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Cr-containing topaz crystal growth on a seed in supercritical aqueous-fluoride fluids and some properties of as-grown crystals

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For the first time the Cr-containing topaz single crystals with unusual alexandrite effect and intensive fluorescence under influence of ultra-violet light are grown up. Growth conditions and the external and internal morphology of crystals and their physical properties is studied.

Key words: Cr-containing topaz, hydrothermal growth of crystals, morphology of crystals, physical properties of topaz

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Introduction

The topaz, as it is known **[***Naumov, etc., 1977***]**, is a polygene mineral. Its crystallisation is occurred in magmatic, pegmatic and hydrothermal stages of mineralization, covering a wide range of temperatures (from 250 to 900°C) and pressures (from 30 to 200 MPa). Conditions of topaz formation in the nature have been determined after many experimental and thermodynamic studies of its stability and mineral equilibriums. Experimental researches, as a rule, were accompanied by obtaining of microscopic crystals of topaz **[***Rosenberg, 1972; Balitsky et al., 2002***]**. The single crystals of topaz were never grown on seeds until recently. It is related to a limited practical application of the natural topaz only in jewellery which is extracted in sufficient quantity for the market requirements. The exception is the rarest and valuable form – Cr-containing topaz. The presented work is devoted to finding-out about conditions of crystal growth such kind of topaz.

Technique, equipment and materials

At a choice of technique of single crystal growth of Cr-containing topaz the early results on experimental studies of its isothermal reactions with aqueous solutions of HF and KF (molarity from 10^{-4} to 10m and from 0 to 1.0m, accordingly) in the range of 300-600°C and 100 MPa have been considered. It has allowed taking in account the stability field of topaz depending on concentration of the HF and KF in fluid **[***Shapovalov, 1988***].** In particular, it has appeared, that for stability of topaz at the specified reactions the solutions should have a high concentration of HF ($3\cdot10^{-3} - 8\cdot10^{-1}$ m) and low concentration of KF ($<7\cdot10^{-3}$ m). It being known that with rise of temperature from 300 to 600°C the field of stability of topaz in the diagram lg (m_{HF})-lg (m_{KF}) is considerably narrowed and displaced to the area of higher concentration of HF. The boundary values of maximum concentration of KF change insignificantly and lay close to lg (m_{KF}) = −2.0.

In the same time, the influence of thermobaric parameters and composition of fluids on streamline of silica and alumina was simultaneously found out at separate and simultaneous dissolution of quartz and topaz in hydrothermal fluids of various compositions under thermo-gradient conditions at 500-780°C and up to 150 MPa **[***Balitsky, etc., 2006***].** It has been found that the topaz in hydrothermal fluoride fluids under thermo-gradient conditions is always transferred from rather low temperature zone to high-temperature zone. It is connected to retrograde character of dissolution of topaz, i.e. the temperature factor of solubility (TFS) has a negative sign. Topaz dissolution becomes more intensive at excess of silica in the system. The behaviour of quartz in the same solutions is ambiguous and differs from behaviour of topaz: at low density of fluid (less than 0.4 g/cm^3) quartz is characterised by retrograde solubility. The silica in such fluids is similar to the alumina transfer which goes to high-temperature zone. But in more dense fluids the TFS of quartz becomes positive and dissolved silica is moving from hotter zone to less hot zone.

The growth of single crystals of topaz was realised in autoclaves of 280 cm^3 made from Cr–Ni alloy A437b. The autoclaves were heated in a group electric furnace with two-section resistant heaters. The duration of runs was 30-60 days. The crystals were grown at temperatures from 500 to 780°C, pressures from 20 to 180 MPa. The difference of temperatures between bottom and top ends of autoclaves was from 20 to 100°C. The pressure and density of fluid in autoclaves were estimated by filling factors on *P–V–T* diagrams of pure water **[***Naumov, etc., 1971***]**. The temperature control was carried out by means of the thermo-measuring device Termodat - 25M1 equipped by chromel-coupel thermocouples with accuracy ± 2°C.

The initial solutions were prepared on basis of bi-distilled water and aluminium fluoride (AlF_3) which were placed in the bottom of autoclave. The fluoride fluid was formed at heating of autoclave at the expense AlF_3. The chrome admixture was not specially added into autoclave, since it came to solution at rather insignificant dissolution of Cr-Ni body of autoclave. Topaz crystal growth was carried out on seed plates of 2÷4x6x50÷70 mm, cut out parallel to faces {001}, {110} and {120} of natural topaz crystals from Volynsk deposit (Ukraine). Seeds were placed in the bottom zone of autoclave with help of copper wire. Nutrient, consisting of mix of fragments of topaz of 10–12 mm in diameter and synthetic quartz of ZY- and ZX-bars of 2x4x30÷50 mm, was placed in the top zone of autoclave. For creation of more contrast temperature gradient, the nutrient and seed zones were separated from each other by diaphragm of 10–15%.

Morphology and internal structure of as-grown crystals were studied by binocular (MBS-9) and polarising (Amplival po - d) microscopes; optical characteristics were defined by immersion method. The chemical composition was defined by microprobe analyser CamScan MV2300. X-ray characterisation was carried out by difractometry on ADP2-01 Co at wavelength 1.79021 Å. The luminescence of topaz was observed under a standard mercury lamp and UV laser EnSpectrR532 with recording of spectrum. The influence of ionizing irradiation on the as-grown topaz crystals was studied by γ-irradiation (^{60}Co, 5 Mrad,) and under irradiation by linear electron accelerator (12 Mv).

Results and discussion

The most intensive growth of topaz is fixed in [001] direction at 700-730°C as at low (10–20 %), and at high (40-50 %) fillings of autoclaves (pressure in order of 40–70 and 150–200 MPa, accordingly). Absolute values of growth rates did not exceed the first tenth of millimetre per day. Almost all faces known for natural topaz crystals were observed on as-grown crystals (pinacoid {001}, prisms {110}, {120}, rhombohedrons {111}, {021}, etc.) (Fig. 1). Their surface, as a rule, is smoothed or covered by growth hillocks of regular and complex shape often with distinct concentric layers (Fig. 2a,b,c).

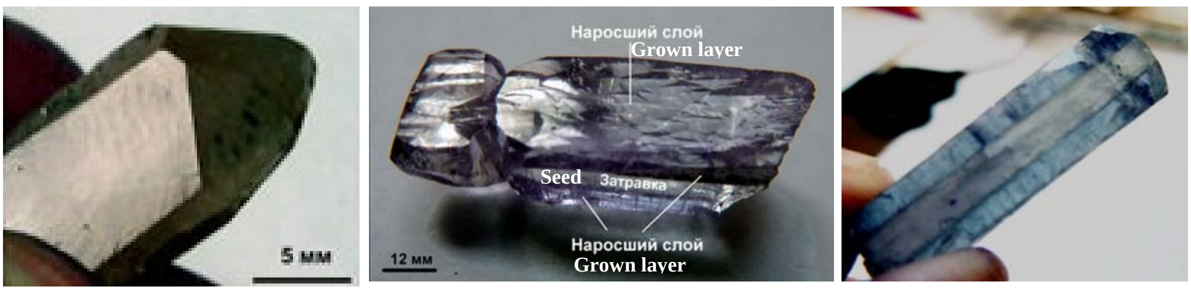

Figure 1. Morphology of single crystal of Cr-containing synthetic topaz

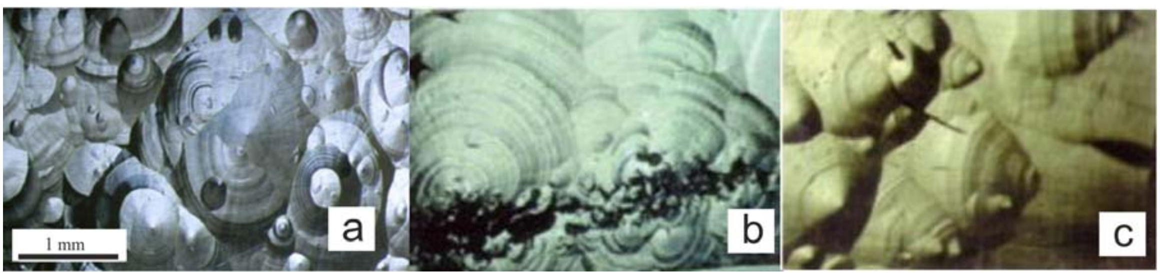

Figure 2. Vicinal relief of faces of pinacoid {001} (a), prisms {101} (b) and bi-pyramid {113} (c) of synthetic Cr-containing topaz

Irrational surfaces of growth are rough; their relief is combined by rhombohedrons and prismatic pyramids with cross-section size of 0.5 mm. The crystals are characterised by the distinct sectorial-zone structure revealed in cross-section cuts, by reason of changing in the direction of zones, which are parallel to certain faces (Fig. 3). The zones are often decorated by presence of numerous primary fluid inclusions with the size from thousand to tenth shares of millimetre. Besides sectors and growth zones, sometime, a thin fibrous structure of the grown layers is observed under polarised light. It was induced by regenerating growth mechanism of some faces. As-grown layer of the topaz crystals has a primary bluish-green colouring (Fig. 4a).

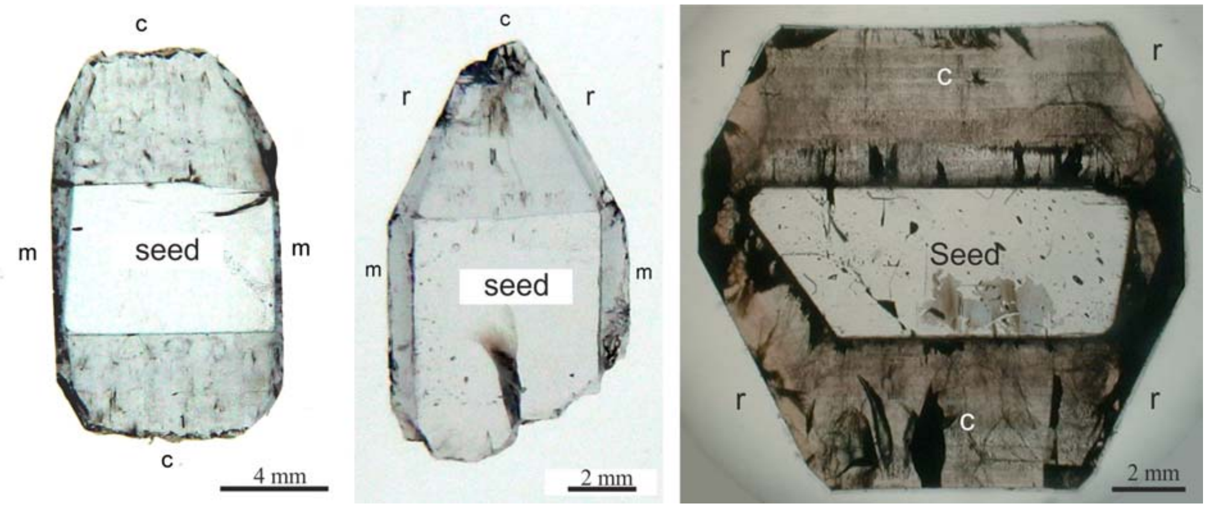

Figure 3. Internal sectorial-zone structure of synthetic Cr-containing topaz

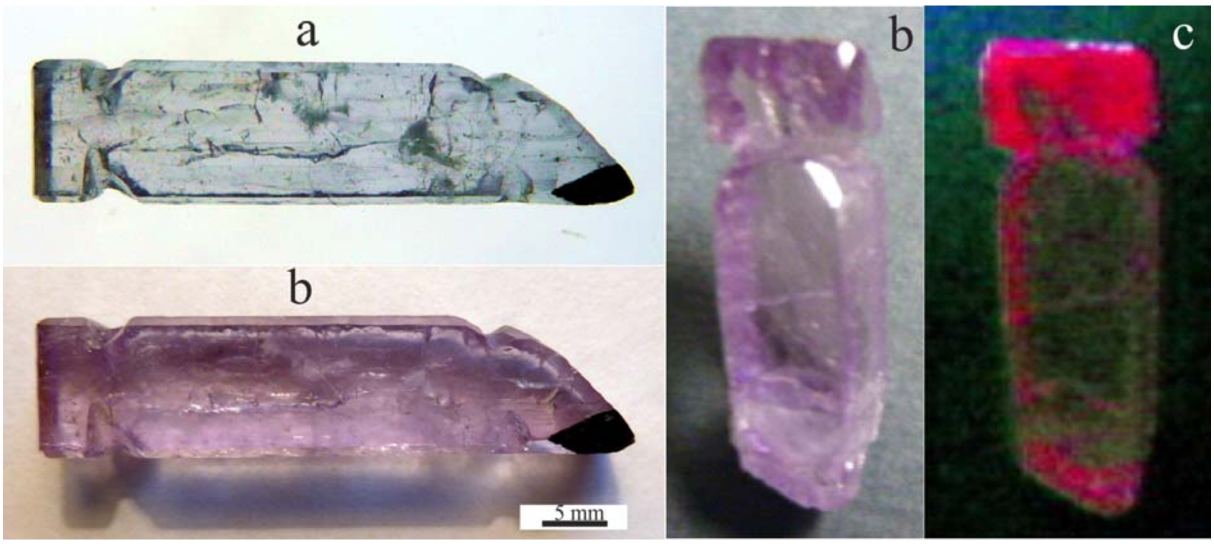

Figure 4. Colour of synthetic Cr-containing topaz at day (a), fluorescent lamp (b) and UV (c) illumination

Like a natural topaz, the synthetic topaz is colored to intensive red-brown under ionising irradiation which disappears after heat treatment at 200-250°C. The microprobe X-ray analysis has shown a concentration of Cr in as-grown layers of topaz up to 0.5 mass%. The green-bluish colour of as-grown topaz crystals changes to red-violet under fluorescent lamp (Fig. 4b), and to brightly red colour under UV. Optical and fluorescence spectra specify that primary colouring of the topaz crystals is related to isomorphic occurrence of Cr^{3+} in structure.

Conclusion

Thus, the single crystals of Cr-containing topaz were grown for the first time. Crystals possess unusual alexandrite effect which is manifested by change of green-bluish colour at daylight to red-violet under fluorescent lamp illumination. The grown crystals are characterised also by intensive fluorescence of red colour under UV irradiation.

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