Anomalous X-ray scattering study of local structures in the superionic conducting glass \((\text{AgBr})_{0.4}(\text{Ag}_2\text{O})_{0.3}(\text{GeO}_2)_{0.3}\)

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Abstract

The local structural information in the near-neighbor region of superionic conducting glass \((\text{AgBr})_{0.4}(\text{Ag}_2\text{O})_{0.3}(\text{GeO}_2)_{0.3}\) has been estimated from the anomalous X-ray scattering (AXS) measurements using Ge and Br K absorption edges. The possible atomic arrangements in the near-neighbor region of this glass were obtained by coupling the results with the least-squares variational method so as to reproduce two differential intensity profiles for Ge and Br as well as the ordinary scattering profile. The coordination number of oxygen around Ge is found to be 3.6 at a distance of 0.176 nm, suggesting the GeO\(_4\) tetrahedral unit as the probable structural entity in this glass. Moreover, the coordination number of Ag around Br is estimated as 6.3 at a distance of 0.284 nm, suggesting an arrangement similar to that in crystalline AgBr.

Keywords: Superionic conducting glass; Silver bromide; Silver oxide; Germanium oxide; Anomalous X-ray scattering; Local structure

1. Introduction

Recently, there is an increasing need for understanding of the structure of glasses which exhibit high ionic conductivity. The conductivity of these glasses called as “superionic conducting glasses” \([1]\) is of the order of \(10^{-2} \Omega^{-1} \text{cm}^{-1}\) at room temperature, comparable to those of the aqueous electrolytes containing NaCl and AgNO\(_3\) \([2]\). Electrical conductivities of several superionic conducting glasses are exemplified by Fig. 1 together with those of typical crystalline systems. Glass conductors have several advantages over the crystalline counterparts due to the unique property peculiar to the glassy state \([3,4]\). Firstly, the good workability makes it possible to fabricate them into thin films or complex shapes. Secondly, since they are isotropic and lack grain boundaries, conductivities are not only higher than those of crystalline ones, but also do not reduce even at low temperatures. Thirdly, wide compositional flexibility allows for optimization of the electrolyte’s properties through compositional control.

For these reasons, there have been extensive studies on superionic conducting glasses for practical applications such as sensors and power sources \([5,6]\). Solid state battery is one of the most typical fields having high potential for practical applications. Along with the recent development of wireless electronic equipment such as mobile telephone, notebook computer, video camera, there have been intense demands for development of rechargeable miniature batteries with high performance. Lithium secondary batteries \([6]\) have been studied for this purpose. Although secondary lithium batteries using liquid electrolyte have been developed as a practical application, all-solid-state batteries are more preferable in some areas such as in medical equipment which require high reliability. Lithium superionic conducting glass such as the Li\(_2\)S–SiS\(_2–\text{Li}_2\text{GeO}_4\) glass \([7]\) is one of the potential materials attracting attention in the field of development of such an all-solid-state battery. Moreover, the attractive properties of superionic conducting glass described above make it possible, in principle, to provide a micro-battery capable of maintaining its memory during a power outage when coupled with the shape of combined thin films \([8]\). The combination of thin film configuration and the low current drain requirements (1–10 nA cm\(^{-2}\)) allow us to use electrolytes with much low conductivity. It may also be stressed that the potential capability is well recognized in the field of clean energy. For example, P\(_2\)O\(_5–\text{ZrO}_2–\text{SiO}_2\) glass \([9,10]\) having conductivity of \(10^{-2} \Omega^{-1} \text{cm}^{-1}\) at room temperature is a...
sort of superprotonic conducting glass. Intensive studies on these glass systems have been initiated for practical applications such as hydrogen fuel cells and hydrogen gas sensors.

In attempting to achieve the goals for development of superionic conducting glasses applicable for practical use, it is important to understand the structure–property correlation in these glass systems. Hence, more recent works have been concerned with an understanding of the structure relevant for the superionic conducting phenomenon. The glass belonging to the system AgBr–Ag₂O–GeO₂, first synthesized by Minami and Yamane [11], is one of the typical superionic conducting glasses. This glass system has been studied by different techniques to delineate the relationship between structure and properties, particularly with reference to their high ionic conductivity [11,12]. Although some spectroscopic measurements are available, it is difficult to obtain conclusive evidence for structural moieties in multi-component disordered systems. For example, the structural information around the germanium atoms—whether germanium atoms prefer tetrahedral positions coordinated by four oxygen atoms or octahedral positions surrounded by six oxygen atoms—is still far from complete, and there have been some conflicting results [11,12].

Based on infrared absorption spectroscopy, Minami and Yamane [11] have suggested that the six-coordinated octahedral GeO₆ is predominant in the AgBr–Ag₂O–GeO₂ glass when the molar ratio Ag₂O/GeO₂ is unity. On the contrary, Morikawa et al. [12,13] have explored the environment around the germanium atoms by EXAFS analysis and suggested that germanium atom is surrounded by four oxygens without regard to the Ag₂O/GeO₂ molar ratio. The disagreement between these two studies reflects the difficulty in determining the structure of Ge–O units in this system by using only the spectroscopic data. For this reason, further structural studies are needed for providing critical information on the structural aspects that may be relevant for understanding the enhanced ionic conductivity.

The purpose of this work is to explore the local atomic configurations including interatomic distances and coordination numbers in the (AgBr)₀.₄(Ag₂O)₀.₃(GeO₂)₀.₃ glass using the anomalous X-ray scattering (AXS) technique coupled with the least-squares variational method.

2. Experimental procedure

The (AgBr)₀.₄(Ag₂O)₀.₃(GeO₂)₀.₃ glass sample was prepared from high-grade chemical reagents AgBr, Ag₂O and GeO₂. Calculated amounts of the materials were weighed, dried in an oven and then melted in a silica glass tube. After melting at 820 K, the melt was quenched between two copper plates. The final thickness of the sample obtained was about 450 μm. A mass density of the sample, determined by the Archimedean method with toluene as the liquid medium, was 6.32 Mg m⁻³.

The AXS measurements on the (AgBr)₀.₄(Ag₂O)₀.₃(GeO₂)₀.₃ glass sample were carried out with synchrotron radiation at BL–7C beam line with a Si(111) double-crystal monochromator covering the energies ranging from 4 to 21 keV at the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. The sample was mounted on a double axis goniometer placed vertically to eliminate the polarization effect. The incident beam was monitored with a nitrogen gas flow-type ion chamber placed
in front of the sample so as to keep the number of incident photons on the sample constant. The scattering intensity was measured with a Si(Li) solid state detector so that the fluorescent radiation from the sample could be removed from the elastic scattering with a pulse height analyzer. Ordinary X-ray scattering was measured with monochromatic Mo Kα radiation. After corrections for air scattering, polarization and absorption, the measured intensity was converted to electron units per atom with the generalized Krogh–Moe–Norman method using the X-ray atomic scattering factors, including their anomalous dispersion terms [14] (public database of SCM-AXS: http://www.iamp.tohoku.ac.jp). The Compton scattering was also corrected using the tabulated values [15]. Details of the data analysis of the AXS measurement have been described elsewhere [16]. Only some fundamental points necessary for the present work are given below.

When the energy of the incident X-ray beam is close to the absorption edge $E_{\text{abs}}$ of one of the constituent elements, the atomic scattering factor becomes a complex function due to resonance scattering; it can be expressed in the form $f(Q, E) = f^c(Q) + f^r(E) + if^i(Q)$, where $Q$ and $E$ are the wave vector and the incident X-ray energy, respectively. The normal atomic scattering factor is represented by $f^c(Q)$. The terms $f^r(E)$ and $f^i(Q)$ are the real and imaginary parts of the anomalous dispersion term, which depend upon the energy of the incident X-ray. Fig. 2 shows the energy dependence of the anomalous dispersion terms $f^r(Q)$ and $f^i(Q)$ for Ge and Br in the energy range including their K absorption edges, calculated using the relativistic Cromer–Liberman scheme [17]. When the incident energy is set in the close vicinity of the absorption edge of a specific constituent, for example Ge atom, the detected variation in intensity $\Delta I_{\text{Ge}}(Q)$ can be attributed only to the change of the anomalous dispersion terms of Ge, $f_{\text{Ge}}'$ and $f_{\text{Ge}}''$. Furthermore, in the lower energy side of the absorption edge, the imaginary part $f_{\text{Ge}}''$ is small and almost constant. Hence, we have only to consider the energy dependence of intensity due to the real part $f_{\text{Ge}}'$. Therefore, the following relation is readily obtained [18].

$$
\Delta I_{\text{Ge}}(Q) = \frac{1}{c_{\text{Ge}} f_{\text{Ge}}'(E_1) - f_{\text{Ge}}'(E_2)} W(Q) 
$$

$$
= \int_0^\infty 4\pi r^2 \sum_k \Re[f_k(Q, E_1) + f_k(Q, E_2)] W(Q) 
\times (\rho_{\text{Ge}}(r) - \rho_{0k}) \frac{\sin (Qr)}{Qr} \, dr 
$$

(1)

where $E_{\text{abs}} > E_2 > E_1$, $I(Q, E)$ is the coherent X-ray scattering intensity in electron units per atom, $c_t$ the atomic fraction of the k-element, $\rho_{\text{Ge}}(r)$ the radial density function of the k-element around Ge at a radial distance of $r$, and $\rho_{0k}(r)$ is the average number density of the k-element in the system. $\Re$ denotes the real part of the parameters in brackets. The environmental radial distribution function (RDF) for Ge in the glass sample is estimated by Fourier
transformation of the quantity of $\Delta_i(Q)$ in Eq. (1)

$$4\pi r^2 \rho_{Ge}(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{\infty} Q\Delta_i(Ge)(Q) \sin (Qr) dQ$$

(2)

where $\rho_0$ is the average number density in the system. Consequently, the environmental structure around Ge atom can be obtained by measuring the X-ray scattering intensity at more than two energies near the absorption edge of Ge. The environmental structure around Br atom can also be estimated from the anomalous X-ray scattering measurements at the Br K absorption edge, using a similar procedure.

3. Results and discussion

Fig. 3 shows the environmental interference functions, $Q\Delta_i(Ge)(Q)$ and $Q\Delta_i(Br)(Q)$, of the (AgBr)$_{0.4}$(Ag$_2$O)$_{0.3}$(GeO$_2$)$_{0.3}$ glass. They are calculated using Eq. (1) from the difference between the two intensities at the incident energies 300 and 25eV below the Ge K (11.104 keV) or Br K (13.470 keV) absorption edges, respectively. The ordinary interference function, $Q(i)(Q)$, obtained from the measurements using Mo Kα radiation is also displayed in this figure.

These profiles essentially show typical structural features of glasses, except for the characteristic shoulder in the high-$Q$ side of the principal peak of the environmental interference function $Q\Delta_i(Br)(Q)$.

Fig. 4 shows the environmental RDFs obtained from $Q\Delta_i(Ge)(Q)$ and $Q\Delta_i(Br)(Q)$ by Fourier transformation, together with the ordinary RDF obtained from $Q(i)(Q)$. A direct comparison among these three curves is possible only for the values on the abscissa, because different weighting factors are used on the ordinate. At first, we note that it is quite difficult to unequivocally identify the peaks from the ordinary RDF data alone because the ordinary RDF is a weighted sum of ten kinds of correlations for the Ag–Br–Ge–O quaternary system. The AXS results enable us to provide the answer by making available the scattering contrast of a desired element. For example, by comparing the ordinary RDF with two environmental RDFs, it is readily found that the correlation located in the region between 0.15 and 0.22 nm is completely lost in the environmental RDF for Br. On the other hand, an isolated peak can be found at about 0.18 nm in the environmental RDF for Ge. Thus, we safely assign the first peak at 0.18 nm in the ordinary RDF to the correlation of Ge–O pair, which is quite likely to overlap with the Ag–O correlation at about $r = 0.2$ nm. The shoulder observed on the left-hand side of the ordinary RDF ($r = 0.28$ nm) almost completely disappears in the environmental RDF for Ge, while the pronounced first peak can be seen at about 0.28 nm in the environmental RDF for Br. For this reason, the corresponding peak is attributed to the correlation of Br–Ag pair, and this is consistent with the distance of the nearest-neighbor bromine and silver in the crystalline case [19]. Nevertheless, some reservation is called for regarding the reliability of the absolute values of the coordination number. The finite

Table 1

| Pairs         | Present glass sample | c-AgBr | α-Quartz type GeO$_2$ | Rutile type GeO$_2$ | c-Ag$_2$O |
|---------------|----------------------|--------|-----------------------|---------------------|-----------|
| Ge–O          | $r$ (nm)             | 0.176 ± 0.002 | – | 0.174 | 0.188 | – |
|               | $N$                  | 3.6 ± 0.3 | – | 4 | 6 | – |
| Ag–O          | $r$ (nm)             | 0.217 ± 0.004 | – | – | – | 0.205 |
|               | $N$                  | 0.6 ± 0.3 | – | – | – | 2 |
| Br–Ag         | $r$ (nm)             | 0.284 ± 0.002 | 0.289 | – | – | – |
|               | $N$                  | 6.3 ± 0.3 | 6 | – | – | – |
| Br–Br         | $r$ (nm)             | 0.391 ± 0.002 | 0.409 | – | – | – |
|               | $N$                  | 11.8 ± 0.3 | 12 | – | – | – |
| $r_{Br-Bd}/r_{Br-Ge}$ |               | 1.38 | 1.41 | 0.315 | 0.342 |
| Ge–Ge         | $r$ (nm)             | 0.315 ± 0.002 | – | 0.315 | 0.342 |
|               | $N$                  | 3.4 ± 0.3 | – | 4 | 8 | – |
termination of the Fourier transformation frequently prevents us from obtaining sufficiently high resolution RDF, so that a careful interpretation is required [16]. The use of the least-squares variational method, originally proposed by Narten and Levy [20], provides one useful method to minimize the problem by using the interference functions instead of RDFs. According to Narten and Levy, the interference function is given by

\[
Q_iQ_\dagger X_jX_kci_{f_ik}f_{lj}2N_{jk}exp(-bjkQ^2)sin(Qr_{jk})
\]

where \(N_{jk}\) is the number of type-\(k\) atoms around any type-\(j\) atom at the distance \(r_{jk}\) and the value of \(bjk\) is mean square variation. The quantities of \(R_{ab}\) and \(b_{ab}\) correspond to the mean and the variance of the boundary region, which need not be sharp. The first term on the right-hand side of Eq. (3) represents a discrete Gaussian-like distribution, and the second term represents a continuous distribution with an average number density at long distance. The distances and coordination numbers of interest in the near-neighbor correlations are estimated by the least-squares calculation using Eq. (3) to reproduce the experimental interference data from both the AXS method and the conventional diffraction.

The least-squares variational method was executed by iteration with the local structural information in crystals as starting parameters. The resultant structural parameters are summarized in Table 1, together with those of the components in their crystalline state for comparison. The uncertainties were estimated from the variance–covariance matrix in the least-squares variational method and they are also included in the table. The structural parameters listed in this table reproduce three independent interference functions of \(Q\Delta_i_{Ge}(Q), Br\Delta_{Br}(Q)\) and \(Q\Delta_i(Q)\), as shown by dotted lines in Fig. 3. This agreement is the evidence that the present approach basically works well. We would like to stress that these structural parameters are not mathematically unique. However, the structural parameters determined through this data processing satisfy the necessary condition at best for explaining the three independent experimental results.

Crystalline germanium oxide has two forms, each with a different coordination of oxygens around the central germanium at room temperature. One is the \(\alpha\)-quartz type structure [21] with tetrahedral GeO\(_4\) unit (Fig. 5a), the other is the rutile type [22] structure with octahedral GeO\(_6\) unit (Fig. 5b). The average Ge–O distances are: 0.174 nm for the tetrahedral coordination and 0.188 nm for the octahedral coordination. As shown in Table 1, a germanium atom is surrounded with 3.6 oxygens at 0.176 nm in the \((AgBr)_{0.4}(Ag_2O)_{0.3}(GeO_2)_{0.3}\) glass. These values seem to be rather close to those of the \(\alpha\)-quartz type GeO\(_2\) crystal. Therefore, the GeO\(_4\) tetrahedron is more likely to be the fundamental local unit of the host matrix in the present glass, similar to the case of GeO\(_2\) glass [23]. This finding does not support the inference from the infrared absorption spectroscopic study [11], but agrees with the result obtained from the EXAFS measurement [12,13]. A germanium atom is also surrounded by 3.4 germanium atoms with its distance of 0.315 nm. Such correlation can be also found in the pure GeO\(_2\) glass case with the coordination number of 4.4 at the distance 0.316 nm [23], suggesting a network structure formed by the GeO\(_4\) tetrahedra joined at their corners.

Table 1 indicates that the atomic distance for Ag–O pair in the glass is 0.217 nm with the coordination number 0.6. This distance is not far from the value of crystalline Ag\(_2\)O (0.205 nm) although the coordination number drastically decreases upon vitrification. Some of Ag\(^+\) ions may be coordinated to the non-bridging oxygens. When assuming that such Ag\(^+\) ions were attached to some oxygens of the GeO\(_4\) tetrahedra, the correlations of the Ge–Ag pair are

\[
Q_jQ_{\dagger}X_aX_bai_{fa}f_{fb}24\pi\rho_0exp(-b_{ab}Q^2)
\]

\[
\times OR_{ab}\cos(QR_{ab})-\sin(QR_{ab})Q^2\]
quite likely to share a part of the second peak in the environmental RDF around Ge with the coordination number of 2 which is estimated from the molar ratio \( \text{[Ag]} / \text{[Ge]} = 3.3 \) of the present glass multiplied by the Ag–O coordination number (0.6). It may be also worthy of note that the remaining area of the second peak involves the contributions from other possible atomic correlations such as Ge–Br and second nearest-neighboring Ge–O pairs, although their numerical values cannot be quantitatively estimated from the present data alone.

On the other hand, the estimated coordination number of nearest-neighbor Ag around Br is 6.3 with the distance of 0.284 nm. The coordination number for Br–Br pairs is 11.8 with the distance of 0.391 nm. The ratio of peak positions defined as \( n_{\text{Br–Br}} / n_{\text{Br–Ag}} \) is 1.38, which is close to the value for an octahedron (1.41). These results indicate that the local environment around Br in the glass is not much different from that in the crystalline AgBr. Furthermore, the first peak of environmental interference function \( Q \Delta I_p(Q) \) in Fig. 3 has a shoulder around 30 nm \(^{-1} \), indicating the existence of a certain ordering relevant to Br ion configuration at a distance beyond the first nearest-neighbor region. In order to reproduce the characteristic profile, at least a pair correlation with the distance of about 0.57 nm from a central Br ion should be considered. The correlation with this length may correspond to the pair correlation of second nearest neighbor Br–Br pair in the crystalline AgBr, though it is difficult to quantify it exclusively from the present data. Nevertheless, it can be suggested that AgBr gets into host matrix of glass while keeping its local structure in the range of second nearest-neighbor distance.

4. Concluding remarks

By applying the AXS method with least-squares variational analysis to a superionic conducting glass of the composition \( \text{(AgBr)}_{0.4} \text{(Ag}_2\text{O)}_{0.3} \text{(GeO}_2\text{)}_{0.3} \), the local structural information such as interatomic distance and coordination number around Ge and Br has been determined. The \( \text{GeO}_4 \) tetrahedron is favored in the glass as the fundamental local ordering entity. The Br ions appear to be surrounded by six Ag ions, and this locally ordered structure gets into the glassy oxide matrix keeping the environment of Br ions similar to that in crystalline AgBr.

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