

TOURMALINE STABILITY AND POSSIBILITY OF ITS SYNTHESIS IN HYDROTHERMAL SOLUTIONS AT TEMPERATURES OF 450-750°C AND PRESSURES UP TO 1.5 KB

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Tourmaline is a widespread mineral of granite pegmatites, pneumatolite-hydrothermal and hydrothermal formations. However, it is often encountered as a rockforming mineral both in granites themselves and metasomatites and metamorphic rocks. Due to its bright and variable coloration, high hardness and the absence of cleavage tourmaline monocrystals are widely used as cutting material. Herewith, tourmaline possesses valuable piezo- and pyroelectric properties and being used in piezoengineering allows to essentially increasing the sensibility of the equipment. However, many of the peculiarities of its formation still remain obscure in spite of numerous geological, mineralogical, geochemical and crystallochemical investigations. In particular, such important tourmaline characteristics as its stability and solubility in hydrothermal solutions of different composition within a wide range of temperatures and pressures are not determined yet. The reliable and reproducible methods of growing its monocrystals are not developed either.

Experiments were run in order to determine tourmaline stability and to develop the methods of its growing. The experiments were carried out in water solutions of boric acid, its mixture with hydrofluoric and hydrochloric acids and fluorides and chlorides of alkaline and heavy metals at 450-750°C and pressures up to 1.5 kbar. The experiments were run in autoclaves 20, 30 and 50 ml in volume made of titanium and chrome-nickel alloys. Prismatic elbaite monocrystals from Malkhansky deposit (Transbaikalia) 3x3x10 – 5x5x10 in size were used as samples and seeds to study tourmaline stability. Nourishing charge was either elbaite monocrystals with the addition of quartz or the mixture of quartz and corundum monocrystals in the ratios close to tourmaline stoichiometry. The experiments were carried out under thermogradient conditions in the absence of dividing diaphragm in the autoclave. The temperature was measured with chromel-alumel thermocouple with the accuracy of $\pm 5^\circ\text{C}$, the pressure was set by the coefficient of autoclave filling. The character of tourmaline dissolution and newly formed phases were studied under a binocular magnifying glass and polarization microscope as well as by X-ray and microprobe analyses on an electron scanning microscope CamScan MV2300 (VEGA TS 5130MM) TPPT equipped with YAG detectors of secondary and reflected electrons and energy-dispersion X-ray microanalyser with a semiconductor Si(Li) detector INCA Energy.

As a result it was found that elbaite in slightly acid water-borate solutions (H_3BO_3 concentration less than 6 wt%) at the above P-T parameters is extremely inert. However, with increasing H_3BO_3 concentration to 12 wt% both seed and charge elbaite are replaced by a thin film of schorl (probably by diffusion due to iron entering the solution upon the corrosion of autoclave walls). Herewith, at the surface of a seed crystal there appear regularly cut small prismatic schorl crystals up to 1 mm in size and elbaite debris in the charge bear the traces of dissolution. The addition of quartz into the charge caused no changes in the character of dissolution and elbaite transfer. The presence of elbaite did not have any effect on the intensity of dissolution and redeposition of quartz either.

In acid alumino-fluorine solutions at 700°C elbaite is unstable and dissolves intensively with the formation of at least two thin crystalline phases quartz and topaz covering the surface of charge debris and seed crystals.

In the solutions of 5 wt% NH_4F and 5 wt% NH_4F + 10 wt% H_3BO_3 at 600 and 750°C and pressures of about 1 kbar the surface of seed crystals and charge get covered with a phase with regularly formed AlF_3 crystals, which prevent both dissolution and growth of elbaite. The most evident dissolution of elbaite seed and charge is observed in the experiments with the solution 10wt% LiF. The dissolution is followed by the formation of small concretions (some tenths and hundredths of mm) of well-formed kyanite and cristobalite crystals.

Seed stimulated tourmaline growth was observed only in the experiments where solutions of 10 wt% NaCl + 15 wt% H_3BO_3 + 20 wt% $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 wt% NaCl + 15 wt% H_3BO_3 + 20 wt% $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were used at 500°C and a pressure of about 1 kbar. Monocrystal corundum and quartz

rods placed at the bottom of an autoclave were used as a charge in those experiments. Elbaite seeds were placed in the upper and bottom zones of the autoclave. Run duration was 20 days.

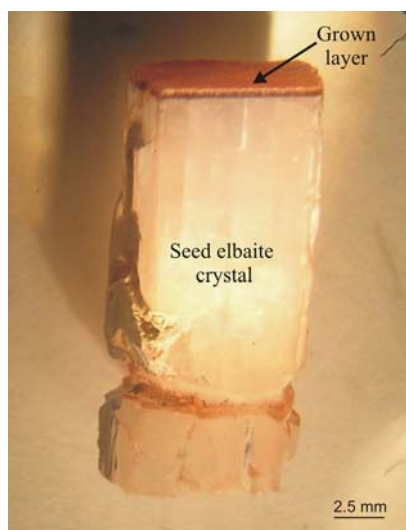


Fig.1. Seed elbaite crystal and Co-tourmaline layer grown on it.

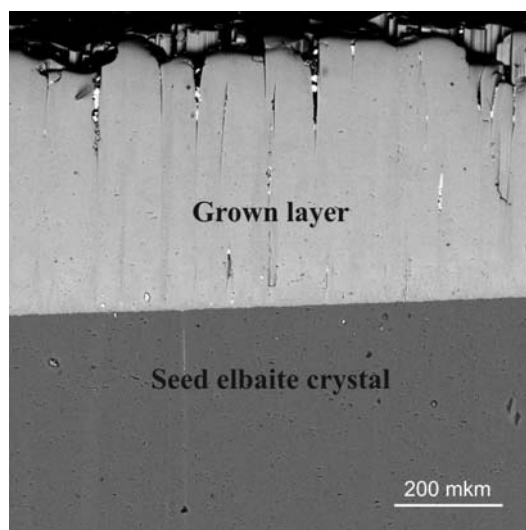


Fig.2. Magnified part of Fig.1 in reflected electrons.

Tourmaline growth on the seeds took place both in the upper and bottom zones on the face $\{+001\}$. In case $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was used the newly formed layer had an intensive pink coloration (Fig.1,2), in the experiments with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ it was pale green. The thickness of the grown layer did not exceed 0.5-0.06 mm, accordingly. Moreover, a great amount of spontaneous Co-tourmaline crystals up to 50 mkm in size were observed on the seeds and charge. They had the same composition as the grown layer. Microprobe and X-ray study of the newly formed layers shows that they belong to the synthetic analogs of cobalt and nickel tourmaline, accordingly.

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