

## Brillouin scattering from amorphous materials at high pressures

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Recent Brillouin experiments on  $\alpha$ -SiO<sub>2</sub> have shown that it undergoes an amorphous-to-amorphous-phase transition as a function of pressure. Here we report Brillouin scattering results from  $\alpha$ -GeO<sub>2</sub>,  $\alpha$ -As<sub>2</sub>S<sub>3</sub>,  $\alpha$ -B<sub>2</sub>O<sub>3</sub>, and a polymeric glass. Irreversible effects under pressure are found for  $\alpha$ -GeO<sub>2</sub> and  $\alpha$ -B<sub>2</sub>O<sub>3</sub> which we also interpret as due to phase transitions. The polymeric glass and  $\alpha$ -As<sub>2</sub>S<sub>3</sub> show no evidence of unusual behavior.

### I. INTRODUCTION

A number of recent experiments have shown that amorphous systems can exist in different polymorphic phases: a new high-pressure phase of  $\alpha$ -H<sub>2</sub>O has recently been found,<sup>1</sup>  $\alpha$ -Si is also reported to have features attributed to two different phases,<sup>2</sup> and  $\alpha$ -SiO<sub>2</sub> was found to have a high-pressure polymorph that is stable at atmospheric pressure.<sup>3-5</sup> Given the current interest in the amorphous state, we thought it worthwhile to investigate the generality of the behavior observed in  $\alpha$ -SiO<sub>2</sub> in an effort to determine what kind of amorphous materials are likely to have a variety of phases. Since two of the three examples mentioned above occur under pressure, it is reasonable to attempt to create other amorphous polymorphs also using high pressures.

Using the Brillouin scattering technique combined with diamond-anvil-cell (DAC) technology as used in Refs. 3 and 4, we have studied a number of different amorphous systems to determine if they would also exhibit the same type of behavior as  $\alpha$ -SiO<sub>2</sub>. For this purpose we have chosen to study a wide range of amorphous systems ranging from  $\alpha$ -GeO<sub>2</sub> which has a structure similar to that of  $\alpha$ -SiO<sub>2</sub>, through to a polymeric solid (Lucite).<sup>6</sup> The reason for choosing Brillouin scattering to study these types of structural changes is that many of the more conventional techniques are difficult to apply to high-pressure studies in DAC. Although x-ray investigations are now possible in DAC, the use of these techniques to study amorphous systems poses very severe problems. Raman scattering, which is also a powerful technique in high-pressure studies, is hampered by the fact that the usually broad features observed in amorphous materials are easily masked by luminescence of the diamonds. In spite of this, recent Raman scattering experiments have been performed in  $\alpha$ -SiO<sub>2</sub> at high pressures<sup>5</sup> and also show the existence of irreversible effects.

The experimental setup used in this study is the same as that used in previous experiments,<sup>3,4,7,8</sup> and will not be described here. The only parameter which is changed for the different materials is the wavelength of the exciting radiation; this is indicated in each case.

### II. RESULTS

#### A. $\alpha$ -GeO<sub>2</sub>

In this material it is difficult to follow the Brillouin line as a function of pressure above  $\sim 5$  GPa. The reasons for this are that the intensity of the Brillouin line decreases as the pressure is increased, the frequency of the Brillouin lines of some of the liquids used as pressure media is very close to that of the material itself, and it appears that the sample may be reacting chemically with some of the liquids. (In H<sub>2</sub>O the sample dissolves completely at a few GPa.) In spite of these difficulties our results using 515 nm radiation are shown in Fig. 1; the spread in the results is due to the above-mentioned factors. In order to transform the measured frequency shift (in cm<sup>-1</sup>) into the product of refractive index ( $n$ ) times the sound velocity ( $v$ ) it must be multiplied by  $7.72 \times 10^5$  yielding  $nv$  in cm/sec. The solid and open symbols in Fig. 1 denote increasing and decreasing pressure, respectively. It is clear, however, that the sample recovered at one atmosphere has a different sound velocity than that of the original sample; its Raman spectrum is also different from that of the original material as shown in Fig. 2. It is therefore safe to conclude from these measurements that the behavior of  $\alpha$ -GeO<sub>2</sub> is very similar to that found in  $\alpha$ -SiO<sub>2</sub>.<sup>3-5</sup> Unlike  $\alpha$ -SiO<sub>2</sub> however, the sound velocity of the recovered sample does not appear to depend strongly on the maximum pressure attained provided it is above  $\sim 10$  GPa, indicating that the transformation occurs over a much narrower pressure range than in  $\alpha$ -SiO<sub>2</sub>.

#### B. $\alpha$ -As<sub>2</sub>S<sub>3</sub>

A complete study of this material to high pressures was not possible because it becomes opaque as pressure is applied. Even using 647 nm radiation we were only able to observe a Brillouin signal up to 4 GPa from which the slope  $\Delta v/\Delta P = 0.19 \pm 0.02$  cm<sup>-1</sup>/GPa can be obtained. This change in Brillouin frequency corresponds to  $d(nv)dP = (1.8 \pm 0.2)10^5$  cm/sec. In spite of not being

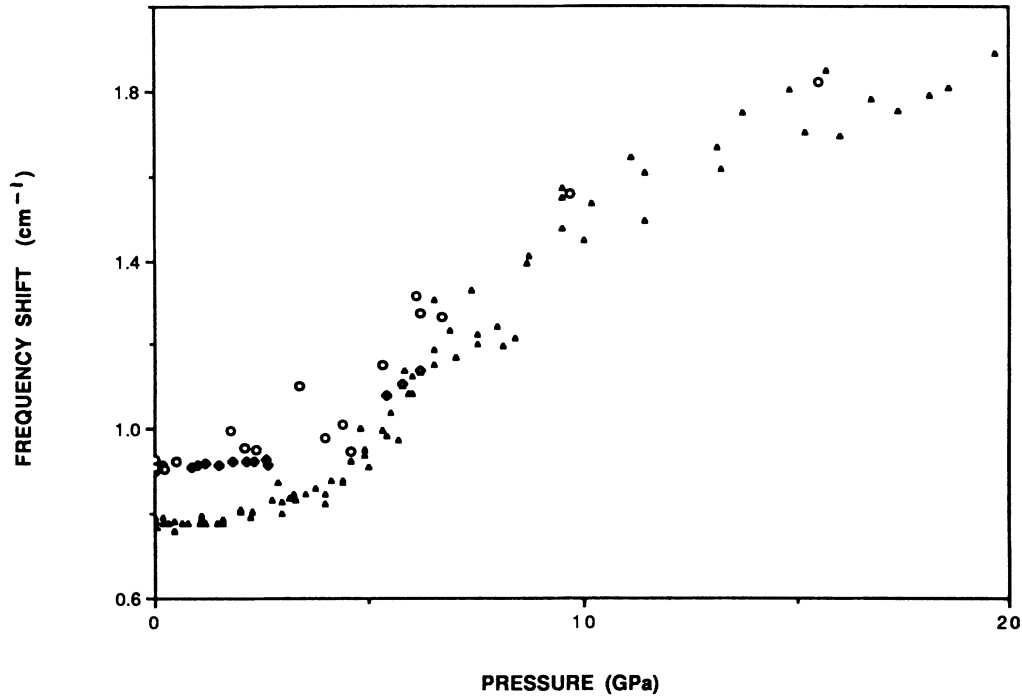


FIG. 1. Brillouin frequency shift of  $\alpha$ -GeO<sub>2</sub> as a function of pressure; triangles denote increasing pressure, circles decreasing pressure, diamonds are increasing pressure on a sample that had already been cycled.

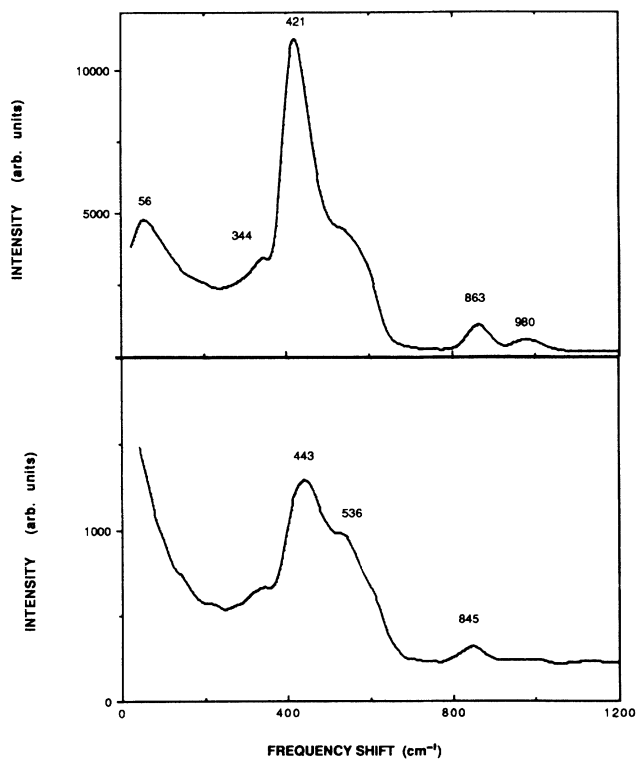


FIG. 2. Raman spectra of  $\alpha$ -GeO<sub>2</sub>: upper, sample before compression; lower, taken at one atmosphere after compression to 14.5 GPa.

able to follow the Brillouin signal to high pressures we did pressurize the sample to  $\approx 15$  GPa; on reducing the pressure we obtained the same results as we had with increasing pressure. We conclude from this that  $\alpha$ -As<sub>2</sub>S<sub>3</sub> does not undergo any irreversible changes in this pressure range.

### C. $\alpha$ -B<sub>2</sub>O<sub>3</sub>

Figure 3 shows the measured Brillouin frequency shift ( $\lambda_{\text{exc}} = 521$  nm) from  $\alpha$ -B<sub>2</sub>O<sub>3</sub> as a function of pressure.

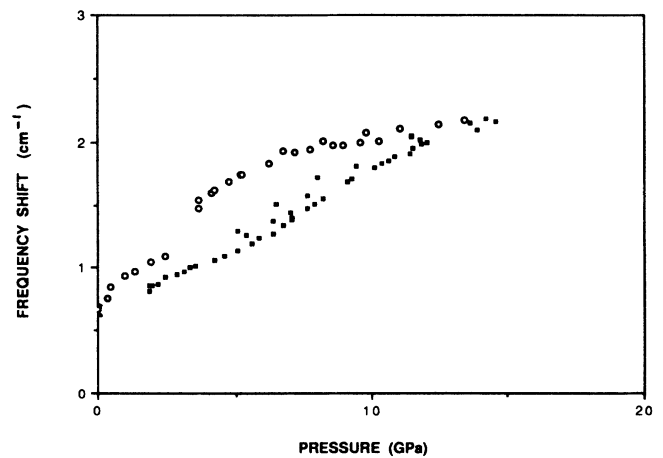


FIG. 3. Brillouin frequency shift of  $\alpha$ -B<sub>2</sub>O<sub>3</sub> vs pressure. The solid and open symbols are for increasing and decreasing pressure, respectively.

Here, as for  $\alpha$ -SiO<sub>2</sub><sup>3,4</sup> there is a clear indication of irreversible behavior as the pressure is increased (solid symbols) and decreased (open symbols). The results shown in Fig. 3 are reminiscent of hysteresis loops encountered in many types of phase transitions. Contrary to the results for  $\alpha$ -SiO<sub>2</sub> however, the "hysteresis" loop in this case appears to be almost closed indicating that even though "irreversible" changes are occurring as pressure is applied, and that at  $\approx 6$  GPa the material on the increasing side is substantially different from that on the decreasing side, at zero pressure the material has reverted back to its original form. Samples held overnight at  $\sim 5$  GPa (decreasing pressure) show no changes.

#### D. Lucite

Figure 4 shows the frequency shift versus pressure for Lucite ( $\lambda_{\text{exc}} = 515$  nm). The solid (open) symbols indicate increasing (decreasing) pressure. There appears to be no evidence for irreversible changes.

### III. CONCLUSIONS

The results indicate that the existence of amorphous polymorphs is not a particularly rare occurrence. In SiO<sub>2</sub> and H<sub>2</sub>O, which exist in many crystallographic forms, it is not unreasonable that different packing arrangements of the basic building blocks can also occur in the amorphous state. On the other hand,  $\alpha$ -B<sub>2</sub>O<sub>3</sub> and  $\alpha$ -As<sub>2</sub>S<sub>3</sub> are both extremely difficult to crystallize and yet in our experiments one shows irreversible behavior while the other does not. Perhaps a common thread for the absence or presence of an effect can be found using arguments based on the "basic building blocks" of each material. In Lucite the lack of any changes can be blamed on its large structural units which would require cooperative changes over large volumes. The compounds that have been shown to have amorphous polymorphs (H<sub>2</sub>O,<sup>1</sup> SiO<sub>2</sub>,<sup>3-5</sup> GeO<sub>2</sub>, and B<sub>2</sub>O<sub>3</sub>) all have small basic units; on the other

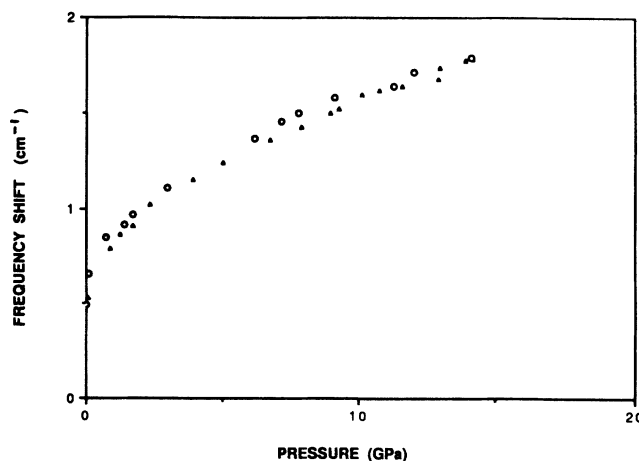


Figure 4 shows the frequency shift versus pressure for Lucite ( $\lambda_{\text{exc}} = 515$  nm). The solid (open) symbols indicate increasing (decreasing) pressure. There appears to be no evidence for irreversible changes.

hand, As<sub>2</sub>S<sub>3</sub> also has a small unit and hence, based on the above considerations, should also show polymorphic behavior. Considerably more work is required before any general conclusions can be drawn. Further insight into this type of polymorphism would benefit enormously from structure studies. The fact that one is dealing with small amorphous samples which are composed of relatively light elements makes these studies extremely difficult. In spite of these problems, efforts are currently underway to determine the structure of recovered samples of  $\alpha$ -SiO<sub>2</sub>.

#### ACKNOWLEDGMENT

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