Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 39 (2013) 7571–7575
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Dielectric properties of Bi-doped $Ba_{0.8}Sr_{0.2}TiO_3$ ceramic solid solutions

Fathi Bahri*, Hamadi Khemakhem

Laboratoire d'Études des Matériaux Multifonctionnels (LÉMM), Unité de Physique-Mathématiques 05UR15-04, Université de Sfax,
Faculté des Sciences de Sfax (FSS), Route de Soukra km 3.5, B.P. 1171, 3000 Sfax, Tunisie

Received 19 January 2013; received in revised form 1 March 2013; accepted 2 March 2013
Available online 14 March 2013

Abstract

Bismuth-doped barium–strontium–titanate ceramics of the formula $(Ba_{0.8}Sr_{0.2})_{(1-1.5y)}Bi_yTiO_3$ were prepared using a conventional solid-state reaction method. The structure, dielectric properties, and ferroelectric relaxor behaviour of all compositions were thoroughly investigated. The findings revealed a broad dielectric anomaly and a shift in dielectric maxima towards higher temperatures with increasing frequency. The diffuseness degree indicator γ was about 1.68, and dielectric relaxation was noted to follow the Vogel–Fulcher relationship, with $T_f = 185$ K, $f_0 = 1.18 \times 10^{10}$ Hz, and $Ea = 0.35$ eV, which further supported the spin-glass-like properties of BBSTs. The latter were also noted to display significant ferroelectric relaxor behaviour that could be attributed to the presence of Bi^{3+} doping ions. The degree of relaxation behaviour was noted to increase with the increase in bismuth concentration. Raman spectra were investigated as a function of temperature, and the findings confirmed the results from X-ray and dielectric measurements. Among the compositions assayed in this solid solution, 10% Bi-doped $Ba_{0.8}Sr_{0.2}TiO_3$ yielded promising relaxor properties that make it a strong candidate for future industrial application in the production of efficient and eco-friendly relaxor ferroelectric materials.

Keywords: C. Dielectric properties; C. Ferroelectric; C. Relaxors; D. Perovskite

1. Introduction

Due to their attractive physical properties, such as high dielectric permittivity, diffuse phase transition and strong electrostriction, relaxor ferroelectric materials have attracted special attention during the last few decades. They have been successfully applied in a wide range of systems and technologies, including sensors, actuators, transducers, and memory elements [1–4]. Most of these materials belong to complex lead-based perovskite compounds, such as PMN–PT and PMN–PZT, whose superior dielectric properties and relaxor behaviour have had considerable contributions in the development of relaxor ferroelectric materials. These materials have, however, often been reported to pose a number of environmental and health concerns due to the volatility and toxicity of lead.

These disadvantages have motivated the search for new, efficient, and eco-friendly lead-free relaxor materials. Several lead-free materials with perovskite structure, such as $BaTiO_3$ (BT) and $SrTiO_3$ [5], have been investigated in terms of their dielectric relaxation, ferroelectric phase transition and electrical properties. Lead-free compositions belonging to $BaTiO_3$ have often been reported to offer special candidate alternatives. In fact, $BaTiO_3$ presents a model lead-free ferroelectric perovskite-type oxide (ABO_3) that displays several polymorphic phase transitions and is, therefore, used to correlate important dielectric/ferroelectric properties, such as variations in polymorphic phase transition temperatures, permittivity, and dielectric loss with chemical doping and ceramic microstructure. $BaTiO_3$-based materials have also been reported to offer a wide range of commercial applications. In several cases involving the disappearance of orthorhombic and tetragonal phases, doped $BaTiO_3$ also presents a ferroelectric-Tc-paraelectric transition, depending on both the substitution and the compositions [6].

Recently, the quantum paraelectric material $SrTiO_3$ has attracted considerable attention for showing exceptional dielectric and ferroelectric behavior, which is of interest for various technological applications. Due to its high lattice polarizability, $SrTiO_3$ is very sensitive to doping. The substitution of Sr^{2+} by Pb^{2+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Mn^{2+}, or Bi^{3+} ions has often been

---

*Corresponding author. Tél.: +21653394715; fax: +21674274437.
E-mail address: thiftrriyosr@yahoo.fr (F. Bahri).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.03.010

reported to exert strong effects on the dielectric properties of $SrTiO_3$ and to induce various types of polar phases (dipole glass, ferroelectric) [7]. In $Ba_{(1-x)}Sr_xTiO_3$, the permittivity maxima related to the cubic-to-tetragonal phase transition of $BaTiO_3$ was previously shown to display relaxor features for $x \geq 0.12$ [8]. This relaxor behaviour has often been ascribed to a random field-induced domain state wherein Bi^{3+} incorporates into an ABO_3-type structure such as that of $BaTiO_3$.

Considering the promising opportunities that lead-free materials, such as $BaTiO_3$ (BT) and $SrTiO_3$ might open with regards to the development of improved and eco-friendly ferroelectric materials, the present study was undertaken to investigate the relaxor behaviour, dielectric properties, and Raman spectroscopy of the Bismuth-doped barium–strontium–titanate ceramics of the formula $(Ba_{0.8}Sr_{0.2})_{(1-1.5y)}Bi_yTiO_3$. The latter have strong diffuse phase transition with frequency dispersion, a valuable property for lead-free ferroelectric applications.

2. Experimental procedures

$(Ba_{0.8}Sr_{0.2})_{(1-3/2y)}Bi_yTiO_3$ ceramic compositions were prepared using the solid state reaction method. The starting materials, $BaCO_3$ (99.9%), TiO_2 (99.9%), $SrCO_3$ (99.9%), and Bi_2O_3 (99.9) (Aldrich chemical) were weighed according to the following reaction:

$$0.8\left(1-\frac{3}{2}y\right)BaCO_3+0.2\left(1-\frac{3}{2}y\right)SrCO_3+\frac{1}{2}yBi_2O_3+TiO_2$$
$$\downarrow$$
$$(Ba_{0.8}Sr_{0.2})_{(1-3/2y)}Bi_yTiO_3+(1-y)CO_2$$

After drying, the powders were calcined at 850 °C for 12 h and then mixed, dried, and pressed into disks. The pellets were sintered at 1220 °C for 2 h and cooled in a furnace. The phase purity of the sample compounds was confirmed by the X-ray diffraction (XRD) technique using a PW-3020 Philips diffractometer with Cu–Kα ($\lambda = 1.5418$ Å) radiation in a wide range of 2θ ($5° < 2\theta < 90°$) and a scanning rate of $2°\ min^{-1}$.

Gold electrodes were sputtered on the samples for dielectric measurements. The relative dielectric permittivity (ε'_r) and loss tan(δ) of the compounds were measured in a cryogenic system and high temperature oven using an HP4284 LCR meter at a frequency range of 100 Hz–1 MHz, temperature range of 85–500 K, and heating rate of $2\ °C\ min^{-1}$. Raman spectra were collected by means of a Raman spectrometer (HORIBA Jobin-Yvon Labram, HR 800) using the He–Ne laser excitation line of 632.8 nm (1.96 eV). All spectra were obtained in normal and side-view backscattering geometries using a microprobe device that allows the incident light to be focused on the sample as a spot with a diameter of about 2 μm.

3. Results and discussion

Fig. 1, shows the XRD patterns of BBSTs recorded at room temperature for Bi doping concentrations of 5%, 10%, and 15%. The findings revealed that 10% Bi doped in $Ba_{0.8}Sr_{0.2}TiO_3$ was the limit for pure phase formation. In fact, when the Bi doping concentration was lower than 10%, all peaks belonged to the pure tetragonal perovskite phase, with a space group of P4mm as determined with the FullProf program. This indicated that Bi^{3+} ions occupied the BST perovskite lattice. The composition $y = 15\%$ showed more than one perovskite phase structure.

Fig. 2, shows the temperature dependence of the dielectric permittivity of BBST doped with 5% Bi as a function of temperature at different frequencies (0.1–1000 kHz). The variation of ε'_r as a function of temperature showed a relatively broad peak with a low dispersion of permittivity in the ferroelectric phase. This behaviour can be attributed to the early onset of the relaxor feature in this composition.

Fig. 3(a and b) shows the dielectric permittivity (ε'_r) and loss tan (δ) of the BBST doped with 10% Bi as a function of temperature at different frequencies (0.1–1000 kHz). Fig. 3(a) illustrates that while the temperature T_m corresponding to the maximum value of the dielectric permittivity increased with the increase in frequency, the maximum value of the dielectric permittivity decreased with the increase in frequency. This

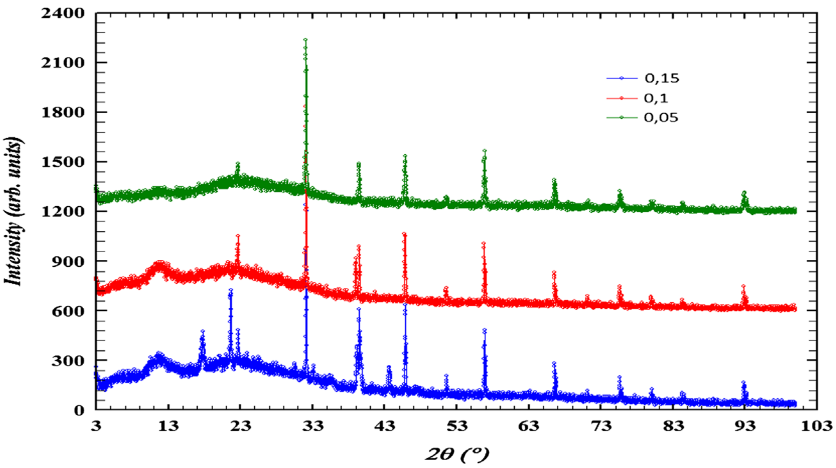

Fig. 1. X-ray diffraction patterns of BBST for different Bi_2O_3 concentrations recorded at room temperature.

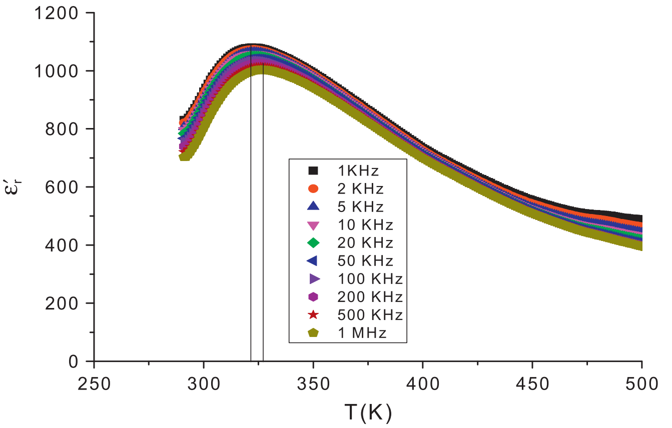

Fig. 2. The temperature dependence of the dielectric permittivity of BBST 5% Bi ceramic at different frequencies.

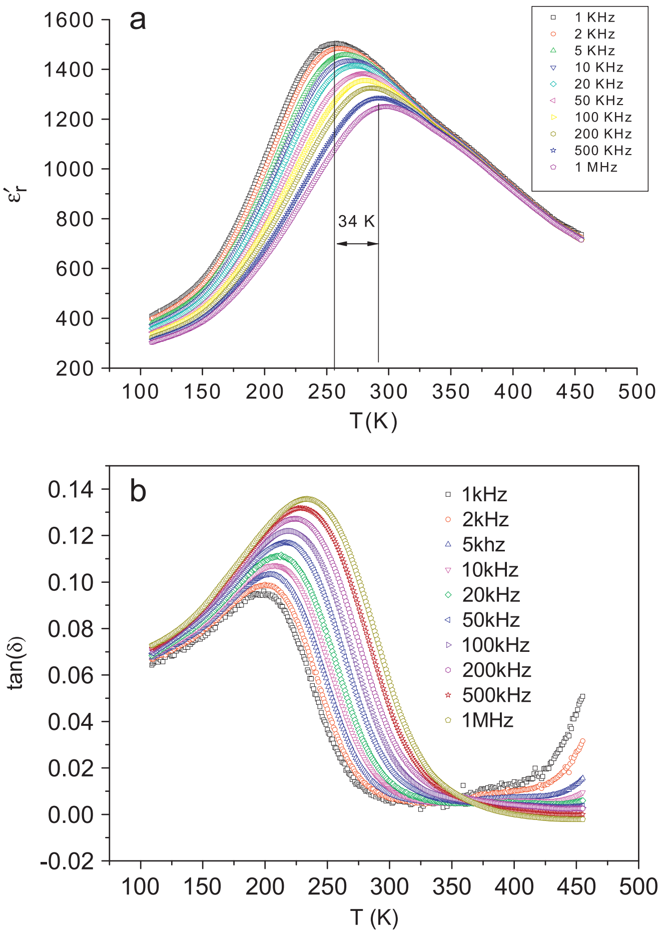

Fig. 3. Temperature dependence of dielectric constant (ε'_r) and tan(δ) at various frequencies for BBST 10 at%.

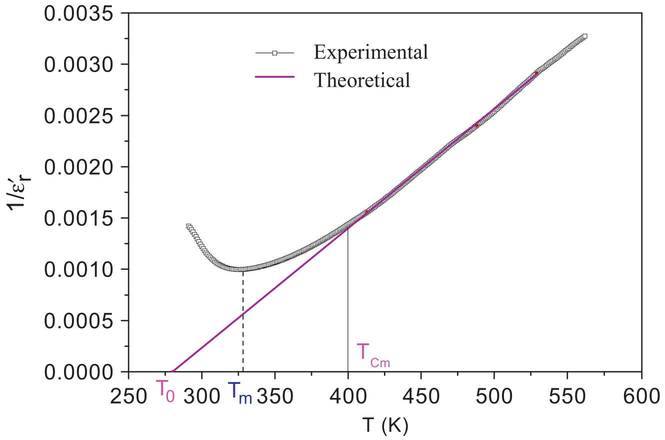

Fig. 4. The plot of the inverse dielectric constant vs. temperature at 10 kHz for BBST [Symbols: experimental data; the solid line: fitting to Eq. (1).].

phenomenon indicated that the BBST sample doped with 10% Bi exhibited typical relaxor behaviour. Another exterior indication of relaxor behaviour is that the dielectric permittivity curves of different frequencies merge at high temperature, which is usually observed in Pb-based relaxors [9]. The loss tangent (Fig. 3(b)) peak was also noted to shift to higher temperatures with the increase in frequency.

For a classical ferroelectric, the dielectric permittivity above the Curie temperature follows the well known Curie–Weiss law:

$$\varepsilon = \frac{C}{T - T_C}(T > T_C) \tag{1}$$

where T_C refers to the Curie temperature and C to the Curie–Weiss permittivity.

Fig. 4 shows the plot of inverse dielectric permittivity versus temperature at 10 kHz for the BBST doped with 10% Bi. The deviation from the Curie–Weiss law for relaxor ferroelectrics can be defined by ΔT_m as follows:

$$\Delta T_m = T_{cm} - T_m, \tag{2}$$

where T_{cm} refers to the temperature from which dielectric permittivity starts to deviate from the Curie–Weiss law and T_m to the temperature at which dielectric permittivity reaches the maximum. The ΔT_m value calculated at 10 kHz was 75 K and was noted to be almost invariable with the increase in frequency. The dielectric characteristics of relaxor ferroelectrics are known to deviate from the typical Curie–Weiss behaviour and can be well described by the Uchino and Nomura function, a modified Curie–Weiss relationship:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^{\gamma}}{C} \quad 1 < \gamma < 2 \tag{3}$$

where ε_m refers to the maximum value of dielectric permittivity, ε to the dielectric permittivity at temperature T, T_m to the temperature at the peak of the dielectric permittivity, C to the Curie constant, and γ to the diffuseness degree indicator, taking the value between 1 (for a normal ferroelectric) and 2 (for a complete diffuse phase transition). The value of γ can, therefore, be used to characterize the relaxor behaviour. The plot of log ($1/\varepsilon - 1/\varepsilon_m$) as a function of log ($T - T_m$) is shown in Fig. 5. By fitting the Uchino equation, the exponent γ which determines the diffuseness degree of the phase transition, was obtained from the slope of log ($1/\varepsilon - 1/\varepsilon_m$)-vs-log ($T - T_m$) plot. The value obtained for the parameter was 1.68, suggesting that the prepared ceramic (BBST 10% Bi) was a

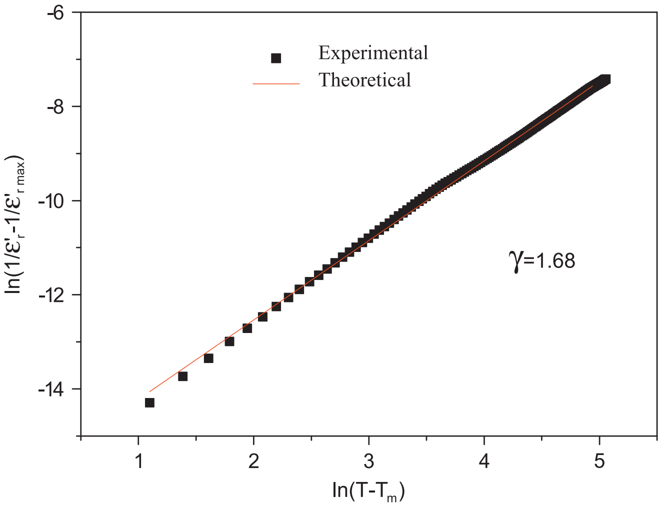

Fig. 5. ln ($1/\varepsilon - 1/\varepsilon_m$) as a function of ln ($T - T_m$) at 10 kHz for BBST 10% Bi. [Symbols: experimental data; the solid line: fitting to Eq. (3).].

relaxor ferroelectric with strong diffuse phase transition [10,11].

The ΔT_{relax} and $\Delta T_{\text{diffuse(1 kHz)}}$ parameters were also introduced to investigate the relaxor feature of BBST 10% Bi. The degrees of relaxation behaviour and diffuseness were defined as [12].

$$\Delta T_{\text{relax}} = T/\varepsilon_m(100\ \text{kHz}) - T/\varepsilon_m(100\ \text{Hz}), \tag{4}$$

$$\Delta T_{\text{diffuse(1kHz)}} = T_{\ 0.9}/\varepsilon_m(1\text{kHz}) - T/\varepsilon_m(1\text{kHz}). \tag{5}$$

Based on the experimental data, the values calculated for ΔT_{relax} and $\Delta T_{\text{diffuse(1 kHz)}}$ of the sample under investigation were 34 and 51 K, respectively. The characterization performed on the basis of the Curie–Weiss law mentioned above and the values calculated for empirical parameters, such as ΔT_m, γ, $\Delta T_{\text{diffuse(1 kHz)}}$ and ΔT_{relax}, provided evidence that the BBST 10% Bi is a relaxor ferroelectric with strong diffuse phase transition and frequency dispersion.

Relaxors have often been reported to behave like spin-glass systems in magnetism, and the relaxation effects to follow an empirical Vogel–Fulcher relationship [13,14]. In this model, the dielectric relaxation appears as a result from thermally activated polarization reversals between two equivalent variants, and the polarization flipping frequency f_0 is related to the activation energy E_a (the barrier between two equivalent polarization states) as follows:

$$f = f_0 exp\left(-\frac{E_a}{k(T_m - T_f)}\right) \tag{6}$$

where f_0 refers to the Debye frequency, k to the Boltzmann constant, and T_f to the static freezing temperature. The parameters obtained by fitting were T_f=185 K, f_0=1.18 × 10^{10} Hz, and Ea=0.35 eV.

All the optically active Raman modes in the tetragonal phase of BT can be represented as follows: Γ_{OPtet}=3[A_1 (TO)+A_1 (LO)]+B_1+ 4[E (TO)+E (LO)]. The Raman spectra of the BT tetragonal phase are known to consist of four dominant bands with positions at 250 (A_1 (TO)), 307 (B_1, E (TO+LO)), 515 (A_1 (TO), E (TO)), and 715 cm^{-1} (A_1 (LO), E (LO)) [15,16]. These Raman bands have been assigned to more than one phonon mode because the wavenumbers of some A_1 and E modes are so close that the observable modes become mixed [16]. The Raman spectra of the tetragonal BT phase could also contain weak bands at 185 cm^{-1} (A_1 (TO)) and a negative dip at 180 cm^{-1} (E (TO), E (LO)).

The Raman spectra recorded for the BBST ceramics under investigation at room temperature are shown in Fig. 6. The characteristic bands observed for two samples at about 250, 300, 518, and 725 cm^{-1} were typical to the tetragonal structure. Since Raman scattering can be observed at around 250 and 518 cm^{-1} for both the tetragonal and cubic symmetries of BT [17], the tetragonal phase can be determined by observing the relative intensity of the bands at 300 and 725 cm^{-1}. The band at 300 cm^{-1} was assigned to the B_1 mode, indicating asymmetry within the [TiO_6] octahedral, while the band at 725 cm^{-1} was ascribed to the highest wavenumber of the longitudinal optical mode (LO) of A_1 symmetry. Although the two observed bands clearly confirmed the presence of the tetragonal phase, possible phase coexistence could not be excluded. The development of the ferroelectric phase transition with temperature was monitored by observing the intensity ratio of the band at 725 cm^{-1} and 518 cm^{-1}. The gradual decrease of the intensity and the sharpness of the tetragonal band at 307 cm^{-1} indicated a diffuse phase transition from the tetragonal to the cubic phase (Fig. 7).

For nearly half a century since the discovery of relaxors, several theoretical models, including the superparaelectricity, dipolar glass, and random-field models, have been proposed to explain relaxor behaviour. A common point between these models relates to the local order–disorder of the crystal structure that gives rise to polar clusters embedded in the matrix. The relaxor behaviour may exist irrespective of whether the matrix is ferroelectric or paraelectric, which is the dynamic response of the polar clusters induced in the system [18,19]. According to the electronic configurations of Xe $4f^{14}5d^{10}6s^26p^3$ for Bi, the Bi^{3+} with the $6s^2$ single ion pair can be deduced to have a large stereochemical activity similar

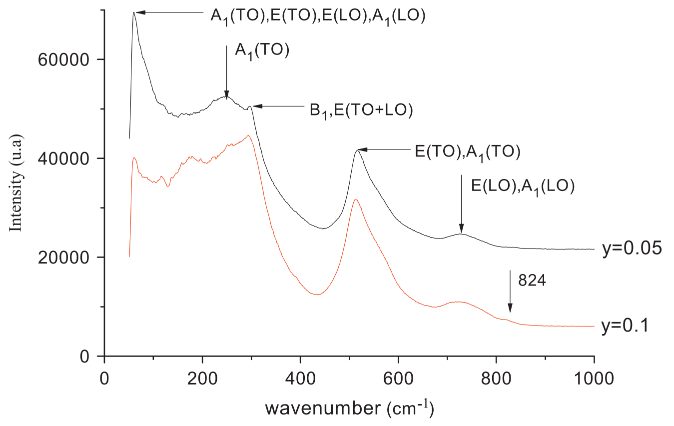

Fig. 6. Raman spectra of the BBST 5% and 10% Bi ceramics at room temperature.

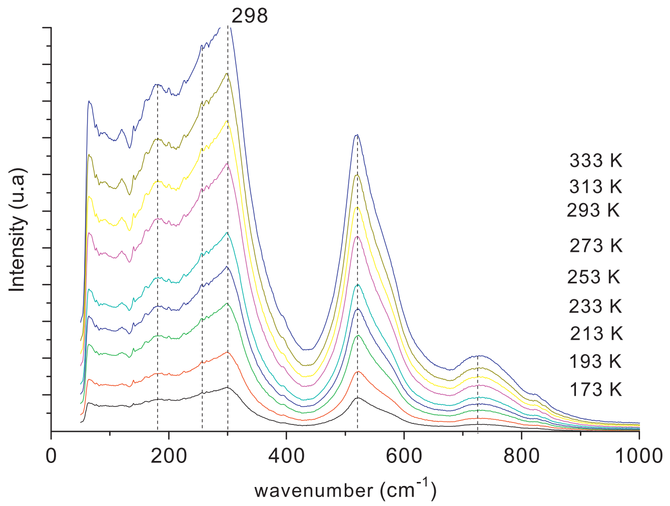

Fig. 7. Raman spectra of BBST 10% Bi at various temperatures.

to the neighbour element of Ba^{2+}. Considering the stereochemical activity of the Bi single pair and the large difference of ionic radii between the host Ba^{2+} ion and the added Bi^{3+} ion, Bi impurity can drive the large displacement at the off-centered A position, resulting in the formation of the polar clusters, which induced the transformation from normal ferroelectrics to relaxors.

4. Conclusions

$(Ba_{0.8}Sr_{0.2})_{(1-1.5y)}Bi_yTiO_3$ ceramic compositions were prepared by the conventional solid-state method. Bi^{3+} ions entered the unit cell and substituted for A-site ions up to $y = 10\%$, maintaining the perovskite structure of the solid solution. The incorporation of Bi_2O_3 induced the ferroelectric relaxor behaviour in the $Ba_{0.8}Sr_{0.2}TiO_3$ system. The quantitative characterization and comparison of the relaxor behaviour based on empirical parameters (ΔT_m,γ, $\Delta T_{\mathrm{relax}}$, $\Delta T_{\mathrm{diffuse\ (1\ kHz)}}$) confirmed its relaxor behaviour with strong diffuse phase transition. The relaxor behaviour originated from the micropolar clusters, which stemmed from the heterovalent substitutions of Bi^{3+} at Ba^{2+} and/or Sr^{2+} site. The findings from Raman spectroscopic analysis confirmed the results from dielectric and RX measurements. Overall, this work presents a simple composition-controlled perovskite system for the study of relaxors and provides ample evidence for the potential candidacy of BBST ceramics as alternative sources for the development of new and eco-friendly lead-free ferroelectric materials.

Acknowledgements

The authors would like to express their sincere gratitude to Anouar Smaoui from the English Language Unit at the Sfax Faculty of Science for his valuable proofreading and language polishing services.

References

[1] B. Jaffe, W. Cook, H. Jaffe, Piezoelectric Ceramics, Academic, London, 1971.

[2] G.H. Haertling, Ferroelectric ceramics: history and technology, Journal of American Ceramic Society 82 (1999) 797–818.

[3] S.E. Park, T.R. Shrout, Ultrahigh strain and piezoelectric behaviour in relaxor based ferroelectric single crystals, Journal of Applied Physics 82 (1997) 1804–1811.

[4] L. Bellaiche, David Vanderbilt, Intrinsic piezoelectric response in perovskite alloys: PMN-PT versus PZT, Physical Review Letters 83 (1999) 1347–1350.

[5] J. Ravez, A. Simon, Some solid state chemistry aspects of lead-free relaxor ferroelectrics, Journal of Solid State Chemistry 162 (2001) 260–265.

[6] H. Khelifi, M. Zannen, N. Abdelmoula, D. Mezzane, A. Maalej, H. Khemakhem, M. Es-Souni, Dielectric and magnetic properties of $(1-x)BiFeO_3$–$xBa_{0.8}Sr_{0.2}TiO_3$ ceramics, Ceramics International 38 (2012) 5993–5997.

[7] V.V. Lemanov, Defects and Surface-Induced Effects in Advanced Perovskites, in: G. Borstel, A. Krumins, D. Millers (Eds.), Kluwer Academic Publishers, 2000, pp. 329–340.

[8] V.S. Tiwari, N. Singh, D. Pandey, Diffuse ferroelectric transition and relaxational dipolar freezing in $(Ba,Sr)TiO_3$, Journal of Physics: Condensed Matter 7 (1995) 1441–1460.

[9] M.M. Kumar, K. Srinivas, S.V. Suryanarayana, Relaxor behaviour in $BaTiO_3$, Applied Physics Letters 76 (2000) 1330–1332.

[10] C. Ang, Z. Jing, Z. Yu, Ferroelectric relaxor $Ba(Ti,Ce)O_3$, Journal of Physics: Condensed Matter 14 (2002) 8901–8912.

[11] X. Chou, J. Zhai, J. Sun, X. Yao, Preparation and dielectric properties of B_2O_3–Li_2O-doped $BaZr_{0.35}Ti_{0.65}O_3$ ceramics sintered at a low temperature, Ceramics International 34 (2008) 911–915.

[12] W. Chen, X. Yao, X.Y. Wei, Tunability and ferroelectric relaxor properties of bismuth strontium titanate ceramics, Applied Physics Letters 90 (2007) 182902–182904.

[13] G.S. Fulcher, Analysis of recent measurements of the viscosity of glasses, Journal of American Ceramic Society 8 (1925) 339–355.

[14] A.K. Tagantsev, Vogel–Fulcher relationship for the dielectric permittivity of relaxor ferroelectrics, Physical Review Letters 72 (1994) 1100–1103.

[15] A.J. Upendra, Y. Songhak, B. Sungg, S.L. Jae, Surfactant-free hydrothermal synthesis of highly tetragonal barium titanate nanowires: a structural investigation, Journal of Physical Chemistry B 110 (2006) 12249–12256.

[16] U.D. Venkateswaran, V.M. Naik, R. Naik, High-pressure Raman studies of polycrystalline $BaTiO_3$, Physical Review B 58 (1998) 14256–14260 and references therein.

[17] Y. Shiratori, C. Pithan, J. Dornseiffer, R. Waser, Raman scattering studies on nanocrystalline BaTiO3 part I—isolated particles and aggregates, Journal of Raman Spectroscopy 38 (2007) 1288–1299.

[18] C. Ang, Z. Yu, Z. Jing, Impurity-induced ferroelectric relaxor behavior in quantum paraelectric $SrTiO_3$ and ferroelectric $BaTiO_3$, Physical Review B 61 (2000) 957–961.

[19] H. Zaghouene, H. Khemakhem, A. Simon, X-ray diffraction, dielectric, pyroelectric, piezoelectric and Raman spectroscopy studies on $(Ba_{0.95}Ca_{0.05})_{0.8875}Bi_{0.075}TiO_3$ ceramic, Ceramics International 38 (2012) 3135–3139.