

Synthesis of KNbO_3 in Water

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Fine particles of potassium niobate KNbO_3 were prepared by a new colloid chemistry method. A rock-salt-type KF block in layered perovskite, $\text{K}_2\text{NbO}_3\text{F}$, with a K_2NiF_4 type structure was selectively dissolved in water to produce perovskite nanosheets at room temperature. The self-assembly of perovskite nanosheets in a colloidal solution gave well crystalline potassium niobate powders. The crystal structure was determined by a Rietveld refinement of a neutron powder diffraction pattern.

Key words: Soft Chemistry, Nanosheet, Niobate, Perovskite, Crystal Structure

1. INTRODUCTION

Poisonous lead causes serious damage to both humans and the environment. Therefore, many lead-free ferroelectric materials such as potassium niobate, KNbO_3 , and Bi-based layered perovskites have been extensively investigated for application in lead-free piezoelectric devices. Perovskite-type potassium niobate is the most promising material for lead-free piezoelectrics due to its large electromechanical coupling factor [1, 2]. However, KNbO_3 powder prepared by conventional solid state reactions exhibited poor sinterability in a subsequent sintering process at higher temperature. In order to obtain submicron powders with good sinterability, many solution processes such as hydrothermal reaction have been investigated [3-5].

The aim of the present work was to prepare and to characterize nano-scaled powders of lead-free perovskite type piezoelectrics, KNbO_3 . Interlayer KF block in a layered perovskite, $\text{K}_2\text{NbO}_3\text{F}$, can be selectively dissolved in water to produce niobate nanosheets at room temperature [6-9]. Subsequent self-assembly process among perovskite nanosheets in a colloidal solution could yield a nanosized KNbO_3 particles at room temperature. The crystal structure of KNbO_3 synthesized by a new soft chemical method was investigated by a Rietveld refinement using neutron powder diffraction pattern.

2. EXPERIMENTAL

High-purity KF, K_2CO_3 and Nb_2O_5 powders were weighed at a ratio of $\text{KF} : \text{K}_2\text{CO}_3 : \text{Nb}_2\text{O}_5 = 2.6 : 1 : 1$, finely ground, mixed and pressed into a disk-shaped pellet of 10 mm diameter at a pressure of 30 MPa for 10 min. A 30% molar excess of KF was added to

compensate for loss due to volatilization. The pellet was heated at 1063 K for 1 h in air. A precursor of $\text{K}_2\text{NbO}_3\text{F}$ was cooled to room temperature and finely ground.

Preparation of colloidal solutions containing the perovskite nanosheets was carried out using distilled water by stirring precursor, $\text{K}_2\text{NbO}_3\text{F}$, powders at room temperature for 2 h. Simple test tubes or test cups can be used as the reaction vessels. After the colloidal solution was filtered by a membrane filter (pore size, 450 nm), the colloidal particle can be separated by a centrifugation of the solution. The precipitate was washed with distilled water and air-dried.

The resultant products were characterized by an electron probe microanalysis (EPMA), X-ray fluorescence spectroscopy (XRF) and powder X-ray diffraction (XRD) analysis. The powder neutron diffraction data for structural analysis were collected using a Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, of Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai [10]. An incident neutron wavelength λ was 0.18207(7) nm. The fine powder sample was enclosed in a cylindrical vanadium vessel. The data were collected on thoroughly ground powders by a multi-scanning mode in the 2θ range from 3° to 153° with a step width of 0.1° . Rietveld structure refinement was carried out with the program RIETAN2000 [11]. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used to observe the morphology of powder products.

3. RESULTS AND DISCUSSION

An existence of colloidal particles in the solution was identified by an observation of the Tyndall effect for the filtered solution. Clearly, the filtered solution is a colloidal solution consisting of many fine particles suspended in water. The colloidal particles were also examined by TEM observation to directly observe the morphology of the particles. As shown in Fig. 1, the colloidal particles consist of nanolayer sheets of the precursor, $\text{K}_2\text{NbO}_3\text{F}$. Therefore, these observations show that layered niobate-perovskite, $\text{K}_2\text{NbO}_3\text{F}$, is exfoliated into single layers in water without any intercalants such as tetrabutylammonium [12].

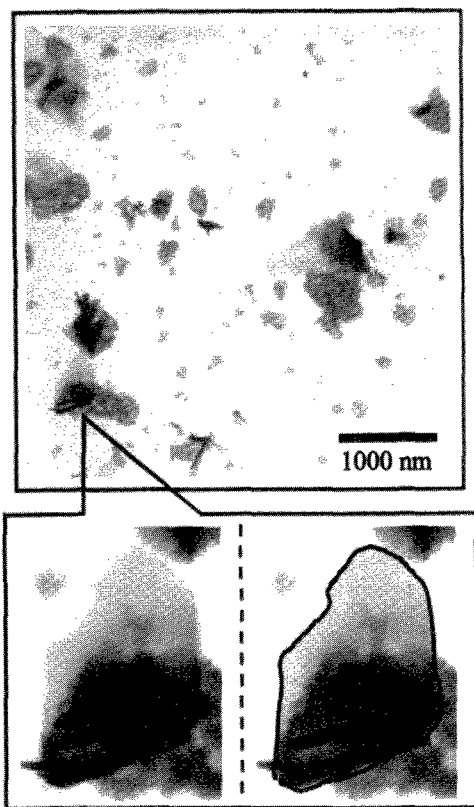


Fig. 1 TEM images of the perovskite nanosheet after immersion in water.

In the centrifugation process, the exfoliated nanosheets of niobate were stacked layer-by-layer on other nanosheets by a self-assembling reaction. The reaction mechanism of this new colloid chemistry technique is explained as follows. When a layered perovskite precursor, $\text{K}_2\text{NbO}_3\text{F}$, is immersed in water at room temperature, the rock-salt-type block, KF , is selectively dissolved in water. Subsequent to the release of fluoride and potassium ions to the liquid phase, restacking of perovskite nanosheets is possible. EPMA data indicates

that all of the fluoride ions and half of the interlayer potassium ions were removed from the solid phase upon the filtration of the solution. From XRF analysis, K/Nb ratios of the soft chemical samples were found to be nearly equal to the stoichiometric K/Nb ratio (± 0.05).

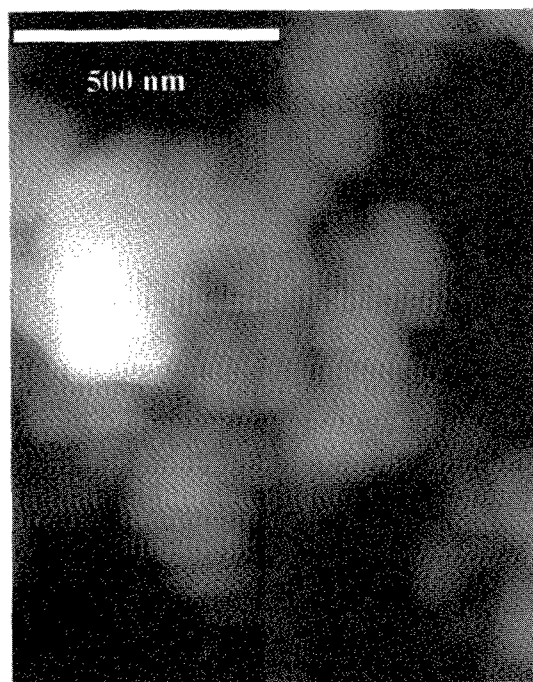


Fig. 2 AFM image of the soft chemical KNbO_3 .

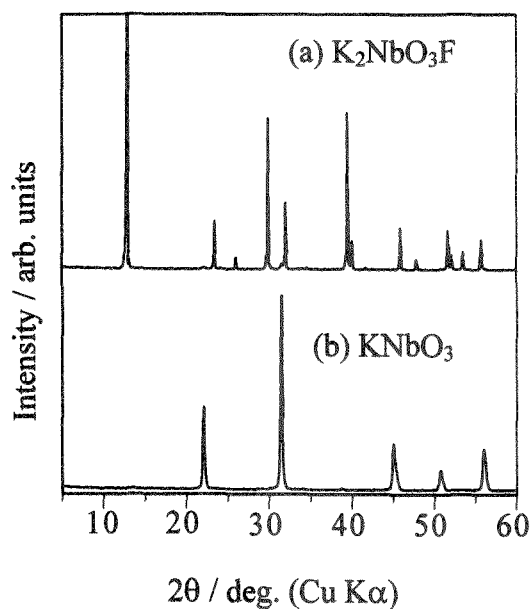


Fig. 3 XRD patterns of precursor, $\text{K}_2\text{NbO}_3\text{F}$ and KNbO_3 prepared by the colloid chemistry method.

The AFM image of the soft chemically produced KNbO_3 powders is shown in Fig. 2. The particles with a size of about 100 - 300 nm were observed in the powder samples after centrifugation. Figure 3 shows the XRD patterns of the precursor, $\text{K}_2\text{NbO}_3\text{F}$, and KNbO_3 prepared by the colloid chemistry method. The XRD pattern of the sample before immersion is consistent with the previously reported literature values ($a = 0.3956$ and $c = 1.3670$ nm) [6]. $\text{K}_2\text{NbO}_3\text{F}$ crystallized in a tetragonal symmetry with space group $I4/mmm$ with $a = 0.39569(1)$ and $c = 1.37010(5)$ nm. On the other hand, the XRD pattern of the fine powder sample after centrifugation shows formation of cubic-like perovskite at room temperature. As shown in Fig. 3, powder XRD pattern seems that the crystal structure of the soft chemically produced sample is different from the orthorhombic form of the KNbO_3 prepared by a high-temperature process (solid state reaction). A similar behavior is also observed in the hydrothermal synthesis of perovskite BaTiO_3 at low temperatures [13, 14]. This effect can be attributed to the incorporation of an OH group into the perovskite lattice or to the particle size effect on the microscopic cooperative phenomenon.

From the XRD analysis, the reasons for the crystallization of different crystal structures for KNbO_3 are not difficult to be explained. To investigate the precise crystal structure, the powder neutron diffraction data were collected from the soft chemical KNbO_3 . Preliminary Rietveld analysis indicated that the superstructure peaks could not be indexed on the basis of the cubic space group. Figure 4 shows the powder neutron diffraction pattern fitting for KNbO_3 prepared by the soft chemistry method. All of the reflections matched with those of the orthorhombic symmetry.

The Rietveld refinement of the neutron powder diffraction pattern show that the crystal structure of the soft chemical sample essentially maintained the orthorhombic form which is the same as that of KNbO_3 by high-temperature solid state reaction. The crystallographic data of soft chemical KNbO_3 are shown in Table I. However, relaxation of the crystal structure by room temperature synthesis greatly relieves the orthorhombic distortion of KNbO_3 product. The origin of their crystallographic behavior is unclear at present.

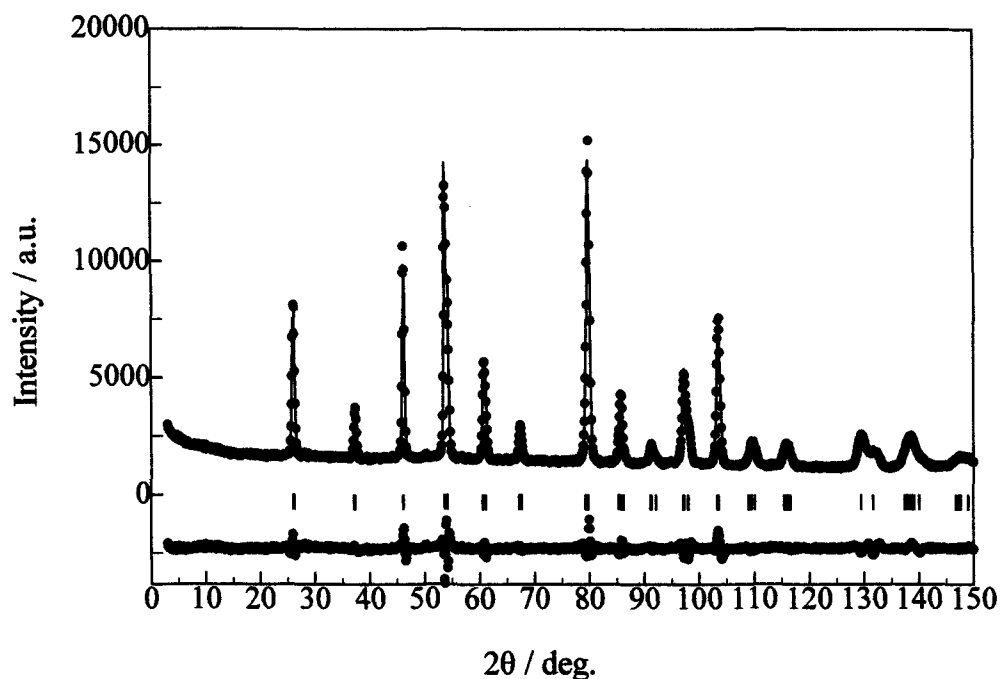


Fig. 4 Powder neutron diffraction pattern fitting for soft chemical KNbO_3 . The calculated and observed patterns are shown on the top by the solid line and dots, respectively. The vertical marks in the middle show the positions calculated for Bragg reflections. The trace on the bottom is a plot of the difference between the calculated and observed intensities.

Table I. Structural parameters and reliable factors of soft chemical KNbO_3 .

Atom	Site	x	y	z	$B_{eq}(\times 10^{-2}\text{nm}^2)$
K	2a	0.5	0	0.486(7)	0.9(1)
Nb	2b	0	0	0	0.5(1)
O(1)	2a	0.5	0	0.962(2)	0.4(2)
O(2)	4e	0	0.254(1)	0.732(3)	0.9(1)
Lattice parameters (nm)		: $a = 0.39906(6)$, $b = 0.5688(1)$, $c = 0.5698(1)$			
Reliable factors		: $R_{wp} = 3.65\%$, $R_p = 2.84\%$, $R_I = 3.57\%$, $R_F = 1.39\%$			

4. CONCLUSIONS

A new colloid chemistry process was developed for synthesizing nanosize KNbO_3 particles using water as a reaction medium at room temperature. The exfoliation - restacking mechanism for reconstruction of perovskite nanosheets can explain the observed soft chemical reaction. That is a typical build-up process. The submicron sized KNbO_3 fine particles may be advantageous for subsequent sintering of the product or fabrication of thin films.

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