A New Flux, NaCl, to Grow Layered Perovskite-Type $Na_2Ca_2Nb_4O_{13}$ Crystals

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Sodium chloride was successfully used as a new flux to grow the layered perovskite-type $Na_2Ca_2Nb_4O_{13}$ crystals by a slow cooling method. The rectangular thin plate-shaped crystals with sizes up to 1.2 mm × 1.2 mm × 0.03 mm were grown. The obtained crystals were colorless and transparent. The most suitable solute content was 0.4 mol%.

Layered perovskite-type compounds are attractive because of their properties such as luminescence and ionic conduction through the interlayer. A considerable number of the layered perovskite-type niobates have been synthesized by the solid state reaction, ion-exchange reaction, and intercalation method.[1-8] One of the niobates is $Na_2Ca_2Nb_4O_{13}$ with four cubes of perovskite layer. The powder crystals of $Na_2Ca_2Nb_4O_{13}$ have been synthesized by the solid state reaction and ion-exchange reaction methods.[3,4] The well-formed single crystals have been grown for the first time from Na_2SO_4 flux.[9] On the basis of the single crystal X-ray diffraction technique, the crystal structure had an orthorhombic symmetry with space group $Bb2_1m$.[10,11] Perovskite-type layers with formula $[(Ca_2Na)Nb_4O_{13}]^-$ are concatenated by Na^+ cations near the interlayer.[10,11] No report on the growth of $Na_2Ca_2Nb_4O_{13}$ crystals from the other fluxes has been published. The present paper describes the growth of $Na_2Ca_2Nb_4O_{13}$ crystals from a NaCl flux by a slow cooling method. The effect of the solute content on the crystal growth was studied. The morphology and crystal structure were also examined.

In this work, NaCl was chosen as a flux to grow crystals of $Na_2Ca_2Nb_4O_{13}$. Sodium chloride has a low melting point with sufficient solubility in water. In addition, NaCl is nontoxic to humans.

Reagent-grade Na_2CO_3, $CaCO_3$, Nb_2O_5, and NaCl were used for the growth of $Na_2Ca_2Nb_4O_{13}$ crystals. A mixture of $Na_2CO_3+2CaCO_3+2Nb_2O_5$ powders was used as a solute. Sodium chloride powder was used as the flux. Mixtures containing solute of 0.1 to 1.5 mol% were prepared in 0.1 mol% increments. The masses of the mixtures were in the region of 25.1 to 25.7 g (25.0 g as $Na_2Ca_2Nb_4O_{13}$-NaCl). The mixtures were put into platinum crucibles of 30 cm^3 capacity. After closing the lids, the crucibles were placed in an electric furnace with silicon carbide heating elements. The crucibles were heated to 1373 K at a rate of 45 K h^{-1}, held at this temperature for 10 h, and then cooled to 723 K at a rate of 5 K h^{-1}. When the cooling program was completed, the crucibles were 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 an optical microscope and a scanning electron microscope (SEM). The width (W: perpendicular to the ⟨001⟩ directions) of two sides and the thickness (T: parallel to the ⟨001⟩ directions) of rectangular crystals were measured. After each growth run, the average width (W_{av}) and thickness (T_{av}) of the first 20 largest crystals were calculated. Crystals were identified by the powder X-ray diffraction (XRD). The crystallinity and symmetry of the crystals were examined by the precession camera. Cell dimensions were determined from 25 reflections measured by a four-circle diffractometer with MoKα radiation. The mass loss of the grown crystals was checked by the thermogravimetry (TG).

Rectangular thin plate-shaped $Na_2Ca_2Nb_4O_{13}$ crystals with widths up to 1.2 mm × 1.2 mm and thicknesses of 0.03 mm were grown from the NaCl flux in all the growth experiments. The obtained crystals were colorless and transparent. They were identified as $Na_2Ca_2Nb_4O_{13}$ by their XRD patterns, using published data.[10,11] Typical $Na_2Ca_2Nb_4O_{13}$ crystals are shown in Figure 1. The W_{av} value of the grown crystals is plotted against the solute content in Figure 2. Small crystals with W_{av}= 0.21 mm were grown from a mixture containing 0.1 mol% solute. The W_{av} value increased with increasing solute content. Large crystals with W_{av}=0.58 mm were grown from a mixture containing 0.4 mol% solute. Any further increase in the solute content resulted in a decrease in the W_{av} value. This indicates that the solute was consumed during the formation of nuclei in preference to the crystal growth. On the other hand, the T_{av} values of the crystals grown at all the experiments were about 0.01 mm. The values were independent of the solute content since the growth rate of the ⟨001⟩ directions was very low. Well-formed plate crystals were grown from mixtures containing 0.1 to 0.8 mol% solute. Taking the sizes and forms of grown crystals into account, the optimum solute content for the growth of $Na_2Ca_2Nb_4O_{13}$ crystals was 0.4 mol%. During these growth runs, the ratios of evaporation of the NaCl flux were in the region of 20 to 40 mass%. The platinum crucibles

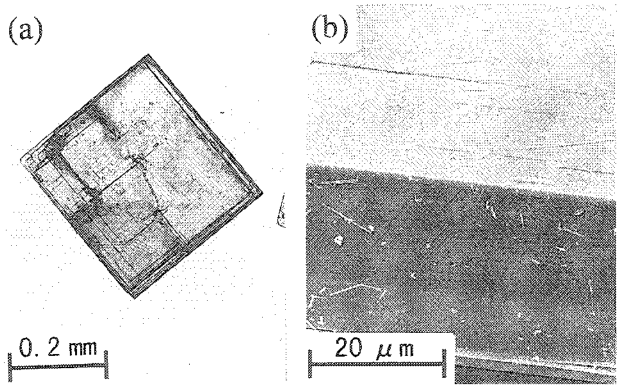

Figure 1. Optical micrograph (a) and SEM photograph (b) showing $Na_2Ca_2Nb_4O_{13}$ crystals grown from NaCl flux.

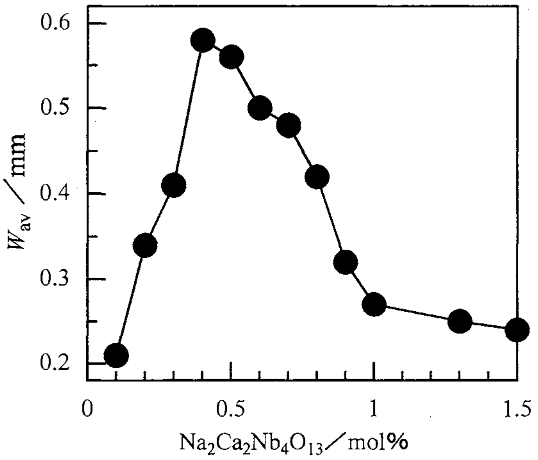

Figure 2. Variation in average width, W_{av}, of plate crystals of $Na_2Ca_2Nb_4O_{13}$ with solute content.

were found to be undamaged after use. The resulting crystals could be readily separated from the flux in warm water because NaCl was easily soluble.

The basal faces of $Na_2Ca_2Nb_4O_{13}$ crystals obtained were flat as shown in Figure 1. The XRD patterns of orientated plate crystals showed that the diffraction intensities of the (00*l*) were predominant. The indices of well-developed basal faces were {001}. On the {001} faces, very thin growth layers were observed. It can therefore be presumed that growth on the basal faces occurred by spreading of layers. The two-dimensional growth is consistent with the layered structure of $Na_2Ca_2Nb_4O_{13}$. The side faces were also flat and there were often parallel lines or grooves on the flat side faces. The TG data showed that the loss of dry crystals was only 0.4 mass% when the pulverized crystals were heated from room temperature to 773 K. No water was detected in the crystals obtained in this work. The precession photographs showed a similar diffraction pattern to that of $Na_2Ca_2Nb_4O_{13}$ crystals grown in the Na_2SO_4 flux.[11] Therefore, it was suggested that the crystal structure is essentially of the layered perovskite type with the layer thickness corresponding to the four corner-shared octahedra. The lattice parameters were determined as a=0.5489 (1) nm, b=0.5519 (1) nm, and c=3.6360 (7) nm, suggesting an orthorhombic symmetry. The $Na_2Ca_2Nb_4O_{13}$ crystals obtained from the Na_2SO_4 flux were reported to have the orthorhombic space group $Bb2_1m$ with a=0.5474 (3) nm, b=0.5510 (3) nm, and c=3.6150 (10) nm.[11] The a and b lengths of these crystals agreed with each other within the experimental errors. However the c length of the crystal grown in the NaCl flux is about 0.02 nm longer than that grown in the Na_2SO_4 flux. The difference in c length between these crystals may originate in different atomic arrangement of the interlayer, as was inferred in our previous paper.[11] A detailed structure analysis of the present crystal is in progress.

As a by-product, rectangular thin plate-shaped $NaCa_2Nb_3O_{10}$ crystals with sizes up to 0.1 mm × 0.1 mm × 0.01 mm were also grown. The $NaCa_2Nb_3O_{10}$ crystals were much smaller than the $Na_2Ca_2Nb_4O_{13}$ crystals. The $NaCa_2Nb_3O_{10}$ crystals amounted to approximately 20% of all crystals with widths up to 0.1 mm. The structure of $NaCa_2Nb_3O_{10}$ crystals had a monoclinic symmetry. The lattice parameters were a=0.5509 (2) nm, b=0.5475 (1) nm, c=2.8456 (10) nm, and β=90.48 (3)°.

Sodium chloride was successfully used as a new flux to grow the layered perovskite-type $Na_2Ca_2Nb_4O_{13}$ crystals. The NaCl flux was preferable in the sizes of grown crystals to the use of Na_2SO_4 flux. However, the NaCl flux had the disadvantage of producing the by-product crystals.

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