Growth of Layered Perovskite-Type $Na_2Ca_2Nb_4O_{13}$ Crystals by the Na_2SO_4 Flux Method

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(Received January 5, 1998; CL-980006)

Rectangular thin plate-shaped crystals of layered perovskite-type $Na_2Ca_2Nb_4O_{13}$ were grown from a Na_2SO_4 flux by a slow cooling method. The crystals of sizes up to 0.8 mm × 0.8 mm × 0.05 mm were grown. The obtained crystals were colorless and transparent. The most suitable solute content was 6 mol%. The structure had a pseudotetragonal symmetry.

Homologous series with layered perovskite-type structure are attractive because of their properties such as ionic conduction and superconductivity. A considerable number of the layered perovskite niobates have been synthesized by the solid state reaction, ion-exchange reaction, and intercalation methods.[1-8] There have been reported three series of layered perovskites; Ruddlesden-Popper, Auriviellius, and Dion-Jacobson series.[9] The compound of $Na_2Ca_2Nb_4O_{13}$ is the n=4 member of the Dion-Jacobson series $Na^+[Ca_2Na_{n-3}Nb_nO_{3n+1}]^-$. The n denotes the thickness of the corresponding perovskite layers. The crystals of $Na_2Ca_2Nb_4O_{13}$ have been synthesized by the solid state reaction and ion-exchange reaction method.[1,2] The form of the obtained crystals was powder.[1,2] No report on the flux growth of $Na_2Ca_2Nb_4O_{13}$ crystals has been published. The present paper describes the growth of $Na_2Ca_2Nb_4O_{13}$ crystals from a Na_2SO_4 flux by a slow cooling method. The effect of the solute content on the crystal growth was studied. The morphology, crystal structure, and imperfections of the resulting crystals were examined.

In the flux growth of crystals, the choice of flux for a desired material is difficult because of the lack of fundamental data such as phase diagrams. A good flux should have a crystal-chemical similarity between solute and flux. On the other hand, crystal-chemical differences should exist in order to prevent solid solubility between solute and flux. In this work, Na_2SO_4 was chosen as a flux to grow the crystals of $Na_2Ca_2Nb_4O_{13}$. Sodium sulfate has a common cation (Na^+) with the solute. The anionic valency (SO_4^{2-}) of the flux is different from that ($Ca_2NaNb_4O_{13}^-$) of the solute. In this way, there are a similarity and a difference between Na_2SO_4 and $Na_2Ca_2Nb_4O_{13}$. Sodium sulfate was expected to be a suitable flux.

Reagent-grade Na_2CO_3, $CaCO_3$, Nb_2O_5, and Na_2SO_4 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 sulfate powder was used as a flux. Mixtures containing solute of 2, 4, 6, 8, 10, 12, 14, and 16 mol% were prepared. The masses of the mixtures were about 30 g. The mixtures were put into platinum crucibles of 30 cm^3 capacity. The lids were fitted and the crucibles were placed in an electric furnace with silicon carbide heating elements. The furnace was heated at a rate of about 45 $℃h^{-1}$ to 1100 ℃, held at this temperature for 10 h, and then cooled at a rate of 5 $℃h^{-1}$ to 500 ℃. When the cooling program was completed, the furnace 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 an optical microscope and a scanning electron microscope (SEM). The crystal width (W: perpendicular to the <001> direction) of two sides and the thickness (T: parallel to the <001> direction) of rectangular crystals were measured. During respective growth runs, the average width (W_{av}) and thickness (T_{av}) of the first 30 largest crystals were calculated. An electron prove microanalyser (EPMA) and an inductively coupled plasma (ICP) spectrometer were used to determine the atomic ratio of Na:Ca:Nb of the grown crystals. The crystal structure was determined by the use of a four-circle diffractometer employed with MoKα radiations monochromated by a graphite plate at room temperature. The crystals were identified by X-ray diffraction (XRD). The mass loss of the grown crystals was checked on the basis of the measured differential thermal analysis (DTA) curves.

Rectangular thin plate-shaped $Na_2Ca_2Nb_4O_{13}$ crystals of widths up to 0.8 mm × 0.8 mm and thicknesses of 0.05 mm were

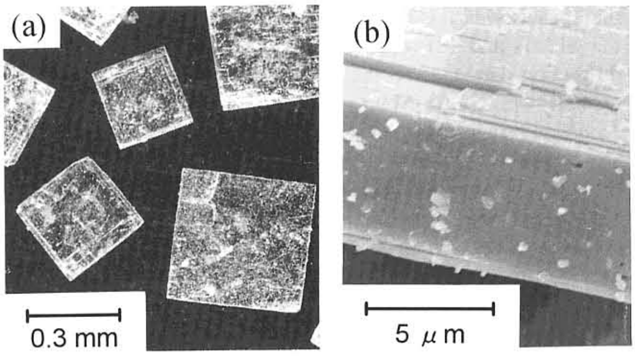

Figure 1. Optical micrograph (a) and SEM photograph (b) showing $Na_2Ca_2Nb_4O_{13}$ crystals grown from Na_2SO_4 flux.

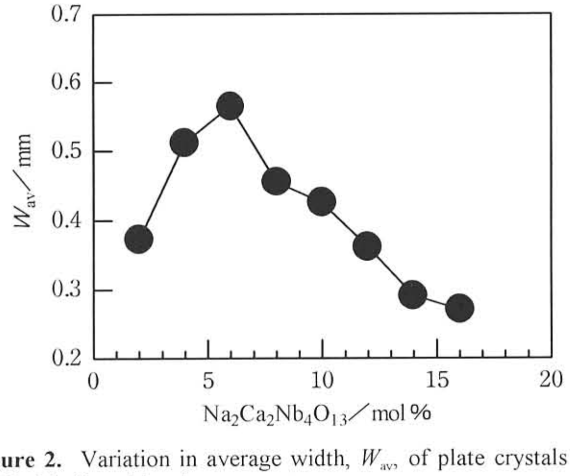

Figure 2. Variation in average width, W_{av}, of plate crystals of $Na_2Ca_2Nb_4O_{13}$ with solute content.

grown from the Na_2SO_4 flux in all the growth experiments. The obtained crystals were colorless and transparent. Typical 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 of W_{av}=0.37 mm were grown from a mixture containing 2 mol% solute. The W_{av} value increased as the solute content increased. Large crystals of W_{av}=0.57 mm were grown from a mixture containing 6 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 0.02 mm. The values were independent of the solute content since the growth rate of the <001> direction was low. Well-formed plate crystals were grown from mixtures containing 2-8 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 6 mol%. During these growth runs, evaporation of the Na_2SO_4 flux was less than 3 mass%. The influence of the evaporation on the crystal growth was negligible. The resulting crystals could be readily separated from the flux in warm water because Na_2SO_4 was easily soluble.

As shown in Figure 1, the basal faces of $Na_2Ca_2Nb_4O_{13}$ crystals obtained were flat. On the basal faces, very thin growth layers were observed. It can therefore be presumed that growth on the basal faces occurred by a spreading of layers. The side faces were also flat. Sometimes there were parallel lines or grooves on the flat side faces. The atomic ratio of Na:Ca:Nb of the crystals was 1:1:2 within experimental errors on the basis of the EPMA and ICP data. In addition, the single crystal X-ray diffraction data showed that the chemical formula of the grown crystals was $Na_2Ca_2Nb_4O_{13}$ in the member n=4 of the Dion-Jacobson series. No water was observed in the crystals. The peak search procedure using a four-circle diffractometer suggested a tetragonal symmetry with a=0.3883(3) and c=3.617(5) nm, containing two molecules of $Na_2Ca_2Nb_4O_{13}$ in the unit cell. However, a detailed analysis revealed a slight deviation of γ angle by 0.37° from 90°. The true cell appeared to be orthorhombic with a=0.5479(2), b=0.5517(2), and c=3.617(2) nm, by taking the a and b axes along [110] and $[\bar{1}10]$ of the tetragonal cell, respectively. In spite of small orthorhombic distortion of the lattice, the structure was solved assuming tetragonal $I4/mmm$ because no significant difference was found among the intensities of equivalent reflections. A schematic representation of the crystal structure of $Na_2Ca_2Nb_4O_{13}$ is shown in Figure 3. Layers with formula $[Ca_2NaNb_4O_{13}]^-$ were concatenated by Na^+ cations near the interlayers. These lattice parameters are close to the ones (a=0.38716(2) and c=3.6937(2) nm: tetragonal system) of $Na_2Ca_2Nb_4O_{13}$ powder obtained by the ion-exchange reaction method.[2] The powder was stable in the temperature range from 350 to 600 ℃.[2] The stable phase at room temperature was a hydrated compound $Na_2Ca_2Nb_4O_{13}\cdot 1.7H_2O$ (a=0.38740(1) and c=4.1605(2) nm: tetragonal system).[2] The lattice parameter c is sensitive to the amount of water. The DTA data showed that the loss of dry plate crystals obtained in this work was only 0.2 mass% when the crystals were heated from room temperature to 500 ℃. The XRD patterns of orientated plate crystals showed that the diffraction intensities of the (00l) were predominant. The indices of well-developed rectangular faces were {001}. The EPMA data showed that sodium, calcium, niobium, and oxygen were almost homogeneously distributed. Flux inclusions were rarely found in the crystals. Impurity incorporation of Pt from the crucible material was also not detected in the crystals.

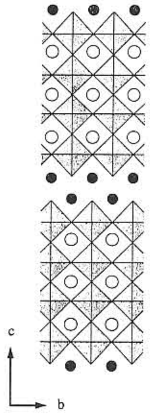

Figure 3. Schematic representation of the structure of $Na_2Ca_2Nb_4O_{13}$ viewed along the a axis. Neighboring perovskite-type slabs with corner-shared NbO_6 octahedra are shifted along the body diagonal direction. Black and white circles represent Na atoms at the interlayer, and Ca and Na atoms in the layer, respectively.

The detailed crystal structure of $Na_2Ca_2Nb_4O_{13}$ will be published elsewhere.

A part of this work was carried out under the Collaborative Research Project of the Materials and Structures Laboratory, Tokyo Institute of Technology.

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