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Neutron Inelastic Scattering of Densified GeO_2 Glass

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Neutron inelastic measurements have been performed on normal and pressure-compacted GeO_2 glasses using LAM-D spectrometer at KENS spallation pulsed neutron source. Two cylindrical GeO_2 samples, which had been subjected to pressures of 0 (ambient pressure) and 6 GPa, respectively, were studied. The boson peak of the dynamical structure factor, $S(Q,E)$, shifts to higher energy transfer magnitude with increasing density (preparation pressure), indicating a modification of the intermediate range order resulting from a compaction of the germania rings. The vibrational density of states, $G(E)$, does not change drastically on densification, except for an energy shift of spectrum.

KEYWORDS: densified glass, inelastic neutron scattering, boson peak, intermediate-range order

§1. Introduction

The nature of intermediate range order in glasses remains one of the outstanding problems in condensed matter physics. Thus, the dependence of the degree of intermediate range order in glasses on an applied pressure is of great interest, although the effects of hydrostatic pressure on the structures of even the simplest glasses have not been widely researched to date. In most cases, the application of pressure has both reversible and irreversible components. This means that, after the pressure is released, the glass has a higher density than that prior to compaction.

Studies have been carried out by several authors into the effects of pressure on the structure of SiO_2 glass.[1–5] Susman *et al.*[4] have published results of a neutron diffraction experiment performed permanently densified SiO_2 glass and it has been shown that both pressure compaction and fast neutron irradiation[6] give similar changes in the short range order. A reduction in the mean Si-Ô-Si bond angle, together with a small increase in the Si-O bond length[3] is observed in both cases. The above modes of sample densification both lead diffraction patterns in which first peak in reciprocal space is broadened and exhibits a reduced height, together with a slight shift to a higher scattering vector magnitude, Q, which implies a reduction of the intermediate order and in the average size of the network cages. Very little research has been carried out on pressure-compacted GeO_2 glass so far, even through the results from studies of this glass are expected to have significance with respect to the compaction mechanism previously put forward for SiO_2.

For GeO_2, the radius ratio, r_{Ge}/r_O, is close to the value for the change from tetrahedral to octahedral co-ordination. Previously published XANES and EXAFS results[7] suggest that, under pressures of 7-9 GPa, the mean Ge(O) co-ordination number, $n_{Ge(O)}$, for the glass increases from 4 to 6. In SiO_2 glass, SiO_6 octahedra are formed but less suddenly and at much greater pressures.[8]

Limited, *in situ*, high-pressure Raman scattering experiments have previously been carried out.[9] For pressure-compacted GeO_2 glass, Raman scattering studies have been performed by several authors.[8,10,11] To the author's knowledge, prior to these experiments, there have been no detailed neutron inelastic studies of pressure-compacted GeO_2 glass.

§2. Experimental Procedures

GeO_2 glass, prepared by melt quenching, was cut into cylindrical pieces of length about 8 mm and diameter about 5 mm, which were then densified in a multi-anvil high-pressure apparatus, using the procedure described elsewhere.[10] The glass piece was compressed at pressure of 6 GPa, and then heated at 673 K for 2 minutes, under pressure. The pressure was released after heating. The densities of the glass pieces were measured by the Archimedes method, using carbon tetrachloride as the immersion fluid, and the average values are 3.639 g/cm^3 and 4.232 g/cm^3 for normal and densified glasses, respectively. The pieces were contained in a thin-walled aluminum can for the inelastic neutron scattering experiments. The total weights of the glass samples were 10.301 g (18 pieces) and 3.188 g (6 pieces) for normal and densified glasses, respectively.

The pulsed neutron inelastic scattering experiment was carried out at room temperature using crystal analyzer, medium-resolution spectrometer, LAM-D,[12] installed on the pulsed spallation neutron source, KENS, at the High Energy Accelerator Research Organization, Japan. The LAM-D spectrometer is an inverted-

geometry time-of-flight (TOF) instrument in which the scattered neutrons with a fixed final energy are selected by the pyrolitic graphite (PG) (002) Bragg reflection (corresponding to $E_f = 4.59$ meV). The scattering vector, Q, and energy transfer, E, characterizing each scattering event, are derived from the measured incident wave vector, k_i, the fixed scattered wave vector, k_f, and the scattering angle, ϕ. All measurements were made at $\phi = 85°$. Energy transfers are observed from 0 to 200 meV with a resolution width, $\delta E/E$, of less than 6 % throughout the entire energy range. The momentum transfer range corresponding to the above energy range is from 1.9 to 9.8 $Å^{-1}$ at $\phi = 85°$. After subtracting the empty sample cell signal, the TOF raw spectra were normalized, using incident beam spectrum, $I_0(\lambda)$, and transformed into energy spectra. No corrections were made for multiple scattering and multi phonon scattering.

§3. Results

The dynamic structure factors, $S(Q,E)$, for GeO_2 glass before and after pressure compaction are shown in Fig. 1. These structure factors were obtained along a (Q,E) path from $Q = 1.9$ $Å^{-1}$ ($E = 0$ meV) to 3.8 $Å^{-1}$ ($E = 25$ meV). Boson peaks of normal and densified glasses are observed in $S(Q,E)$ at 3.4 meV and 5.3 meV, respectively. A polynomial fit was performed to the Boson peak and is noted by the full line in Fig. 1.

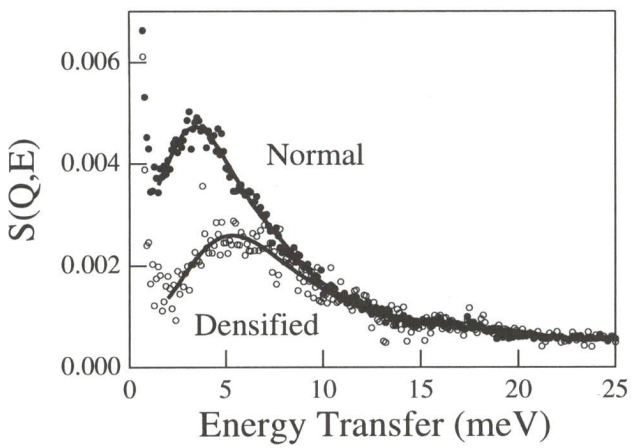

Fig. 1. Dynamic structure factors, $S(Q,E)$, for normal (0 GPa, 3.639 g/cm^3) and densified (6 GPa, 4.232 g/cm^3) GeO_2 glasses. The solid lines are polynomial fitting curves as a guide to the eye only.

The vibrational density of states (VDOS), $G(E)$, are shown in Fig. 2. The VDOS of the densified glass in the range from 20 to 30 meV was scaled to be matched to that of the normal glass, because of negligible difference in $S(Q,E)$ for two samples above 12 meV, as in Fig. 1. The spectrum of normal GeO_2 glass is in agreement with that of Galeener *et al.*[13] The two spectra of normal and densified glasses are similar to each other. However, in spite of the large statistical errors of the spectra for densified glass, it is shown that the high-energy broad peaks above 90 meV shift to lower energy by densification. Galeener *et al.*[13] and Ishihara *et al.*[10] applied the

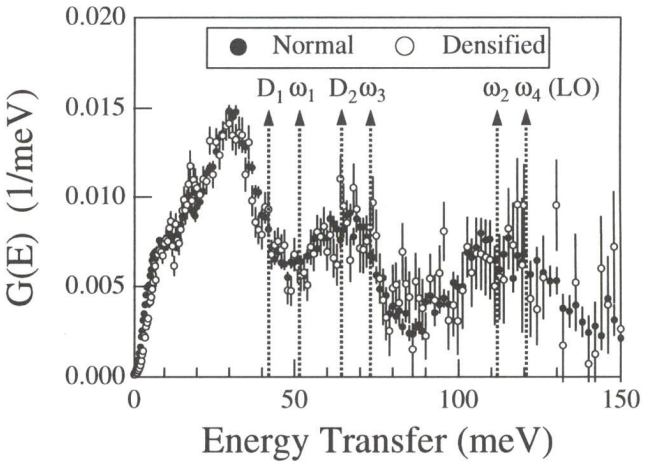

Fig. 2. Generalized vibrational density of states, $G(E)$, (VDOS) for normal (0 GPa, 3.639 g/cm^3) and densified (6 GPa, 4.232 g/cm^3) GeO_2 glasses. The arrows indicated the vibrational modes as specified by Ishihara *et al.*[10] using the Sen and Thorpe model.[14]

Sen and Thorpe (ST) model[14] to the results of the Raman scattering spectra. The arrows in Fig. 2 denote the vibrational modes assigned by Ishihara *et al.*[10]

§4. Discussions

From Fig. 1, it can be seen that the Boson peak moves to higher energy with increasing density. This peak shift is consistent with the results of Raman scattering.[10,11] Further, peak intensity decreases drastically whereas the intensities above 12 meV do not change on pressure densification. For SiO_2 glass, which is the same AX_2 tetrahedral network glass as GeO_2 glass, the Boson peak has been interpreted as arising from the localized collective motions of SiO_4 tetrahedra in the extent of intermediate range order associated with n-membered rings of SiO_4 tetrahedra ($n = 4 \sim 10$).[15] Hence it may be concluded that the average size of the ring of GeO_4 tetrahedra decreases with increasing density, which is expected when densification occurs with little structure reorganization. A neutron diffraction study was performed on normal and pressure-compacted GeO_2 glass recently and it shows that first diffraction peak of the diffraction pattern shifts to higher Q with increasing density, indicating a modification of the intermediate range order resulting from a compaction of the network cages.[16] This suggestion is consistent with the above interpretation of the boson peak shift.

The significant change in the VDOS involves the broad optical band over 90 meV, which moves to lower energy by pressure compaction. In the Raman scattering study,[10] the ω_4 (TO) and ω_4 (LO) modes, assigned to the asymmetric stretching vibration of Ge-Ô-Ge, shift to the lower energy with increasing pressure compaction. By the application of the ST model to the Raman scattering data, it is pointed out that the peak shifts indicate a reduction in the mean Ge-Ô-Ge bond angle with increasing density.[10] Hence the change in the VDOS over 90 meV with increasing density suggests a decreasing

mean Ge-Ô-Ge bond angle. As mentioned in section 3, it is not possible to extract the exact Ge-Ô-Ge bond angle by the application of the ST model, due to the large statistical errors of the VDOS for the densified glass.

These features of $S(Q,E)$ and $G(E)$ for densified GeO_2 glass are similar to those of recent inelastic neutron scattering study for densified SiO_2 glass.[17] It will therefore be necessary perform a more detailed structural study for AX_2 tetrahedral network glass system. To obtain a more detailed understanding of the transformation of the intermediate range order or the germania rings on pressure compaction, three-dimensional static structural models of the normal and densified GeO_2 glasses are being created from the reverse Monte Carlo (RMC) fits[18] to the recent neutron diffraction data[16] and additional X-ray diffraction results using high-energy photons,[19] to be reported elsewhere.[20]

§5. Conclusions

A neutron inelastic scattering study has been performed into the effects of pressure compaction on the dynamical structure of GeO_2 glass. By pressure densification, the Boson peak moves to higher energy, indicating a reduction in the average size of the germania ring. Similarly there is corresponding decrease in most probable Ge-Ô-Ge bond angle with increasing sample density. These are in agreement with the published Raman scattering data.[10]

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