Crystal Growth of KNbO₃ by Solution-Dropping Method

T. Yoshiguchi¹,a, T. Ota¹,b, N. Adachi¹,c

¹Ceramics Research Laboratory, Nagoya Institute of Technology, 10-6-29, Asahigaoka, Tajimi, Gifu 507-0071, Japan
a takashi@crl.nitech.ac.jp, b t.ota@nitech.ac.jp, c nadachi@nitech.ac.jp

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Abstract

By the solution-dropping method imitating the growth of stalagmite in nature, piezoelectric KNbO₃ crystal was prepared onto a substrate by dropping metastable K₂NbO₃F aqueous solution. The transformation from K₂NbO₃F to KNbO₃ was accelerated by separately dropping H₂O₂ solution at the same time. Under the conditions of K₂NbO₃F concentration of 4.2×10⁻² mol/l, H₂O₂ concentration of 9mol/l, dropping rate of 1.7ml/min, dropping time of 2 h, and substrate temperature of 20°C, KNbO₃ crystals of 2 to 5µm and polycrystalline film composed of KNbO₃ crystals of < 1µm were grown at aqueous temperatures of 20°C and 60°C, respectively.

Introduction

Potassium niobate(KNbO₃; KN) is a lead-free piezoelectric material having high electro-optic and non-linear optical coefficients. This material attracts a great interest for its multiple applications, such as optical wave guides, frequency doublers and holographic storage systems[1-3]. Also KN has large electromechanical coupling constants in bulk acoustic waves[4,5] and in surface acoustic wave[6,7]. As KN is entirely undissolved in water, the crystal growth must be usually done at high temperatures by a melt growth, flux growth and so on.

On the other hand, it was recently reported that KN precipitated from metastable K₂NbO₃F(KNF) aqueous solution[8]. By taking advantage of this phenomenon, we tried the crystal growth of KN from a metastable KNF aqueous solution using by the solution-dropping method. This method is imitating the growth of stalagmite in nature[9]. For example, calcite (CaCO₃) crystals could be grown by continuously dropping a supersaturated calcium carbonate aqueous solution on a substrate. An unique characteristic of this growth method is that the supplying place of the source is different from the place of crystal growth. Consequently, growth factors such as source-temperature and growth-temperature can be separately controlled. Further, this enables continuous chemical reaction and crystal growth on a substrate by separately dropping two types of aqueous solutions in analogy with a chemical vapor deposition. So, calcite crystal was also grown on a substrate by separately dropping Na₂CO₃ solution and CaCl₂ solution in the same time. In this work, H₂O₂ solution was separately dropped at the same time, in order to accelerate the transformation from KNF to KN.
Experimental

$K_2NbO_3F$ powder was synthesized as follows. KF, $K_2CO_3$ and $Nb_2O_5$ powders were weighed out in the ratio $KF/ K_2CO_3/ Nb_2O_5 = 2.6: 1: 1$, ground and pressed into disk-shape pellets. The pellets were heated at 1063 K for 1 h in air. A 30% molar excess of KF was added to compensate for loss due to volatilization on firing. The precursors, KNF, were cooled to room temperature, thoroughly ground, and added to distilled water with concentration of $4.2 \times 10^{-2}$ mol/l [8].

The crystal growth of KN was done as shown in Fig.1. The KNF aqueous solution at temperatures of 20 to 60°C was dropped at a rate of 1 to 2 ml/min for 2 to 5 h on a substrate that was maintained at a temperature of 20°C. The (001) $KNbO_3$ or SrTiO$_3$ crystal was used as a substrate. In some runs, $H_2O_2$ aqueous solution with concentration of 0 to 9 mol/l was separately dropped at the same time. The obtained precipitates were characterized by XRD (Rigaku RINT1100) and FE-SEM (JEOL-7000FO).

Results and discussion

In the beaker, KN crystals were precipitated from KNF aqueous solution after stirring for about 12h. So, the KNF aqueous solution was dropped at a rate of 1 ml/min for 5 h onto a substrate. Figure 2 shows the SEM images of the deposits. They were identified by EDS, in which the ratio of K, Nb, O and F were detected for each deposit. There were a few amount of KN crystals (Fig.2(a)) along with a large amount of KNF deposits (Fig.2(b)). Consequently, it was essential to accelerate the transformation from KNF to KN.

Fig.2 SEM images of (a)KN and (b)KNF deposited by dropping KNF aqueous solution on a (001) $KNbO_3$ substrate.
As the authors heard that fluorine in a volcanic rock could be eliminated by the treatment with H$_2$O$_2$ solution. So, H$_2$O$_2$ was added into KNF aqueous solution. As a result, KN crystals precipitated after stirring for a few minutes. Figure 3 shows the XRD pattern of the precipitate after mixing KNF aqueous solution and H$_2$O$_2$ aqueous solution for 5 minutes in the beaker. The amount of KN crystals increased with increasing concentration of H$_2$O$_2$ and/or temperature of aqueous solution. The transformation from KNF to KN occurred immediately under the conditions of aqueous temperature of 60°C and H$_2$O$_2$ concentration of 9mol/l. The particle size of the precipitates was about 0.1 µm as shown in Fig.4.

Then, KNF (4.2×10$^2$ mol/l) and H$_2$O$_2$ (9mol/l) aqueous solutions were separately dropped for 5 h onto a (001) KNbO$_3$ substrate at the same time. As shown in Fig.6, some KN crystals of 2 to 5µm were grown on the substrate at an aqueous temperature of 20°C. At an aqueous temperature of 60°C, the substrate was covered with a great number of KN crystals of < 1µm.
Summary

KNbO$_3$ crystals were prepared from metastable K$_2$NbO$_3$F aqueous solution. The transformation from K$_2$NbO$_3$F to KNbO$_3$ was accelerated by adding H$_2$O$_2$ solution.

KNbO$_3$ crystals of 2 to 5µm were grown by separately dropping KNF aqueous solution and H$_2$O$_2$ solution at the same time. In addition, a polycrystalline film composed of KN crystals of < 1µm formed by the control of growth conditions.

References

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