

NEW METHODOLOGIES FOR THE IDENTIFICATION OF THE MORPHOTROPIC PHASE OF BOUNDARY REGION IN THE (BINA)TiO₃–BaTiO₃ LEAD FREE PIEZOCERAMICS

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Abstract:

On ferroelectric materials, the piezoelectric activity is enhanced near the so-called morphotropic phase boundary (MPB) separating the rhombohedral and tetragonal phases in the binary phase diagram. Here, we report the identification of the morphotropic phase boundary (MPB) region in the $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – $x\text{BaTiO}_3$ (BNT-BT) ceramic system by Confocal Raman Microscopy (CRM), emphasizing on the relationships between structure and piezoelectric properties. CRM results reveal the presence of the morphotropic phase boundary, between rhombohedral and tetragonal structures when BT concentration is close to 0.06-0.07. Raman spectroscopy can be used to rapidly identify the MPB on ferroelectric ceramics as seen in our model system (BNT-BT-based ceramics), since Raman spectra can be taken in few seconds, being then a very useful technique for material testing on industrial processes. Specifically, the methodology here showed represents an interesting way to correlate the micro and nanostructure with the properties in lead-free piezoceramics, which are controlled in part by the distribution of their different crystal phases. We believe that our results can benefit the understanding of BNT-BT ceramics expanding its applications range.

Keywords: Piezoelectric properties, Raman spectroscopy, Lead-free piezoelectric.

1. Introduction

The solid solutions close to the morphotropic phase transition (MPB) region, which is

characterized by the coexistence of different structural phases for the same material composition, are known to exhibit high ferroelectric properties such as dielectric permittivity, piezoelectric constant, and electromechanical coupling factors [1–3]. Consequently, lead titanate-zirconate ceramics ($\text{Pb}(\text{Ti,Zr})\text{O}_3$ - PZT), which are the most widely used piezoelectric ceramics, are formulated near the MPB region to optimize the ferroelectric properties [4,5]. However, due to the toxicity of lead, a wide range of regulations concerning environmental preservation are increasingly being introduced [6,7]. PZT ceramics are still allowed because of the lack of an adequate alternative. Therefore, research for the development of lead-free materials with properties

comparable to that of PZT has been in progress for the last few years [8]. In lead free ceramic systems, bismuth-based material can potentially replace lead-based piezoelectric materials because of the presence of stereo-chemically active lone pair electrons [9] of Bi. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) pure ceramic exhibits much weaker piezoelectric properties as compared to PZT ceramics [10,11]. To circumvent these problems, various types of compounds were added into BNT system to form solid solutions. In recent years, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - BaTiO_3 (BNT-BT) solid solutions have received considerable attention, mainly by its interesting electromechanical properties at the morphotropic phase boundary [12,13]. The presence of MPB in different BNT-BT solutions has been reported [1,14–16], and it has been considered as one of the principal candidates for replacing of PZT. However, a necessary condition for successful synthesis of high performing materials lies in the knowledge of their physical properties [17–22], especially the peculiarities accompanying the phase transitions in BNT-based systems which are not fully understood.

The Raman spectroscopy is a very sensitive tool to study at a local scale the structural deformations of perovskites, which are induced both by the tilting of BO_6 octahedra and by the

cationic displacements, as it was well known for piezoelectrics, such as PZT, and PMN-PT systems and lead-free KNN modified ceramics [23-30] In this work, we have used a $(1-x)\text{Bi}_0.5\text{Na}_0.5\text{TiO}_3-x\text{BaTiO}_3$ ($(1-x)\text{BNT}-x\text{BT}$) based lead-free piezoelectric as a model system to investigate the evolution of the phases involved around a MPB region using Confocal Raman Microscope. For that [31-37], X-ray diffraction (XRD) and Confocal Raman Microscopy (CRM) measurements are performed in a wide range of compositions in order to determine the crystallographic evolution of the material. Further, the high sensitivity of CRM to subtle changes in the crystal symmetry allow to spatially detect the phase distribution closed to MPB in the system, providing a complementary tool to XRD for unraveling the presence of phase's coexistence. Specifically [38-45], the results indicate that the piezoelectric properties are governed by the stabilization of a Rhombohedral–Tetragonal (R-T) phase boundary close to room temperature which is controlled in part by the distribution of their different crystal phases.

2. Experimental details

Sample preparation:

The BNT- BT ceramic samples with composition $(1-x) (\text{Bi}_0.5\text{Na}_0.5\text{TiO}_3) - x (\text{BaTiO}_3)$ ($x = 0.04, 0.06, 0.07, 0.08, 0.09$) were synthesized through solid state reaction. For the synthesis of BNT, Bi_2O_3 (Aldrich 99.9%), Na_2CO_3 (Biopack 99.5%), TiO_2 (Aldrich 99%) were used. Powders were mixed and milled using zirconia balls in an alcoholic medium in a planetary mill for 3 h (Fritsch, Pulverisette 7, 1450rpm). Powders were dried and calcined at 750°C for 2h. For the synthesis of BT BaCO_3 , (Biopack 99.5%), TiO_2 (Aldrich 99%) were used [46-50]. Powders were mixed and milled for 3h, and then dried and calcined at 900°C for 2h. For each

composition, the BNT and BT resulting powders were mixed again in a planetary mill, pressed into disks and sintered at 1150°C for 2h.

X-ray Diffraction (XRD):

Crystalline phases were characterized by X-ray diffraction (XRD) (PANalytical, X'pert Pro) The patterns were recorded over the angular range 20–80° (2 θ) with a step size of 0.0334° and a time per step of 100 seconds, using CuK α radiation (λ = 0.154056 nm) with working voltage and current of 40 kV and 40 mA, respectively. Peaks positions were fitted assuming a Gaussian peak shape.

Electron Microscopy:

Microstructures were evaluated using a Field Emission Scanning Electron Microscope, FE-SEM (Hitachi S-4700) equipped with energy dispersive spectroscopy, EDS. Density values were determined using the Archimedes method. Confocal Raman Microscope (CRM): The Raman scattering analyses were carried out under an air atmosphere and at room temperature. The experiments were performed using a Confocal Raman Microscope coupled to an AFM (Witec alpha-300R). Raman spectra were obtained using a 532-nm excitation laser and a 100x objective lens (NA = 0.9). The incident laser power was 0.5 mW. The optical diffraction resolution of the

Confocal Microscope was limited to about ~200 nm laterally and ~500 nm vertically. Raman spectral resolution of the system was down to 0.02 cm⁻¹. Samples were deposited on a

microscopy glass slide and mounted on a piezo-driven scan platform having 4 nm lateral and 0.5 nm vertical positioning accuracy.

Conclusions :

A $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$ (BNT-BT) system based material is used as a model to evaluate the phase's coexistence relevance to the material properties in a morphotropic phase boundary (MPB) by Confocal Raman Microscopy (CRM). Further, the high resolution of CRM to identify the phase distribution around to MPB region allow detected subtle changes in the crystal symmetry, providing a complementary tool to XRD to resolve the presence of phase's coexistence. Under the synthesis conditions (that is solid-state reaction), it is shown that the stabilization of the MBP region is located in the compositional range between $x = 0.06$ and 0.07 . CRM analyses allow to determinate that two overlapping modes associated with the vibrations of the TiO_6 octahedral in the frequency range between 450 and 650 cm^{-1} show a change in the Raman intensities of the both modes as the composition increase. The study of the phases location involved in MPB region using Raman imaging reveals a relationship between the phase transition at room temperature and the functional properties, which is attributed to the appearance of a high degree of polarization directions close to phase's coexistence (that is, the coexistence between a tetragonal symmetry, T, and a rhombohedral symmetry, R).

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