Effect of Ba addition on the structural, dielectric and ferroelectric properties of $Na_{0.5}Bi_{0.5}TiO_3$ ceramics[*]

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Lead-free $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3$ (x = 0, 0.04 and 0.06) ceramics were fabricated by conventional solid phase sintering process. X-ray diffraction analysis shows that obtained specimens possess the perovskite structure. The microstructure study shows a dense structure, in good agreement with the relative density determined by the Archimedes method (above 95 %). Electric permittivity anomaly is shifted to low temperature after Ba doping of NBT. The pyroelectric and hysteresis loops measurements show that polarization and coercive field increases and decreases, respectively, after Ba doping of NBT. The obtained results are discussed in terms of ions/lattice imperfections, which create local electromechanical fields. The investigated ceramics are considered to be promising candidates for lead-free electronic materials.

Keywords: *$(Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3$; structural properties; ferroelectric properties*

1. Introduction

Piezoelectric materials have been widely used as elements of actuators, sensors and transducers. These materials are mostly based on lead containing compounds. But due to high toxicity of lead oxide (PbO) the lead-free piezoelectric materials are highly required nowadays. Sodium-bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) and NBT-based solid solutions are considered as the most promising candidates for replacing lead-containing materials.

Structural investigations using X-ray [1, 2] and neutron [3–5] diffraction evidenced three phases in NBT: the cubic paraelectric phase above about 520 to 540 °C, a tetragonal ferroelastic phase in the temperature range down to about 330 to 260 °C, and a rhombohedral ferroelectric state in low-temperature range [6–8]. The dielectric study revealed that the room-temperature ferroelectric state disappeared at $T_d \sim$ 200 to 230 °C (on heating),

where a hump in electric permittivity and dielectric loss tanδ was observed, and then electric permittivity exhibited a maximum at about 320 °C (T_m) [9]. This inconsistency between the structural and the dielectric results is poorly understood.

In the present work, the $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3$ (x = 0, 0.04 and 0.06) ceramics were fabricated by a conventional solid phase sintering process, and their structural, dielectric and ferroelectric properties were investigated.

2. Experimental

$(1-x)Na_{0.5}Bi_{0.5}TiO_3–xBaTiO_3((1-x)NBT–xBT)$ ceramics (x = 0, 0.04 and 0.06) were prepared by a solid state reaction synthesis, in the same way as NBT [10]. High quality Na_2CO_3, Bi_2O_3 and TiO_2 powders were used. The powders, weighed in suitable proportions, were mixed by ball milling, and then primary sintered under the following conditions: 700 °C (1.5 h), 750 °C (1 h) and 800 °C (2 h) in a closed corundum crucible. In this process we

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obtained the white material, which was ground, pressed and sintered for the second time (800 °C: 1.5 h, 1000 °C: 1.5 h and 1100 °C: 1.5 h). After the second sintering, the ceramics were disintegrated, ground, pressed and sintered for the third time (1100 °C: 1 h and 1150 °C: 1.5 h). Ceramics obtained under these technological conditions were cream-colored, translucent, with a density greater than 95 % of the theoretical value and exhibited very good mechanical properties.

The crystalline structure of the obtained ceramics was examined using X-ray diffraction analysis with CuKα radiation. The bulk densities were measured by Archimedes method. The microstructure was examined by scanning electron microscopy (Hitachi S-4700). The electric permittivity was measured on silver electrode samples as a function of temperature (30 to 600 °C) and frequency (100 Hz to 1 MHz) with a GW INSTEK LCR-8110G meter. The measuring electric field of 20 kV/cm was applied. In order to reduce any aging effect, prior to the measurements the samples were annealed for 1 h at 600 °C. The data were collected regularly with a step of 0.1 °C upon heating and cooling, with a temperature change rate of 2 °C/min., using an automatic temperature controller. Ferroelectric hysteresis loops were evaluated by a Sawyer-Tower circuit. The remnant polarizations were obtained independently from pyroelectric measurements. The pyroelectric currents were recorded using Keithley 6517A electrometer by a quasistatic method after polarizing in dc electric fields of 5 kV/cm, from 250 °C to room temperature.

3. Results and discussion

X-ray measurements reveal that all ceramics show perovskite structure without a secondary phase. This means that Ba ions have completely diffused into NBT lattice. The mean lattice parameter increased after Ba-doping NBT, due to higher ionic radius of Ba^{2+} than that of (Na$_{0.5}$Bi$_{0.5}$)$^{2+}$. Scanning electron microscopy observations indicate that the average grain size slightly decreases with increasing x (from ∼3.5 µm for pure NBT to ∼2.5 µm for x = 0.06).

Fig. 1 shows the temperature dependence of electric permittivity of the samples from room temperature to 600 °C at frequencies of 100 Hz to 1 MHz. A broad maximum at about T$_m$ ∼ 320, 296 and 310 °C for x = 0, 0.04 and 0.06, respectively, is observed, indicating diffuse phase transition. An anomaly at T$_d$ ∼ 190, 120 and 95 °C for x = 0, 0.04 and 0.06, respectively, is observed. Electric permittivity increases and is more frequency dependent after Ba^{2+} doping of NBT. While T$_m$ is frequency independent, T$_d$ shows relaxor behavior (inset in Fig. 1b).
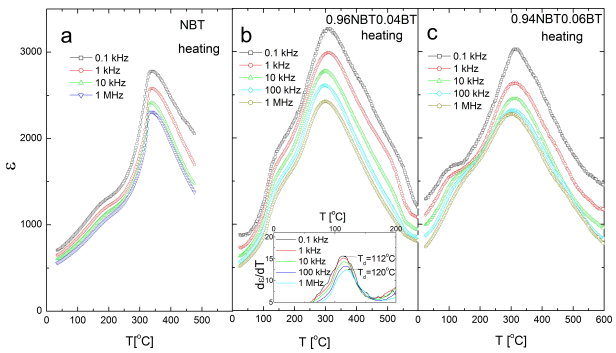

Fig. 1. Temperature dependence of electric permittivity of (1 − x)NBT–xBT ceramics: x = 0 (a), x = 0.04 (b) and x = 0.06 (c).

The shape of the room temperature hysteresis loops is typical of ferroelectric materials (Fig. 2). Note that hysteresis loop for 0.94NBT–0.06BT ceramics is slightly deformed, indicating that polar regions exist with nonpolar phase, which transforms into ferroelectric phase due to the applied electric field [11, 12] (Fig. 3). After Ba^{2+} doping of NBT, polarization increases and coercive field decreases.

Fig. 3 shows the temperature evolution of the remnant polarization obtained from pyroelectric measurements showing very good agreement with P-E hysteresis loops results. It can be noted that two anomalies in the temperature dependence of pyroelectric current i$_p$(T) are visible (approximately at T$_d$ and T$_m$; insets a and b in Fig. 3). This means that in Ba-doped NBT, the polar regions, which are oriented by applying electric field, exist also above T$_d$, as suggested by hysteresis loops measurements.
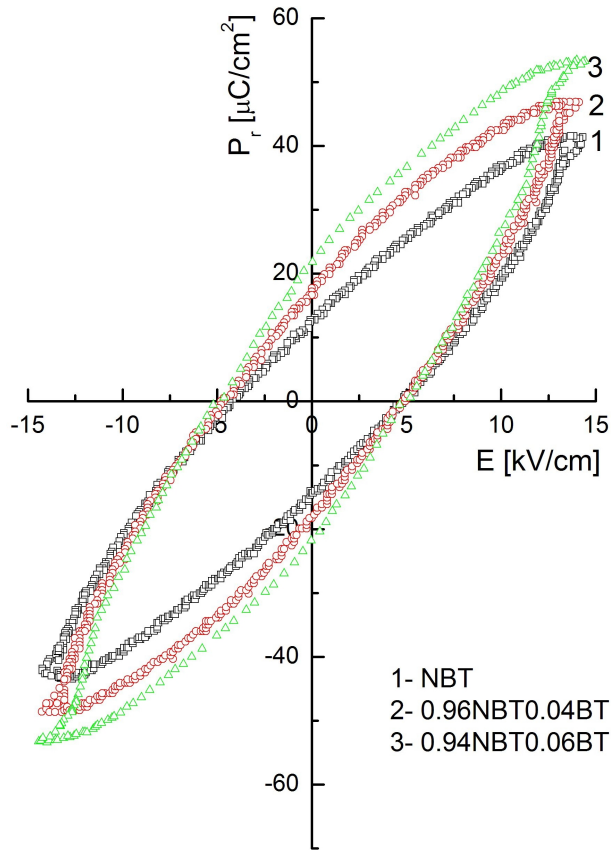
Fig. 2. P-E hysteresis loops of $(1-x)$NBT–xBT ceramics: $x = 0$ (1), $x = 0.4$ (2) and $x = 0.06$ (3).

The increase of dielectric dispersion by Ba^{2+} can arise from the different ionic size of Ba^{2+} and $(Na_{0.5}Bi_{0.5})^{2+}$, which gives rise to the local strain [13]. The inhomogeneity of the ions distribution, which is expected in solid solutions, may cause additional internal strain. This strain promotes the formation of polar regions, which can be responsible for the increase of dielectric dispersion and relaxor behavior. The improvement of the dielectric and ferroelectric properties of NBT after Ba^{2+} doping can be related to a larger ionic radius of this ion in comparison to $(Na_{0.5}Bi_{0.5})^{2+}$. This should lead to an increase in dipole-dipole interactions and, thus, influence the ferroelectric properties. In addition, the increase in the size and volume of oxygen octahedra with the rise in Ba^{2+} content extends the degree of freedom of the Ti^{4+} ions displacement from the oxygen octahedral centre, which also can influence the ferroelectric properties.
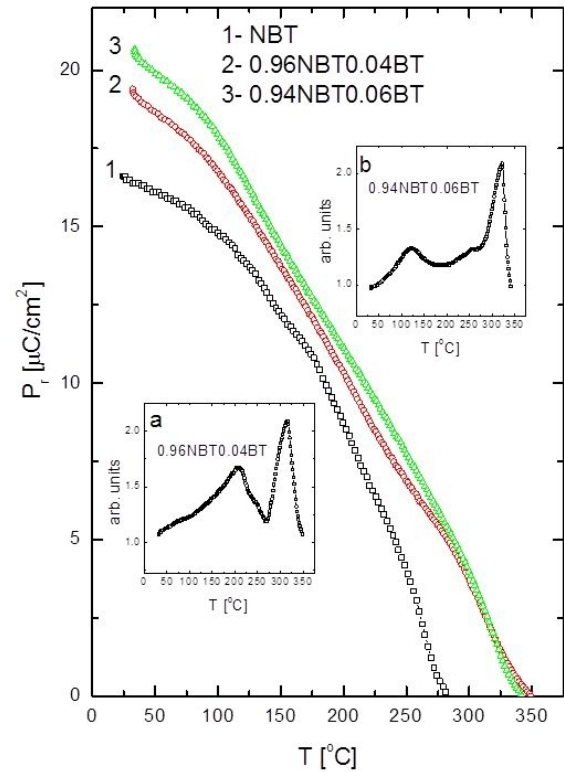

Fig. 3. Temperature dependence of the remanent polarization of $(1-x)$NBT–xBT ceramics. Insets a and b show pyroelectric current of $(1-x)$NBT–xBT ceramics for $x = 0.04$ and 0.06, respectively.

4.   Conclusion

Dense lead-free $(1-x)$NBT–xBT ($x = 0$, 0.04 and 0.06) ceramics were fabricated by conventional sintering method. The ceramics possess a pure perovskite structure. It has been shown that Ba^{2+} ion substitution to NBT causes an increase of electric permittivity and its dispersion as well as an enhancement of ferroelectric properties. The results were interpreted in terms of the difference of ionic size of Ba^{2+} and $(Na_{0.5}Bi_{0.5})^{2+}$, which can promote the formation of polar regions and the increase in the size and volume of oxygen octahedra.

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