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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 (CaBi2Nb2O9, Ca0.9Ba0.1Bi2Nb2O9, Bi2NbTiO6, Bi2Nb1.2Ti0.8O9), three-layer (Bi4Ti3O12), and four-layer [CaBi3Ti2O15, Ca0.94(Na, Ce)0.06Bi3Ti4O15] compounds. All of them have a high Curie point (Tc ≃ 675 °C). The orthorhombic structured materials show good resistance to thermal depoling up to temperatures close to their Curie points. However, Bi4Ti3O12, which has a monoclinic structure, shows a significant reduction in d33 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 Bi2NbTiO6 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 relaxor1–3 and multiferroic4–6 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 (Bi2O3)2n(Am−xBxO3m+n)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 Pz of even-layer compounds is only along the a-axis. Based on their orthorhombic space group A2αμm, the polarization along the c-axis is cancelled because of mirror symmetry. However, in odd-layer compound Bi4Ti3O12 (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-axes.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, Tc, of the selected compounds is not less than 675 °C. The compounds include even-layer compounds CaBi2Nb2O9 (CBNO, m=2), Bi3NbTiO6 (BNTO, m=2), CaBi3Ti4O15 (CBT, m=4) and odd-layer compound Bi4Ti3O12 (BIT, m=3). In order to study the effect of substitution on the thermal depoling, three substituted compounds Ca0.96Ba0.04Bi2Nb2O9 (CBBNO, m=2), Bi3Nb1.2Ti0.8O9 (BNTO-D, m=2) and Ca0.94(Na, Ce)0.06Bi3Ti4O15 (CNBT, m=4) were also prepared.

Polycrystalline ceramic samples were prepared by conventional ceramic processing. The starting raw materials were Bi2O3 of 99.975% purity, CaCO3 of 99% purity, BaCO3 of 99% purity, Na2CO3 of 99.5% purity, CeO2 of 99.9% purity, TiO2 of 99.6% purity, and Nb2O5 of 99.9% purity. The materials were mixed by ball milling in ethanol, dried and sieved to under 250 μm. 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 μm, 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., C2011004DS).

X-ray diffraction (XRD) patterns for the sintered ceramics were obtained with an x-ray diffractometer (Siemens D5000) using Cu Kα 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, d33, was measured...
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, except BNTO and BNTO-D. In the XRD patterns for BNTO most of the diffraction peaks match the main phase of the BNTO structure with the exception of a small peak at about $2\theta=30^\circ$, which matches the strongest peak (117) for BIT. The doped BNTO-D ceramics also contain BIT phase. The amount of second phase in BNTO is higher than that in BNTO-D. The strongest diffraction peak for two layer compounds CBNO, CBBNO, BTNO, and BNTO-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.

Figure 2 shows the temperature dependence of the dielectric 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, BNTO, BNTO-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. After substitution, the room temperature $d_{33}$ value of CBBNO, BNTO-D, and CNBT is higher than that of CBNO, BNTO and CBT, respectively.

Figure 3 shows the 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.
eoelectric hysteresis. 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. 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. 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 SrBi$_4$Ti$_4$O$_{15}$ ($m=4$).

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 $T_c/T_c$. There is about 40% drop in $d_{33}$ for BIT below 0.6 $T_c/T_c$. While Messing et al. reported that for Nb doped BIT Bi$_{4}$Ti$_{3-3x}$Nb$_x$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 walls. 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 BNTO-D below 0.6 $T_c/T_c$ could also be attributed to a possible, but as of yet unconfirmed, monoclinic distortion caused by excess Nb doping in BNTO. There is a small decrease of $d_{33}$ for CBNO, CBBNO, and BNTO below 0.6 $T_c/T_c$. While for the four-layer CBT and CNBT the $d_{33}$ does not drop until the temperature is greater than 0.6 $T_c/T_c$. 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.