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Growth of Hexagonal Bipyramidal Ruby Crystals by the Evaporation of a Li_2O–MoO_3 Flux

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The growth of hexagonal bipyramidal ruby crystals by the flux evaporation method in the Li_2O–MoO_3 flux system has been reported. Ruby crystals were grown by heating a mixture of a solute (Al_2O_3 + 0.5 wt % Cr_2O_3) and a flux (Li_2O–MoO_3) at 1050, 1100, or 1200 °C, followed by holding the solution at these temperatures for 5 h. The crystal size was dependent on the evaporation loss of the flux. The evaporation loss of the flux gradually decreased with increasing amount of Li_2O added to MoO_3, and increased with the holding temperature. The obtained ruby crystals had lengths of up to 2.6 mm and widths of up to 2.1 mm, and had a transparent-red color. Their form was a bipyramid, bounded by well-developed $\{11\bar{2}3\}$ faces. The most suitable flux composition for high-quality and large ruby crystal growth was found to be 2 mol % Li_2O–98 mol % MoO_3.

Ruby, which is a form of aluminum oxide (corundum) doped with chromium, has been the world's most attractive gemstone for thousands of years. Chromium ions give corundum its red color. Ruby has found wide applications thanks to its excellent properties, including its optical property, chemical stability, and mechanical strength. Chemically and physically speaking, ruby is dense (specific gravity), hard, and with a high melting point. In particular, ruby is the second-hardest natural material (next to diamond) known to humankind. The hardness of ruby can be ascribable to the strong, short-distance binding between aluminum and oxygen. Concerning its optical property, the first successfully optical laser consisted of a ruby crystal (a rod of synthetic ruby), and was created in 1960.[1] The excited electrons from the Cr^{3+} ground state into higher electron states fall back to their initial states while emitting light with a wavelength of 694 nm, corresponding to red light. The focused red light gains a tremendously greater power than normal light.

The history of ruby synthesis includes one century or more, and a variety of techniques are commonly used to synthesize ruby crystals, such as Verneuil, Czochralski, hydrothermal, vapor phase, and flux.[2–10] Each and every synthetic method has unique advantages. Among these techniques, flux growth is very convenient, and can produce ruby crystals at temperatures well bellow the melting point of the solute. Furthermore, this technique is suitable for the synthesis of crystals having an enhedral habit. Many kinds of studies have been reported on the growth of ruby crystals by slow cooling of a flux using a system of lead compounds.[3–8] In those cases, almost all of the ruby crystals grown from these fluxes were of plate-like habit with well-developed {0001} faces. Though some studies have reported on the evaporation growth of emerald crystals,[11–13] few studies have considered with ruby crystals.

In our previous study,[2] hexagonal-bipyramidal ruby crystals were grown for the first time by the evaporation of a molybdenum trioxide flux. The present paper describes the growth of ruby crystals from a Li_2O–MoO_3 flux by an isothermal technique involving the evaporation of a flux. The effect of Li_2O addition to the MoO_3 flux on the crystal growth was investigated. Because Li_2O works as an evaporation inhibitor, its addition could effectively cause an enlargement and quality improvement of ruby crystals.

Experimental

Single crystals of hexagonal-bipyramidal ruby were grown by a flux evaporation method. A mixture of reagent-glade Al_2O_3 (Wako Pure Chemical Industries, Ltd.) and Cr_2O_3 (Wako Pure Chemical Industries, Ltd.) was used as a solute, and reagent-grade MoO_3 (Allied Material Co., Ltd.) and Li_2CO_3 (Junsei Chemical Co., Ltd.) powders were chosen as the flux. The typical growth conditions are given in Table 1. Al_2O_3 and Cr_2O_3 were added, respectively, at a concentration of 7.0 mol % of the flux and 0.5 wt % (0.007–0.008 g) of the Al_2O_3. The concentrations of Li_2O in the flux were varied from 0 to 8 mol % (0 to 0.503 g). The solute (1.526–1.624 g) and flux (28.384–28.481 g) powders were weighed, mixed together, and put into platinum crucibles with a

Table 1. Typical Growth Conditions of the Ruby Crystals

Run No.	Solute	Flux (basic)		Flux (acidic)	Holding temperature /°C
	Al_2O_3 /g	Content (mol %)	Li_2O /g	MoO_3 /g	
1	1.519	0	0	28.481	1100
2	1.542	2	0.120	28.338	1100
3	1.566	4	0.244	28.190	1100
4	1.590	6	0.372	28.038	1100
5	1.616	8	0.503	27.881	1100
6	1.542	2	0.120	28.338	1000
7	1.542	2	0.120	28.338	1050
8	1.542	2	0.120	28.338	1200

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diameter of 36 mm and a height of 40 mm. These weights of the reagents were kept at approximately 30 g for all growth runs. The lids were loosely fitted and the crucibles were inserted into an electric furnace with silicon carbide heating elements. The crucibles were heated in air from room temperature to the holding temperatures (Table 1) at 45 °C•h^{-1}. They were held at the holding temperatures for 5 h. After that, they were removed from the furnace and allowed to cool rapidly to room temperature. Subsequently, the crystal products were separated from any remaining flux matrix in warm water.

The grown crystals were observed using an optical microscope (Keyence, VH-Z450 + VH-7000C) and a scanning electron microscope (SEM, Hitachi, S-5000). The obtained crystals were investigated by means of X-ray diffraction (XRD, Rigaku, RINT-1500) and electron probe microanalysis (EPMA, JEOL, JXA-8900R). The length, L (parallel to the c axis) and width, W (perpendicular to the c axis) of the ruby crystals were measured. The average length, L_{av}, and width, W_{av}, of the crystals were calculated for each growth run.

Results and Discussion

Many ruby crystals of good quality were isothermally grown up to a size of $L = 2.6$ mm and $W = 2.1$ mm from Li_2O–MoO_3 flux in Runs 1–4, 7, and 8. No growth of ruby crystals was observed in Runs 5 and 6. The grown ruby crystals were basically colored transparent-red. However, crystals grown at a holding temperature of 1050 °C were semitranslucent and dark-red (or black). The basic form of grown crystals was not related to the growth conditions. The crystals were hexagonal bipyramids, that is, double six-sided pyramid bounded by 12 similar triangle faces, with very flat surfaces. Typical ruby crystals are shown in Fig. 1. The grown crystals were investigated by XRD in order to identify the bipyramidal red crystals and to determine the Miller indices of the crystal faces. Figure 2 shows XRD profiles of data for the bipyramidal crystals, pulverized crystallites, and α-Al_2O_3 (corundum) JCPDS.[14] In Fig. 2a, only the diffraction pattern of the $(11\bar{2}3)$ plane can be seen in the bipyramidal crystals. The pulverized crystallites pattern (Fig. 2b) was found to be the same as that of α-Al_2O_3 (Fig. 2c). The presence of Cr atoms, which gave its characteristic red color, was confirmed using EMPA. Furthermore, the variations in the concentration of the major constituents in the grown crystals were investigated using EPMA. Al, O, and Cr atoms were distributed almost homogeneously in the crystals. On the contrary, Mo atoms from the flux and Pt from the crucible were not detected. In addition, based on the XRD pattern, the interfacial angles and the shape of triangular faces, the bipyramidal ruby crystals were found to be surrounded by $\{11\bar{2}3\}$ faces. Figure 3 shows an optical photograph and a drawing of the crystal habit bounded by hexagonal-bipyramidal $\{11\bar{2}3\}$ faces. By a visible observation and EPMA, no inclusion, such as flux or a by-product, was found in ruby crystals grown from the Li_2O–MoO_3 flux as well as the only MoO_3 flux.[2] Furthermore, Li_2O addition, which greatly influences nucleus formation, improved the crystal shapes and color qualities due to dopant homogeneity.

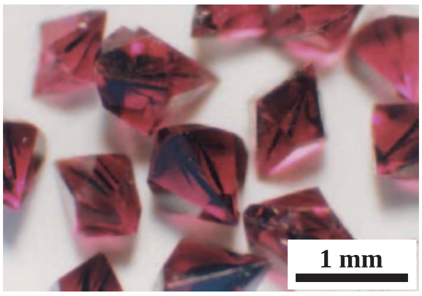

Fig. 1. Optical micrograph showing ruby crystals grown from Li_2O–MoO_3 flux.

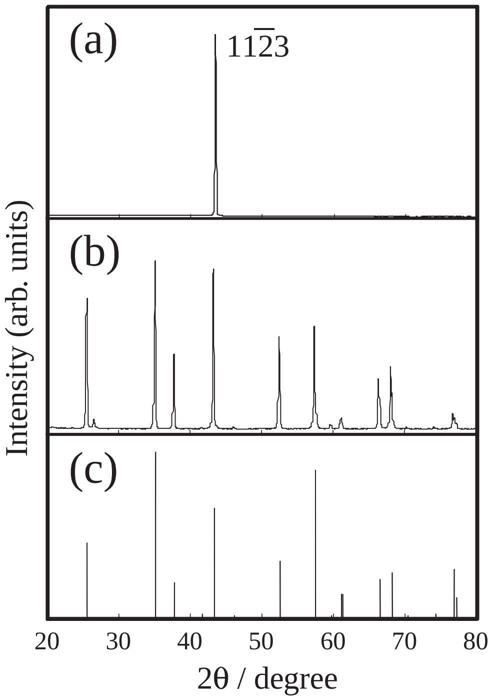

Fig. 2. X-ray diffraction patterns (Cu Kα) of ruby crystals. (a) Hexagonal-bipyramidal crystal of which well-developed face was laid in parallel with the holder plate; (b) pulverized crystallites; (c) α-Al_2O_3 JCPDS data.[14]

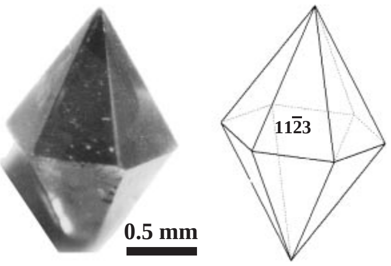

Fig. 3. Typical ruby crystal and drawing of crystal habit bounded by the $\{11\bar{2}3\}$ faces.

The relationship between the flux loss upon evaporation and the concentration of Li_2O added to MoO_3 is shown in Fig. 4. Approximately 99.4 wt % of the MoO_3 flux evaporated over a period of 5 h in the absence of Li_2O. The rate of evaporation was calculated as ca. 1.26×10^{-3} g•h^{-1}•mm^{-2}. The evaporation loss decreased linearly with an increase in the amount of Li_2O. The addition of Li_2O to MoO_3 could make the high-temperature solution relatively involatile owing to the interaction between a basic oxide (Li_2O) and an acidic oxide (MoO_3).

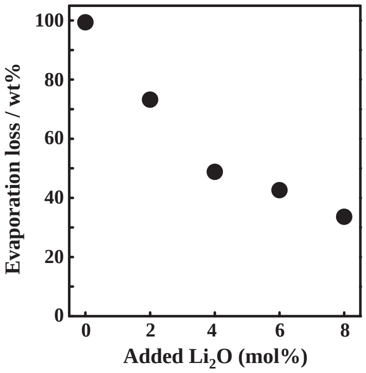

Fig. 4. Relationship between evaporation loss of flux and amount of Li_2O added to MoO_3 (Runs 1–5).

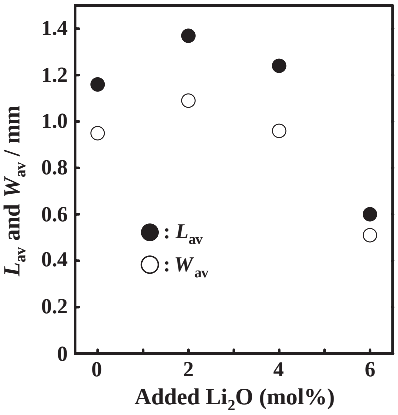

Fig. 5. Variation of average length (L_{av}) and width (W_{av}) values of ruby crystals grown with amount of Li_2O added to MoO_3 (Runs 1–4).

When 0.503 g of Li_2O was added to MoO_3 (8 mol % Li_2O–92 mol % MoO_3), the evaporation loss was only 33.6 wt % and the evaporation rate was calculated to be ca. 4.22×10^{-4} $g \cdot h^{-1} \cdot mm^{-2}$. The flux evaporation loss was found to be determinable by controlling the amount of added Li_2O. Ruby crystals grew from the MoO_3 flux containing up to 0.372 g (6 mol %) of Li_2O (Runs 1–4).

Figure 5 shows the variation in the average length (L_{av}) and width (W_{av}) of the ruby crystals grown with the amount of Li_2O added to MoO_3. As clearly indicated in the Fig. 5, the crystal sizes obviously depended on the Li_2O amounts, that is, the evaporation loss of flux. A great number of slightly small crystals with $L_{av} = 1.16$ mm and $W_{av} = 0.95$ mm, greater than 800, were grown from a solo MoO_3 flux. Because of the high evaporation loss of the flux, the rate of nucleus formation was relatively large, and many small crystals grew onto these nuclei. At 2 mol % Li_2O–98 mol % MoO_3 (Run 2), L_{av} and W_{av} increased to 1.37 mm and 1.09 mm, respectively. The number of crystals was ca. 400 and the yield was 0.949 g. The average weight of the crystals was approximately 2.46×10^{-3} g. Furthermore, the figure and size of grown ruby crystals were relatively uniform, and their faces were well-developed. When the amount of $Li_2O > 2$ mol %, the L_{av} and W_{av} values gradually decreased with an increase in the amount of Li_2O. At 6 mol % Li_2O–94 mol % MoO_3 (Run 4), L_{av} and W_{av} became 0.6 mm and 0.51 mm, respectively, resulting from the low evaporation loss of the flux (ca. 42.6 wt %). The size and number of grown crystals were evidently dependent on the Li_2O amount, in other words, the evaporation loss of the flux. Without Li_2O addition, numerous nuclei are crystallized because of the high evaporation rate, and each of them cannot grow greatly. On the other hand, not only nucleus formation, but also crystal growth is restrained with an increase in Li_2O addition, since the flux evaporation, that is, the driving force of crystal growth is lowered. In the case of 8 mol % Li_2O–92 mol % MoO_3 (Run 5), no ruby crystals grew from the Li_2O–MoO_3 flux. Taking the crystal sizes and qualities into account, 2 mol % of Li_2O added to MoO_3 was found to be the most suitable flux for growing ruby crystals in this study.

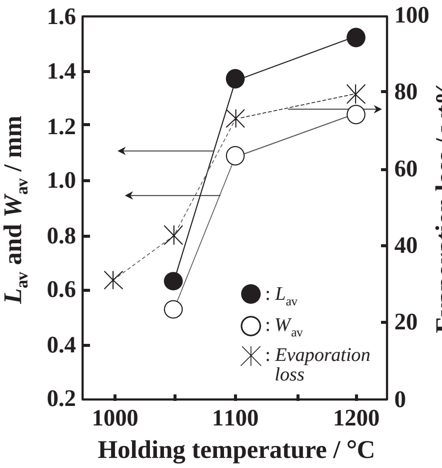

Fig. 6. Relationship between holding temperature and evaporation loss of flux or grown crystal sizes (L_{av} and W_{av}).

The effect of the holding temperature on ruby growth from a high-temperature solution was investigated in Runs 2 and 6–8. Figure 6 shows the relationship between the flux-evaporation loss or the grown crystal size (L_{av} and W_{av}) and the holding temperature. The flux composition was fixed at 2 mol % Li_2O–98 mol % MoO_3. At 1000 °C the evaporation loss was about 30.0 wt %, thereafter linearly increasing with the holding temperature, and reaching approximately 42.9 wt % at 1050 °C, 73.2 wt % at 1100 °C, and 79.6 wt % at 1200 °C. Concerning the averages, at holding temperatures of 1050, 1100, and 1200 °C, the L_{av} and W_{av} values were 0.63 and 0.53 mm, 1.37 and 1.09 mm, and 1.52 and 1.24 mm, respectively. The number and the average weight of the crystals grown at 1200 °C were, respectively, ca. 300 and 4.0×10^{-3} g. The averages gradually increased with increasing the holding temperature. On the other hand, no crystal products were grown at a holding temperature of lower than 1000 °C. These results indicate that the holding temperature, that is, the evaporation loss is closely related to the size of the grown crystals. It is reasonable to suppose that the holding time is elongated in order to grow large crystals.

Platinum crucibles were found to be undamaged after use, with no evidence of an attack from the Li_2O–MoO_3 flux. The flux was thus compatible with platinum at the intentional temperature. The grown crystals could be easily separated from the flux in warm water. In particular, the MoO_3 flux containing large amounts of Li_2O was readily soluble in warm water. The flux-evaporation method using Li_2O–MoO_3, therefore, easily allowed the isothermal crystal growth of ruby.

Conclusion

Red and transparent ruby were easily grown by the evaporation of Li_2O–MoO_3 flux. The forms of the ruby crystals were hexagonal bipyramids, bounded by well-developed $\{11\bar{2}3\}$ faces. The size and number of ruby crystals depended on the evaporation losses of the flux due to the flux compositions and the holding temperatures. The evaporation loss of the flux gradually decreased with an increase in the amount of Li_2O added to MoO_3. The Li_2O acted to control the amount of flux evaporation. The most suitable composition of the flux was 2 mol % Li_2O–98 mol % MoO_3. The ruby crystals grown from the 2 mol % Li_2O–98 mol % MoO_3 flux were up to 2.6 mm (*L*) and 2.1 mm (*W*), and much larger than that grown from the only MoO_3 flux. Furthermore, the addition of Li_2O to the MoO_3 flux improved not only the sizes of the ruby crystals, but also their shapes and qualities. In fact, molybdenum trioxide flux containing a small amount of Li_2O was found to be much more suitable for the growth of bipyramidal ruby crystals than only the MoO_3 flux.

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