

Optical Silica Glass Based on Super Quartzites from the Eastern Sayan Mountains

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Abstract—The results of examining high-purity quartzites retrieved from the Eastern Sayan Mountains (namely, the Bural–Sardag deposit), extracting ultra-high purity quartz concentrates from them, and depositing silica glass using the vacuum-compression method are reported. The flowsheet for their beneficiation is elaborated. The characteristics of quartz concentrates and silica glass based on them are provided.

Keywords: quartz, quartzites, super quartzites, crystallization, silica glass, quartz ceramics

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INTRODUCTION

Natural quartz raw material is the main source of high-purity quartz concentrates for manufacturing transparent silica glass and quartz ceramics. Quartz crystal and vein varieties of quartz of various types are conventionally used to obtain high- and ultra high purity quartz concentrates [1]. The content of the mineral in veins is typically rather low and the veins are characterized by high heterogeneity.

The increased demand for high-quality raw materials and the depletion of the traditional deposits, especially quartz crystal ones, have made assessing the quality and the potential of using quartz rocks in industry rather relevant [2]. As opposed to the vein varieties of quartz, quartzites from the Eastern Sayan region are characterized by a high degree of homogeneity and purity [3, 4]. The findings reported in this study are based on examination of quartzites from the Bural–Sardag deposit.

The Bural–Sardag deposit is located in the northwestern part of the Garganskii Block [3, 4]. Its basement is exposed in the eastern part of the Tyva–Mongolia microcontinent that is adjacent to the Siberian Craton along the Main Sayan Fault Zone. The basement of the Garganskii Block is represented by gneisses, plagiomigmatites, tonalite gneisses, and amphibolites with the U–Pb age estimated as 2.7 billion years. The basement of the block is overlain by a schist–siliceous–carbonate cover. Its bottom bench carrying high-purity quartzites is composed of Neo-

proterozoic carbonate–quartzite deposits of the Irkutnaya Suite that is well-developed in the northern and northwestern margins of the heart of the block. The productive quartzite layer is pinching out on the eastern and southeastern flanks of the block. The block cover is flanked by ophiolites of the Neoproterozoic age on the western, northern, and eastern sides. Composed of harzburgites, dunites, websterites, orthopyroxenites, and a complex of parallel dykes, as well as massive and pillow lavas, the ophiolite complex is a hollowed-out allochthon that is overthrust onto the block from the northeastern side in modern coordinates. The Gargan suprasubduction granitoid massif of the Sumsunur complex (U–Pb age, 790 million years) lies southwestward from the Bural–Sardag deposit zone and northeastward from the Urda–Gargan occurrence. Granitoids of the Sumsunur complex have cut through the basement of the Gargan Block, the quartzite complex of the cover, and the ophiolite overthrust sheet [5].

CHARACTERISTICS OF QUARTZITES

The high-purity (according to visual examination) quartzite varieties retrieved from the Bural–Sardag deposit, earlier referred to as super quartzites [3], are a monomineral white rock with a subporphyritic structure. Transparent colorless elongated quartz grains, up to 3 mm in size, stand out sharply against a milk-white fine-grained (Fig. 1a) or microgranular (Fig. 1b) groundmass. These quartz grains either have a subpar-

allel orientation or do not have a distinct orientation at all. The mineralogical and petrographic studies identified two quartz generations: relic (first generation) and newly formed (second generation) ones.

First-generation quartz is represented by large (up to 3 mm) elongated grains that typically show wavy extinction and have fractures associated with plastic and brittle deformations. Relic quartz grains are typically characterized by serrate boundaries and fine-dispersed graphite growing along the fractures and inter-grain boundaries. Furthermore, quartz contains primary gas–liquid inclusions (GLIs) confined to the growth zones or secondary GLIs in the resistive fractures. Second-generation quartz is composed of fine (0.01–0.1 mm) grains without a noticeable plastic or brittle deformation. This type of quartz is formed along the grain boundaries of relic quartz and in the fracture propagation zones and often divides the initial quartz grains. Inclusions of various mineral phases (dickite, alunite, pyrite, and muscovite) were revealed in quartzites retrieved from the Bural–Sardag deposit.

EXPERIMENTAL

The contents of the volatile components in super quartzite were determined by kinetic thermal desorption mass spectrometry involving the quantitative analysis of flows of the compounds released into a high vacuum when a sample of a certain fineness was heated stepwise from room temperature to 1400°C. The samples were prepared as quartz grits with the granulometric composition of 174–450 µm. The sample preparation scheme for thermal desorption mass spectrometry involves the following processes: manual disintegration of a quartzite lump to obtain a 50 mm fraction; washing the lump; disintegrating the lump in a jaw crusher using tungsten carbide jaws until a 25 mm fraction was obtained; classifying into a fraction of 5–25 mm; chemical etching of the lump with a 10% HCl solution; drying the lump; thermal disintegration; manual disintegration in a quartz mortar to obtain a 5 µm fraction; grinding in a quartz grinder; and isolating a 174–450 µm fraction. Samples prepared both with and without the thermal disintegration stage were analyzed. The kinetics of the release and the composition of volatile components were measured by V.A. Kreisberg at the laboratory of the Division of Physical Chemistry, Chemistry Department, Moscow State University. The disintegrated sample was loaded into an ampoule made of annealed silica glass and placed in a vacuum for 24 h. All the weakly bound impurities physically adsorbed onto the surface were removed in a high vacuum (10^{-7} – 10^{-8} Torr) before the mass spectrometry annealing was started. The kinetics of water release were recorded during the subsequent stepwise heating with a step of 200°C; a mass spectrum of releasing gaseous products was recorded in the sections of isothermal heating [6].

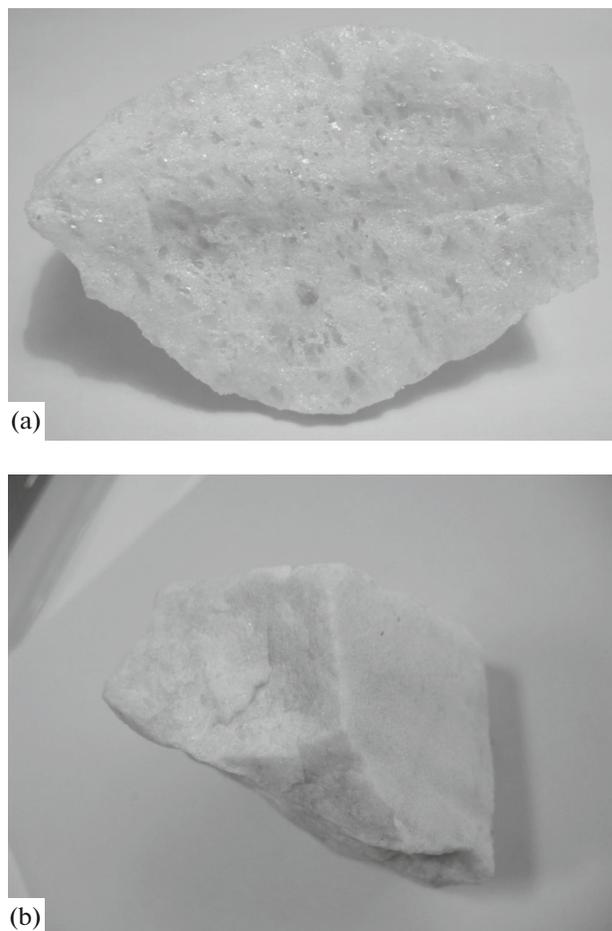


Fig. 1. Super quartzites retrieved from Bural–Sardag deposit: samples 7 cm in cross section.

The weight fractions of impurities were measured by inductively coupled plasma mass spectrometry (ICP-MS) on a NexION 300D quadrupole mass spectrometer (Perkin Elmer, United States) with a cyclone sputtering chamber: intensity of the high-frequency generator, 1350 W; sputtering argon gas flow rate, 1.1 L/min; cooling argon flow rate, 16 L/min; and auxiliary argon flow rate, 0.8 L/min. The samples (0.2–0.5 g) were dissolved in an HF–HNO₃ mixture with a 1% mannite solution, which was added to prevent the loss of boron in autoclaves (ANKON-AT-2, Russia) at 160–180°C (depending on the granulometric composition of the samples). The main compound of the sample was distilled with HF in the form of silicon tetrafluoride at 60–80°C, while the impurities were transferred into 3% nitrate solutions. The resulting solutions of the samples were additionally diluted before recording the spectra to weaken the mutual effect of the elements. In order to reduce the concentrations of the elements in the control experiment solutions and enhance the measurement accuracy, chemical sample preparation was performed in a class 1000 cleanroom; laboratory glassware made of poly-

Table 1. Contents of main impurities in gas–liquid inclusions in super quartzite at different beneficiation stages

Sample	Compounds in GLI, mln ⁻¹										
	H ₂ O			CO ₂	CO	C _x H _x	ΣC	H ₂	HCl	H ₂ S	SO ₂
	<600°C	>600°C	total								
Super quartzite	58.2	65.7	123.9	2.4	9.4	3.7	7.9	0.21	1.87	0.78	0.15
Fine-grained quartz	77.9	77.0	154.9	4.3	6.9	3.8	7.4	0.28	0.32	0.09	0.04
Super quartzite after thermal disintegration at 900°C	11.1	27.8	38.9	1.3	3.6	3.0	4.5	0.10	0.02	0.16	0.01
Super quartzite after calcination at 1455°C	42.0	3.9	45.9	0.4	4.4	4.8	6.2	0.05	0.02	0.01	–
IOTA-standard (Unimin)	18.6	17.2	35.8	1.3	4.5	3.9	5.7	0.51	0.21	0.01	0.03

meric materials and reagents of extra purity grade (acids of special purity grade additionally purified by sub-boiling distillation (DST-1000, Savillex) and deionized water with specific resistance > 18.2 MΩ/cm (Simplicity, Millipore, France)) were used. Calibration was carried out using CLMS-2 and CLMS-4 multielement standard solutions (Spex, United States), ICP solution X Certipur (Merck, Germany), and IQC-026 (Ultrascientific, United States). Rhodium in a concentration of 3 ng/mL was added as an internal standard. The impurity detection threshold calculated using the 3S criterion was 10⁻⁷–10⁻⁴ wt %. The correctness of determining the impurity content was controlled using the IOTA STANDARD and IOTA 4 reference samples of quartz concentrates (UNIMIN, United States), which were employed to produce transparent vitreous silica, or using the standard addition method. The results were obtained for 2 or 3 parallel weighed samples; the relative error of measurements ranges from 4 to 45%, depending on the element being determined and its content.

X-ray diffraction analysis was performed on a D8 ADVANCE automated X-ray diffractometer equipped with a Göbel mirror and a VANTEC-1 PSD detector in the step scan mode in the range of diffractions angles 2θ = 10°–60°; CuK_α radiation, 40 kV, 40 mA, exposure, 1 s; scan step, 0.02°. The X-ray diffraction patterns were calculated using the software built into the diffractometer. The PDF-2 database of powder XRD patterns was used for phase identification.

The absorption spectra of 1.5–3.5 mm thick transparent polished plane-sided plates made of silica glass were recorded on a Lambda 950 double-beam spectrophotometer (Perkin Elmer) in the spectral range of 190–3000 nm. The resulting spectra were adjusted for reflectance using Fresnel's formula for a normally incident beam.

The silica glass samples were prepared using a modernized OKB-8093 single-crystal growing unit by vacuum compression melting at a maximum pressure up to 6 bar. The resistive heater, the elements of the heating unit, and the crucible were made of graphite.

The temperature was monitored using a BP thermocouple and a digital pyrometer. Quartz concentrates were loaded into a graphite crucible, and the unit chamber was evacuated using a backing and a diffusion pump. After drying the raw material at ~150°C for several hours, the temperature was increased. In the case of a vacuum failure as the temperature was increased, we waited for some time for it to be restored and started a program to increase the temperature at a rate of ~300°C/h until melting began. When the melting point of quartz was attained, excessive heat (by ~100°C) was supplied and the chamber was filled with argon until it reached a pressure of 6 bar; the target temperature was maintained stable. The melt was exposed to this pressure for 1 h; then the heating was stopped. In this melting regime, the weight loss was 10–20%. Transparent colorless silica glass samples without visible bubbles were prepared in this regime.

RESULTS AND DISCUSSION

Gas–liquid inclusions in quartzites were studied by kinetic thermal desorption mass spectroscopy with the quantitative analysis of the flows of the compounds released into a high vacuum when a sample of a certain fineness was heated stepwise from room temperature to 1400°C by fluid inclusion analysis and laser ablation ICP mass spectrometry. The contents of the GLIs were determined by thermal desorption mass spectrometry (Table 1). The contents of the gas–liquid impurities in quartz grit is the key parameter showing the quality of the raw material, while the high-temperature form of water released above 600°C is the most important characteristic of quality. In terms of the content of the high-temperature form of water, super quartzite calcined at 1450°C is better than the Unimin reference quartz samples.

A flowsheet for their advanced beneficiation of quartz concentrates extracted from the quartz raw material of two types retrieved from the Bural–Sardag deposit, super quartzite and fine-grained quartzite, has been elaborated. The procedure of breaking quartz

Table 2. Weight fractions of impurities in quartz concentrates

Concentrate	Impurities, mln ⁻¹												
	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 CB	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
Calcination in Ar at 1450°C + CB	1.1	4	0.6	0.4	0.2	0.18	0.006	0.2	0.3	0.18	7.2	0.1	0.16
IOTA-4	0.3	8	1.4	0.7	0.07	0.004	0.01	1	0.4	0.2	12.09	0.1	0.05

Engineer, O.N. Solomein; analyses were carried out by V.Yu. Ponomareva at Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences. CB—chemical beneficiation.

by thermal disintegration was described in the Experimental section. It is followed by chemical beneficiation (CB) in a 20% HCl–10% HF mixture at a 2 : 1 solid-to-liquid (S–L) ratio, drying the quartz grits, controlling the quality of the quartz concentrate, and packaging. The second stage of the processes included calcination of the quartz concentrate to 1450°C followed by CB and drying. Transformation of high-temperature quartz into cristobalite starts under its calcination at 1450°C in argon [7]. The specific volume changes significantly during the quartz–cristobalite transition, resulting in an intense opening of the fluid inclusions, while the subsequent CB contributes to the removal of the exposed impurity elements.

The elemental composition of the impurities was determined by ICP-MS. The results of super quartzite beneficiation are summarized in Table 2. It is clear that the total content of the ten main impurities (Σ10) in the resulting concentrates after the first beneficiation stage is 10 mln⁻¹, and 7 mln⁻⁷ after the second

stage. One can state that in the simple flowsheet of deep beneficiation, even without using manual ore sorting and magnetic or electrostatic separation methods, the super quartzites retrieved from the Bural–Sardag deposit give rise to quartz concentrates with ultra high purity comparable to that of the IOTA 4 reference samples.

The experimental glass samples were prepared by vacuum compression melting of beneficiated super quartzite concentrates in graphite crucibles; their absorption spectra at 1300–280 nm do not feature the bands corresponding to OH groups (Fig. 2). With respect to its characteristics, the glass corresponds to grade KI silica glass according to the State Standard GOST 15130–86 [8].

Crystallization resistance is one of the key characteristics of silica glass used to produce thermally stable quartz ceramics. The thermal characteristics of the glasses produced from super quartzites were studied. Crystallization resistance tests were carried out according to the following scheme: quartz plates were heated in a muffle furnace in air on a quartz substrate to 1000–1250°C at a heating rate of 180°C/h. At temperatures between 1000 and 1250°C, the plates were kept for 2 h every 50°C; then the plates were cooled at a rate of 300°C/h. Visual monitoring, photoregistration of the appearance of plates before and after tests, and X-ray diffraction analysis were used to control crystallization. The results of visual monitoring showed that crystallization did not take place on the surface of the glasses produced from quartz concentrates of super quartzite and cristobalitized fine-grained quartzite exposed to 1200°C for 2 h, since the plate surface remained transparent without any noticeable turbidity. X-ray diffraction analysis demonstrates that cristobalite formation begins at 1150°C and accelerates at 1200°C in glasses produced from quartz concentrates of super quartzite (Fig. 3) and cristobalitized fine-grained quartzite. X-ray diffraction analysis of the surface is needed in addition to visual monitoring as this has been regulated by the technical specifications TU 1-596-476–2011 [9].

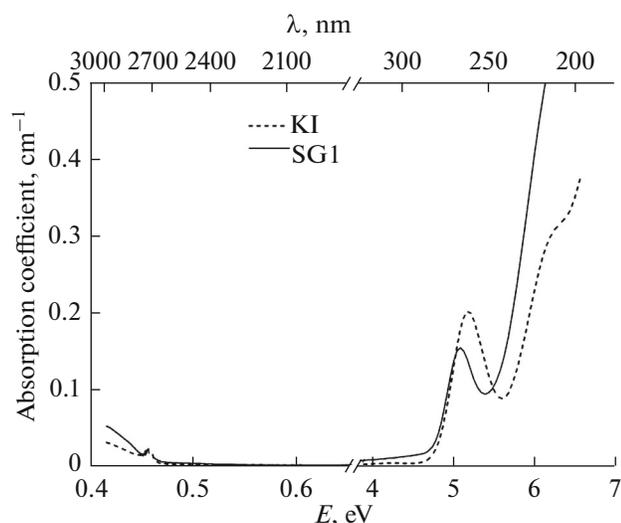


Fig. 2. Electron absorption spectra of KI glass and silica glass (SG1) produced by vacuum-compression method at 5 bar.

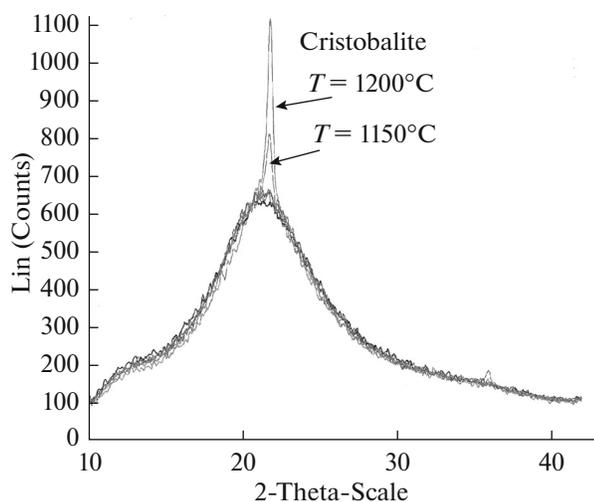


Fig. 3. X-ray diffraction patterns of silica glass manufactured from super quartzite grits during thermal tests at 1150 and 1200°C.

Quartz tubes were obtained by melting the resulting quartz concentrates of super quartzite and cristobalitized super quartzite on a K-2000 setup at OOO Silica Glass Research and Production Company (St. Petersburg, Russia). Melting of silica glass involved continuously feeding grits into a smelting crucible made of molybdenum or tungsten. Tungsten rods 5 mm in diameter and 1300 mm long were used as heating elements in the setup. The crucible was heated by the radiation emitted by the tungsten rods. The temperature of the tungsten rods was maintained at a level of 2200–2300°C. The raw material in the smelting crucible was melted and degassed (clarified) as it moves from the feeder to the forming unit; and the resulting molten glass flowed out through the forming nozzle under gravity and was caught by the pulling rolls. The pulling rate of the product as a tube or a rod depends on the viscosity of the molten glass and on the specified size of the products. The characteristics of quartz tubes produced from cristobalitized super quartzite fully comply with the technical specifications TU 1-596-476–2011 for tubes and rods [9] intended for manufacturing special products from quartz ceramics.

CONCLUSIONS

The study demonstrates that super quartzites retrieved from the Eastern Sayan Mountains are a

promising material for the production of ultra high-purity quartz concentrates for optical silica glass and high-temperature quartz ceramics.

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