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Phase transformation in BST ceramics investigated by internal friction measurements

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Abstract

Ferroelectric (BaSr)TiO_3 materials are widely used for numerous applications in microelectronic ranges. This paper concerns investigation of variation of internal friction and shear modulus versus temperature in a low frequency range for $Ba_xSr_{1-x}TiO_3$ systems (x = 0.4, 0.55, 0.7 and 0.8). This makes it possible to report energy dissipation phenomena such as phase transitions and relaxation processes due to interactions between domain walls and oxygen vacancies. Temperature of loss peak for each phase transition decreases and peaks become more diffuse with increasing Sr content in BST materials. An experimental phase diagram has been established for $Ba_xSr_{1-x}TiO_3$ systems. Effects of MgO doping have been investigated for the composition x = 0.8. Both level of mechanical loss and temperatures of phase transitions are sensitive to the Mg dopant.

Keywords: Ferroelectric properties; Mechanical properties; Internal friction; $BaTiO_3$ and titanates

1. Introduction

Ferroelectric materials as barium strontium titanate, $Ba_xSr_{1-x}TiO_3$ (BST) are potential candidates for use in microwave circuit devices. High tunability and low dielectric loss at room temperature[1] make it possible to use those materials in voltage tuneable microwave components. It has been shown that composition influences the tunability and dielectric loss depends on microstructure and thickness for films.[2] In $BaTiO_3$ (x = 1) materials, an elastic modulus anomaly and a mechanical loss peak are induced at three phase transitions: cubic–tetragonal (ferroelectric–paraelectric), tetragonal–orthorhombic and orthorhombic–rhombohedral. Some losses due to relaxation processes have been observed in materials having coarse grains in ferroelectric phase.[3] Some works have shown that they are ascribed to the interaction between domain walls and oxygen vacancies diffusion. In $BaTiO_3$ ceramics, permittivity anomalies and dielectric loss peaks are respectively connected to modulus anomalies and mechanical loss peaks. As a result, either dielectric spectra or mechanical spectra make it possible to show the occurrence of different phenomena responsible for energy dissipation.

Previous work[4] reported dielectric measurements on $Ba_xSr_{1-x}TiO_3$ (x = 0.5, 0.6, 0.7 and 1) ceramics. The aims were to determine the phase transitions temperatures and evaluate the dielectric losses level for each composition in order to reach optimal performance. This paper deals with mechanical losses and shear modulus as a function of temperature for $Ba_xSr_{1-x}TiO_3$ (x = 0.4, 0.55, 0.7 and 0.8) ceramics at low frequencies. The last part shows the MgO doping effects for the $Ba_{0.8}Sr_{0.2}TiO_3$ composition.

2. Materials and experimental

$Ba_xSr_{1-x}TiO_3$ ceramics with x = 0.8, 0.7, 0.55 and 0.4 were prepared by conventional solid-state reaction and

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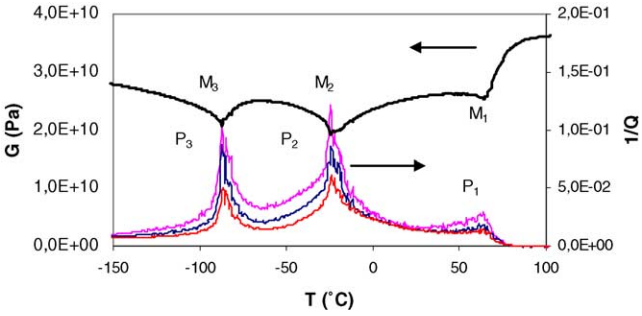

Fig. 1. Mechanical loss (Q^{-1}) and shear modulus (G) as a function of temperature in BST80/20 ceramic at 0.1, 0.3 and 1 Hz.

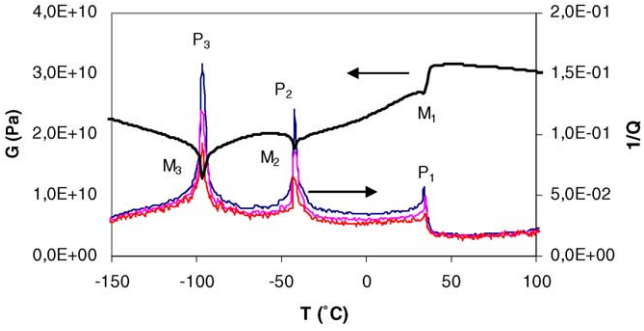

Fig. 2. Mechanical loss (Q^{-1}) and shear modulus (G) as a function of temperature in BST70/30 ceramic at 0.1, 0.3 and 1 Hz.

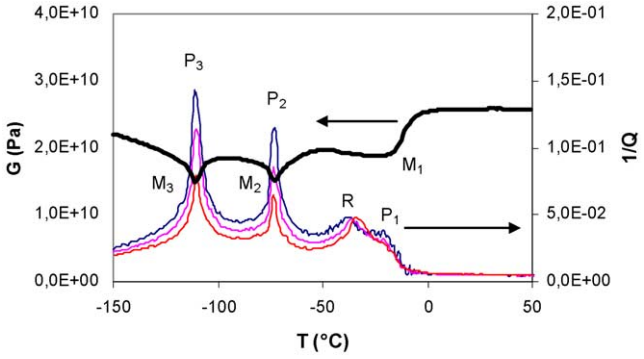

Fig. 3. Mechanical loss (Q^{-1}) and shear modulus (G) as a function of temperature in BST55/45 ceramic at 0.1, 0.3 and 1 Hz.

followed by viscous polymer processing (VPP) route. Those compositions are denoted as BST80/20, 70/30, 55/45 and 40/60, respectively. Barium carbonate (Fluka, >99%), strontium carbonate (Fluka, >99%), and titania powders were mixed in acetone with zirconia media, then calcined at temperatures from 900 to 1150 °C for 2 h. The calcined powders were mixed with polymer (PVB) and binders in a twin roll mill (Interdisciplinary Research Centre, University of Birmingham, UK); a final lamination makes it possible to obtain sheets of 1.3–1.4 mm in thickness. Samples with dimensions 55 mm × 5 mm × 1.3 mm were sliced up from the dried paste. To remove additive polymer, samples were first heated up to 600 °C at a heating rate of 1 °C/min before sintering at 1400 °C for 2 h with a heating rate of 10 °C/min.

The mechanical loss (Q^{-1}) and the shear modulus (G) were simultaneously measured[5] versus temperature at low frequencies (0.1 to 1 Hz) with an inverted pendulum. Internal friction (or mechanical loss) is deduced from the loss angle between applied stress (about 2 MPa) and resulting strain. Shear modulus corresponds to stress–strain ratio. All measurements were performed at a heating rate of 1 °C/min in vacuum ($\cong 10^{-3}$ Torr).

3. Results and discussion

Su et al.[6] have reported that microstructure and dielectric properties depend strongly on calcination and sintering conditions in BST materials. The microstructures of the $Ba_xSr_{1-x}TiO_3$ ceramics with x = 1, 0.7, 0.6, and 0.5 compositions processed in the same way are described by Cheng et al.[4] For BST80/20 (x = 0.8) and BST70/30 (x = 0.7) ceramics, an abnormal grain growth is obtained with coarse grains of about 50 μm surrounded by fine grains of about 2 μm. The grain size increases with Ba content or, in other words, substitution of Ba by Sr inhibits grains growth. The mechanical loss (Q^{-1}) and the shear modulus (G) of the BST80/20, 70/30, 55/45 and 40/60 compositions as a function of temperature for frequencies of 0.1, 0.3 and 1 Hz are respectively shown in Figs. 1–4.

The $G(T)$ curves show three modulus anomalies M_1, M_2, and M_3 connected to loss peaks P_1, P_2, and P_3 which correspond to the phase transitions: cubic to tetragonal, tetragonal to orthorhombic and orthorhombic to rhombohedral, respectively. Those modulus anomalies are denoted M because they are often ascribed to a minimum value on $G(T)$ curves.

The temperatures of phase transitions decrease with increasing Sr content in BST materials and the loss peaks become broader (see Figs. 1–4). The microstructure of such ceramics has a core-shell structure, which leads to more diffuse phase transitions with rising Sr content. For the BST55/45 and BST40/60 compositions, it is observed that the anomaly M_1 does not become a modulus minimum and the phase transition loss peak cubic (paraelectric)–tetragonal (ferroelectric) noted P_1 appears like a step. This agrees with previous observations

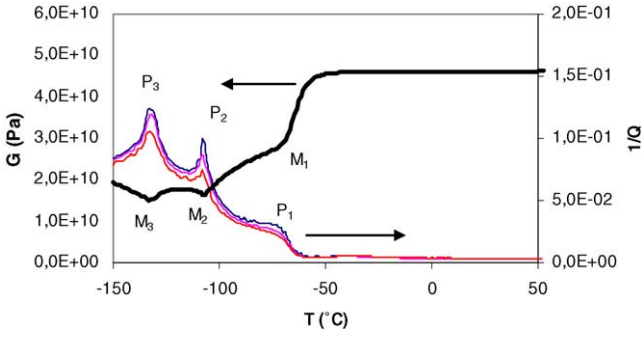

Fig. 4. Mechanical loss (Q^{-1}) and shear modulus (G) as a function of temperature in BST40/60 ceramic at 0.1, 0.3 and 1 Hz.

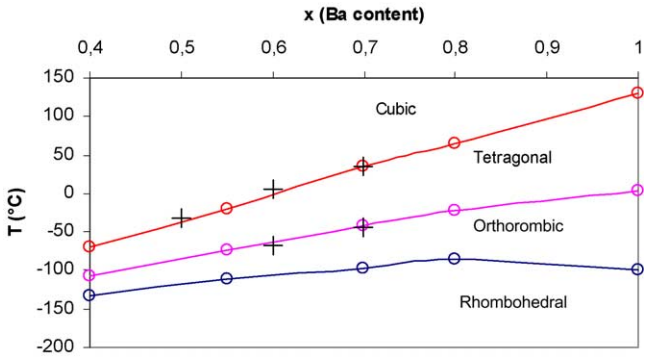

Fig. 5. Experimental phase diagram of $Ba_xSr_{1-x}TiO_3$ systems. The circles (◯) correspond to mechanical measurements and the crosses (+) correspond to dielectric measurements.

of the curve of dielectric loss as a function of temperature[4] the BST50/50 composition.

Fig. 5 shows the experimental phase diagram plotted from the mechanical spectroscopy measurements for the $Ba_xSr_{1-x}TiO_3$ materials. Some previous results[4] obtained with dielectric measurements are shown in the same figure. The case $x = 1$ corresponds to $BaTiO_3$ ceramic and the mechanical measurements have been carried out in a previous work.[7] Such comparison makes it possible to show that dielectric and mechanical measurements are fully connected.

Fig. 3 shows the $Q^{-1}(T)$ curves of the BST55/45 composition. A broad relaxation peak R exists in the ferroelectric phase in addition to the phase transition peak P_1. The R peak is also frequency dependent, so it is controlled by a relaxation process. The calculation of its activation parameters with the Arrhenius plot might help to determine the nature of relaxation process. Activation energy (H) and limit relaxation time (τ_0) are linked as:[8]

$$\tau = \tau_0 \exp\left(\frac{H}{kT}\right)$$

where T is the absolute temperature and k is the Boltzmann constant. The R peak is considered as a Debye peak so $\omega\tau = 1$ ($\omega = 2\pi f$). This gives:

$$\ln(2\pi f) = -\ln(\tau_0) - \frac{H}{kT_p}$$

T_p corresponds to the temperature of peak maximum. The activation energy and the limit relaxation time are calculated to be 2.9 eV and 3×10^{-63} s. Activation energy smaller than 1.1 eV has been measured in BST systems[9–11] leading to conclusion that the relaxation peaks could be attributed to the diffusion of oxygen vacancies. In the present case, the activation energy and the relaxation limit time are respectively larger and shorter than the found values in the literature. Postnikov et al.[12] proposed that the relaxation peaks are ascribed to the diffusion of point defects in ferroelectric materials. He et al.[13] measured a larger activation energy and a smaller relaxation limit time than those found in PZT materials. Those authors described the phenomenon by using the coupling model[14]

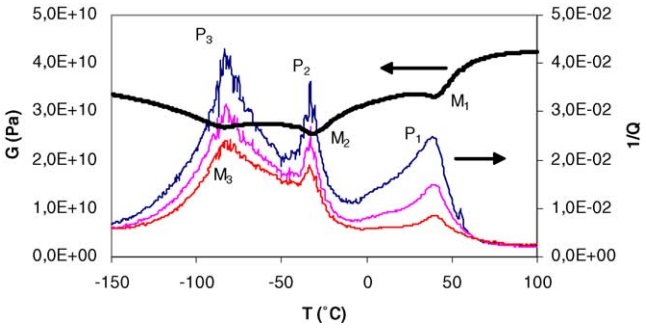

Fig. 6. Mechanical loss (Q^{-1}) and shear modulus (G) as a function of temperature in BST80/20 ceramic with 1 at.% MgO doping at 0.1, 0.3 and 1 Hz.

where the activation energy is given by:

$$H = \frac{H_0}{1-n}$$

H_0 is the activation energy which describes the interacting system, H is the apparent activation energy, and n is the coupling parameter describing the degree of the correlation of the system. If $n > 0$ then correlation effects play a significant role and H becomes larger. It is thought that the relaxation peak R for the BST55/45 composition can be induced by the relaxation of oxygen vacancy clusters near 90° domain walls. Further investigations are needed to improve the understanding of this proposed loss mechanism.

Fig. 6 shows the $G(T)$ and $Q^{-1}(T)$ curves of the BST80/20 material doped with 1 at.% MgO. The ceramic has been prepared to investigate the doping influence. The three modulus anomalies are connected to three loss peaks (P_1, P_2 and P_3) induced by three phase transitions as for non-doped BST. In Table 1, the cubic–tetragonal, tetragonal–orthorhombic and orthorhombic–rhombohedral transition temperatures are respectively noted $T_{C\text{-}T}$, $T_{T\text{-}O}$ and $T_{O\text{-}R}$ in both doped and undoped materials. Significant changes in the transition temperatures from tetragonal to orthorhombic phase and cubic to tetragonal phase are observed. Moreover, the heights of loss peaks P_2 and P_3 decrease with Mg dopant. As regards the P_1 peak at the Curie temperature, its height is not influenced by the use of Mg dopant. This implies that the Mg doped BST80/20 material has lower mechanical losses than that of undoped material except between 20 and 50 °C. As mechanical and dielectric losses are linked one to each other, it is thought that lower dielectric losses can be obtained when using dopant. The level of loss decreases with increasing frequency (see Figs. 1–4). This indicates that the properties of doped material are improved for application in microwave devices.

Table 1
Temperatures of phase transitions in undoped and 1 at.% MgO doped BST80/20 ceramics

Compositions	$T_{O\text{-}R}$ (°C)	$T_{T\text{-}O}$ (°C)	$T_{C\text{-}T}$ (°C)
BST80/20 doped	−82	−32	39
BST80/20 undoped	−86	−23	65

4. Conclusion

Mechanical measurements as a function of temperature have been carried out on BST ceramics with different compositions. Each phase transition induces a modulus anomaly and a mechanical loss peak. This makes it possible to determine the temperatures of transition: cubic to tetragonal phase, tetragonal to orthorhombic phase and orthorhombic to rhombohedral phase. An experimental phase diagram is deduced from those measurements and from previous dielectric measurements for $Ba_xSr_{1-x}TiO_3$ systems. An additional relaxation loss peak appears in the $Q^{-1}(T)$ curves for the BST55/45 ceramic. Taking into account the activation parameters, it is thought that the relaxation process is induced by the relaxation of oxygen vacancy clusters near 90° domain walls. Undoped and doped BST80/20 materials have also been investigated. The doping effects change the temperatures of phase transitions and the level of mechanical loss. A trade-off between quantity of dopant and choice of composition can be found to obtain a high performance material (low dielectric or mechanical loss) for microwave applications.

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References

1. Davis Jr., L. and Rubin, L. G., Some dielectric properties of barium-strontium titanate ceramics at 3000 megacycles. *J. Appl. Phys.*, 1953, **24**, 1195.
2. Su, B., Holmes, J. E., Meggs, C. and Button, T. W., Dielectric and microwave properties of barium strontium titanate (BST) thick films on alumina sustrates. *J. Eur. Ceram. Soc.*, 2003, **23**, 2699–2703.
3. Cheng, B. L., Gabbay, M., Maglione, M. and Fantozzi, G., Relaxation motion and possible memory of domain structures in barium titanate ceramics studied by mechanical and dielectric losses. *J. Electroceram.*, 2003, **10**, 5–18.
4. Cheng, B. L., Su, B., Holmes, J. E., Button, T. W., Gabbay, M. and Fantozzi, G., Dielectric and mechanical losses in (Ba,Sr)TiO_3 systems. *J. Electroceram.*, 2002, **9**, 17–23.
5. Schaller, R., Fantozzi, G. and Gremaud, G., *Mechanical Spectroscopy Q^{-1} 2001 with Applications to Materials Science*. Trans Tech Publications, Switzerland, 2001.
6. Su, B., Holmes, J. E., Cheng, B. L. and Button, T. W., Processing effects on the microstructure and dielectric properties of barium strontium titanate (BST) ceramics. *J. Electroceram.*, 2002, **9**, 111–116.
7. Cheng, B. L., Gabbay, M., Fantozzi, G. and Duffy Jr., W., Mechanical loss and elastic modulus associated with phase transitions of barium titanate ceramics. *J. Alloys Compounds*, 1994, **211/212**, 352–355.
8. Nowick, A. S. and Berry, B. S., *Anelastic Relaxation in Crystalline Solids*. Academic Press, New York, 1972 (Chapter 3).
9. Cheng, B. L., Gabbay, M., Duffy Jr., W. and Fantozzi, G., Anelastic relaxation associated with motions of domain walls in $BaTiO_3$ ceramics. *J. Mater. Sci.*, 1996, **31**, 4141–4147.
10. Zafar, S., Jones, R. E., Jiang, B., White, B., Chu, P., Taylor, D. and Gillespie, S., Oxygen vacancy mobility determined from current measurements in thin $Ba_{0.5}Sr_{0.5}TiO_3$ films. *Appl. Phys. Lett.*, 1998, **73**, 175–177.
11. Saha, S. and Krupanidhi, S. B., Microstructure related influence on the electrical properties of pulsed laser ablated (Ba,Sr)TiO_3 thin films. *J. Appl. Phys.*, 2000, **88**, 3506–3513.
12. Postnikov, V. S., Pavlov, V. S., Gridnev, S. A. and Turkov, S. K., Interaction between 90° domain walls and point defects of the crystal lattice in ferroelectric ceramics. *Sov. Phys. Solid State*, 1968, **10**(6), 1267–1270.
13. He, L.-X., Li, C.-E., Wang, Z.-Y., Yan, H.-X. and Liu, W., Study on low frequency internal friction for Pb(Zr,Ti)O_3 ferroelectric ceramics. *Phys. Stat. Sol. (a)*, 2000, **179**, 275–283.
14. Haneczok, G. and Weller, M., Analysis of mechanical loss spectra in Zirconia ceramics by applying the coupling model. *J. Phys. IV*, 1996, **6**, C8-703–C8-706.