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Onset Temperatures and Kinetics of Quartz Glass Crystallization

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Abstract—A complex analysis of the crystallization of quartz glass from quartzites of the Bural-Sardyk deposit (the Eastern Sayan) has been performed. A mineralogical and petrographic characterization of the quartzites of this deposit is presented, and techniques of quartz grit preparation and quartz glass formation are described. Quartz glass samples prepared from grits of two types have been thermally tested, and crystallization onset temperatures and character of their crystallization were determined for them.

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INTRODUCTION

The stability of quartz glass to crystallization is one of its most important characteristics, which determines the functioning of quartz glass products at high temperatures upon rapid heating. These parameters must be taken into account when designing, e.g., ceramic radio-transparent coverings of antenna fairings of high-speed aircrafts [1], optical fiber claddings [2], and microelectronic devices. Analysis of the quartz glass crystallization is also important for determining the general regularities of glass–crystal phase transitions.

The tendency of glasses to crystallization is determined by their chemical composition and external parameters (such as temperature and pressure). Glass crystallization is facilitated by the presence of interfaces, regions of contact with refractory materials, gas bubbles in the glass mass, foreign solid inclusions, etc. On the whole, glass crystallization occurs in two stages: formation of crystallization centers (nuclei) and crystal growth thereon [3–5]. The crystallization centers are microparticles with an ordered composition and structure, having an interface with the environment.

Glass crystallization may have either surface or bulk character. Generally, bulk crystallization follows the surface one.

Quartz glass is generally stable to crystallization at temperatures below 1000°C, and crystallization temperatures range from 1000 to 1650°C. Cristobalite is released in the entire temperature range of quartz glass crystallization. However, the presence of alkali metal oxide impurities in quartz glass may induce formation of tridymite crystals. The presence of alkali metal oxides and aluminum impurities may significantly increase the quartz glass crystallization rate.

The purpose of this study was to analyze the quartz glass obtained from high-purity quartzite species from the Bural-Sardyk deposit (the Eastern Sayan) [6]. During the analysis, we compared glasses obtained from chemically enriched quartz concentrates of two types, one of which was subjected to initial calcination at 1550°C for 6 h, while the other was not.

EXPERIMENTAL

Rock crystal and vein varieties of quartz of different geological and commercial types are traditionally used to obtain quartz concentrates of high and ultrahigh purity [7, 8]. Generally, veins are poor and highly inhomogeneous. In contrast to the vein varieties of quartz, the quartzites from the Eastern Sayan are characterized by high homogeneity and purity [6, 9]. The results reported here are based on the use of superquartzites from the Bural-Sardyk deposit. The visually high-purity quartzites from the Bural-Sardyk deposit, which were previously referred to as "superquartzites" [6], are a monomineral white rock with a porphyry structure. Transparent colorless elongated quartz grains of up to 3 mm in size are clearly seen against the background of the fine-grain or micrograin milky white main mass (Fig. 1). They are either orientated subparall or have no clear orientation. Mineralogical and petrographic analyses showed the presence of two quartz generations: relict (Fig. 2, region *1*) and newly formed (Fig. 2, region *2*) ones. The first-generation quartz consists of large (up to 3 mm) elon-

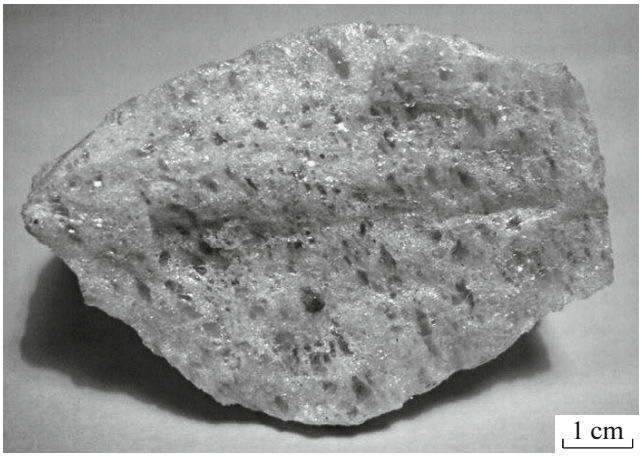

Fig. 1. Superquartzite from the Bural-Sardyk deposit.

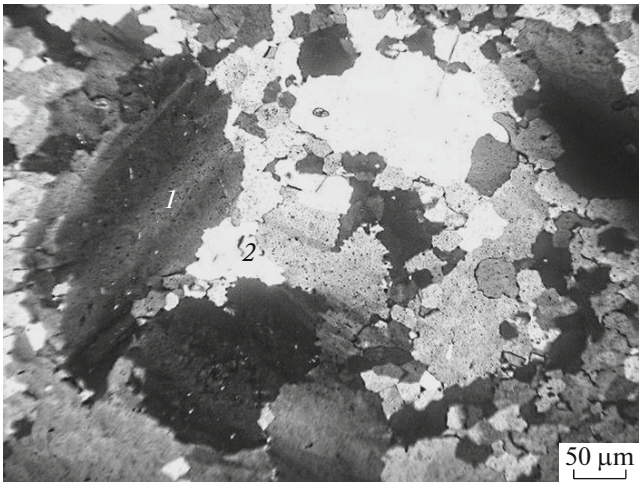

Fig. 2. Quartz generations in superquartzite: the (*1*) first (relict) and (*2*) second generations.

gated grains, which are characterized by block-wavy extinction and presence of cracks; these features are related to plastic and brittle deformations, respectively. Relict quartz grains have jaggy boundaries and are characterized by the presence of fine-grained graphite, which develops along cracks and grain boundaries. In addition, there are primary (timed to growth zones) and secondary (timed to healed cracks) fluid inclusions in relict quartz. The second-generation quartz consists of small (from 0.3 to 0.7 mm), almost isometric, grains without any traces of plastic or brittle deformation. The newly formed quartz, which is due to the recrystallization of relict quartz, develops along the grain boundaries and in the crack-development regions, often dissecting initial quartz grains.

The quartz concentrates were obtained from superquartzite according to the following algorithm: manual fragmentation of a piece into 50-mm fractions, washing, fragmentation in a jaw breaker using tungsten carbide jaws to 25-mm fraction, classification to 5–25-mm fraction, chemical etching of piece in a 10% HCl solution, drying, thermal fragmentation, manual fragmentation in a quartz mortar to 5-μm fraction, attrition in a quartz attritor, and selection of 174–450-μm fraction [10]. Then the quartz grit was subjected to chemical enrichment (CE) in a 20% HCl : 10% HF acid mixture at a liquid-to-solid ratio of 2 : 1 and dried. The results of the chemical analysis of the initial material and quartz concentrate by inductively coupled-plasma mass spectrometry [10] are listed in Table 1.

Quartz was transformed into cristobalite as a result of annealing the quartz concentrate in air at a temperature of 1450°C for 3 h.

The experiments on quartz glass formation were carried out on specially modified "REDMET 10-M" and "REDMET 8" commercial systems for growing single crystals. Glass samples were welded both in vacuum and in argon (at a pressure up to 6 bar, using the vacuum-compression method). The glass formation procedure was described in detail in [10].

An experimental study of the stability to crystallization was carried out as follows: 3-mm-thick quartz glass plates on a quartz-ceramic substrate were heated stepwise in the temperature range from 1000 to 1250°C in a muffle furnace in air. The plate heating rate was 180°C/h. The plates were exposed at a specified temperature for 2 h, after which they were cooled at a rate of 300°C/h. Along with polished, unpolished plates were analyzed to exclude contamination of the surface by elements from abrasives). The dynamics of crystallization-center formation was investigated by X-ray diffraction (XRD) on an automatic D8 ADVANCE X-ray diffractometer, equipped with a Goebel mirror and VANTEC-1 PSD detector. The collection was per-

Table 1. Mass fractions of impurities in quartz concentrates (ppm)

Concentrate	Impurity												
	Fe	Al	Ti	Ca	Mg	Cu	Mn	Na	K	Li	Σ10	P	B
Initial	6	27	1.7	0.8	1	0.17	0.02	3.5	6.3	0.13	46.6	0.2	0.2
After CE	0.9	4.5	0.8	0.4	0.2	0.14	0.005	2.5	0.5	0.12	10.1	0.1	0.18

Technologist O.N. Solomein, the analyses were carried out by V.Yu. Ponomareva (Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences).

formed using Cu radiation in the step mode in the range of 2θ angles from 10° to 60°. The experimental conditions were as follows: 40 kV, 40 mA, exposure 1 s, and 2θ step 0.02°. X-ray diffraction patterns were calculated using the diffractometer software. Phases were identified applying the PDF-2 database of powder diffraction patterns.

The surfaces of the glass samples cut (cut with a diamond saw) from superquartzite and superquartzite cristobalite, polished by diamond pastes and unpolished, were investigated by electron-probe X-ray microscopy using a JXA8200 microanalyzer (JEOL, Japan), equipped with five wave spectrometers and an EX-84055MU energy-dispersive spectrometer (JEOL, Japan). The experiments were carried out at an accelerating voltage of 20 kV and a probe current of 20 mA. The composition of the found inclusions was determined with an energy-dispersive spectrometer (EDS). The EDS spectra were processed using the microanalyzer software.

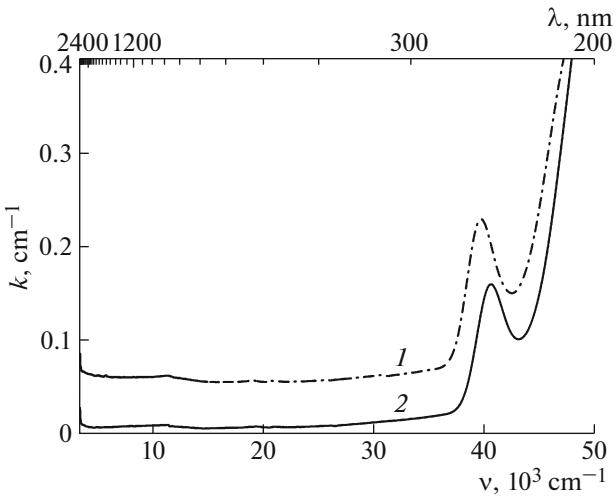

Fig. 3. Absorption spectra of the quartz glasses obtained from superquartzite cristobalite grit molten at pressures of (*1*) 1 and (*2*) 5 bar.

RESULTS AND DISCUSSION

The optical quality of the glasses obtained in vacuum from quartz concentrates of superquartzite and superquartzite cristobalite is practically the same: they are transparent with inclusion of small bubbles; the latter can be practically completely removed by glass welding using vacuum-compression method. Nevertheless, one can see that the glass samples obtained from cristobalitized superquartzite contain fewer bubbles than those obtained from non-cristobalitized concentrates.

Figure 3 shows the optical absorption spectra of the glasses fabricated at pressures of 1 and 5 bar (their absorption spectrum corresponds to that of KI glass). It can be seen that the total absorption of the glass obtained at a pressure of 1 bar is higher due to the presence of a bubble and the presence of a 250-nm absorption band of germanium impurity [10].

Glass from superquartzite cristobalite is most resistant to crystallization under thermal tests. A visual inspection showed the presence of small single crystal-

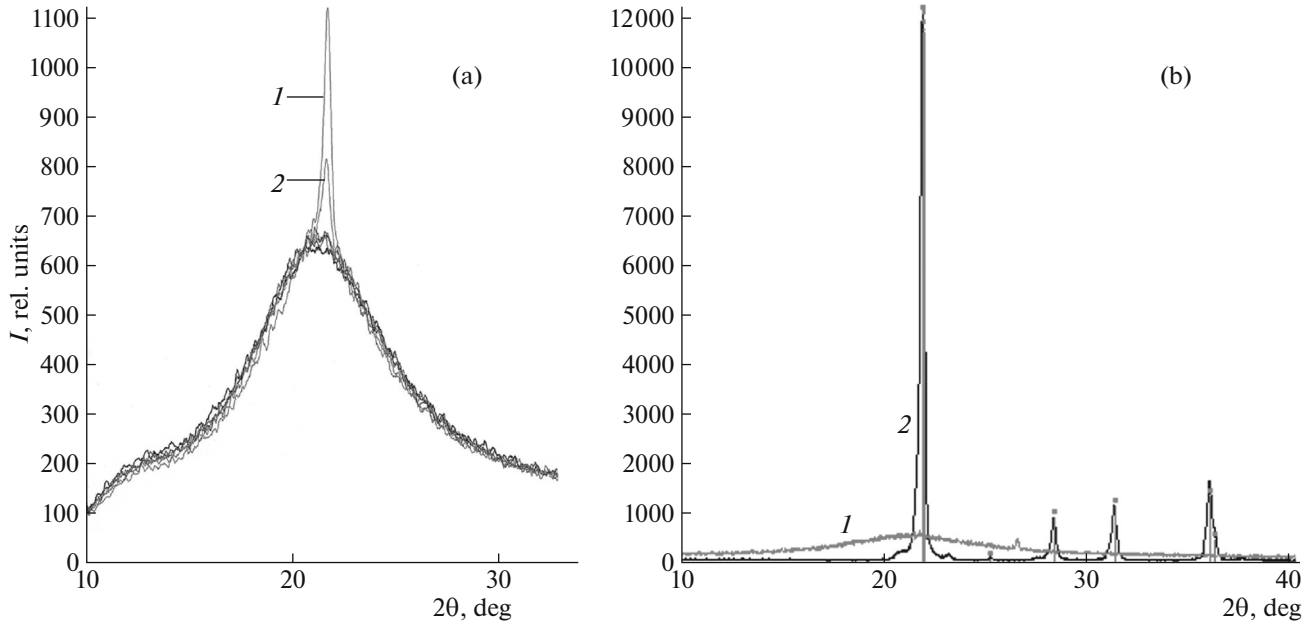

Fig. 4. Fragments of diffraction patterns: (a) quartz glass after plate annealing at (*1*) 1150°C and (*2*) 1200°C and (b) (*1*) ground quartz glass sample, previously annealed at 1200°C, and (*2*) ground glass sample after repeated annealing to 1300°C.

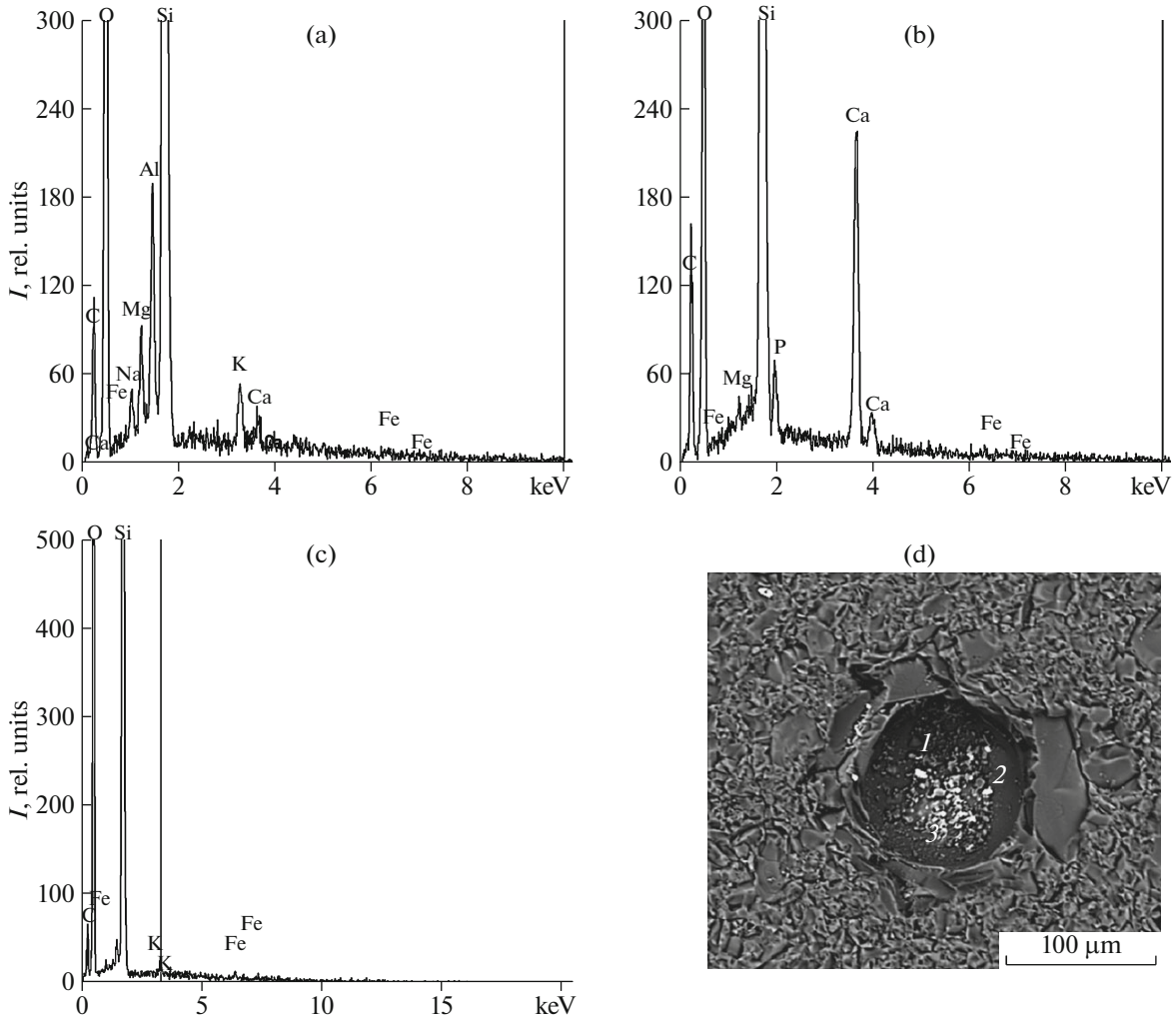

Fig. 5. (a–c) EDS spectra characterizing the elemental composition of specific inclusions, which are indicated in the (d) backscattered electron image of the surface of the central part of the glass plate obtained from superquartzite.

lization regions on the surface of the plates heated at 1300°C for 2 h, whereas the glass plates obtained from superquartzite grit are almost completely crystallized. These conclusions are also confirmed by the crystal optics estimation of the surface of the plates under study. Observation of all samples annealed at 1150°C in transmission using polarized light revealed an isotropic crystalline phase in them, up to 0.05 × 0.1 mm in size; the refractive index of this phase greatly exceeds that of the bearing material of the plates under study.

During thermal tests, the crystallization kinetics of the glass plates obtained from superquartzite grit and superquartzite cristobalite was investigated by XRD. Characteristic lines of the cristobalite phase were found to arise in the XRD spectra of all glass samples at a temperature of 1150°C (Fig. 4a). The intensity of the cristobalite lines in the XRD spectra increased after annealing at 1200°C for 2 h (Fig. 4a). After this annealing, a central part of about 1 cm^2 in size was cut from each plate and ground in a quartz mortar. The cristobalite lines were not observed in the XRD spectra of all ground samples. After repeated annealing of ground quartz glass samples, strong cristobalite bands arise again in their XRD spectra (Fig. 4b).

The disappearance of the cristobalite lines in the spectra of ground quartz glass samples means that the plate crystallization after annealing at a temperature of 1200°C for 2 h has a surface character. These measurements were carried out upon step heating of the samples to the plate deformation temperature. In all experiments with annealed plates, cristobalite bands were not observed in their XRD spectra after grinding their central parts. This fact suggests that the crystallization of the quartz glass samples under study has a surface character up to a temperature of 1700°C.

The quartz glass plates were also annealed in vacuum in the same way. No cristobalite bands were observed in the XRD spectra of ground quartz glass

samples annealed at 1300°C for 2 h in vacuum. Therefore, the cristobalite formation on the glass surface upon heating to above 1150°C occurs only in air.

The surface images of the superquartzite and superquartzite cristobalite plates annealed to 1200°C, which were analyzed on a microanalyzer in backscattered and secondary electrons, exhibit significant differences in structure. At ×40 and ×150 magnifications, the glass sample from superquartzite has a fine-grained structure, whereas the structure of the glass sample from superquartzite cristobalite is much more coarse-grained. This effect unambiguously indicates a difference in the processes occurring during preparation of the quartz concentrates used for glass production.

Inclusions containing different elements (phosphorus, potassium, sodium, calcium, aluminum, iron, silicon, and magnesium) were found on the surface of polished and unpolished plates of both superquartzite and superquartzite cristobalite. However, a distinctive feature of the superquartzite cristobalite plate surface is the presence of "pure" regions and individual inclusions. At the same time, clear-shaped crystallized regions and inclusions of clusters ("daisies"), around which crystallization begins as well, are observed on the superquartzite plate surface (Fig. 5).

CONCLUSIONS

As a result of the complex analysis by methods of XRD, optical microscopy, and electron-probe microscopy, it was found that the quartz-glass samples obtained from superquartzite and superquartzite cristobalite grits have different structures. The crystallization onset temperature was almost the same (1150°C) for both glass types; however, the glass obtained from superquartzite cristobalite grit is more resistant to crystallization. A visual analysis of the plates revealed the presence of individual crystallization regions; the number of these regions is smaller than that for the glass obtained from superquartzite grit.

According to the electron-probe microscopy data, the microinclusions may play the role of crystallization centers.

It was shown that the plate crystallization after annealing at temperatures of up to 1700°C for 2 h has a surface character. In addition, the cristobalite formation on the glass surface upon heating to above 1150°C occurs only in air.

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