

Silica and Alumina Transfer in Supercritical Aqueous Fluids and Growing of Topaz Monocrystals in Them

V. S. Balitsky*, D. V. Balitsky**, S. D. Balitsky***, C. Aurisicchio****, and M. A. Roma****

**Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

***University of Montpellier II, Montpellier, France*

****Division of Geology, Moscow State University, Vorob'evy gory, Moscow, 119992 Russia*

*****Rome University, Rome, Italy*

Received March 3, 2004

Abstract—Silica and alumina transfer during the dissolution and growth of quartz, corundum, and topaz in supercritical aqueous fluids have been experimentally studied under a direct temperature gradient, and the possibility for growing of topaz monocrystals in them have been determined. It was demonstrated that the directions of silica and alumina transfer shows no unambiguous correlation with the composition, *PT* conditions, pH, and density of the fluids, and, in some cases, can be opposite. This defines simultaneous spatially associated or separated growth of quartz and topaz, as is often observed in camera pegmatites. Our experimental data made it possible to develop a reproducible seed growth of topaz monocrystals and to study their structure, morphology, and physical properties.

DOI: 10.1134/S0016702906020066

INTRODUCTION

Topaz is known [1–4] to usually occur in pegmatite, greisen, and hydrothermal deposits, but occasionally crystallizes directly from magmatic melts. The physicochemical conditions of topaz crystallization, including the experimental synthesis of its microscopic crystals, have been studied by many scientists [2, 3, 5–7 etc.]. However, topaz macrocrystals have never been grown as of yet. This is primarily related to the fact that topaz has no physical properties that would make it valuable not only in the jewelry industry but also in promising fields of science and technologies, while the reserves and mining of topaz satisfy the jewelry market. The only exception is its scarce and valuable variety, purple–violet Cr-bearing topaz, whose formation conditions have not been exactly constrained. However, topaz crystal chemistry indicates the principal possibility of the incorporation of a much higher amount of Cr³⁺ as compared to those in the natural mineral. This fact indirectly indicates that synthetic topaz “doped” with Cr³⁺ might be suitable for creation of a new type of the working medium for quantum generators.

Evidently, many problems of the crystal genesis and use of topaz in science and technologies can be solved on the basis of a reliable and reproducible method of growing its synthetic analogues. This problem was briefly discussed previously [8, 9]. This publication summarizes our earlier experimental data.

EXPERIMENTAL TECHNIQUE, EQUIPMENT, AND MATERIALS

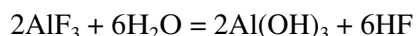
The study of fluid inclusions in topaz [1, 4], paragenetic analysis and thermodynamic calculations of equi-

librium topaz-bearing mineral assemblages [2, 3], as well as the experimental synthesis of fine-crystalline topaz [2, 3, 5–7] indicate that it can be formed in hydrothermal fluids within wide temperature and pressure ranges. Evidently, topaz and associated minerals, mainly quartz, often crystallized under temperature gradient owing to local silica and alumina transfer. For example, quartz and topaz can dissolve and grow in camera pegmatites [4]. Given this fact, we used gradient hydrothermal synthesis to simulate the transfer of major topaz components, silica and alumina, and the growth of its monocrystals. The first problem was to determine the behavior of silica and alumina in hydrothermal fluids of different composition. For this purpose, we simulated both separate and combined dissolution of topaz and minerals entirely consisting of either SiO₂ (quartz) or Al₂O₃ (corundum) under a direct temperature gradient. Two modifications of the temperature-gradient hydrothermal method were used for experiments. In one modification, the autoclave was split by a perforated diaphragm into two equal zones with sharply different temperatures, and monocrySTALLINE rods of quartz, topaz, and corundum of certain crystallographic orientation were placed in different combinations, together or separately, in the upper and lower zones of the autoclaves. In the other modification, the diaphragm was absent, while monocrystal rods of the minerals were placed vertically over the entire length. In this case, the temperature gradually changed along the autoclave axis, while zones with sharply different temperature were absent.

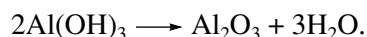
As is known [10, 11], the dissolution and crystallization of minerals under temperature gradient occur in

different temperature zones depending on the sign of the temperature coefficient of solubility (t.c.s.). Under a direct t.c.s., crystals dissolve in the higher temperature lower zone of the autoclave and grow in its lower temperature upper zone. Under a reverse t.c.s., the dissolution and growth zones are inverted. The identification of dissolution and growth zones makes it possible to reliably determine the transfer direction of mineral-forming components of a given hydrothermal fluid during congruent dissolution, as well as to estimate the influence of fluid temperature and density on the growth and morphology of the crystals, the incorporation and distribution of trace elements, etc.

The starting solutions were made on the basis of doubly distilled water and chemicals whose components occur in fluid inclusions in topaz (AlF_3 , KF, LiF, NaCl), as well as Na_2CO_3 of analytical grade. The required amount of low soluble dry AlF_3 was loaded in the autoclave at its bottom. Acidic fluids (pH 1–2 after experiments) formed when the autoclave was put in the operating mode, according to the reaction



with the Al hydroxide–corundum transition at temperature higher than 500°C



Solutions from the other reagents were prepared immediately before the loading of the autoclaves.

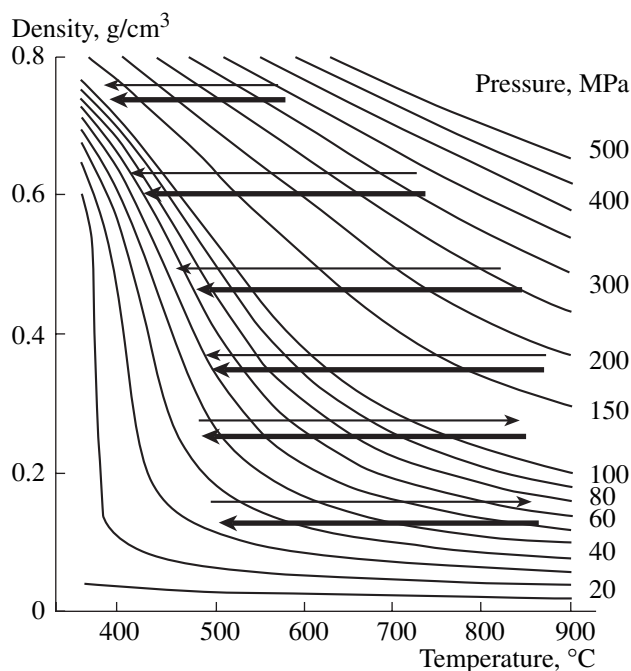


Fig. 1. Direction of silica transfer during quartz dissolution in the pure water, neutral chloride and alkaline solutions (thin arrows) and in the acidic aqueous–fluoride fluids (heavy arrows) under a direct temperature gradient. Hereinafter, isobars are given for pure water.

The starting minerals were cut in the form of rods of given crystallographic orientation from synthetic quartz, corundum, and natural topaz from the Volhynia deposit, Ukraine.

The experiments on studying silica and alumina transfer were carried out at the maximum operating temperature of 800°C and a pressure of 180 MPa in the autoclaves, which were made of EI-437B heat-resistant Cr–Ni alloy and had volumes of 30 and 50 ml. The autoclaves were mounted in sectional electric furnaces with two-section (in the presence of a diaphragm in the autoclaves) or one-section (in the absence of a diaphragm) heaters. Experiments lasted for 10–30 days. The pressure and density of the solutions during the experiments were estimated from the filling coefficient, using P – V – T diagrams for the starting and compositionally similar solutions [12], or from a P – V – T dependence for pure water if diagrams are unavailable [13]. The temperature was controlled using standard measurement devices with an accuracy of $\pm 1^\circ\text{C}$.

Most experiments were carried out at temperatures from 500 to 780°C , pressures from 20 to 180 MPa, and a temperature difference 20 – 100°C between the higher and lower temperature zones. The direction of silica and alumina transfer was determined from the weight change of the initial rods after experiments and the appearance of dissolution pits and furrows, and growth features (vicinals, faces). The congruent or incongruent dissolution of minerals was recognized, respectively, from the absence or appearance of newly formed mineral phases in the autoclaves or on the rods.

The dissolution and growth surface topography of the rods after experiments, as well as the morphology and internal structure of the grown crystals and inclusions formed during their growth were studied under binocular (MBS-9) and polarized-light (Amplival po-d) microscopes. Optical characteristics were measured with a theodolite table and by immersion techniques. Chemical composition was analyzed on a CamScan MV2300, MBX electron microscope equipped with a Link 860 EDS. Density was determined by hydrostatic weighting. Unit cell parameters were calculated from powder XRD patterns recorded on a ADP2-01 diffractometer, (Co anode, wavelength 1.79021 \AA). IR spectra were recorded on an AVATAR 320 FTIR (Nicolet) spectrometer. To determine the influence of ionizing irradiation, the grown topaz crystals were subjected to γ -irradiation (dose 5 Mrad, ^{60}Co source) and a high energy electron beam on a linear accelerator (dose 12 mV).

RESULTS AND DISCUSSION

Features of silica and alumina transfer in supercritical aqueous fluids. The results of experiments on the separate and combined dissolution of quartz, topaz, and corundum are shown in plots (Figs. 1–3). It can be seen that, during quartz dissolution in the supercritical field in pure water, neutral chloride, and alkaline fluids, silica is

transferred into the lower-temperature zone (Fig. 1). However, in acidic aqueous–fluoride fluids, the direction of silica transfer shows distinct correlation with the fluid density (ρ). Silica is transferred from the higher to lower temperature zones at $\rho > 0.34\text{--}0.37\text{ g/cm}^3$, and in the opposite direction at lower ρ . The direction of silica transfer does not depend on the presence or absence of topaz. Topaz interacts differently with fluids of similar compositions. Regardless of the presence or absence of quartz, topaz is unstable in alkaline and neutral chloride fluids, and is replaced by either feldspars (at high alkalinity) or mica (at low alkalinity). In fluoride near-neutral and acidic fluids and in the absence of quartz, topaz is slightly dissolved and transferred at temperatures of up to 780°C and a pressure of 180 MPa. However, in the presence of quartz, the extent of dissolution of both minerals becomes similar. Unlike quartz, topaz always dissolves in the lower temperature zone and is transferred into the higher temperature zone regardless of the density of the aqueous–fluoride fluids (ρ from 0.05 to 0.52 g/cm^3) (Fig. 2). A similar behavior is typical of silica under a direct temperature gradient during interaction between corundum and aqueous–fluoride fluids (Fig. 3). This indicates that alumina behaves similarly during the dissolution of topaz and corundum in aqueous–fluoride fluids. However, unlike corundum, the intense dissolution of topaz and the transfer of alumina in these fluids occur only in the presence of quartz. If both corundum and quartz are present in the aqueous–

fluoride fluids, they are replaced by topaz or (at low F contents) X-andalusite.

During the dissolution of corundum in alkaline fluids at $500\text{--}700^\circ\text{C}$, alumina, like silica during quartz dissolution, is transferred from the higher temperature lower zone to the lower temperature upper zone. This phenomenon is used to grow quartz and corundum monocrystals and their color varieties in alkaline hydrothermal solutions at a direct temperature gradient [10, 11]. However, the simultaneous presence of quartz and corundum in strongly alkaline solutions leads to the instability of both minerals and their replacement by feldspathoids.

Experimental results also showed that a narrow (“pseudoequilibrium”) zone with no indications of dissolution and growth develops between the zones of dissolution and growth of quartz and topaz during their interaction with acidic aqueous–fluoride fluids at free temperature convection (without diaphragm). The spatial and temporal position of this zone is defined by both the volume and the total surface of the dissolving minerals, as well as by the value and character of the temperature gradient. At restricted fluid convection (porous environments), the direction of silica and alumina transfer is controlled by the same relations as in an open cavity, but the extent of their transfer decreases by more than one order of magnitude, without any distinct boundary between dissolution and crystallization zones.

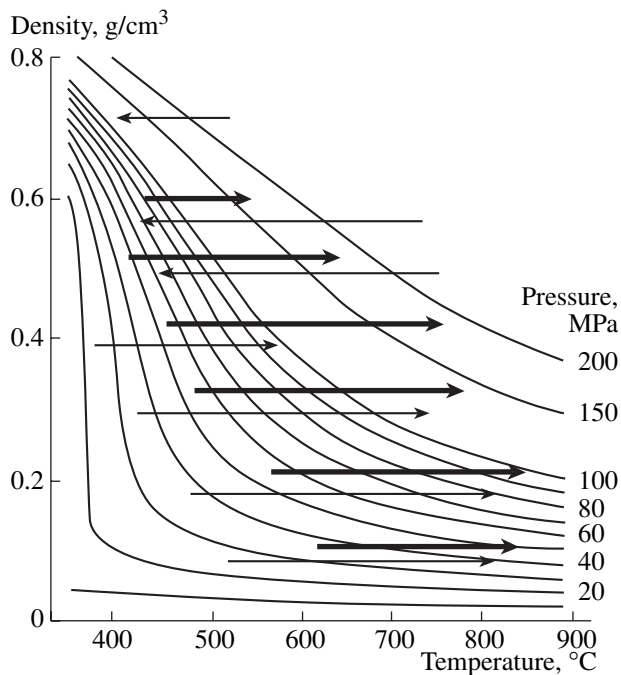


Fig. 2. Direction of transfer of silica (thin arrows) and alumina (heavy arrows) during the simultaneous dissolution of quartz and topaz in the acidic aqueous–fluoride fluids under a direct temperature gradient.

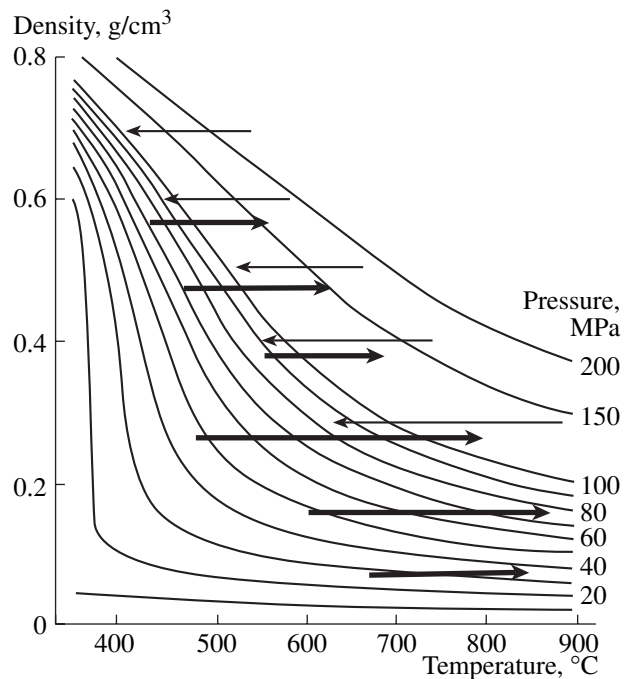


Fig. 3. Direction of alumina transfer during corundum dissolution in alkaline (thin arrow) and acidic aqueous–fluoride fluids (heavy arrows) under a direct temperature gradient.



Fig. 4. Monocrystal of synthetic topaz grown on a seed parallel to {001} in acidic aqueous–fluoride fluids at 730°C and 150 MPa.



Fig. 5. Vicinal surface of the {011} plane of synthetic topaz.

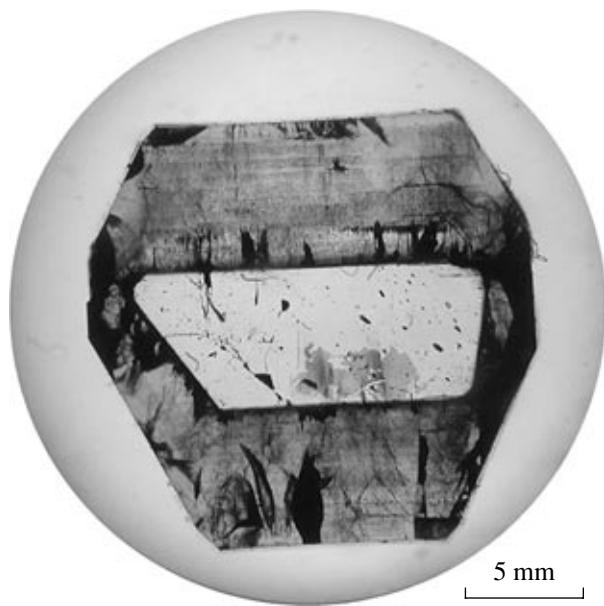


Fig. 6. Zoned structure of synthetic topaz. Section parallel to {100}. The seed of natural topaz is at the center (white band). The overgrowing layer contains numerous tiny (0.001–0.01 mm) fluid inclusions.

Growing topaz monocrystals. Structural–morphological characteristics and some properties of topaz. Our study of silica and alumina transfer in supercritical aqueous fluids served as the basis for the development of a reproducible method for the seed growth of topaz monocrystals. According to this method, topaz is grown in fluoride-bearing near-neutral or acidic aqueous fluids within wide ranges of temperature (550–780°C) and pressure (20–180 MPa). The relatively low fluid densities require a high temperature gradient (from 50 to 80°C) between the lower and upper autoclave zones to maintain the necessary mass transfer. Topaz seeds in the form of monocrystal plates $\sim 2 \times 8 \times 40$ mm of ZX- and ZY-orientations were loaded in the lower, higher temperature zone, and a charge (a mixture of equal proportions of topaz and quartz fragments) was loaded into the upper, lower temperature zone. To provide more contrasting temperature gradient, the zones were separated by a perforated diaphragm with total area of the holes equal to 10–15%.

The crystals were grown mostly in autoclaves with a volume of 300 cm³, internal diameter of 30 mm, and length of 400 mm. Experiments lasted 20–60 days. As a result, the grown topaz monocrystals were from 2.5 to 5.0 mm thick (on the one side of the seed), from 8.0 to 15 mm wide, and from 20 to 40 mm tall (Fig. 4). The crystal most rapidly grew along the [001] direction at temperatures of 700–730°C at both low (10–20%) and relatively high (40–50%) fillings (pressure of 40–70 and 150–200 MPa, respectively). The maximum growth rate was no more than a few tenths of a millimeter a day. In spite of the relatively brief duration of the experiments, the crystal was overgrown by practically all faces typical of natural topaz: {001} pinakoid, {110} and {120} prisms, {111} and {021} rhombohedra, and others. Their surface is typically even or is covered by growth hillocks of regular or complicated shape, often with distinct concentric layers (Fig. 5). The irrational growth surfaces have a rough regeneration topography, composed of rhombohedral and prismatic pyramids 0.2–0.5 mm across. The crystals show a clearly pronounced sectorial–zoned structure in cross sections owing to a change in the direction of zones parallel to certain faces (Fig. 6). The zones are often accentuated by numerous fluid inclusions, from a few thousandths to tenths of a millimeter (Fig. 7). The overgrowing layer also often contains large (up to a few tenths of a millimeter across) fluid inclusions, elongated along the growth direction of the face (Fig. 8). Along with growth sectors and zones, overgrowing layer reveals a thin fibrous texture in polarized light, which is caused by the regeneration growth of some faces (Fig. 9). The overgrowing topaz layer is typically colorless, occasionally pale pink. This color is presumably caused by elevated (up to a few tenths of a weight percent) contents of Cr, which can be supplied in fluid during the corrosion of autoclave walls.

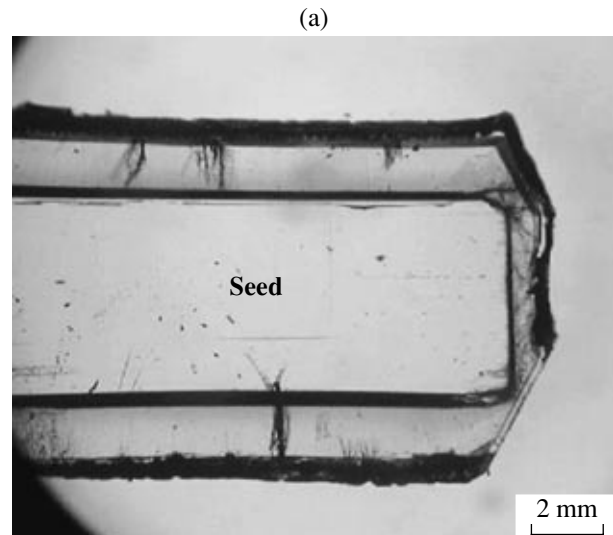
Like natural topaz, its synthetic analogues acquire reddish–brown color under the effect of ionizing irradi-



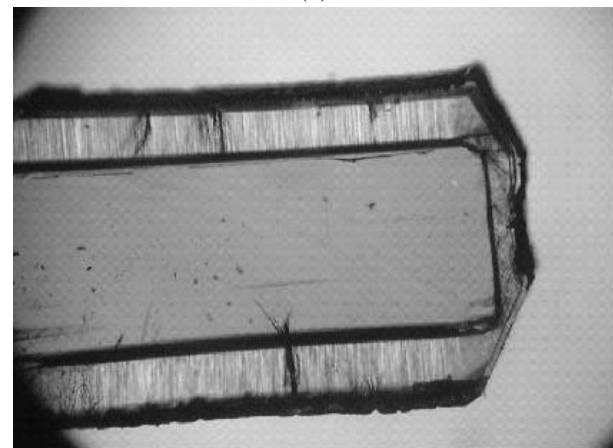
Fig. 7. Magnified fragment of Fig. 6 with an overgrowing layer of synthetic topaz with numerous fluid inclusions.



Fig. 8. Large three-phase fluid inclusion consisting of gas, liquid, and a solid phase (fluoride-silicate glass?) in synthetic topaz.



(a)



(b)

Fig. 9. Fragment of seed plate of natural topaz of XZ orientation overgrown by synthetic topaz. (a, b) in polarized and unpolarized light, respectively. Unpolarized light revealed that the layer has a thin-laminar structure, with laminae oriented parallel to the crystal growth direction.

ation, with this color disappearing at high temperature (200–250°C). In this case, the crystals acquire a pale blue (sky-blue) color, which is stable up to 400°C. Both types of irradiation colors can be restored by repeated irradiation. A similar behavior is observed in synthetic topaz upon its irradiation by high-energy electrons and subsequent thermal treatment.

Microprobe analysis revealed no differences between the chemical compositions of natural and synthetic topaz. They have the following contents of the major components, respectively (wt %): 35.97 and 35.07–35.53 SiO₂; 55.02 and 54.67–54.79 Al₂O₃; 16.33 and 16.17–16.87 F, and 7.31 and 6.62–6.80 O. These results are well consistent with homogeneous reflected-electron pattern and images in characteristic Si, Al, F, and O X-rays in natural seed topaz and the overgrowing layer of the synthetic analogue (Fig. 9). This is also cor-

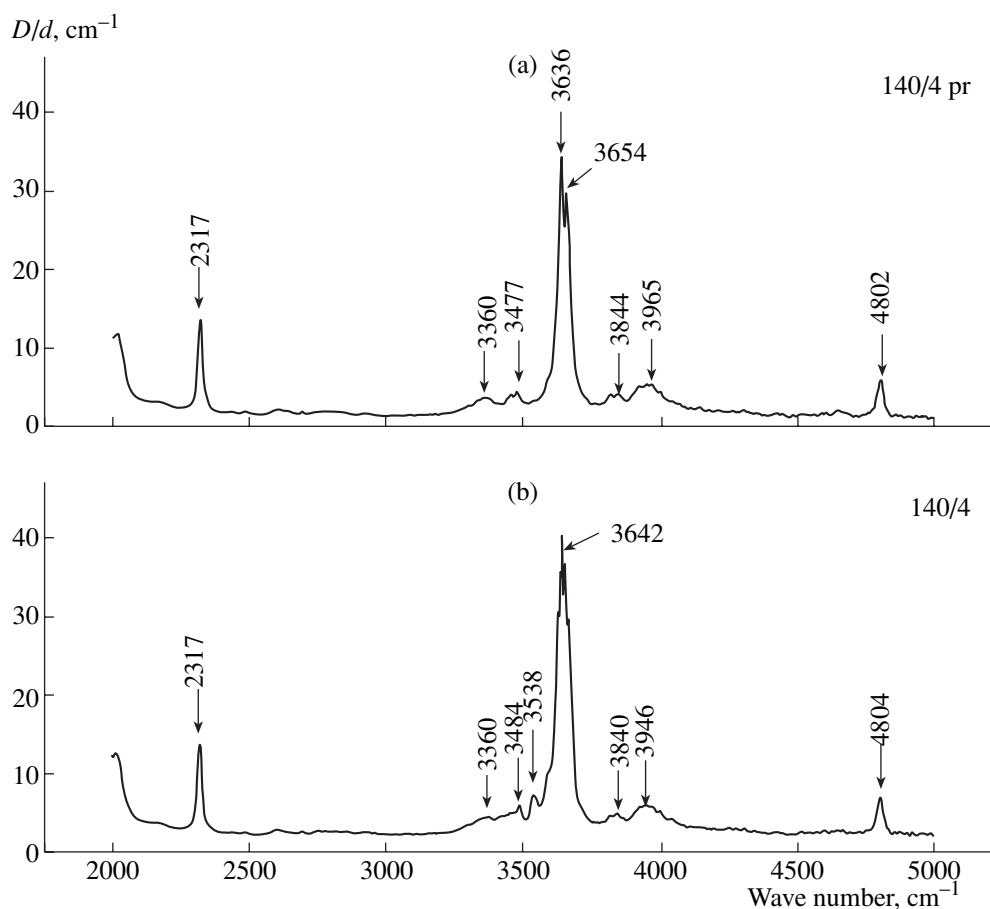


Fig. 10. Typical IR spectra of natural (a) and synthetic (b) topaz showing their complete similarity.

roborated by the similar unit cell parameters of natural and synthetic topaz, which were calculated from high-precision XRD patterns. These parameters were as follows: $a = 4.649 \text{ \AA}$, $b = 8.792 \text{ \AA}$, $c = 8.394 \text{ \AA}$, $V = 343.096 \text{ \AA}^3$ for natural seed topaz; $a = 4.649 \text{ \AA}$, $b = 8.789 \text{ \AA}$, $c = 8.391 \text{ \AA}$, $V = 342.857 \text{ \AA}^3$ for the overgrowing layer of synthetic topaz.

The refractive indices of synthetic topaz ($N_g = 1.615\text{--}1.620$, $N_m = 1.610\text{--}1.618$, and $N_p = 1.607\text{--}1.615$) practically do not differ from those of natural topaz. The density of natural and synthetic topaz seemed to be nearly identical (3.55–3.57). No differences were found between the IR-spectra of natural and synthesized topazes either (Fig. 10).

CONCLUSIONS

The transfer of silica and alumina during the simultaneous dissolution of quartz, topaz, and corundum in hydrothermal supercritical fluids (580–780°C, pressure up to 180 MPa) were studied at a direct temperature gradient. It was shown that, during quartz dissolution in neutral hydrothermal and alkaline fluids, silica is transferred from high-temperature to low-temperature zones

regardless of the presence or absence of topaz. During corundum dissolution in the same fluids, alumina is transferred in the same direction. Under these conditions, topaz is an unstable phase and is replaced by micas and feldspars depending on the pH of the fluid. The direction of silica transfer during quartz dissolution in acidic aqueous–fluoride fluids distinctly depends on the fluid density (ρ). At $\rho > 0.34\text{--}0.37 \text{ g/cm}^3$, silica is transferred from the higher temperature zone into the relatively lower temperature zone, and *vice versa* at lower ρ . At the same time, during the dissolution of corundum and topaz in the presence of quartz in similar aqueous–fluoride fluids, alumina is always transferred from the lower temperature into higher temperature zones, regardless of the density. This maintains the simultaneous transfer of silica and alumina in aqueous–fluoride fluids in the same or opposite directions and, hence, the simultaneous spatially combined or separated growth of quartz and topaz. A change in the direction of silica and alumina transfer during the dissolution of the minerals in hydrothermal fluids of different composition and density under a temperature gradient is explained by a change in the t.c.s. sign.

Our experimental data make it possible to develop a technique for the reproducible growing of topaz monocrystals, which are nearly identical to natural topaz in chemistry, structure, and main physical properties.

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