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Abstract

Full Text

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Synthesis of Dense Modifications of Silica in the Presence of Water at a Pressure of $150 \cdot 10^3$ kg/cm^2 *

It was established by one of us (L. F. Vereshchagin) that, when HgI_2 crystallizes from a methyl iodide solution, the tetragonal red modification of mercuric iodide is always precipitated, stable at atmospheric pressure and ordinary temperatures. In the case of crystallization from an acetone solution at the same P and T, however, the rhombic yellow modification of HgI_2 is formed, stable at temperatures above 129°. The appearance of a phase in a region not stable for it made it possible to suppose that in some cases the solvent can substantially affect the position of the equilibrium curve of the P–T diagram. From this point of view it was of interest to ascertain the possibility of crystallizing silica in the form of its various modifications, stable at high pressures, in the presence of water.

The choice of silicon dioxide as the substance to be investigated is explained, first, by the large role that this compound plays in processes of mineral formation, and, second, by the availability of data on the synthesis and study of the stability of the dense modifications of interest to us ($^{3-6}$). Comparison of these data with the results of our investigations would make it possible to judge the validity of the supposition expressed above.

The difficulties encountered in attempts to obtain the rutile-like modification of SiO_2 at temperatures below 850–900° and pressures below $160 \cdot 10^3$ kg/cm^2 are well known; therefore it was of interest to synthesize stishovite at lower temperatures and corresponding pressures.

Experiments carried out in the presence of water led to the obtaining of a dense modification of silica, crystallizing in the rutile structure, at a pressure of $150 \cdot 10^3$ kg/cm^2 and a temperature of 450°. When the phase obtained was observed in an immersion preparation under a microscope, individual needle-like and tabular crystals up to 0.3 mm in size (Figs. 1 and 2) were found against a background of a fine-grained groundmass, the formation of which can be explained by the conditions of the experiments, which did not have the aim of growing single crystals. The Debyegram of the synthesized substance (Fig. 3) indicates that the entire crystallized phase is represented by stishovite. The values of the interplanar spacings, given in Table 1, correspond fully to values known from the literature (^{3}).

Further, at the same temperature of 450°, but at different pressures, a series of experiments was carried out, as a result of which, by subsequent interpolation of the data obtained, it was possible to mark a point on the coesite—stishovite equilibrium curve corresponding to a temperature of 450° and a pressure of $130 \pm 5 \cdot 10^3$ kg/cm^2. In discussing this work the question arose of the phase state of water at the indicated values of pressures and temperatures. A recent communication by Pistorius et al. (^{7}) permits the assertion that, under the conditions of our experiments, water was in a supercritical state. Several attempts to obtain stishovite in the region of existence of ice VII were not crowned with success; however, it should be expected that, upon addition to the system of salts readily soluble in water, which lower the temperature of the melting curve of ice, crystallization of dense modifications of silica may be possible in the region of lower temperatures.

The study of processes occurring under hydrothermal conditions at high pressures, it seems to us, opens favorable prospects for further investigations in the

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Fig. 1. Needle-like crystal of the rutile-like modification of SiO_2. Without analyzer. 150×

Fig. 2. Tabular crystal of the rutile-like modification of SiO_2. Without analyzer. 600×

Fig. 3. Debyegram of the rutile-like modification of SiO_2

Table 1

Interplanar spacings for the Debye pattern of the rutile-like modification of SiO_2. Copper filtered radiation. RKD-57 camera. Line intensities are given by visual estimate.

d, Å	I	d, Å	I	d, Å	I	d, Å	I
2.95	strong	1.290	weak	1.011	weak	0.830	medium
2.23	medium	1.230	medium	0.987	medium	$0.8019\alpha_1$	medium
1.97	strong	1.210	medium	0.946	medium	$0.8020\alpha_2$	weak
1.85	medium	1.180	weak	0.936	weak	$0.7974\alpha_1$	medium
1.52	strong	1.083	weak	0.882	weak	$0.7975\alpha_2$	weak
1.472	medium	1.060	weak	0.870	weak	$0.7921\alpha_1$	medium
1.322	medium	1.043	weak	0.850	weak	$0.7923\alpha_2$	weak

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* As reference points for constructing the calibration curve of the dependence of pressure in the chamber on the force of the press, jumps in the electrical resistance in Bi, Ba, and Tl at 25.6; 27; 45; 80; and $125 \cdot 10^3$ kg/cm^2 were used (^{1,2}).

field of phase equilibria; in addition, one may hope that the corresponding development of the technique will make it possible to obtain single crystals whose dimensions would meet the requirements for a more complete study of their physicochemical properties.

The methodological aspects of the work and its further results will be presented in subsequent communications.

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