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Growth of $MgNb_2O_6$ crystals from a $Na_2Mo_2O_7$ flux

S. OISHI, Y. KAWATANI, T. SUZUKI
Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380-8553, Japan
E-mail: oishish@gipwc.shinshu-u.ac.jp

N. ISHIZAWA
Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Single crystals are essential for a variety of scientific and industrial purposes. The major advantage of a flux method is that crystals grow at a temperature well below the melting point. Another advantage is that well-formed crystals are obtained. Magnesium niobate, $MgNb_2O_6$, exhibits luminescence in the blue region [1, 2]. Crystals of $MgNb_2O_6$ have the orthorhombic columbite-type structure [3, 4]. The compound $MgNb_2O_6$ melts congruently at about 1570 °C [5]. A crystalline powder of $MgNb_2O_6$ has been prepared by a solid state reaction method [1, 3, 4, 6]. Crystals of $MgNb_2O_6$ have been grown by laser-heated pedestal growth [2], chemical transport growth [7, 8], Czochralski growth [9], Verneuil growth [10], and flux growth [6, 11] methods. In flux growth, $Na_2B_4O_7$ [11] and $Na_2B_4O_7$-B_2O_3 [6] have been used successfully as fluxes. The form of the crystals is rod-shaped [6, 11]. Well-formed crystals of $LiNbO_3$ and $CaNb_2O_6$ crystals from Li_2MoO_4 [12, 13] and $Na_2Mo_2O_7$ [14] fluxes, respectively, have been grown. In this work, $Na_2Mo_2O_7$ was chosen as a flux to grow crystals of $MgNb_2O_6$ on the basis of previous experience in growing niobate crystals [12–14]. Sodium dimolybdate has a low melting point with sufficient solubility in water. No report on the growth of $MgNb_2O_6$ crystals from a $Na_2Mo_2O_7$ flux has been published neither has the solubility of $MgNb_2O_6$ crystals in $Na_2Mo_2O_7$ flux been reported. The present paper describes the growth of $MgNb_2O_6$ crystals from a $Na_2Mo_2O_7$ flux by a slow cooling method. The morphology, density and lattice parameters of the resulting crystals were examined.

The solubility of $MgNb_2O_6$ in $Na_2Mo_2O_7$ was determined by measuring the mass loss of $MgNb_2O_6$ crystals in $Na_2Mo_2O_7$ melts at temperatures between 600 and 1100 °C. Mixtures of excess crystals (1–2 mm in length; 0.7–1.5 g) of $MgNb_2O_6$ and $Na_2Mo_2O_7$ powder (1.5–2.3 g) prepared by quenching $Na_2CO_3 + 2MoO_3$ melt were put into platinum vessels. After the mixture was heated for 3 h at a preset temperature, undissolved crystals were present upon quenching. The undissolved crystals were separated from the solidified saturated solution by washing with warm water and reweighed. The loss in mass due to dissolution represents the solubility at that temperature. The eutectic temperature of the $MgNb_2O_6$-$Na_2Mo_2O_7$ system was determined on the basis of differential thermal analysis (DTA). In the flux growth of $MgNb_2O_6$ crystals, reagent-grade MgO (Wako Pure Chemical Industries, Ltd.), Nb_2O_5 (Wako Pure Chemical Industries, Ltd.), Na_2CO_3 (Wako Pure Chemical Industries, Ltd.) and MoO_3 (Tokyo Tungsten Co., Ltd.) were used. An equimolar mixture of MgO and Nb_2O_5 powders was used as a solute. A mixture of $Na_2CO_3 + 2MoO_3$ powders was used as the flux. On the basis of solubility data, a mixture containing 12 mol% solute was prepared. The mass of the mixture was 27.8 g (25.0 g as pseudo-binary system $MgNb_2O_6$-$Na_2Mo_2O_7$). The mixture was put into 30 cm^3 platinum crucible. After the lid was fitted, the crucible was placed in an electric furnace with silicon carbide heating elements. The crucible was heated at a rate of about 45 °C/h to 1100 °C, held at this temperature for 10 h, and then cooled to 500 °C at a rate of 5 °C/h. When the cooling program was completed, the crucible was allowed to cool down to room temperature. The crystalline products were then separated by dissolving the flux in warm water. The obtained crystals were examined using a light microscope and a scanning electron microscope (SEM). The crystal phases were identified by X-ray diffraction (XRD) and the lattice parameters were obtained. The length and width of the grown crystals were measured. The interfacial angles of the crystals were also measured by use of light micrographs of grown crystals. The density of crystals was determined pycnometrically. A SEM equipped with an energy dispersive X-ray spectrometer (EDS) was used to study any variations in the concentration of the major constituents in the grown crystals.

The temperature dependence of the solubility of $MgNb_2O_6$ crystals in $Na_2Mo_2O_7$ is shown in Fig. 1. At 600 °C, $MgNb_2O_6$ was dissolved in $Na_2Mo_2O_7$ at a concentration of about 3.2 mol% (about 2.89 g in 100 g $Na_2Mo_2O_7$). The solubility gradually increased with increasing temperature, with $MgNb_2O_6$ reaching a solubility of about 12.4 mol% (about 12.4 g in 100 g $Na_2Mo_2O_7$) at 1100 °C. The obtained solubility curve had an appreciable temperature coefficient of solubility so that $MgNb_2O_6$ could be crystallized by slowly cooling the solution from 1100 °C. Thus, it was confirmed in solubility experiments that $Na_2Mo_2O_7$ was a suitable flux for growing $MgNb_2O_6$ crystals. The $MgNb_2O_6$-$Na_2Mo_2O_7$ system had a eutectic

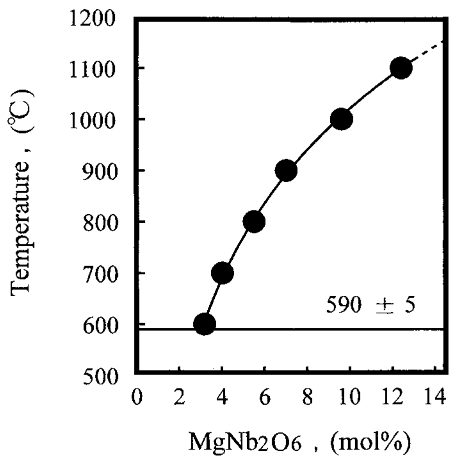

Figure 1 Solubility of $MgNb_2O_6$ in $Na_2Mo_2O_7$ as a function of temperature.

temperature of $590 \pm 5\,^{\circ}C$ on the basis of the DTA data. Judging from the solubility curve and eutectic temperature, the eutectic composition was considered to be around 3 mol% $MgNb_2O_6$–97 mol% $Na_2Mo_2O_7$. Fig. 1 shows that mixture containing 12 mol% solute is unsaturated at a soak temperature of $1100\,^{\circ}C$. It was expected that large crystals could be grown from the solution on subsequent slow cooling.

Well-formed rod-shaped $MgNb_2O_6$ crystals having lengths of up to 5.1 mm and widths of 2.7 mm were grown from the $Na_2Mo_2O_7$ flux. The obtained crystals were identified as $MgNb_2O_6$ by their powder XRD patterns, using data given on the ICDD PDF [3]. The crystals were light brown and transparent. Typical rod crystals of $MgNb_2O_6$ are shown in Fig. 2. The aspect ratios of the grown crystals were in the region of 1.5–3.1. In this high-temperature solution, the difference between the soak and liquidus temperatures was about $20\,^{\circ}C$ on the basis of the solubility curve shown in Fig. 1. It was found that large crystals were obtained when the soak temperature was above the liquidus temperature. This tendency is similar to that for the growth of $CaWO_4$ crystals from Na_2WO_4 flux [15]. The mixture containing 12 mol% solute produced 1.71 g crystals. This means that about 64 mass% of the solute (2.67 g) was retrieved as rod crystals from the solution. The theoretically expected yield of $MgNb_2O_6$ crystals was calculated to be 2.06 g on the basis of the Lever Rule. The mass of the obtained crystals was about 83% of the calculated value. The agreement between the observed and calculated mass of grown crystals was good. In the flux growth run, evaporation of $Na_2Mo_2O_7$ flux was less than 2 mass%.

Crystals of $MgNb_2O_6$ were hexagonal rods with prominent faces. The surfaces of these crystals were very flat as shown in Fig. 2. In order to determine the Miller indices of the crystal faces, the orientated well-developed crystals were investigated by XRD. Only the diffraction intensities of the (020), (040) and (060) planes were predominant, indicating that the indices of the prismatic faces were {010}. The interfacial angle between the (010) and adjacent prismatic faces was $62 \pm 1\,^{\circ}$. This value was in good agreement with the calculated interfacial angle of $62.0\,^{\circ}$ between the (010) and (032) faces. It was found that the {010} and {032} faces were arranged as prisms. The interfacial angle between the (010) and the prominent faces was $40 \pm 1\,^{\circ}$. The indices of the prominent face was found to be {130}. In this manner, it was concluded that the rod crystals were bounded by the {010}, {032} and {130} faces as shown in Fig. 3. The rod crystals were elongated in the $\langle 100 \rangle$ directions, which correspond to the directions for the length mentioned before. The EDS data showed that the magnesium and niobium atoms were distributed almost homogeneously in the grown crystals. According to the results, it was considered that oxygen atoms were also distributed almost homogeneously. Sodium and molybdenum from the flux were not detected in the crystals. In addition, flux inclusions were rarely found in the crystals. Based on the powder XRD data, the lattice parameters of the $MgNb_2O_6$ crystals were $a = 5.702(3)$ Å, $b = 14.191(3)$ Å and $c = 5.033(2)$ Å. These values agree approximately with

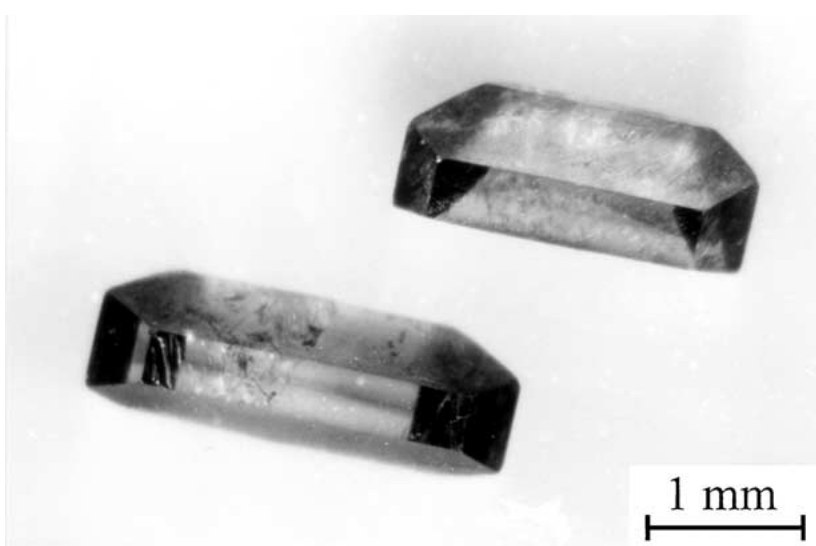

Figure 2 $MgNb_2O_6$ crystals grown from $Na_2Mo_2O_7$ flux.

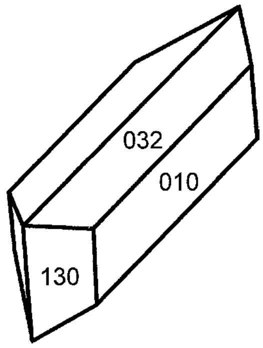

Figure 3 Schematic drawing of the habit of $MgNb_2O_6$ crystal.

those ($a = 5.700$ Å, $b = 14.193$ Å and $c = 5.032$ Å) from the literature [3]. The density was pycnometrically determined to be 5.01 ± 0.02 g/cm^3. This was in good agreement with the calculated (4.99 g/cm^3) and literature (4.995 g/cm^3)[3] values.

Light brown and transparent $MgNb_2O_6$ crystals with lengths of up to 5.1 mm and widths of 2.7 mm were grown from a $Na_2Mo_2O_7$ flux for the first time by the slow cooling method. The resulting rod crystals were well-formed and elongated in the ⟨100⟩ directions. The solubility of $MgNb_2O_6$ crystals in $Na_2Mo_2O_7$ flux gradually increased with a rise in temperature. Sodium dimolybdate was found to be a suitable flux to grow $MgNb_2O_6$ crystals.

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