Local atomic order in GaGeS and GaGeSe glasses

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1. Introduction

Chalcogenide glasses are characterized by remarkable physical properties, such as large photosensitivity or high ionic conductivity. In general, their properties can be fine-tuned by varying the composition of the constituent elements. There are, however, only a small group of compositions containing a group 13 element, and even less that are good glass formers. One of the few pseudo-binary alloys that exhibits a high glass forming ability over a wide composition range is $(GeS_2)_{1-x}(Ga_2S_3)_x$ or $(GeSe_2)_{1-x}(Ga_2Se_3)_x$. An accurate structural characterization still proves to be difficult, and thus, the link to understand the unique glass properties is complex. One of the main problems to investigate structures with usual x-ray techniques is that the elements possess very similar atomic numbers (Z = 31, 32, and 34 for Ga-Ge-Se alloys, respectively) and have similar backscattering amplitudes in XAFS analysis.

We performed anomalous x-ray scattering (AXS) on $(GeSe_2)_{0.75}(Ga_2Se_3)_{0.25}$ glass near the Ga, Ge, and Se K absorption edges, and the data were analyzed using reverse Monte Carlo (RMC) modeling [1]. From this result, we conclude that the local atomic arrangements around the Ge and Se atoms are similar to those in pure $GeSe_2$ obtained by the previous AXS experiments [2]. Furthermore, the differential spectrum near the Ga edge looks quite similar to that near the Ge edge, but the first sharp diffraction peak (FSDP) is different from each other. Thus, the intermediate range order (IRO) may be different.

To confirm these findings, the measurements on similar Ga-Ge-S alloys would be very helpful. Since S is a light element, however, AXS and XAFS measurements are difficult due to the low energy of the S K absorption edge. On the other hand, the contrast between the x-ray and neutron diffraction (XRD and ND) can be expected, i.e., about 30% stronger in ND than in XRD for the scattering length (atomic form factor) of S. Thus, the combinational use of neutrons and x-rays can provide the partial atomic configurations around the S atoms.

Moreover, since the neutron $g_N(r)$ data obtained from neutron $S_N(Q)$ in a wide Q range provide the sum of partial pair correlation functions, $g_{ij}(r)$ with exact weighting factors, W_{ij}, which is very helpful for the detailed RMC analysis [3]. Note that W_{ij}s for x-ray $S_X(Q)$ highly depend on the Q values, and those for x-ray $g_X(r)$ are difficult to determine due to the Q dependence of x-ray atomic form factors. The use of $g_N(r)$ is also useful for the RMC modeling on the Ga-Ge-Se alloys even though these elements have mostly no difference in the neutron scattering lengths.

2. Experiment

The glassy samples of $(GeS_2)_{0.90}(Ga_2S_3)_{0.10}$ and $(GeSe_2)_{0.75}(Ga_2Se_3)_{0.25}$ were manufactured by a usual melt-quenching method by Dr. M. Krbel at Center of Materials and Nanotechnologies, University of Pardubice, Czech Republic. The powder samples were contained in standard cylindrical V cans with an inner diameter of 12 mm and a wall thickness of 0.01 mm. The ND measurements were carried out at room temperature in a wide Q range over 300 nm^{-1} using the NOVA neutron diffractometer at BL-21 in MLF/J-PARC. The beam power of the neutron source is 400 MW, and each ND experiment

took 4 h. A standard data analysis was performed, such as the subtraction of the empty can data and the normalization using the scattering data of a V rod.

3. Results

The left panel of Fig. 1 shows the $S(Q)$ spectra of $(Ga_2S_3)_{0.10}(GeS_2)_{0.90}$ (top) and $(Ga_2Se_3)_{0.25}(GeSe_2)_{0.75}$ (bottom) glasses. Excellent statistic qualities are realized up to about 100 Å^{-1}, and the Fourier transformations were performed to obtain $g(r)$ spectra as shown in the right panel of Fig. 1. Although small truncation ripples are seen around the first peaks at 2.2 Å, they have enough quality to utilize for the RMC calculations, which are now in progress in combination with the AXS data measured at ESRF.

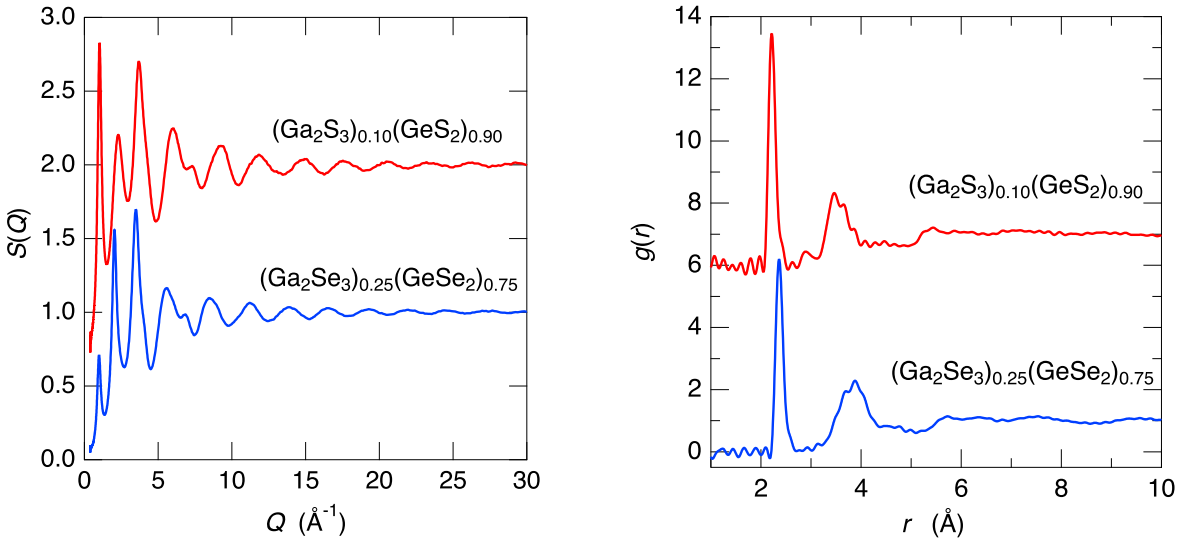

Fig. 1. $S(Q)$ (left) and $g(r)$ (right) ND spectra of $(Ga_2S_3)_{0.10}(GeS_2)_{0.90}$ (top) and $(Ga_2Se_3)_{0.25}(GeSe_2)_{0.75}$ (bottom) glasses.

4. Conclusion

We have successfully measured ND on the $(Ga_2S_3)_{0.10}(GeS_2)_{0.90}$ and $(Ga_2Se_3)_{0.25}(GeSe_2)_{0.75}$ glasses using the NOVA neutron diffractometer at BL-21 in MLF/J-PARC with excellent statistical qualities. The $S(Q)$ and $g(r)$ data will be used for the RMC in combination with the AXS data to clarify the role of the constituent elements for the excellent functionalities of these glasses.

[1] B. D. Klee et al., Chalc. Lett. **15**, 1 (2018).

[2] S. Hosokawa et al., Phys. Rev. B **84**, 014201 (2011).

[3] O. Gereben et al., J. Optoelect. Adv. Mater. **9**, 3021 (2007).