Dielectric properties of bismuth doped $Ba_{1-x}Sr_xTiO_3$ ceramics

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Abstract

The dielectric properties of bismuth (5 at.%) doped $Ba_{1-x}Sr_xTiO_3$ ($x = 0$, 0.2, 0.4, 0.6 and 0.8) ceramics are investigated. Bi doping significantly decreases the dielectric permittivity maximum of ferroelectric–paraelectric phase transition of $Ba_{1-x}Sr_xTiO_3$ solid solutions and shifts the ferroelectric–paraelectric phase transition temperature to lower temperatures for the $x = 0$, 0.2, 0.4 and 0.6 compositions but to higher temperature for the $x = 0.8$ composition. Bi doped $BaTiO_3$ still exhibits normal ferroelectric characteristic while a relaxor behavior was observed in Bi doped $Ba_{1-x}Sr_xTiO_3$ and the degree of the diffuseness and the relaxation increases as x increases. A random electric field is suggested to be responsible for the relaxor behavior observations. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: (Ba,Sr)TiO₃; Dielectric properties; Ferroelectric properties; Perovskite; Relaxors

1. Introduction

Barium titanate ($BaTiO_3$) is known as a typical ferroelectric material with three phase transtions: a ferroelectric–paraelectric phase transition (cubic–tetragonal) around 130°C (also called Curie temperature T_c), a tetragonal–orthorhombic phase transition around 5°C and an orthorhombic–rhombohedral phase transition around −80°C. $BaTiO_3$ based solid solutions have been a subject of extensive studies since the early 1950s. Among them, many papers were devoted to $BaTiO_3$–$SrTiO_3$ solid solutions.[1,2] Previous studies on the dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions have shown that the compositions with $x \leqslant 0.8$ exhibited normal ferroelectric behavior while a relaxor characteristic was observed in the $SrTiO_3$ rich region ($x > 0.8$).[3,4]

$SrTiO_3$ is a quantum paraelectric which shows high dielectric permittivity at low temperature.[5] No ferroelectric phase transition occurs down to almost 0 K.[5] However, a low temperature relaxation behaviour, similar to that observed in ferroelectric relaxors, has been observed in doped $SrTiO_3$ such as $Sr_{1-x}Ca_xTiO_3$[6] and $Sr_{1-1.5x}Bi_xTiO_3$.[7] A widely accepted viewpoint is that the relaxation of these systems is due to a random field induced domain state.

The present paper investigates the dielectric properties of bismuth doped $Ba_{1-x}Sr_xTiO_3$ ceramics for $x \leqslant 0.8$. A ferroelectric relaxor behavior is observed. The degree of the diffuseness and the relaxation of the ferroelectric–paraelectric phase transition increases as x increases. The possible mechanism responsible for the relaxor observation is discussed.

2. Experimental

Ceramic samples were prepared by the conventional mixed oxide method. Reagent grade $BaCO_3$, $SrCO_3$, TiO_2 and Bi_2O_3 were weighed according to the composition $((Ba_{1-x}Sr_x)_{1-1.5y}Bi_yTiO_3$ ($x = 0$, 0.2, 0.4, 0.6 and 0.8, $y = 0$ and 0.05). After ball-milled in alcohol for 6 h using agate pots and agate balls in a planetary mill, the powders were dried, and then calcined between 1100 and 1200°C for 6 h. The calcined powders were milled again for 8–10 h, to obtain powders of less than 5 μm of particle size. Pellets of 10 mm in diameter and 2–3 mm in thickness were uniaxially pressed at 100 MPa and then isostatically pressed at 250 MPa. For undoped $Ba_{1-x}Sr_xTiO_3$ ceramics (i.e. $y = 0$), the sintering was conducted at 1300, 1300, 1320, 1350 and 1380°C corresponding to $x = 0$, 0.2, 0.4, 0.6 and 0.8 respectively for 4 h, followed by a furnace cooling. For 5 at.% Bi doped $Ba_{1-x}Sr_xTiO_3$ ceramics (i.e. $y = 0.05$), the sintering temperature was 1250, 1250, 1280, 1300 and 1300°C corresponding to $x = 0$, 0.2, 0.4, 0.6 and 0.8 respectively. The

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sintering conditions had to be adjusted for each sample composition to obtain high relative densities (>95% of theoretical density).

For X-ray diffraction (XRD) analysis, some of the sintered samples were ground into powders in order to avoid possible orientation effects. The XRD was conducted at room temperature using CuKα radiation.

The microstructure of the samples was observed in polished sections, using scanning electron microscopy (SEM) with X-ray energy dispersive spectroscopy (EDS), for chemical analysis.

For the dielectric measurements, sintered samples were polished and gold electrodes were sputtered on both sides. Dielectric permittivity was measured, at different frequencies between 100 Hz and 1 MHz, as a function of temperature, using a Solartron 1260 Impedance/Gain-Phase Analyzer and a Displex APD-Cryogenics cryostat during heating up at a rate of 1 K/min in the temperature range of 12–320 K. Measurements in the range of 320–600 K were done in a furnace during heating up at a rate of 1 K/min.

3. Results

It has been reported that the solubility limit of Bi in $BaTiO_3$ is around 5 at.%[8] and it is around 10 at.% in $Ba_{0.2}Sr_{0.8}TiO_3$[9] at 1250°C. It is then possible to assume that 5 at.% of Bi doping can be fully incorporated into the perovskite lattice of $Ba_{1-x}Sr_xTiO_3$ ($x \leqslant 0.8$). XRD analysis confirmed this assumption. The XRD patterns of all the compositions showed a single perovskite phase. Fig. 1 shows the XRD patterns of 5 at.% Bi doped $Ba_{1-x}Sr_xTiO_3$ for $x = 0$ and 0.8 compositions.

The SEM micrographs of undoped and 5 at.% Bi doped $Ba_{1-x}Sr_xTiO_3$ samples showed a dense and homogeneous microstructure, as can be seen in Fig. 2, representatively for Bi doped $x = 0.8$ composition. The
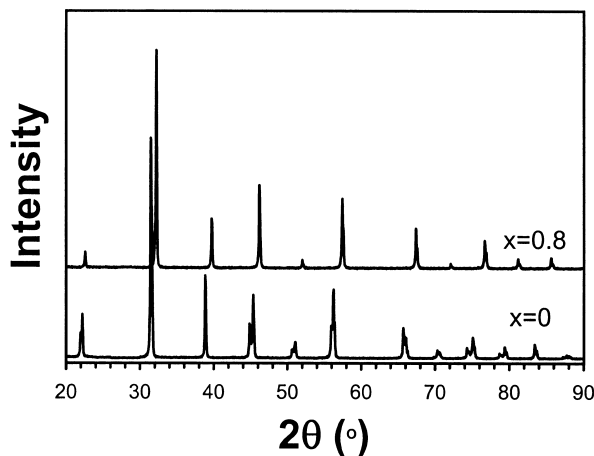
grain size of the studied ceramics vary between 2.3 and 15 μm with lower values for compositions with higher x-values and Bi doping. The chemical nature of the grains was checked by EDS analysis. No evident composition difference was found between different grains.

Evident hysteresis loops were observed for all the compositions, indicative of a ferroelectric state. Fig. 3 shows the hysteresis loop of 5 at.% Bi doped $Ba_{0.6}Sr_{0.4}TiO_3$ composition.

Fig. 4 shows the temperature dependence of the dielectric permittivity at various frequencies for the $Ba_{1-x}Sr_xTiO_3$ ($x = 0$, 0.4, 0.6 and 0.8) compositions undoped and doped with 5 at.% of Bi. Bi doped $BaTiO_3$ still exhibits sharp ferroelectric–paraelectric transition while the trasition is diffused and relaxed for Bi doped
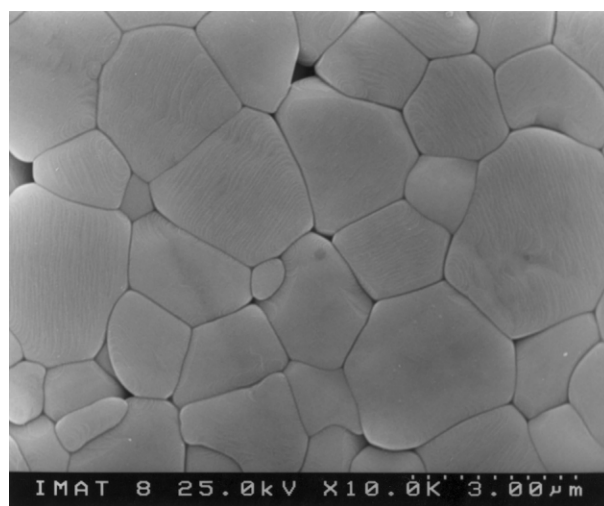

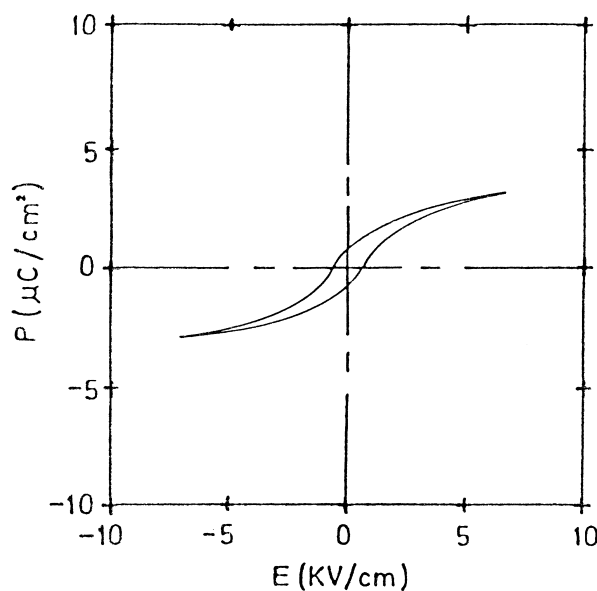Fig. 2. SEM micrograph of 5 at.% Bi doped $Ba_{0.2}Sr_{0.8}TiO_3$ ceramics.

Fig. 3. Hysteresis loops (50 Hz) of 5 at.% Bi doped $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics at 210 K.

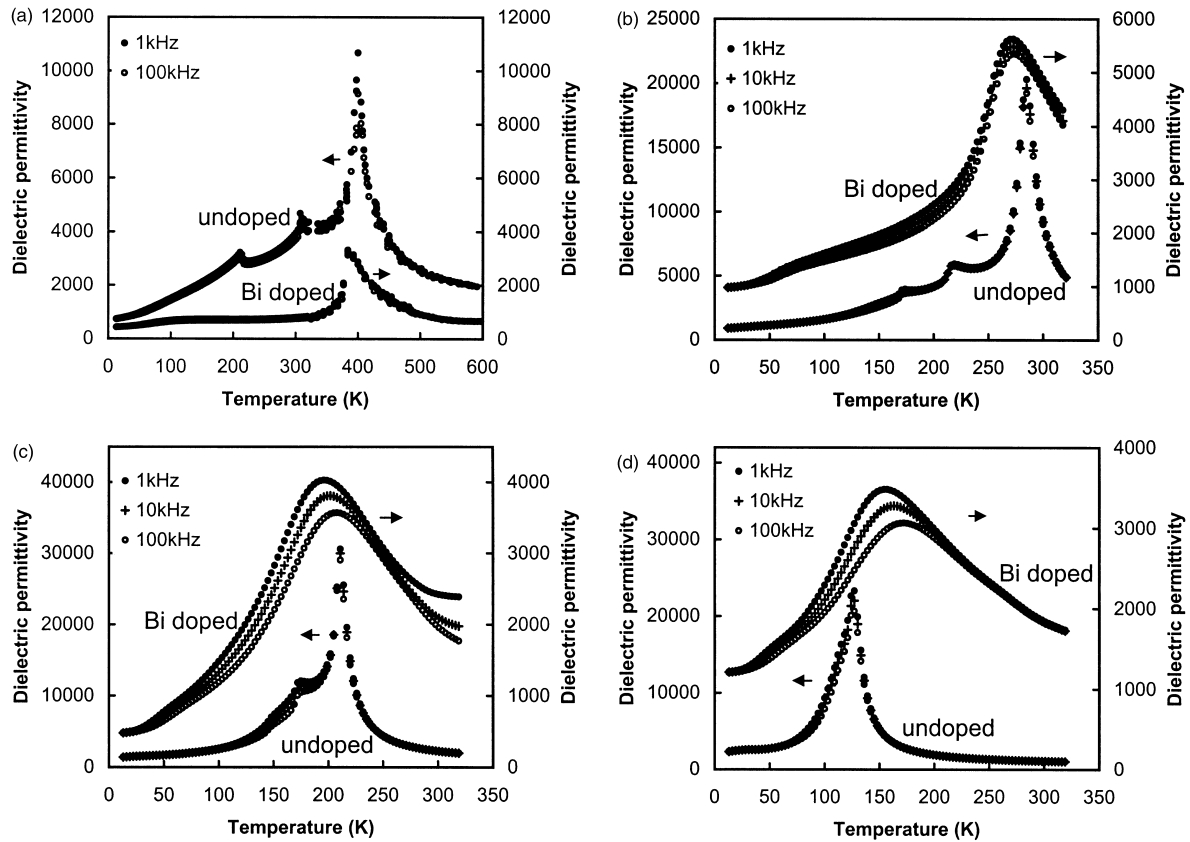Fig. 1. XRD patterns of 5 at.% Bi doped $Ba_{1-x}Sr_xTiO_3$ ($x = 0$ and 0.8) ceramics.

Fig. 4. Temperature dependence of dielectric permittivity at various frequencies for undoped (left *y*-axis) and 5 at.% Bi doped (right *y*-axis) $Ba_{1-x}Sr_xTiO_3$ ceramics where $x = 0$ (a), 0.4 (b), 0.6 (c) and 0.8 (d). Note the scale difference between the left *y*-axis and the right *y*-axis in (b), (c) and (d).

$Ba_{1-x}Sr_xTiO_3$, this becoming more obvious as x increases. The low temperature phase transitions of $BaTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ solid solutions vanish after Bi doping. The reason is being explored.

The permittivity maximum, ϵ_{max}, and the temperature where the permittivity maximum occurs (transition temperature), T_{max}, at 1 kHz, for all the studied compositions are shown in Table 1. ϵ_{max} of $Ba_{1-x}Sr_xTiO_3$ significantly decreases after Bi doping. The temperature of the permittivity maximum shifts by Bi doping to lower temperatures for the $x = 0$, 0.2, 0.4 and 0.6 compositions but to higher temperature for the $x = 0.8$ composition.

The diffuseness of the phase transition can be empirically described by the parameter $\Delta T_1 = T_{0.9\epsilon max(100\ Hz)} - T\epsilon_{max(100\ Hz)}$, i.e. the difference between the temperature corresponding to 90% of the permittivity maximum ϵ_{max} in the high temperature side and $T_{\epsilon max(100\ Hz)}$. The ΔT_1 values for Bi doped samples are shown in Table 1. ΔT_1 increases as x increases.

In order to quantify the frequency dispersion of T_{max}, i.e. the relaxation degree, a parameter ΔT_2 defined as $\Delta T_2 = T_{max(1\ MHz)} - T_{max(100\ Hz)}$ was used. ΔT_2 for the Bi doped samples are also shown in Table 1. ΔT_2 also increases as x increases.

Table 1
Dielectric permittivity maximum (ϵ_{max}) (1 kHz), transition temperature (T_{max}) (1 kHz), $\Delta T_1 = T_{0.9\epsilon max(100\ Hz)} - T_{\epsilon max(100\ Hz)}$ and $\Delta T_2 = T_{max(1\ MHz)} - T_{max(100\ Hz)}$ for undoped and Bi (5 at.%) doped $Ba_{1-x}Sr_xTiO_3$ ceramics

Composition		ϵ_{max}	T_{max}	ΔT_1	ΔT_2
$x = 0$	Undoped	10 670	400	–	–
	5 at.% Bi doped	3400	385	–	–
$x = 0.2$	Undoped	19 750	342	–	–
	5 at.% Bi doped	5400	328	10	0
$x = 0.4$	Undoped	20 310	285	–	–
	5 at.% Bi doped	5630	273	24	3
$x = 0.6$	Undoped	30 590	211	–	–
	5 at.% Bi doped	4030	200	28	21
$x = 0.8$	Undoped	23 310	127	–	–
	5 at.% Bi doped	3480	154	33	33

4. Discussion

As can be seen in Fig. 4, Bi doped $BaTiO_3$ still shows a sharp dielectric permittivity peak with no frequency dispersion of the peak temperature at the ferroelectric–paraelectric phase transition. However, in Bi doped $Ba_{1-x}\ Sr_xTiO_3$ solid solutions, a relaxor type behavior was observed, characterized by a diffuse dielectric peak

with frequency dependence. The degree of the diffuseness (characterized by ΔT_1) and the relaxation (characterized by ΔT_2) significantly increases as the Sr^{2+} concentration increases (Table 1). These indicate that the relaxor behavior of Bi doped $Ba_{1-x}Sr_xTiO_3$ is related to the Sr^{2+} concentration.

In pure $SrTiO_3$ no ferroelectric phase transition occurs at temperature down to almost 0 K.[5] However, evident hysteresis loops were observed in Bi doped $SrTiO_3$ ceramics[7], indicating that the ferroelectricity was induced by Bi doping. A ferroelectric relaxor behavior was observed in heavily Bi doped $SrTiO_3$ ceramics.[7] It was suggested that Bi ions were located at off center positions of Sr^{2+} sites,[7] similarly as suggested for Ca^{2+} doped $SrTiO_3$[6] and Li doped $KTaO_3$.[10,11] It was also suggested that strontium vacancies (V''_{Sr}) may occur in Bi doped $SrTiO_3$ in order to balance the charge misfit caused by trivalent Bi^{3+} ions substituting divalent Sr^{2+} ions.[7] Off-center Bi^{3+} ions and $Bi^{3+} - V''_{Sr}$ centers form dipoles and thus set up local electric fields. The ferroelectric relaxor behavior of Bi doped $SrTiO_3$ was then attributed to the random field induced domain state.[7]

According to the suggestions for Bi doped $SrTiO_3$,[7] the Bi^{3+} ions substituting for Sr^{2+} in $Ba_{1-x}Sr_xTiO_3$ solid solutions can also be located at off-center positions and A site (strontium and/or barium) vacancies (V''_A) may also appear to compensate the charge imbalance arising from the substitution of A sites by Bi^{3+} ions. A random electric field formed by off-center Bi^{3+} ions and $Bi^{3+} - V''_A$ dipoles would then suppress the ferroelectricity of $Ba_{1-x}Sr_xTiO_3$ solid solutions, resulting in the relaxor behavior of Bi doped $Ba_{1-x}Sr_xTiO_3$ ceramics. Following this idea, the Bi^{3+} ions substituting for Ba^{2+} ions should not be at off-center positions since Bi doped $BaTiO_3$ does not show dielectric diffuseness and frequency dispersion. The ionic radius of Bi^{3+} is smaller than the ionic radius of Sr^{2+} and Ba^{2+}[12] and the calculated polarizabilities[13] of Ba^{2+} (6.40×10^{-24} cm³), Sr^{2+} (4.24×10^{-24} cm³) and Bi^{3+} (6.12×10^{-24} cm³) indicate that the polarizability of Bi^{3+} will be between those of Sr^{2+} and Ba^{2+}. Vugmeister et al.[11] have suggested that the substituting ions with smaller ionic radius and greater polarization forces than the lattice ions will favor off-center location. This can offer an explanation for the effect above described i.e. that the degree of the diffuseness and the relaxation of Bi doped $Ba_{1-x}Sr_xTiO_3$ increases as x increases since the tendency of Bi^{3+} to be off-center located in the $Ba_{1-x}Sr_xTiO_3$ lattice should increase as the Sr^{2+} concentration increases.

5. Conclusions

The dielectric properties of bismuth (5 at.%) doped $Ba_{1-x}Sr_xTiO_3$ ($x = 0, 0.2, 0.4, 0.6$ and 0.8) ceramics are investigated.

Bi doping significantly decreases the dielectric permittivity maximum of $Ba_{1-x}Sr_xTiO_3$ and shifts the maximum temperature to lower temperatures for the $x = 0, 0.2, 0.4$ and 0.6 compositions but to higher temperature for the $x = 0.8$ composition.

Undoped $Ba_{1-x}Sr_xTiO_3$ compositions ($x \leqslant 0.8$) are normal ferroelectrics. Bi doped $BaTiO_3$ still exhibited a sharp paraelectric–ferroelectric phase transition while a relaxor behavior was observed in Bi doped $Ba_{1-x}Sr_xTiO_3$, becoming more obvious as x increases. The relaxor behavior was characterized. It was shown that the degree of the diffuseness and the relaxation of the phase transition increases as x increases. A random electric field is suggested to be responsible for the relaxor behavior observations.

References

1. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London, 1971.
2. Smolenskii, G. A., Bokov, V. A., Isupov, V. A., Krainik, N. N., Pasynkov, R. E. and Sokolov, A. I., *Ferroelectrics and Related Materials*. Gordon Breach, New York, 1984.
3. Lemanov, V. V., Smirnova, E. P., Syrnikov, P. P. and Tarakanov, E. A., Phase transitions and glasslike behavior in $Sr_{1-x}Ba_xTiO_3$. *Phys. Rev. B*, 1996, **54**, 3151–3157.
4. Zhou, L., Vilarinho, P. M. and Baptista, J. L., Dependence of the structural and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions on raw material processing. *J. Eur. Ceram. Soc.*, 1999, **19**, 2015–2020.
5. Müller, K. A. and Burkhard, H., $SrTiO_3$: an intrinsic quantum paraelectric below 4 K. *Phys. Rev. B*, 1979, **19**, 3593–3602.
6. Bednorz, J. G. and Müller, K. A., $Sr_{1-x}Ca_xTiO_3$: an XY quantum ferroelectric with transition to randomness. *Phys. Rev. Lett.*, 1984, **52**, 2289–2292.
7. Cheng, A., Zhi, Y., Vilarinho, P. M. and Baptista, J. L., Bi:$SrTiO_3$: a quantum ferroelectric and a relaxor. *Phys. Rev. B*, 1998, **57**, 7403–7406.
8. Zhou, L., Vilarinho, P. M. and Baptista, J. L., Solubility of bismuth oxide in barium titanate. *J. Am. Ceram. Soc.*, 1999, **82**, 1064–1066.
9. Zhou, L., Vilarinho, P. M. and Baptista, J. L., Relaxor behavior of $(Ba_{0.2}Sr_{0.8})TiO_3$ ceramic solid solution doped with bismuth. *J. Electroceram.*, 2000, **5**, 191–199.
10. Toulouse, J., Vugmeister, B. E. and Pattnaik, R., Collective dynamics of off-center ions in $K_{1-x}Li_xTaO_3$: a model of relaxor behavior. *Phys. Rev. Lett.*, 1994, **73**, 3467–3470.
11. Vugmeister, B. E. and Glinchuk, M. D., Dipole glass and ferroelectricity in random-site electric dipole systems. *Rev. Mod. Phys.*, 1990, **62**, 993–1026.
12. Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystall.*, 1976, **A32**, 751–767.
13. Shannon, R. D., Dielectric polarizabilities of ions in oxides and fluorides. *J. Appl. Phys.*, 1993, **73**, 348–366.