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Temperature-induced amorphization of SiO_2 stishovite

M. Grimsditch
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

S. Popova
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
and Institute of High Pressure Physics, 142092 Troick Moscow Region, Russia

V. V. Brazhkin and R. N. Voloshin
Institute of High Pressure Physics, 142092 Troick Moscow Region, Russia

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A Raman-scattering investigation of stishovite, a high-pressure crystalline polymorph of SiO_2, shows that at around 650 °C it becomes amorphous. The amorphous material produced during the initial stages of amorphization is not identical to ordinary silica since it exhibits features of the high-pressure amorphous polymorph. Above 800 °C there is little remaining evidence of stishovite but the amorphous material has transformed to a state indistinguishable from that of silica. Annealing effects in densified silica are also presented and compared with the stishovite results.

It is somewhat surprising, given that the classical method of preparing amorphous materials involves "rapid" cooling from the melt, that heating can also lead to amorphization. However, in the relatively new field of solid-state amorphization it has been found that in certain cases (changing of thermodynamical parameters,[1,2] accumulation of defects,[3] or fabrication of metastable structures[4]) the initial crystal structure can become unstable and, if the rate of growth of the new stable crystalline phase is negligibly small, the material can become amorphous. In this context heating may also act as a destabilizing factor and produce amorphization. Amorphization of some quenched high-pressure phases during subsequent heating has been discussed in Ref. 5.

Of particular interest in the field of amorphous materials is SiO_2. Its most common noncrystalline form is produced by cooling from the melt but other forms, such as those found in meteor impact craters or produced from fused quartz under high pressures,[6] are also known to exist. In Ref. 6 it was proposed that since the elastic and vibrational properties of the pressure-densified material were so different from ordinary fused quartz, that the term "amorphous polymorph" may be appropriate. It is known that the quartz and coesite crystalline polymorphs[7,8] transform into an amorphous phase under hydrostatic pressure. Furthermore it was found that the material produced from quartz under these conditions was elastically anisotropic.[9,10] This latter finding is controversial and is currently under discussion.[11]

Stishov[12] reported the temperature-induced amorphization of the high-pressure crystalline polymorph of SiO_2 stishovite. The kinetics of the transformation have been investigated using optical and x-ray techniques.[13–15] Optical techniques[13] showed that the transformation rate increases rapidly as the temperature is raised and that the final product has the same refractive index as fused quartz. X-ray investigations[15] indicate that the amorphous material produced during the initial stages of the transformation is not identical to fused quartz. Although this observation is consistent with the suggestion[13] that a sixfold-coordinated glass is produced during the initial stages, a recent NMR investigation[16] finds no evidence of sixfold-coordinated Si atoms in the amorphized material.

Here we present a Raman-scattering investigation of the temperature-induced amorphization of stishovite. Our results show that at the beginning of the amorphization process the material is different from fused quartz but that as the temperature is raised it reverts to a material whose Raman spectrum is indistinguishable from that of fused quartz. We also include a similar temperature study of pressure-densified amorphous silica, the results of which are then compared with those on stishovite.

Two samples of stishovite synthesized in Pd foil using the high-pressure technique previously described[12,15] were used in our experiments. Raman spectra were recorded in a backscattering geometry on a triple spectrometer using a CCD detector and 100 mW of 482.5-nm radiation. The samples were placed in a furnace and heated in air. A grating filter was used in the incident laser beam to eliminate plasma lines from the laser. Plasma lines closer than ~150 cm^{-1} are not removed by the filter: they are observed in the spectra and indicated by asterisks. The two stishovite samples investigated exhibited different degrees of luminescence; since most of the luminescent background disappeared as the temperature increased we believe it is due to the presence of organic impurities.

Figure 1 shows Raman spectra obtained from stishovite at various temperatures. We can distinguish two stages during heating: (1) pure crystalline, (2) mixture of crystalline and amorphous materials. The temperature boundaries between the two stages are slightly different for the two samples: glass appeared at 550 °C and the

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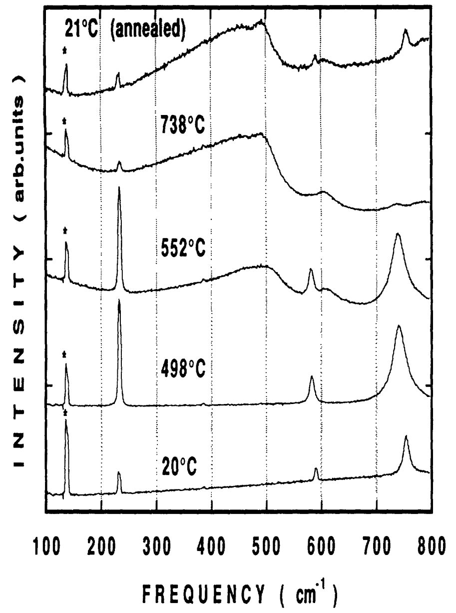

FIG. 1. Temperature dependence of the Raman spectra of stishovite. The asterisk indicates a plasma line from the laser.

crystal essentially disappeared at 750 °C in one of the samples but for the second one the temperatures were 670 and 850 °C, respectively. This discrepancy could be due to different grain sizes in the two samples and the concomitant defected regions at their boundaries. Furthermore the second sample was annealed at 400 °C for 12 h prior to the experiment in an effort to reduce the luminescence (no significant change in the luminescence was observed). In the spectrum from the recovered sample it appears that a weak luminescent background is again present. Presumably it is due to some impurity which has not been completely eliminated by heating.

At room temperature the Raman peak positions are 231 cm^{-1} (B_{1g} mode), 590 cm^{-1} (E_g mode), and 754 cm^{-1} (A_{1g} mode); they are in a good agreement with literature values.[17,18] None of the Raman lines shift significantly with temperature. The low-frequency B_{1g} mode shows only a very small increase in frequency (5×10^{-3} cm^{-1}/°C) up to 500 °C. The two other modes decrease in frequency with relatively small slopes of 0.01 cm^{-1}/°C for E_g and 0.03 cm^{-1}/°C for A_{1g}. A comparison with other substances with the rutile structure $\mathrm{TiO_2}$,[19,20] $\mathrm{SnO_2}$,[21] and $\mathrm{GeO_2}$ (Ref. 22) shows similarities in the temperature behavior of the Raman modes.

In stage 2 stishovite coexists with an amorphous phase. The phonons of the crystalline parts still do not exhibit any unusual behavior, while the portions of the spectra corresponding to the amorphous regions show (as will be discussed in detail below) that both prominent peaks in the disordered phase are shifted to higher energy than in regular fused quartz. At the highest temperatures the amorphous material becomes indistinguishable from regular silica glass and the crystalline peaks are almost no longer observable.

An examination of the amorphous portions of the spectra in Fig. 1 shows that, although they are very similar to those of fused silica, they do exhibit some notable differences. To highlight the differences we have plotted in Fig. 2 the temperature dependence of Raman spectra from (a) amorphized stishovite, (b) 20% pressure-densified silica,[23,24] and (c) ordinary fused silica. The complete transparency of our fused quartz sample compared to the multigrain-translucent samples of stichovite and densified material account for the differences in signal to noise and the absence of the laser plasma lines below 150 cm^{-1}. The amorphous material produced during the initial stage of amorphization of stishovite exhibits features of the high-pressure amorphous polymorph in as much as both broad peaks are shifted to higher frequencies. The evolution of the Raman spectra shown in Fig. 2 for the stishovite glass and the densified glass are similar; in both materials the peaks shift to lower energies as the temperature is raised and both become indistinguishable from spectra of silica at high temperatures. The spectra for ordinary fused silica, included for completeness in Fig. 2, show almost no change with temperature. The annealing effect in the pressure-densified material is consistent with earlier Brillouin-scattering results which showed that on heating, the sound velocity in the densified material reverts to that of ordinary fused silica.[25]

The similarities between amorphized stishovite and

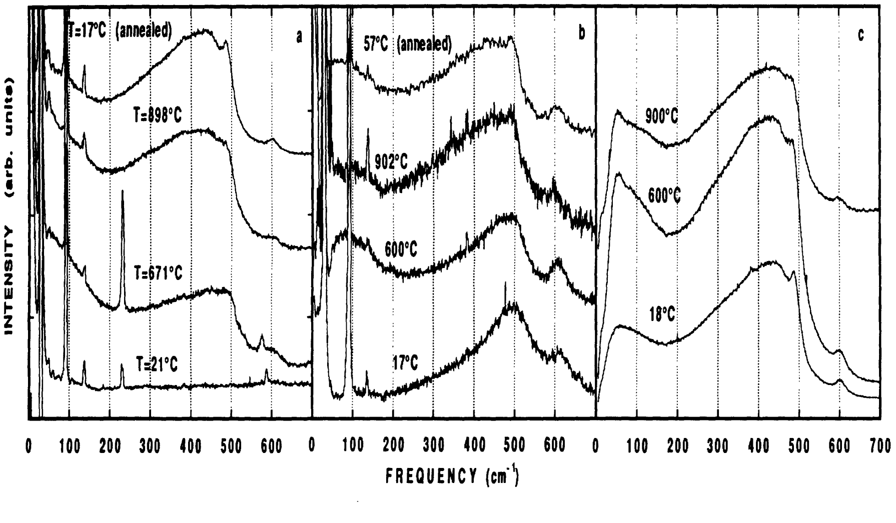

FIG. 2. Raman spectra of (a) stishovite, (b) densified silica, and (c) ordinary silica. The sharp lines below 150 cm^{-1} are plasma lines from the laser.

densified silica can be qualitatively understood as due to a "memory" of sixfold coordination. It has been shown[26] that, under compression, silica develops a sixfold-coordinated structure. Although after pressure release there appears to be no remnant sixfold coordination in the structure,[23] it is not unreasonable that the local fourfold structure, originating from a spontaneous change from six- to four-coordinated Si atoms, is not identical to the fourfold structure obtained in thermodynamical equilibrium.

In conclusion, Raman scattering has been used to study the temperature-induced amorphization of stishovite. The onset of amorphization is at ~600 °C and is complete by ~800 °C. Upon amorphization stishovite does not transform directly to a silicalike glass but to an intermediate amorphous phase similar to that of an irreversibly densified glass. At higher temperatures the Raman spectra are indistinguishable from those of ordinary fused silica. In agreement with the conclusions of Ref. 16 we conclude that the amorphization is associated with the transformation from the sixfold-coordinated stishovite to a fourfold-coordinated network very similar to ordinary fused SiO_2. Furthermore, due to the large expansion at the transition from a six- to a fourfold-coordinated structure (60% in the case of quartz to stishovite), extremely large local stresses should arise. The presence of such stresses is indirectly confirmed by visual observation: since the amorphous material probably grows at the grain boundaries, the local stresses break apart the polycrystalline sample leading to the observed 5–20 times volume increase.

It has been proposed[27] that the lattice instability which gives rise to amorphization during different disordering techniques may result in a softening of an elastic constant. In the case of pressure-induced amorphization of quartz this has actually been shown using molecular dynamics.[28,29] Since during amorphization there are no signs of an instability in the optical phonons observed by Raman scattering, it will be interesting to perform a similar investigation using Brillouin scattering to study the acoustic phonons; this however will require "large" single crystals.

Although the present investigation shows that by 800 °C stishovite has transformed into a material indistinguishable (based on Raman spectra) from silica, it is noteworthy that in Refs. 15 and 16 it was shown that amorphized stishovite crystallizes into the cristobalite phase at $T \sim 1100$ °C. Since a regular glass does not crystallize at these temperatures it is clear that, at the microscopic level, subtle differences must remain which distinguish amorphized stishovite from fused silica. The small change in the Si-O-Si angle observed with NMR (Ref. 16) could be a signature of this structural difference.

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