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Preparation and Properties of $(Ba_{0.6}Sr_{0.4})Bi_2Ta_2O_9$ Ceramic

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Abstract

$(Ba_{0.6}Sr_{0.4})Bi_2Ta_2O_9$ (BSBT) ceramic materials with plate-like grains were prepared by the conventional mixed oxide method. The microstructures of BSBT ceramic sintered at different temperatures were studied. The variations of the saturation polarization (P_s), remanent polarization (P_r) and coercive field (E_c) with applied electric field and temperature were studied by hysteresis (D–E loop) measurements. The permittivities, piezoelectric and pyroelectric coefficients of BSBT ceramic poled at various electric fields and temperatures were measured. © *1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

The layer-structured bismuth compound is one of the most technologically interesting materials. It has the general formula: $A_{n-1}Bi_2B_nO_{3n+3}$, where A is usually a divalent ion, such as Sr, Ba or Pb, and B is Ti^{4+} Nb^{5+} or Ta^{5+}. Within the bismuth family, $SrBi_2Ta_2O_9$ has attracted the most attention in the past several years because of its fatigue-free property,[1–6] which is a very important factor for the memory application of ferroelectric thin films. The good fatigue performance arises mainly from its domain configuration and composition. $BaBi_2Ta_2O_9$ is another important member of the layer-structured bismuth ferroelectric family. It has a lower Curie temperature and a higher permittivity at room temperature compared to $SrBi_2Ta_2O_9$. Since $SrBi_2Ta_2O_9$ and $BaBi_2Ta_2O_9$ have similar structures, it would be interesting to investigate ceramic materials based on $(Ba\text{-}Sr)Bi_2Ta_2O_9$ solid solutions. Such a study may help to produce materials with enhanced ferroelectric properties that are useful in applications.

In this paper, bulk $(Ba_{0.6}Sr_{0.4})Bi_2Ta_2O_9$ (BSBT) ceramic materials were sintered at different temperatures and their microstructures were examined. The relative permittivity, piezoelectric and pyroelectric coefficients, saturation polarization, remanent polarization, and coercive field were investigated as functions of the applied electric field and temperature.

2 Sample Preparation and experimental details

The ceramic material $(Ba_{0.6}Sr_{0.4})Bi_2Ta_2O_9$ was prepared by the conventional mixed oxide method. The raw materials used, Ta_2O_5, Bi_2O_3, $SrCO_3$ and $BaCO_3$, are all of chemically pure grade. The above raw materials in the ratio of stoichiometry of the composition were mixed by ball-milling. The $(Ba_{0.6}Sr_{0.4})Bi_2Ta_2O_9$ compound was obtained after calcining the mixture at 675°C for 2 h. The calcined compound was ball-milled again to reduce the particle size and then disc samples about 0·4 mm thick were fabricated by pressing the binder-mixed powder. After removal of the binder, the disc samples were sintered in sealed Al_2O_3 crucibles at 1155–1185°C for 1 h. The sintered samples were then electroded with air-dried silver paint.

The fracture surfaces of BSBT ceramic samples were examined in a Stereoscan 440 scanning electron microscope (SEM, Leica Cambridge Ltd.). Hysteresis (D-E loop) measurements were carried out at 23–120°C in a Radiant Technology RT66A ferroelectric test system equipped with a Trek P0621 power amplifier. The looping frequency is about 2·5 Hz. The permittivities of the ceramic before and after poling were measured using a HP4194A impedance analyzer. In order to elicit piezo- and pyroelectric activities, the BSBT samples were poled at various electric fields and temperatures. The piezoelectric coefficient d_{33} was

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measured using a Pennebaker Model 8000 tester (American Piezo-Ceramic Inc.) and the pyroelectric coefficient was determined by the digital integration method.[7] For the poled samples, the dielectric, piezoelectric and pyroelectric properties were measured 24 h after poling.

3 Results and Discussion

3.1 Microstructure

The SEM micrographs of the fracture surfaces of BSBT samples sintered at 1155 and 1170°C for 1 h are shown in Fig. 1. The morphology of the sample sintered at 1185°C is similar to that sintered at 1170°C and is not shown here. It is seen that the anisometric plate-like crystallises are randomly oriented in the matrix. The size of the crystalline grains is about 2–5 μm and does not depend significantly on sintering temperature.

Comparing with the morphology of SBT,[8] the size of the crystalline grains in BSBT is much smaller than that in SBT sintered at 1230°C, which is about 30 μm in the longitudinal direction. The preferential alignment of crystallites, observed in SBT samples sintered at 1230°C, is not observed in BSBT samples. This may arise from the substitution of the Sr atoms by the larger Ba atoms. It is also seen that the samples are not 100% dense and some pores exist in the matrix.

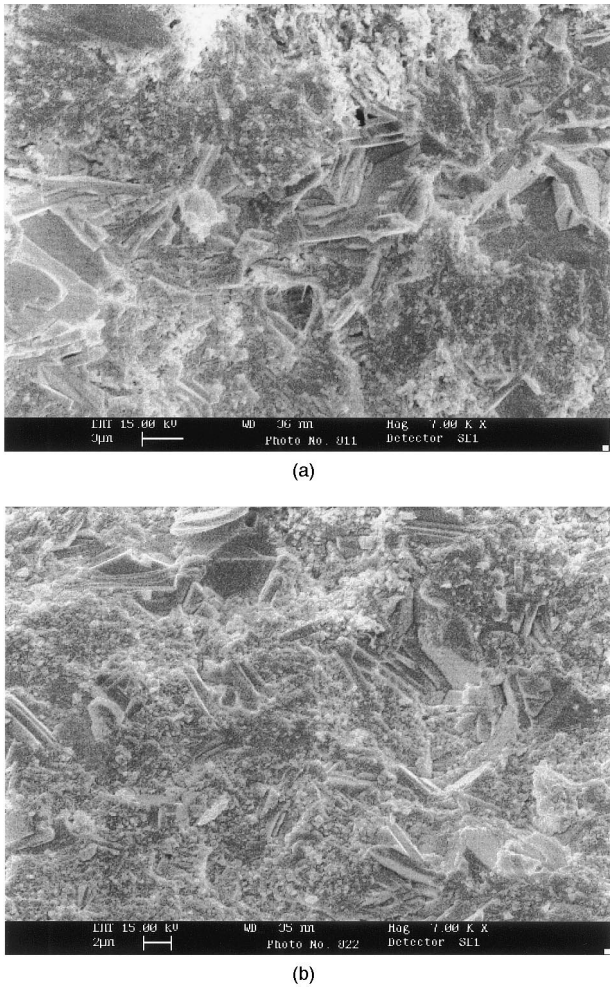

Fig. 1. SEM micrographs of fracture surfaces of BSBT ceramic samples sintered at (a) 1155°C, and (b) 1170°C.

3.2 Saturation and Remanent Polarization

The hysteresis loops for the samples sintered at 1155 (Sample A), 1160 (Sample B), 1170 (Sample C) and 1185°C (Sample D) were determined at different temperatures (from ambient temperature to 120°C) and applied electric fields (from 3·3 to 6·8 kV/mm). Typical D–E loops for Sample A measured at 23 and 80°C are shown in Fig. 2. A fully saturated square hysteresis loop had not been attained because there was electric breakdown when the electric field was further increased. This may arise from the existence of pores in the matrix of BSBT samples.

From the D–E loops shown in Fig. 2 it can be seen that the saturation polarization P_s, remanent polarization P_r and coercive field E_c of Sample A increase with the increase of applied field and measuring temperature. Although not shown, P_S, P_r and E_c, for Samples B, C and D exhibit similar trends. Figure 3 shows that P_s, P_r and E_c, measured at ambient temperature for BSBT sintered at 1155°C increase linearly with applied field. At a low applied field of 3·3 kV/mm, P_s, P_r are 0·82 and 0·26 μC cm^{-2}, respectively, and increase linearly to 2 and 0·7 μC cm^{-2}, respectively, as the applied field increases to 6·8 kV/mm^{-1}. E_c increases from 0·8 to 1·9 kV mm^{-1} over the same range of applied field. Figures 4–6 show that P_s, P_r and E_C measured at other temperatures also increase linearly with the applied electric field. Figure 5 shows that, at 120°C, P_r increases from 0·9 μC cm^{-2} at $E = 3{\cdot}3$ kV mm^{-1} to 2 μC cm^{-2} at $E = 6{\cdot}8$ kV mm^{-1}, and it has not

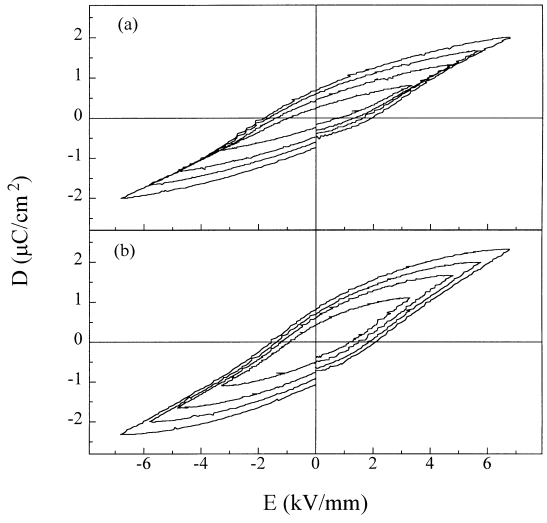

Fig. 2. Hysteresis behaviour of BSBT samples sintered at 1155°C. (a) measured at 23°C; (b) measured at 80°C.

reached saturation at the highest field applied. A higher P_s cannot be achieved because electrical breakdown limits the magnitude of the field that can be applied.

3.3 Relative permittivity

Figure 7 shows the relative permittivity ε at 23°C as a function of frequency for BSBT samples sintered at 1155 (Sample A) and 1170°C (Sample C). At 100 Hz ε is 158 for unpoled Sample A and 147 for unpoled Sample C. The ε values for both unpoled samples decrease by about 20% as the frequency increases from 100 Hz to 2 MHz. The slightly larger ε value for Sample A may result from the slightly larger crystallites in Sample A. It can be seen that poling under an applied electric field of 3 kV mm^{-1} at 90°C for 1 h leads to a 2–5% decrease in ε, (Fig. 7). There is a further decrease in ε when the applied field increases to 6 kV mm^{-1}. The poled samples show the same frequency dependence as the unpoled samples.

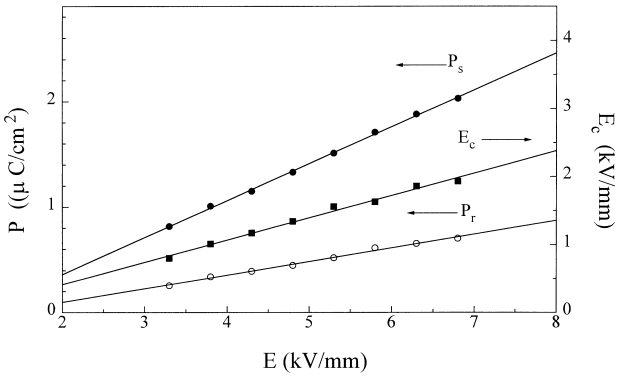

Fig. 3. P_s, P_r, and E_c of BSBT sintered at 1155°C as functions of the applied electric field at 23°C.

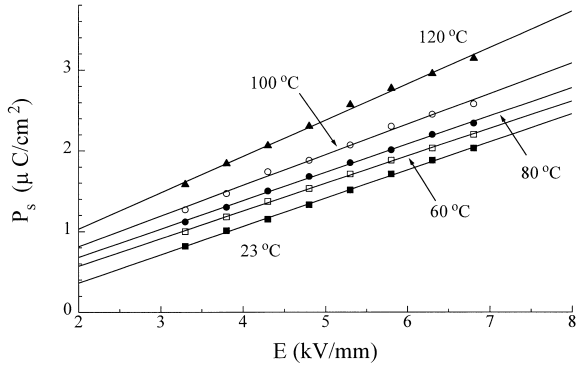

Fig. 4. Saturation polarization of BSBT sintered at 1155°C as a function of the applied electric field measured at various temperatures.

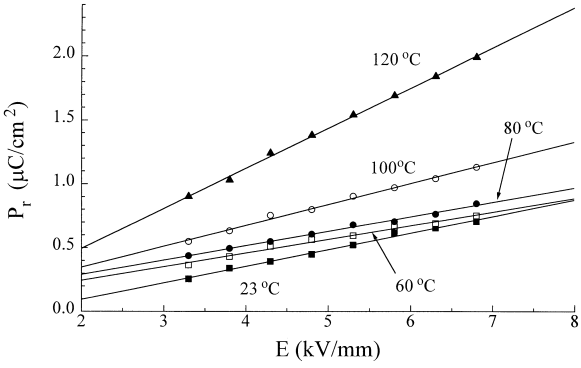

Fig. 5. Remanent polarization of BSBT sintered at 1155°C as a function of the applied electric field measured at various temperatures.

3.4 Piezoelectric and pyroelectric coefficient

The piezoelectric coefficient d_{33} was measured for BSBT samples sintered at 1155 and 1170°C after poling at 90°C for 1 h. The values of d_{33} for both samples are quite low, being about 5·8 and 6·4 pC/N after poling at 3 and 6 kV mm^{-1}, respectively. Figure 8 shows the pyroelectric coefficient p as a function of temperature for samples sintered at 1155 (Sample A) and at 1170°C (Sample C), both poled at 6 kV mm^{-1} and 90°C for 1 h. A similar

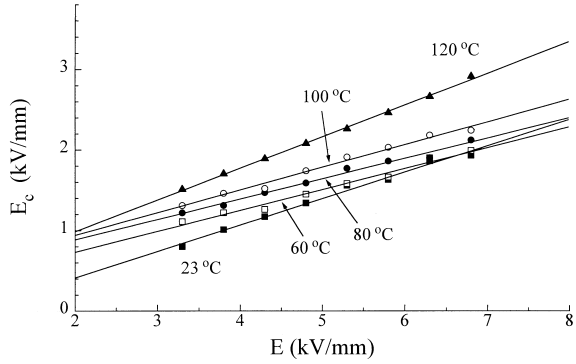

Fig. 6. Coercive field of BSBT sintered at 1155°C as a function of the applied electric field measured at various temperatures.

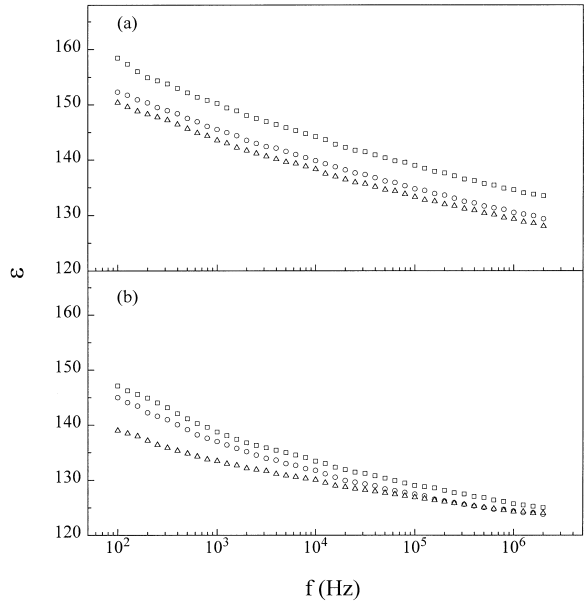

Fig. 7. Frequency dependence of relative permittivity at 23°C for (a) BSBT sintered at 1155°C, (b) BSBT sintered at 1170°C. Data □:, unpoled; ○, poled at 3 kV mm^{-1} and 90°C for 1 h; △, poled at 6 kV mm^{-1} and 90°C for 1 h.

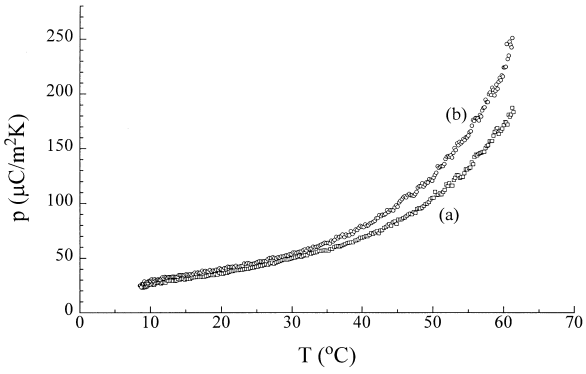

Fig. 8. Pyroelectric coefficient as a function of temperature for BSBT sintered at (a) 1155°C (b) 1170°C.

temperature dependence of the pyroelectric coefficient was found for the samples poled in DE loop measurements. The values of p for both samples are almost the same from 10 to 35°C, but p for the sample sintered at 1170°C exhibits a stronger temperature dependence above 35°C.

4 Conclusion

$(Ba_{0.6}Sr_{0.4})Bi_2Ta_2O_9$ (BSBT) ceramic materials were prepared by the conventional mixed oxide method using different sintering temperatures. Randomly oriented anisometric plate-like crystalline grains with size 2–5 μm were observed in the ceramic, thus revealing the layered structure of the material. The saturation polarization (P_s), remanent polarization (P_r) coercive field (E_c) were measured at various applied electric fields and temperatures. P_s, and P_f and E_c increase linearly as the applied field increases and also increase with increasing poling temperature. The relative permittivity of the poled ceramic samples is lower than that of the unpoled one. The higher the poling field, the lower the relative permittivity. BSBT has a low piezoelectric coefficient. Its pyroelectric coefficient is also low at ambient temperature, but becomes quite high above 50°C because of its strong positive temperature dependence.

Acknowledgements

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