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Evolution of crystalline phases and morphotropic phase boundary of the (Bi,Na)TiO_3-(Bi,K)TiO_3-$BaTiO_3$ lead-free ceramic system

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ABSTRACT

In this work, high density $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$-$BaTiO_3$ (BNBK) lead-free ceramics with nominal compositions crossing the morphotropic phase boundary region were prepared and their crystalline phases were investigated by a combination of the X-ray diffraction and Raman spectroscopy techniques, at room temperature. Results show that the BNBK82 sample has a single tetragonal phase (*P4mm*) and the BNBK91 and BNBK93 samples, single rhombohedral phase (*R3c*), while the BNBK88 and BNBK86 compositions showed coexistence of the above two phases with a not previously reported additional tetragonal *P4bm* phase. The Raman spectra deconvolution, for the BNBK86 and BNBK88 samples, also demonstrates the coexistence of rhombohedral and tetragonal phases, with phase fractions in very good agreement with the Rietveld refinement results, evidencing these compositions are located in the MPB region of the BNBK system. Results in this work suggest the MPB region proposed by Takenaka, for the BNBK system, is more appropriate than the one proposed by Trelcat.

1. Introduction

Lead-based piezoelectric ceramics, like $Pb(Zr_{1-x}Ti_x)O_3$, $0 \leq x \leq 1$ or PZT, are widely used in several applications, such as actuators, sensors, filters, transducers, among others [1,2]. For compositions with Zr/Ti ratio close to 52/48, the PZT ceramics show a morphotropic phase boundary (MPB) characterized by the presence of two or more energy states with compatible values (sometimes related to the coexistence of two or more structural phases at the same temperature) [1]. The MPB presence in PZT results in an abnormal enhancement of the dielectric, piezoelectric, ferroelectric and electromechanical properties [3–6]. However, the technological success of PZT-related materials has caused serious environmental and health hazard for humans, plants and animals, mainly during the fabrication process where a large amount of volatile and toxic *PbO* is released to the atmosphere [7]. In this way, some directives that restrict and/or regulate the use of certain hazard substances, including lead-based compounds, have been adopted in several countries, and therefore, lead-free piezoelectric materials have been widely investigated to replace PZT ceramics in technological applications [4,5,8–10].

Among the lead-free piezoelectric materials that have received considerable attention in the last years, stand out those based on $Bi_{0.5}Na_{0.5}TiO_3$ (BNT). The BNT is a ferroelectric material with perovskite structure at room temperature and with several structural phase transitions with the temperature increasing, going from rhombohedral phase with *R3c* space group, at room temperature, to tetragonal (*P4bm*) and cubic ($Pm\bar{3}m$) phases for high temperatures [11]. Although the piezoelectric, dielectric and ferroelectric properties of BNT are not sufficiently good for most applications, it is an important basis for various important solid solutions [11]. The $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$-$BaTiO_3$ (BNT-BKT-BT or BNBK) ternary system, for instance, was investigated mainly due to its high piezoelectric properties and relatively high Curie temperature near the MPB between rhombohedral and tetragonal symmetries [12–15].

Despite of the MPB vital influence in the physical properties of piezoelectric materials, in the case of the BNBK ternary system, the morphotropic phase boundary region is complex and therefore, only few conclusive works can be found in literature [4,13]. The first MPB region for this system was proposed by Takenaka et al. [12–14] in 2003. The authors proposed the MPB region as the intersection

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between four compositions of the $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xBi_{0.5}K_{0.5}TiO_3$ (BNKTx) and $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xBaTiO_3$ (BNBTx) binary systems. Most recently, in 2012, Trelcat et al. using the Rietveld refinement of X-ray diffraction experimental data for four binary compositions of BNKT (similar to those studied by Takenaka [12–14]) and other three ternary BNBK compositions, proposed a MPB region for the BNBK system [16] wider than that proposed by Takenaka and coauthors. The two works, mentioned above, are the main contributions to the knowledgement about the MPB region in the BNBK system and they are still controversial. Like this, further elucidations about the actual MPB region for the BNBK system are necessary.

Taking into consideration the aforementioned, the aim of this work was to carry out a detailed study of the crystalline structure and the phase evolution as a function of the concentration of K^+ and Ba^{2+} ions in the BNBK ternary system, by using X-ray diffraction measurements and Raman spectroscopy.

2. Experimental procedure

In order to choose the materials to be studied in this work, two initial compositions (from literature) of BNBK with high piezoelectric and dielectric constants (0.852BNT-0.11BKT-0.038BT and 0.862BNT-0.1025BKT-0.035BT) [17,18] were represented at the phase diagram of this system and the line joining these compositions was used to generate the five chosen compositions in this work, which cross the MPB region proposed by Takenaka [12–14], and the other proposed by Trelcat [16], following the nominal formula:

$$xBi_{0.5}Na_{0.5}TiO_3 - 0.72(1-x)Bi_{0.5}K_{0.5}TiO_3 - 0.28(1-x)BaTiO_3 \quad (1)$$

with $x = 0.82$, 0.86, 0.88, 0.91 and 0.93 mol% (labeled BNBK100x). Fig. 1 shows a ternary phase diagram of the BNBK system, highlighting the studied compositions in this work, and the proposed MPB regions by Takenaka and by Trelcat [12,16].

The ceramic powders were synthesized by solid state reaction using precursors with purity higher than 99.8% ($BaCO_3$, Na_2CO_3, Bi_2O_3, TiO_2 and K_2CO_3), which were weighed according to the nominal composition designed by equation (1) and then mixed in a ball mill using isopropyl alcohol and Y_2O_3-stabilized zirconia as liquid and grinding media, respectively, for 24 h. The mixed powders were calcined at 850 °C for 3 h and milled for 24 h in order to obtain a homogeneous particle size distribution. At the sequence, they were uniaxially pressed at 150 MPa into a cylinder mold, isostatically pressed at 220 MPa, and conventionally sintered at 1150 °C for 2 h.

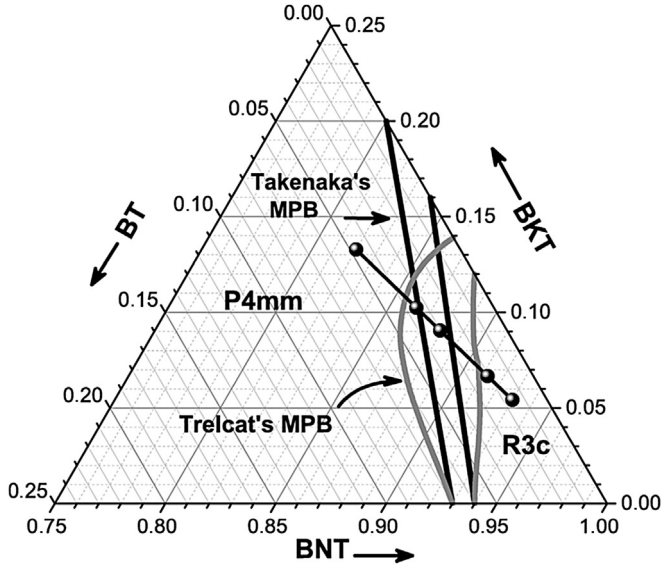

Fig. 1. Phase diagram of the BNBK system with the proposed MPB regions by Takenaka, and by Trelcat. The spheres represent the studied compositions in this work.

The resulting ceramic samples were cut in different geometries and sizes and then, annealed at 600 °C for 1 h.

The microstructure was investigated by scanning electron microscopy (SEM) using a microscopy (JSM 5800 LV, JEOL) in the secondary electron imaging mode (SEI). BNBK100x samples employed to SEM analysis were mechanically polished using abrasive paper (silicon carbide) with successively finer grades of and then thermally etched in air at 1050 °C for 2 min.

The samples density was determined by the Archimedes method, using a precision balance (AUW220D, Shimadzu) and distillate water as liquid media.

X-ray diffraction (XRD) patterns were measured at room temperature, between 10° and 90°, using a diffractometer (XRD-6000 Shimadzu) operating at 40 kV and 30 mA with CuKα radiation. The analysis of the XRD patterns was carried out using the Rietveld refinement method with the graphical user interface (EXPGUI, 2001) for GSAS [19,20].

Raman spectroscopy measurements were performed using a Raman spectrometer (T64000, Jobin Yvon) with resolution of 1 cm^{-1}. The line of 514.5 nm of an Ar^+ laser was used as excitation source. The Raman spectra evolution between 30 cm^{-1} and 730 cm^{-1} was analyzed by considering the Raman peaks as Lorentzian functions, related to active Raman modes theoretically predicted for the crystalline structure [21].

Molecular weight, phase fraction and lattice parameters obtained by Rietveld refinement method and apparent density were used to compute the relative density for all the samples.

3. Results and discussion

Values of apparent and relative densities of the BNBK100x ceramics are listed in Table 1. All the samples showed a relative density higher than 95%, which denotes the effectiveness of the used preparation parameters to obtain high quality samples.

Fig. 2 shows the SEM micrographs for all BNBK100x samples. The ceramics showed microstructures with low porosity levels which is in line with the high relative density of these materials. Also, the increase of the K^+ and Ba^{2+} ions (decrease of x in the nominal formula) induces a decreasing of the grain size in similar way as reported in literature [15,22–24].

XRD patterns of the BNBK100x samples are illustrated in Fig. 3. All the patterns can be identified as perovskite-type structure without spurious phases, suggesting the K^+ and Ba^{2+} ions have fully incorporated into the BNBK lattices. The diffraction peaks shifts towards smaller angles when the K^+ and Ba^{2+} content is increased have been associated with the ionic radius of K^+ ($\gamma = 0.133\ nm$) and Ba^{2+} ($\gamma = 0.136\ nm$) ions which are larger than those of Na^+

Table 1
Apparent and relative densities for the BNBK100x ceramics studied in this work.

Sample	Apparent density (g/cm^3)	Relative density (%)
BNBK93	5.862	98.8
BNBK91	5.793	97.6
BNBK88	5.798	97.0
BNBK86	5.781	97.2
BNBK82	5.678	95.6