Phase transformation in BST ceramics investigated by internal friction measurements

H. Frayssignes a,∗, B.L. Cheng b, G. Fantozzi a, T.W. Button c

a GEMPPM UMR CNRS 5510, INSA de Lyon, Batiment Blaise Pascal, 20 Avenue Albert Einstein, 69621 Villeurbanne Cedex, France
b Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China
c IRC in Materials Processing, University of Birmingham, Edgbaston B15 2TT, UK

Received 10 April 2004; received in revised form 13 July 2004; accepted 16 July 2004
Available online 29 September 2004

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 x Sr 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 x Sr 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.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Ferroelectric properties; Mechanical properties; Internal friction; BaTiO 3 and titanates

1. Introduction
Ferroelectric materials as barium strontium titanate, Ba x Sr 1−x TiO 3 (BST) are potential candidates for use in microwave circuit devices. High tunability and low dielectric loss at room temperature 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. 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. 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 reported dielectric measurements on Ba x Sr 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 x Sr 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 Ba0.8Sr 0.2TiO 3 composition.

2. Materials and experimental
Ba x Sr 1−x TiO 3 ceramics with x = 0.8, 0.7, 0.55 and 0.4 were prepared by conventional solid-state reaction and
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 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 (≈10^{-3} Torr).

3. Results and discussion

Su et al. have reported that microstructure and dielectric properties depend strongly on calcination and sintering conditions in BST materials. The microstructures of the Ba\(_x\)Sr\(_{1-x}\)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. 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.
of the curve of dielectric loss as a function of temperature \( T \) the BST50/50 composition. Fig. 5 shows the experimental phase diagram plotted from the mechanical spectroscopy measurements for the Ba\(_x\)Sr\(_{1-x}\)TiO\(_3\) materials. Some previous results \(^6\) 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. \(^1\) Such comparison makes it possible to show that dielectric and mechanical measurements are fully connected.

\[ Q_o = \frac{H}{kT_p} \]

\( T_p \) corresponds to the temperature of peak maximum. The activation energy and the limit relaxation time are calculated to be 2.9 eV and 3 \( \times 10^{-15} \) s. Activation energy smaller than 1.1 eV has been measured in BST systems \(^9\) 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. \(^1\) proposed that the relaxation peaks are ascribed to the diffusion of point defects in ferroelectric materials. He et al. \(^1\) 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\(^1\)

**Table 1**

<table>
<thead>
<tr>
<th>Compositions</th>
<th>( T_{C,K} ) (°C)</th>
<th>( T_{C,O} ) (°C)</th>
<th>( T_{C,T} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BST80/20 doped</td>
<td>–82</td>
<td>–32</td>
<td>39</td>
</tr>
<tr>
<td>BST80/20 undoped</td>
<td>–86</td>
<td>–23</td>
<td>65</td>
</tr>
</tbody>
</table>

**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:

\[ H = \frac{H_o}{1 - \eta} \]

\( H_o \) is the activation energy which describes the interacting system, \( H \) is the apparent activation energy, and \( \eta \) is the coupling parameter describing the degree of the correlation of the system. If \( \eta > 0 \) 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.
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$_x$Sr$_{1-x}$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.

Acknowledgements

The samples were prepared at the IRC in Materials Processing (UK) and the internal friction measurements were carried out at the laboratory GEMPPM (France). The authors would like to thank French EGIDE and British Council for the financial support of Alliance Partnership Programme 2002, Project No.: 04015YC and PN 02.006.

References