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Flux Growth of Hexagonal Bipyramidal Ruby Crystals

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Ruby (Al_2O_3:Cr), a most attractive red gemstone, is a form of aluminum oxide doped with chromium. There have been many studies on the synthesis of ruby single crystals by various techniques such as Verneuil, Czochralski, hydrothermal, vapor phase, and flux.[1] The flux growth is particularly preferred because it readily allows crystal growth at temperatures well below the melting point of the solute. Other important advantages of flux growth are that the grown crystals have an enhedral habit and a reasonably lower degree of dislocation density. Many researchers have reported on the flux growth of gem crystals, such as ruby and emerald.[1,2] Supersaturation states are required in flux growth and can be obtained by a slow-cooling, flux-evaporation, or temperature-gradient technique. Some works report on the growth of emerald crystals by the flux evaporation method.[3−5] However, few studies have discussed the evaporation growth of ruby crystals. The slow cooling method, using a system of lead compounds, such as PbF_2, $PbO-B_2O_3$, and $PbO-PbF_2$ as solvents, has been most widely used for ruby crystallization.[2] Almost all ruby crystals grown from these fluxes were of platelike habit with well-developed {0001} faces. The effect of growth conditions on the ruby habits is only understood for some of the platelike habits.

We have grown emerald crystals ($Be_3Al_2Si_6O_{18}$:Cr) from molybdate system fluxes using the evaporation method.[3−5] Emerald is a beryl (beryllium aluminum silicate) doped with chromium. It was grown from a solute composed of BeO, Al_2O_3, and SiO_2 powders and the same fluxes mentioned above. From our experience with emerald growth, it can be assumed that ruby crystals can most likely be grown from molybdate system fluxes since Al_2O_3 is dissolved in the MoO_3-based fluxes. In our previous paper, only the platelike ruby crystals were grown by the flux slow-cooling method using $PbF_2-B_2O_3$ flux.[6] The purpose of this study, therefore, is the growth of hexagonal bipyramidal ruby crystals from a MoO_3 flux. In addition, the morphology of the resulting crystals was also examined.

Ruby crystals were grown using reagent grade MoO_3 as a flux. A mixture of a reagent grade Al_2O_3 and an oxide dopant (Cr_2O_3) was used as a solute. Cr_2O_3 was added at a concentration of 0.5 mass % of the Al_2O_3. The solute (1.52 g) and flux (28.48 g) powders were weighed out, mixed together, and put into a platinum crucible (30 cm^3 capacity) with a diameter of 36 mm and height of 40 mm. The lid was loosely fitted and the crucible placed in an electric furnace with silicon carbide heating elements. The crucible was heated at about 45 °C·h^{-1} to 1100 °C and held at this temperature for 5 h. After that, the crucible was removed and allowed to cool rapidly to room temperature. Subsequently, the crystal products were separated from the flux in warm water. The grown crystals were observed using an optical microscope. The obtained crystals were investigated by means of X-ray diffraction (XRD) and electron probe microanalysis (EPMA). The length (parallel to the *c* axis) and width (perpendicular to the *c* axis) of the ruby crystals were measured, and their averages were calculated.

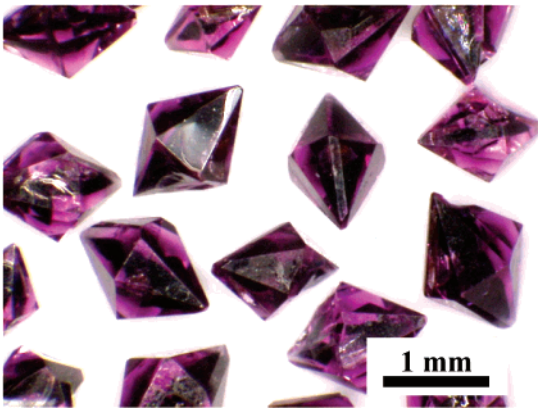

Figure 1. Optical micrograph showing ruby crystals grown from MoO_3 flux.

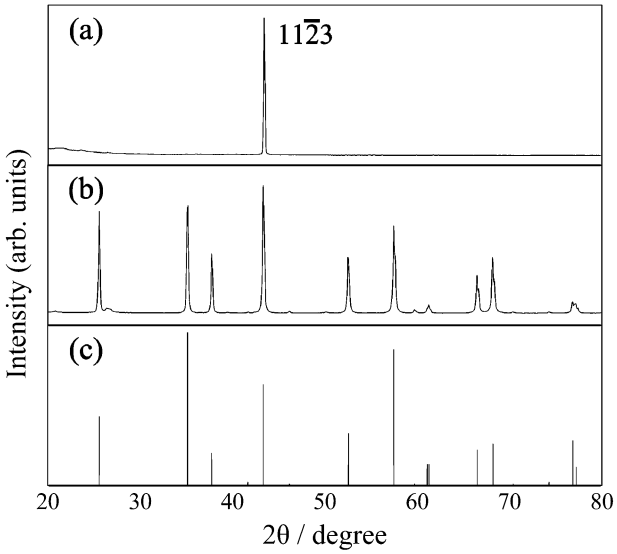

Figure 2. X-ray diffraction patterns (Cu K_α) of ruby crystals. (a) Hexagonal bipyramidal crystal of which well-developed face was laid in parallel with the holder plate; (b) pulverized crystallites; (c) corundum JCPDS data.[7]

Bipyramidal ruby crystals (double six-sided pyramid bounded by 12 similar triangle faces) could be grown by the MoO_3 flux-evaporation method. The typical ruby crystals are shown in Figure 1. The grown crystals were red and transparent. The maximum crystal grown reached 1.8 mm in length and 1.7 mm in width. The average crystal sizes were approximately 1.2 mm in length and 1.0 mm in width. The evaporation ratio of MoO_3 flux after 5 h was approximately 99.4 mass %, and its evaporation rate was

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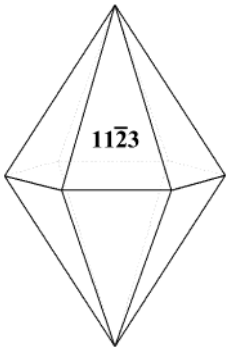

Figure 3. Drawing of ruby crystal with hexagonal bipyramidal {11$\bar{2}$3} faces.

calculated as 1.26×10^{-3} g·h^{-1}·mm^{-2}. Such high evaporation rate is known to be caused by the high volatility of MoO_3.

To identify the bipyramidal red crystals and determine the Miller indices of the crystal faces, the obtained crystals were laid on a holder plate and investigated by the XRD. Figure 2 shows XRD profiles of data for the bipyramidal crystals, pulverized crystallites, and α-Al_2O_3 (corundum) JCPDS.[7] Only the diffraction pattern of the (11$\bar{2}$3) plane was detected in the bipyramidal crystals, as shown Figure 2a. The XRD pattern of crystals grown in this study indicates good crystallinity, and the pulverized crystallites pattern (Figure 2b) was found to be the same with that of α-Al_2O_3 (Figure 2c). The presence of chromium, which gave its characteristic red color, was confirmed using EPMA. Therefore, there is no doubt about the hexagonal bipyramidal crystals grown in this study being ruby.

The usual morphology of ruby crystals obtained from lead-based fluxes is well-known as thin hexagonal plates with well-developed {0001} faces.[1,2,6] On the other hand, the most unique feature of ruby crystals grown from MoO_3 flux is their unusual habit. Figure 3 shows the drawing of the crystal habit surrounded by the {11$\bar{2}$3} faces. This figure shows the crystal habit in which the lattice constants are fixed at $a = 4.759$ Å and $c = 12.993$ Å.[7] As clearly seen in Figure 1, spontaneously formed ruby crystals grown from MoO_3 flux are of hexagonal bipyramid form with well-developed {11$\bar{2}$3} faces, and the surfaces of the crystals are very flat. The dominance of the {11$\bar{2}$3} faces is thought to be attributed to adsorption of a layer of molybdate ions on these faces, which is the most favorable for epitaxial adsorption of MoO_3 chains. In addition, the interfacial angles and the shape of triangle faces were also identical to the theoretical values and forms, respectively. From the XRD analysis and morphology estimation, thus, the crystal habit shown in Figure 3 was found to be correct.

In conclusion, transparent ruby crystals were readily grown for the first time by an isothermal technique involving the evaporation of MoO_3 used as a flux. The crystals formed as hexagonal bipyramids bounded by well-developed {11$\bar{2}$3} faces. They exhibited the typical red color and were up to 1.8 mm × 1.7 mm in size. Molybdenum trioxide was found to be a suitable flux for the growth of bipyramidal ruby crystals.

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