

# MORPHOTROPIC PHASE BOUNDARY IN $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-BaTiO}_3$ LEAD FREE SYSTEM: XRD AND RAMAN SPECTROSCOPY STUDIES

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*In this paper, we report a raman spectroscopy and X-ray diffraction investigations on lead-free  $(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-xBaTiO}_3$  (NBT-BT) solid solution ceramics over a composition range of  $0 \leq x \leq 0.10$  at room temperature. The Raman curves were fitted to the individual Raman peaks. The obtained peaks were analyzed by observing the changes in their respective peak positions and intensities with increasing of  $\text{BaTiO}_3$ . In light of the obtained observations, it is suggested that a MPB of rhombohedral and tetragonal phases of the studied system lies at the composition of  $x = 0.065$ . Further support for the obtained MPB was drawn from X-ray diffraction measurements.*

## INTRODUCTION

Piezoelectric are materials that generate a voltage in response to a mechanical strain (and vice versa). The most useful piezoelectric materials display a transition region in their composition phase diagrams, known as a morphotropic phase boundary [1-2], where the crystal structure changes abruptly and the electromechanical properties are maximal. Originally the term 'morphotropic' referred to phase transitions due to changes in composition, but it has come to be used mainly for the common 'morphotropic phase boundaries' (MPB) that separate regions of tetragonal symmetry from those of rhombohedral symmetry by varying the composition in ferroelectrics [3].

For the last few decades, lead zirconate titanate  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) ceramics have been the material of choice for actuator, sensor, and transducer applications, because the piezoelectric activity is enhanced near the so-called morphotropic phase boundary (MPB) in the binary phase diagram at  $x = 0.48$  [4-5]. However, environmental issues call for the use of nonhazardous substances for device fabrication. Consequently, many researches are today carried out to develop lead-free solid solution exhibiting an MPB. Research activities have mainly been focused on  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  -based solid solutions [6-11]. Among these solid solutions,  $(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-xBaTiO}_3$  (NBT-xBT) system

exhibits excellent piezoelectric properties at the rhombohedral-tetragonal MPB [6]. It was anticipated that the structure of solid solution with a low  $\text{BaTiO}_3$  (BT) content would become tetragonal due to the rather large lattice distortion of BT compared to the rhombohedral distortion in NBT. Although this structural modification was confirmed in previous works, the exact composition of MPB remains unclear [6], [12-15].

Takenaka et al. studied the NBT-BT lead free system and found the MPB around the composition  $x = 0.06 - 0.07$  [6]. Chen et al suggest that a MPB of rhombohedral and tetragonal phases resides at  $0.06 < x < 0.10$ , whereas Parija et al. observed the MPB at  $x = 0.07$  on their studies on NBT-BT system [12-13]. For NBT-BT single crystals, Hosono et al. reported maximum dielectric and piezoelectric constants in the composition range of  $x = 0.05 - 0.09$  [14]. Pengpat et al. estimated the MPB at  $x = 0.10$  in their work on the NBT-xBT [15]. A number of investigations were carried out on the NBT-BT system near MPB compositions; however, exact and exclusive studies concerning the MPB were not found in the literature.

In this work, we present a study based on X-ray diffraction and Raman spectroscopy investigations of the room temperature phase in NBT-xBT lead-free solid solution with special emphasis focused on searching the morphotropic phase boundary (MPB).

## EXPERIMENTAL

A conventional powder solid-state reaction method was used to prepare the samples: weighted powder of  $\text{Na}_2\text{CO}_3$ ,  $\text{BaCO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  (at least of 99 % purity) were ball-milled by planetary milling in ethanol for 1 h. After calcining at  $825^\circ\text{C}$  for 4 h in air atmosphere, the powder was ball-milled again and then isostatically pressed. The compacted samples were sintered at  $1200^\circ\text{C}$  for 4 h in air atmosphere. The as-prepared samples were cut into disks of 12 mm in diameter and 1 mm in thickness. The crystal structures of sintered ceramics were determined by means of a X-ray diffractometer (RIGAKU Miniflex) using  $\text{Cu K}\alpha$  radiation. Raman scattering experiments were performed using a micro Raman spectrometer (LABRAM, HR800), working in a back scattering configuration, equipped with a  $\text{He}^+$  ion ( $\lambda = 633 \text{ nm}$ ) laser. The spectral resolution of the system was  $3 \text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

## Raman study

BNT is the classic example of a rhombohedral ferroelectric material at ambient temperature and belongs to the space group  $R3c$ . The irreducible representation of optical phonons in this phase is  $\Gamma_{\text{opt}} = 4A_1 + 5A_2 + 9E$ , where the  $A_1$  and  $E$  modes are both Raman and infrared active, whereas the  $A_2$  mode is inactive both in Raman and infrared [16]. Figure 1 represents the Raman spectra of  $(1-x)\text{NBT}-x\text{BT}$  ceramics for compositions ( $x = 0, 0.03, 0.05, 0.065, 0.07, 0.08$  and  $0.10$ ) at room temperature performed in the range from 100 to  $1000 \text{ cm}^{-1}$ . The deconvolution of the spectrum of pure NBT with LabSpec 5 software using the pseudo-Voigt function, shows six vibration modes observed at 130, 276, 521, 590, 784 and  $855 \text{ cm}^{-1}$  (Figure 2).

These results are in good agreement with those reported by Petzelt et al. [16] and Siny et al. [17]. The first mode at  $130 \text{ cm}^{-1}$  was attributed to the Na-O bonds of the A-site vibration in the perovskite of general formula  $\text{ABO}_3$ . The second situated at  $276 \text{ cm}^{-1}$  is associated with the vibration of the  $\text{TiO}_6$  group and is observed in many perovskite materials [18, 19]. Modes observed at  $521 \text{ cm}^{-1}$  and  $590 \text{ cm}^{-1}$  are dominated by vibrations involving mainly oxygen displacements. The two latest modes (i.e. at  $784 \text{ cm}^{-1}$  and  $855 \text{ cm}^{-1}$ ) can be correlated to the presence of oxygen vacancies [20, 21].

When  $\text{Ba}^{2+}$  is introduced in the NBT structure, remarkable changes are observed in the Raman spectra. The overall evolution of the frequency and intensity of individual modes mentioned with BT addition are plotted in Figure 3.

The first mode (i.e. at  $130 \text{ cm}^{-1}$ ), displays a shift to low frequencies as BT concentration increases (up to about  $106 \text{ cm}^{-1}$  for  $x = 0.10$ ). Changes in position and

shape are observed only on bands characterising the A site in BT compositions (assigned to the Na/Ba–O vibration), because vibrations involving the B site are expected to be unaffected by the substitution. The observed shift of this mode toward lower frequencies can be mainly caused by the increase in the mass of the anions in A site. However, the mode reveals a sudden drop in the frequency around the composition of  $x = 0.065$  and then remains mostly unchanged. The mode intensity undergoes a slope change around the same composition.

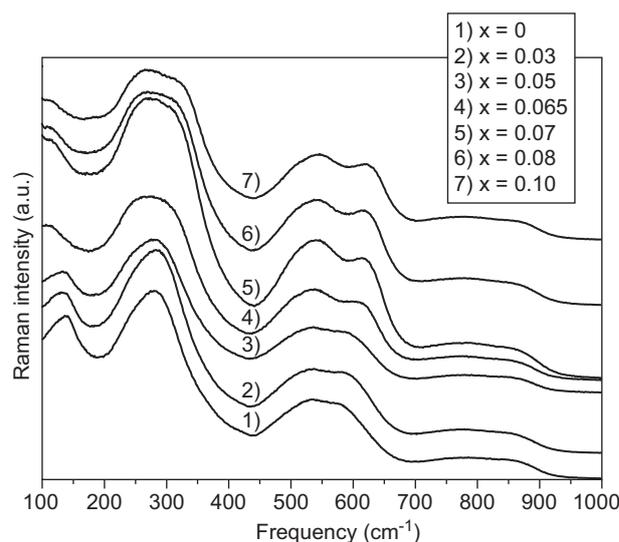


Figure 1. Raman spectra of  $(1-x)\text{NBT}-x\text{BT}$  ( $x = 0.0, 0.03, 0.05, 0.065, 0.07, 0.08$  and  $0.1$ ).

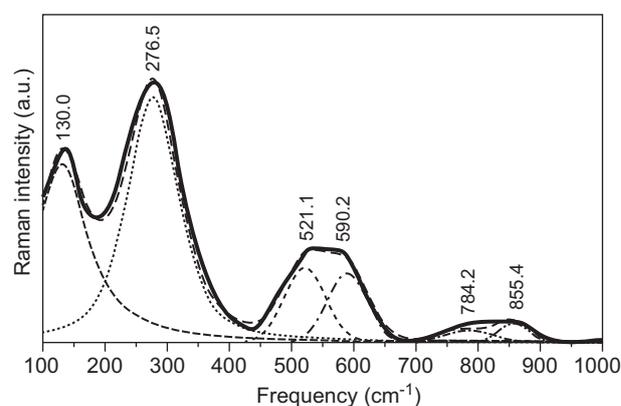


Figure 2. Fitting of the Raman spectra of NBT ceramic by the pseudo-Voigt function.

The Ti-O vibration which is located at the region from 200 to  $400 \text{ cm}^{-1}$  is characterized by the change accompanied by the arising of the additional line ( $\sim 310 \text{ cm}^{-1}$ ) for  $x \geq 0.065$  in the high frequency part of this band. The negative frequency shift and the anomaly observed for this mode suggest that this particular phonon is directly involved in the structural phase transition. The arising of the additional line ( $\sim 310 \text{ cm}^{-1}$ ) is probably connected with the appearance of tetragonal symmetry [22].

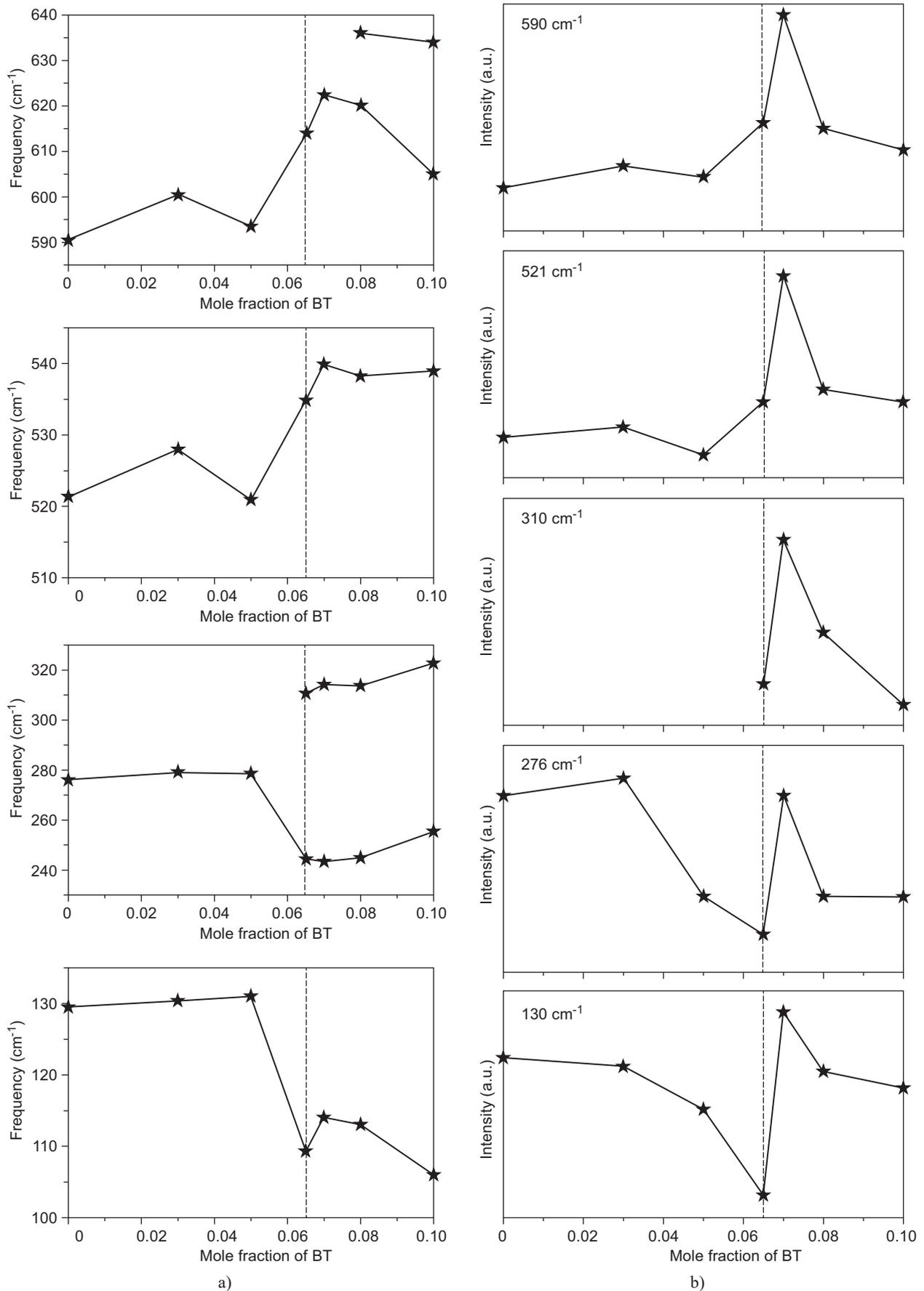


Figure 3. Evolution of: a) the peak frequency, b) the intensity of different modes in the Raman spectra with BT content.

The bands at  $521\text{ cm}^{-1}$  and  $590\text{ cm}^{-1}$  should be sensitive to the changes of structure according to the results of studies of another perovskites materials-type [24]. The high-frequency Raman bands, in the case of oxide materials, are usually caused by the vibrations resulting from the shift of oxygen [25]. For this reason one can expect, that they do not depend on the mass of the anion. There are interesting changes in these region, particularly concerning the band  $590\text{ cm}^{-1}$ ; a new band at about  $636\text{ cm}^{-1}$  appears from  $x = 0.08$  with weak intensity and then increases in intensity to  $x = 0.10$  (this peak is shown in Figure 3a, but not included in Figure 3b). This behavior is similar to the additional band at  $310\text{ cm}^{-1}$  which appears in the spectral region from 200 to  $300\text{ cm}^{-1}$  and is probably connected to the change of symmetry to the tetragonal phase.

No significant changes with composition were observed for the two deconvoluted peaks at  $784$  and  $855\text{ cm}^{-1}$  for NBT, apart from their broadening and weakening in the frequency region between  $700$  and  $900\text{ cm}^{-1}$ . Because of no significant change of these modes, there are not included in Figure 3.

The variations of frequency and the intensity of all peaks show a similar type of anomaly at a composition of  $x = 0.065$ . These anomalies observed in the Raman spectroscopy analysis let us suggest that the MPB of the NBT- $x$ BT lies at the composition of  $x = 0.065$ .

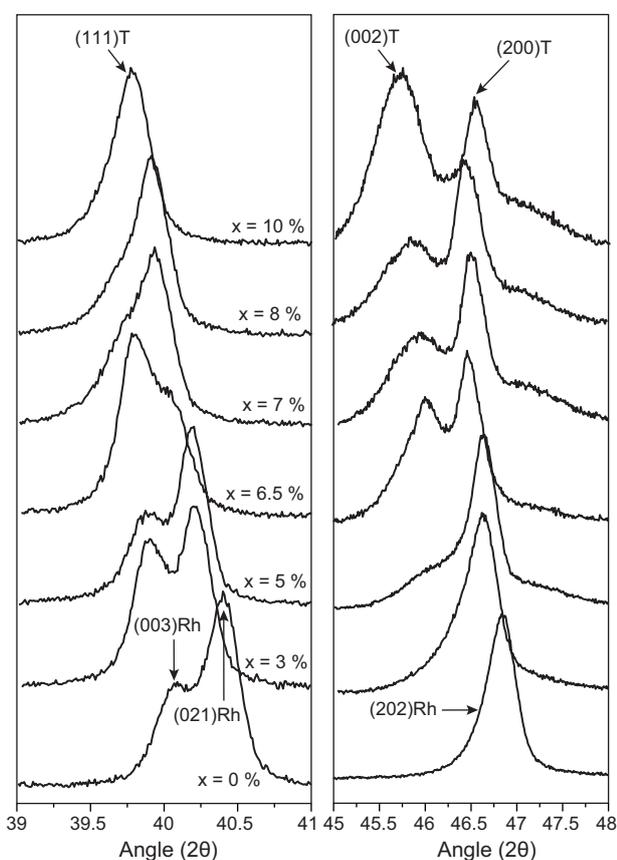


Figure 4. XRD patterns of  $(1-x)$ NBT- $x$ BT ceramics in the  $2\theta$  ranges of: a)  $39-41^\circ$  and b)  $45-48^\circ$ .

X-ray diffraction investigation was carried out on the NBT-BT system to give insight into the change in their crystal structure as the BT content increases and to verify the obtained Raman spectroscopy results. Figure 4 shows the X-ray diffraction (XRD) patterns of NBT- $(x)$ BT ceramics in the  $2\theta$  ranges of  $39-41^\circ$  and  $45-48^\circ$ , respectively. The peaks shift to a lower angles indicating an increase in the lattice parameter with an increase in the BT content. This can be explained by the larger ionic radii of  $\text{Ba}^{2+}$  compared to  $\text{Na}^+$  and  $\text{Bi}^{3+}$ . The rhombohedral symmetry is characterized by a  $(0\ 0\ 3)/(0\ 2\ 1)$  peak splitting between  $39^\circ$  and  $41^\circ$  at lower composition and the tetragonal symmetry is characterized by split in  $(2\ 0\ 2)$  peak at higher compositions, between  $45^\circ$  and  $48^\circ$ . This is a clear demonstration that the structure of the solid solution transformed from rhombohedral to tetragonal symmetry due to the large distortion caused by BT. In Figure 4a the  $(0\ 0\ 3)/(0\ 2\ 1)$  peak splitting is gradually decreases to a composition  $x = 0.065$  and, then disappears. In Figure 4b, a distinct peak splitting can be seen at  $x \geq 0.065$  and beyond, corresponding to a tetragonal symmetry above the stated composition.

The results obtained from the Raman spectroscopy and X-ray diffraction are complimentary to each other.

Therefore, in light of the present results and observations, it can be said that the MPB of the NBT- $x$ BT solid solution lies at the composition of  $x = 0.065$ . Various compositional ranges of the MPB have been reported for NBT- $(x)$ BT ceramics in the introduction. According to the theoretical model for the MPB in  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  solid solution, the MPB, is inversely proportional to the grain size of the ceramics [26]. Therefore, it is not surprising that the MPB obtained by different processing techniques are quite different. The result of this work is generally in agreement with those of previous studies.

## CONCLUSION

A systematic study based on XRD and Raman spectroscopy was carried out in the  $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $x\text{BaTiO}_3$  lead-free system. Distinct changes in the Raman spectra and X-ray diffraction patterns were discussed in the light of a rhombohedral to tetragonal phase transition. The deconvoluted modes in the Raman spectra were analyzed in terms of the wave number and intensity as the BT content increased. Remarkable changes were observed:

- The low frequency mode at  $130\text{ cm}^{-1}$  shows an anomaly at the composition of  $x = 0.065$
- The mode centered at  $276\text{ cm}^{-1}$  associated with the structural phase transition starts splitting into two at  $x = 0.065$ , which is a clear indication of a rhombohedral to tetragonal phase change.

- The appearance of a new mode for  $x = 0.08$  and  $x = 0.10$  near the band  $590\text{ cm}^{-1}$  in the region between  $440$  and  $700\text{ cm}^{-1}$ .

These features allow us to conclude that the MPB in the present system lies at the composition, of  $x = 0.065$ . This conclusion is supported by the X-ray diffraction analysis results.

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