Dielectric and pyroelectric properties of barium strontium calcium titanate ceramics

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Abstract

$(Ba_{0.6}Sr_{0.3}Ca_{0.1})TiO_3$ powders were prepared by the sol-gel method using a solution of Ba, Sr and Ca acetate and Ti isoprop-oxide, and the specimens doped with $MnCO_3$ (0.1 mol%) and Y_2O_3 (0.5 mol%) were fabricated by the cold isostatic press method. The urethane pot and zirconia ball were used in the mixing and grinding process, and the green pellets were sintered at 1450 °C for 2 h in the alumina crucible. The specimen exhibited a dense and void-free grain structure with grain size of about 3 μm. The dielectric constant and the dielectric loss at Curie temperature were 16,600 and 1.2%, respectively. The specimen under a 4 kV cm^{-1} DC bias field showed the maximum pyroelectric coefficient of 550×10^{-9} C cm^{-2} K^{-1} at Curie temperature. The figure of merit F.M.D* for specific detectivity (D^*) of the specimen, applied with DC 8 kV cm^{-1} bias field, was the highest value of 17.6×10^{-9} C cm J^{-1} at Curie temperature. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: (Ba,Sr,Ca)TiO$_3$; Dielectric properties; Pyroelectric properties; Sol-gel processes

1. Introduction

Ferroelectric Pb(Zr,Ti)O$_3$ and BaTiO$_3$ ceramics have received much attention for their possible application to the Gbit-scale ferroelectric random access memories (FRAMs), piezo micro-actuator, tunable microwave device and non-linear optical devices, due to their unique properties.[1–3] BaTiO$_3$ system ceramics, which exhibit spontaneous polarization and a high dielectric constant, were widely investigated because of their potential for various electrical properties obtained by varying the minor modification of the dopants without seriously affecting other properties and the lack of hazardous lead in the composition. In particular, the polarization and dielectric constant change rapidly near the Curie temperature, which makes this the most sensitive operation regime to detect infrared radiation. In general, BaTiO$_3$ and (Ba,Sr)TiO$_3$ ceramics are prepared by the conventional mixed oxide method, based on calcining mixtures of oxide and/or carbonate powders. However, the resultant products usually consist of chemically inhomogeneous particles with large grain sizes ($G_s > 10$ μm) and can not be used as raw materials for advanced electronic components. For large grain-size materials, several problems exist, such as poor mechanical strength at the final devices thickness and large pixel-to-pixel variation in the pyroelectric response properties for IR detection application. Uncooled infrared detector requires a grain size typically between 1 and 3 μm and a transition temperature near ambient room temperature to maximize detector performance.[4]

In this paper, (Ba,Sr,Ca)TiO$_3$ powders, doped with Y- and Mn-ions, were prepared by the sol-gel method in order to decrease the grain size and to improve the dielectric properties and chemical homogeneity in materials. Especially, the urethane pot and zirconia ball were used in the mixing and grinding process in order to prevent the contaminations from the pot. The dielectric and pyroelectric properties, as a function of the temperature and applied DC bias field, were investigated for infrared detectors.

2. Experimental

The chemical composition of the sample was given according to the following formula: $(Ba_{0.6}Sr_{0.3}Ca_{0.1})$-

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TiO_3 + 0.1 mol% $MnCO_3$ + 0.5 mol% Y_2O_3. This $(Ba_{0.6}Sr_{0.3}Ca_{0.1})TiO_3$ (BSCT) composition gave a transition temperature near the ambient room temperature. Doped BSCT specimens with 0.1 mol% $MnCO_3$ and 0.5 mol% Y_2O_3 were selected for their basic composition on the basis of previous experiments.[5] BSCT powders, started with a mixture of Ba acetate [$Ba(CH_3COO)_2$], Sr acetate hemihydrate [$Sr(CH_3COO)_2 \cdot 0.5H_2O$], Ca acetate monohydrate [$Ca(CH_3COO)_2 \cdot H_2O$] and Ti isopropoxide $Ti[OCH(CH_3)_2]_4$, were prepared by the sol-gel method. Acetic acid and 2-methoxyethanol were used as solvents. In the initial stage, Ba, Sr and Ca acetate were dissolved in acetic acid with a molar ratio of 1:15, and then the solution was heated for the evaporation of water. After cooling, Ti-isopropoxide, dissolved in 2-methoxyethanol, was added to the solution. This mixed solution was refluxed, and then 2-methoxyethanol and water were added to the solution for stabilization and hydrolysis, respectively. The powder precursors were dried slowly at 100 °C for 48 h and then calcined at 800 °C for 2 h in a high-purity alumina crucible. After dopants of Y_2O_3 and $MnCO_3$ were added to the calcined BSCT powders, these powders were mixed and ground for 24 h with urethane pot and zirconia grinding media in order to prevent contamination. The granular powders, mixed with polyvinyl alcohol of 2 wt.%, were prepared by the spray-dry method and were pressed by using the cold isostatic press method. The green pellets were sintered at 1450 °C for 2 h in the alumina crucible.

The crystallinity and the microstructure of BSCT specimens were observed using X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.
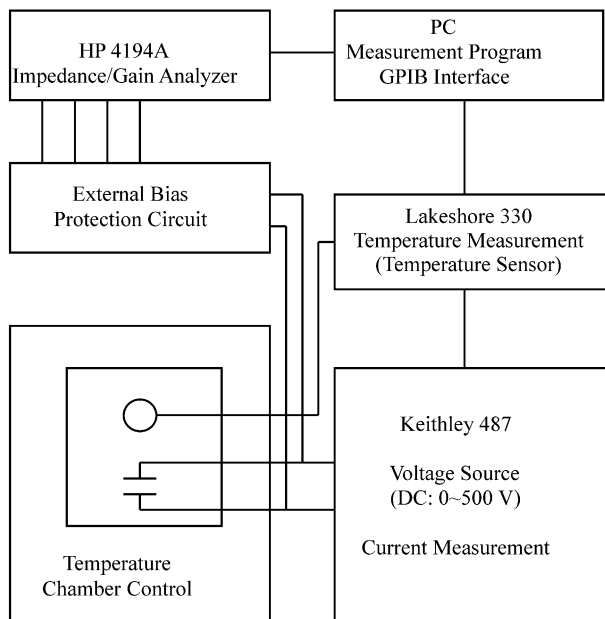
The dielectric and pyroelectric properties with variation of temperature and DC bias field were measured using an impedance/gain analyzer (HP 4194A). The measurement temperature was 26 °C. Fig. 1 shows the block diagram for the dielectric and pyroelectric properties measurement system, which depicts the varying temperature and DC bias field of the BSCT specimen.
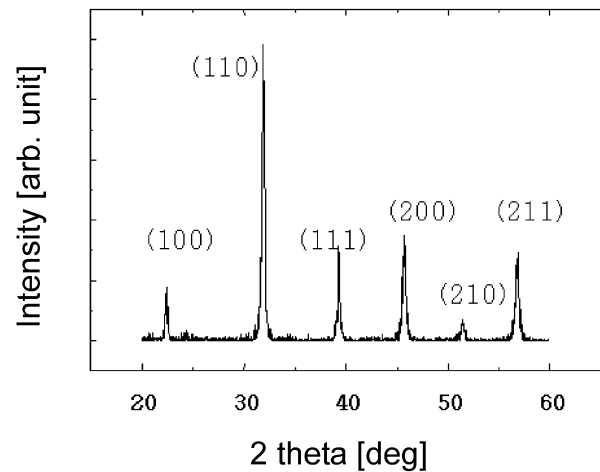

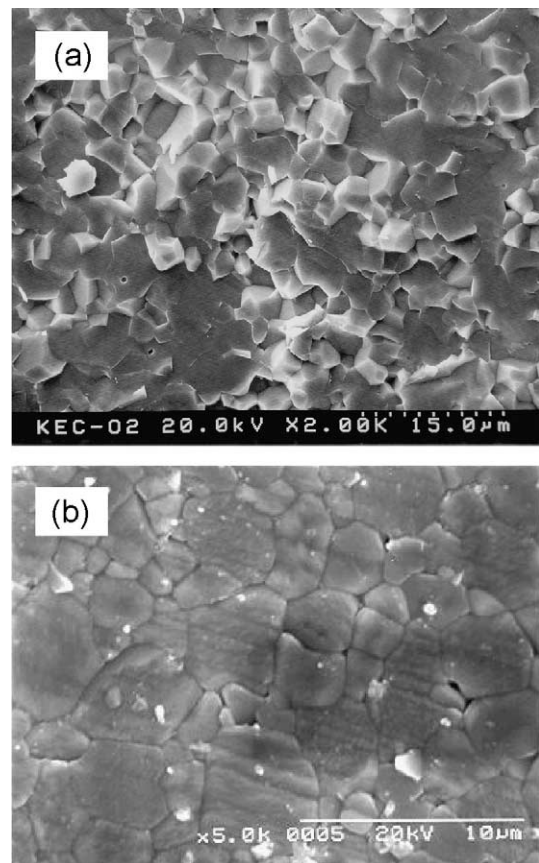Fig. 2. XRD patterns of the BSCT specimen sintered for 2 h at 1450 °C.

Fig. 3. SEM micrographs of the BSCT specimen: (a) cross section and (b) surface morphologies.

Fig. 1. Block diagram of the measurement of dielectric and pyroelectric properties under temperature and DC bias field variation.

3. Results and discussion

The X-ray diffraction analysis of BSCT specimen, sintered at 1450 °C for 2 h, showed the formation of the complete solid solution in a single cubic perovskite structure with a lattice constant of 0.3973 nm and non-second phase, as shown in Fig. 2.

Fig. 3 shows the cross-section and surface SEM micrographs of BSCT specimen. The specimen exhibited a dense and void-free grain structure with a grain size of about 3 μm. If the Al_2O_3 pot and ball were used in the mixing and grinding processes of $BaTiO_3$ system powders, Al ions give rise to a formation of vacancies due to addition in the specimen as the dopant.[6] But, in this study, the urethane pot and zirconia ball were used in the ball-milling process in order to prevent the contaminations, and as a result the dense and void-free grain structure were formed. The sintered density of the specimen used the urethane pot was 5.54 g cm^{-3} which was in the range of 98% of the theoretical value, and this was much higher than that (5.45 g cm^{-3}) of the specimen used in the alumina pot.
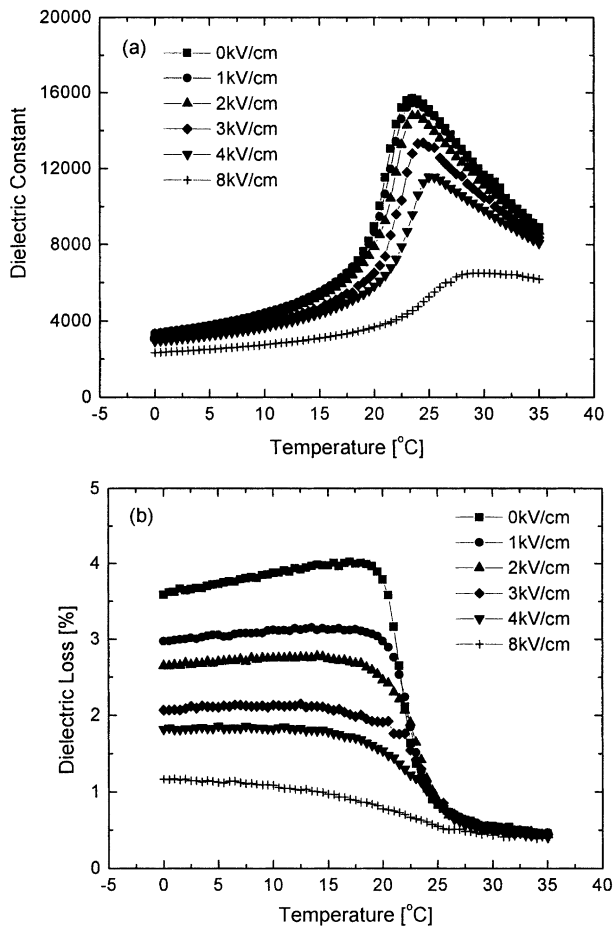
The relative dielectric constant and dielectric loss of BSCT specimens as a function of temperature and applied DC bias field are shown in Fig. 4. The Curie temperature of the zero biased BSCT specimens was 23.5 °C, and the dielectric constant and the dielectric loss at this temperature were 16,600 and 1.2%, respectively. The maximum dielectric constant and dielectric loss decreased and the Curie temperature increased as the DC bias field increased. The good dielectric constant slope and low dielectric loss up to 4 kV cm^{-1} suggest that specimens with reasonable pyroelectric responsivity can be expected.

Fig. 5 shows the relative dielectric constant and dielectric loss of BSCT specimens as a function of DC bias field, and the measurement temperature was 25 °C. From the results shown in Fig. 5, it is evident that the relative dielectric constant of the specimens decreased with increasing the DC bias field. The nonlinearity of dielectric constant with DC biasing field at the paraelectric states results from the anharmonic interaction of Ti ions in the perovskite cubic structure.[7] The real part of the relative dielectric constant ε'_r in paraelectric states was represented as

$$\varepsilon'_r / \varepsilon'_{ro} = (1 + a\varepsilon'_{ro}E^2)^{-1/3} \tag{1}$$

Fig. 4. (a) Relative dielectric constant and (b) dielectric loss of BSCT specimens as a function of temperature and DC bias fields.
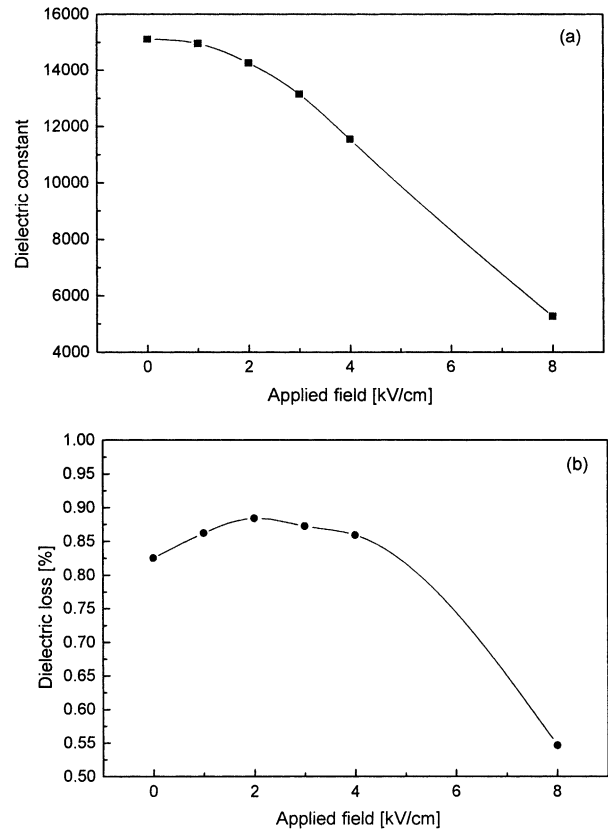

Fig. 5. Relative dielectric constant and dielectric loss of BSCT specimens as a function of applied DC bias fields.

where ε'_{ro} and ε'_r are the real part of the relative dielectric constant at 1 kHz under zero bias field an under bias field E and a is the phenomenological coefficient. The ε'_r of the samples decreased with increasing bias field. The phenomenological coefficient, a, is used to determine the effects of the DC bias field on the real part of the relative dielectric constant, and increased with increase an DC bias field. The values of the phenomenological coefficient are 9.17×10^{-21} (cm $V^{-1})^2$ and 1.03×10^{-19} (cm $V^{-1})^2$ with an applied field of 1 kV cm^{-1} and 8 kV cm^{-1}, respectively. The dielectric loss of the specimens is influenced little by the DC bias field. But the specimen applied with DC 8 kV cm^{-1} bias field showed a good value of 0.546%, due to the suppression of the movement of charges by the high field.

Fig. 6 shows the pyroelectric coefficient of BSCT specimens with variation of DC bias field and temperature. The specimens under a 4 kV cm^{-1} DC bias field showed the maximum value of 550×10^{-9} C cm^{-2} K^{-1} at Curie temperature. This is due to the fact that the dielectric

constant-temperature curve of the specimen applied with DC 4 kV cm^{-1} bias field display a sharp shape near the Curie temperature, as shown in Fig. 4.

Fig. 7 shows the dependence of the figure of merit F.M.D* for specific detectivity D* (where, F.M.D*= $p/c_v(K \cdot \tan\delta)^{1/2}$ and p is the pyroelectric coefficient, c_v ($= 3.2$ J cm^{-3} K^{-1}) is the volume specific heat, K is the dielectric constant and $\tan\delta$ is the dielectric loss)[8] on DC bias field for BSCT specimens. The F.M.D* for specific detectivity increased with an increase in applied DC field, and the specimen applied with DC 8 kV cm^{-1} bias field show a maximum value of 17.6×10^{-9} C cm J^{-1} at Curie temperature. Even the specimens biased at 4 kV cm^{-1} had good pyroelectric coefficient and showed a low F.M.D*, due to their high dielectric constant and dielectric loss.

4. Conclusions

BSCT specimen doped with $MnCO_3$ (0.1 mol%) and Y_2O_3 (0.5 mol%) have been fabricated by the sol-gel method and characterized for uncooled infrared detector materials. The urethane pot and zirconia ball were used in the mixing and grinding process, and as a result the dense and void-free grain structure were formed. The relative dielectric constant of the specimens nonlinearly decreased with increasing the DC bias field. The specimen, which was displayed a sharp shape of the relative dielectric constant-temperature curve near the phase transition temperature, showed the high pyroelectric coefficient.
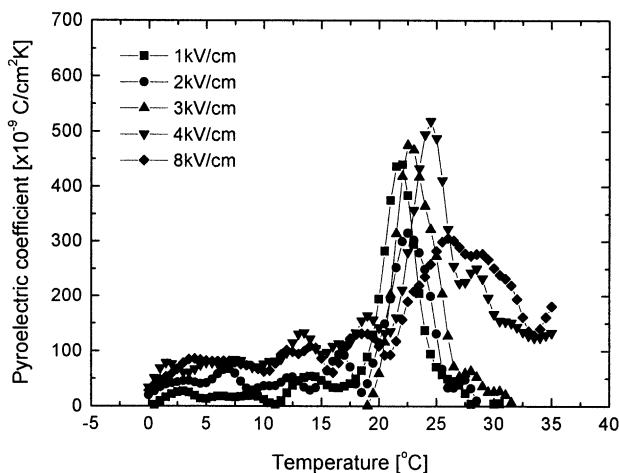

Fig. 6. Pyroelectric coefficient of BSCT specimens as a function of temperature and DC bias fields.

Fig. 7. Figure of merit F.M.D* of BSCT specimens as a function of temperature and DC bias fields.

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