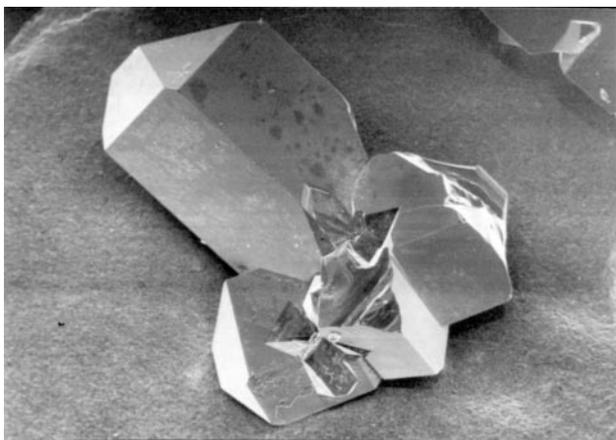
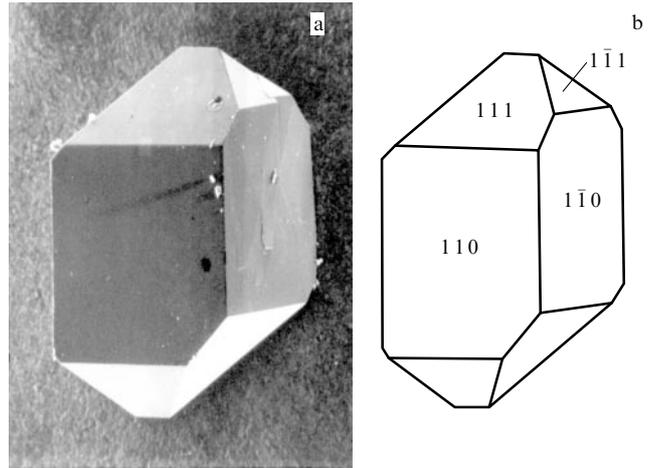


**Figure 2.** Part of the  $(T, x)$  phase diagram of the  $\text{SiO}_2\text{-H}_2\text{O}$  system at 9 GPa.

Usually, in each experiment three to four such crystals or aggregates of such crystals (Fig. 3) are obtained along with crystals of larger or smaller dimensions, i.e. the situation inevitable in spontaneous crystallization is realized. All the crystals have the same habit, but differ in the width-to-length ratio, e.g.  $750 \times 750 \times 1000 \mu\text{m}$  and  $500 \times 500 \times 2400 \mu\text{m}$ . The parameters of the unit cell were  $a = (4.177 \pm 0.004) \text{ \AA}$  and  $c = (2.666 \pm 0.003) \text{ \AA}$ , which practically coincide with the tabulated values obtained by Stishov and Popova [1] and Sinclair and Ringwood [2]. Full structural analysis done with the R ED-4 single-crystal diffractometer reproduced, within experimental error, the values of the structural and thermal parameters given in Sinclair and Ringwood's paper [2].



**Figure 3.** Aggregate of stishovite crystals.



**Figure 4.** Morphology of a stishovite crystal: (a) real crystal, and (b) crystal face symbols

The face indices were determined from X-ray diffraction of optically oriented crystals in a precession Buerger camera. As expected, the habit of the crystals is formed by the most densely packed faces (110) and (111) (Fig. 4).

Some indications of the role that impurities play in the formation of the amber coloring of crystals have been given by the experiments involving a 1 M solution of NaOH with the same values of the other growth parameters. The emergence of sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) in the precipitate made it possible to assume that the origin of the color centers is in some way related to the diffusion of carbon from the heater into the ampoule.

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## Temperature-induced solid-phase amorphization of stishovite

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The very fact that silica is one of the main rock-forming minerals in the Earth has determined the special interest in studies of the  $(P, T)$  conditions needed for its formation. Such studies were to resolve the questions related to the location of the various phases of silica (quartz, coesite, and stishovite) in nature and to the depth intervals in the Earth's mantle within which these phases are stable.

This is apparently the reason why in the 30 years that have passed from the time of the first publication concerning the

experimental production of stishovite [1] there have been many more works on the conditions of high-pressure synthesis than on the transition to the equilibrium state of stishovite itself at normal pressure. Actually, however, this process is not as trivial as it might seem: it proceeds through an intermediate nonequilibrium phase with a disordered (vitreous) structure.

The stishovite–glass transformation is important if one wants to understand solid-phase amorphization. In contrast to many other substances (tetrahedral semiconductors,  $\text{SnI}_4$ , etc. [2–4]), the transformation of stishovite occurs when the substance is heated under normal pressure and allows for quantitative measurement of such quantities as the heat of transition and the activation energy and for structural and spectral studies of the amorphous phase.

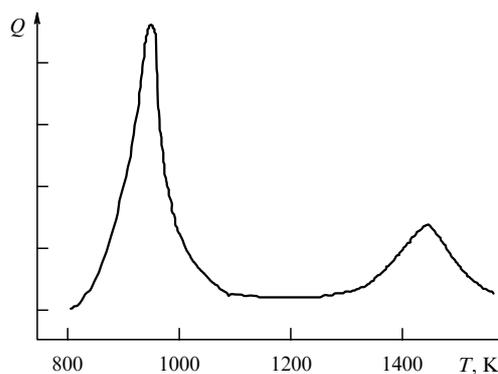
In the present report we give the results of calorimetric measurements of the parameters of phase transformations in stishovite under atmospheric pressure, of studies of the pressure influence on the transition temperatures, and of structural studies (X-ray and Raman spectra). We also make certain assumptions concerning the model of solid-phase amorphization [5, 6].

Stishovite samples were made from amorphous silica ( $\text{H}_2\text{O}$  impurities less than 3%, other impurities less than 1%) in containers made of graphite or a metal (Ta or Pt) under a pressure of 9 GPa in the temperature interval 1050 to 1500 K.

To determine the transition temperature ( $T_{tr}$ ), transition heat ( $Q$ ), activation energy ( $\Delta G$ ), and the Avrami index ( $n$ ), the stishovite samples were annealed on a MOM ‘C’ derivatograph at rates ranging from 2 to 20  $\text{K min}^{-1}$ . There are two exothermic peaks on the isochronal annealing curve: one corresponds to the formation of the amorphous phase, while the other corresponds to the crystallization of cristobalite (Fig. 1).

The values of the parameters of the temperature-induced transition in stishovite heated at the rate of 20  $\text{K min}^{-1}$  are listed in Table 1 [5].

The pressure influence on the transition temperature was studied by means of thermobaric analysis [7]. It was found that the temperature of solid-phase amorphization grows with pressure, while the glass crystallization temperature drops, and already at  $P > 0.5$  GPa crystallization of  $\alpha$ -quartz occurs. The boundaries of these transitions are crossed near the quartz–coesite equilibrium line. Thus, at pressures higher than the pressure of transition to the coesite phase there is a direct stishovite–coesite transformation, i.e. a



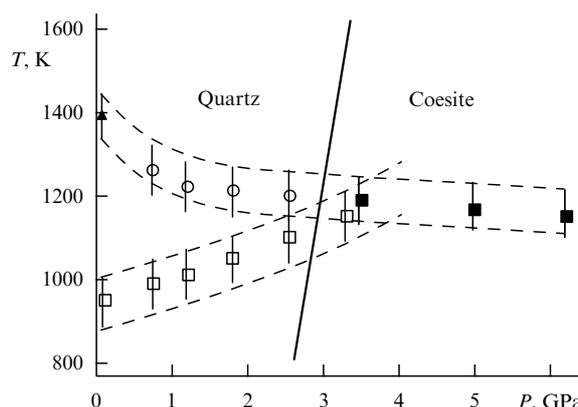
**Figure 1.** Heat-release peaks in the heating of stishovite. The rate of isochronal annealing of stishovite is 20  $\text{K min}^{-1}$ .

**Table 1.**

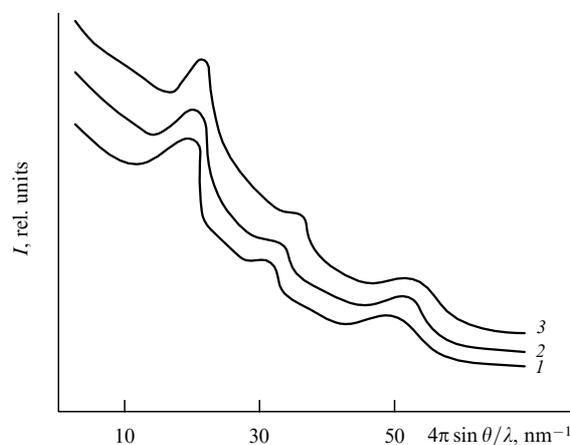
Transition	$\Delta T_{tr}$ , K	$Q$ , $\text{kJ mol}^{-1}$	$\Delta G$ , $\text{kJ mol}^{-1}$	$n$
Stishovite–glass	890–950	$41 \pm 3$	$220 \pm 30$	$\sim 1$
Glass–cristobalite	1370–1470	$5 \pm 1.5$	$400 \pm 50$	$3 \pm 0.5$

transformation that does not pass through the amorphous state (Fig. 2). This suggests that solid-phase amorphization takes place within a limited pressure and temperature range in the stability region of silica phases in which silicon is in four-coordination to oxygen.

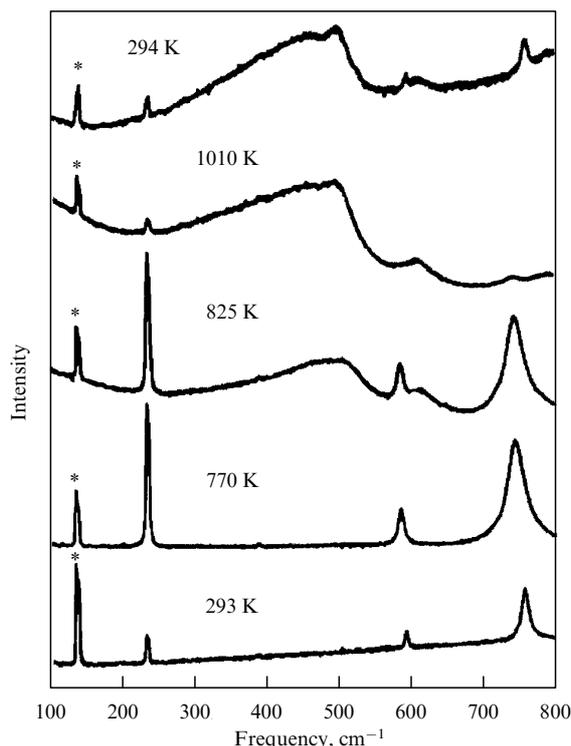
The X-ray spectra of the amorphous phase recorded at different annealing stages do not differ from the angular dependence of the intensity of X-ray scattering for ordinary quartz glass (Fig. 3). However, the Raman spectra taken at different annealing temperatures of stishovite have certain characteristic features. Figure 4 depicts the results of measurements of Raman spectra of stishovite at different temperatures. The data obtained at room temperature agree with the data taken from the literature [8, 9]. The corresponding



**Figure 2.** Effect of pressure on the temperatures of the following transitions: stishovite–amorphous phase  $\square$ , amorphous phase–cristobalite  $\blacktriangle$ , amorphous phase–quartz  $\circ$ , and stishovite–coesite  $\blacksquare$ .



**Figure 3.** X-ray spectra of amorphous silica: ordinary quartz glass (1), and glass produced at different annealing stages in the solid-phase amorphization of stishovite (2, 3).



**Figure 4.** Raman spectra for different stishovite annealing temperatures; the peaks of the crystalline phases of stishovite are  $B_{1g}$  ( $230\text{ cm}^{-1}$ ),  $E_g$  ( $590\text{ cm}^{-1}$ ) and  $A_{1g}$  ( $754\text{ cm}^{-1}$ ); \* 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  $\sim 500\text{ cm}^{-1}$  and is shifted to higher frequencies in comparison to the peak in the Raman spectrum of ordinary quartz glass ( $\sim 450\text{ cm}^{-1}$ ). 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  $\sim 1200\text{ K}$  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,  $\Delta G = 220\text{ kJ mol}^{-1}$ , proves to be much lower than the activation energy of diffusion processes, equal to  $400\text{--}500\text{ kJ mol}^{-1}$  [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:  $210\text{ GPa} < B < 520\text{ GPa}$  and  $150\text{ GPa} < G < 250\text{ GPa}$ . 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  $50\text{--}100\text{ }\mu\text{m}$ .