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Irreversible structural changes in vitreous B_2O_3 under pressure

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The disappearance of the boroxol rings has been identified as the microscopic structural change which occurs in a-B_2O_3 upon pressure induced densification. Although changes in ''ring statistics'' is often assumed to be responsible for densification, our results provide the first unambiguous experimental verification. [S0163-1829(96)06925-1]

Amorphous solids exhibit continuous polymorphism, as opposed to the discrete polymorphism of the crystalline state. In the crystalline state, a material can exist with one or more well-defined structures, whereas the structure of an amorphous solid is a continuous function of the preparation conditions as characterized, for example, by the fictive temperature of a glass. It has been known for a long time[1] that amorphous materials can exist metastably within a range of densities and it is apparent that this densification process must not only involve the elimination of free volume but also produce structural changes. There has so far been very limited identification of the microscopic nature of the structural changes but, for example, the distribution of Q_n species in alkali silicate glasses (SiO_4 tetrahedra with different numbers n of bridging oxygen atoms) at a given composition varies as a function of the fictive temperature.[2] In pure a-SiO_2 changes are seen in the first peak in the diffraction pattern, which reflect variations in the intermediate-range order.[3] In the case of chalcogenide systems vapor deposited films may have a structure very different from that of the melt-quenched glass of the same composition, in terms of both the short- and intermediate-range order.[4] Similarly, structural changes have also been inferred from techniques such as Raman scattering, where differences in the vibrational frequencies are interpreted as due to unidentified structural modifications.[5] One of the great successes of the random network theory of Zachariasen[6] is that it incorporates such continuous changes, with both preparation conditions and composition, in a simple way.

One of the most elusive aspects in the study of amorphous polymorphs has been to identify the microscopic origins of the observed structural changes. In the case of SiO_2, for example, all the crystalline polymorphs (except stishovite) comprise SiO_4 tetrahedral networks which are easily distinguished by their space group; this classification technique, however, cannot be applied to noncrystalline materials. It is also possible to distinguish crystalline polymorphs in terms of their ''ring statistics''[7] and, although this latter concept is transferable to amorphous polymorphs, its usefulness to date is academic since the ring statistics are not experimentally measurable. Here a study is presented of pressure effects in a-B_2O_3 which clearly shows the validity of the ''ring statistics'' concept as well as providing a clear identification of the microscopic origin of densification.

Vitreous B_2O_3, is a fascinating but extremely controversial material, particularly in respect to the structural role played by the B_3O_6 boroxol group. The basic structural units in vitreous B_2O_3 are BO_3 triangles.[8] The B_3O_6 boroxol group is a three-membered ring of BO_3 triangles constrained to be planar by delocalized π bonding. The structure of vitreous B_2O_3 may thus be envisioned as a mixed random network of BO_3 triangles and B_2O_3 groups. The presence of boroxol groups in vitreous B_2O_3 was suggested by Goubeau and Keller[9] and further evidence is summarized by Krogh-Moe.[10] In a recent paper,[11] the evidence for boroxol groups playing a major role in the structure of B_2O_3 quenched at conventional cooling rates under ambient pressure is discussed and neutron-scattering data are presented which indicate that the fraction f of boron atoms in boroxol groups is 0.80 ± 0.05, in excellent agreement with earlier NMR data[12] which gave $f=0.82\pm 0.08$.

It has been known for some considerable time that it is possible to densify vitreous B_2O_3 by the application of pressure.[13] Concomitant irreversible changes in sound velocity have also been reported.[14] Pressure experiments therefore provide an ideal method of investigating the relationship between the density and the fraction of boron atoms in boroxol groups. Here we report the results of a Raman-scattering study of a-B_2O_3 under pressure—an experiment originally suggested by Chason and Spaepen.[15] The Raman spectrum of a-B_2O_3 is unusual because it contains a sharp feature not normally found in amorphous materials. The origin of the sharp Raman line at 808 cm^{-1} has been unquestionably assigned to boroxol rings: the B isotope substitution experiments of Galeener and Geissberger[16] showed that it involves almost exclusively O motion, while the O substitution experiments of Risen *et al.*[17] showed that it involves three oxygen atoms. By monitoring the pressure dependence of the intensity of the Raman peak, it will be shown that this feature disappears at high pressures and only partially recovers

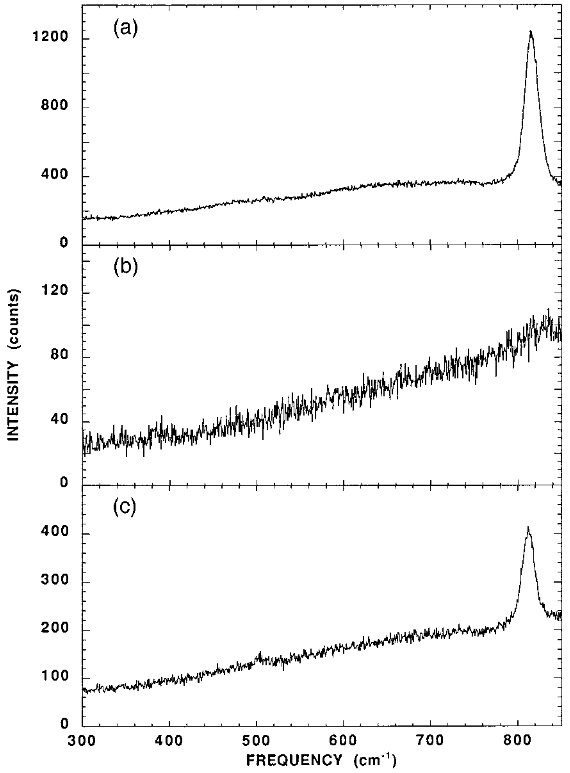

FIG. 1. Raman spectra of a-B_2O_3 at (a) 6 GPa just after loading, (b) at the maximum pressure 16 GPa, and (c) at 0 GPa after pressure release (still in the DAC).

as the pressure is released. The pressure dependence of the intensity and the frequency of the Raman peak thus indicate that, at high pressures, the boroxol rings have been eliminated from the material.

The a-B_2O_3 used in the present experiments was heated overnight at 1000 °C to guarantee that it was free from water contamination. It was loaded into a diamond-anvil cell (DAC) with argon as a pressure medium to avoid any effects of chemical reactions. Due to the method used to load the DAC with liquid argon there was little control over the initial pressure; this explains the lack of low-pressure data on the increasing pressure runs.

Raman spectra were recorded with $\approx$60 mW of 482.5 nm radiation from a Kr laser using a triple spectrometer with a CCD detector. Figure 1 shows spectra recorded at (a) an initial pressure of 6 GPa after loading, (b) at the maximum pressure of 16 GPa, and (c) at 0 GPa (still inside the cell) after pressure release. The most striking feature in Fig. 1 is the complete disappearance of the feature at 810 cm^{-1} at high pressures. The broad background is mostly due to the density of vibrational states of a-B_2O_3 but there is also a contribution from the luminescence of the diamonds. No attempt has been made to deconvolute or interpret these broad features.

Figure 2 shows the pressure dependence of the frequency of the sharp peak. The solid (open) symbols are taken with increasing (decreasing) pressure. The figure contains data from various different runs. At zero pressure the peak position agrees with the values found in the literature: 809 cm^{-1}.[9,10] The frequency increase with pressure (1.06 ± 0.10 cm^{-1}/GPa) is indicative of a strengthening of the B-O bond: as such it provides no insight as to why the boroxol rings should vanish at high pressures.

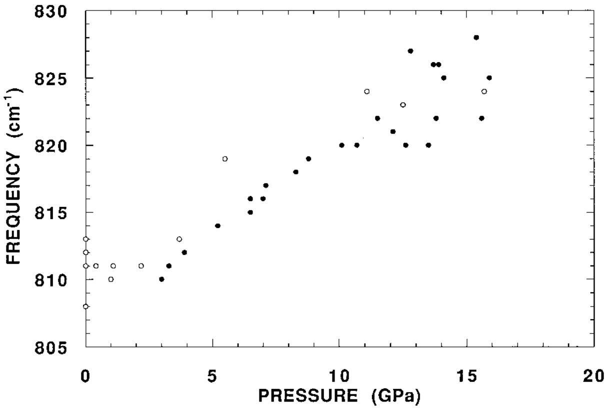

FIG. 2. Pressure dependence of the frequency of the sharp Raman peak. The solid (open) symbols are taken with increasing (decreasing) pressure.

Figure 3 shows the peak intensity (no broadening was observed) of the sharp feature; again the solid (open) symbols were taken with increasing (decreasing) pressure. Since it is not possible to reliably normalize the intensities between different runs, this figure contains data from a single run. Other runs showed the same overall trends. The intensity of the sharp Raman feature drops rapidly in the range 5–14 GPa and is virtually unobserved at higher pressures. The weakness of the peak also explains the larger spread in the high-pressure results in Fig. 2. On pressure decrease, the intensity of the peak never recovers to its original value; at zero pressure it remains at least five times weaker than in the starting material. Because there were no visible changes in the appearance of the a-B_2O_3 sample as pressure was increased, the disappearance of the Raman peak cannot be attributed to changes in the sample transparency. Even at the highest pressures the laser beam transmitted through the sample showed no obvious attenuation.

The irreversible effects shown in Fig. 3 are consistent with the irreversible changes in the sound velocity found in this material[14] and also with the measured densification un-

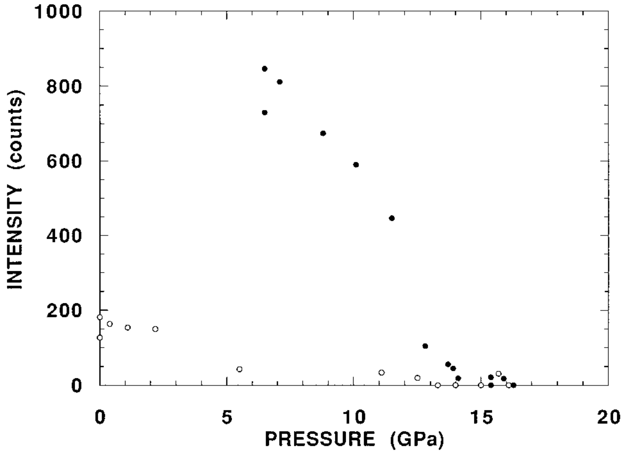

FIG. 3. Intensity of the sharp peak vs pressure. The solid (open) symbols are taken with increasing (decreasing) pressure.

der pressure.[13] Since, at around 4 GPa, there is a large hysteresis in the intensity but not in the line position, it may be concluded that it is not the local environment of each boroxol ring which is producing the observed changes. A more self-consistent picture is that the rings are ''dissolved'' at high pressures and that there is a nucleation barrier which must be overcome before they can renucleate as the pressure is reduced. In this picture the rings do not break apart because the bonding forces become weak but because an alternative structure becomes more stable. On pressure release the formation of the boroxol rings is hindered by a barrier so that there are fewer of them than at the same increasing pressure. The vibrational frequency of the rings however is not greatly affected because, once they have formed, they are relatively insensitive to the local environment.

Simple size and geometrical arguments show that the formation of a boroxol ring in a network of BO_3 triangles leads to a decrease in local density.[8] Hence it is reasonable that, under pressure, the boroxol rings will be less favored and will disappear.

The results described above provide one of the very few clear pictures of microscopic changes during pressure induced densification: viz., in a-B_2O_3 the boroxol rings vanish. This mechanism is the same as that considered in Ref. 15 where it is concluded ''If they (boroxol rings) exist in large numbers, they must break up to allow the densification of the glass.'' At the time, however, it was not possible to ascertain with certainty if rings were present in the starting material. The model developed in Ref. 15 to explain densification consistent of planar regions composed of BO_3 triangles (and no boroxol rings) which puckered as pressure was applied. If, as suggested in Ref. 15, the model were generalized to include boroxol rings, and if puckering and breaking of rings were concomitant, it may well provide an explanation of densification and our results as well.

Our results do not provide direct information on the process by which the rings disappear. However, based on the model suggested to explain the viscosity of liquid B_2O_3,[10,18] it is possible to propose a plausible mechanism for the elimination of the rings. The ambient pressure crystalline modification of B_2O_3,[19] B_2O_3-I, does not contain boroxol groups, but comprises ribbons of B_2O_3 triangles and has a density ($\rho = 2.55$ g/cm^3) very much higher than that of the glass [$\rho = 1.8$ g/cm^3 (Ref. 8)]. The shortest path rings are 10 and 11-fold. A crystal seeded into the anhydrous supercooled melt does not grow, even over a period of several months,[20] indicating an extremely high activation energy of crystallization and hence very different structures for the crystal and melt. The high-pressure crystalline polymorph, B_2O_3-II, which exists metastably under ambient conditions, is formed at pressures in excess of ~ 2 GPa and temperatures higher than 673 K and has a structure which involves distorted BO_4 tetrahedra and both twofold and threefold coordinated oxygen atoms.[21] Under pressure therefore it is likely that some fourfold coordinated B atoms could be formed. These units could act as intermediate (or final) configurations which allow the boroxol rings to deform or break. On pressure release these local structures may prove topologically/stereochemically unfavorable for the reformation of boroxol rings. The Raman technique does not allow us to identify the nature of the new local structures.

Based on the microscopic processes proposed above, relaxation phenomena should occur. We did not observe such effects in our experiments which typically involved small pressure changes over time periods of tens of minutes. It may be possible to observe relaxation phenomena by performing experiments with sudden large pressure changes (e.g., an increase from 5 to 10 GPa) and then monitor the evolution of the intensity of the Raman line.

The information obtained here on the microscopic origins of densification in B_2O_3 must be compared with what is known in other systems: SiO_2 and GeO_2 are probably the materials about which most is known. Both SiO_2 and GeO_2 are known to form sixfold coordinated structures under pressure[22,23] and to produce a densified state on pressure release. On the other hand 20% densified SiO_2 is known to be almost purely fourfold coordinated.[3] So, while the sixfold coordinated state may play a role in the densification process it does not persist into the material recovered on pressure release. The extended x-ray-absorption fine structure results on GeO_2 (Ref. 23) also show that the pressure-induced (at around 7 GPa) sixfold coordination is not stable at ambient pressure and that here also the changes on densification are not due to nearest-neighbor modifications but to changes in intermediate-range order.

In summary: the microscopic changes which occur in B_2O_3 during pressure-induced densification have been identified. The disappearance of the sixfold boroxol rings under pressure provides clear evidence of changes in ring statistics in an amorphous material. It appears therefore that ring statistics could provide the first quantitative measure of structural changes in amorphous polymorphs. A severe problem however is that, for most materials, it is still necessary to develop experimental tools which allow the statistics to be accurately determined.

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