Abstract. Superionic conducting glasses are the important materials as solid electrolytes. Amorphous Ag-Ge-Se system is well known to exhibit the superionic conducting behavior where silver ions easily migrate into the mixed structure of Ag₂Se and Ge-Se chalcogenide glass. It will be good material to study how the superionic conducting region distributes in the glassy network, and whether the conducting paths extends to the entire of the material, or the localized and limited area in an isolated region. In this paper, we will present the results of the static structure of Ag-Ge-Se system by high-energy X-ray diffraction measurements.

1. Introduction

Superionic conducting glasses are the important materials as solid electrolytes. Amorphous material of Ag-Ge-Se system is well known to exhibit superionic conducting behavior where the silver ions easily migrate into the mixed structure of Ag₂Se and Ge-Se chalcogenide glass. Since this system has a wide compositional range where amorphous state can be easily obtained by quenching through water or even air [1], it could be good material to study on how the fast ionic conducting region is distributed in the glassy media, and also whether the conducting paths extend to the entire of the material, or the localized and limited area in an isolated region. Kawamura et al. [2] reported a large jump in the value of electrical conductivity at the composition around x=0.3 for Agₓ(GeSe₃)₁₋ₓ, which may support a percolation threshold of the superionic conducting behavior in the glassy network [3,4]. How does the structural change occur when the composition of Ag is systematically increasing? We want to find out structural change around the transition area of ionic conductivity.

In this paper, we will present the results of static structure of Ag-Ge-Se system by high-energy X-ray diffraction measurements.

2. Experimental

The powder sample was put into the quartz capillary with inner diameter of 2.5 mm and the wall thickness was 10 μm. The diffraction data were observed by transmitting method with high energy X-
ray (113,4 keV) and the wavelength was 0.1093 Å. The data of structure factor S(Q) of Ag\(_x\)(GeSe\(_3\))\(_{1-x}\) (x=0, 0.15, 0.28, 0.305, 0.33, 0.5) were obtained at room temperature with high accuracy. The observed Q region was from 0.3 Å\(^{-1}\) to 30 Å\(^{-1}\).

### 3. Results

The observed structural data S(Q) are excerpted up to 8.0 Å\(^{-1}\) for the convenience of discussion in the figure 1. The pre-peak can be seen in the low wavelength region. This FSDP (First Sharp Diffraction Peak) becomes small with increasing the density of silver ions. The position of the third peak of the structure factor moves systematically to the low wave-number with increasing the density of silver ion.

Figure 2 shows the pair distribution functions g(r), obtained by the Fourier transform of the structure factor S(Q). There exist the two characteristic peaks around 2.36 Å and 3.82 Å, and these values may correspond to the length of tetrahedral units of three Se atoms around the central Ge atom. And the glassy network can be formed by these tetrahedral units and the chain of Se-Se.

The first peak at 2.35 Å corresponds to the both lengths of Se-Se and Ge-Se, and also the intensity of these peaks decreases with increasing the density of silver ion. On the other hand, the peak at 2.64 Å suggests the Ag-Se correlation and this peak becomes to grow up with the density of silver ion. The peak around 3.8 Å also moves systematically to the long distance with the density of silver ion.

There exist two peaks around 2.36 Å and 3.82 Å, and these may correspond to the length of tetrahedral units of three Se atoms around centered Ge atom. And the glass network is formed by these tetrahedral units and the chain of Se-Se.

Figure 3 shows the difference of the total pair correlation functions at two temperatures at 113 K and 300 K, which corresponds to the non-super ionic state and superionic state, respectively. This may also indicate the structural change due to the mobility of silver ions at two different temperatures; how the distribution of silver ions can be affected by temperature.

The peak at 2.64 Å in the figure 3 may corresponds to the Ag-Se coordination, and this peak becomes sharp at low temperature, 113K, and rather small peak at room temperature. The distribution of the silver ions around the Se changes largely with decreasing temperature.

### 4. Discussion

As shown in figure 1, the pre-peak can be seen in the low wavelength region. This FSDP becomes small with increasing the density of silver ions. The position of the third peak of the structure factor moves to the low wave-number region with increasing the density of silver ion. As shown in figure 2, there exist the two characteristic peaks around 2.36 Å and 3.82 Å, and these values may correspond to the length of tetrahedral units of three Se atoms around the central Ge atom. And the glassy network can be formed by these tetrahedral units and also the bonding of Se-Se chains as shown in figure 4. The first peak at 2.35 Å corresponds to the both lengths of bonding of Se-Se chains and Ge-Se bond in the tetrahedral units, and this peak decreases with increasing the density of silver ion.

On the other hand, the peak at 2.64 Å suggests the correlation of Ag-Se, and this peak becomes to grow up with the density of silver ions. The peak around 3.8 Å also shifts to the long distance with the density of silver ion.

From the compositional change of the structure of Ag\(_x\)(GeSe\(_3\))\(_{1-x}\), we obtained the clear change of the network structure composed of Ge-Se and this is modified easily by the additional density of Ag ions. From the temperature change of the pair correlation functions, we could find out the difference of the structure due to the difference between the mobility of the Ag ions at the low and high temperature. It is interesting to know the relation between the structural change in the network and the conducting path of Ag ions, and it may also be interesting to express the picture of Ag ions from the atomic assignment, which is trapped in the network at low temperature, and also the behavior of beginning to move in the conducting paths.
Figure 1. Observed structure factors $S(Q)$ of $Ag_x(GeSe_3)_{1-x}$ at room temperature. The data of $S(Q)$ are excerpted up to $8.0 \text{ Å}^{-1}$.

Figure 2. Pair distribution functions $g(r)$ obtained from the structure factors $S(Q)$ at room temperature.
Figure 3. The difference between the obtained pair distribution functions $g(r)$, at two different temperatures, at 113 K and room temperature, 300 K.

Figure 4. Schematic structural model and the relation between the Se-Se bonds and Ge-Se bonds in GeSe$_3$.

References

[1] Mitkova M, Wang Yu and Boolchand P 1999 Phys. Rev. Lett. 83 3848
[2] Kawasaki M, Kawamura J, Nakamura Y and Aniya M 1999 Solid State Ionics 123 259
[3] Kluge G, Thomas A, Klabes R, Grotzschel R and Suptitz P 1990 J. Non-Cryst. Solids 124 186
[4] Ressel R, Kluge G and Suptitz P 1987 J. Non-Cryst. Solids 97–98 1247