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High-energy x-ray diffraction study of amorphous $(\text{Si}_{0.71}\text{Ge}_{0.29})\text{O}_2$

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Abstract

Synthetic amorphous $(\text{Si}_{0.71}\text{Ge}_{0.29})\text{O}_2$ has been investigated by high-energy synchrotron x-ray diffraction ($E = 130.1$ keV), in order to achieve a better understanding of amorphous structures built from the two network-forming oxides SiO_2 and GeO_2 . The interatomic distances and bond angles that were determined are predominantly the same as in pure a- SiO_2 and a- GeO_2 , respectively. According to the first coordination shell, the total coordination number $CN(TO) = 3.4(5)$ ($T = \text{Si}, \text{Ge}$) indicates the existence of a considerable amount of cations that are connected to less than four oxygen ions. This result is clearly different with respect to the coordinations found in the structures of the respective pure amorphous oxides. If the second coordination shell is also taken into account, a second average (Ge–O) interatomic distance at $r = 2.23(1)$ Å can be determined and $CN(TO)$ increases to 4.2(1.1), indicating that all cations are actually connected to four anions. However, regular $[\text{GeO}_4]$ tetrahedra are no longer supposed to be the only possible germanium–oxygen coordination polyhedra in the structure investigated. Based on these findings, we infer that SiO_2 and GeO_2 predominantly form a homogeneous but not completely continuous random network.

1. Introduction

In the past six years, essential progress has been made possible in determining the structure of amorphous GeO_2 [1–7]. The results indicate that the glass structure of GeO_2 can be

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described by a continuous random network of corner-sharing $[\text{GeO}_4]$ tetrahedra. A similar structure model has been proposed for amorphous silica [8–12]. Germano-silicate glasses are widely used as, for example, optical fibres, and much research has been done on the physical (i.e. optical) properties of such fibres. However, surprisingly little is known about the structure of germano-silicate glasses [13–23], even though this knowledge is essential for a comprehensive understanding of the material properties.

The aim of this study is to find out whether the structure of germano-silicate glass forms a homogeneous network, similar to the structure of pure amorphous silica and germania, respectively. To this end we performed x-ray diffraction experiments on a germano-silicate glass containing 29 mol% GeO_2 . We used high-energy synchrotron x-ray diffraction ($E = 130.1$ keV) to achieve a resolution in direct space that enables the reliable determination of average interatomic distances, bond angles and coordination numbers. The Ge content of our sample is somewhat higher than in most conventional optical fibres, since we intended to perform further high-quality diffraction experiments on the same sample using resonant scattering at the Ge K-absorption edge, in order to gain additional information about the local environment of germanium. The results of these AWAXS experiments will be presented in a forthcoming paper.

2. Experimental details

2.1. Sample preparation

Mixtures of ultra-pure amorphous SiO_2 and ultra-pure amorphous GeO_2 powder, respectively, were homogenized and melted in a covered Pt/Rh crucible at a temperature of 1750 °C. This temperature was kept constant for two days before the melt was quenched by simply pouring it on a cold steel plate. The solid sample was crushed, ground up and heat-treated for two days in a dry atmosphere at $T = 120$ °C to keep hydration as low as possible. The chemical composition and the homogeneity were determined by ICP-OES (inductive coupled plasma optical emission spectroscopy) and by laser ablation ICP-MS (inductive coupled plasma mass spectrometry). The average ratio of Si:Ge amounted to $26.92 \pm 0.36:28.82 \pm 0.15$ wt%, and the distribution of both elements was homogeneous. The atomic density is 0.0664 ± 0.0001 atoms \AA^{-3} , which is in good agreement with data in the literature [24].

2.2. High-energy x-ray diffraction (HXD)

The sample was investigated by HXD ($E = 130.1$ keV) at the BW5 wiggler synchrotron beamline at HASYLAB/DESY (Germany) using a Si(111) Laue single-crystal incident-beam monochromator [25]. Hard x-rays were used because a high resolution in real space, as desired for disordered materials, can be achieved and the required data corrections are small, particularly for absorption. Due to the small scattering angles, even the polarization correction is almost negligible [10]. The experiments were carried out in the Debye–Scherrer geometry. The sample holder was a pure silica glass capillary with a wall thickness of 0.01 mm and a diameter of 3.0 mm. The sample was placed in a vacuum chamber (with $p = 0.012$ mbar) to reduce significantly the air scattering at low values of Q ($=4\pi \sin \Theta / \lambda$). Data were recorded in a range of Q between 0.45 and 32.27 \AA^{-1} (with a stepwidth = 0.039 \AA^{-1}). The total data acquisition time at each step was 120 s, and data were recorded in 12 separate scans (at 10 s/step) to minimize the influence of beam fluctuations and drifts in general. The effective absorption coefficient, $\mu(E)$, was determined from sample transmission experiments. The maximum absorption at $E = 130.1$ keV is only 9.8% for the low-density sample that was investigated. Counting statistics yielded relative errors of $|\Delta I/I| = 0.06\%$ obtained at Q_{max} .

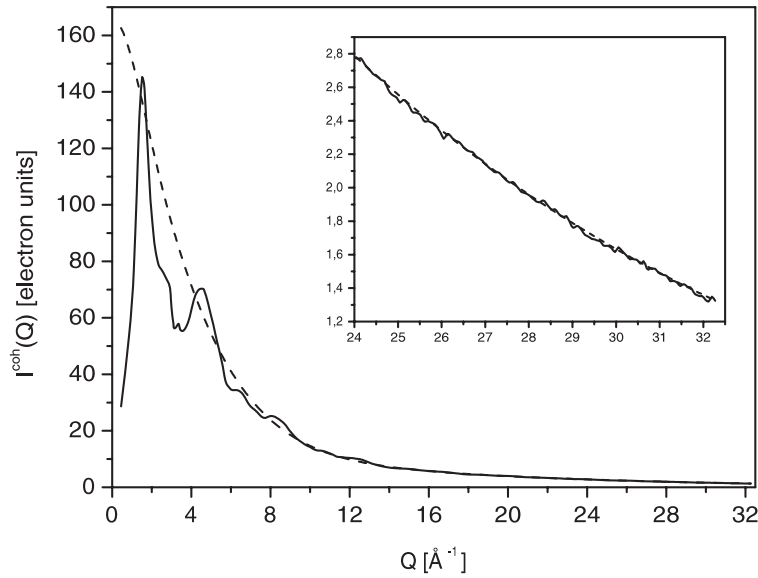


Figure 1. Fully corrected and normalized intensity data, $I^{\text{coh}}(Q)$ (for $E = 130.1$ keV). The full curve shows experimental data; the dashed curve shows the isotropic part of the scattering intensity (self-scattering + Compton scattering). The inset is a magnified view of the high- Q region.

The data reduction included corrections for background scattering, scattering of the empty capillary, dead time, polarization, absorption, inelastic scattering (Compton) [26] and the variable sample–detector distance, which is caused by a linear movement in the Ge solid-state detector normal to the primary beam. After data reduction, the scattering intensities were normalized to electron units [27–30] (figure 1). For the calculation of the independent coherent scattering intensities, the analytical scattering-factor functions for free ions of Waasmaier and Kirfel [31] were used.

3. Results

The average interatomic distances r_{ij} (Å) that were determined by HXD are summarized in table 1. The values of the r_{ij} and the associated uncertainties were calculated from the total pair correlation function, $G(r)$, and the radial distribution function, RDF:

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q[S^{\text{FZ}}(Q) - 1]M(Q) \sin(Qr) dQ \quad (1)$$

$$\text{RDF} = r[G(r) + 4\pi r \rho_0] \quad (2)$$

where $S^{\text{FZ}}(Q)$ denotes the Faber–Ziman (FZ) total structure factor [32, 33], ρ_0 is the atomic density, and $M(Q)$ is a smoothing function [34] that reduces truncation effects in the Fourier transform $G(r)$. In table 1, the r_{ij} (Å) are also compared to the corresponding interatomic distances in a-SiO₂ and a-GeO₂. These distances represent the mean values that were calculated exclusively from x-ray diffraction data for a-SiO₂ [8, 10, 11, 35, 36] and a-GeO₂ [1, 2, 7, 37–40], respectively, except the first O–O correlation for a-GeO₂, which has been taken from neutron diffraction results [40]. Figure 2 shows the interference function $Q[S^{\text{FZ}}(Q) - 1]$ and figure 3 shows the related total pair correlation function $G(r)$. Figure 4 depicts the 1.4–3.6 Å range of the total RDF (first-neighbour distances), which was fitted by a linear combination of

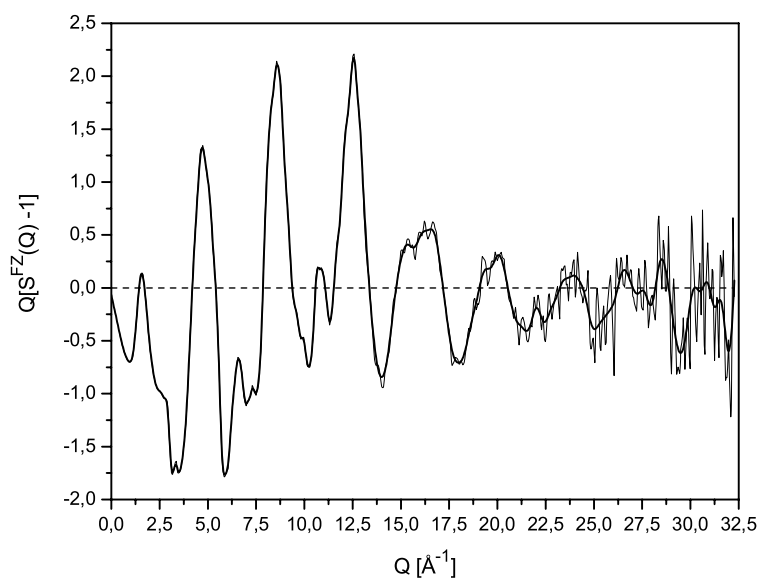


Figure 2. The interference function $Q[S^{\text{FZ}}(Q) - 1]$, where $S^{\text{FZ}}(Q)$ denotes the total FZ structure factor [32, 33]: bold curve—smoothed function; thin curve—unsmoothed function.

six variable Gaussian functions whose final parameters are summarized in table 2. The total coordination number $CN(TO) = 3.4(5)$ ($T = \text{Si}, \text{Ge}$) indicates the existence of a considerable amount of cations that are connected to less than four anions, contrary to the coordinations found in the structures of the pure oxide glasses. The partial coordination numbers CN_{ij} given in table 2 must be handled with care, because it is usually not advisable to calculate partial coordination numbers from the total RDF of a ternary system. Therefore, the values in table 2 can only serve as a hint that the total coordination number $CN(TO) < 4.0$ is mainly caused by a reduced germanium–oxygen coordination. However, if the third maximum in the total RDF (second coordination shell) is considered as a second average (Ge–O) interatomic distance, then $CN(TO)$ increases to 4.2(1.1) and, on average, all cations are connected to four oxygen ions. As a consequence, regular tetrahedra are no longer the only possible germanium–oxygen coordination polyhedra.

Ge is known to form hexa-coordinated environments in oxide crystals [41, 42], so we considered the possibility that part of the Ge atoms assume a hexa-coordinated environment as a result of the stress induced by the presence of a SiO_2 matrix. This hypothesis was dismissed for the following reasons. The Ge–O distance in Rutile-type GeO_2 is, at 1.87–1.90 Å, considerably smaller than the peak distance observed. So far, six-fold coordinated Ge has been observed only in binary oxide samples that have undergone some kind of pressure treatment. This is not the case for our sample.

It is noted that similar peaks at $r \approx 2.2$ Å were also found in other germanate glasses [43, 44] and were not assigned to interatomic correlations. Therefore, we also considered the possibility that the maximum at $r = 2.23(1)$ Å might be just an artefact of the Fourier transformation of unknown origin. In this case, the peak must not be assigned to any interatomic correlation. But, with respect to the calculated coordination numbers, this seems to us to be the less likely possibility.

According to the r_{ij} given in table 1, the calculated bond angle $(\text{O–Si–O}) = 107.4(1.8)^\circ$ is comparable to the corresponding average bond angle in a- SiO_2 [$(\text{O–Si–O}) = 109.5^\circ$].

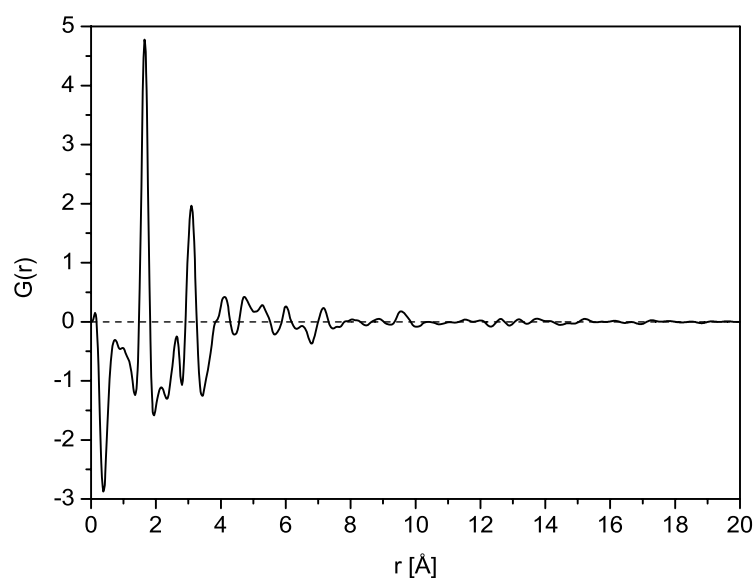


Figure 3. The total pair correlation function $G(r)$.

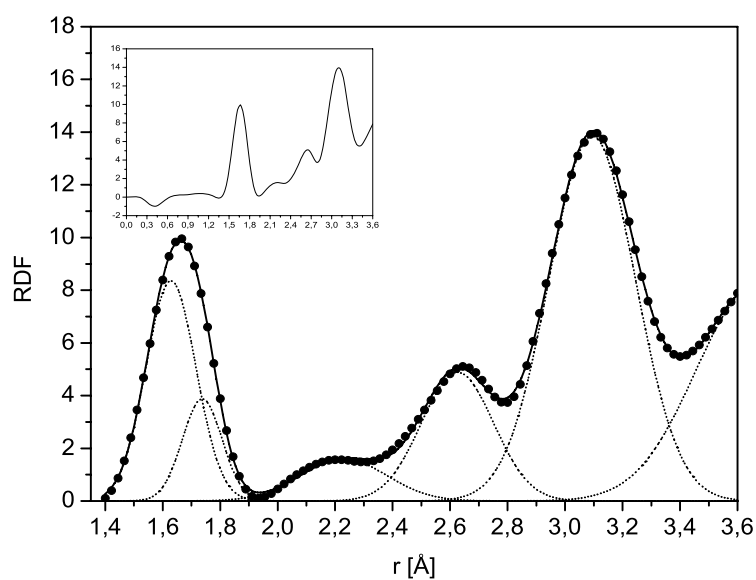


Figure 4. Part of the radial distribution function RDF (first-neighbour distances), fitted by six Gaussian functions: full circles—experimental; solid curve—overall fit; points—single Gaussian functions. The inset shows a larger part of the experimental RDF, starting at $r = 0$ Å.

Because $r(\text{O}-\text{O}) = 2.63$ Å is significantly smaller in $\text{a}-(\text{Si}_{0.71}\text{Ge}_{0.29})\text{O}_2$ than in a-GeO_2 ($r(\text{O}-\text{O}) = 2.84$ Å; see table 1), the $(\text{O}-\text{Ge}-\text{O})$ bond angle is calculated to be $98.1(1.3)^\circ$ for $\text{a}-(\text{Si}_{0.71}\text{Ge}_{0.29})\text{O}_2$, which is clearly different from 109.9° in a-GeO_2 .

Table 1. Interatomic distances, r_{ij} (Å), compared to the corresponding mean distances in a-SiO₂ [8, 10, 11, 35, 36] and a-GeO₂ [1, 2, 7, 37–40], respectively. $T = \text{Si, Ge}$. Standard deviations are given in parentheses.

a-(Si _{0.71} Ge _{0.29})O ₂	$\langle \text{a-SiO}_2 \rangle$	$\langle \text{a-GeO}_2 \rangle$	Correlation
1.629(17)	1.613		Si–O
1.738(15)		1.734	Ge–O
2.229(9)			Ge–O
2.626(2)	2.64	2.84	O–O
3.095(2)	3.09	3.18	T – T
4.12(1)	4.15	4.11	T –O
4.72(1)		4.88	T –O
5.27(1)	5.10	4.96/5.38	T – T , T –O, O–O
6.00(1)		6.00	T – T
6.50(2)	6.40		T –O
7.17(1)			T – T , T –O, O–O
9.55(3)			T – T , T –O, O–O

Table 2. The parameters of the Gaussian functions, obtained from a fit of the first-neighbour distances. CN_{ij} denotes partial coordination numbers, which must be considered with care (see text). $\langle u^2 \rangle = (\text{FWHM}^2/8 \ln 2)$ is the mean-square variation in r_{ij} (where FWHM is the full width at half maximum). $T = \text{Si, Ge}$. Standard deviations are given in parentheses.

Correlation	CN_{ij}	r_{ij} (Å)	FWHM	$\langle u^2 \rangle^{1/2}$
Si–O	4.7(1.0)	1.629(17)	0.2055(144)	0.087
Ge–O	1.9(1.0)	1.738(15)	0.1625(149)	0.069
Ge–O	1.7(0.1)	2.229(9)	0.3557(197)	0.151
O–O	5.0(0.2)	2.626(2)	0.2956(71)	0.126
T – T	5.9(0.1)	3.095(2)	0.3552(40)	0.151

4. Discussion

The structure of a-(Si_{0.71}Ge_{0.29})O₂ reveals a well developed short-range and medium-range order with detectable interatomic distances up to 9.55 Å. The first-neighbour distances (tables 1 and 2; figure 4) are comparable to the r_{ij} found in a-SiO₂ and a-GeO₂, respectively, with the exception of the clearly shorter O–O distance in a-GeO₂. Therefore, the conclusion appears reasonable that the short-range order around Si is nearly identical to that in a-SiO₂, i.e. [SiO₄] tetrahedra are basic building units. The local environment of Ge, however, differs from that in a-GeO₂. The [GeO₄] tetrahedra are no longer regular. The existence of non-bridging oxygen ions could explain the shorter mean O–O distance as well as the smaller average (O–Ge–O) bond angle. The reduced germanium–oxygen coordination in the first shell, which has been addressed in the previous chapter, leads to the next assumption that a considerable number of Ge cations may be connected to only three or two anions. Consequently, direct Ge–Ge bonds are very likely to be present in the structure. Direct Ge–Si and Si–Si bonds can be excluded with high certainty due to the ideal short-range order around Si, as mentioned above. Bernard *et al* [22] concluded, from molecular dynamics (MD) simulations performed on a doped germano-silicate glass (Ge/Si = 1; 1.17 mol% Eu³⁺), that the lower Ge–O bond energy enables the structure to be more flexible around Ge. Our results provide additional supporting evidence for this assumption. The r_{ij} calculated by Bernard *et al* [22] are $r(\text{Si–O}) = 1.62$ Å and $r(\text{Ge–O}) = 1.70$ Å—the first distance is close to our results (tables 1 and 2). But there are also inconsistencies with the diffraction results. Bernard *et al* [22] assumed that exclusively regular

tetrahedra were present in the structure ($\text{CN}(\text{SiO}) = \text{CN}(\text{GeO}) = 4$) and that a homogeneous distribution of the tetrahedra formed a three-dimensional network. According to our sample, this structure model is not very likely, though the MD results are partly supported by Raman experiments performed by Duverger *et al* [18, 19] on amorphous GeO_2 - SiO_2 waveguides. These authors also assume a homogeneous distribution of regular $[\text{SiO}_4]$ and $[\text{GeO}_4]$ tetrahedra, with Si–O–Si, Si–O–Ge and Ge–O–Ge bonds, forming a mixed network rather than phase segregation. However, we consider the maximum in the total RDF at $r = 2.23(1)$ Å (figure 4) to be a second average (Ge–O) interatomic distance. Therefore, on average, all cations are connected to four anions, but the network is not only formed by regular tetrahedra.

In discussing different structure models for germano-silicate glasses, one must however keep in mind that all the samples that have been investigated so far [13–23] were prepared differently. Our sample was prepared directly from the melt; other samples were prepared via the sol–gel route, by CVD or by MCVD. Some samples were additionally heat-treated at higher temperatures, hydrated or UV irradiated. The effect of sample preparation on the structure of amorphous germano-silicates is not yet really understood and therefore experimental results received from different samples should be interpreted with care.

5. Conclusion

The aim of this study is a better understanding of amorphous structures built from the two network-forming oxides SiO_2 and GeO_2 . To this end, we performed x-ray diffraction experiments on amorphous $(\text{Si}_{0.71}\text{Ge}_{0.29})\text{O}_2$ using high-energy synchrotron x-ray diffraction to achieve a high resolution in direct space. The results allow for the determination and identification of most of the interatomic distances in the range between 1.61 and 9.55 Å and for the concomitant calculation of some coordination numbers and bond angles. A clearly developed short-range and medium-range order can be noticed, exhibiting some structural features different to those of a- SiO_2 and a- GeO_2 . The interatomic distances that were determined are predominantly the same as in pure a- SiO_2 and a- GeO_2 , respectively. The total coordination number, according to the first coordination shell $\text{CN}(TO) = 3.4(5)$ ($T = \text{Si}, \text{Ge}$), indicates the existence of a considerable number of cations that are connected to less than four oxygen ions. This result is clearly different to the coordinations found in the structures of the pure amorphous oxides. If the second coordination shell is also taken into account, then a second average (Ge–O) interatomic distance at $r = 2.23(1)$ Å can be determined and $\text{CN}(TO)$ increases to 4.2(1.1), indicating that all cations are actually connected to four anions. However, regular $[\text{GeO}_4]$ tetrahedra are no longer supposed to be the only possible germanium–oxygen coordination polyhedra in the structure that was investigated. Based on these findings, we infer that SiO_2 and GeO_2 predominantly form a homogeneous but not completely continuous random network.

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