# GROWTH DEVICE, CRYSTAL GROWTH AND CHARACTERIZATION OF ALEXANDRITE

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Alexandrite is beryllium aluminate Al2O3•BeO doped with minor levels of chromophores, Cr2O3 being the major one. The engineering application of single crystals of synthetic alexandrite is currently limited to active elements of tunable IR-lasers for remote sensing and medicine. In the design of the mechanical components of any crystal-growth systems, especially high-temperature systems, there are two basic requirements: long-term stability of the dimensions of the heating equipment; and uniform rotary and translational motion of the crystal over a wide speed range. Accordingly, it is assumed for the heating system that the heater and internal screens are made of tungsten and the heater is cylindrical. In the present work, authors describe a new high-temperature furnace for a crystal-growth system, with new designs of the heater, screens, copper leads, and the lid. To eliminate the sealed input, which is the primary source of non-uniform crystal motion, the kinematic system, including the motor, is placed in a volume connected to the furnace.

Conference participants

To permit ongoing change in configuration of the heating system, the power-supply system takes the following form. Rectangular copper plates are pressed against the current lead by pin and nut. Two copper rods are screwed into the plates, on different sides of the common longitudinal axis. A thermocouple junction is attached to the upper end of one of the rods, for temperature monitoring. Leads connected to the top ends of the rods carry the voltage signal directly to the heater. The 4-mm internal channels in rods accommodate grooved tungsten bars, which are the power leads of the heater. The heater takes the form of a coil (height 10 mm, diameter 63 mm, with a strip thickness of 1 mm. The coil is inserted in gaps in the upper part of the bars, to which it is soldered by molybdenum. Bars are fixed to rods by two M4 bolts. The screen system consists mainly of molybdenum sheet (thickness 0.2 mm), with upper and lower caps, a coaxial cylindrical lateral section, upper and lower inserts, and an intermediate screen cover. It is possible to change the number of constituent sheets, the axial temperature gradient may be adjusted during crystal growth, without affecting the rest of the structure. The first internal screen is made of tungsten. The supporting components of the screen system are the upper and lower plates, made of titanium sheet (thickness 1 mm). The screen system is mounted on supporting plate by means of six rods; plate is mounted on the base furnace by means of three rods. The heating volume is sufficient to accept a molybdenum or tungsten crucible with a diameter up to 55 mm and height up to 40 mm. The crucible is mounted on a molybdenum table, which is centered in the furnace by means of attachment to thermocouple tube. The latter is not a supporting element; the legs of the table are three tungsten bars in bushes, which, in turn, are held in intermediate washer 6 within the central hole of supporting plate. The junction of the VR-5/20 thermocouple is in direct contact with the bottom of the crucible.

The extension and rotation device has a clearly defined function: the growth of singe crystals (predominantly high-temperature oxides), by a method resembling the Kiropoulos method. Single crystals may be grown not from melt but (formally) from a solution in which the solvent is one of the components of the compound introduced in quantities slightly exceeding stoichiometry. The Kiropoulos method does not provide for extension of the crystal. However, experimental results show that such extension (at a slow speed, around 0.1–0.5 mm/h), which is one of the primary aspects of the Czochralski method, permits more massive crystals to be grown.

Thus, it is difficult to precisely classify the method, which includes aspects of the Kiropoulos method (melt), the Czochralski method (melt), and the flux method (solution).

Alexandrite is beryllium aluminate $Al_2O_3{\cdot}BeO$ doped with minor levels of chromophores, Cr2O3 being the major one. The engineering application of synthetic alexandrite single crystals is currently limited to active elements of tunable IR lasers for remote sensing and medicine. The underlying idea of this process is that the feed contains an overstoichiometric proportion of one component, namely, beryllium oxide (3–6 wt %) or alumina (5–6 wt %), with the proper decrease in the proportion of the other component. Single-crystal seeding was performed at temperatures below the phase transition inchrysoberyl (about 1853 °C [1]), and growth was carried out while temperature was depressed below the temperatures of the neighboring eutectic (1835°C for beryllium-rich feeds and 1850°C for alumina-rich feeds). The process was worked out for the following two compositions, wt %: 75 $Al_2O_3$—25 BeO,85 $Al_2O_3$—15 BeO. Chromium oxide and vanadium oxide were added in an excess of up to 0.3 and 0.1 wt %, respectively. In all experiments, the feed weight was 50 g. The crucible used was molybdenum 26 mm high and an outer diameter of 47 mm.

Temperature depression rates during crystal growth were 0.5–4 K/h; rotation speeds were 1–5 rpm. The feed could contain network-forming cations, for example, $B^{3+}$ or $Si^{4+}$, in the form of oxides in proportions of 0.3–0.5 wt %. Alexandrite yields reached 75% of the feed weight.

The use of seed crystals oriented along the major crystallographic axes affected crystal habit only insignificantly. The only exclusion was [100] orientation: crystals grown on such seeds frequently had a mirrorsmooth upper facet. In our opinion, the above-indicated feed compositions are optimal. In some experiments, the high-temperature phase was grown directly from the seed or soon after seeding; its growth then stopped, apparently, at the transition temperature 1853°C . Further temperature depression even induced partial dissolution, followed by intensive eutectic solidification on this substrate. In the other experiments, the low-temperature phase was seeded, but in the form of a polycrystal. The mot perfect crystal consisted of four twins. Under certain conditions, the high-temperature phase was seeded in the form of a completely clear regular- shaped single crystal with hexagonal habit. This stab was pulled to heights of 5–10 mm, but a horizontal phase-transition interface always appeared at these heights. X-ray powder diffraction showed only chrysoberyl chrysoberyl, without any specific features or foreign phases, in samples that experienced the transition.

This work is an embodiment of the process for growing bulk alexandrite single crystals using resistive heating with reduced temperature gradients. We have determined the feed compositions for stable seeding and growing up a single crystal of the low temperature alexandrite phase in the range of its thermodynamic stability.

Experiments with the proposed crystal-growth system show that the furnace ensures long-term stability of the geometric dimensions of the thermal unit. The extension and rotation unit ensures smooth (jerk-free) rotation of the crystal at 0.8–10 rpm. The nonuniformity of the rotary speed is not observed visually over a 15-cm radius. The carriage path is 100 mm and may be easily increased by changing the size of the extension and rotation unit. With a maximum carriage speed of 135 mm/h, no nonuniformity of its motion is observed at 100-fold magnification. The proposed system is currently in use for the growth of alexandrite single crystals. The effectiveness of the system is evident from electron-microscope images of etched samples obtained on a Jeol JSM-6460 LV scanning instrument (Fig. 1).

The dislocation density in the sample is $5.8*10^4$ $cm^{-2}$, which is in good agreement with the literature values of $10^4$–$10^5$ $cm^{-2}$ [2].

We have also determined the ranges of the major process parameters (including crystal rotation speeds and cooling rates) that do not cause gas or feed melt occlusion. Visually perfect single crystals have been grown. Combined or separate doping with chromophores $V_2O_3$and $Cr_2O_3$ yields crystals with colors ranging from bright bluish-green (with $V_2O_3$solely) to dark red (with $Cr_2O_3$ solely). Faceted insets of this material demonstrate good color inversion from purple-red to green in response to a change in light.

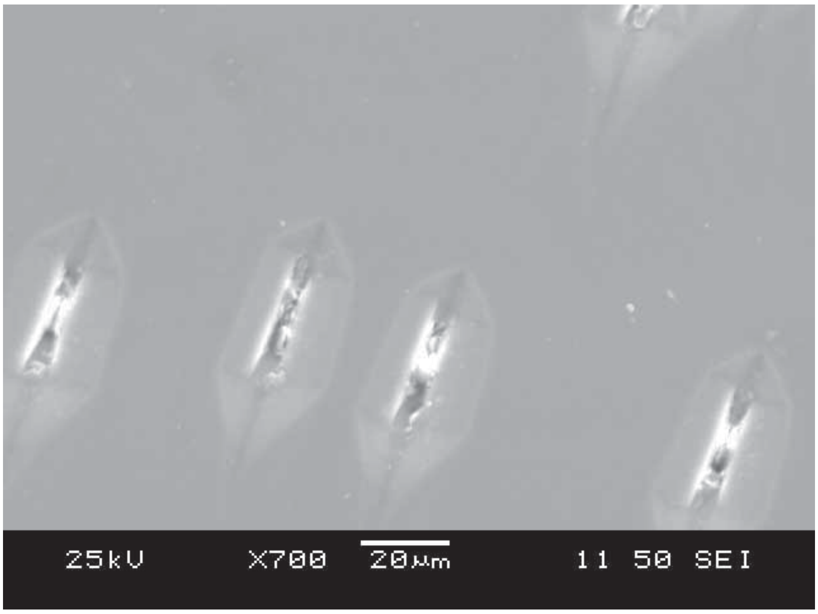

**Fig. 1. Typical etch pits at dislocations in alexandrite single crystals.**

## References:

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