Inelastic neutron scattering in superionic conducting glass Ag$_2$GeSe$_3$

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Abstract. The results of inelastic neutron scattering measurements for Ag$_2$GeSe$_3$ are reported in association with a low energy excitation and Ag diffusion. A low energy excitation peaked at 2.4 meV and underling tail below 10meV are observed from 120K to 300K. Glass structure based on Ge-Se covalent bond persists in this material, that is confirmed by observation of stretching and bending modes of Ge-Se bond.

1. Introduction

Superionic conducting glasses are one of important materials as solid electrolytes. Ag-Ge-Se amorphous system is well known to exhibit superionic conducting behavior where silver ions easily migrate into a random media of Ge-Se chalcogenide network glass [1,2]. There are many superionic conductors involving silver fast conducting ions such as AgI, Ag$_2$Se, AgI-AgPO$_3$ and so on [3-5]. Among those superionic conductors, ionic conduction appears at a lower temperature in glass materials than in crystalline materials. It is well known that there appears a low energy excitation at a energy transfer, $E$, of few meV in glass materials which is called as boson peak because the intensity is scaled by Bose factor. Since mobile Ag ions have a quasi-elastic tail in this $E$ region, diffusion of Ag ion can be mixed to the low frequency oscillations by boson peak. To understand dynamics of Ag ions from microscopic viewpoint, revealing silver conduction path and driving force for ionic conduction, is important. Mitokova et al. [1] revealed the compositional region of Ag-Ge-Se system where glass material is easily obtained by rapid quenching. Ag$_2$GeSe$_3$ composition is located at the edge of this glass region with highest Ag amount. In this paper, we discuss the dynamics of Ag$_2$GeSe$_3$ glass from inelastic neutron scattering measurements.

2. Experimental Procedure

The glass material of Ag$_2$GeSe$_3$ was prepared by water quenching from the melts of mixtures among Ag, GeSe$_2$ and Se. Quasi- and inelastic neutron-scattering experiments were performed using the LAM-40, LAM-D and CAT installed at KENS spallation neutron source in the High Energy
Accelerator Research Organization, KEK, Tsukuba, Japan. The powder sample was lapped in Al foil (30 μm thickness) to form a flat plate with 1.5mm thickness. For the LAM-40 and LAM-D experiments, this plate was wound and put into an Al container with 20mm inner diameter and 0.5mm wall thickness, which was located in an evacuated chamber. For the CAT experiment, the flat plate sample was located in a chamber. The low temperatures were achieved by using a cold head cooling.

Those spectrometers are an inverted-geometry time-of-flight spectrometers, where the energy of the final neutron is 4.59meV by Bragg reflection with PG002 mirrors. The LAM-40 spectrometer is connected to the cold-neutron source and gives information on relatively low-energy excitations including the quasi-elastic region in the wavenumber space from 0.2 to 2.6Å⁻¹ with an energy resolution of about 0.2meV [6]. LAM-40 consists of seven sets of assemblies of pyrolytic graphite (PG) analyzer mirrors and detectors with the angle interval of 16°. On the other hand, LAM-D and CAT are connected to the thermal neutron source and gives a 0.5 meV resolution. Relatively high-energy-transfer region can be detected in these spectrometers. LAM-D consists of two scattering-angle sets of about 40 and 80 degrees. CAT has one analyzer mirror at a scattering angle at around 80 degree. For both inelastic spectrometers, analyzer mirrors with a relatively wide window of scattering angle give us information on the generalized vibrational density-of-states under the incoherent approximation without any integration on $Q$.

To extract the dynamic structure factor, $S(Q,E)$, as a function of momentum transfer, $Q$, and energy transfer, $E$, from the TOF-spectra for LAM-40, a background contribution was carefully removed and the scattering contribution from the container material was subtracted taking into account an absorption correction. Counter efficiency was considered using the spectra of a vanadium standard sample. Each spectrum was normalized to the incident intensity. Since a TOF spectrum under the measuring condition of a constant scattering angle is not on a constant-$Q$ trajectory, we usually interpolate values on a $Q-E$ lattice using a surface spline technique. At this stage, this interpolation has not been carried out yet, and therefore we will present the $S(2\theta,E)$ spectra in this paper and denote representative $Q$-values at the energy transfer of zero, $E=0$.

3. Results
The obtained dynamic structure factors, $S(Q,E)$, of Ag2GeSe3 are shown in figure 1 at Q values. One can see the low energy excitations peaked at around 2.4 meV and having a tail in a high-energy region at $Q = 2.47 \text{ Å}^{-1}$ in figure 1b. As increasing temperature, the intensity of this low energy excitation increases but the excitation energy is almost constant. The low energy excitation is observed at all $Q$ values but the intensity decreases at lower $Q$ values.

Figure 1. Temperature dependence of dynamic structure factors of Ag2GeSe3 obtained by quasi-elastic neutron scattering experiments using LAM-40 at (a) $Q = 1.92 \text{ Å}^{-1}$ and (b) $Q = 2.47 \text{ Å}^{-1}$.
The dynamic structure factors in a higher energy-transfer region were obtained by the inelastic neutron scattering measurements using CAT (a) and LAM-40 (b) as shown in figure 2. At the scattering angle of 80°, significant temperature dependence was observed below 10 meV associated with the low energy excitation. The spectrum at 50K exhibits slightly different profile as that at the lowest temperature of 120K in figure 1a. This means that the boson peak of Ge-Se glassy media is located at a much lower energy than 2.4 meV, the energy where the peak profiles are seen in figure 1. At 300K, a tail structure similar to that in figure 1a was observed, although the hump like structure around 2 meV is smeared out by a relatively low energy resolution of CAT spectrometer. At 18 meV and 36 meV, other excitations are observed which is emphasized in the spectra obtained at scattering-angle of 40° by LAM-40 (see figure 2b). The excitation energies are slightly shifted to 17meV and 33meV.

4. Discussions

From the comparison between S(Q,E) at 50K and at higher temperatures, the tail structure below 10 meV is related to the fast conduction of Ag ions that can be a quasi-elastic tail of Ag ion diffusion, however the FWHM (full width at half maximum) of 10 meV is two diffusive, higher than liquid metals and Cu diffusion in molten CuI. Since boson peak in glassy materials is usually restricted below few meV, it is suggested that this tail may be originated from the combination effect between Ag ion conduction and a low energy excitation of glassy media.

To see the higher excitations in detail, the generalized vibrational density-of-states, g-DOS, were deduced from the $S(Q,E)$ as shown in figure 3. The excitation at 34 meV is assigned as the stretching mode of Ge-Se covalent bond since silver ions migrates in the glassy media of GeSe₃ at 300K and the...
similar excitation was observed for crystalline GeSe$_2$. The defined stretching mode at 34 meV and the bending mode at 17 meV suggest that the covalent network in Ge-Se amorphous material persists by adding Ag.

5. Summary
Quasi-elastic and inelastic neutron scattering measurements of superionic conducting glass of Ag$_2$GeSe$_3$ have been performed. The low energy excitation at 2.4 meV is observed for all temperatures from 120K to 300K and underling tail below 10 meV. The intensity of those excitation increases as increasing temperature, which might be a combination effect between boson peak for glass media and Ag conduction. It is confirmed from the generalized vibrational density-of-state that covalent glass network of Ge-Se persists in this material.

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