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Thermal depoling of high Curie point Aurivillius phase ferroelectric ceramics

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The thermal depoling behavior of several different Aurivillius phase ferroelectric ceramics has been studied. This includes two-layer ($\text{CaBi}_2\text{Nb}_2\text{O}_9$, $\text{Ca}_{0.9}\text{Ba}_{0.1}\text{Bi}_2\text{Nb}_2\text{O}_9$, $\text{Bi}_3\text{NbTiO}_9$, $\text{Bi}_3\text{Nb}_{1.2}\text{Ti}_{0.8}\text{O}_9$), three-layer ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$), and four-layer [$\text{CaBi}_4\text{Ti}_4\text{O}_{15}$, $\text{Ca}_{0.94}(\text{Na}, \text{Ce})_{0.03}\text{Bi}_4\text{Ti}_4\text{O}_{15}$] compounds. All of them have a high Curie point ($T_c \geq 675^\circ\text{C}$). The orthorhombic structured materials show good resistance to thermal depoling up to temperatures close to their Curie points. However, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, which has a monoclinic structure, shows a significant reduction in d_{33} well before its Curie point. The monoclinic distortion produces more non- 180° ferroelectric domain structures, and it is the thermal instability of these that accounts for their thermal depoling behaviour. Excess Nb doping of $\text{Bi}_3\text{NbTiO}_9$ produces a significant reduction in its resistance to thermal depoling, suggesting that the doping produces a lowering of the crystallographic symmetry. © 2005 American Institute of Physics. [DOI: 10.1063/1.2034121]

Some Aurivillius phase compounds show interesting relaxor^{1,2} and multiferroic^{3,4} properties when Ba and Fe are on the *A*- and *B*-site in the general formula, respectively. In recent years many investigations have concentrated on their potential use in nonvolatile ferroelectric random-access memory (FRAM) (Refs. 5 and 6) and high-temperature piezoelectric applications,^{7,8} because of their fatigue-free properties and high Curie point, respectively.

The general formula of Aurivillius phase materials is $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where *A* is a mono-, di- or trivalent element (or combination) with cuboctahedral coordination. *B* is a transition element suited to octahedral coordination, and *m* is the number of octahedral layers in the perovskite slab. The *m* value can vary from 1 to 6.⁹ It can also be fractional and compounds with $m=1.5$, 2.5, and 3.5 are widely known.¹⁰ It is found that the ferroelectric properties for even ($m=2n$) and odd layer ($m=2n+1$) Aurivillius phase compounds are different.¹¹ The spontaneous polarization P_s of even-layer compounds is only along the *a*-axis. Based on their orthorhombic space group $A2_1am$, the polarization along the *c*-axis is cancelled because of mirror symmetry. However, in odd-layer compound $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=3$, monoclinic, space group *Pc*) a small degree of spontaneous polarization along the *c*-axis can be observed besides the major polarization along the *a*-axis.^{12–14}

In Damjanovic's review¹⁵ of high-temperature piezoelectric materials, Aurivillius phase ferroelectric ceramics were highlighted as important for sensor application. Thermal depoling of ferroelectrics determines the upper temperature limit of their application as piezoelectrics. However, there is very limited information on the thermal depoling of Aurivillius phase materials. In the present work the thermal depoling of Aurivillius phase compounds was studied. For the purpose of high-temperature piezoelectric application, the Curie

point, T_c , of the selected compounds is not less than 675°C . The compounds include even-layer compounds $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO, $m=2$), $\text{Bi}_3\text{NbTiO}_9$ (BNTO, $m=2$), $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (CBT, $m=4$) and odd-layer compound $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT, $m=3$). In order to study the effect of substitution on the thermal depoling, three substituted compounds $\text{Ca}_{0.9}\text{Ba}_{0.1}\text{Bi}_2\text{Nb}_2\text{O}_9$ (CBBNO, $m=2$), $\text{Bi}_3\text{Nb}_{1.2}\text{Ti}_{0.8}\text{O}_9$ (BNTO-D, $m=2$) and $\text{Ca}_{0.94}(\text{Na}, \text{Ce})_{0.03}\text{Bi}_4\text{Ti}_4\text{O}_{15}$ (CNBT, $m=4$) were also prepared.

Polycrystalline ceramic samples were prepared by conventional ceramic processing. The starting raw materials were Bi_2O_3 of 99.975% purity, CaCO_3 of 99% purity, BaCO_3 of 99% purity, Na_2CO_3 of 99.5% purity, CeO_2 of 99.9% purity, TiO_2 of 99.6% purity, and Nb_2O_5 of 99.9% purity. The materials were mixed by ball milling in ethanol, dried and sieved to under $250\ \mu\text{m}$. The calcination conditions were 950°C 2 h for CBNO and CBBNO, 900°C 4 h for BNTO and BNTO-D, 850°C 4 h for BIT and 900°C 2 h for CBT and CNBT. After calcination, the powders were remilled, dried and sieved to under $500\ \mu\text{m}$, and then finally pressed into disks of 10 mm diameter in a steel die at a pressure of about 200 MPa. The pressed specimens were sintered for 1 h at 1150°C for CBNO, 1050°C for CBBNO, 1080°C for BNTO and BNTO-D, 1150°C for BIT, 1175°C for CBT, and 1150°C for CNBT in air. Electrodes for high-temperature electrical property measurements were fabricated with fired-on platinum paste (Gwent Electronic Materials Ltd., C2011004D5).

X-ray diffraction (XRD) patterns for the sintered ceramics were obtained with an x-ray diffractometer (Siemens D5000) using $\text{Cu } K\alpha$ radiation. The samples, except BIT, for piezoelectric measurements were poled by applying a dc electric field of 8–15 kV/mm for 5–15 min in silicone oil at 200°C . The maximum poling field that could be achieved for BIT was below 1 kV/mm because of its high conductivity.¹⁶ The piezoelectric constant, d_{33} , was measured

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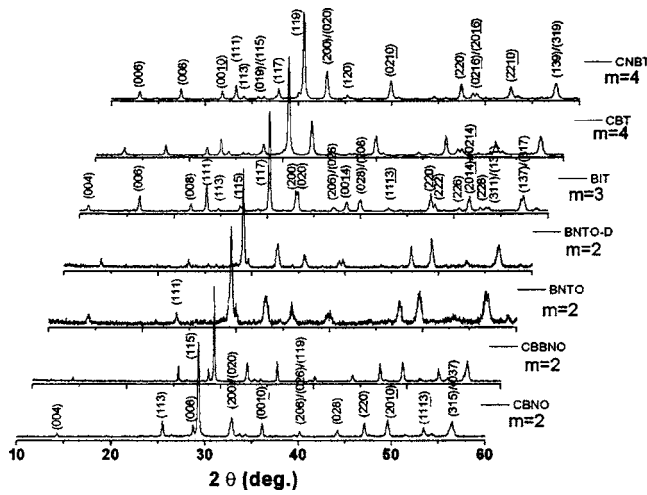


FIG. 1. XRD patterns of sintered ceramic powders.

using a piezo d_{33} meter (ZJ-3B, Institute of Acoustics, Academia Sinica). The temperature dependence of dielectric constant and loss were measured at 1 MHz using a LCR meter (Agilent 4284A) connected to a furnace. Thermal depoling experiments were conducted by holding the poled samples for 2 h at high temperatures, cooling to room temperature, measuring d_{33} , and repeating the procedure at intervals of 100 °C up to a temperature above T_c .

Figure 1 shows the XRD patterns of sintered ceramic powders of these compounds. The materials are all single-phase within the sensitivity of the technique based on related crystal structure parameters,^{17–19} except BNT0 and BNT0-D. In the XRD patterns for BNT0 most of the diffraction peaks match the main phase of the BNT0 structure with the exception of a small peak at about $2\theta=30^\circ$, which matches the strongest peak (117) for BIT. The doped BNT0-D ceramics also contain BIT phase. The amount of second phase in BNT0 is higher than that in BNT0-D. The strongest diffraction peak for two layer compounds CBNO, CBBNO, BNT0, and BNT0-D is (115), for three layer BIT it is (117) and for four layer CBT and CNBT it is (119), which is consistent with the strongest diffraction peak ($1\ 1\ 2m+1$) of Aurivillius phases generally.²⁰

Figure 2 shows the temperature dependence of the di-

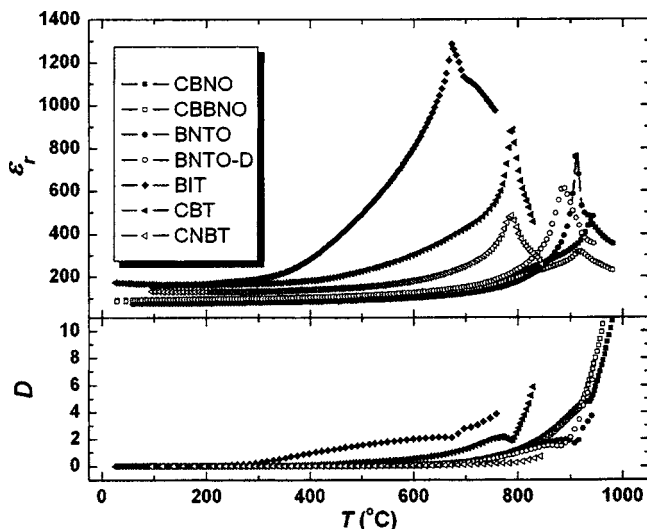
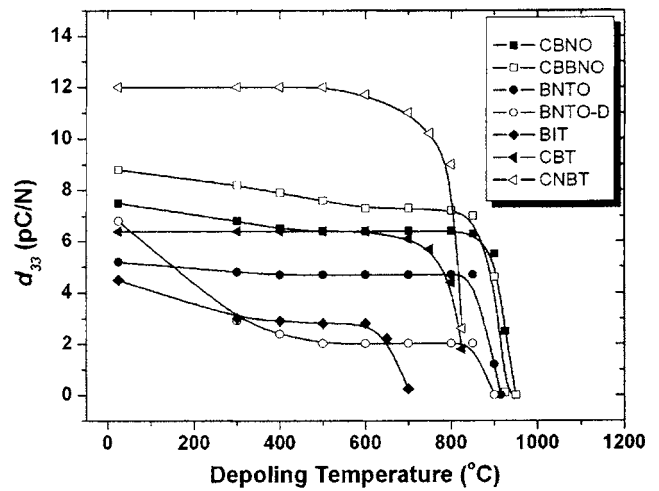
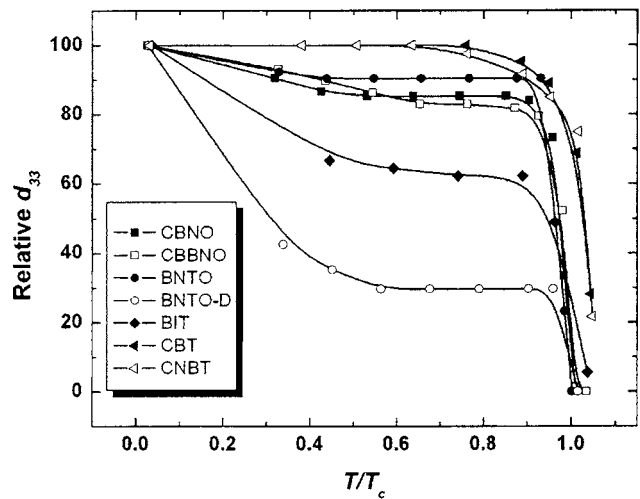


FIG. 2. Temperature dependence of dielectric constant and loss at 1 MHz.



(a)



(b)

FIG. 3. Effect of thermal depoling on piezoelectric properties: (a) the change of d_{33} after annealing for 2 h; (b) the same data plotted as relative d_{33} and homologous temperature.

electric permittivity and loss of the compounds at 1 MHz. The Curie point is 940 °C, 918 °C, 913 °C, 886 °C, 675 °C, 790 °C, and 787 °C within an error of ± 2 °C for CBNO, CBBNO, BNT0, BNT0-D, BIT, CBT, and CNBT, respectively. There is a loss peak at a few degrees below the Curie points. A possible explanation for this peak is that it is associated with the movement of ferroelectric domain walls. Displacement of domain walls contributes to the dielectric and mechanical losses of ferroelectric materials and, particularly near the phase transition temperature, may dominate other loss mechanisms.²¹ The room temperature d_{33} values of the Aurivillius phase compounds are relatively low (Fig. 3) compared with those of PZT (lead zirconate titanate, 200–600 pC/N). This is because of their high coercive fields and the two-dimensional orientation restriction of the switching of the P_s between the a - b axes.²² After substitution, the room temperature d_{33} value of CBBNO, BNT0-D, and CNBT is higher than that of CBNO, BNT0 and CBT, respectively.

In ferroelectric materials, domain wall movement can produce a significant contribution to the piezoelectric properties.^{23,24} In Aurivillius phase materials, even-layer materials, such as $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ($m=4$), show relatively little pi-

electronic hysteresis.^{25,26} A possible reason for this is the absence of a contribution from piezoelectrically active non-180° domain walls. This is not the case for the odd-layer BIT ($m=3$), which has several types of non-180° domain walls.^{25–27} However, a nearly hysteresis-free and constant d_{33} as a function of the frequency and applied ac pressure was found for Nb doped BIT at room temperature.²⁶ A possible reason for this is that the Nb doping suppresses the monoclinic distortion in BIT so that the structure is similar to that of the orthorhombic $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ($m=4$).²⁶

Figure 3 shows the effect of thermal depoling on the piezoelectric properties. The d_{33} values were measured at room temperature after annealing for 2 h at the x -axis temperature. When the annealing temperature is near T_c , the d_{33} values of all the compounds decrease rapidly, and tend to zero when the temperature is increased above T_c . The thermal depoling behavior of the materials differs when the annealing temperature is below $0.6 T/T_c$. There is about 40% drop in d_{33} for BIT below $0.6 T/T_c$. While Messing *et al.*²⁸ reported that for Nb doped BIT $\text{Bi}_4\text{Ti}_{3-x/5}\text{Nb}_{x/5}\text{O}_{12}$ ($x=0.2$) there was no obvious drop of d_{33} below 500 °C. The monoclinic distortion of BIT produces more types of non-180° domain wall. These observations suggest that these non-180° domain walls are thermally unstable well below the Curie point, and give rise to the observed degradation of d_{33} . The obvious depoling of BNT0-D below $0.6 T/T_c$ could also be attributed to a possible, but as of yet unconfirmed, monoclinic distortion caused by excess Nb doping in BNT0. There is a small decrease of d_{33} for CBNO, CBBNO, and BNT0 below $0.6 T/T_c$. While for the four-layer CBT and CNBT the d_{33} does not drop until the temperature is greater than $0.6 T/T_c$. Based on the similar depoling behaviors of two-layer CBNO, CBBNO and four-layer CBT, CNBT, orthorhombic structured materials are more stable to thermal depoling than monoclinic materials.

In summary, it is suggested that some non-180° domain walls are thermally unstable below T_c and give rise to thermal depoling. In Aurivillius phase materials, monoclinic distortion produces more types of non-180° domain walls, which therefore makes the materials less resistant to thermal depoling.

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