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Preparation and characterisation of the magneto-electric xBiFeO$_3$–(1 − x)BaTiO$_3$ ceramics

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Abstract

The solid solutions of BiFeO$_3$–BaTiO$_3$ have been prepared via solid state with a view to obtaining magnetoelectric properties, i.e. ferroelectric and magnetic activity in the same range of temperatures. Optimum calcination and sintering strategy for obtaining pure perovskite phase, dense ceramics (>97% relative density) and homogeneous microstructures have been determined. The sample of composition 0.7BiFeO$_3$–0.3BaTiO$_3$ reported in the present work is pseudo-cubic at room temperature. The permittivity is $\varepsilon_r \approx 150$ at the room temperature and shows a broad ferro-para phase transition at around 175 °C where $\varepsilon_r \approx 1600$. This diffuse maximum of the permittivity, similar to that in relaxors, is due to the chemical inhomogeneity in both A and B sites of the perovskite unit cell ABO$_3$. Higher losses, $\tan\delta > 1$, appear above 200 °C and other different conduction mechanisms start to be active particularly at temperatures higher than 400 °C, when the ceramic becomes conductive. The magnetic properties show a succession of transitions from weak ferro/ferrimagnetism-to-antiferromagnetism and antiferromagnetism-to-paramagnetism at $T_{N1} \approx 10$ K and $T_{N2} \approx 265$ K. Below T_{N2} the ceramic 0.7BiFeO$_3$–0.3BaTiO$_3$ can present magnetoelectric coupling, due to the fact that is simultaneously ferroelectric and antiferromagnetic.

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1. Introduction

The ferroic systems have an order parameter reversible by an adequate driving force and this switching process is accompanied by hysteresis. Ferroelectrics, ferromagnetics and ferroelastics are typical examples of ferroics: the electric polarization, magnetic moment or strain can be reversed between two ordered states by means of electric, magnetic or stress fields, respectively. The magnetoelectric (ME) multiferroics possess two order parameters (magnetic and electrical polarization) coexisting in the same temperature range.[1–3] The conditions for the occurrence of ferroelectric and magnetic order in the same material require: (i) the presence of adequate structural building blocks permitting ferroelectric-type ionic movements, i.e. off-centre displacement associated with the spontaneous polarization in ferroelectrics, (ii) magnetic-interaction pathways for the magnetic order, usually of the super-exchange type, and (iii) symmetry conditions.[4] Although highly exciting for potential applications, the single-phase ME multiferroism is quite rare, being restricted to only few systems, due to the apparently opposite requirements concerning the d-orbital occupancy for ferroelectric and magnetic order.[5] Recently a few different mechanisms have been proposed to explain this contradiction and to find the possible compatibility of the two types of orders.[6,7]

BiFeO$_3$ is a single-phase ME, being ferroelectric (Curie temperature $T_C \approx 830$ °C) and antiferromagnetic (Néel temperature $T_N = 310$ °C), also showing a weak ferro/ferri magnetic characteristic in some temperature ranges.[8] In its bulk state, BiFeO$_3$ has a rhombohedral-distorted perovskite structure $R3c$ ($a = b = c = 5.63$ Å, $\alpha = \beta = \gamma = 59.4°$) at room temperature. Although promising for its multiferroic character, only poor dielectric and ferroelectric properties (low values of the polarization and of the dielectric constant) were found at room

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temperature in the bulk ceramics, mainly due to the semiconducting character which does not allow proper electrical poling and leads to high dielectric losses. Some better $P(E)$ loops ($P_s = 8.9\ \mu C/cm^2$, $P_r = 4.0\ \mu C/cm^2$, $E_c = 39$ kV/cm under an applied field of 100 kV/cm) were observed recently at room temperature in $BiFeO_3$ ceramics obtained by rapid liquid phase sintering.[9] Only in epitaxial or polycrystalline films of $BiFeO_3$ obtained by Pulsed Laser Deposition (PLD), were better dielectric properties reported.[10,11] Therefore, even these results and their interpretation are presently under debate between a few groups of researchers.[12,13]

In order to reduce the problems mentioned above, the method of forming binary solid solutions with other perovskites with good dielectric properties as $BaTiO_3$,[14] $PbTiO_3$[15] or others[16] was adopted. Therefore, even in solid solutions, the problems of losses were only partially solved and the reported data are often "author dependent". In the present work, the possibility of obtaining ferroelectric and magnetic activity in solid solutions of $xBiFeO_3$–$(1-x)BaTiO_3$ was investigated.

2. Sample preparation and experiment

Ceramics with compositions $(1-x)BiFeO_3$–$xBaTiO_3$ were prepared via solid state using Bi_2O_3, Fe_2O_3, TiO_2 (99.9% Aldrich) and $BaCO_3$ (99.9%, Solvay Bario Derivati) in appropriate proportions. The precursors were mixed, milled for 24 h and calcined at various temperatures in the range (600–750 °C) for 4–8 h with intermediate milling steps. Optimum calcinations parameters to obtain the pure perovskite phase were found for each composition. The calcined powders were milled, isostatically pressed at 2×10^8 Pa and then sintered at 900 °C for 2 h in oxygen. Phase composition and crystal structures at different calcinations steps and after sintering were checked by X-ray diffraction (XRD, Co Kα radiation, Philips PW1710, Philips, Eindhoven, The Netherlands). The microstructures were characterized by scanning electron microscopy (SEM, LEO 1450VP, LEO Electron Microscopy Ltd., Cambridge, UK). The dielectric measurements, in the frequency range 10^{-1} to 10^7 Hz, were performed at temperatures of 30–400 °C with a heating/cooling rate of 0.5 °C/min using an impedance analyzer Solartron SI1260. Differential scanning calorimetry (DSC) measurements were performed on samples of ≈100 mg (cut from the sintered disks) in the range 20–250 °C at a heating/cooling rate of 10 °C/min. The enthalpy of transition was estimated from the area of the DSC peaks. The magnetic moments of ceramic samples were measured using a superconducting quantum interferometric device SQUID magnetometer (Quantum Design) in the range of temperatures 5–350 K. The results presented below concentrate on ceramics with the composition $x = 0.7$.

3. Results and discussions

The X-ray diffraction patterns of Fig. 1 show phase formation of the solid solution with the composition $0.7BiFeO_3$–$0.3BaTiO_3$. The pure perovskite phase, not yet formed after the calcinations at 600 °C for 2 h, is completely formed by calcination at 750 °C for 8 h and it is preserved after the sintering at 900 °C for 2 h. The possible secondary phases are below the XRD detection limit (≈1 wt.%). The phase symmetry is very close to cubic (pseudo-cubic), Rietveld refinement gave similar results, with either rhombohedral symmetry or a very low rhombohedral distortion of cubic with $a = 3.9945$ Å. Therefore, the presence of some Raman modes, not allowed for a centrosymmetric state, clearly showed that $0.7BiFeO_3$–$0.3BaTiO_3$ is not really cubic, but slightly distorted, as in the case of the relaxor systems.[17] This result agrees with the phase diagram of $xBiFeO_3$–$(1-x)BaTiO_3$ proposed in ref. [14] in which the composition $x = 0.7$ should be in the range of the morphotropic phase boundary, rhombohedral-to-cubic.[14] The particle size of the calcined powders is around 200–300 nm (Fig. 2a). The ceramic shows a homogeneous microstructure (Fig. 2b, where a SEM image obtained inside a macro-pore, without any etching is presented), having the average grain size of around 2 μm and a good densification (97% relative density).

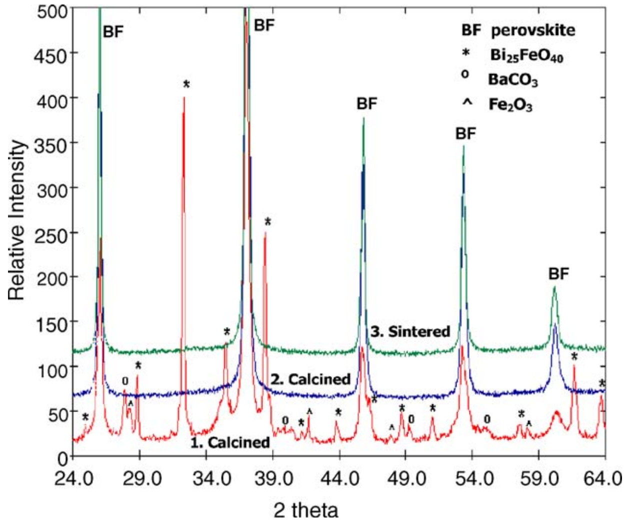

Fig. 1. X-ray diffractograms of the $0.70BiFeO_3$–$0.30BaTiO_3$ solid solutions at selected processing steps: (1) calcination at 600 °C for 2 h, (2) calcination at 750 °C for 8 h and (3) sintering at 900 °C for 2 h.

The dielectric data were obtained on Au-electroded samples in plan-parallel configuration. At room temperature, the imaginary part of the impedance exhibits a continuous reduction with increasing frequency and a few relaxations around the frequencies of 1 Hz, 0.6 kHz and 60 kHz (Fig. 3). The Cole–Cole plot represented in the inset of Fig. 3 shows more than one component, indicating inhomogeneities of the electrical properties at microscopic level, grain-boundary or/and interface effects. The dielectric constant measured at $f = 4$ kHz shows a broad maximum at the temperature of around 175 °C (Fig. 4) accompanied by a maximum of the dielectric losses $\tan\delta$ in the same range of temperatures (shown in the inset of Fig. 4). This maximum corresponds to the ferro-para phase transition. The losses are reduced at high frequency (considering the particularities of the present system), for example at $f = 4$ kHz they are below 20% for temperatures lower than 200 °C. Therefore, by increasing the temperature, $\tan\delta$ increases and presents also other stronger anomalies associated with mechanisms other than the phase transition, as for example one visible in the inset of Fig. 4 around

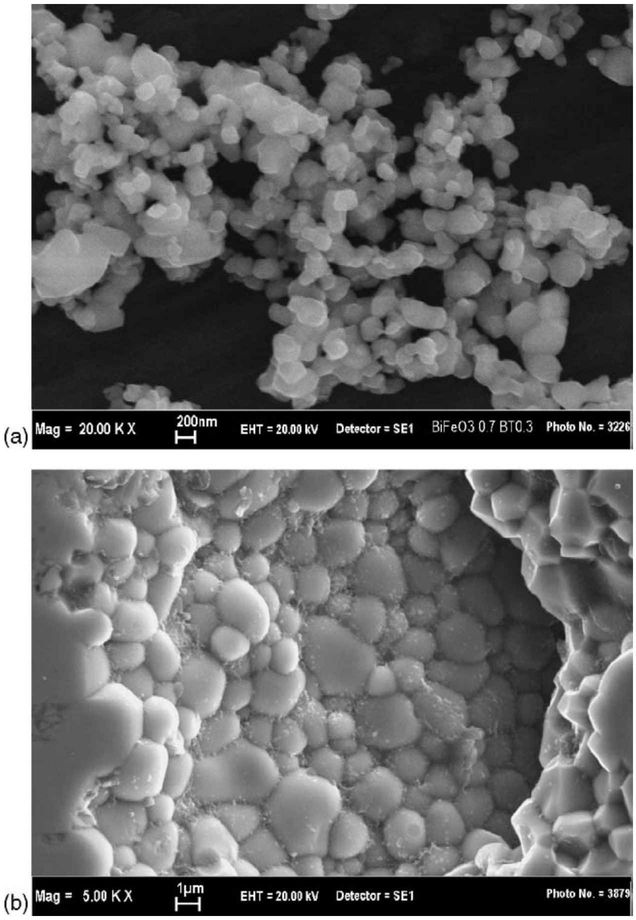

Fig. 2. SEM micrographs of the $0.70BiFeO_3$–$0.30BaTiO_3$ solid solution: (a) after calcination at 750 °C for 8 h (bar: 200 nm) and (b) after sintering at 900 °C for 2 h (bar: 1 μm).

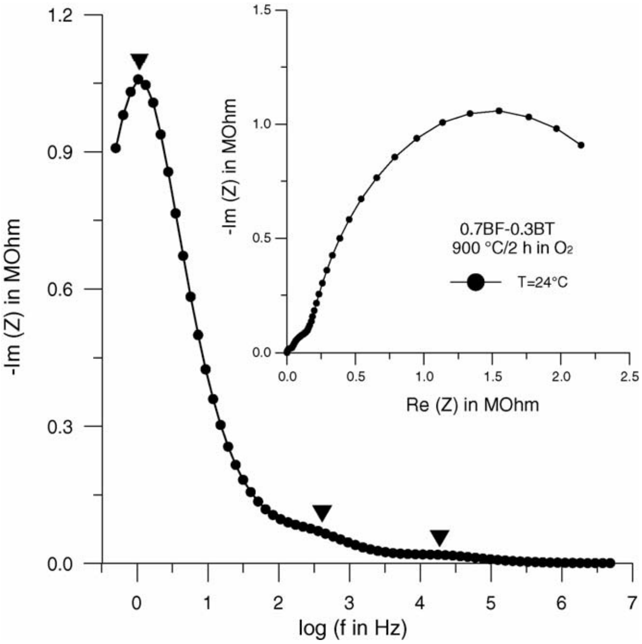

Fig. 3. Imaginary part of the impedance vs. frequency spectrum for $0.70BiFeO_3$-$0.30BaTiO_3$ ceramic showing a few relaxations. Inset: plot of the imaginary vs. the real part of the impedance for the same sample.

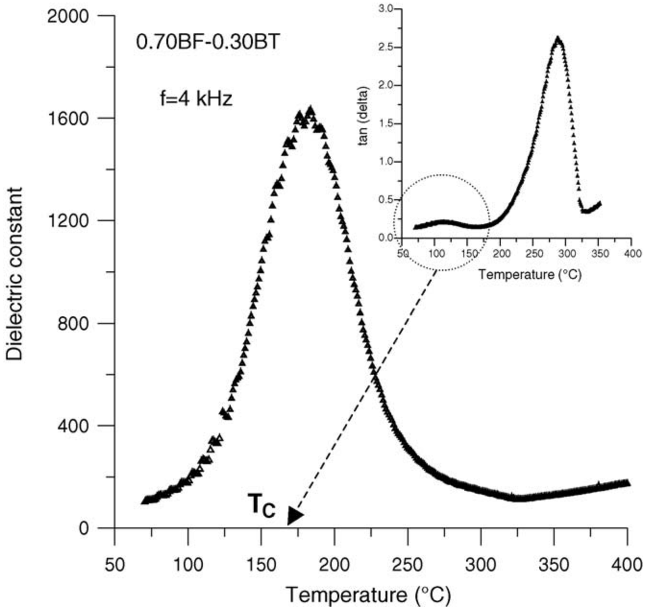

Fig. 4. The temperature dependence of the dielectric constant and losses at the frequency $f = 4$ kHz for $0.70BiFeO_3$–$0.30BaTiO_3$.

280 °C. Moreover, repeated cycles heating/cooling over 400 °C activate other loss mechanisms giving rise to very high losses (tan δ of hundreds, the ceramic being no longer a dielectric) and low reproducibility of dielectric properties even at room temperatures. Our results are similar to ones reported for similar ceramic systems as $BiFeO_3$–$PbTiO_3$, for which dielectric constant versus temperature with a few maxima and $\tan\delta \gg 20$ for $T > 300$ °C were reported.[15] This high conductivity and leakage, especially at higher temperatures in $BiFeO_3$-based ceramics, were considered to be caused in part by the difficulty of producing this material in its single phase, so that even very small impurities segregated to boundaries can have a doping effect and transform the dielectric into a semiconductor.[9] Therefore, the problem persists even in very pure $BiFeO_3$ ceramics and it was explained as originating from the spontaneous change of the oxidation state of Fe^{3+}/Fe^{2+}. This results in the formation of oxygen vacancies for preserving the local electrical neutrality and causes thermally activated hoping conduction. In addition, an important contribution to the losses is given in bulk ceramics by defects associated with the grain boundaries.[18] All these phenomena often make difficult the detection of the ferro-para phase transition by electrical investigations. Therefore, in the case of $0.7BiFeO_3$–$0.3BaTiO_3$ ceramic, the phase transition around 175 °C was also confirmed by a non-electrical method (by the presence of a small DSC peak with an enthalpy of the transition of 0.25 J/g at the same temperature). According to the present data, this ceramic has a ferroelectric character (most probably relaxor-like) at temperatures below 175 °C. The diffuse character of the phase transition can be understood in terms of the inhomogeneous composition both in A and B sites of the ABO_3 perovskite cell. Thus, the composition $0.7BiFeO_3$–$0.3BaTiO_3$ can be a candidate for magnetoelectric effect, if showing magnetic activity.

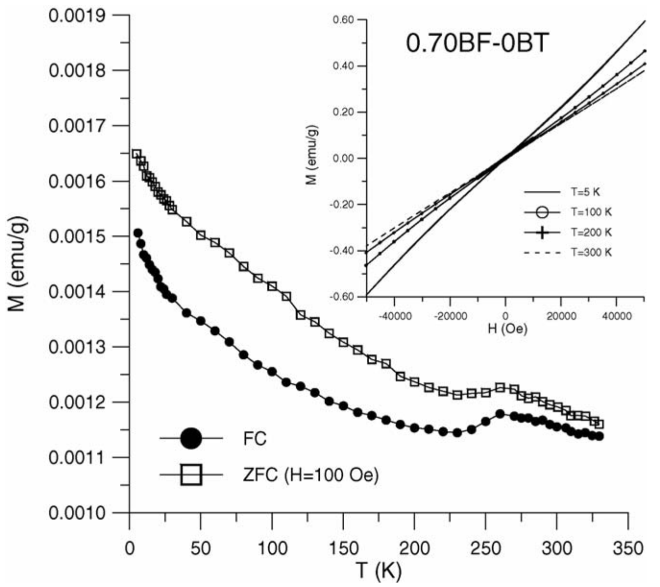

Fig. 5. Temperature dependence of the magnetization for the ceramic 0.70BF–0.30BT, indicating two magnetic transitions at $T_{N1} \approx 10$ K and $T_{N2} \approx 265$ K. Inset: $M(H)$ curves at a few temperatures: $T = 5$, 100, 200 and 300 K.

The results of the magnetic measurements obtained by SQUID are presented in Fig. 5, where the evolution of the magnetization $M(T)$ with temperature is shown. From anomalies in the $M(T)$ dependence, two magnetic transitions at $T_{N1} \approx 10$ K and $T_{N2} \approx 265$ K were identified, in spite of the apparent linearity of the $M(H)$ loops at different temperatures, represented in the inset of Fig. 5. Pure $BiFeO_3$ was classified as antiferromagnetic with the Néel temperature $T_N = 310$ °C, but some other features like weak ferro/ferrimagnetic characteristic in some temperature ranges were also found.[8,19] The present data for the solid solution show that the presence of the non-magnetic $BaTiO_3$ phase causes a reduction of the magnetic interaction by diminishing the Neel temperature below room temperature. A succession of transitions takes place with increasing temperature, from weak ferro/ferrimagnetism-to-antiferromagnetism and antiferro-magnetism-to-paramagnetism at T_{N1} and T_{N2}, respectively. Thus, the ceramic xBiFeO$_3$–$(1-x)$BaTiO$_3$ with the composition $x = 0.7$ should present magnetoelectric coupling below T_{N2}, where it is expected to be simultaneously ferroelectric and antiferromagnetic.

4. Conclusions

In the present work, the possibility of producing bulk magnetoelectric ceramics of xBiFeO$_3$–$(1-x)$BaTiO$_3$ with pure perovskite phase, homogeneous microstructure and high density has been investigated. The composition $x = 0.7$ was found to be pseudo-cubic at room temperature, with high permittivity and a broad ferro-para phase transition at around 175 °C (relaxor-like character). Losses above unity, at temperatures above 200 °C, and strong conduction particularly at temperatures higher than 400 °C were found. A succession of magnetic transitions were detected: weak ferro/ferrimagnetism-to-antiferromagnetism and antiferro- magnetism-to-paramagnetism at $T_{N1} \approx 10$ K and $T_{N2} \approx 265$ K. The solid solution 0.7BiFeO$_3$–0.3BaTiO$_3$ is expected to show magnetoelectric coupling below T_{N2}, since in this temperature range it was shown to be simultaneously ferroelectric and antiferromagnetic.

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References

1. Smolenskii, G. A. and Bokov, V. A., Coexistence of magnetic and electric ordering in crystals. *J. Appl. Phys.*, 1964, **35**, 915–918.
2. Wood, V. E. and Austin, A. E., In *Magnetoelectric Interaction Phenomena in Crystals*, ed. A. J. Freeman and H. Schmid. Gordon and Breach, 1975.
3. Schmid, H., Multi-ferroic magnetoelectrics. *Ferroelectrics*, 1994, **162**, 317–338.
4. Ryu, J., Priya, S., Uchino, K. and Kim, H. E., Magnetoelectric effect in composites of magnetostrictive and piezoelectric materials. *J. Electroceram.*, 2002, **8**, 107–119.
5. Hill, N. A. and Filippetti, A., Why are there any magnetic ferroelectrics? *J. Magn. Magn. Mater.*, 2002, **242–245**, 976–979.
6. Ederer, C. and Spaldin, N. A., A new route to magnetic ferroelectrics. *Nature Mater.*, 2004, **3**, 849–851.
7. Efremov, D. V., Van der Brink, J. and Khomskii, D. I., Bond- versus site-centred ordering and possible ferroelectricity in manganites. *Nature Mater.*, 2004, **3**, 853–856.
8. Fischer, P., Polomska, M., Sosnowska, I. and Szymanski, M., Temperature dependence of the crystal and magnetic structures of $BiFeO_3$. *J. Phys. C: Solid State Phys.*, 1980, **13**, 1931–1940.
9. Wang, Y. P., Zhou, L., Zhang, M. F., Chen, X. Y., Liu, J. M. and Liu, Z. G., Room-temperature saturated ferroelectrics polarization in $BiFeO_3$ ceramics synthesized by rapid liquid phase sintering. *Appl. Phys. Lett.*, 2004, **84**, 1731–1733.
10. Wang, J. *et al.*, Epitaxial $BiFeO_3$ multiferroic thin film heterostructures. *Science*, 2003, **299**, 1719–1722.
11. Yun, K. Y., Ricinschi, D., Kanashima, T., Noda, M. and Okuyama, M., Giant ferroelectric polarization beyond 150 μC/cm^2 in $BiFeO_3$ thin film. *Jpn. J. Appl. Phys.*, 2004, **43**, L647–L648.
12. Eerenstein, W., Morrison, F. D., Dho, J., Blamire, M. G., Scott, J. F. and Mathur, N. D., Comment on "Epitaxial $BiFeO_3$ Multiferroic Thin Film Heterostructures". *Science*, 2005, **307**, 1203a.
13. Wang, J. *et al.*, Response to comment on "Epitaxial $BiFeO_3$ Multiferroic Thin Film Heterostructures". *Science*, 2005, **307**, 1203b.
14. Kumar, M. M., Srinivas, A. and Suryanarayana, S. V., Structure property relations in $BiFeO_3/BaTiO_3$ solid solutions. *J. Appl. Phys.*, 2000, **87**, 855–862.
15. Zhu, W. M. and Ye, Z. G., Effects of chemical modification on the electrical properties of 0.67BiFeO$_3$−0.33PbTiO$_3$ ferroelectric ceramics. *Ceram. Int.*, 2004, **30**, 1435–1442.
16. Kim, J. S., Cheon, C., Lee, C. H. and Jang, P. W., Weak ferromagnetism in the ferroelectric $BiFeO_3$–$ReFeO_3$–$BaTiO_3$ solid solutions (Re = Dy,La). *J. Appl. Phys.*, 2004, **96**, 468–475.
17. Ye, Z. G., Relaxor ferroelectric complex perovskites: structure, properties and phase transitions. *Key Eng. Mater.*, 1998, **155–156**, 81–122.
18. Kalinin, S. V., Suchomel, M. R., Davies, P. K. and Bonnell, D. A., Potential and impedance imaging of polycrystalline $BiFeO_3$ ceramics. *J. Am. Ceram. Soc.*, 2002, **85**, 3011–3017.
19. Ruette, B. *et al.*, Magnetic-field-induced phase transition in $BiFeO_3$ observed by high-field electron spin resonance: cycloidal to homogeneous spin order. *Phys. Rev. B*, 2004, **69**, 064114.