- 4. Knittle E, Jeanloz R Geophys. Res. Lett. 13 1541 (1986)
- 5. Dubrovinsky L et al. Nature 412 527 (2001)
- 6. Mazin I I et al. Am. Mineral. 83 451 (1998)
- 7. Dubrovinsky L S et al. Eur. J. Mineral. 13 857 (2001)
- 8. Pasternak M P et al. *Phys. Rev. Lett.* **79** 5046 (1997)
- 9. Funamori N, Jeanloz R Science 278 1109 (1997)
- 10. Helffrich G R, Wood B J Nature 412 501 (2001)
- 11. Finger L W, Hazen R M Acta Crystallogr. B 47 561 (1991)
- Scott H P, Williams Q, Knittle E *Phys. Rev. Lett.* 88 015506 (2002)
 Stishov S M, Popova S V *Geokhimiya* (10) 837 (1961) [*Geochem.* (10) 923 (1961)]
- 14. Hazen R, Finger L Science **201** 1122 (1978)
- 15. Fiquet G Z. Kristallogr. 216 248 (2001)
- Kazantsev S S et al., in *Tezisy III Nats. Konf. po Primeneniyu* Rentgenovskogo, Sinkhrotronnogo Izlucheniĭ, Neĭtronov i Élektronov dlya Issledovaniya Materialov (RSNÉ), Moskva, 2001 (Abstracts of 3rd National Conference on the Use of X-ray and Synchrotron Radiations, Neutrons, and Electrons in the Studies of Materials (XSNE), Moscow 2001) (Moscow: Izd. Inst. Kristallografii Ross. Akad. Nauk, 2001) p. 83
- 17. Pushcharovskiĭ D Yu *Strukturnaya Mineralogiya Silikatov i ikh Sinteticheskikh Analogov* (Structural Mineralogy of Silicates and their Synthetic Analogs) (Moscow: Nedra, 1986)
- 18. Finger L W et al. *Nature* **341** 140 (1989)
- 19. Fleet M E, Henderson G S Phys. Chem. Mineral. 22 383 (1995)
- 20. Fleet M E Am. Mineral. 83 618 (1998)
- 21. Fleet M E Am. Mineral. 81 1105 (1996)
- 22. Gasparik T et al. Am. Mineral. 80 1269 (1995)

PACS numbers: 81.10.-h

DOI: 10.1070/PU2002v045n04ABEH001160

Hydrothermal growth of stishovite (SiO₂)

N A Bendeliani

1. Introduction

Single stishovite crystals have been grown by the hydrothermal method in the SiO₂-H₂O system under a pressure of 9–9.5 GPa in the 1170–770 K temperature interval. The method produced well-cut, transparent crystals of prismatic habit with the faces (110) and (111) and maximum dimensions of $500 \times 500 \times 2400$ µm.

The advances in growing and studying single stishovite crystals achieved during the last 40 years, starting with the discovery of this silica phase which plays an important role in geophysics and planetary sciences, have been limited to the results of three experiments [1-3]. Using accidentally grown single-crystal grains with sizes of $200-300 \mu m$, the researchers were able to measure the refractive index and microhardness [1] and decipher the crystal structure [2]. Ramley et al. [3] studied the effects of hydrogen infusion into the lattice and observed acicular crystals that were up to 1000 µm long but only 25 µm wide. The ever growing interest in the properties of stishovite has led to the need for developing a fairly simple and reliable method of growing large and perfect single crystals of this phase. This problem has been solved at the Institute for High Pressure Physics of the Russian Academy of Sciences [4].

2. Experiment

Crystal growth was done in a Konak-type high-pressure cell with automatic monitoring of loading and programmed control of the current strength in the heater. The dependence of the temperature on the current strength was determined in a preliminary experiment. Figure 1 shows a schematic of the



Figure 1. Schematic of a high-pressure cell: *1*, input lead; *2*, metal disk; *3*, graphite heater; *4*, ampoule; *5*, container

high-pressure cell. The active volume of the hermetically sealed platinum ampoule was $\sim 25 \text{ mm}^3$. The temperature gradient along the ampoule's height did not exceed 20 at 1200 K. The source materials were a powder of natural quartz with a grain size of $10-20 \mu \text{m}$ and distilled water. The amount of water was estimated by the ratio of the volumes of the components and ampoule.

3. Results and discussion

Using the example of coesite, a high-pressure phase of SiO_2 less dense than stishovite, Dyuzheva et al. [5] showed that the classical method of hydrothermal growth in modified form is realized fairly simply in conditions of extreme compression. Hence, provided that the necessary equipment is available, the solution of this problem is reduced primarily to determining the solubility of stishovite in an aqueous fluid.

The pressure of 9-9.5 GPa (the phase transition in Sn) under which the growing process took place proved to be sufficiently high for the system not to leave the stishovite regime in the course of the entire experiment (six to seven hours). The position of the liquidus on the (*T*, *x*) phase diagram under such pressure for a mixture consisting of the solution and stishovite was estimated by registering the sizes of stishovite grains in experiments with different component ratios in cooling from various temperatures. These data were then used to build the relevant part of the phase diagram (Fig. 2), which while being inaccurate in detail was quite sufficient for use as a working diagram. The melting temperature of ice-VII on the diagram has been taken from the paper by Pistorius et al. [6].

The best results were achieved with 6 mol.% of SiO₂ in the source mixture. The temperature was lowered from 1170 to 770 K with a cooling rate of roughly 1 K min⁻¹. Under such conditions the growth process produces transparent colorless, sometimes clear amber-coloured crystals of a prismatic habit with characteristic dimensions of $600 \times 600 \times 1200 \ \mu m$.



Figure 2. Part of the (T, x) phase diagram of the SiO₂-H₂O 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 $a = (4.177 \pm 0.004)$ Å and $c = (2.666 \pm 0.003)$ Å, which practically coincide with the tabulated values obtained by Stishov and Popova [1] and Sinclair and Ringwood [2]. Full structural analysis done with the RÉD-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 ($Na_2C_2O_4$) 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.

References

- 1. Stishov S M, Popova S V Geokhimiya (10) 837 (1961) [Geochem. (10) 923 (1961)]
- 2. Sinclair W, Ringwood A E *Nature* **272** 714 (1978)
- 3. Pawley A R, McMillan P F, Holloway J R Science 261 1024 (1993)
- 4. Lityagina L M et al. J. Cryst. Growth 222 627 (2001)
- Dyuzheva T I et al. Kristallografiya 43 554 (1998) [Crystallogr. Rep. 43 511 (1998)]
- 6. Pistorius C W et al. J. Chem. Phys. 38 600 (1963)

PACS numbers: 61.43.Er, 81.30.Hd

DOI: 10.1070/PU2002v045n04ABEH001161

Temperature-induced solid-phase amorphization of stishovite

S V Popova, V V Brazhkin, R N Voloshin, M Grimsditch

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