Phys. Chem. Glasses., 2005, **46** (4), 345–349

Infrared spectroscopy of germanium dioxide (GeO_2) glass at high pressure

P. V. Teredesai,[1]* *D. T. Anderson,*[1] *N. Hauser,*[1] *K. Lantzky*[2] *& J. L. Yarger*[3]*

[1]*Department of Chemistry, University of Wyoming, Laramie, WY 82071, USA*
[2]*Department of Chemistry, St. John Fisher College, Rochester, NY 14618, USA*
[3]*Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA*

Room temperature infrared studies have been performed on GeO_2 glass under quasi-hydrostatic pressures of 9.5 GPa. The mid-infrared absorption spectrum of GeO_2 glass (g-GeO_2) shows two distinct vibrational modes, one at 560 cm^{-1} (mid frequency peak) and another at 870 cm^{-1} (high frequency peak). At pressures above 6 GPa, these two absorption peaks broaden and intensity in the region between them (~700 cm^{-1}) increases dramatically. We interpret this change in the infrared spectrum at high pressure as the onset and progression of the amorphous to amorphous transformation from a low-density tetrahedral glass to a high density octahedral network glass.

Recently, many tetrahedral oxide glasses have been shown undergo a polyamorphic[1] or amorphous to amorphous phase transitions (AAT) at high pressure.[2] Examples include glasses in the silicate, germanate and chalogenide families as well as amorphous H_2O.[3] High pressure studies of SiO_2 and GeO_2 glasses show evidence for an AAT above 30 GPa and 6 GPa, respectively,[3] the new amorphous phase in both SiO_2 and GeO_2 being a high density six-coordinated glass.[4–10]

While the glasses of amorphous silicates and germanates can undergo transitions to a new high density amorphous phase, so can the tetrahedral crystalline phase, which often shows a crystal-to-amorphous transition in a similar pressure region as the AAT seen in the amorphous materials.[11] Hence, either pressurising the ambient glass or tetrahedral crystalline material can be used to reach the high density amorphous phase in SiO_2 and GeO_2.

Amorphous GeO_2 is known to respond to pressure either through modifications of the medium range order[12] or through coordination changes of the cations in the tetrahedral network.[7–10] High pressure Raman study[8] carried on GeO_2 glass (g-GeO_2) indicated an AAT between 6–12 GPa where the gradual coordination change was marked by a change in the pressure derivative of the frequency shifts of the main Raman band, broadening and weakening of this band, and the appearance of a low frequency feature at 240 cm^{-1}. A high pressure Raman study carried out on crystalline GeO_2 of quartz type (q-GeO_2),[9] showed a crystal to amorphous transition with an onset at 7 GPa. These studies pointed to saturation in the pressure dependence of the frequency of the main A_1 (441 cm^{-1}) Ge–O–Ge symmetric stretching mode and a marked increase in the intensity of this mode near 7 GPa. Above 7 GPa, the intensity of A_1 mode dramatically decreases and a broad band on the high frequency side of this mode develops.[9] Infrared study of q-GeO_2 carried to 30 GPa, shows a gradual amorphisation towards an almost 6 coordinated amorphous GeO_2 between 6–12 GPa.[13]

The average Ge–O distance, <Ge–O>, in both g-GeO_2 as well as q-GeO_2 was found to increase from 1·73 Å (tetrahedral structure) to 1·85 Å (octahedral structure) between 6–12 GPa.[7] The wide range of pressure (6–12 GPa) where both coordinates exist indicated that the 4–6 coordination change was gradual. On decompression, only g-GeO_2 showed complete reversibility to four-fold coordination with a large hysterisis, having <Ge–O> around 1·73 Å at 2 GPa, whereas <Ge–O> in q-GeO_2 dropped down only to 1·8 Å, somewhere intermediate between the Ge–O distances of octahedral and tetrahedral structures. This observation forces one to think about two possibilities: on decompression from high pressures, (a) there is co-existence of 50% tetrahedral and 50% octahedral GeO_2 and (b) the high coordinated GeO_2 structure doesn't relax back to four-fold structure instead stabilises in the intermediate five-coordinated GeO_2 structure. Recent *in situ* x-ray and neutron diffraction measurements on g-GeO_2 have shown g-GeO_2 to undergo a metastable phase of average coordination number five between 6–12 GPa.[14] As an analogy, the existence of five-coordinated Si cations has

* Corresponding authors. Email: pallavi.teredesai@gmail.com, Jeff.Yarger@asu.edu