Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B, April 2006, **47** (2), xxx–yyy

High pressure Raman spectroscopy study of $GeSe_2$ glass

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For many years, germanium diselenide, $GeSe_2$ has been investigated for possible amorphous to amorphous transitions (AAT). In this report, the possibility of an AAT in $GeSe_2$ glass has been explored by Raman spectroscopy under quasi-hydrostatic pressures up to 9 GPa. A typical Raman spectrum of amorphous $GeSe_2$ at ambient conditions shows a main Raman band A_1 at 200 cm^{-1}, corresponding to the symmetric stretching vibrations of the corner sharing tetrahedra (CST) and a companion mode A_1^c at 216 cm^{-1}, corresponding to the stretching vibrations of the dimerised Se atoms on the edge sharing tetrahedra (EST). Pressure causes some reduction in the Raman intensity along with loss of peak features. Decompressed samples from about 9 GPa show a dramatic increase in the Raman intensity, while the peak frequencies and shape remaining the same as that of the uncompressed sample. This suggests that the network of the CST and EST in the $GeSe_2$ glass remains similar even after compression to 9 GPa.

1. Introduction

At ambient conditions the structure of $GeSe_2$ glass is similar to the β phase ($P2_1/c$) consisting of 66% $GeSe_4$ tetrahedra connected together by their corners (CST), and the remaining 34% $GeSe_4$ tetrahedra connected together through their edges (EST).[1–4] This existence of edge sharing and inhomogeneously distributed homopolar bonds makes $GeSe_2$ distinct from other tetrahedral glasses. Currently a lot of interest is involved in the study of amorphous $GeSe_2$ in the search for possible amorphous to amorphous transitions (AAT), as was observed in tetrahedral network oxides, SiO_2[5–7] and GeO_2.[8–14]

There are several reports indicating that the structure of $GeSe_2$ has a polyamorphic behaviour. Starting from amorphous $GeSe_2$, Shimada *et al*[15] synthesised three different polymorphs : orthorhombic α-$GeSe_2$ or LT phase (P_{mmm} or P_{mn}) at 0 GPa, T_1-cristobalite phase ($I\bar{4}2d$) at 1–5 GPa and CdI_2 type phase ($P\bar{3}m1$) at 7–8 GPa, all at the same temperature of 400°C, see Table 1. In addition, three more polymorphs of $GeSe_2$ have been synthesised.[16–18] Electrical resistivity measurements carried out on amorphous Ge_xSe_{100-x} ($0 \le x \le 40$) showed an irreversible and discontinuous glassy semiconductor to crystalline metallic transition at 7 GPa.[19] The crystalline β phase, $P2_1/c$ $GeSe_2$ was shown to amorphise reversibly between 11 and 14 GPa,[20] whereas a sequence of amorphisation, crystallisation to LT phase and reamorphisation was observed taking place in β-$GeSe_2$ at 6·2, 7 and 8 GPa respectively.[21]

Table 1.

Phase	*Temperature*	*Pressure (GPa)*
α-$GeSe_2$/LT phase (P_{mmm} or P_{mn})[15]	400°C	0
T1-cristobalite ($I\bar{4}2d$)[15]	400°C	1–5
[16]	500°C	3
CdI_2 type ($P\bar{3}m1$)[15]	400°C	7–8
$I\bar{4}$ [17]	698 K	2
$P\bar{4}$ [17]	773 K	6
HgI_2 type ($P4_2/nmc$)[18]	400°C	3

Ab initio molecular dynamic (MD) simulations revealed that amorphous $GeSe_2$ undergoes a gradual reversible transition to a metallic phase and is associated with increase in coordination from 4 to 6 for Ge, and from 2 to 4 for Se atoms.[22] Calculations based on *ab initio* density functional techniques predicted a pressure induced phase transition of crystalline $GeSe_2$ to a CdI_2 type at 3.56 GPa and an HgI_2 type at 2·30 GPa, where both phases of $GeSe_2$ are metallic.[23] Recent high temperature–high pressure x-ray diffraction experiments showed the change from monoclinic 2D to tetragonal 3D structure of liquid $GeSe_2$ below 2.5 GPa.[24]

It is understood that when the amorphous tetrahedral network system undergoes transitions to a new high density amorphous phase, the tetrahedral crystalline phase often shows a crystal-to-amorphous transition in a similar pressure region to the AAT seen in the amorphous material.[25] Hence, application of pressure either on the ambient glass or tetrahedral crystalline material can lead to the high density amorphous phase in tetrahedral network systems. In other words, with prior knowledge of the pressure effects on crystalline $GeSe_2$, it can be expected that amorphous $GeSe_2$ should show some signatures of AAT with pressure.

In this study, the possibility of AAT in $GeSe_2$ glass

Paper presented at the American Ceramics Society Glass and Optical Materials Division (GOMD) Fall Meeting and 14th International Symposium on Non-Oxide Glasses, Florida, USA. 7–12 November 2004.
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