

Characteristics of BNT films synthesized by a hydrothermal method

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Abstract. Thin films of lead-free piezoelectric ceramics ($\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$) (abbreviated as BNT) were prepared on pure titanium substrates by a hydrothermal method. Several properties of BNT films deposited in various Bi^{3+} and Ti^{4+} concentrations of starting materials were investigated using SEM and XRD. Moreover, the effects of ion concentrations of starting materials on permittivity and piezoelectric effect of BNT films were discussed. The Bi_2O_3 crystals were more deposited on the surface of films with the increase of the concentration of Bi^{3+} . The relationship between the deflection and applied electric field was measured on unimorph cantilever type actuators made from three deposits which had different XRD patterns. The results showed that the piezoelectric effect of BNT films was dependent on the crystallization level of BNT.

Introduction

Piezoelectric materials have wide applications in intelligent systems. Lead zirconate titanate $\text{Pb}(\text{Zr}_x, \text{Ti}_{1-x})\text{O}_3$ (abbreviated as PZT), one of piezoelectric materials, is widely used due to its high dielectric and piezoelectric coefficients. It has been reported by T. Kanda et al. that a touch probe sensor was made from PZT films hydrothermally deposited on pure titanium substrates [1]. However, the toxicity of lead oxide in PZT does harm to human and environment [2]. Therefore, to reduce and eliminate lead pollution, more and more attentions have been paid to lead-free piezoelectric ceramics.

Bismuth sodium titanate ($\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$) (abbreviated as BNT) is considered to be one of promising lead-free piezoelectric ceramics. In this work, BNT films were deposited on pure titanium substrates by a hydrothermal method. The hydrothermal method, one of liquid phase process techniques, has two outstanding advantages: films can grow on “3D” shaped substrates and deposited films require no post treatment (annealing or polarization) [3]. The hydrothermal synthesis of BNT powder was reported by P. Pookmanee et al.[4]. However, there has been no report about the relation between the conditions of starting materials and the properties of BNT films. In this work, the characteristics of BNT films were investigated with varying the concentrations of starting materials.

Experimental

Hydrothermal synthesis. BNT films were synthesized on pure titanium substrates ($40 \times 20 \times 0.05 \text{ mm}$) in an autoclave with a Teflon cup of 40ml. Bismuth nitrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, hereinafter referred to as $\text{Bi}(\text{NO}_3)_3$] and titanium oxide [TiO_2] was used as bismuth precursor and titanium precursor respectively, and sodium hydroxide [NaOH] was used as sodium precursor and mineralizer. As shown

in Fig. 1, the hydrothermal process of BNT films is a 2-step process: the “nucleation” step and then the “crystal growth” step which was repeated once more to obtain thicker films in this study. The experimental conditions of starting materials are shown in Table 1.

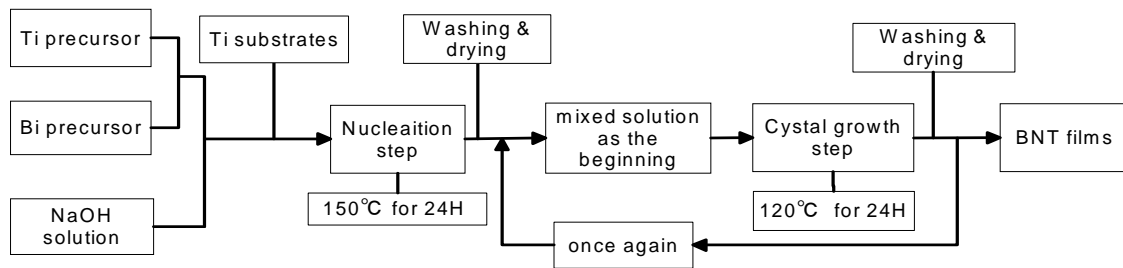


Fig. 1 The process of the hydrothermal method

Characterization. The morphology and microstructures of BNT films were observed by a scanning electron microscopy (SEM, Philips XL303). Crystal structures and crystallization levels of BNT films were analyzed by X-ray diffraction (XRD, JEOL JDX-3500) with the detection range(2θ) of $10-90^\circ$. Dielectric measurements of BNT films were carried out by LCR Meter (Agilent 4284A). The piezoelectric constant d_{33} of BNT films was measured using a piezo-meter system (UK, Piezotest). The converse piezoelectric effect of BNT films was examined by the actuation testing. The unimorph cantilever type specimens (cf. Fig.2) of the actuation test were made from three different samples(G, K and O) which were synthesized at the same TiO_2 concentration of 0.5mol/l (cf. Table 1). Applying a DC field on the specimen, we measured the deflection of the tip of its free end by a laser displacement meter (Keyence, LC-2400), and then investigated the converse piezoelectric effect of BNT films.

Table 1. Conditions of starting materials and symbols of samples

16 ml solution of NaOH(10mol/l)		4ml solution of $Bi(NO_3)_3$ (mol/l)			
		1.0	1.2	1.4	1.6
8 ml solution of TiO_2 (mol/l)	0.3	A	E	I	M
	0.4	B	F	J	N
	0.5	C	G	K	O
	0.6	D	H	L	P

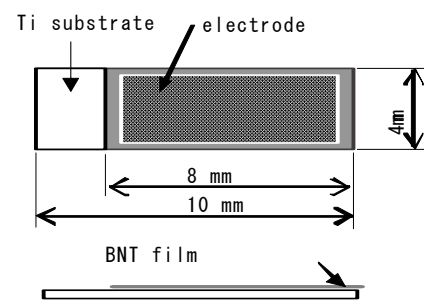


Fig.2 Dimensions of cantilever type specimen

Results and discussion

Film thickness. The thicknesses of as-deposited films are shown in Fig. 4, which shows that the films deposited at the $Bi(NO_3)_3$ concentration of 1.4 mol/l are comparatively large in thickness. The mean thickness of deposited films was about $25.4\mu m$ calculated from all the samples.

Surface observation. Fig. 5(a) shows the microstructure of as-deposited film surface of sample G. It was found that granular BNT crystals (approximately $2\mu m$ grain size) and tetrahedral Bi_2O_3 crystals were generated on the substrate surface, and Bi_2O_3 crystals were scattered on the surface of BNT film. The amount of Bi_2O_3 crystal increased dramatically with increasing the $Bi(NO_3)_3$ concentration of the

starting solution. The Bi_2O_3 crystals were able to be removed by the immersion of concentrated nitric acid. After the removal of Bi_2O_3 crystals, the thickness of BNT film was about $7\mu\text{m}$ for every sample, and the microstructure of BNT film surface is shown in Fig. 5(b) corresponding to Fig. 5(a).

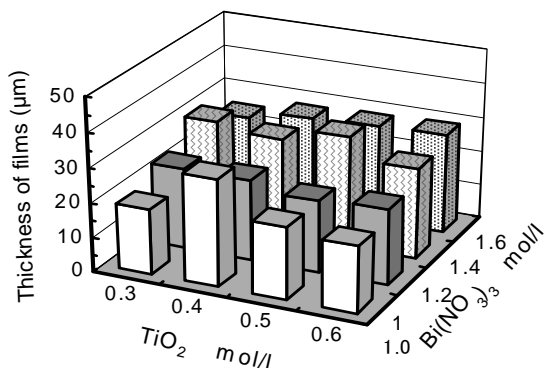
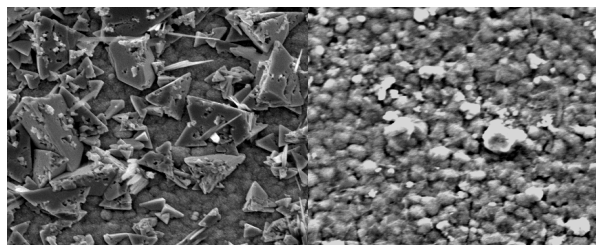


Fig.3 Thicknesses of deposited films



(a) after 3 depositions (b) treated in nitric acid
10 μm

Fig.4 SEM images of BNT films (Sample G)

XRD. The XRD patterns of sample G, K and O are shown in Fig. 5. It shows that the BNT diffraction peak of sample K was more intense than that of sample G and O, and the generation of Bi_2O_3 was confirmed for each sample. The diffraction peaks of sample O was comparatively low, indicating that the crystallization level of sample O was not so high as that of sample G and K.

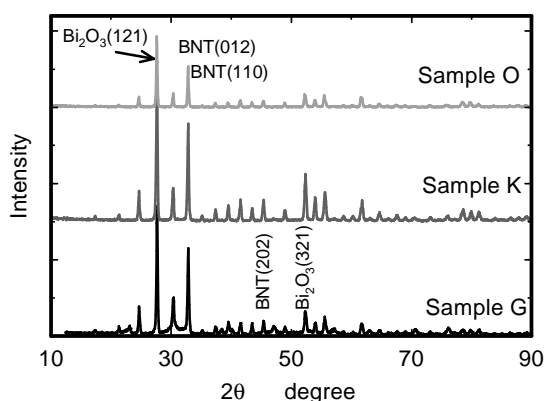


Fig. 5 XRD patterns of sample G, K and O

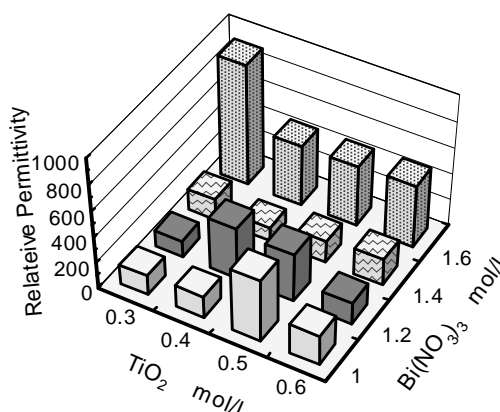


Fig. 6 Relative permittivity of films

Permittivity. Fig. 6 shows relative permittivity of the as-deposited films for all the samples. It shows that the relative permittivity was much larger in the case of the $\text{Bi}(\text{NO}_3)_3$ concentration of 1.6 mol/l, comparing to the case of 1.4 mol/l. It can be also seen that the well crystallized sample K was very low in the relative permittivity.

Piezoelectric performance. Fig. 7 shows piezoelectric constants d_{33} of as-deposited films for all the samples. It indicates that the piezoelectric constant d_{33} may tend to be large in the case of low concentration of TiO_2 . The correlation between the relative permittivity and piezoelectric constant d_{33} of as-deposited films can not be found by comparing Fig. 6 with Fig. 7.

Fig. 8 shows the relation of the driving voltage and deflection of unimorph cantilever type specimens for sample G, K and O. It can be seen that the relatively large deflections were obtained for sample G and K in the case of the positive electric field. An obvious hysteresis was observed in Fig. 8

and the deflection was hardly obtained in the negative electric field. On the other hand, it can be also seen that the deflection for sample O was not almost generated in the positive or negative electric field. This was considered the result of the insufficiency of BNT crystallization on the sample O. However, the piezoelectric constant d_{33} of sample O was larger than that of sample G and K (cf. Fig.7). It is suggested from the above results that the materials with an excellent effect of direct piezoelectricity are not necessary to be good in the converse piezoelectric effect.

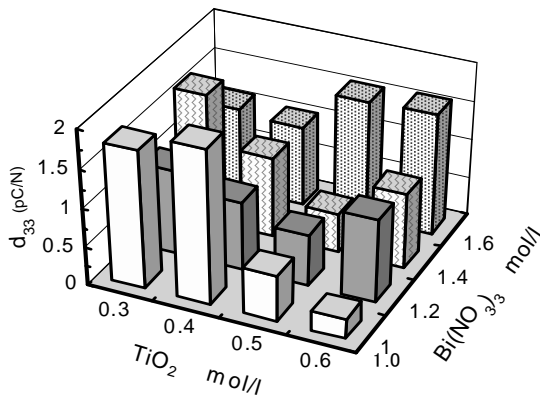


Fig. 7 Piezoelectric constant of films

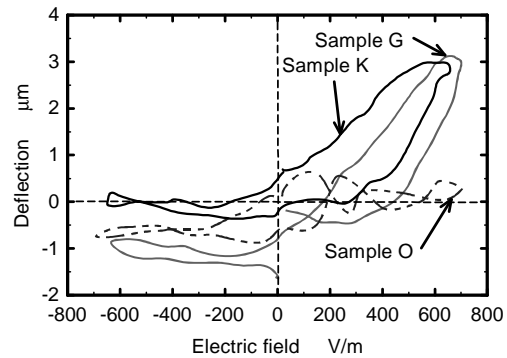


Fig. 8 Deflections of cantilever type actuator

Conclusions

BNT films were hydrothermally synthesized on pure titanium substrates with varying the concentrations of the starting materials. The amount of Bi_2O_3 crystal on the as-deposited film surface increased with increasing the $\text{Bi}(\text{NO}_3)_3$ concentration of the starting solution. The relative permittivity tended to increase greatly in the case of the $\text{Bi}(\text{NO}_3)_3$ concentration of 1.6 mol/l. In addition, the piezoelectric effect of BNT films greatly depended on the crystallization level of BNT, and so the converse piezoelectric effect was not obviously observed in the case of low BNT diffraction peaks.

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