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The potential application of BNT-based ceramics in large displacement actuation

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$Bi_{1/2}Na_{1/2}TiO_3$-based ceramics are a group of promising lead-free piezoelectric materials that are being studied more and more intensely at present. Large displacement actuation is one of the important applications of piezoelectric materials. Because the piezoelectric constant of BNT-based ceramics measured by the Berlincourt method is no more than 150pC/N, it seems that the materials are not suitable for large displacement actuation. However, in our work it was found that BNT-BT ceramic wafers could produce very large displacement under DC electric field, although the piezoelectric constant measured by Berlincourt method was very small. It makes them possible to be used as large displacement actuator. There are two possible mechanisms for this phenomenon. The first mechanism may be related to the semiconductivity of BNT-BT ceramics. In this case, the BNT-BT ceramic wafers are similar to a monomorph device. The other possible mechanism may be associated with the anomalously intense space charge effect in the materials.

Key words: $Bi_{1/2}Na_{1/2}TiO_3$, Lead-free, Piezoelectric ceramics, Large displacement, Monomorph, Space charge.

Introduction

Sodium bismuth titanate, $Bi_{1/2}Na_{1/2}TiO_3$, (abbreviated as BNT), is a compound with strong ferroelectricity. It was first discovered by Smolenskii *et al.* in 1960 [1]. At present, BNT-based ceramics are intensely studied as lead-free piezoelectric materials to take the place of lead-containing piezoelectric ceramics because of health and environmental concerns with lead-containing materials. The main shortcomings of BNT ceramics are that they are not easily poled because of their high conductivity nor are they easily sintered. In order to obtain useful lead-free piezoelectric ceramics, $Bi_{1/2}Na_{1/2}TiO_3$-$Bi_{1/2}K_{1/2}TiO_3$ (BNT-BKT), $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$ (BNT-BT) and $Bi_{1/2}Na_{1/2}TiO_3$-$NaNbO_3$ (BNT-NB) systems have been studied [2-6]. The addition of BKT, BT or NB in BNT can increase the electric resistance and improve the piezoelectric and sintering properties. Doping in BNT-based ceramics can further improve their piezoelectric properties [7].

Large displacement actuation is one of the important applications for piezoelectric materials. The materials for large displacement piezoelectric actuators normally need relatively large piezoelectric constant d_{33}. BNT-based ceramics seem to be not suitable for this kind of application. But when BNT-BT ceramics were studied, it was discovered that the ceramic wafers could produce very large displacement under DC electric fields. This means that BNT-based ceramics can be used as large displacement actuators.

In the present work, two kinds of BNT-BT specimens were prepared. The normal specimens exhibit common piezoelectric properties. Under DC electric field, they did not produce large displacement. Special specimens were prepared by raising the synthesis temperature and increasing the sintering time. These BNT-BT specimens exhibit anomalous properties. Under DC electric field, they can produce very large displacement, although the piezoelectric constant d_{33} measured by the Berlincourt method is very small. Two possible mechanisms were proposed for this phenomenon in this paper.

Experimental Procedure

Conventional techniques for fabrication of mixed oxides were used to prepare BNT-BT ceramics. Reagent grade Bi_2O_3, Na_2CO_3, $BaCO_3$ and TiO_2 were used as raw materials. The raw materials were weighed according to the formula of $(Bi_{1/2}Na_{1/2})_{0.92}Ba_{0.08}TiO_3$. Two kinds of BNT-BT specimens, designated normal and special specimens, were prepared. To prepare the normal BNT-BT specimens, the weighed powders were mixed and then calcined at about 900-1000°C for two hours. After calcination, the ceramic powder was pressed into pellets 20 mm in diameter and 0.5 mm thick and sintered at 1150°C-1200°C for one hour. The procedure to prepare special specimens was the same as that of normal specimens, but the synthesis temperature was higher and the sintering time was much longer. The ceramic disks were polished and covered with silver electrode. The normal specimens were poled under a DC electric field of 3-4 kV/mm at 80 to 100°C for half an hour. The special specimens were

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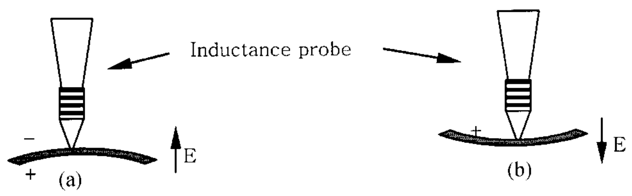

Fig. 1. Two patterns for the measurement of displacement-voltage relation of BNT-BT ceramics. (a) The negative electrode of poled specimen upward. (b) The positive electrode upward. It should be noted that BNT-BT wafers arch toward negative electrode a little after they are poled. In this figure the arch degree is overdrawn deliberately.

poled under 1 kV/mm for the same time at the same temperature. The poling field of special specimens was decreased because of the large conductivity.

The piezoelectric constant d_{33} was measured by the Berlincourt method at a frequency of 100 Hz. The dielectric constant and dielectric loss were measured using a CY2611 capacitance meter. The coupling coefficients were determined using the resonance method. The thermally stimulated depolarization current (TSDC) was measured by the instrument used in Ref. 3. The displacement under DC electric field was obtained by a DGS-6 micro-displacement instrument. The resolution of the instrument was 0.01 μm. The displacement of BNT-BT ceramics under DC electric field was measured using two measurement patterns. One pattern is with the negative electrode of the poled specimen upward, the other is with the positive electrode upward, as shown in Figs. 1(a) and 1(b).

Results and Discussions

Table 1 shows the piezoelectric and ferroelectric properties of normal BNT-BT ceramics. From the table, it can be seen that d_{33} of the ceramics is 112pC/N. As a rule, d_{33} obtained by the Berlincourt method is the same as that obtained by the displacement-voltage relation (e.g. inverse piezoelectric effect). This means the displacement of normal BNT-BT ceramics should be about 0.01 μm, if the applied voltage is 100 V. The measurement of displacement of normal BNT-BT ceramics under electric field in this study confirms this supposition; the displacement under 100 V was about 0.02 μm.

Compared with normal BNT-BT specimens, the physical properties of special BNT-BT ceramics changed greatly, especially the electric resistance. The electric resistivity decreases from ~10^8 Ωm for normal BNT-BT specimens to ~10^5 Ωm for special BNT-BT ceramics. The poling voltage of special BNT-BT ceramics was lowered because of the large conductivity. This may be one reason for the decrease of d_{33} in the special BNT-BT ceramics, which is about 60pC/N. Strangely enough, unlike normal BNT-BT ceramics, the displacement under DC electric field of special BNT-BT ceramics, measured as shown in Fig. 1(a), was very large, as shown in Fig. 2(a). The displacement under 100 V is larger than 1 μm, which is more than fifty times larger than the 0.02 μm displacement of normal BNT-BT ceramics under same voltage.

The original compositions of normal and special BNT-BT ceramics were the same, but the physical properties turned out to be greatly different. The large differences should originate from the different calcining temperatures and sintering times. S. E. Park *et al.* have reported the volatilization of Bi and Na elements during the preparation of BNT crystal [8]. In our case, the difference of conductivity between the two kinds of BNT-BT specimens may also be caused by the evaporation Bi and Na. The higher calcining temperature and longer sintering time enhance the evaporation. The nonstoichiometry of BNT-BT ceramics caused by the evaporation increases the conductivity of BNT-BT ceramics.

As proposed by A K. Uchino *et al.*, semiconductive piezoelectric ceramics can curve and produce very large displacement under electric field because of the uniform distribution of electric field in the piezoelectric ceramics [9]. They can be used as a large-displacement actuator, which was called a monomorph. Because the special BNT-BT ceramics became semiconductive, the

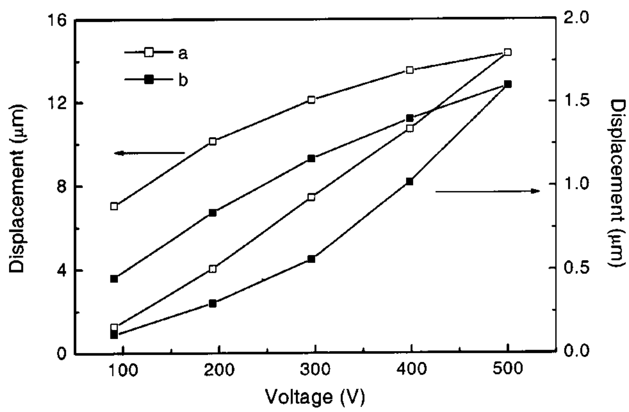

Fig. 2. The displacements of special BNT-BT ceramics under various DC voltages. (a) Before heat treatment. (b) After heat treatment.

Table 1. The piezoelectric and ferroelectric properties of normal BNT-BT ceramics

Piezoelectric Constant	Dielectric Constant	Dielectric Loss	Planar Coupling Factor	Thickness Coupling Factor	Remnant Polarization	Coercive Field
d_{33} (pC/N)	ε_{33}^T	tgδ	k_p	k_t	P_r (μC/cm^2)	E_c (V/mm)
112	841	0.0204	0.13	0.42	36	3200

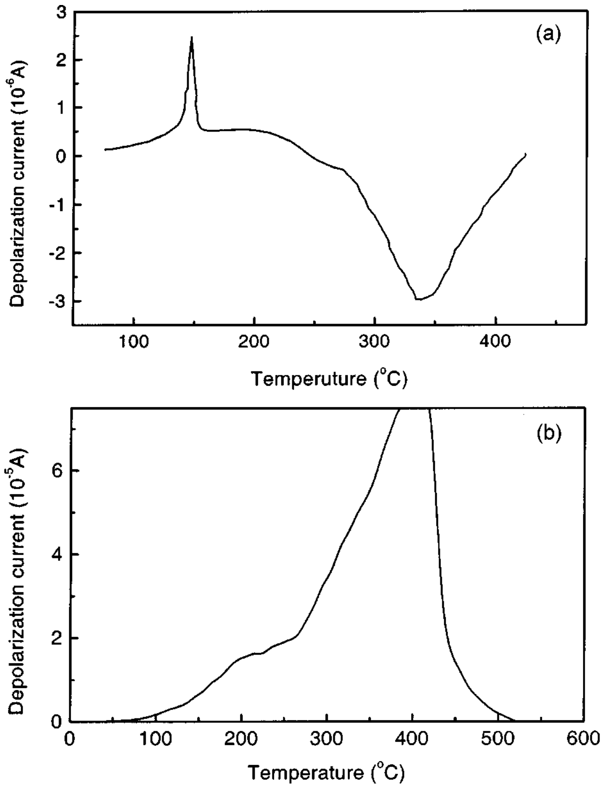

Fig. 3. TSDC curves of poled BNT-BT ceramics (a) normal specimens (b) special specimens.

monomorph effect was sure to contribute in some degree to the large displacement.

Besides the difference of conductivity between the two kinds of BNT-BT ceramics, there was another great difference that suggests the possible existence of another mechanism for the large displacement of special BNT-BT ceramics. Figure 3 shows the TSDC curves of normal and special BNT-BT ceramics, respectively. The first sharp depolarization current at about 140°C in Fig. 3(a) is caused by the disappearance of spontaneous polarization. The piezoelectric constant d_{33} measured by the Berlincourt method became zero after the normal specimens were heated to this temperature. Another depolarization current peak at higher temperature is due to the space charge polarization, which may also be caused by the evaporation of Bi and Na elements [10, 11]. Compared with normal specimens, as shown in Fig. 3(b), the depolarization current of special specimens was about ten times more intense and the first peak in Fig. 3(a) was not observed. The depolarization current of spontaneous polarization in special specimens was blanketed by much more intense space charge polarization. It is well known that piezoelectric ceramics can produce displacement under an electric field due to the existence of spontaneous polarization, which is called the inverse piezoelectric effect. It is possible that space charge polarization can contribute to the large displacement of BNT-BT ceramics. This supposition was partially confirmed by the experiment described below.

As seen in Fig. 3(a), the depolarization current of normal BNT-BT ceramics caused by spontaneous polarization occurs at about 140°C. Because normal and special specimens have the same composition, the depolarization temperature of spontaneous polarization in special specimens should also be about 140°C. Due to the intense depolarization current of space charge polarization, this depolarization peak cannot be observed in Fig. 3(b). The special BNT-BT specimens were heated to 200°C and held at that temperature for about 20 min and then cooled down. It is obvious that the contributions to displacement of spontaneous polarization and part of the space charge polarization were eliminated by the heat treatment. The ceramics lost their piezoelectric properties and the piezoelectric constant d_{33} was about zero after heat treatment. But the ceramics still had large displacement under DC electric field, as shown in Fig. 2(b). Under a voltage of 100 V, the displacement is about 0.11 μm. This displacement should mainly originate from space charge polarization.

It was found that BNT-BT ceramics curved toward negative electrodes after they were poled, but the curvature is very small, only 0.07 mm. The curvature may contribute to the displacement to some degree, similar to a RAINBOW device [12]. However, this is not the main reason for the large displacement because normal BNT-BT ceramics also curved toward negative electrodes for about 0.09 mm and they did not produce large displacement. The curvature effect mixed with the monomorph effect and space charge effect contribute to the large displacement. The curvature has influence on the electromechanical properties of special BNT-BT specimens. The displacement of special BNT-BT specimens under a voltage of 100 V is only 0.03 μm measured by the pattern in Fig. 1(b), which is much less than that measured by the Fig. 1(a) pattern.

It is possible that BNT-BT ceramics can be used as lead-free piezoelectric actuators that are easily prepared by conventional ceramic preparation procedure.

Conclusions

It was found that BNT-BT ceramics could produce very large displacement and could possibly be used as an actuator. The monomorph effect and space charge effect may be the two main mechanisms for this phenomenon. The curvature of the ceramic wafers may also help to produce the large displacement.

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