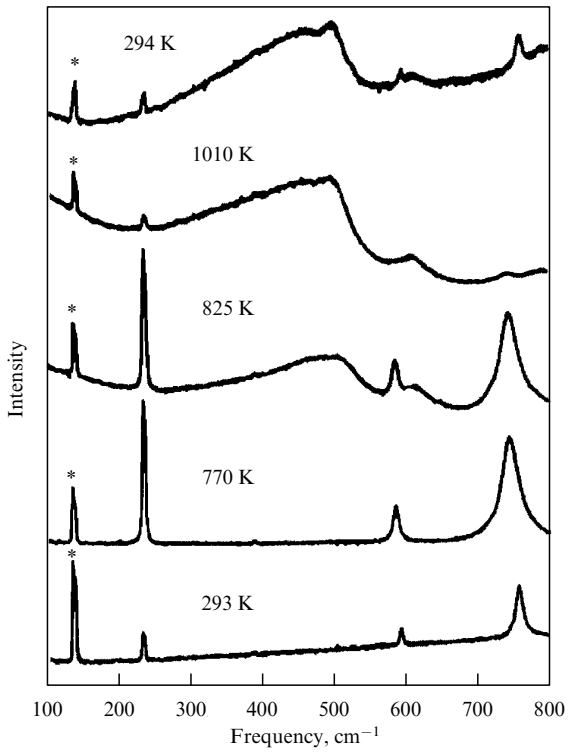

Figure 4. Raman spectra for different stishovite annealing temperatures; the peaks of the crystalline phases of stishovite are B_{1g} (230 cm^{-1}), E_g (590 cm^{-1}) and A_{1g} (754 cm^{-1}); * indicates the plasma lines; the temperature after annealing is 294 K.

frequencies are weakly dependent on temperature, which also is characteristic of other compounds with a rutile-type structure [10, 11]. When the samples are heated, the spectra clearly exhibit a smeared peak, which is testimony to the emergence of a disordered phase (see Fig. 4). Gradually the lines of the crystalline phase disappear almost completely, and the entire spectrum begins to consist only of the broad peak. The top of the peak is at $\sim$ 500 cm^{-1} and is shifted to higher frequencies in comparison to the peak in the Raman spectrum of ordinary quartz glass ($\sim$ 450 cm^{-1}). It is common knowledge that this is a characteristic feature of what is known as dense quartz glass, produced under pressures higher than 10 GPa [12, 13]. The heating of the disordered phases, glass obtained through amorphization of stishovite and dense glass, up to $\sim$ 1200 K reduces the frequency of the broad-peak maximum in the Raman spectrum, with the result that the observed spectrum becomes identical to the Raman spectrum of ordinary quartz glass [6].

The above experimental data make it possible to formulate a model of solid-phase amorphization based on the instability of the metastable phase.

Loss of stability of the lattice with a rutile-type structure leads to a situation in which the value of the activation energy of the crystal – glass transition, $\Delta G = 220$ kJ mol^{-1}, proves to be much lower than the activation energy of diffusion processes, equal to 400 – 500 kJ mol^{-1} [14]. As a result there is massive formation of nuclei of the stable phase in which silicon is in four-coordination to oxygen under such (P, T) conditions that growth becomes impossible, a fact corroborated by the value $n \sim 1$ of the Avrami index.

In contrast to the well-known model of 'cold' melting, the proposed model gives a correct prediction for both the sign of the thermal effect and the structure of the short-range order in the amorphous phase.

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Elastic moduli and the mechanical properties of stishovite single crystals

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In the beginning of the 1960s it was realized that the Earth's lower mantle consists mainly of silicates, in which silicon is in six-coordination to oxygen. The high-density phase of silica, stishovite, became the first, most important, and the simplest example of substances determining the behavior of the Earth's interior [1]. Thus, the importance of stishovite studies cannot be too strongly emphasized. Until recently, however, the studies of stishovite characteristics were restricted by the absence of large high-quality single crystals of high-density silica. In particular, this is true of studies of the mechanical properties and elastic moduli. The information on the elastic and mechanical properties of high-density silica may shed light on mass transfer in, and the elastic characteristics of, the lower mantle.

Earlier studies of the elastic moduli of stishovite were conducted primarily with polycrystalline samples. Here both the study of the compressibility by the X-ray diffraction under compression and the measurements of the bulk (B) and shear (G) moduli based on ultrasonic data led to a large spread in the values of the moduli: 210 GPa $< B <$ 520 GPa and 150 GPa $< G <$ 250 GPa. Until recently there was only one work by Weidner et al. [2] in which all the elastic constants of stishovite were studied by the Brillouin scattering method. The researchers used single crystals with sizes of 50 – 100 μm.

As for the macroscopic mechanical properties of stishovite, we know of only three attempts to measure the hardness of high-density silica [1, 3, 4], with obtaining the values 21, 32, and 33 GPa, differing quite strongly. Up till now the other mechanical properties have not been measured.

Recently a group of scientists at the Institute for High Pressure Physics (IHPP) of the Russian Academy of Sciences have used the method of hydrothermal synthesis at pressures of about 9 GPa to grow large (up to 3 mm long) high-quality single crystals of stishovite [5]. We report the use of these single crystals in precision measurements of the elastic characteristics by the Brillouin scattering method and of the mechanical properties (hardness and fracture toughness) by the indentation method. Note that this is the first time that the coefficient of fracture toughness K_{IC} for stishovite has been measured.

As a result we have obtained the most reliable values (for the present) for the elastic constants of stishovite (in GPa): $C_{11} = 463$, $C_{33} = 757$, $C_{66} = 298$, $C_{44} = 252$, $C_{12} = 205$, and $C_{13} = 203$.

Vought and Royce averaging led to the following values of the bulk and shear moduli for isotropic polycrystals (in GPa): $B_V = 323$, $G_V = 232$, $B_R = 309$, and $G_R = 212$.

Realistic values of the moduli can, apparently, be obtained by averaging the Vought and Royce values: $B_{V-R} = 316$ GPa and $G_{V-R} = 222$ GPa. The errors in determining the moduli did not exceed 5 GPa.

Note that these results agree fairly well with those of Weidner et al. [2]. The microhardness of stishovite single crystal was determined from the Vickers diamond pyramid hardness tests under $2N$ loads. The imprint proved to be anisotropic: the average imprint diagonal along the c axis of a single crystal was $d_{||} = (10.8 \pm 0.2)$ μm, while the diagonal perpendicular to this axis was $d_{\perp} = (11.9 \pm 0.2)$ μm, which correspond to hardnesses $H_{||} = (31.8 \pm 1.0)$ GPa and $H_{\perp} = (26.2 \pm 1.0)$ GPa. The true hardness values for a single crystal exceed the values measured by Stishov and Popova [1], but are smaller than the values obtained by Leger et al. [3] and Dubrovinsky et al. [4]. Note that the hardness of stishovite is much greater than that of corundum (20 GPa), which allows one to consider high-density silica as a superhard material.

The fracture toughness of stishovite single crystals was studied by the length of cracks along indentation corners. The measured coefficient of fracture toughness $K_{IC} = (1.6 \pm 0.3)$ MN m$^{-3/2}$ places stishovite in the class of very brittle materials (for diamond $K_{IC} = (6-12)$ MN m$^{-3/2}$, and for corundum $K_{IC} = (2-2.5)$ MN m$^{-3/2}$), which limits the potential application of stishovite. In addition, the heating of stishovite to fairly moderate temperatures ($\sim 600\,^{\circ}$C) under normal pressure leads to its transformation into amorphous silica, which also limits the possible use of stishovite as a superhard material.

In the future the elastic properties and lattice dynamics should be investigated, say, by the methods of Brillouin scattering, inelastic neutron scattering, and so on, at high pressures and high temperatures. High-pressure studies will reveal the nature of the transformation of stishovite to the post-stishovite phase with $CaCl_2$ structure and will shed light on the properties of the Earth's lower mantle. The study of stishovite's properties at high temperature will lead to an understanding of the mechanism of solid-phase amorphization of the high-pressure phases. At present these two research directions are being realized with the use of large single crystals of stishovite grown at IHPP.

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