

## Synthesis of $\text{KNbO}_3$ thin film by self-assembly of perovskite nanosheets

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A  $\text{KNbO}_3$  thin film was synthesized on a quartz substrate by self-assembly of exfoliated perovskite nanosheets suspended in the aqueous solution. XAFS experiments show a difference of the bonding distance between Nb and O in colloidal suspensions and  $\text{KNbO}_3$  bulk samples. The thin film was characterized using XRD analysis. The molar extinction coefficient of the colloidal suspension and absorbance of the thin film were examined using UV-vis absorption spectra. Respective thickness of perovskite nanosheet aggregate thin films were examined using AFM and SEM. The UV-vis absorption spectra of the films showed an increase in absorbance with increasing the thickness of thin film, suggesting growth of a self-assembled multilayer comprising perovskite nanosheets and  $\text{K}^+$  ions.

Keywords: Soft chemistry, Perovskite, Layered perovskite, nanosheet, self-assembly

### 1. INTRODUCTION

Potassium niobate ( $\text{KNbO}_3$ , denoted as KN) has a large electromechanical coupling factor [1-2]. Superior ferroelectric properties make it a very promising material for high-quality lead-free piezoelectric and nonlinear optical devices. Several papers have described the preparations of the KN thin films. The KN thin film can be prepared by following method: metalorganic chemical vapor deposition (MOCVD) [3], pulsed-laser deposition [4], sputtering [5], liquid-phase epitaxy (LPE) [6] and sol-gel technique [7]. However, these preparation methods have similar disadvantages as high-temperature requiring temperature ranging between 873 K and over 1173 K to obtain crystalline  $\text{KNbO}_3$  phase. We recently found that a self-assembly process is useful as a low-temperature process for KN thin film fabrication [8].

Self-assembly is one of the few practical strategies for making ensembles of nanostructures. This approach, involving exfoliation and restacking process, has provided a new technique for the design of new nanostructured thin films. Additionally, recent development in soft chemistry has given birth to a new type of nanosized materials, namely nanosheet. Nanosheets are usually obtained via delamination of precursor layered materials into their elementary layers which possess a thickness of several nanometers. The present study demonstrates a new method for the fabrication of  $\text{KNbO}_3$  thin films consisting of exfoliated

nanosheets and positively charged  $\text{K}^+$  ions as an inorganic binder. Usually the electrostatic self-assembly method has been carried out by alternate immersion in a metal ion solution and an organic ligand solution. The electrostatic self-assembly process does not require alternate immersion operations.

### 2. EXPERIMENTAL

$\text{K}_2\text{NbO}_3\text{F}$  (denoted as KNF) was prepared as a precursor using a conventional solid state reaction. High-purity KF,  $\text{K}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$  powders were weighed in the ratio of KF :  $\text{K}_2\text{CO}_3$  :  $\text{Nb}_2\text{O}_5$  = 2.6 : 1 : 1; then they were intimately ground and pressed into a pellet under a pressure of 30 MPa for 10 min. A 30% molar excess of KF was added to compensate for the loss caused by volatilization. The pellet of the starting materials mixture was heated at 1063 K for 1 h in air [8]. Perovskite nanosheet precursor solutions were prepared by dissolving KNF in a 100–10000 times volume of distilled water; then the solutions were stirred at room temperature for 2 h. After the reaction, a colloidal suspension was obtained with a membrane filter (pore size: 450 nm) through suction filtration. Procedures to construct KN thin films are as follows. A quartz substrate was washed with a nitric acid solution (25 wt%). The KN thin film was prepared: (1) the substrate was immersed slowly into the colloidal suspension; (2) then it was dried in air.

Extended X-ray Absorption Fine Structure (EXAFS) spectra of Nb-K edge were measured at the BL-10B beamline of the Photon Factory

(Tsukuba, Japan) in the transmission mode utilizing a Si [311] double crystal monochromator (ring energy 2.5 GeV and stored current of 250-350mA). The X-ray was detected ion chambers with a  $\text{N}_2$  (50%) / Ar (50%) mixed gas and Ar gas for  $I_0$  and I detectors, respectively.

A thin film formed on quartz substrate was characterized using powder X-ray diffraction (XRD) data obtained using X-ray diffractometer (MX-Labo; Mac science Ltd.). The molar extinction coefficient of colloidal suspension and optical properties of the thin film were measured using an Ultraviolet-visible (UV-vis) spectrophotometer (V-550; Jasco Inc.). The thickness of perovskite nanosheet aggregates was examined using an atomic force microscopy (AFM, SPM-9500; Shimadzu Corp.). We measured the thin film thickness using a scanning electron microscope (SEM, JSM-5310LV; JEOL). Morphology and selected area electron diffraction (SAED) pattern of perovskite

nanosheets were examined using a transmission electron microscopy (TEM, JEM-1200EX; JEOL).

### 3. RESULTS AND DISCUSSION

Fourier transform (FT) spectra of Nb-K edge EXAFS oscillations are shown in Fig. 1. For a comparison, the data for four different samples are also shown in Fig. 1. The Nb-K edge EXAFS spectra of the colloidal suspension in Figure 1 (a) shows two types Nb-O bonding distance. The long bond distance is nearly equal to that of bulk  $\text{KNbO}_3$  crystal. One can also notice a fairly shorter bond distance of Nb-O-Nb in the colloidal suspension. Based on these facts, we can propose a possible model for the exfoliated perovskite nanosheet single layer, as shown in Figure 2 (a). Nb atoms are located in a middle of fine coordinated square pyramid, as shown Figure 2 (b). The bond distance between apical oxygen and

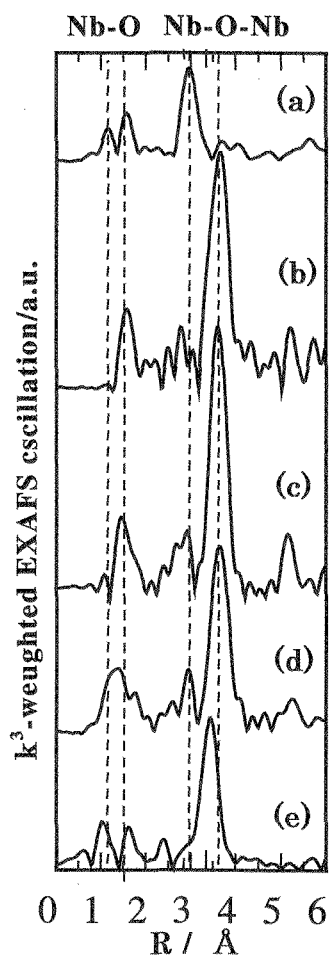


Fig. 1 Fourier transformed spectra of  $k^3$ -weighted EXAFS for (a) colloidal suspension, (b)  $\text{KNbO}_3$  prepared by soft chemical reaction, (c)  $\text{KNbO}_3$  prepared by sintering sample of (b) at  $1000^\circ\text{C}$ , (d)  $\text{KNbO}_3$  prepared by solid state reaction, and (e) starting material of  $\text{Nb}_2\text{O}_5$ .

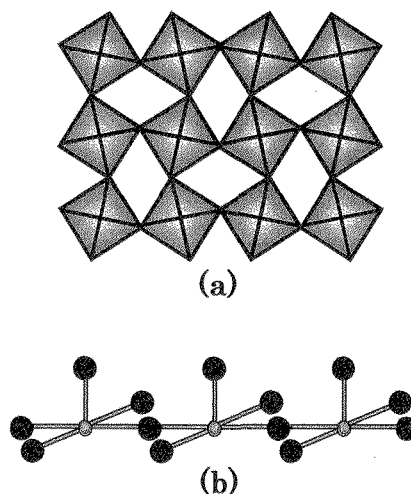


Fig. 2 Ideal model for (a) single layer and (b) square pyramid of perovskite nanosheet.

Nb atoms should be shorter than the other Nb-O distance within a plane. Since such square pyramids may be so electrostatically stressed, the squares within the layer plane could be tilted each other, so that the Nb-O-Nb bond distance becomes shorter. When the layered perovskite precursors of KNF are immersed in water at room temperature, the rock-salt-type blocks, KF, are selectively dissolved in water. Since the perovskite layers in the bulk should be so unstable at this stage, the single layered perovskite nanosheets are exfoliated. Figure 3 shows absorbance spectra of colloidal suspensions with various concentrations of nanosheets. It showed a decrease in absorbance with decreasing the colloidal suspension concentration. A molar extinction coefficient for the colloidal suspension was determined from the spectra by Lambert-Beer's law [9], as shown in the inset of Figure 3.

The molar extinction coefficient obtained is  $1.74 \times 10^2$  l/mol-cm, well agreement with the value of  $1.68 \times 10^2$  l/mol-cm reported for titania

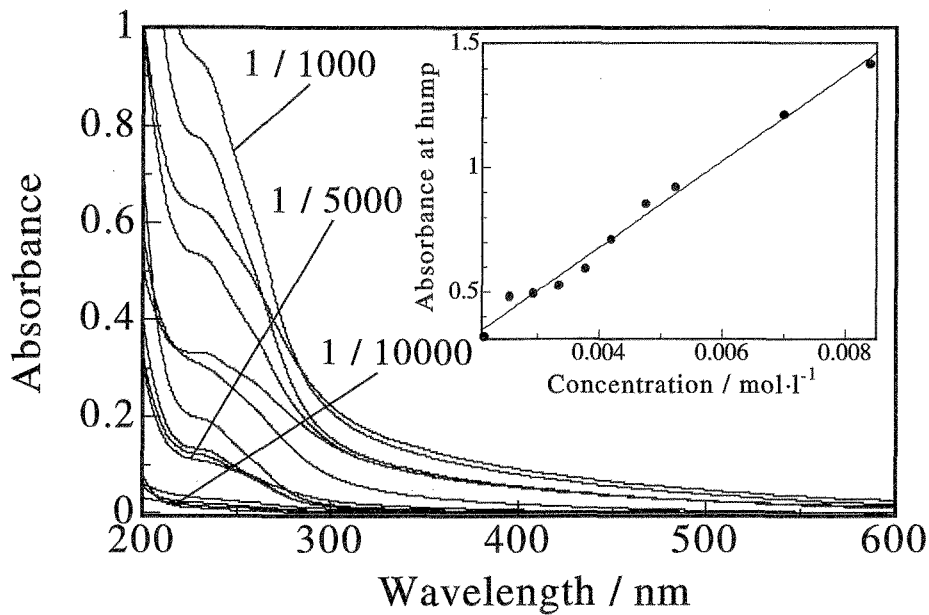


Fig. 3 UV-Vis spectra of colloidal suspension ( Conc. KNF (g) / H<sub>2</sub>O (g) = 1 / 1000–1 / 10000 ). The insert shows determination of molar extinction coefficient.

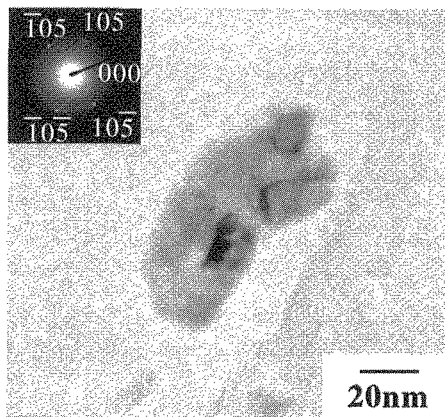


Fig. 4 TEM micrograph and SADE pattern (inset) of perovskite nanosheet.

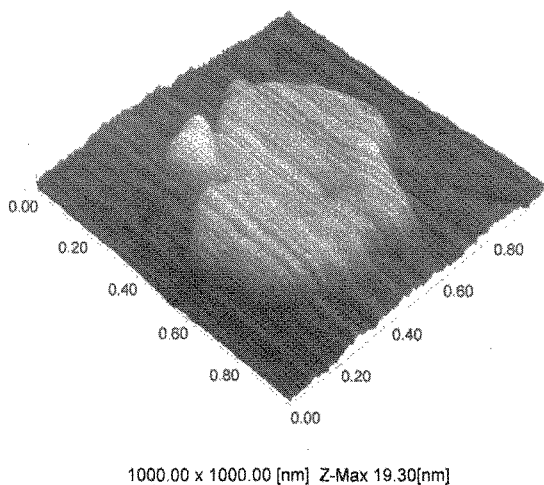


Fig. 5 AFM image of perovskite nanosheet aggregates.

nano-sheet colloidal suspensions [10].

Fig. 4 shows the TEM micrograph and the SADE pattern of the perovskite nanosheet. The perovskite nanosheets are plates with a size of about 60 nm × 40 nm. The SADE pattern indicates that the perovskite nanosheet is composed of a single domain.

The AFM image of the perovskite nanosheet aggregates is shown in Figure 5, indicating the perovskite nanosheet aggregates with ca. 800 nm length and ca. 19 nm in height. Considering the lattice parameter  $a = 0.399$  nm for the bulk crystal of cubic KNbO<sub>3</sub>, the thickness of the perovskite nanosheet corresponds to 47 units of KNbO<sub>3</sub>.

Figure 6 shows the XRD patterns of the thin film on the quartz substrate immersed for 7 day. Interestingly, a crystalline KNbO<sub>3</sub> thin film with single phase was formed even at room temperature.

This fact suggests that the exfoliated niobate nanosheets are stacked layer-by-layer through this self-assembling reaction. The self-assembled thin films were grown by adsorption of colloidal perovskite nanosheets.

Figure 7 shows the UV-Vis absorption spectra of various thin films prepared by varying the time of immersion into the colloidal suspension. An increase in absorbance with increasing the immersion time is observed, suggesting the growth of a self-assembled multilayer consisting of perovskite nanosheets and K<sup>+</sup> ions. However, no liner relationship between thin film thickness and immersion time exists for KN thin film growth. In addition, the thickness of the KN thin film with 7 day immersion was 3 μm (Figure 8), good agreement was found with the value of 2.8

$\mu\text{m}$  that was calculated from the molar extinction coefficient and the absorbance of the colloidal suspension.

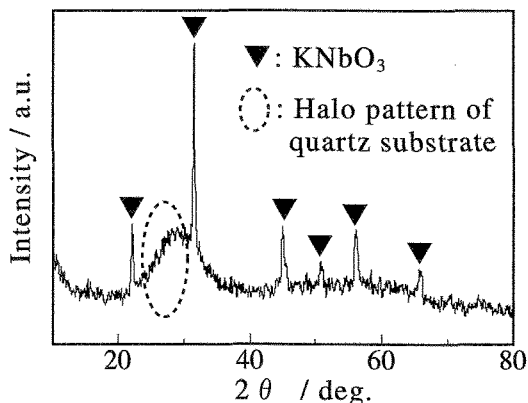


Fig. 6 XRD pattern of thin film prepared by self-assembly for 7 day immersion.

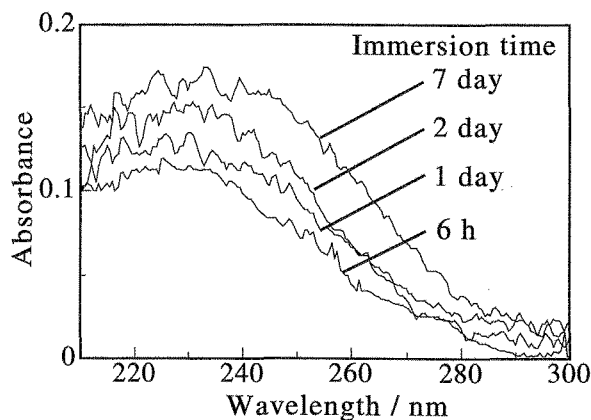


Fig.7 UV-Vis absorption spectra of thin film prepared by self-assembly.

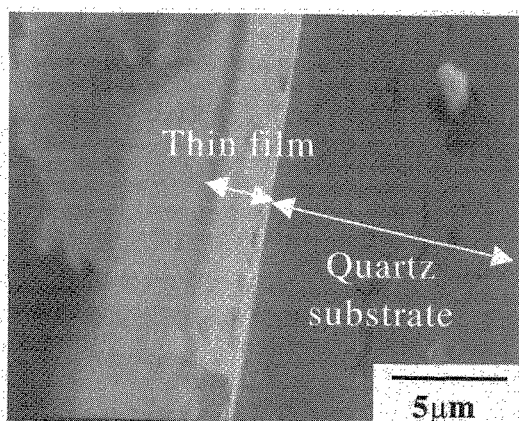


Fig. 8 SEM image of KN thin film prepared by immersion times for 7days.

#### 4. CONCLUSION

We prepared the colloidal suspension involving perovskite nanosheets colloids by a soft chemical reaction. Nb-K edge EXAFS spectra proved an existence of perovskite nanosheets in the colloidal suspension. No ring SADE pattern was observed on the perovskite nanosheet. Furthermore, we have demonstrated KN thin film fabrication at room temperature via self-assembly of perovskite nanosheets and  $\text{K}^+$  ions. This process can occur without any intercalants such as quaternary ammonium ions, which are often used in other self-assembly processes [11]. Furthermore, the self-assembly proceeds without any inorganic binders such as aluminum keggin ions [12] because  $\text{K}^+$  ions as a binder exist as a binder in colloidal suspension. Therefore, this approach may be regarded as a new type of built-up process.

#### 5. REFERENCES

- [1] K. Yamanouchi, H. Odagawa, T. Kojima and T. Matsumura, *Electron. Lett.*, 33 (1997), p. 193
- [2] K. Nakamura and Y. Kawamura, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* 47 (2000), p. 750
- [3] S. Nichols, B. M. Hwang, J. H. Mason, B. W. J. Mater. Res., 17 (2002), p. 275
- [4] S. Yilmaz, T. Venkatesan and R. Gerhard-Multhaupt, *Appl. Phys. Lett.*, 58 (1991), p.2479
- [5] S. S. Lehmann, H. W. Gunter, *P. Appl. Phys. Lett.*, 61 (1992), p. 373
- [6] K. Kakimoto, S. Ito, I. Masuda and H. Osato, *J. Appl. Phys.*, 41 (2002), p. 6908
- [7] D. Bao, A. Kuang and H. Gu, *Phys. Stat. Sol., A* 163 (1997), p. 67
- [8] K. Toda, N. Ohtake, M. Kawakami, S. Tokuoka, K. Uematsu and M. Sato, *J. Appl. Phys.*, 41 (2002), p.7021
- [9] T. Sasaki, M. Watanabe, *J. Photochem. Photobiology., A* 148 (2002), p. 275
- [10] L. Wang, Y. Ebina, K. Takada and T. Sasaki, *J. Phys. Chem., B* 108 (2004), p. 4283
- [11] M. Fang, C. H. Kim, A. C. Sutorik, D. M.Kaschank and T. E. Mallouk, *Mat. Res. Soc. Symp. Proc.*, 446 (1997), p. 377
- [12] P. J. Ollivier, N. I. Kovtyukhoba, S.W. Keller and T.E. Mallouk, *Chem. Commun.*, (1998), p. 1563

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