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Abstract

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MORPHOLOGY AND SOME PROPERTIES OF Al_2O_3 CRYSTALS GROWN FROM TUNGSTATE MELTS

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For the growth of single crystals of ruby and leucosapphire, crystallization of Al_2O_3 from solution in a melt of certain low-melting substances— PbF_2 , PbO , cryolite, etc.—is now often used. Single crystals obtained by this method are free of elastic stresses, have a low dislocation density, and are optically more perfect than those grown by the Verneuil method. However, the known solvents have a number of disadvantages, among which are their volatility and toxicity, as well as the growth from them of Al_2O_3 crystals with a sharply nonisometric, plate-like form. The present work describes a method for growing single crystals of leucosapphire and ruby from solution in a melt of sodium and strontium tungstates, and examines the morphology and several other characteristic properties of the crystals obtained.

Investigation of the ternary systems $\text{Al}_2\text{O}_3\text{—WO}_3\text{—Me}_2\text{O}(\text{MeO})$, where $\text{Me} = \text{Li; Na; K; Sr; Ba, etc.}$, carried out with a heating microscope, showed that no ternary compounds are formed in these systems and that all of them are suitable for growing Al_2O_3 single crystals. A characteristic feature of these systems, especially the alkaline ones, is their low tendency toward spontaneous nucleation of aluminum oxide crystallization centers, as well as the relatively low solubility of Al_2O_3 . From the standpoint of growing aluminum oxide crystals, the optimum compositions are those corresponding to the ternary peritectics between Al_2O_3 , aluminum tungstate $\text{Al}_2\text{O}_3 \cdot 3\text{WO}_3$, and the corresponding tungstates of alkali and alkaline-earth elements. In the $\text{Al}_2\text{O}_3\text{—WO}_3\text{—Na}_2\text{O}$ system, this peritectic has the composition 28 mol.% Na_2O , 2 mol.% Al_2O_3 , and 70 mol.% WO_3 , and melts at 725° . In the $\text{Al}_2\text{O}_3\text{—WO}_3\text{—SrO}$ system, this eutectic has the composition 18 mol.% SrO , 9 mol.% Al_2O_3 , and 73 mol.% WO_3 , and a melting point of 1080° . The dependence of the solubility of Al_2O_3 in solvents of these two compositions on temperature was determined by saturating a melt of specified temperature with corundum rods grown by the Verneuil method. The resulting curves are shown in Fig. 1.

The relatively low solubility of aluminum oxide in these solvents, their low

Figure 1 plot: solubility of Al₂O₃ vs temperatureFigure 1: Figure 1 plot: solubility of Al₂O₃ vs temperature

volatility, and their lack of tendency toward spontaneous formation of crystallization centers, already noted above, make tungstates especially promising for growing Al₂O₃ single crystals by the seeded-growth method at a constant temperature gradient.

In experiments on growing crystals by this method, a small quantity (about 10 g) of dissolving material—fragments of corundum ceramics or crystals of leucosapphire and ruby—was placed on the bottom of a platinum crucible with a capacity of 25 ml. The crucible was then filled with the solvent melt and placed in a platinum gradient furnace. The maximum temperature at the bottom of the crucible was usually 1250° (sodium tungstate solvent), and at the surface of the melt about 1200°. After satur-

the melt with aluminum oxide for 6 hours, a seed—a crystal of leucosapphire or ruby about 3–4 mm in size—was lowered into the melt. The growth rate of the seed under the indicated conditions is 0.5–0.75 mm per day. A considerably higher growth rate could be achieved at higher temperatures. Thus, in a strontium tungstate solvent, when heated to 1500° in an induction furnace and with a temperature at the seed of about 1300°, the growth rate of Al₂O₃ crystals could be brought up to 0.5 mm per hour. By this method, leucosapphire and ruby crystals 6–8 mm in size were grown. The crystals obtained often had well-formed faces, were free from solvent inclusions, and were transparent and colorless (leucosapphire).

Fig. 1. Dependence of the solubility of Al₂O₃ in a melt of composition 28 mol.% Na₂O, 2 mol.% Al₂O₃, and 70 mol.% WO₃ (1), and 18 mol.% SrO, 9 mol.% Al₂O₃, and 73 mol.% WO₃ (2), on temperature.

Experiments were also carried out on the growth of Al₂O₃ single crystals by spontaneous crystallization during cooling of the melt. Such crystallization was observed only in the strontium tungstate solvent. Crystallization was carried out under the following regime: heating to 1500° in a rhodium furnace, holding for 2 hours, and cooling to 1100° at a rate of 16° per hour. In this way leucosapphire crystals up to 1.5–2 mm in size were obtained.

One of the most characteristic properties of Al₂O₃ crystals grown from solution in a melt of tungstates is their unusual habit.

It was noted that the usual form of ruby and leucosapphire crystals obtained from PbF₂ and other previously used solvents is thin hexagonal plates with developed {0001} faces^(1,2). On the edges of the plates, faces {10 $\bar{1}$ 1}^(1,3) and, more rarely, {10 $\bar{1}$ 2}, {20 $\bar{2}$ 1}^(3,4), {11 $\bar{2}$ 1}⁽⁴⁾, and {22 $\bar{4}$ 3}⁽⁵⁾ were observed. Along with plates, small, more isometric crystals are sometimes formed, having the shape of rhombohedra with {22 $\bar{4}$ 3} faces and of the basal pinacoid {0001}

Figure 2 micrograph: typical corundum crystal form

Figure 2: Figure 2 micrograph: typical corundum crystal form

(⁵). It is difficult to obtain such crystals with dimensions of several millimeters even with a solvent quantity of 5–6 kg (⁶). Crystals in the form of rhombohedra with faces $\{10\bar{1}1\}$, $\{01\bar{1}2\}$, $\{0001\}$ can also be obtained by introducing small (up to 1 mol.%) amounts of La_2O_3 additives into the $\text{PbF}_2\text{--Bi}_2\text{O}_3$ solvent (⁷).

Spontaneously formed leucosapphire or ruby crystals grown from tungstate melts have the form of hexagonal bipyramids with $\{22\bar{4}3\}$ faces. The form of such crystals is clearly visible in Fig. 2, which shows a leucosapphire crystal about 0.3 mm in size, grown on the filament of a heating microscope after evaporation of the solvent. In the initial stage of growth of Al_2O_3 crystals on a seed, the faceting of the crystals is more varied. Here, along with developed $\{22\bar{4}3\}$ faces, prism faces $\{11\bar{2}0\}$ and the basal pinacoid $\{0001\}$ were observed. The formation of such faces is only a temporary phenomenon. Thus, the growth rate of seeds in the direction of the c axis was maximal in all cases, and the $\{0001\}$ faces rapidly overgrow.

Fig. 2. Typical form of corundum crystals obtained from solution in a melt of tungstates—hexagonal bipyramid $\{22\bar{4}3\}$.

In spontaneously formed crystals, basal pinacoid faces are never observed.

Crystallization of leucosapphire or ruby in tungstate melts in the form of hexagonal bipyramids is unusual not only for artificial, but also for natural crystals of Al_2O_3 . The only exception, apparently, is the corundum of the Ilmen deposit, which occurs with such a form (⁸).

Another feature of Al_2O_3 crystals grown from solution in a tungstate melt is their twinning. Most crystals larger than 1–1.5 mm consist of regions rotated relative to one another by 180° about the c axis. Similar twinning, but to a lesser extent, is also noted in synthetic Al_2O_3 crystals grown from other solvents, and in natural crystals (⁹). The presence of twins does not affect the crystal form described above or their optical properties, but is readily detected by X-ray methods.

Leucosapphire single crystals grown from tungstate melts are colorless, but they give bright orange-red luminescence under ultraviolet excitation, indicating incorporation of a tungsten impurity into the Al_2O_3 lattice. In rubies, the orange-red luminescence is suppressed by the usual luminescence with R lines characteristic of ruby. According to spectral-analysis data, the amount of tungsten impurity is of the order of 0.1 at. %. The value of the specific gravity (3.99 g/cm^3) and the refractive index ($n_g = 1.77$; $n_p = 1.76$) do not differ from those for pure synthetic leucosapphire crystals.

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