j} \beta c_{\alpha} c_{\beta} f_{\alpha} f_{\beta} \quad (8)$$

The intensity for coherent scattering yields:

$$I_c = \sum_i \sum_j f_j^* f_i e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} \quad (9)$$

Separating out the self-scattering from the sum:

$$I_c = \sum_i f_i^* f_i + \sum_{i \neq j} f_i^* f_j e^{i\vec{q} \cdot \vec{r}_{ij}} = N \langle f^2 \rangle + \sum_{i \neq j} f_i^* f_j e^{i\vec{q} \cdot \vec{r}_{ij}} \quad (10)$$

Subtracting the self-scattering term from I_c defines the discrete scattering Intensity I_d :

$$I_d = \sum_{i \neq j} f_i^* f_j e^{i\vec{q} \cdot \vec{r}_{ij}} \quad (11)$$

The total scattering structure function $S(\vec{q})$ is defined as the geometry-, polarization- and intensity-per-atom-normalized coherent intensity, subtracted by a Laue monotonic scattering term, due to imperfect cancellation of intensity for destructive interference, in case of different types of scatterers present [1]:

$$S(\vec{q}) = \frac{I_c}{N\langle f \rangle^2} - \frac{\langle (f - \langle f \rangle)^2 \rangle}{\langle f \rangle^2} \quad (12)$$

Knowing this we can use expression (10) to find $S(\vec{q})$ for our case:

$$\frac{I_c}{N} - \langle f^2 \rangle = \frac{1}{N} \sum_{i \neq j} f_i^* f_j e^{i\vec{q} \cdot \vec{r}_{ij}} \quad (13)$$

Division on both sides by $\langle f \rangle^2$ yields:

$$\frac{I_c}{N\langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2} = \frac{1}{N\langle f \rangle^2} \sum_{i \neq j} f_i^* f_j e^{i\vec{q} \cdot \vec{r}_{ij}} \quad (14)$$

Which gives us the expression for $S(\vec{q})$:

$$S(\vec{q}) - 1 = \frac{I_c}{N\langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2} = \frac{I_d}{N\langle f \rangle^2} = \frac{1}{N\langle f \rangle^2} \sum_{i \neq j} f_i^* f_j e^{i\vec{q} \cdot \vec{r}_{ij}} \quad (15)$$

With our structure function in hand we can continue with an inverse fourier transform to obtain the atomic PDF, for that the **reduced structure function** $F(q)$ is used:

$$F(q) = q(S(q) - 1) \quad (16)$$

And finally the atomic PDF:

$$G(r) = \frac{2}{\pi} \int_{q_{min}}^{q_{max}} dq F(q) \sin(qr) \quad (17)$$

Where q_{min} and q_{max} are to be obtained from the experiment.

Considering a system of two or more atomic species, a partial atomic pair distribution function $G_{\alpha\beta}(r)$ can be constructed by considering only histograms of occurrences where type β atoms are found around type α atoms. $G_{\alpha\beta}(r)$ is then calculated by division of these histograms by the total number of the respective spheres in an ideal gas of the same density n_0 [24]. This can be used for the derivation of the partial structure function [1]. A definition of the partial atomic PDF takes the form:

$$G_{\alpha\beta}(r) = \frac{1}{4\pi N \rho_0 r^2} \sum_{\nu \in \{\alpha\}} \sum_{\mu \in \{\beta\}} \delta(r - r_{\nu\mu}) \quad (18)$$

With the total atomic PDF, and similarly the total scattering function, being the sum over all components:

$$\begin{aligned} G(r) &= \sum_{\alpha} \sum_{\beta} G_{\alpha\beta}(r) \\ S(q) &= \sum_{\alpha} \sum_{\beta} S_{\alpha\beta}(q) \end{aligned} \quad (19)$$

The function can thus be built up as a superposition of its sub-distributions. And finally, both distributions are related to each other via Fourier-transformation analogous to (17):

$$S_{\alpha\beta}(q) = 1 + 4\pi \frac{N}{V} \int_0^{\infty} dr r^2 \frac{\sin(qr)}{qr} (G_{\alpha\beta}(r) - 1) \quad (20)$$

Figure 5 shows a plot of simulated partial atomic PDFs of $30\text{Rb}_2\text{O}70\text{B}_2\text{O}_3$.

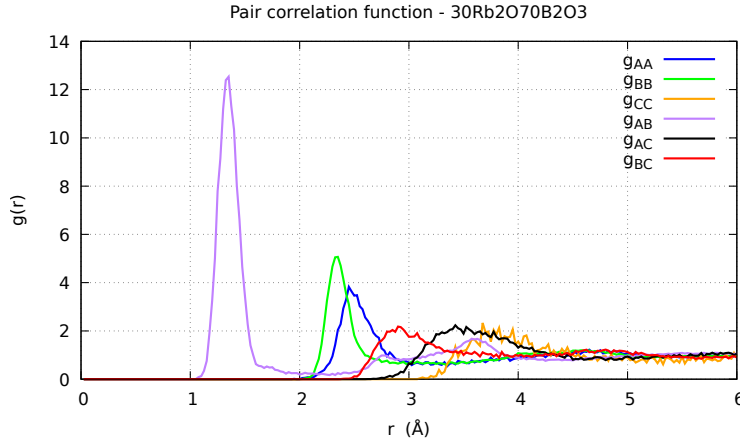


Figure 5: Simulated atomic pair correlation function of $30\text{Rb}_2\text{O}70\text{B}_2\text{O}_3$. Boron atoms denoted by A, oxygen atoms by B and rubidium atoms by C.

1.2.3 The Laue monotonic-scattering term

The Laue monotonic scattering Term in (12) requires further explanation, in this section the term will be derived.

As introduced above the total scattering intensity is the sum from the coherent and incoherent intensity contributions, in a system of two atomic species A and B, I_{Scat} takes the form:

$$I_{Scat} = N_A f_A^2 + N_B f_B^2 + \sum_{i \neq j} (c_A f_A + c_B f_B)^2 e^{-i\vec{q} \cdot \vec{r}_{ij}} \quad (21)$$

Where $N_A f_A^2 + N_B f_B^2$ is the incoherent scattering intensity and $\bar{f} = c_A f_A + c_B f_B$ can be introduced for a randomly distributed configuration, or solid solution. Adding and subtracting the term $\sum_{i=j} \bar{f} e^{-i\vec{q} \cdot \vec{r}_{ij}}$ yields:

$$\begin{aligned} I_{Scat} &= \\ &= N_A f_A^2 + N_B f_B^2 - \sum_{i=j} (c_A f_A + c_B f_B)^2 e^{-i\vec{q} \cdot \vec{r}_{ij}} + \sum_{i,j} (c_A f_A + c_B f_B)^2 e^{-i\vec{q} \cdot \vec{r}_{ij}} \\ &= N_A f_A^2 + N_B f_B^2 - N (c_A f_A + c_B f_B)^2 + \sum_{i,j} \bar{f}^2 e^{-i\vec{q} \cdot \vec{r}_{ij}} \\ &= N ((c_A f_A^2 + c_B f_B^2) - (c_A f_A + c_B f_B)^2) + \bar{f}^2 \sum_{i,j} e^{-i\vec{q} \cdot \vec{r}_{ij}} \end{aligned} \quad (22)$$

The averaged atomic scattering factors can thus be expressed as:

$$\begin{aligned} \langle f^2 \rangle &= c_A f_A^2 + c_B f_B^2 \\ \langle f \rangle^2 &= (c_A f_A + c_B f_B)^2 \end{aligned} \quad (23)$$

And in general for any number of atomic species:

$$\begin{aligned} \langle f^2 \rangle &= \frac{1}{N} \sum_i f_i^2 \\ \langle f \rangle^2 &= \frac{1}{N^2} \sum_{i,j} f_i f_j \end{aligned} \quad (24)$$

With this information the total scattered Intensity can be written as:

$$I_{Scat} = N (\langle f^2 \rangle - \langle f \rangle^2) + \langle f \rangle^2 \sum_{i,j} e^{i\vec{q} \cdot \vec{r}_{ij}} \quad (25)$$

Where the Laue monotonic-scattering term is identified as $var(f) = \langle f^2 \rangle - \langle f \rangle^2$, which is the variance of the atomic scattering factor and makes up the incoherent term in the total intensity.

The scattering function defined from the total scattered intensity takes the form:

$$\frac{S(q)}{N} = \frac{\frac{I_{Scat}}{N} - var(f)}{\langle f \rangle^2} \quad (26)$$

The Laue monotonic-scattering term itself is a small, slowly varying function that represents continuous diffuse scattering. Since it is only relevant for the incoherent scattered intensity it contains no structural information [10]. As such using only the coherent scattering term for the definition of the scattering function is appropriate:

$$\frac{S(q)}{N} = \frac{I_c}{N \langle f \rangle^2} \quad (27)$$

2 Experimental Set-up and Measurement

This chapter covers the main methods, utilities and software tools used in the experiment, as well as sample preparation and calibration of the X-ray source and detector. A detailed description of the set-up is given and the measurement process is explained.

2.1 Set-Up

An illustration of the complete experimental set-up is provided in figure 6. The bulk of the experimental utilities is based on the proprietary Bruker AXS Nanostar modular system, which provides the Cu $K\alpha$ X-ray source, mirror collimation system, vacuum chamber and a 2D detector array. Additionally an energy resolving detector was attached inside the vacuum chamber to avoid fluorescent intensity and allow measurement of the elastic scattering peaks. The components are explained in detail below.

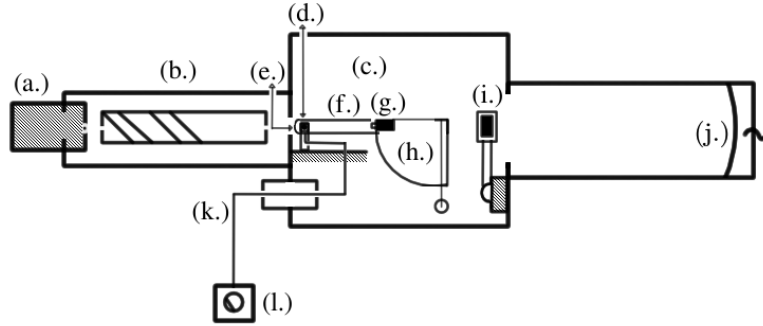


Figure 6: Sketch of the experimental set-up. (a.): Cu $K\alpha$ X-ray source, (b.): pinhole and mirror collimation system, (c.): sample chamber, (d.): sample holder, (e.): rotation stage, (f.): rotating aluminium arm, (g.): primary energy resolving detector, (h.): protractor with weighted down string for angle measurement, (i.) glassy carbon for intensity calibration [11], can be rotated into the beam path, (j.): secondary angle resolving 2D detector, (k.): flexible drill extension, (l.): dial for setting the angle.

2.1.1 Detectors

Our primary detector is an energy resolving Amptek XR-100 CR Si-PIN X-ray detector. It is internally, thermo-electrically cooled with an energy resolution of , at best, 139eV FWHM. In the experiment it is used to differentiate the elastic energy line, i.e. the characteristic $K\alpha$ energy of 8.041keV , and the fluorescent line, caused by excitation of fluorescent atoms. The detector is mounted on a rotatable aluminium arm, which can move in a range from 0° to 70° relative to the incoming horizontal beam. This allows the measurement of the elastic intensity modulation within this range.

The secondary detector is the built in VANTEC-2000 2D microgap detector, usually used for small angle X-ray scattering experiments. In our case this detector allowed us to choose a good spot on the sample for measurement, by scanning the beam over its surface and seeking the best transmitted intensity. This transmission, in relation to the intensity gained from an empty sample holder will also yield the thickness of the sample.

2.1.2 Goniometer

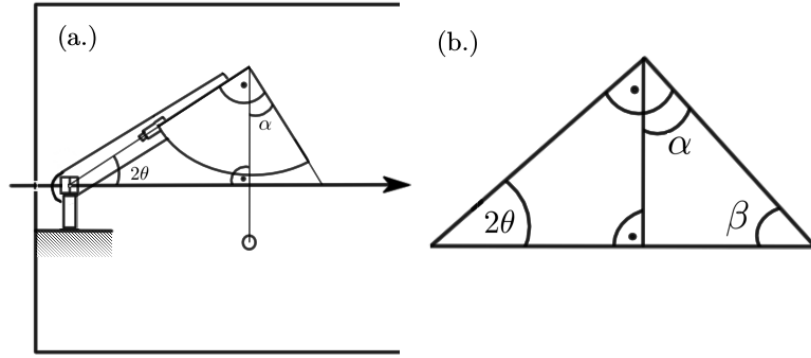


Figure 7: Sketch of the measurement situation inside the sample chamber. The angle α , read from the protractor, is equal to 2θ .

In order to manipulate the angle, at which the scattered beam is detected, while maintaining the vacuum conditions within the chamber, we engineered a simple mechanical device, based on a mechanical rotating platform, at which the detector arm is fixed. This platform is then connected to a flexible drill extension, which leads through a vacuum conduit outside of the chamber and is connected to a dial. The rotating platform has a resolution of 0.9° , a plastic protractor is connected in parallel to the detector arm and a string, weighted down by a tungsten ring, allows reading the set angle from the vacuum chamber's window. A sketch of the construction can be seen in figure 7 (a.).

As depicted in figure 7 (b), a right angled triangle is spanned from the scattering angle 2θ , furthermore another right angled triangle exists with the angle α on the scale, where the right angle is constructed by the string being pulled downwards by its weight. The angle α is also part of the 90° angle from the first triangle, being split in two by the string. Both triangles have the unknown angle β in common. It can be shown that α is indeed equal to 2θ :

$$\begin{aligned}
 2\theta + 90^\circ + \beta &= 180^\circ \\
 \alpha + \beta + 90^\circ &= 180^\circ \\
 \Rightarrow 2\theta + 90^\circ + \beta &= \alpha + \beta + 90^\circ \\
 \Rightarrow 2\theta + 90^\circ &= \alpha + 90^\circ \\
 \Rightarrow 2\theta &= \alpha
 \end{aligned} \tag{28}$$

2.2 Sample Preparation

Among the 19 investigated samples, 14 pertain to B_2O_3 and its modifications with alkali-oxides, two are lead-silicate glasses and another two vanadium-phosphates. Table 1 details a comprehensive list of the alkali-borate glasses, where the sample-names are written in the form $xAl_2O(100 - x)B_2O_3$ with x being the fraction of alkali-oxide in percent.

AI	%Al ₂ O			
Li	5	20		
Na	5	20		
Ka	5	20		
Rb	2	15	20	30
Cs	2	15	20	

Table 1: Measured alkali-borate glasses, not included here is the unmodified B_2O_3 glass, which was also measured.

The other samples include 30PbO70SiO₂ and 60PbO40SiO₂ for the lead-silicates and furthermore 50V₂O₅50P₂O₅ and 75V₂O₅25P₂O₅ for the vanadium-phosphates. Since there was already a large population of these samples available, none of them was manufactured from scratch.

2.2.1 Attenuation length and sample thickness

In order to facilitate the optimal scattering intensity from the samples they had first to be ground down to a thickness that closely matches the attenuation length of the sample at our photon energy.

The attenuation length is defined as the depth into the material, where the intensity drops to $\frac{1}{e}$ th of its value at the surface [1]. In our case of perpendicular entry by the beam into the sample, the intensity is modulated via:

$$I = I_0 e^{-\frac{\mu}{\rho} \rho l} \quad (29)$$

Where ρ is the density and $\frac{\mu}{\rho}$ and ρl are the mass attenuation coefficient and the mass thickness respectively. At the attenuation length d we thus have $I = \frac{I_0}{e}$ and can write:

$$\frac{I_0}{e} = I_0 e^{-\frac{\mu}{\rho} \rho l} \Rightarrow \frac{1}{e} = e^{-\frac{\mu}{\rho} \rho l} \quad (30)$$

And thus:

$$-1 = \frac{\mu}{\rho} \rho d \Rightarrow d = \frac{\rho}{\mu \rho} \quad (31)$$

Since all but three of the sample densities were already calculated from the Archimedes-method [10], the attenuation lengths for each sample were calculated using the website henke.lbl.gov/optical_constants/atten2.html.

2.2.2 Grinding, polishing and storage

Since the sample thickness needs to be close to the attenuation length of the material, most samples needed to be ground. For this grinding paper was fixed on a rotating grinding machine while the grain size was successively decreased. Petroleum was used as a lubricant to avoid recrystallization from the hygroscopic properties of the glasses. Throughout the grinding process samples were measured with a Somet depth gauge micrometer, this was not meant as an exact measurement, as it would not represent the location where the beam would eventually enter the sample, and was used to confirm whether the sample was in the preferred range in thickness. The error on the device was a range of $\pm 3\mu\text{m}$. The true thickness would be later measured from the X-ray scattering experiment.

After having reached the correct range in thickness a very finely grained sandpaper was used for polishing. The aim was to achieve a planar shape as much as possible, since a perfectly perpendicular incidence is assumed in our thickness correction. The more heavily scattering modifier ions in our glass samples, i.e. Rb and Cs, required low thicknesses that were not possible to grind, without destroying the sample. In this case the samples were dimpled to the required depth. Finally the samples were cleaned with acetone and after thoroughly drying kept in glass jars with added silica gel. This was also done for the non-borate glasses, though not necessary.

2.3 Calibration

2.3.1 Detector energy linearity

Our primary detector measures the incoming beam intensity and creates an energy dependent spectrum of counts relative to the detector's channels. These channels can be put into relation to the respective photon energies that are emitted during the scattering process. The channel index should grow proportionally to the registered energy. This can be used to calculate the energy of any peak, or its FWHM from the channel indices.

To achieve this we measured the spectra of titanium-dioxide, iron and steel samples and analysed the peaks resulting from the fluorescent scattering. An example of such a spectrum is depicted in figure 8. Since these materials and their components, such as the steel sample, have known characteristic X-ray lines, that will be emitted as long as a certain threshold of photon energy is passed, it is easy to relate each fluorescent peak to a specific energy. With a list of channel peak positions and characteristic energies a linear regression can be plotted showing the sought after proportional relation between the two. The plot of this calibration is depicted in figure 9. An introduction into the fluorescence mechanism is written in Appendix A.

As can be seen from figure 9, the relation between energy and channel index can be expressed as:

$$Ch = a \cdot E + b \quad (32)$$

Where Ch and E describe channel index and energy respectively and a and b are constants. From the linear fit these constants are found to be:

$$a = (176.12 \pm 0.08) \frac{1}{\text{keV}} \quad b = 9.2 \pm 0.6 \quad (33)$$

Ideally b should be expected to vanish, as the function should go through the centre.

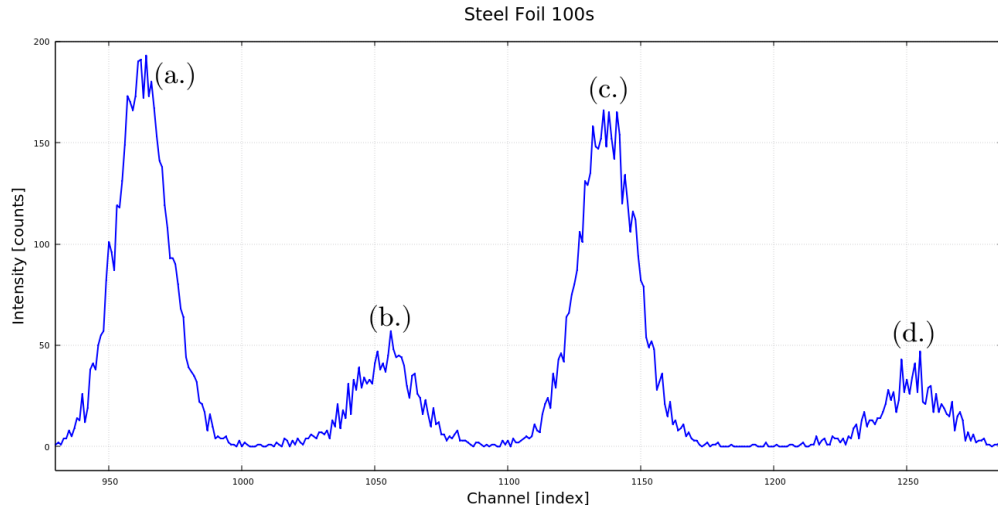


Figure 8: Intensity profile for a measurement of 100 s , characteristic X-ray lines of stainless steel foil, FWHM in channels. (a.): Chromium K_{α_1} and K_{α_2} at 5.412 keV FWHM = 23.8; (b.): Chromium K_{β_1} and K_{β_3} at 5.947 keV, as well as Mn K_{α_1} and K_{α_2} at 5.895 keV, both with an FWHM = 21.8; (c.): Iron K_{α_1} and K_{α_2} at 6.400 keV FWHM = 25.6; (d.): Iron K_{β_1} and K_{β_3} at 7.058 keV FWHM = 27.1 [12].

In order to test the energy resolution of the detector the peaks depicted in figure 8 were fitted with Gaussian functions and the FWHM was extracted. The beam widths were then calculated using 32:

Peak	FWHM [eV]
Cr K_{α}	135 ± 1
Cr K_{β} & Mn K_{α}	123 ± 15
Fe K_{α}	145 ± 1
Fe K_{β}	153 ± 8

Table 2: FWHM for each peak depicted in 8.
The average energy-resolution of all fitted peaks is (141 ± 6) eV.

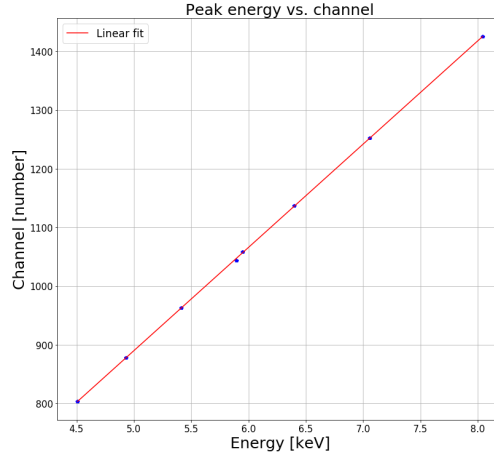


Figure 9: Plot of the fluorescent peak energy vs. the channel numbers, from measurements on TiO_2 , iron-foil and steel-foil (pure iron-chromium alloy). The last data-point on the right represents the elastic peak at 8.041 keV. The linear regression was done using the errors of channel peak-positions as weights.

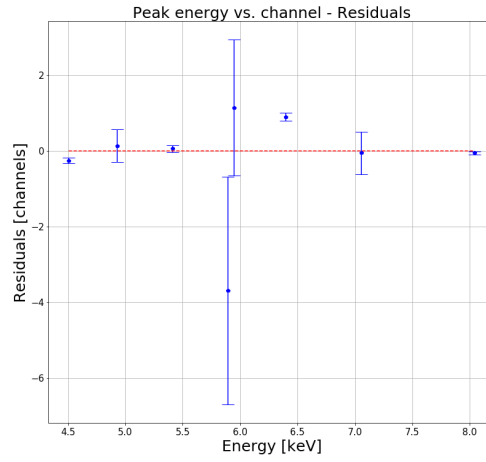


Figure 10: Plotted linear regression residuals of the fit in figure 9.

The detector FWHM can also be plotted as a function of fluorescent energy lines, this relationship is displayed in figure 11.

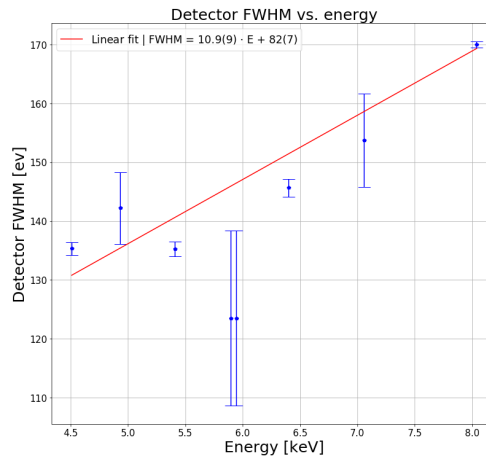


Figure 11: Detector FWHM in channels as function of fluorescent peak energies with a linear regression applied to it. Note that Cr K_β and Mn K_α share the same FWHM and it's error, in order to make the fit viable, see figure 8 and table 2.

2.3.2 Detector Absorption linearity

To test the linearity of absorption of the detector, i.e. detector counts being proportional to the number of incoming photons, we successively attached layers of aluminium foil in front of the sample holder, scattering through a sample of $^{15}\text{Rb}_2\text{O}85\text{B}_2\text{O}_3$, and measured the counted intensity as a function of attenuation degree. The thickness of the foil was calculated by measuring the size of the strips and their weight, and thus calculating the thickness from the volume since the density of aluminium is known. Figure 12 shows the total intensity in counts in relation to the transmitted intensity.

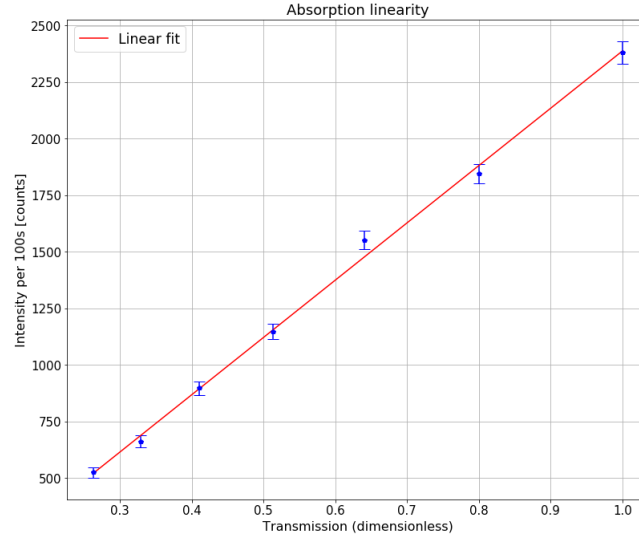


Figure 12: Total intensity normalized for 100 s acquisition time, as function of the transmitted intensity.

Two $10\text{cm} \times 10\text{cm}$ strips of aluminium foil, with an error of $\pm 1\text{mm}$ were weighed at a resolution of $\pm 0.1\text{mg}$. With $\rho_{\text{Al}} = 2.698\text{gcm}^{-3}$ being the density of aluminium at room temperature, and using the average weight of the samples, a thickness of $d = (175.2 \pm 0.2) \cdot 10^{-4}\text{mm}$ per layer of foil was calculated. It can be concluded from figure 12, that the linearity of the AMPTEK detector is completely satisfactory.

2.3.3 Beam Profile

The factory description of the beam profile states it to be of circular shape with a diameter of $d = 0.5$ mm. To test the current dimensions of the beam we scanned the pinhole of the sample holder in both horizontal and vertical directions. These scans resulted in the plots shown below in figures 13 and 14, where the x-axis describes the beam centre position in mm, and the y-axis the intensity in counts. Next these plots were fitted using a sigmoid function and the numerical derivative of the resulting function was taken. These functions are shown in the lower sub-plots of figures 13 and 14, and represent the beam shape in horizontal and vertical direction respectively, these derived points were further fitted with a Gaussian and a Voigt function respectively to extract the FWHM. Using this method the beam is characterized as a slight elliptical shape with a diameter of $d_x = 0.353$ mm along the x-axis and $d_y = 0.332$ mm along the y-axis.

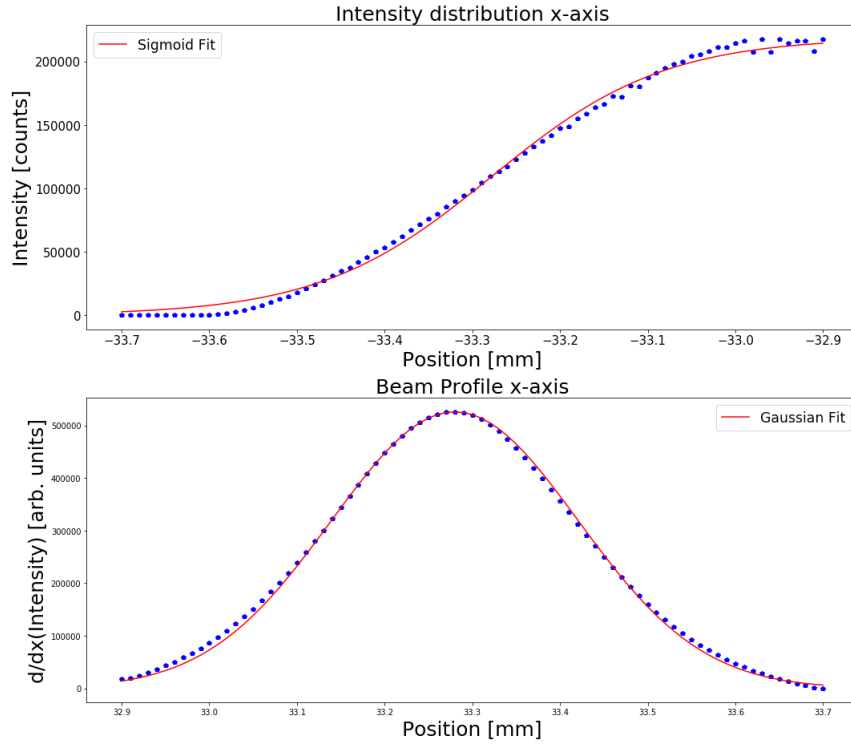


Figure 13: The upper plot shows the change in intensity of the beam moving over the pinhole on the x-axis, with the sigmoid fit in red. The lower plot shows the derivative of this fit, itself fitted with a Gaussian function.

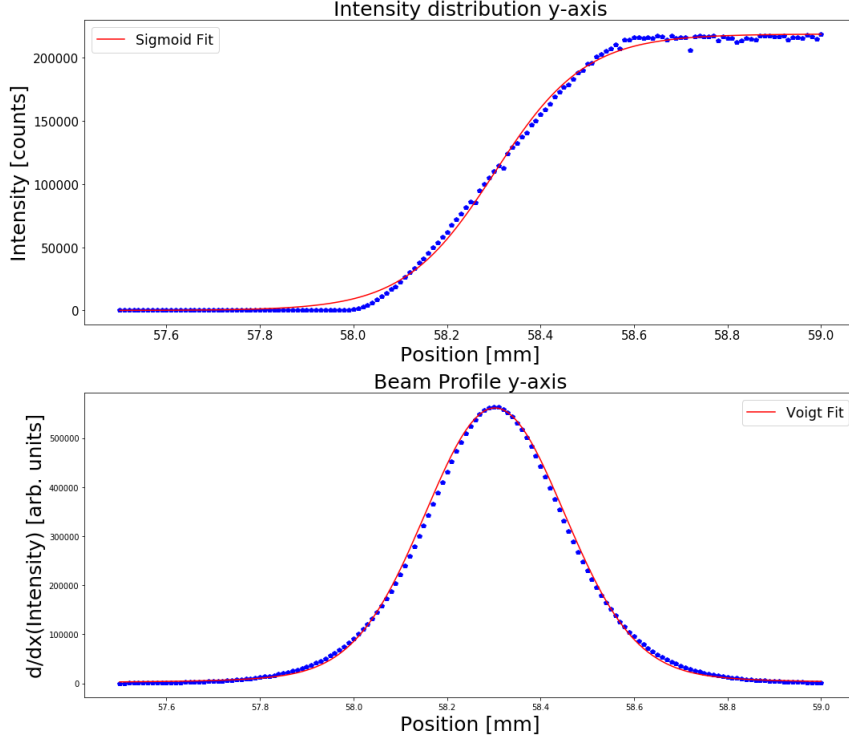


Figure 14: The upper plot shows the change in intensity of the beam moving over the pinhole on the y-axis, with the sigmoid fit in red. The lower plot shows the derivative of this fit, itself fitted with a Voigt function.

A second method to characterize the beam-shape was also accomplished, by measuring the distance between the mid-points of the numerically derived function directly, thus acquiring the FMHW without relying on another fit. This was done by finding the values in the y-axis array most close to the halved maximum value, and calculating the distance from the data points belonging to the respective indices. The procedure for this is explained in Appendix C.

The diameters of the beam are thus to be found as $d_x = 0.330\text{mm}$ and $d_y = 0.340\text{mm}$, less elliptical in shape than from the fit-assisted calculation.

2.4 Measurement

At the start of the measurement the total intensity of the X-ray beam was measured with the secondary 2D detector, this base intensity would later be needed to calculate the transmission of each sample. The arm holding the glassy carbon was rotated into the beam to disperse its intensity for this purpose. The measurement process pertained to mounting each sample to the sample-holder, we then proceeded to scan their surfaces over the 2D detector to choose a decent spot for measurement. The total measured intensity at that spot would be the transmission of that sample. All measurements were taken under vacuum conditions at around 10^{-2} mbar.

Our primary detector would then be rotated in line with the X-ray beam emitting from the sample at 0° , and measurement would start at 2° . After a certain intensity had been gathered, on average between one thousand and two thousand counts, we would increase the angle in 2° steps, however we took special interest in the region of the first maximum between 20° and 30° , where each subsequent measurement was taken at an 1° increase. This was repeated for each sample up to the maximum 2θ angle we could measure, which was 70° .

2.5 Data-Evaluation and Analysis

The scattering measurement of each sample consists of a series of one intensity profile per fixed angle. This data needs to be compiled and prepared, such that it can be displayed in the terms of the Introduction chapter, specifically equations (12) to (17). The analysis of the resulting scattering functions is based on Monte-Carlo models that should bring insight into the underlying glass structures.

2.5.1 Data Preparation

The data preparation and calculation of the scattering function is done by a set of Python-scripts¹. These scripts have six steps in this regard:

- Definition of the elastic peak position within 3σ of the average.
- Loading the angle specific dataset, calculating the momentum transfer q from the angle, summation of all counts within the peak and calculation of the intensity error, which is its square root.
- Calculating the mean-squared atomic scattering factors $\langle f \rangle^2$ for the specific sample per q .
- Applying sample thickness correction on the intensity and its error.
- Loading the measurement time from the datafile and normalizing the intensity and the error to 100s.
- Finally calculation of the scattering function and its error.

¹All scripts and raw data is available at https://github.com/DegreeOfFreedom/total_scattering

Apart from the thickness-correction, all other steps have been explained within the introduction chapter. It is based on a perpendicular incoming X-ray beam and corrects for lost intensity due to variation in the length the beam has to travel through the sample, it is thus angle-dependent. The thickness correction coefficient is defined as [1]:

$$corr(2\theta) = \frac{e^{-\frac{\mu d}{\cos(2\theta)}} - e^{-\mu d}}{1 - \frac{1}{\cos(2\theta)}} \quad (34)$$

This equation is used by first measuring the total intensity of the unperturbed X-ray beam and then the intensity of the beam going through the sample at the desired spot. The ratio of the intensities will yield the transmission at this spot:

$$\begin{aligned} \frac{I_{sample}}{I_{empty}} &= e^{-\mu d} \\ \Rightarrow \mu d &= -\ln\left(\frac{I_{sample}}{I_{empty}}\right) \end{aligned} \quad (35)$$

Next the loss in intensity for the shortest path, and thus least amount of absorption, needs to be calculated, by taking the limit for $2\theta \rightarrow 0$:

$$a_0 = \lim_{2\theta \rightarrow 0} corr(2\theta) \quad (36)$$

And finally the thickness-corrected intensity:

$$I_{corr} = a_0 \cdot \frac{I_0}{corr(2\theta)} \quad (37)$$

Where I_0 stands for the measured intensity at 2θ .

2.5.2 Calculation of scattering-factor functions

As indicated in equation (15), the calculation of the scattering-function $S(q)$ requires the q -dependent atomic scattering factors of the sample atoms, namely the normalized averages $\langle f \rangle^2$ and $\langle f^2 \rangle$, as introduced in (8) and (7). For this purpose we use the values and equations from Waasmaier and Kirfel [25], who used a linear combination of five Gaussians:

$$f(s) = \sum_{i=1}^5 a_i e^{-b_i s^2} + c \quad (38)$$

Where $s = \frac{\sin(\theta)}{\lambda}$. The parameters for each index are tabulated in [25], using this the scattering-factors for our samples could be calculated. Figure 15 shows an example plot.

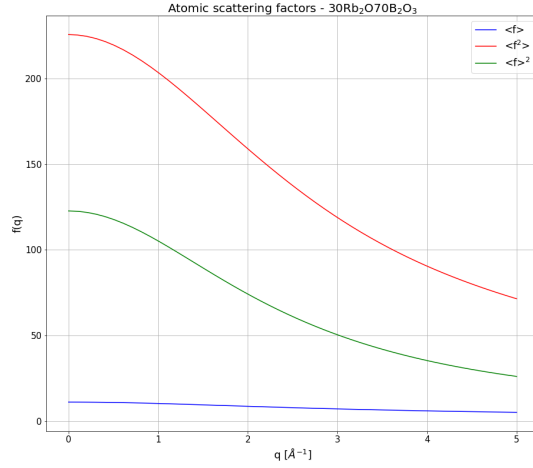


Figure 15: Calculated averaged scattering-factors for 30Rb₂O70B₂O₃.

2.5.3 Data analysis - Simulation of alkali borates amorphous structure

Information which is fundamentally essential for interpretation of experimental autocorrelation time obtained from the aXPCS measurement is the scattering function $S(q)$. The ability to measure the scattering function in various oxide glasses, practically background-free, provides a unique opportunity to analyse structures of amorphous materials with the hope to gain a deeper understanding of their dynamics. Despite all the efforts material scientists put into studies of the structure of glasses, one can attest only moderate success, especially regarding the knowledge of medium-range order in these materials. Thus, any sort of new experimental information should be effectively used to explore structural models in glasses.

In this regard, at least two procedures are available for the extraction of structural information from X-ray diffraction: the application of a reverse Monte Carlo method [14], or the construction of a model structure, using various inter-atomic potentials, to compare to the experiment. One can call the latter a bottom-up method with the former being top-down. Reverse Monte Carlo provides excellent fits to experimental data, but the glass-structures it creates are severely random and difficult to interpret. Moreover, in order to allow any feasible modelling, the data must be of excellent quality and measured over a very large q -range, which discredits measurements based on a copper K_α source. In the following we chose to compare our experimental scattering functions with a $S(q)$ simulated by the Monte Carlo method.

With the dopant of the borate-glasses being alkali-ions, we are in the fortunate position of being able to use a well tested, credible potential used for molecular dynamics (MD) studies in these structures. This is the potential of the Born-Mayer-Huggings (BMH) form and with a set of parameters derived initially by Verhoef and den Hartog [15] for studies of structural and dynamical properties in lithium, caesium and mixed alkali borate glasses and, subsequently, in a number of other studies. This inter-atomic potential has already been used for instance to study the structure and dynamics in lithium [16] and caesium [17] giving reasonable agreement with experimental radial distribution functions and infra-red profiles. The structure of the full series of Li, Na, K, Rb and Cs borate oxide glasses have been investigated with a focus on structural modifications on the B–O network showing reasonable agreement with the neutron-weighted partial static structure factor [18]. Even structural foundations of the mixed-alkali effect (MAE) have been studied on Li – Cs borate oxides via simulations of the structure and infra-red vibrational spectra [19] providing a structural explanation for the MAE.

Due to the fact that we are only interested in the structural information and not at all in vibrational characteristics, we used a faster and, in terms of our requirements, more precise method of Monte Carlo (MC) simulations. Berthier and Kob [20] showed using a standard Monte Carlo algorithm to study the slow dynamics of a binary Lennard-Jones soft-spheres model that the Monte Carlo approach is the most efficient way to simulate a stochastic structure and even long-range dynamics. This means that not only the structure but also the average dynamical behaviour of the system is in quantitative agreement with results obtained by molecular dynamics simulations (i.e. using Newtonian dynamics) apart from simulations of lattice vibrations (phonons) at very short times which are not of interest to us.

The simulation software has been written and simulations computed by Bogdan Sepiol.

3 Results

The following section covers the complete set of results for each sample within the alkali-borate glass group, as well as within the vanadium-phosphate and lead-silicate glass group. The output of the data evaluation, as described in section 2.5, is a list of parameters pertaining to sample thickness, normalization and transmission, respectively. These will be provided in tables for each type of glass, along with the plots of the scattering functions. Since measurements took place in two distinct configurations of the set-up, where the secondary detector was situated further away in the first set than in the second, the intensity of the unperturbed beam, i.e. in the case of an empty sample holder, has two different values used for calculation of the sample transmission via equation (35). These intensities, as counts per second, are as follows:

$$\begin{aligned} I_0^{(1)} &= 182400 \\ I_0^{(2)} &= 212894 \end{aligned} \tag{39}$$

The error in the calculated thickness Δd was calculated on the base of Poisson standard deviation $\Delta I = \pm\sqrt{I}$, thus $\Delta d = \pm\frac{1}{\mu}\left(\frac{I+I_0}{II_0}\right)^{\frac{1}{2}}$. For the relative error $\frac{\Delta d}{d}$, in the best case, we would expect around 0.5%. The results for the thickness are displayed rounded to the significant digit with a 1% relative error.

3.1 Alkali-Borate Glasses

3.1.1 Lithium

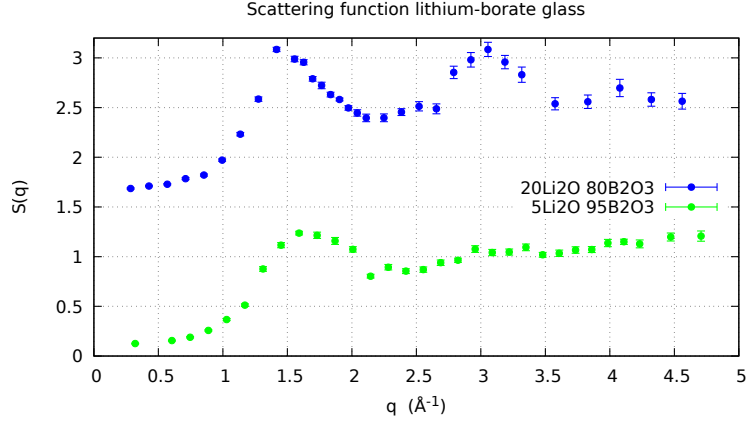


Figure 16: Scattering functions for the $x\text{Li}_2\text{O}(1-x)\text{B}_2\text{O}_3$ sample group, with $x = 5$ represented by the green points and $x = 20$ by the blue points. The plots are shifted vertically by 1.5.

% Li ₂ O	I_0	I	N	$\frac{1}{\mu}$ [μm]	d [μm]
5	$I_0^{(1)}$	39100	80	501.8	772(8)
20	$I_0^{(2)}$	130600	100	450.6	220(2)

Table 3: Gathered intensity on the measurement location for each sample in the lithium-oxide group. N represents the normalization variable according to 12, $\frac{1}{\mu}$ the scattering length according to 35 and d the mean sample thickness at the spot of measurement.

3.1.2 Sodium

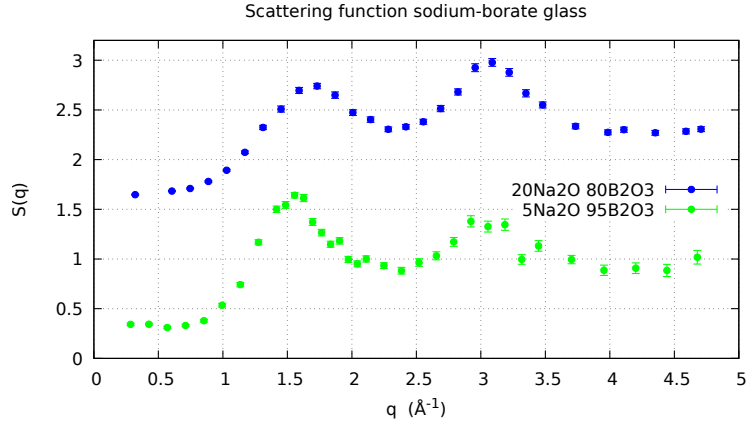


Figure 17: Scattering functions for the $x\text{Na}_2\text{O}(1-x)\text{B}_2\text{O}_3$ sample group, with $x = 5$ represented by the green points and $x = 20$ by the blue points. The plots are shifted vertically by 1.5.

% Na ₂ O	I_0	I	N	$\frac{1}{\mu}$ [μm]	d [μm]
5	$I_0^{(2)}$	88500	120	414.7	364(4)
20	$I_0^{(1)}$	95800	85	374.2	241(2)

Table 4: Gathered intensity on the measurement location for each sample in the sodium-oxide group. N represents the normalization variable according to 12, $\frac{1}{\mu}$ the scattering length according to 35 and d the mean sample thickness at the spot of measurement.

3.1.3 Potassium

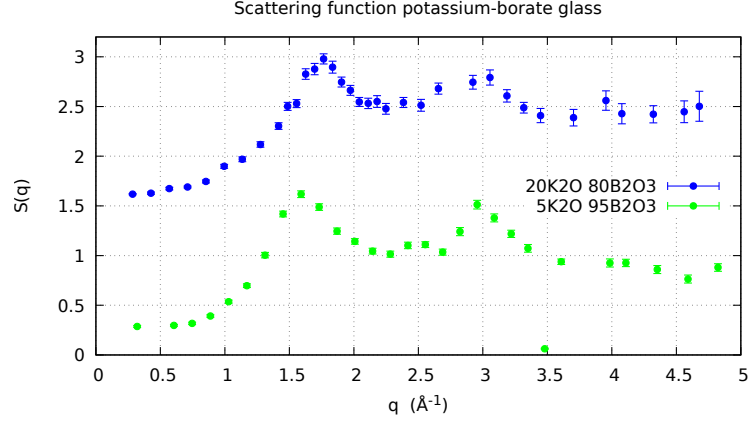


Figure 18: Scattering functions for the $x\text{K}_2\text{O}(1-x)\text{B}_2\text{O}_3$ sample group, with $x = 5$ represented by the green points and $x = 20$ by the blue points. The plots are shifted vertically by 1.5.

% K ₂ O	I_0	I	N	$\frac{1}{\mu}$ [μm]	d [μm]
5	$I_0^{(1)}$	92500	60	178.4	121(1)
20	$I_0^{(2)}$	82450	27	165.3	165(2)

Table 5: Gathered intensity on the measurement location for each sample in the potassium-oxide group. N represents the normalization variable according to 12, $\frac{1}{\mu}$ the scattering length according to 35 and d the mean sample thickness at the spot of measurement.

3.1.4 Rubidium

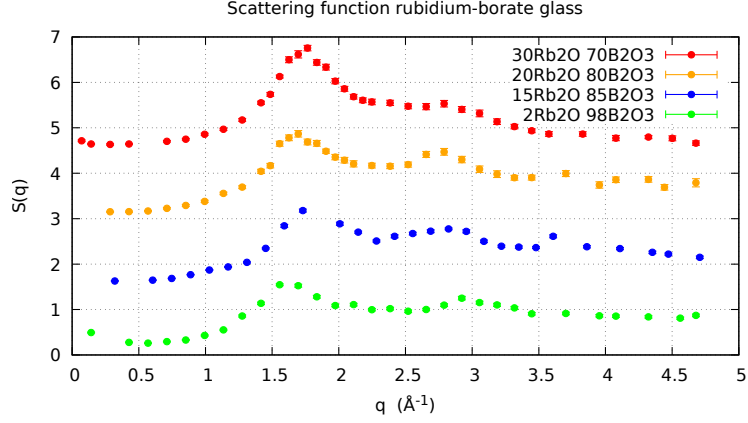


Figure 19: Scattering functions for the $x\text{Rb}_2\text{O}(1-x)\text{B}_2\text{O}_3$ sample group, with $x = 2$ represented by the green points $x = 15$ by the blue points, $x = 20$ by orange points and $x = 30$ by red points. The plots are shifted vertically by 1.5.

% Rb_2O	I_0	I	N	$\frac{1}{\mu}$ [μm]	d [μm]
2	$I_0^{(1)}$	107000	80	155.6	83(1)
15	$I_0^{(1)}$	87800	23	128.6	94(1)
20	$I_0^{(2)}$	124300	13	95.0	51(1)
30	$I_0^{(2)}$	59688	2.5	109.9	139(1)

Table 6: Gathered intensity on the measurement location for each sample in the rubidium-oxide group. N represents the normalization variable according to 12, $\frac{1}{\mu}$ the scattering length according to 35 and d the mean sample thickness at the spot of measurement. The calculation of the scattering length and thickness of the $20\text{Rb}_2\text{O}80\text{B}_2\text{O}_3$ sample was done on basis of the density value measured by Berkemeier et al. in [6], as no measured density was available in house.

3.1.5 Caesium

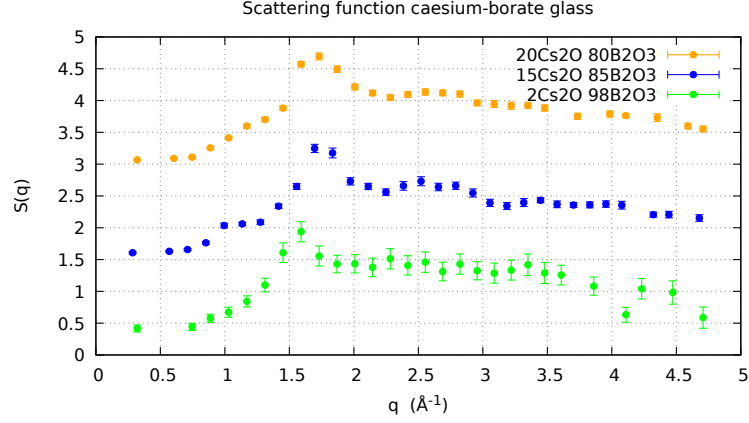


Figure 20: Scattering functions for the $x\text{Cs}_2\text{O}(1-x)\text{B}_2\text{O}_3$ sample group, with $x = 2$ represented by the green points $x = 15$ by the blue points and $x = 20$ by orange points. The plots are shifted vertically by 1.5. A measurement for $x = 10$ was also done but was excluded due to very weak measured scattered intensities resulting from a sample that was too thick.

% Cs_2O	I_0	I	N	$\frac{1}{\mu}$ [μm]	d [μm]
2	$I_0^{(1)}$	17200	17	44.3	104(1)
15	$I_0^{(1)}$	45000	5	33.6	47.(5)
20	$I_0^{(1)}$	41800	4	30.9	45.5(5)

Table 7: Gathered intensity on the measurement location for each sample in the caesium-oxide group. N represents the normalization variable according to 12, $\frac{1}{\mu}$ the scattering length according to 35 and d the mean sample thickness at the spot of measurement.

3.1.6 B₂O₃

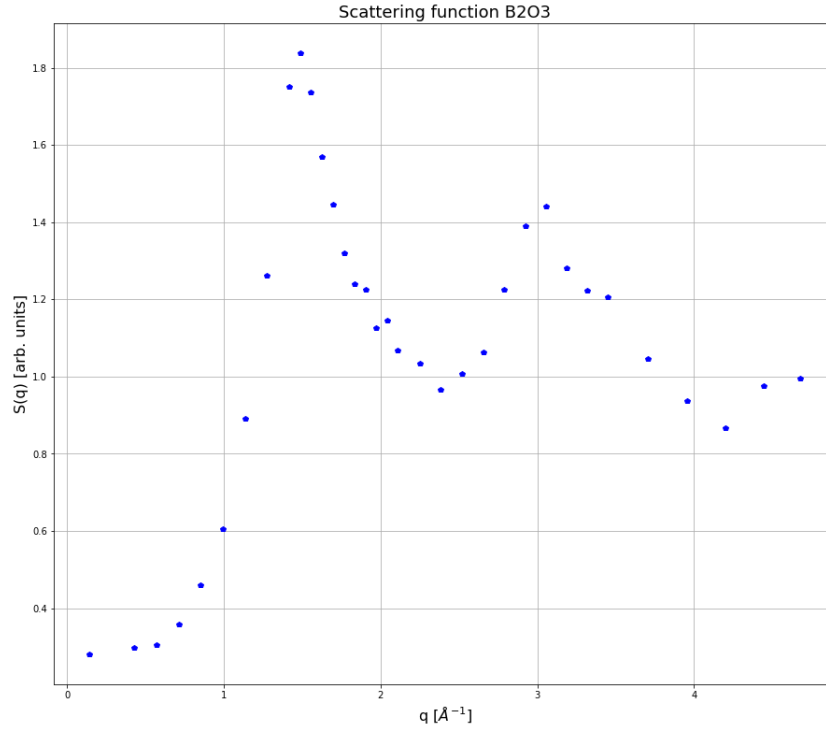


Figure 21: Scattering function for the B₂O₃ sample.

The sample thickness at the measurement location was determined to be $d = 251(3) \mu\text{m}$, with an intensity of 145700 at $I_0 = 212894$, scattering length of $\frac{1}{\mu} = 661.9 \mu\text{m}$ and $N = 85$.

3.2 Vanadium-Phosphate and Lead-Silicate Glasses

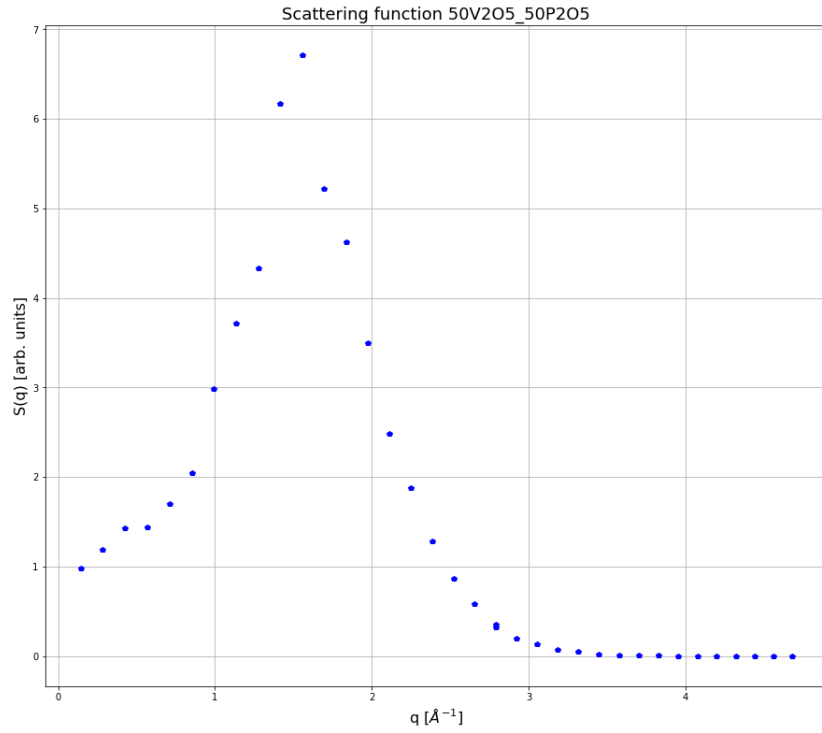


Figure 22: Scattering function for the $50\text{V}_2\text{O}_550\text{P}_2\text{O}_5$ sample.

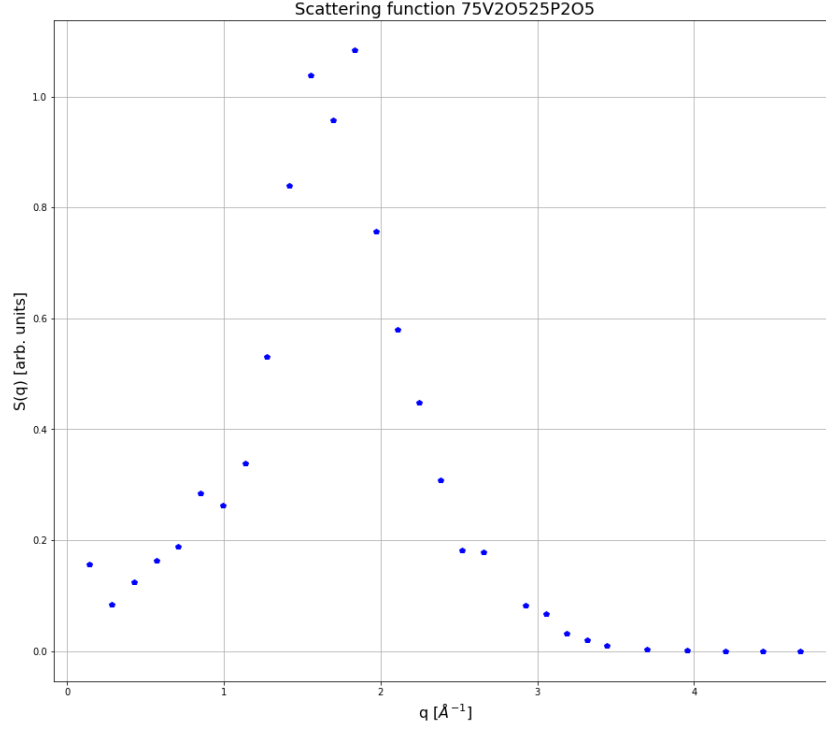


Figure 23: Scattering function for the 75V₂O₅25P₂O₅ sample.

% V ₂ O ₅	I_0	I	N	$\frac{1}{\mu}$ [μm]	d [μm]
50	$I_0^{(2)}$	120200	1	38.6	22.(2)
75	$I_0^{(2)}$	122500	1	31.2	17.(2)

Table 8: Gathered intensity on the measurement location for each sample in the vanadium-phosphate group. N represents the normalization variable according to 12, $\frac{1}{\mu}$ the scattering length according to 35 and d the mean sample thickness at the spot of measurement.

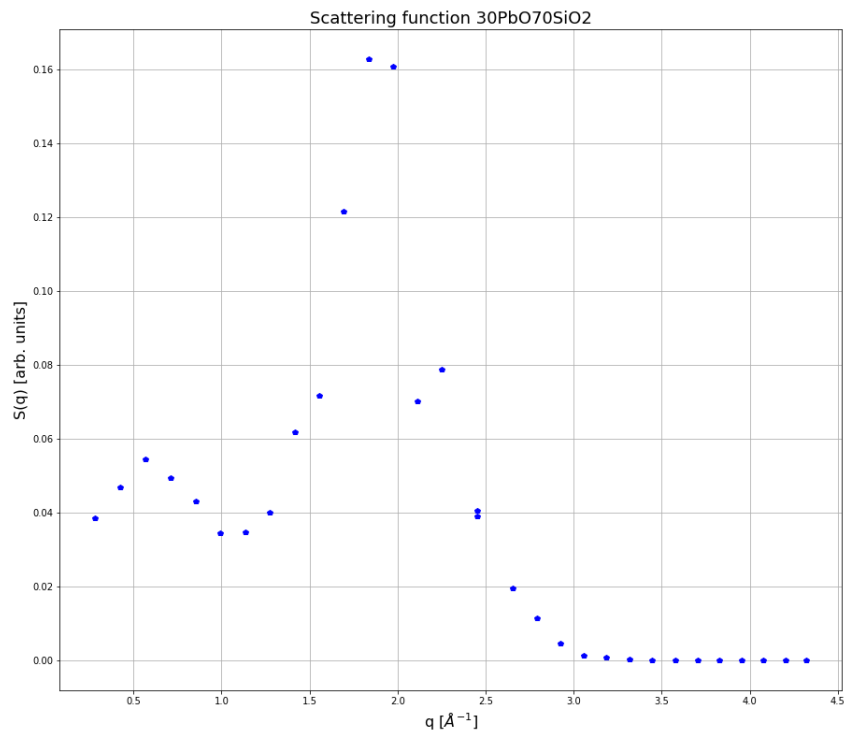


Figure 24: Scattering function points for the 30PbO70SiO₂ sample.

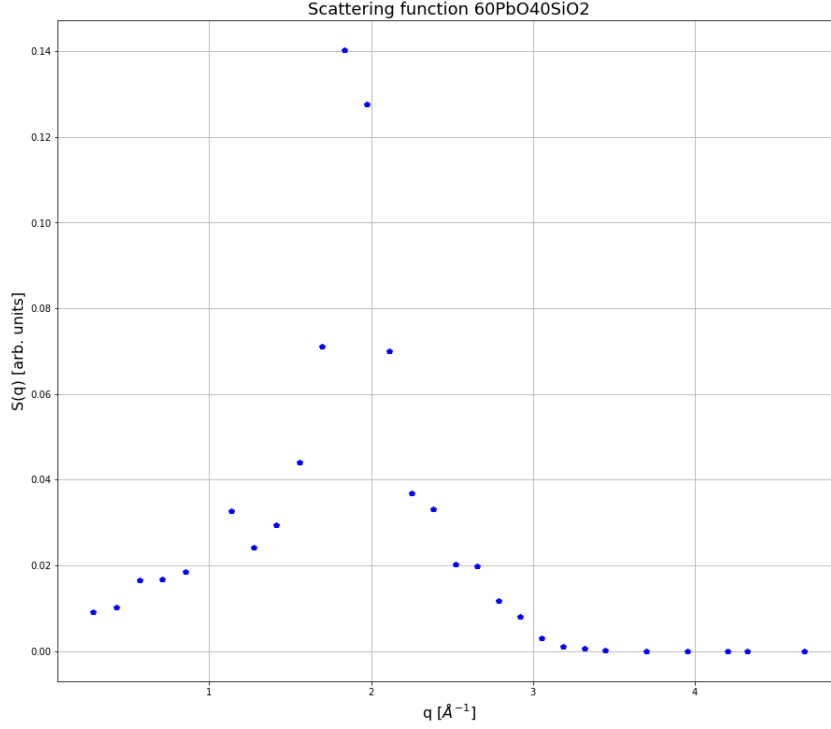


Figure 25: Scattering function points for the 60PbO40SiO₂ sample.

% PbO	I_0	I	N	$\frac{1}{\mu}$ [μm]	d [μm]
30	$I_0^{(2)}$	152000	1	16.5	5.(1)
60	$I_0^{(2)}$	105360	1	12.7	8.(1)

Table 9: Gathered intensity on the measurement location for each sample in the lead-silicate group. N represents the normalization variable according to 12, $\frac{1}{\mu}$ the scattering length according to 35 and d the mean sample thickness at the spot of measurement.

The densities of the lead-silicate glass samples were taken from [29], where the density of the 30PbO70SiO₂ sample was measured to be $\rho = 4.28 \text{ gcm}^{-3}$ and the 60PbOSiO₂ was interpolated to be $\rho = (6.6 \pm 0.7) \text{ gcm}^{-3}$.

3.3 Comparison with the simulated spectra

Almost all glass compositions measured with the AMPTEK detector have been simulated and compared with the measured scattering functions. Simulated structures are denoted $x\text{Al}_2\text{O}(1-x)\text{B}_2\text{O}_3$, where AI is the alkali ion and $x = 0.02 \div 0.30$ is the mole fraction of alkali oxide. Structures consisting of about 10000 to 11000 atoms in a cubic cell with periodic boundary conditions [21] have been generated with a number of components guaranteeing charge neutrality of the simulation box. Interatomic interactions were treated by means of BMH potential [15] and long-range Coulomb forces were handled by the Ewald summation method [21]. It was suggested that the basic BO_3 triangular units in vitreous B_2O_3 can be arranged in planar boroxol rings with a total chemical formula $\text{B}_3\text{O}_{9/2}$ [22]. The fraction of boron atoms in such rings has remained, however, despite decades of investigations an intensively disputed topic. There is now a broad consensus on the fraction of boron atoms inside the rings [23] of about 75% in vitreous B_2O_3 . It is impossible to reproduce a fraction this high with any binary potential and we introduced in our simulation *a priori* boroxol rings via three-body interaction between boron and oxygen atoms. It is also known that the fraction of boron atoms in boroxol rings diminishes with increasing number of alkali ions. In our simulations we used a fraction of between 60 % and 40 % of boron in the rings regarding the $x = 0.02$ and 0.30 structures, respectively.

The starting value of the volume of the simulation box was chosen due to the experimental density measured by the Archimedes method using decahydronaphthalene as an immerse liquid and a silicon single crystal as a density standard. For the details of the method see [10].

The relaxation was performed due to the standard Monte Carlo dynamics [21] with an elementary move performed as follows [20]. An atom i located at the position $\vec{r}_i$ was randomly chosen and moved to a new position $\vec{r}_i + \delta\vec{r}$, $\delta\vec{r}$ being a random vector within a sphere of radial length δ_{max} centred at the original vector $\vec{r}_i$ ($\delta_{max} = 0.3 \text{ \AA}$ [20]). The Metropolis acceptance rate was calculated from the Boltzmann factor $e^{-\beta\Delta E_i}$, where $\beta = 1/k_B T$ and ΔE_i is the energy cost to move the atom between both positions. The relaxation was started at a very high temperature and equilibrated in several steps up to the final temperature of 300 K. The real-space partial radial distribution function $g_{AB}(r)$ where $\{A, B\}$ are B, O or AI atoms, respectively, and, by Fourier sine-transformation, the total scattering function $S(q)$ was calculated. Simulation results for Rb borates are shown in 26.

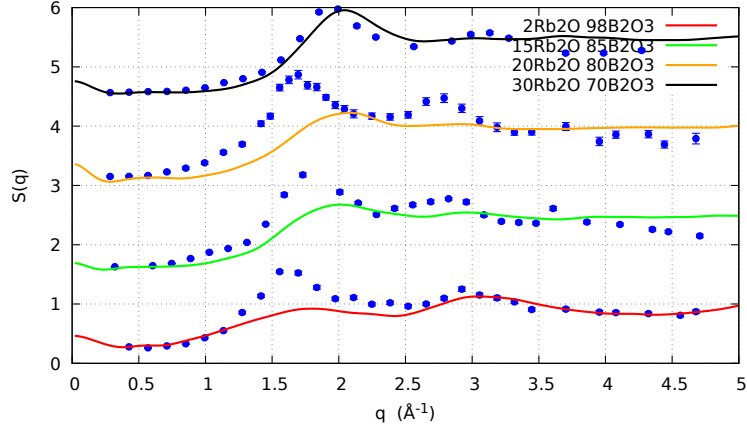


Figure 26: Total scattering function $S(q)$ for $x = 2$ (red lower curve), 15, 20 and 30 (black uppermost curve) mol% $x\text{Rb}_2\text{O}(1-x)\text{B}_2\text{O}_3$ glasses as a function of momentum transfer. The lines are results of MC simulations, blue points are results of scattering measurements as described in chapters 2.4 and 2.5. The plots are shifted vertically by 1.5 for clarity.

Generally one can observe moderate agreement between experimental and MC simulated $S(q)$. The agreement between simulation and experiment tends to be better for ionic glasses with higher concentration of rubidium atoms and less for the lowest one. The position of the first diffraction peak changes continuously from about $q \cong 1.6 \text{ \AA}^{-1}$ for $x = 2$ to almost $2.0 \text{ \AA}^{-1}$ for $x = 30$ at.% Rb_2O . The MC-simulated curves follow this trend to some extent, but not strong enough. Different trials have been undertaken to improve the quality of the fits. E.g. different equilibrium distances between boron and oxygen atoms dependent on the local configuration of boron atoms have been introduced. It is known, that the structure of pure B_2O_3 glass obtained by MD simulation [15] consists of randomly connected BO_3 triangles and BO_4 tetrahedrons. The mean B–O distance is about $1.37 \text{ \AA}$ in triangles and $1.48 \text{ \AA}$ in tetrahedrons. Also different B–O distances in the boroxol rings have been applied, as well as changes in various parameters of inter-atomic potentials. These attempts ended with only little and partial success. Consequently the same set of parameters have been applied for all further simulations and only the radii of the alkali ions have been adapted according to the applied ion kind.

The better experiment-simulation agreement for ionic glasses with higher concentration of rubidium atoms means, that the simulated B–O network does not mirror the real B_2O_3 structure. Especially the first diffraction peak is too small. Further trials are necessary to simulate this network sufficiently well, or even more sophisticated inter-atomic potentials are necessary for that purpose. Attempts to simulate these structure completely without boroxol rings provided even worse results, which means that we still need better order on the medium-range distances between atoms, i.e. distances between about 3 and 10 Å. Simulation results for caesium borates are shown in 27.

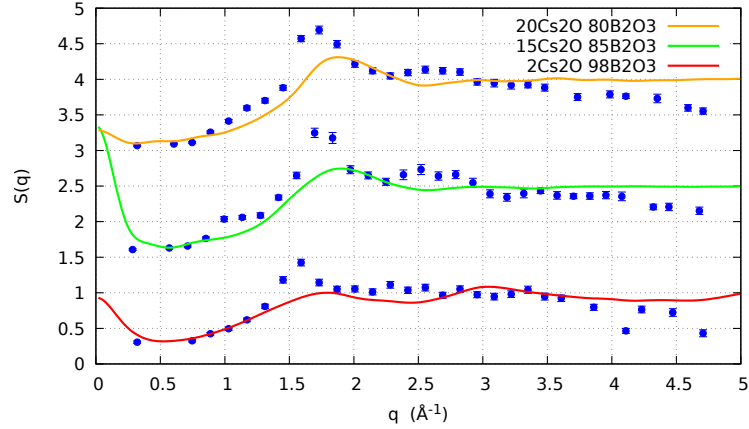


Figure 27: Total scattering function $S(q)$ for $x = 2$ (red lower curve), 15 and 20 (orange uppermost curve) mol% $x\text{Cs}_2\text{O}(1-x)\text{B}_2\text{O}_3$ glasses. The plots are shifted vertically by 1.5.

The position of the first diffraction peak changes only minimally from about $q \cong 1.6 \text{ \AA}^{-1}$ for $x = 2$ to about $1.7 \text{ \AA}^{-1}$ for $x = 20$ at.% Cs_2O . Generally the scattering function in $x\text{Cs}_2\text{O}(1-x)\text{B}_2\text{O}_3$ is very similar to that of $x\text{Rb}_2\text{O}(1-x)\text{B}_2\text{O}_3$. That allows two important conclusions to be drawn: first of all, our measurement with the AMPTEK detector of caesium glass with a very high fraction of fluorescent scattering, which was carefully separated from the elastic signal, was very successful. Secondly, the evaluation of raw scattering intensity due to Eq. (37) shall be correct because very similar $S(q)$ is obtained despite different scattering powers of both alkalis: compare $f_{\text{Rb}^+} = 36$, whereas $f_{\text{Cs}^+} = 54$ which results in the scattering intensity proportion of 1 : 2.25. Simulation results for potassium borates are shown in 28.

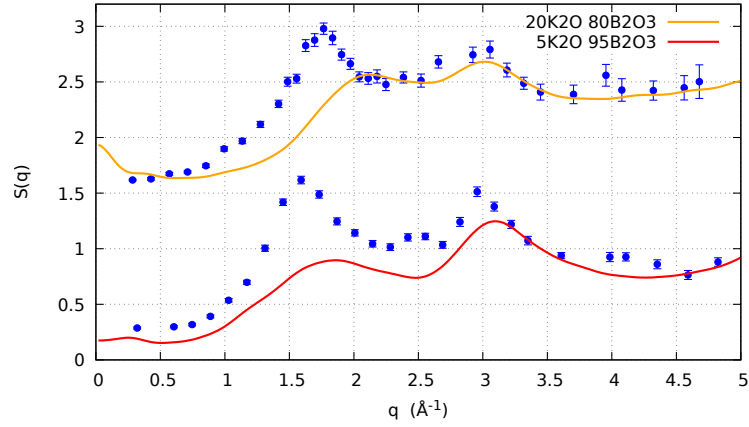


Figure 28: Total scattering function $S(q)$ for $x = 5$ (red lower curve) and 20 (orange upper curve) mol% $x\text{K}_2\text{O}(1-x)\text{B}_2\text{O}_3$ glasses. The plots are shifted vertically by 1.5.

Potassium $x\text{K}_2\text{O}(1-x)\text{B}_2\text{O}_3$ represent a special case in the family of alkali borates. Whereas rubidium and caesium represent large ions with ionic radii used in the BMH potential of 1.70 and 1.84 Å, respectively, lithium and sodium are small ions (0.925 and 1.16 Å). The result is that Rb^+ and Cs^+ not only, to a high extent, influence the B_2O_3 network of BO_3 triangles and BO_4 tetrahedrons, but also scatter X-rays strongly, especially for higher alkali contents. On the other hand small ions left the B_2O_3 network more or less unaffected and also scatter very weakly even in higher ionic concentrations. Potassium borates represent a "transition type" of alkali oxides. The position of the first diffraction peak changes significantly from $q \cong 1.6 \text{ Å}^{-1}$ for $x = 5$ to about 1.76 Å^{-1} for $x = 20 \text{ at.}\%$ K_2O . This is evidence for changes in the structure. The simulated spectrum for $x = 20 \text{ mol}\%$ K_2O fits very poorly to the experimental data, which means that the simulated network does not reflect reality. Simulation results for sodium and lithium borates are shown in 29 and 30.

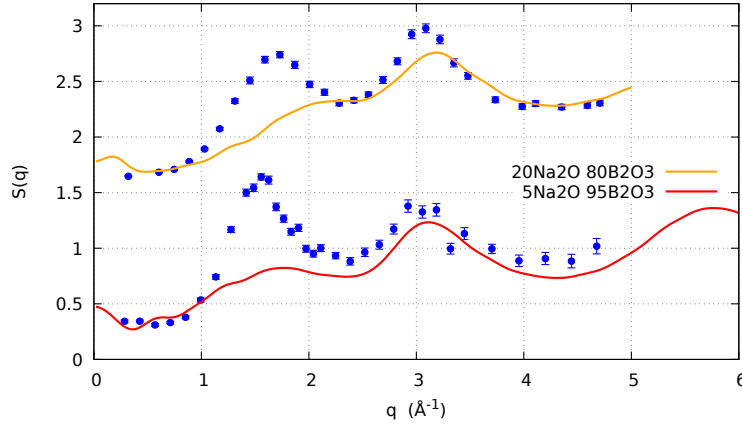


Figure 29: Total scattering function $S(q)$ for $x = 5$ (red lower curve) and 20 (orange upper curve) mol% $x\text{Na}_2\text{O}(1-x)\text{B}_2\text{O}_3$ glasses. The plots are shifted vertically by 1.5.

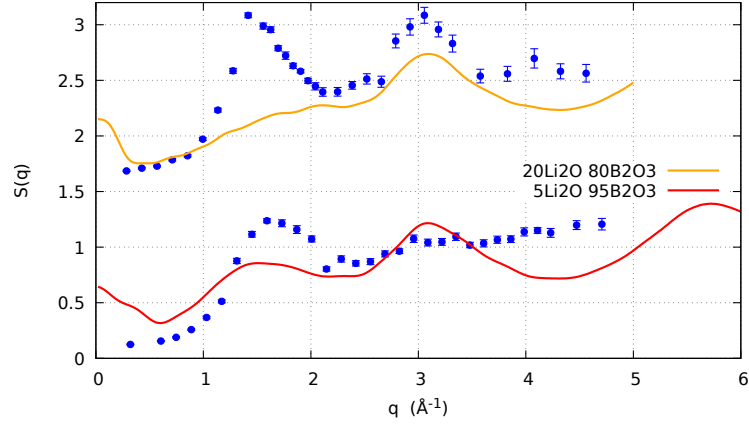


Figure 30: Total scattering function $S(q)$ for $x = 5$ (red lower curve) and 20 (orange upper curve) mol% $x\text{Li}_2\text{O}(1-x)\text{B}_2\text{O}_3$ glasses. The plots are shifted vertically by 1.5.

Together with vitreous B_2O_3 , see 31, these borates eminently represent inadequacies of the BMH model in the simulation of borate glasses.

Concluding, we take note of weaknesses of the simulation model and consider this as a challenge to find a better framework for borate oxides. Especially the weak first diffraction peak of the model glasses can be interpreted as a sign of a network structure, which is much better ordered in the medium-range order as it appears in the Monte Carlo simulated structures. In other words, the simulated B_2O_3 network is still much too random or disordered. In order to create higher medium-range order, an inter-atomic potential with long-range interaction is required.

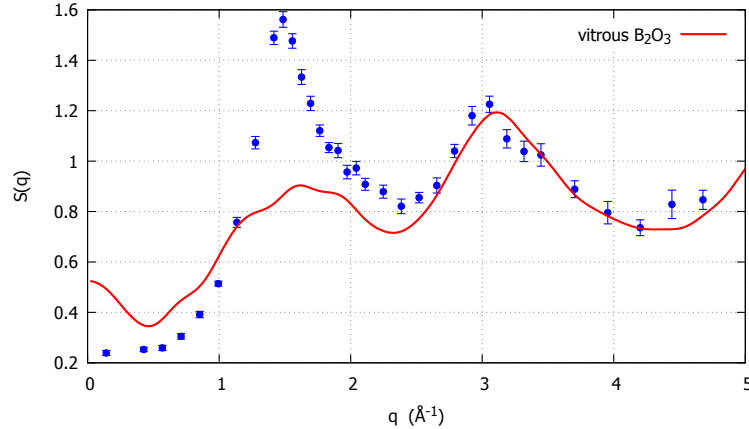


Figure 31: Total scattering function $S(q)$ for vitreous B_2O_3 glass.

3.4 Reverse Monte-Carlo method

In order to gain a qualitative understanding of the possible benefits in using the RMC method we simulated the structures of $5\text{K}_2\text{O}95\text{B}_2\text{O}_3$ and $5\text{Na}_2\text{O}95\text{B}_2\text{O}_3$. The results are displayed in figures 32 and 33.

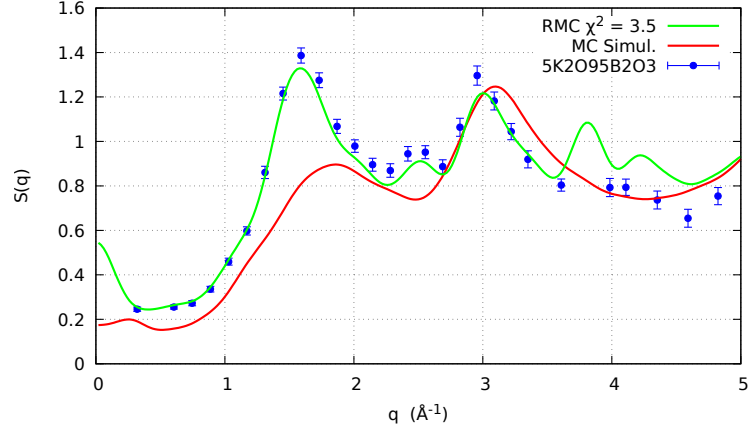


Figure 32: Comparison between the MC-model with BMH potential and RMC models on the scattering function results of $5\text{K}_2\text{O}95\text{B}_2\text{O}_3$.

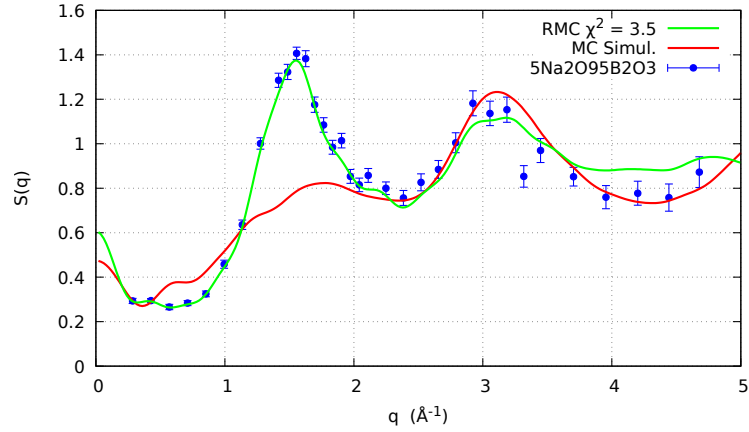


Figure 33: Comparison between the MC-model with BMH potential and RMC models on the scattering function results of $5\text{Na}_2\text{O}95\text{B}_2\text{O}_3$.

The improvements over the BMH Monte-Carlo model are apparent, especially around the first peak, where the former experienced the most severe difficulties. A significant drop in the value of χ^2 also indicates that this approach might be more useful in the simulation of borate-glasses. For higher Q-values the compliance to the data seems to be weaker than in our previous simulations. The respective atomic pair-correlation functions were also plotted and can be seen in figures 34 and 35.

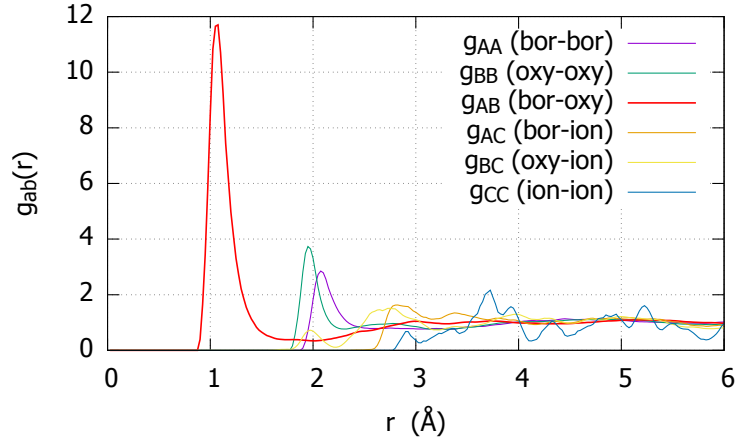


Figure 34: RMC calculated pair-correlation function of $5\text{K}_2\text{O}95\text{B}_2\text{O}_3$.

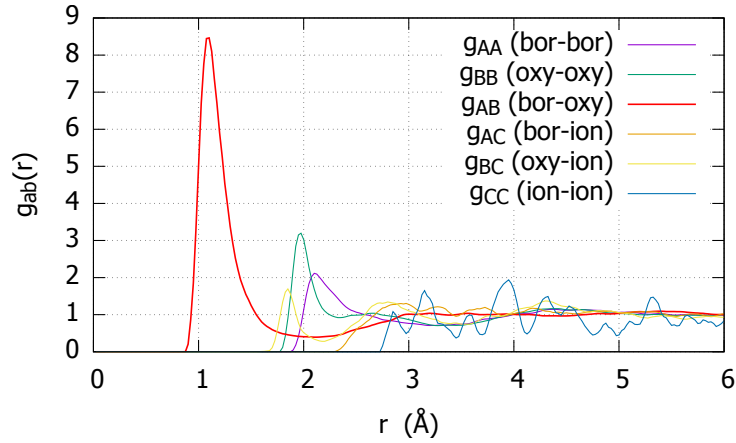


Figure 35: RMC calculated pair-correlation function of $5\text{Na}_2\text{O}95\text{B}_2\text{O}_3$.

In comparison to the previously simulated atomic PDFs, the new simulation creates a broader distribution with slightly smaller amplitudes, which is seen especially at the boron-oxygen peak. An analysis of the resulting numbers of nearest-neighbours, especially in the relative populations of boron atoms and their nearest oxygens, implies more disorder in the simulated structure. In the RMC simulation 3.7% have one oxygen neighbour, 43.3% have two, 50.6% have three and 2.4% have four oxygen neighbours. In the MC-simulated structure this was distributed to 0.04%, 14.5%, 82.5% and 2.9% respectively. This would represent a scenario more adherent to the assumption that the BO_3 unit is the most important fundamental building block of the structure. Since the RMC method yields more disorderly results this is expected, and the shown results are not conclusive, but may represent a template of an accurate approach to simulating our structures.

4 Conclusions and Outlook

The following chapter shall examine and compile the results from the previous sections and give conclusions thereupon. Besides the results of the experiment, the experimental approach and the method of data-collection and evaluation should be discussed regarding to its fitness for purpose within the total X-ray scattering technique. Finally for elements in the experiment, that did not perform as expected, alternatives and improvements are suggested for future experimentation.

Preparing the bulk samples in a polished, planar form was advantageous, in that the grinding and polishing process was simple and easy to accomplish. Most importantly we experienced no, or only very insignificant discrete peaks of intensity due to recrystallization of the hygroscopic samples, even though many of them were already quite old. It can be said that for the lighter alkali-metals this process presents no disadvantages.

Samples with rubidium and caesium modifier ions however were more challenging, since their scattering length required thicknesses beyond what was achievable with grinding. As these were then dimpled to the appropriate thickness they exhibited a geometry different from what was expected by the thickness-correction algorithm, which assumes a perpendicular incoming beam to a planar surface. This affected one sample of $30\text{Rb}_2\text{O}70\text{B}_2\text{O}_3$ especially, whose calculated $S(q)$ did not approach unity for large q . It is possible that this could be remedied by using another algorithm designed to accommodate the spherical shape at the spot of entry, see Appendix B.

One measurement of the dimpled samples, namely $10\text{Cs}_2\text{O}90\text{B}_2\text{O}_3$, was thrown out due to an almost random distribution of gathered intensities. This was most likely due to the fact that the sample was still too thick. For future sample preparation it should be necessary to have a more precise means of measuring these sample-dimensions, as the dimpling process requires a somewhat accurate estimation of how deep the dimpling tool must proceed into the sample. Another option is using a higher energy photon source as the scattering length increases with beam energy.

The experimental set-up using the two detectors, as depicted in figure 6, worked as expected. The use of the goniometer inside the vacuum chamber allowed for a very quick data collection and reduced the time spent measuring from past experiments significantly. The energy resolving detector was successful in separating the fluorescent intensity lines from the elastic lines, giving the opportunity to measure fluorescent materials.

Due to the large amounts of both data and necessary steps for evaluation, the choice to automate the process with a python-script turned out to be a significant help in reducing the time spent processing the datasets. However the script in its current form has one flaw, in that it requires a consistent nomenclature of the input file-names. A measured intensity profile at an certain angle would usually be saved in a text-file with the name including the sample specification and the measured angle. For example a profile measured from $10\text{Cs}_2\text{O}90\text{B}_2\text{O}_3$ at an angle of 6° would be named "10Cs2090B203_DEG_6.mca", the script would expect this file-name format and extract the sample-name and angle via string operations. Some early measurements were conducted with the goniometer being set to 0.5° at the lowest reading, and since our resolution was only slightly lower than 1° subsequent measurements were performed at 2° or 1° steps. To reflect this in the file-name the previous example would be named "10Cs2090B203_DEG_6-5.mca". This meant that not all measurements could be evaluated at once but had to be separated according to their file-names, with a second script only for the latter category.

Concerning the simulation, as already mentioned in the previous section, the results were only moderately successful. From the resulting model structure and the thus derived scattering function, it seems this approach may be too simple in nature, as it doesn't reflect reality adequately. This is evidenced in the fact that the available potentials cannot reproduce the approximately 75% boron concentration in B_3O_6 boroxol rings by themselves. The BMH model generally performs poorly with the glasses modified with lighter alkali-ions, such as Li, Na and Ka. For the heavier alkali-ions, which more severely affect the network structure display higher agreement with the simulation at increasing concentrations, which further underlines the argument that the BMH model is insufficient for simulation of B_2O_3 structures.

In conclusion, it seems as though the BMH approach is too rigid to properly simulate these structures. A sufficient model may require many more parameters to achieve the desired results.

A Fluorescence

The generation of radiation in a conventional X-ray tube is based on emission of electrons in a tungsten cathode and their acceleration towards a metal target acting as an anode within the acceleration voltage of the device. The primary radiation from a X-ray source consists of a continuous spectrum, caused by decelerating electrons (Bremsstrahlung), and a discrete spectrum of characteristic lines from the anode target material, which most commonly consists of chromium, copper, molybdenum or tungsten [26] [27].

An X-ray tube is supplied with several kW of power, achieving a voltage of around $U = 10 - 100\text{kV}$ and a current of $10\text{-}50\text{mA}$, most of the electric input power is lost in heat generation and only around 0.1% is converted into radiation. The average kinetic energy of the generated electrons can be calculated as [26]:

$$E_{kin} = eU - A_K + A_A \quad (40)$$

Where e denotes the elementary charge of the electrons and A_K , A_A the work functions of the cathode and anode materials respectively.

The produced primary radiation, being in part composed of Bremsstrahlung and in part of characteristic lines, can then be filtered or made monochromatic, though this is not strictly necessary, and be brought to interact with other samples. If the photon energy of the primary beam is equal to or exceeds the ionization threshold of the electrons in the sample, it produces secondary X-ray radiation. This is called X-ray fluorescence (XRF).

For XRF to be generated the photon energy of the beam must exceed the binding energy of a bound inner electron in the target atom, also called the critical excitation energy. If the condition is met the electron can be ejected from the atom and a vacancy is created. In the subsequent recombination the atom has two options to regain its stable ground state, either an electron takes the space in the vacancy and imparts the energy difference to an electron in an outer shell, thus emitting an Auger electron, or the difference of previous and subsequent energy states from the other electron occupying the vacancy is converted directly into a photon with energy characteristic to the element in accordance with $E_{ph} = E_p - E_s = h\nu$. This process can continue until finally a free electron takes the place of an outermost valence electron with emission of a photon or Auger electron at each step, thus returning the atom to a stable ground state.

The allowed transitions between shells are subject to selection rules. For a transition between shells of principal quantum numbers n_1 and n_2 to be allowed, firstly the difference between their orbital angular momentum quantum numbers must yield $\Delta l = 1$, and furthermore the difference Δj of the total angular momentum operator, gained by vectorial addition of spin and orbital angular momentum, must conform to either $\Delta j = 0$ or $\Delta j = 1$. Figure 36 displays the possible transitions.

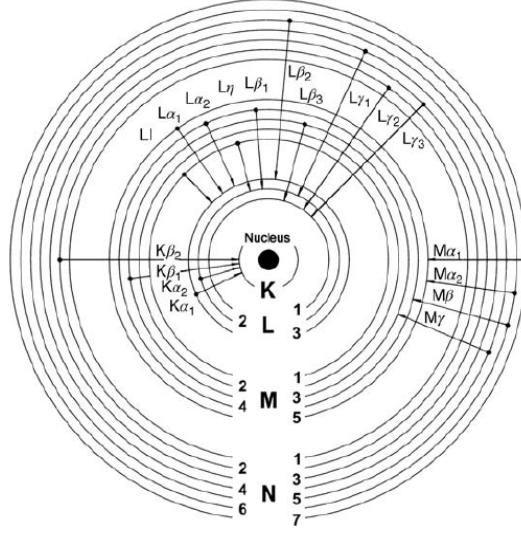


Figure 36: Schematic depiction of allowed transmissions of inner electrons [27] [28].

Since the particle in question is an electron the total angular momentum is written as $j = l \pm \frac{1}{2}$. The nomenclature according to Siegbahn is ordered as such: The series notation is based on the principal quantum number, increasing indices are labelled as K, L, M, etc., transitions between shells are described by Greek symbols according to the difference in principal quantum numbers, therefore $\Delta n = 1 \rightarrow \alpha$, $\Delta n = 2 \rightarrow \beta$ etc., finally the fine-structure splits in energy levels require a further distinction due to degeneracy in the orbital momentum denoted by an index beneath the Greek lettering.

As an example consider a transition between the L and K shell from a p-orbital ($l = 1$) to an s-orbital ($l = 0$). This transition has two distinct lines from $j = \frac{1}{2}$ and $j = \frac{3}{2}$ representing the α_1 , α_2 doublet. The energy terms for each state are in relation to the principal quantum number: $T_n = R_E \frac{1}{n^2}$; Where R_E is the Rydberg constant. Transmission energies can thus be written as:

$$h\nu = R_E \left(\frac{1}{n_i^2} - \frac{1}{n_j^2} \right) \quad (41)$$

The relative intensities of a series' peaks are determined by the probabilities of the transitions. Returning to our prior example of the α_1 , α_2 doublet and considering the number of possible states is expressed as $N_z = 2j + 1$, this means four states for $j = \frac{3}{2}$ and two for $j = \frac{1}{2}$ which yields:

$$\frac{I_{K_{\alpha_1}}}{I_{K_{\alpha_2}}} = 2 \quad (42)$$

The intensity of the K_{α_1} peak should therefore be twice as strong as the peak from K_{α_2} .

B Thickness correction for spherical shaped incident on sample

The total beam intensity gathered in the detector after it's scattered and subsequently attenuated by the sample is the integral of all possible trajectories of the beam within the irradiated sample volume. The specific geometry thus influences the amount of absorption experienced by the beam. In the case of elastic single scattering over the solid angle $d\Omega$ at (θ, ϕ) the the total scattering intensity is calculated with [1]:

$$I_s(E, \theta, \phi) = d\Omega dE \int d\vec{r} J \frac{d^2\sigma}{d\Omega dE} A \rho \quad (43)$$

Where ρ is the number-density of scatterers in the volume element, A represents the attenuation factor at a specific thickness $e^{-\mu d}$, and J is the area and time normalized incident flux. The double differential cross section per scatterer for our case can be expressed as:

$$\frac{d^2\sigma}{d\Omega dE} = \frac{1}{\rho V_s d\Omega dE} \quad (44)$$

Combining (44) and (43) an intensity corrected for absorption in the form of (37) can already be discerned. It is thus the effective volume V_s that the beam travels through that determines the strength of attenuation. In the case of a flat-plate geometry this was already calculated, but a dimpled sample may require a correction where the spherical nature of the geometry is acknowledged. We thus consider the situation depicted in figure 37, where we approximate the spherically shaped dimple as a trapezoid geometry in the two-dimensional plane.

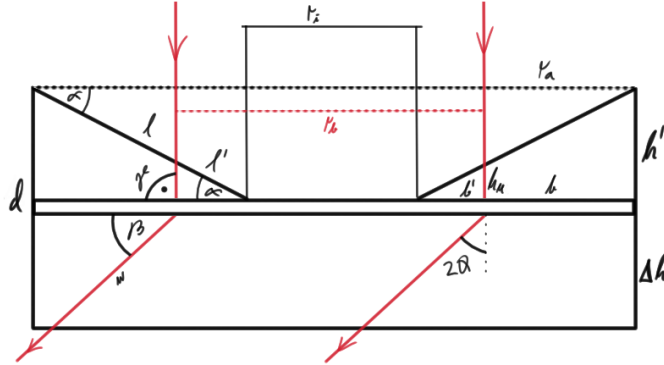


Figure 37: Approximation of a dimpled sample, red lines symbolize the beam travel. r_a , r_i and r_b denote the outer, inner and beam-diameter respectively. The triangles forming slopes on either side are symmetric, both extending a hypotenuse l under the angle α , l' denotes the shorter part of l , likewise b is the downwards facing cathetus with b' the length cut off from it by the beam. h' is the thickness of the sample before the scattering event, Δh the thickness after, with d being the sum of the two. The incident beam enters under the angle of $\gamma = 90^\circ$ and exits under β .

The effective volume is dependent on the length of path the beam has to travel through the sample, and thus the scattering angle $\beta = \frac{\pi}{2} - 2\theta$. The volume for our geometry can be calculated by integrating the attenuation over the total thickness of the sample using the proportions of paths travelled by an unperturbed beam in a flat plate over paths in our geometry scattered by an angle. The two needed fractions are $\frac{h'}{h_u}$ and $\frac{\Delta h}{w}$, the volume is calculated as:

$$V_s = \frac{h'}{h_u} e^{-\mu d \frac{\Delta h}{w}} \int_0^d e^{-\mu h' (\frac{h_u}{h} - \frac{w}{\Delta h})} dh' \quad (45)$$

From simple trigonometry we see that $\frac{\Delta h}{w}$ is simply $\sin(\beta) = \cos(2\theta)$, for the upper half of our sample we get:

$$\tan(\alpha) = \frac{h'}{b} = \frac{h_u}{b'} \quad (46)$$

With $b = \frac{r_a - r_i}{2}$ and $b' = \frac{r_b - r_i}{2}$ we can write:

$$\frac{h'}{h_u} = \frac{b}{b'} = \frac{r_a - r_i}{r_b - r_i} = P \quad (47)$$

Putting those two expressions into (45) yields us:

$$V_s = P \cdot e^{-\frac{\mu d}{\cos(2\theta)}} \int_0^d e^{-\mu h' (P - \frac{1}{\cos(2\theta)})} dh' \quad (48)$$

With the solution of the integral being our correction term:

$$\text{corr}_T(2\theta, P) = P \cdot \frac{e^{-\frac{\mu d}{\cos(2\theta)}} - e^{-\mu d (\frac{2}{\cos(2\theta)} - P)}}{\mu (P - \frac{1}{\cos(2\theta)})} \quad (49)$$

We tested this new correction term by applying it to a measurement where our previous one failed, figure 38 shows the scattering function of $30\text{Rb}_2\text{O}70\text{B}_2\text{O}_2$ with the old thickness correction and figure 39 the same sample evaluated with the new correction term.

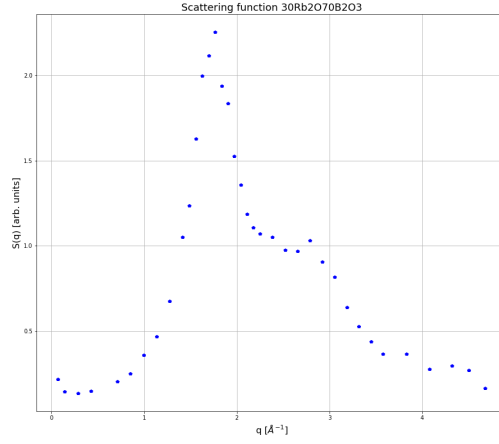


Figure 38: Scattering function for a dimpled $30\text{Rb}_2\text{O}70\text{B}_2\text{O}_2$ sample with the old thickness correction. Despite the correction, the function does not go towards unity for larger q as it should.

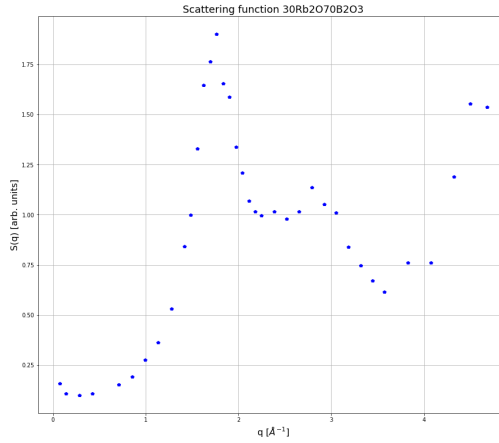


Figure 39: Scattering function for a dimpled $30\text{Rb}_2\text{O}70\text{B}_2\text{O}_2$ sample with the new thickness correction. The values for the parameters are $r_a = 0.4 \text{ mm}$, $r_i = 0.24 \text{ mm}$ and $r_b = 0.353 \text{ mm}$.

Parameters were chosen to be consistent with the model expectations, i.e. $r_a > r_b > r_i$. Values for $S(q)$ increase too harshly for higher q -values and do so stronger the higher the r_a parameter is set. A comparison between this dimpled sample with the new correction and the sample, of the same concentration used in our simulation, is depicted in figure 40. While some improvement is evident, it is still not ideal. It is however reasonable to assume that a dimpled sample geometry has significant influence on the resulting scattering behaviour.

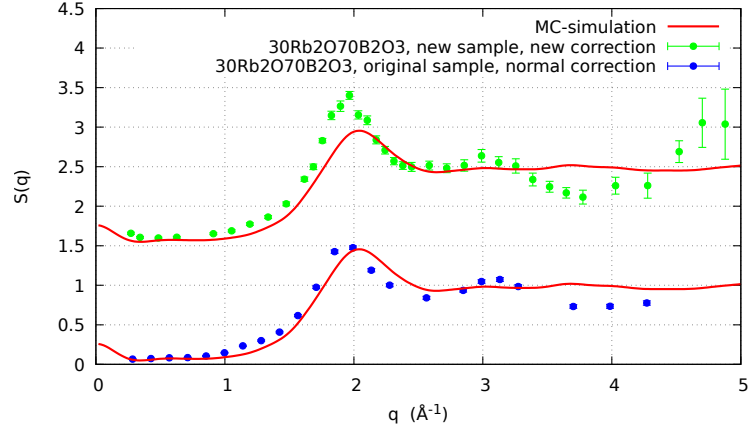


Figure 40: Comparison of two $30\text{Rb}_2\text{O}70\text{B}_2\text{O}_3$ samples. The plots are shifted on the y-axis by 1.5 and the upper plot is shifted on the x-axis by 0.3 to line up better with the simulation.

C Usage of Python scripts for data evaluation

The link provided in [30] encompasses scripts for a variety of applications:

- All calibrations performed in section 2.3.
- Preparation and normalization of gathered intensities and calculation of scattering factors as described in 2.5.1.
- Calculation of the scattering function with the output being a text-file of the data-points and a plot of the function.
- A script for the calculation of the sample thickness.

A complete set of the raw data is also provided in the link. Furthermore a modified script where $S(q)$ is calculated with the trapezoid thickness-correction is included as well. The simulations used in section 3 are not included in the package.

The scripts are written on the basis of Python version 2.7, and require the following external packages:

- Numpy
- Scipy
- Matplotlib
- Sympy
- Natsort
- Scikit-learn [31]

These can be installed via pip or with the platform specific package-manager.

The main script, "auswerter.py", goes through all the steps mentioned above, except for the calibration. It requires a configuration file in which the location of the angle-specific intensity-profiles is specified. The other parameters included in this file are the output-paths for the data-points and plot, the name of the sample, the name of the required module to calculate the sample-specific averaged scattering factors, the concentrations in at.% for the atoms comprising the sample, the intensities I_0 and I for thickness correction, the length of the input array and finally the normalization coefficient N .

The script requires only the location of the configuration files for execution.

The remaining calibration scripts handle calculation pertaining to the detector energy and absorption linearity, as well as the beam profile. The relevant data for our measurements is already provided within them. The beam profile script calculates the FWHM according to the methods laid out in section 2.3.3. To calculate the FWHM via direct distance measurement the following python code can be used, with variable names according to beam_profiler.py:

```
In [1]: points = zip(xx, di_real_0)
In [2]: half = int(max(di_real_0)*0.5)
In [3]: index = np.where((di_real_0 >= half-10000) &
...   : (di_real_0 <= half+10000))
In [4]: index
Out[4]: (array([21, 54]),)
In [5]: abs(points[54][0] - points[21][0])
Out[5]: 0.3299999
```

Code example: Calculating the FWHM for the x-axis of the beam.

In [1] an array consisting of both position and derivated intensity is created, in [2] the half of the peak height is calculated, in [3] array indices within a certain range that fall within the half point of the peak height are identified, in [5] these indices are used to directly calculate the distance both points situated at half maximum on the x-axis.

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