



Dielectric and Mechanical Losses in (Ba,Sr)TiO₃ Systems

B.L. CHENG,^{1,2,*} B. SU,¹ J.E. HOLMES,¹ T.W. BUTTON,¹ M. GABBAY³ & G. FANTOZZI³

¹*IRC in Materials Processing, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

²*Laboratory of Optical Physics, Institute of Physics, Centre for Condensed Matter Physics,
Chinese Academy of Sciences, Beijing 100080, Peoples' Republic of China*

³*GEMPPM, CNRS UMR5510, INSA de Lyon, 69621 Villeurbanne cedex, France*

Submitted June 17, 2002; Accepted September 10, 2002

Abstract. In the application of tuneable microwave devices of ferroelectric (BaSr)TiO₃ systems the two critical parameters needed for optimal device performance are high tunability and low dielectric loss. The dielectric loss of the materials is strongly dependent on microstructure. This paper is concerned with an investigation of the variation in the dielectric and mechanical losses in Ba_xSr_{1-x}TiO₃ systems ($x = 0.5, 0.6, 0.7$ and 1.0) with microstructure (grain sizes from $1 \mu\text{m}$ to $50 \mu\text{m}$). The magnitude of the loss peak and sharpness of the anomaly in the dielectric constant/elastic modulus observed for the phase transitions in Ba_xSr_{1-x}TiO₃, depend not only on the composition and but also on the grain size. A relaxation peak has been observed in large grain material, which is indication of interactions between different configurations of domain walls and the diffusion of oxygen vacancies in the domains.

1. Introduction

Ferroelectric Ba_xSr_{1-x}TiO₃ (BST) ceramics have been widely studied in microelectronic devices such as voltage-tuneable microwave components and in dynamic random access memories [1, 2]. In the application of tuneable microwave devices of ferroelectric BST systems the two critical parameters needed for optimal device performance are high tunability and low dielectric loss. The tunability can be influenced by changes in the composition of bulk and thick films [3–6] and of thin films [7–10]. However, the dielectric loss of the materials is more complicated and depends strongly on microstructure [11–16]. The dielectric loss increases from 0.001–0.01 at 1 kHz to about 0.2 at 20 GHz, preventing the use of many thin films in microwave devices. In order to limit the motion of domain walls in the microwave frequency range, an intra-grain concentration gradient ceramic was developed as for a capacitor with X7R-specification [17]. The microstructure of such ceramics has a core-shell

structure for smoothing the variation of permittivity, ϵ_r , at the phase transitions from paraelectric-ferroelectric, T_c , tetragonal-orthorhombic, T_{o-t} , and orthorhombic-rhombohedral, T_{o-r} , and for limiting the motion of domain walls. However, there are a large number of factors, such as grain size, electrodes, thermal treatment temperature, oxygen pressure, internal stress and internal strains, which can play a role in the origin of the loss in the BST materials.

The study of mechanical loss (Q^{-1}), elastic modulus (Young's modulus E or shear modulus G), dielectric loss ($\tan \delta$) and permittivity (ϵ_r) at frequencies from 0.01 Hz to about 1 MHz on the BaTiO₃-based ceramics has provided interesting information on the phase transitions and the motion of domain walls [18–22]. Each phase transition in BaTiO₃ induces a loss peak and an anomaly in the dielectric constant/elastic modulus. A number of relaxation loss peaks (R 's) have been observed in the ferroelectric phase for large grain materials. All the relaxation peaks can be analysed by an Arrhenius-type relationship for

*To whom all correspondence should be addressed.

a large range of vibration frequencies from 10^{-2} to 10^6 Hz. Furthermore, one relaxation process exists in all the ferroelectric phases, which demonstrates a memory effect of ferroelectric domain configurations. The study of vacuum annealing and doping effects on the materials have confirmed that all the relaxation peaks are due to the interaction between domain walls and the diffusion of oxygen vacancies in the domains [21, 22].

This paper is concerned with an investigation of the dielectric and mechanical losses in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ systems ($x = 0.5, 0.6, 0.7$ and 1.0) with grain sizes ranging from $1 \mu\text{m}$ to $50 \mu\text{m}$.

2. Materials and Experimental

Barium titanate powder (RHONE-POULENC) was mixed with suitable organic binders. After drying and deagglomeration, the powders were pressed uniaxially at 50 MPa to make prismatic bars ($8 \times 8 \times 50 \text{ mm}$), and then isostatically pressed at 380 MPa. The compacts were sintered in air for 2 h at 1300°C , and then sliced into rectangular plates ($1 \times 5 \times 40 \text{ mm}$), denoted as BST 10/0. $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ceramics with $x = 0.5, 0.6$, and 0.7 , denoted as BST 5/5, 6/4, 7/3 respectively, were prepared by a conventional solid-state reaction method from barium carbonate (Fluka, >99%), strontium carbonate (Fluka, >99%) and titania powders. After mixing and ball milling in acetone with zirconia media the powders were calcined at a range of temperatures from 900 to 1150°C for 2 hrs. The calcined powders were remilled with binder and dry pressed at 100 MPa. The pellets were sintered at 1400°C for 2 hrs.

Scanning electron microscopy observations were made on samples polished mechanically and lapped to $1 \mu\text{m}$ using diamond paste, followed by acid etching (5 vol% HCl, 0.5 vol% HF, 94.5 vol% H_2O). The measurements of mechanical loss and Young's modulus were carried out at kilohertz frequencies by forced vibration of the samples driven electrostatically in their fundamental flexural mode. The dielectric measurement for BST 10/0 was carried out using an HP4192A impedance analyser using the same sample as for the mechanical measurements. Two opposite faces of the samples were electroded by gold vapour deposition. The measurements of dielectric properties of BST 7/3, 6/4, and 5/5 were carried out using an HP 4194A impedance analyser.

3. Results and Discussion

The microstructures of the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x = 0.5, 0.6, 0.7$, and 1.0) ceramics are shown in Fig. 1. The grain size is increased dramatically with the increasing percentage of Ba in the BST materials. There is a homogenous grain size distribution ($1\text{--}2 \mu\text{m}$) for the BST 5/5 composition. For the BST 10/0 and BST 7/3 compositions, an abnormal grain growth is observed for samples sintered at 1300 and 1400°C respectively. A bi-modal distribution of grain sizes was established in the materials: coarse grains of about $50 \mu\text{m}$ are surrounded by the fine grains of about $2 \mu\text{m}$. It appears that increasing the proportion of Sr in the BST materials can inhibit grain growth.

The variation of Young's modulus $E(T)$ and mechanical loss Q^{-1} as a function of temperature for the ceramic BST 10/0 is shown in Fig. 2(a) (21). The vibration frequency is about 3 kHz. The curve of $E(T)$ shows three anomalies; A_1 (130°C), A_2 (4°C) and A_3 (-100°C) as the temperature is decreased, which correspond to the three phase transitions in the material: A_1 : cubic to tetragonal phase, A_2 : tetragonal to orthorhombic phase, A_3 : orthorhombic to rhombohedral phase. The sharp anomaly in the modulus enables precise determination of the transition temperatures. These anomalies are respectively associated with three narrow peaks P_1 , P_2 , and P_3 on the $Q^{-1}(T)$ curve. Moreover, the $Q^{-1}(T)$ curve has a large peak R_o^m , and a small peak R_r^m . These peaks are considered to arise from relaxation process and so have been denoted the letter R , with the subscript m denoting a mechanical measurement, and the subscript denoting the phase region, o for orthorhombic and r for rhombohedral. The variation in permittivity $\varepsilon(T)$ and dielectric loss ($\tan \delta$) with temperature for the same BST 10/0 material for the frequencies of 1, 3, 10, and 100 kHz is shown in Fig. 2(b) (23). In addition to the phase transition peaks located at -90°C , 10°C , and 127°C on the loss curve, there are three other peaks R_r^e , R_o^e , and R_t^e located respectively in the rhombohedral, orthorhombic, and tetragonal phases, and the shift of those peaks with frequency confirms the relaxation behaviour. In this case the superscript e denotes an electrical measurement.

The permittivity of the BST 5/5, 6/4, and 7/3 ceramics as a function of temperature at the frequency of 10 kHz is shown in Fig. 3. As the concentration of Ba is decreased, the Curie temperature, T_c , is decreased from 36°C , to 5°C and -32°C for the BST 7/3, BST 6/4, and BST 5/5, respectively.

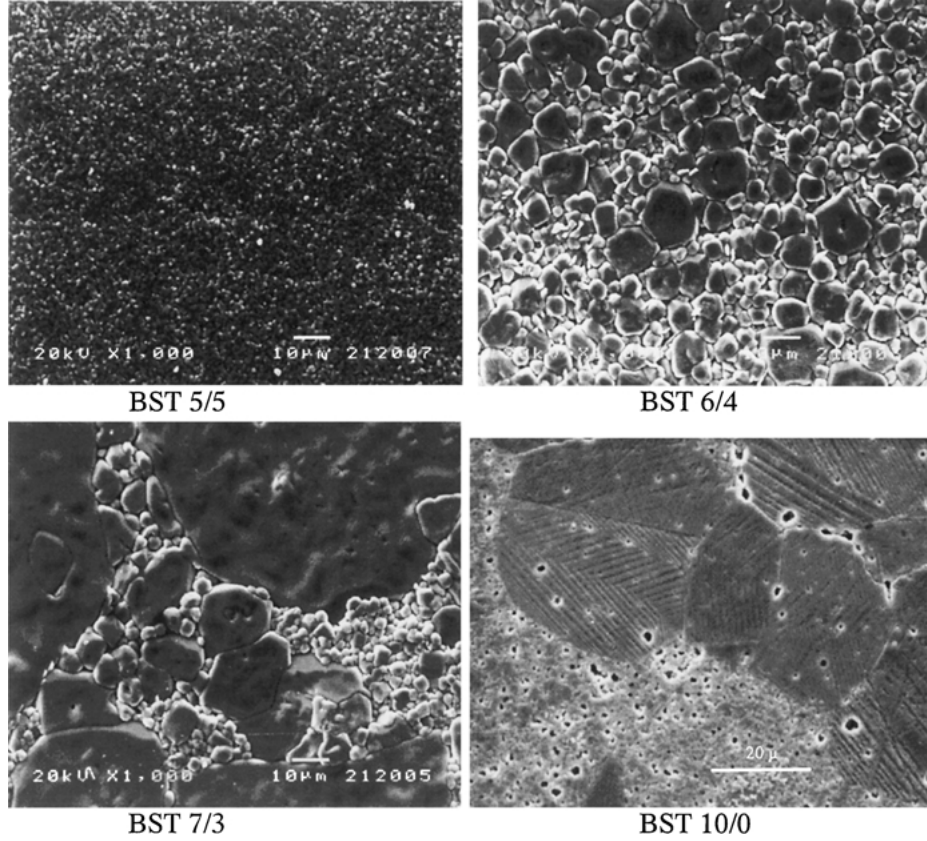


Fig. 1. Microstructure of BST ceramics with different Ba/Sr ratios.

The dielectric loss of the BST 7/3, 6/4 and 5/5 compositions as a function of temperature for measurement frequencies of 0.5, 1, 5, 10, 50, and 100 kHz are shown in Fig. 4(a) (b) and (c) respectively. For the large grain BST 6/4 material (Fig. 4(b)) there are transition peaks P_2 and P_1 located at about -68°C and 5°C corresponding the transition from the orthorhombic to tetragonal, and tetragonal to cubic phases respectively. However, in the tetragonal phase, there is a relaxation peak R . The relaxation peak is clearly shaped for the frequencies of 0.5, 1, and 5 kHz, and the peak temperature increases with frequency. The similar behavior of dielectric loss has been found in the BST 7/3 ceramic as shown in Fig. 4(a). However, for the BST 5/5 ceramic, Fig. 4(c), no dielectric loss peak at the Curie temperature is observed, and there is only a step for the phase transition from the ferroelectric to paraelectric phase. The high loss in the ferroelectric phase demonstrates the effect of ferroelectric domain wall motion. Furthermore, when the concentration of Sr is high, the phase

transition from tetragonal to cubic becomes diffuse, which corresponds to the broad peak in the permittivity versus temperature in Fig. 3 for BST 5/5. All these results indicate that the mechanisms of transition from the paraelectric to ferroelectric phase depend on the concentration of Sr in the BST system and it is possible that the motion of domain walls gives arise to relaxation peaks in the ferroelectric phase.

The relaxation time τ can be written according to the Arrhenius equation as

$$\tau = \tau_0 \exp\left(\frac{H}{kT}\right) \quad (1)$$

where T is the absolute temperature, k is the Boltzmann's constant, H is the activation energy, and τ_0 is the reciprocal frequency. For a Debye peak, the condition for the peak is $\omega\tau = 1$ [23]. This gives:

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

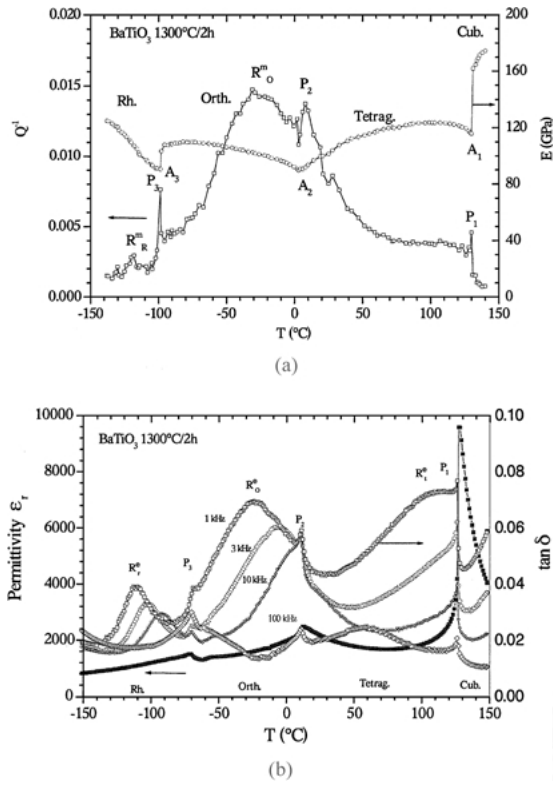


Fig. 2. Mechanical loss and Young's modulus (a) and dielectric loss and permittivity (b) as a function of temperature in BST 10/0 ceramic.

where T_p is the temperature of the peak, $\omega = 2\pi f$, and f is the vibration frequency. The relationship between temperature and vibration frequency for the relaxation peaks, R , shown in Fig. 4, is plotted in Fig. 5 for the

BST 7/3 and BST 6/4 ceramics. The activation energy H and relaxation time τ_0 are calculated to be 0.399 eV, 2×10^{-12} s and 0.360 eV, 2×10^{-11} s for the BST 7/3 and 6/4 compositions, respectively. A summary of the activation parameters from this work and the literature [24, 25] is shown in Table 1.

The values of relaxation time τ_0 for this work are similar to the value of the Debye frequency ν_D^{-1} (about 10^{-14} s). This indicates that all of the relaxation peaks could be attributed to a single atomic diffusion process [21]. The activation energy for oxygen vacancy diffusion in BST systems has been measured as 1.0–1.1 eV by Zafar et al. [24] and 0.38–1.02 eV by Saha et al. [25]. These values of oxygen diffusion energy are similar to those obtained from the dielectric and mechanical loss peaks. This implies that the relaxation peaks observed here could be connected to the diffusion of oxygen vacancies, which can be induced by impurities, vacuum annealing and intentional doping. It is well known that certain impurities, such as Fe^{3+} , Fe^{2+} , Ca^{2+} , K^+ , Na^+ , always substitute for Ti^{4+} [26]. Similar relaxation peaks caused by the interaction between oxygen vacancies and domain walls have also been identified in $Pb(Zr,Ti)O_3$ ceramics [27–29]. Postnikov et al. [30] proposed that the shear stress, σ , causes an increase in the polarisation of the domains oriented in the direction of tension, and a decrease in the polarisation of those oriented in the direction of compression. The domain wall is moved by such stresses. The change of polarisation causes a bound electrical charge to appear at the domain wall. These bound charges induce an electrical field in the grain. The mobile charges associated with

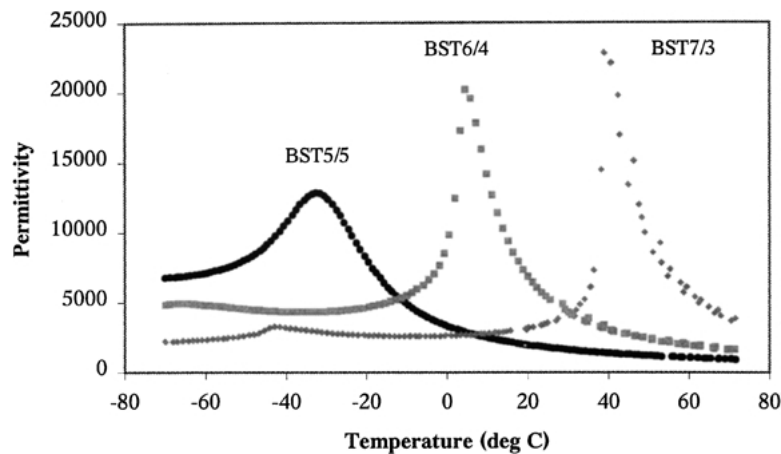


Fig. 3. Permittivity of BST 5/5, 6/4, and 7/3 ceramics as a function of temperature.

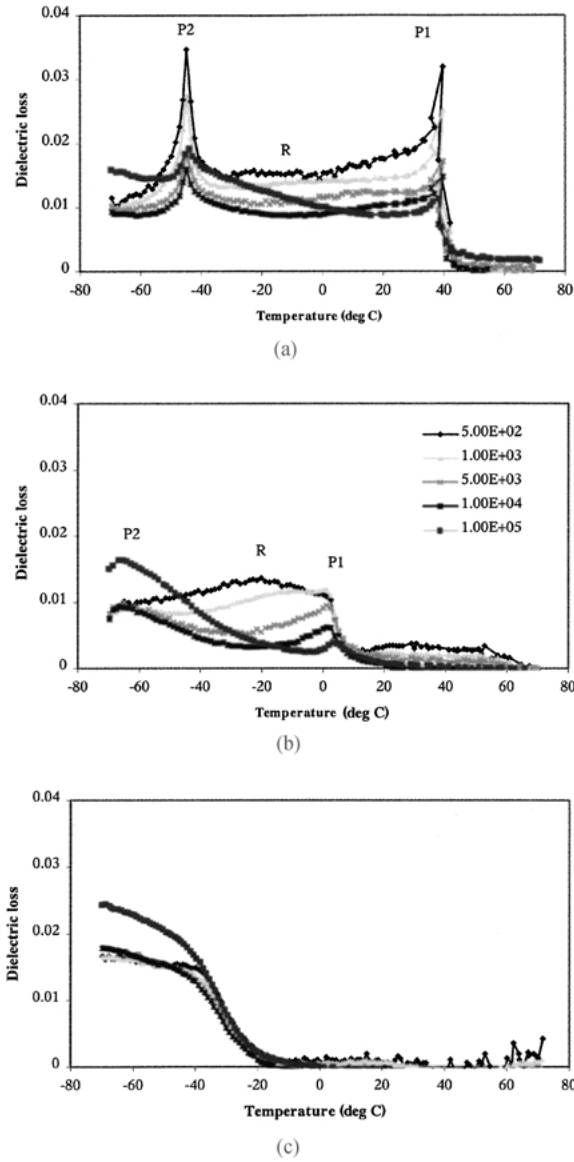


Fig. 4. Dielectric loss as a function of temperature for (a) BST 7/3, (b) 6/4, and (c) 5/5 ceramics. The legends in the figure are measurement frequencies in Hz and the same for all the samples.

point defects will diffuse in the electrical field in order to achieve equilibrium. Establishing the equilibrium takes time and, through the converse piezo-effect, this induces an additional anelastic deformation. A similar situation may occur in the BST materials.

The magnitude of the dielectric loss peaks P_1 and P_2 associated with the phase transitions decreases with increasing frequency from 100 Hz to about 1 MHz,

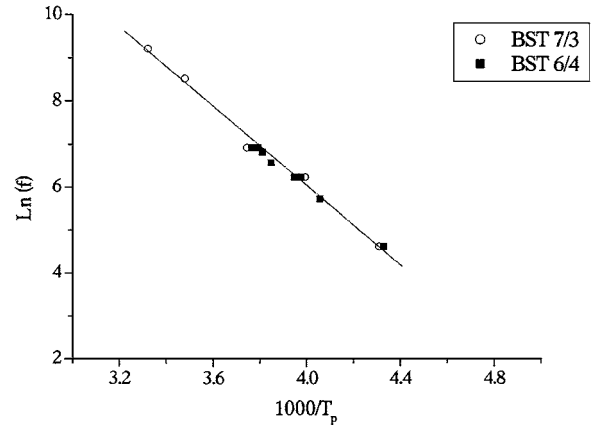


Fig. 5. Relationship between frequency and temperature for relaxation peaks in BST 7/3 and 6/4 ceramics (Best-fit for the BST 7/3 data is shown for clarity).

as demonstrated in Figs. 2 and 4 for the BST 10/0, 7/3, and 6/4 ceramics. Such a variation of loss at the phase transition with frequency is similar to the behaviour of a first-order phase transition as described by Postnikov et al. [31]. Similar behaviour has been widely observed in alloys and in ferroelectric materials (31). The main hypothesis is that the loss at the phase transition is proportional to the transformed portion during one cycle of vibration, and the following relationship was established as,

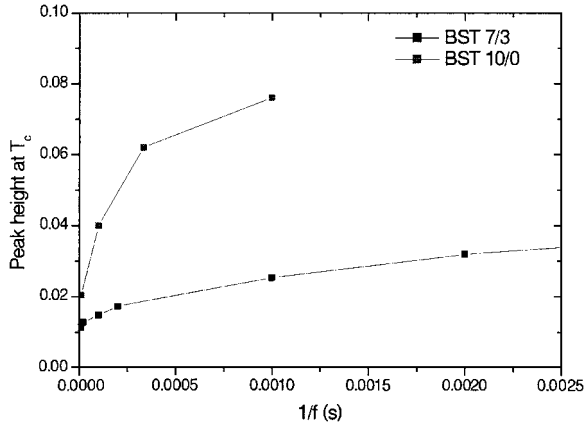
$$Q^{-1} \propto \left(\frac{dT}{dt} \right) / f, \quad (3)$$

where dT/dt is the heating or cooling rate of the measurement, and f is the frequency. In the material with a first-order phase transition, the peak in mechanical loss at the phase transition is a linear function of the frequency. In order to check if this relationship is obeyed in the case of BST, the dielectric loss at the phase transition, P_1 , has been plotted as a function of $1/f$ in Fig. 6 for the BST 7/3 and 10/0 materials.

It is clearly seen in Fig. 6 that the relationship between the loss and reciprocal of frequency is non-linear. Such behaviour indicates that the phase transition in (BaSr)TiO₃ material is only of a soft first-order, and the nucleation of the new phase is very sensitive to the external electric field at the temperature of the phase change. However, the dielectric loss of peak P_2 in the BST 10/0 (Fig. 2(b)) appears stable for frequencies from 1 kHz to 10 kHz. This is thought to be due to

Table 1. Activation energy H (eV) of the relaxation peaks in the BaSrTiO₃ ceramics (see text for full explanation of the terms).

Composition [Reference]	Experimental methods	$R_r^e + R_r^m$ (eV)	$R_{r,o}^m + R_{o,t}^e$ (eV)	$R_o^m + R_t^m$ (eV)	R_t^m (eV)
BST 10/0 [21]	Mechanical and dielectric loss	0.29	0.47	0.68	0.92
BST 7/3	Dielectric loss	0.399			
BST 6/4	Dielectric loss	0.360			
BST 5/5 [24]	Current density				1.0–1.1
BST 5/5 [25]	Conductivity	0.38–1.02	0.5–1.28		1.07–1.3

Fig. 6. Height of the dielectric loss peak at the Curie temperature T_c for BST 10/0 and BST 7/3.

the large relaxation peak associated domain wall motion in the orthorhombic phase, which compensates for the decreasing loss due to the phase transition at high frequencies, so keeping the total loss independent of frequency.

In the Ba_{0.5}Sr_{0.5}TiO₃ ceramic sample the variation of dielectric loss at T_c is different from the behaviour of BST 10/0, 7/3, and 6/4; there is no phase transition peak corresponding to T_c . The dielectric loss reduces continuously from the ferroelectric to paraelectric phase as a function of increasing temperature. The loss could follow a relationship similar to $(1 - c/a)^2$, as observed in Nb₃Sn with A15 structure [32]. Liu et al. [33] have reported a similar variation of the tetragonal distortion, $c/a - 1$, versus temperature for SrTiO₃ by high-resolution dilatometry measurements. Furthermore, Hubert et al. [34] reported the coexistence of both paraelectric and ferroelectric phases in the submicronspatial resolution using confocal scanning optical microscopy. Recently, Tikhomirov

et al. [35] confirmed the local paraelectric/ferroelectric phase transitions over submicron areas of ferroelectric Ba_xSr_{1-x}TiO₃ thin films. Thus the physical reason for the absence of a sharp loss peak in Ba_{0.5}Sr_{0.5}TiO₃ may be due to the intrinsic heterogeneous distributions of the Ba and Sr in the lattice, and this is currently the subject of further investigation.

4. Conclusion

We have established a correlation of mechanical and dielectric losses in Ba_xSr_{1-x}TiO₃ ceramics with different microstructures (grain size from 1 μ m to 50 μ m). Measurements of mechanical loss, elastic modulus, dielectric loss and permittivity have shown the following features. First, each phase transition induces a loss peak and an anomaly of dielectric constants/elastic modulus for Ba_xSr_{1-x}TiO₃ when $x > 0.6$. The phase transition at the Curie temperature T_c appears to be a soft first order from an analysis of the phase transition dynamics. There is no loss peak in the Ba_{0.5}Sr_{0.5}TiO₃ ceramic, which could be due to intrinsic heterogeneous distribution of Ba and Sr in the lattice. Secondly, there are relaxation peaks existing in coarse grain materials. These peaks have been analysed by an Arrhenius relationship for the frequencies from 10⁻² to 10⁶ Hz. A relaxation peak has been identified in the BST 7/3 and 6/4 compositions with a measured activation energy of approximately 0.40 eV. All the relaxation peaks could be explained by the interaction between domain walls and the diffusion of oxygen vacancies in the domains.

Acknowledgments

The authors are very grateful to M. Maglione for help with the dielectric measurements, and C. Meggs and

G. Dolman for help with the sample preparation. We also acknowledge the support of the British Council and French EGIDE Alliance Programmes (Franco-British Partnership Programme 2002, Project No: PN 02.006).

References

1. M.J. Lancaster, J. Powell, and A. Porch, *Supercond. Sci. Technol.*, **11**, 1323 (1998).
2. J.F. Scott, *Ferroelectric Memories* (Springer-Verlag, 2000).
3. B. Su, P.H. Pearce, and T.W. Button, in *Ferroelectrics 2000 UK*, edited by Neil McN Alford and Eric Yeatman (IOM Communications, 2000), pp. 153–160.
4. J.W. Liou and B.S. Chiou, *J. Am. Ceram. Soc.*, **80**, 3093 (1997).
5. L.Q. Zhou, P.M. Vilarinho, and J.L. Baptista, *J. Euro Ceram. Soc.*, **19**, 2015 (1999).
6. S.M. Rhim, H.J. Bak, S.M. Hong, and O.K. Kim, *J. Am. Ceram. Soc.*, **83**, 3009 (2000).
7. C.L. Chen, J. Shen, S.Y. Chen, G.P. Luo, C.W. Chu, F.A. Miranda, F.W. Van Keuls, J.C. Jiang, E.I. Meletis, and H.Y. Chang, *Applied Phys. Lett.*, **78**, 652 (2001).
8. Y. Gim, T. Hudson, F. Fan, C. Kwon, A.T. Findikoglu, B.J. Gibbons, B.H. Pak, and Q.X. Jia, *Applied Phys. Lett.*, **77**, 1200 (2000).
9. B.H. Pak, Y. Gim, Y. Fan, Q.X. Jia, and P. Lu, *Applied Phys. Lett.*, **77**, 2587 (2000).
10. H.D. Wu and F. Barnes, *Integrated Ferroelectrics*, **22**, 291 (1998).
11. J.D. Baniecki, R.B. Laibowitz, T.M. Shaw, P.R. Duncombe, D.A. Neumayer, D.E. Kotecki, H. Shen, and Q.Y. Ma, *Appl. Phys. Lett.*, **72**, 498 (1998).
12. J.Y. Sok, S.J. Park, E.H. Lee, J.P. Hong, J.S. Kwak, and C.O. Kim, *Jpn. J. Appl. Phys.*, **39**(pt.1), 2752 (2000).
13. W.J. Kim, W. Chang, S.B. Qadri, J.M. Pond, S.W. Kirchoefer, D.B. Chrisey, and J.S. Horwitz, *Appl. Phys. Lett.*, **76**, 1185 (2000).
14. J. Im, O. Auciello, P.K. Baumann, S.K. Streiffer, D.Y. Kaufman, and A.R. Krauss, *Appl. Phys. Lett.*, **76**, 625 (2000).
15. W.J. Kim, H.D. Wu, W. Chang, S.B. Qadri, J.M. Pond, S.W. Kichoefer, D.B. Chrisey, and J.S. Horwitz, *J. Appl. Phys.*, **88**, 5448 (2000).
16. E.J. Cukauskas, S.W. Kichoefer, and J.M. Pond, *J. Appl. Phys.*, **88**, 2830 (2000).
17. Lunomirsky, T.Y. Wang, F. Deflaviis, and O.M. Stafstudd, *Integrated ferroelectrics*, **24**, 319 (1999).
18. B.L. Cheng, M.Gabbay, W. Duffy, Jr., and G. Fantozzi, *J. of Alloys and Compounds*, **211/212**, 352 (1994).
19. W. Duffy, Jr., B.L. Cheng, M. Gabbay, and G. Fantozzi, *Metalurgical and Materials Transactions A*, **26**, 1735 (1995).
20. B.L. Cheng, M. Gabbay, W. Duffy, Jr., and G. Fantozzi, *J. of Materials Science*, **31**, 4951 (1996).
21. B.L. Cheng, M. Gabbay, and G. Fantozzi, *J. of Materials Science*, **31**, 4141 (1996).
22. B.L. Cheng, M. Gabbay, M. Maglione, Y. Jorand, and G. Fantozzi, *J. de Physique IV*, **6**, C8, 647 (1996).
23. A.S. Nowick and B.S. Berry, *Anelastic Relaxation in Crystalline Solids* (AP, New Yorks), Ch. 3. 1972.
24. S. Zafar, R.E. Jones, B. Jiang, B. White, P. Chu, D. Taylor, and S. Gillespie, *Applied Phys. Lett.*, **73**, 175 (1998).
25. S. Saha and S.B. Krupanidhi, *J. Applid Phys.*, **88**, 3506 (2000).
26. H. Ihrig, *J. Phys. C: Solid Stat Phys.*, **11**, 819 (1978).
27. E.M. Bourim, H. Tanaka, M. Gabbay, and G. Fantozzi, *Jpn. J. Appl. Phys.*, **39**, 5542 (2000).
28. L.X. He, C.E. Li, Z.Y. Wang, H.X. Yan, and W. Liu, *Phys. Stat. Sol. A*, **179**, 275 (2000).
29. X.B. Chen, C.H. Li, Y. Ding, Z.F. Zhang, H.M. Shen, J.S. Zhu, and Y.N. Wang, *Phys. Stat. Sol. A*, **179**, 455 (2000).
30. P.V. Postnikov, V.S. Pavlov, S.A. Grudev, and S.K. Turkov, *Soviet Phys.—Solid State*, **10**, 1267 (1968).
31. V.S. Postnikov, S.A. Gridnev, B.M. Darinski, and L.M. Sharshakov, *Nuovo Cimento*, **23**, 324 (1976).
32. C.L. Snead, Jr. and D.O. Welch, *J de Physique*, **46** C10, 589 (1985).
33. M. Liu, T. Finlayson, and T.F. Smith, *Phys. Rev. B*, **55**, 3480 (1997).
34. C. Hubert, J. Levy, A.C. Carter, W. Chang, S.W. Kiechoefer, and J.S. Horwitz, *Appl. Phys. Lett.*, **71**, 3353 (1997).
35. O. Tikhomirov, H. Jiang, and J. Levy, *Appl. Phys. Lett.*, **77**, 2048 (2000).