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Elastic constants of stishovite up to its amorphization temperature

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Abstract

Brillouin spectra of stishovite were measured up to the amorphization temperature ($T_{\text{am}} \sim 830$ K) using large (1 mm) defect-free single crystals. At room temperature the sound velocities extracted from the BLS yield all six elastic constants. The derived bulk modulus and the polycrystalline shear modulus of stishovite at ambient conditions are $B = 316$ GPa, $G = 222$ GPa. Between room temperature and 800 K only a small decrease of the elastic constants was observed. This is an indication that the amorphization process is not due to a soft, long-wavelength, acoustic phonon. Room-temperature Raman spectra from samples heated to close to the amorphization temperature show that amorphization occurs more rapidly on the (110) than on the (001) crystallographic face. These results, together with those of x-ray measurements from the literature, allow us to conclude that amorphization in stishovite is most likely a surface phenomenon initiated by large oscillations of the Si atoms within the crystal faces whose normals are perpendicular to the c -axis.

1. Introduction

The silicon dioxide crystal polymorph known as stishovite is the simplest and most important example of a compound with silicon atoms in six-fold coordination [1]. Since the discovery of stishovite it has been established that almost all minerals in the Earth's mantle are silicates with the same six-fold coordination [2]. For this reason the study of stishovite is of great importance in geophysics. Although the high-pressure properties of stishovite, including its anomalous behaviour in the vicinity of the transition to the CaCl_2 structure [3–5], have attracted considerable attention within the geophysical community, there are only a few reports concerning the atmospheric pressure and high-temperature behaviour of stishovite [6–10].

The amorphization of stishovite due to heating at atmospheric pressure provides a striking example of a solid state amorphization (SSA) transition of high-pressure phases [11]. The SSA

phenomenon, discovered a few decades ago, is an interesting problem in condensed matter physics. The amorphization consists of the spontaneous atomic-scale disordering of crystals during compression of low-pressure phases or decompression (or heating) of high-pressure modifications [12]. In spite of the significant effort devoted to its elucidation, the nature of SSA is still unclear. The amorphization of stishovite was the first example of SSA of high-pressure phases observed, having been reported well before the first report of SSA of the GaSb high-pressure phase [13], and the examples of the SSA under compression of H₂O–ice [14], SnI₄ [15], and SiO₂ [16]. It may be said that the observation of SSA in stishovite prompted the subsequent intense study of the SSA phenomenon.

Stishovite, because it offers the unique possibility to study SSA at atmospheric pressure and moderate temperatures (~ 800 K), where many characterization methods can easily be used, is an ideal candidate for a study to detail the SSA process. This is in contrast to the high-pressure conditions of SSA in SiO₂ or H₂O or the low-temperature conditions of SSA of the high-pressure phases of GaSb, Si and Ge [17]. The small number of attempts to date to study stishovite at elevated temperature and atmospheric pressure is partially due to the difficulty in obtaining pure, well-characterized, large single-crystal samples. Nevertheless, it has been observed that under heating stishovite transforms to a densified silica glass [8, 9] and that the corresponding SSA process has a low activation energy [7]. This has been regarded as evidence for a lattice instability as the driving force for the SSA. The model of a lattice instability as the origin of SSA [12] is now well established, and the ‘cold melting approach’ [14] has now only historical importance. Direct experimental evidence for shear softening prior to the SSA was obtained for the first time for H₂O–ice [18], and an elastic constant softening was found in compressed single crystals of quartz [19]. Ultrasonic measurements [18], Brillouin scattering [19] and Raman scattering [8] are now the main methods used to study the lattice dynamics in the vicinity of SSA. However, in the general case it is difficult to say *a priori* which phonon mode will be responsible for the SSA. To obtain a comprehensive picture of the behaviour of all the phonons it would be necessary to use different experimental techniques including inelastic neutron scattering in single crystals. Except for the very recent study of compressed H₂O–ice [20], no other such SSA study has been undertaken to date. Theoretical calculations predict that in many cases the crystalline lattice instability originates from a softening of a short-wavelength acoustic phonon [21]. For example the SSA of compressed quartz is governed by phonons with wavevectors (1/3, 1/3, 0) in the Brillouin zone [22]. For stishovite, previous measurements of single-crystal x-ray diffraction at high temperatures revealed a large increase of the atomic vibration amplitude [9], and there has also been a Raman spectroscopy study of heated polycrystalline stishovite samples [8]. The mechanism responsible for SSA in stishovite has not been discussed in these previous reports. The recent synthesis of defect-free large single crystals (up to 2 mm) of stishovite [23] makes it possible to use a wide spectrum of physical methods for the detailed study of stishovite properties. In the present paper we present the results of a Brillouin and Raman spectroscopy study of large (typically $1.5 \times 0.5 \times 0.4$ mm³ with the *c*-axis along the long direction) stishovite crystals over a wide temperature range from room temperature up to the amorphization temperature.

2. Experiment

Information on the elastic constants was obtained by Brillouin scattering. We used a Sandercock-type tandem Fabry–Perot interferometer [24] with 5 + 4 passes. 200 mW of 514.5 nm radiation from an Ar laser was used as the exciting source. At room temperature we used a combination of backscattering, 90° scattering and platelet geometries [25] to determine all six independent elastic constants. At high temperatures, due to the difficulty of aligning the

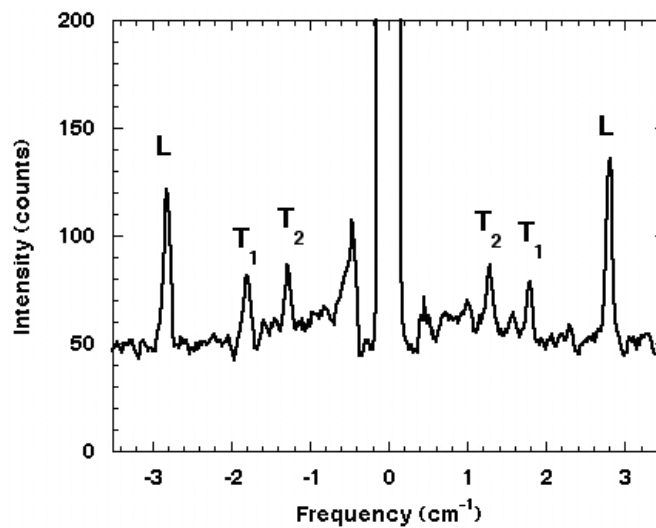


Figure 1. (110) backscattering Brillouin spectrum from stishovite at 150 °C. L, T₁ and T₂ indicate the longitudinal and two transverse phonons.

sample inside the furnace, experiments were limited to the backscattering geometry. A typical spectrum is shown in figure 1. The measured frequency shift $\Delta\omega$ is related to the sound velocity (v) by

$$\Delta\omega = (\omega_L v/c)(n_i^2 + n_s^2 - 2n_i n_s \cos\theta)^{1/2} \quad (1)$$

where ω_L is the frequency of the laser radiation, c the velocity of light, θ the angle between the incident and scattered radiation inside the sample, and n_i and n_s are the refractive indices for the incident and scattered light. The velocity in turn depends on an effective elastic constant X through $X = \rho v^2$, where ρ is the mass density. For any given propagation direction X is a known function of the elastic constants.

In the backscattering geometry ('backscattering' is used to indicate that the scattered light exits through the same surface as that on which the incident beam impinges), the incident beam subtended an angle of $\approx 30^\circ$ with the surface normal, and experiments were performed on the two naturally occurring facets ((110) and (001)) of the single-crystal stishovite needles. The samples were placed in a temperature-controlled oven and experiments were performed until the deterioration of the sample due to its amorphization precluded further measurements. In backscattering experiments on the (001)-face (i.e. phonons with a wavevector along the [001] direction) we observed only the longitudinal mode (which is related to c_{33}); only at the highest temperatures did the shear mode (related to c_{44}) become observable. For light incident on the (110) face (i.e. its wavevector close to the [110] direction) and polarized along $[1, \bar{1}, 0]$, we observed all three allowed phonons: the longitudinal $((c_{11} + c_{12} + 2c_{44})/2)$ and the two transverse (c_{44} and $(c_{11} - c_{12})/2$). In the 90° geometry, with the incident and scattered wavevectors along $[110]$ and $[1\bar{1}0]$ respectively, we observed the longitudinal (c_{11}) and one transverse (c_{44}) mode. The platelet geometry (in which the light exits the sample through the face opposite to that where it entered) yielded information on the quasilongitudinal and quasitransverse branches propagating in the (110) plane, which depend on c_{66} and c_{13} . Thus the combination of measurements in the three geometries yields a complete set of elastic constant values.

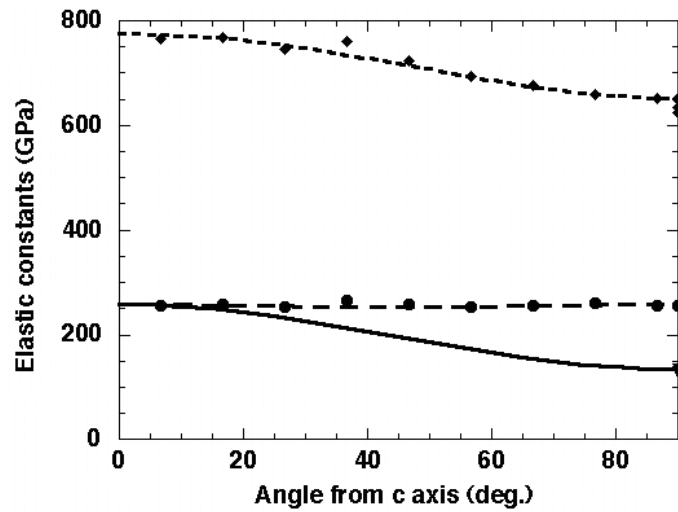


Figure 2. Room-temperature effective elastic moduli versus angle in the (110) plane of stishovite. The symbols are experimental Brillouin data, and the lines are calculated using the c_{ij} obtained from a least squares fit (table 1).

Table 1. Elastic constant values from the present work and from [26].

	c_{11} (GPa)	c_{33} (GPa)	c_{44} (GPa)	c_{66} (GPa)	c_{12} (GPa)	c_{13} (GPa)
Present work	466 ± 3	775 ± 4	258 ± 2	310 ± 6	207 ± 8	204 ± 4
Reference [26]	453 ± 4	776 ± 5	252 ± 2	302 ± 3	211 ± 5	203 ± 4

3. Results

From a fit, with the six independent c_{ij} as free parameters, to all room-temperature data we obtain the c_{ij} listed in table 1. Also listed in table 1 are the values reported in [26]. In analysing our room-temperature data we have used the refractive indices $n_o = 1.799$ and $n_e = 1.826$ and the density 4.28 g cm^{-3} [1]. Overall the agreement between the two sets of c_{ij} is quite good. In figure 2 we plot all our experimental data in the (110) plane (symbols) and compare them with the values calculated from the c_{ij} in table 1.

Previous data on polycrystalline aggregates have yielded a large dispersion of values: from 210 to 520 GPa for the bulk modulus and from 150 to 250 GPa for the shear modulus [27]. By taking the Voigt–Reuss average of our elastic constants we obtain what we believe are reliable values for the bulk modulus and the polycrystalline shear modulus: $B = 316 \pm 4$ GPa, $G = 222 \pm 5$ GPa. These values should be the most accurate available at present and we suggest they be used for the analysis of seismic data and the construction of models for the Earth’s mantle.

In order to interpret the high-temperature Brillouin data with equation (1) it is necessary to know the temperature dependence of the refractive indices. Since they have not been measured, in order to avoid making any assumptions about their temperature dependence, in figure 3 we have plotted the product of sound velocity times refractive index extracted directly from equation (1) with no assumptions. Although unlikely, if future determinations of the refractive index were to show a noticeable temperature dependence, the results in figure 3 could be reanalysed accordingly. We note that, based on the polarization used in the experiments,

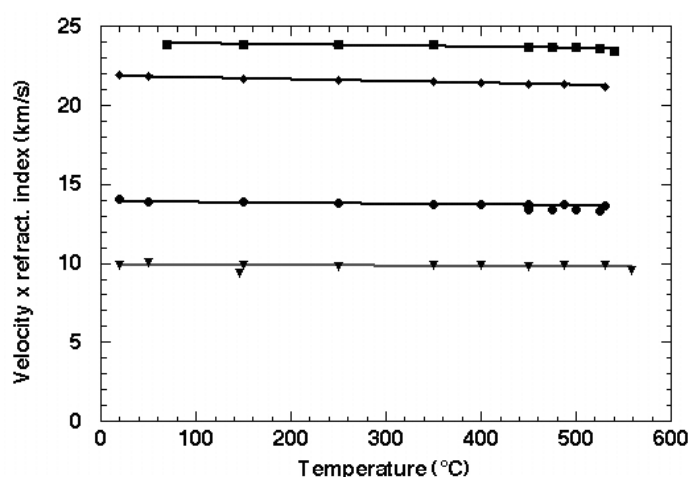


Figure 3. Temperature dependence of various c_{ij} of stishovite. In descending order: c_{33} , $(c_{11} + c_{12} + 2c_{66})/2$, c_{44} and $(c_{11} - c_{12})/2$.

the relevant refractive index for all data in figure 3 is n_o . Assuming that the temperature-induced changes in refractive index are small, and using the measured 0.9% decrease in density at 830 K [9], the results in figure 3 correspond to 4.2, 7.1, 5.2 and 3.2% decreases in c_{33} , $(c_{11} + c_{12} + 2c_{44})/2$, c_{44} and $(c_{11} - c_{12})/2$, respectively between room temperature and the maximum temperatures reached. These changes are typical for most solids and show no evidence of a pronounced softening due to the onset of amorphization. Our results, however, do not rule out the possibility that in a small temperature range (≈ 20 K) around the amorphization temperature, a more rapid change of the c_{ij} could be occurring.

After treatment at 560°C the samples were characterized, at room temperature, using Raman spectroscopy. Backscattering spectra obtained from the (110) and (100) crystallographic faces (the same $[1\bar{1}0]$ polarization was used for both spectra) are shown in figure 4. (The three sharp features indicated by asterisks at 273, 303 and 365 cm^{-1} are plasma lines from the Kr laser and should be ignored.) The features at 755 and 590 cm^{-1} are zone-centre Raman-active modes of crystalline stishovite. The broad Raman features at 480 and 620, as previously identified [8], are from the amorphous phase. From the ratio of the crystalline to amorphous peaks the spectra indicate that there is more amorphous material on the (110) face than on the (001) face. This provides a strong indication that the amorphization process is initiated at the surface and not in the bulk, and furthermore that the (110) surface is less stable than the (001) face.

4. Discussion and conclusions

The observed small softening of the elastic constants of stishovite (with the possible exclusion of temperatures in the close vicinity of the amorphization temperature) is rather typical for ordinary stable oxides that do not exhibit SSA. The weak pressure dependence of the amorphization temperature [7] indicates that SSA in stishovite is dominated by a temperature-induced process. We interpret the absence of significant softening in either the Raman optical mode frequencies [8] or in any of the zone centre acoustic branches as an indication that amorphization is not due to a soft phonon mode. Strictly speaking one cannot rule out that a

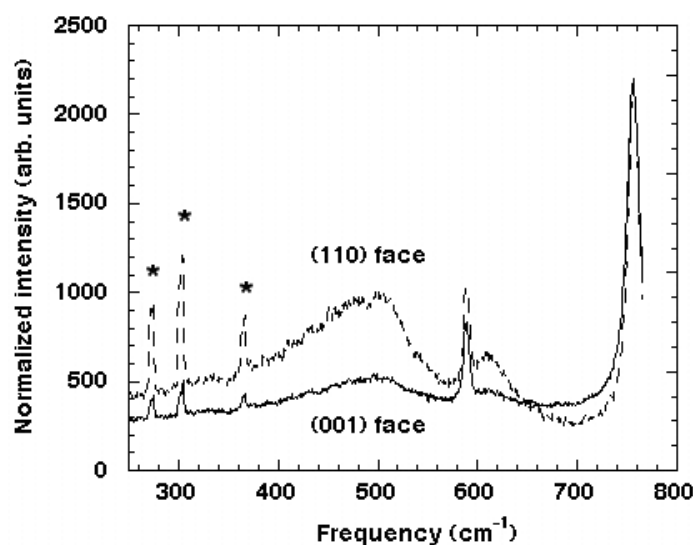


Figure 4. Raman spectra obtained on (110) and (001) facets of stishovite after heating to 560 °C. The asterisks indicate peaks of instrumental origin.

non-zone centre phonon becomes soft; however, since in most cases the softening of a particular phonon is accompanied by some softening across the whole phonon branch, we conclude that this scenario is unlikely and that the amorphization process in the case of stishovite is not a bulk phenomenon.

Our results show that the mechanism for SSA of stishovite is more complicated than a simple elastic softening. One can note in this respect that preliminary results from a molecular dynamics simulation using the standard Tsuneyuki intermolecular potential does not reveal SSA during the heating or expansion of stishovite [28]; this is consistent with our conclusion that amorphization does not occur via softening of a bulk phonon. One can also mention a recent molecular dynamics simulation [29], demonstrating the great influence of defects in the crystalline lattice on the SSA parameters. In polycrystalline samples the SSA of stishovite has also been observed to start from the crystalline grain boundaries [7], and in the present experiments on single crystals we see that it begins preferentially from the (110) surface compared to the (001) surface. It has been observed that the amplitude of the atomic oscillations of the Si atoms along the *c*-axis increases strongly with temperature, becoming larger than the motion along the other axes near the amorphization temperature [9]. This motion lies within the (110) face. If the presence of a free surface or grain boundary were to enhance such motion, this could lead to an instability that initiates the crystal-to-amorphous transformation, which then spreads by thermal activation processes into the bulk crystal. A similar instability should be observed on all crystal faces that contain the *c*-axis, though the different packing of Si atoms on the different faces might also influence the stability. It would therefore be of interest to observe the amorphization as initiated, for example, from the (100) face.

In summary, we have obtained accurate values of the stishovite elastic constants by a Brillouin scattering study of a large defect-free single crystal. From Raman scattering and the temperature dependence of the c_{ij} we also conclude that SSA in stishovite initiates as a surface phenomenon with a large contribution from diffusive temperature-induced atomic motion. A high-temperature, inelastic neutron scattering study of single crystals of stishovite could provide additional insight into the SSA of this substance.

Acknowledgments

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References

- [1] Stishov S M 1961 *Geochemistry* **10** 837 (in Russian)
- [2] Anderson D L 1989 *Theory of the Earth* (Oxford: Blackwell)
- [3] Kingma K J, Cohen R E, Hemley R J and Mao H K 1995 *Nature* **374** 243
- [4] Andraut D, Fiquet G, Guyot F and Hanfland M 1998 *Science* **282** 720
- [5] Shieh S R, Duffy T S and Li B 2002 *Phys. Rev. Lett.* **89** 255507
- [6] Skinner B J and Fahey J J 1963 *J. Geophys. Res.* **68** 5595
- [7] Brazhkin V V, Voloshin R N and Popova S V 1991 *J. Non-Cryst. Solids* **136** 241
- [8] Grimsditch M, Popova S V, Brazhkin V V and Voloshin R N 1994 *Phys. Rev. B* **50** 12984
- [9] Endo S, Akai T, Akahama Y, Wakatsuki M, Nakamura T, Tomii Y, Koto K, Ito Y and Tokonami M 1986 *Phys. Chem. Minerals* **13** 146
- [10] Xue X, Stebbins J F and Kanzaki M 1993 *Phys. Chem. Minerals* **19** 480
- [11] Stishov S M 1962 New dense form of silica and some aspects of the Earth interior *PhD Thesis* Institute of Geochemistry, Moscow
- [12] Brazhkin V V and Lyapin A G 1996 *High Pressure Res.* **15** 9
- [13] McDonald T R, Sard R and Gregory E 1965 *J. Appl. Phys.* **36** 1498
- [14] Mishima O, Calvert L D and Whalley E 1984 *Nature* **310** 393
- [15] Fujii Y, Kowaka M and Onodera A 1985 *J. Phys. C: Solid State Phys.* **18** 789
- [16] Hemley R J, Jeaphcoat A P, Mao H K, Ming L C and Manghnani M H 1988 *Nature* **334** 52
- [17] Tsuji K, Katayama Y, Koyama N, Yamamoto Y, Chen J Q and Imai M 1993 *J. Non-Cryst. Solids* **156** 540
- [18] Gromnitskaya E L, Stal'gorova O V and Brazhkin V V 1997 *J. Exp. Theor. Phys.* **85** 109
- [19] Gregoryanz E, Hemley R J, Mao H-K and Gillet Ph 2000 *Phys. Rev. Lett.* **84** 3117
- [20] Strassle Th, Saitta A M, Klotz S and Braden M 2004 *Phys. Rev. Lett.* **93** 225901
- [21] Binggeli N, Chelikowsky J R and Wentzcovitch R M 1994 *Phys. Rev. B* **49** 9336
- [22] Watson J W and Parker S C 1995 *Phys. Rev. B* **52** 13306
- [23] Lityagina L M, Dyuzheva T I, Nikolaev N A and Bendeliani N A 2001 *J. Cryst. Growth* **222** 627
- [24] Sandercock J R 1982 *Light Scattering in Solids III* ed M Cardona and G Güntherodt (Berlin: Springer) p 174
- [25] Grimsditch M 2001 *Handbook of Elastic Properties of Solids, Liquids and Gases* vol I *Dynamic Methods for Measuring Elastic Properties of Solids* ed M Levy, H Bass and R Stern (New York: Academic) pp 331–47
- [26] Weidner D J, Bass J D, Ringwood A E and Sinclair W 1982 *J. Geophys. Res.* **87** 4740
- [27] Brazhkin V V, Grimsditch M, Guedes I, Bendeliani N, Dyuzheva T I and Lityagina L M 2002 *Phys.—Usp.* **45** 447
- [28] Trachenko K 2004 private communication
- [29] Bustingorry S and Jagla E A 2004 *Phys. Rev. B* **69** 064110