Study of the morphotropic phase boundary in the lead-free $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{--BaTiO}_3$ system by Raman spectroscopy

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Lead-free piezoelectric $(100-x)\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{--}x\text{BaTiO}_3$ solid solution ceramics are investigated by Raman spectroscopy and X-ray diffraction over a composition range of $0 \leq x \leq 10$. Distinct changes in the Raman spectra and X-ray diffraction patterns were discussed in the light of a rhombohedral to tetragonal phase transition. The dominant bands in the Raman spectra were analyzed by observing the changes in their respective peak positions, widths and intensities as the composition increased. Based on these results, it is suggested that the morphotropic phase boundary in the studied system lies at the composition of $x \approx 5.5$. This is further evidenced by the X-ray diffraction analysis.

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Key-words : Lead-free piezoelectric, MPB, Raman spectroscopy

[Received October 20, 2008; Accepted April 16, 2009]

1. Introduction

In last few decades, the most widely used piezoelectric ceramics are lead oxide based ferroelectrics, especially $\text{Pb}(\text{ZrTi})\text{O}_3$ (PZT). PZT exhibits outstanding piezoelectric properties close to a morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases. However, in recent years, lead-free ceramics with excellent electrical properties are of great interest as environmental friendly alternatives to the lead containing piezoelectric materials. $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT) related materials have been considered as one of the promising candidates for the replacement of lead-based piezoelectric ceramics on account of their potential electromechanical properties.

The peculiar phase transition behavior of NBT has also attracted significant attention from a fundamental point of view. It undergoes transitions from a paraelectric (PE) cubic phase to a ferroelectric (FE) tetragonal phase and then to a rhombohedral relaxor ferroelectric (RFE) phase. Compared to lead-based RFEs, the diffuse phase transition in NBT is associated with global structural changes.^{1,2)} A number of studies have been carried out; however, several contradictory explanations have been reported for the interpretation of different structural and dielectric anomalies observed in each phase.²⁻⁶⁾ In the process of understanding the phase transition behavior and subsequently to improve the properties, several NBT-based solid solutions have been developed.^{4,7-9)} Among them, the $(100-x)\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{--}x\text{BaTiO}_3$ (NBT- x BT) system exhibits excellent piezoelectric properties at the rhombohedral-tetragonal MPB.³⁾ It was anticipated that the structure of the solid solution with a low 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 earlier works, the exact composition of the MPB remains unclear.^{3,10-12)}

Takenaka et al. observed relatively good piezoelectric properties

in NBT- x BT at the MPB around the composition of $x = 6\text{--}7$.³⁾ Chu et al. reported the maximum value of the piezoelectric constant and dielectric at $x = 6$ and $x = 8.3$ respectively, whereas Pengpat et al. observed the MPB at $x = 10$ in their work on the NBT- x BT system.^{10,11)} Hosono et al. reported maximum dielectric constants and piezoelectric coupling factors in the composition range of $x = 5\text{--}9$ on single crystals.¹²⁾ Chiang et al. reported an exceptionally high strain of 0.85% at 38 kV/cm on a single crystal with a composition of $x = 5.5$.⁴⁾ A number of studies have been carried out to improve the properties of NBT- x BT near the MPB compositions; however, exclusive studies concerning the MPB are rare in the literature.

Raman spectroscopy has been used as an effective technique to investigate the structural evolution in perovskite-type solid solution ceramics. However, limited reports are available on the Raman scattering studies of NBT-based systems.¹³⁻¹⁷⁾ To the best of our knowledge, Raman spectroscopy has never been used exclusively for NBT-related solid solutions to determine the MPB. The purpose of the present study is the complementary use of Raman spectroscopy and X-ray diffraction for the reinvestigation of the room temperature phase in NBT- x BT solid solution, with special attention paid to the MPB.

2. Experimental procedure

The samples were prepared from commercial powders of Na_2CO_3 (Acros Organics, New Jersey, USA), Bi_2O_3 (Kojundo Chemical Lab Co., Saitama, Japan), BaCO_3 (Sigma-Aldrich, St. Louis, USA) and TiO_2 (Sigma-Aldrich, St. Louis, USA). The conventional solid state reaction method was used to process powders of polycrystalline $(100-x)\text{NBT-}x\text{BT}$, $x = 0, 3, 5, 5.5, 6, 6.5, 8$ and 10 . Stoichiometric mixtures of high purity oxides and carbonates were ball-milled inside a polypropylene bottle using zirconia balls in ethanol medium for 24 h. The dried slurries were crushed, sieved and then calcined at 800°C for 4 h. The powders were lightly pressed into disks and cold isostatically pressed at 200 MPa. The disk samples were sintered at 1200°C for 4 h.

The crystal structure and phase purity of powders ground from

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the sintered samples were examined using a SWXD X-ray diffractometer (Rigaku Co., Japan). For the Raman spectroscopic study, the sintered pellets were polished on one side using diamond paste and then cleaned thoroughly with acetone. The samples were subsequently annealed at 400°C for 8 h to remove the residual surface stress left from polishing. Raman spectra were recorded at room temperature in back scattering geometry with a Horiba-Jobin-Yvon HR800 spectrometer equipped with a liquid N_2 -cooled back thinned charge couple device (CCD) detector. The output power of the Ar-ion laser operated at 514.5 nm was set at 2.5 mW . The results were analyzed by fitting the spectra to the Lorentzian line shape using the Jandel peak fit program.

3. Results and discussion

As mentioned earlier, NBT has rhombohedral symmetry with space group $R3c$ (C_{3v}^6) and BT has tetragonal symmetry with space group $P4mm$ (C_{4v}^1) at room temperature. As far as BT is concerned, in the tetragonal ferroelectric phase of the C_{4v}^1 point group, each of the T_{1u} modes splits into a double degenerate E mode and non-degenerate A_1 mode while the T_{2u} silent mode splits into $B_1 + E$ modes. All the A_1 and E modes are Raman and infrared active and the B_1 mode is only Raman active. Furthermore, the existence of long-range electrostatic forces in the tetragonal ferroelectric phase splits each of the A_1 and E modes into longitudinal and transverse modes. However, in the present case most of the analysis has been done with respect to the rhombohedral symmetry of NBT. As per the Group theory analysis, NBT (rhombohedral, $R3c$) should show 13 Raman active modes; in irreducible representation $\Gamma_{\text{Raman}} = 7 A_1 + 6 E$.¹⁵⁾

Before discussing the spectral changes in detail, it is useful to inspect the spectra of the end compositions of the present study. **Figure 1(a)** shows the Raman spectra of the NBT and NBT–10BT along with the curves fitted to the individual Raman peaks. The overall spectral signature demonstrates a relatively broad feature; which is in good agreement with previous reports. This can be attributed to the A-site disorder and the overlapping of Raman modes due to the lattice anharmonicity. Moreover, some Raman

active modes are also infrared active; thus, their frequency depends on their longitudinal and transverse character that lead to a broadening of the bands in the polycrystalline samples.

The spectra of NBT–10BT show two additional peaks at 188 (relatively weak) and 325 cm^{-1} (strong) compared to the peaks at 138 , 256 , 514 and 581 cm^{-1} observed for NBT. Moreover, the high frequency overlapping bands in the range of $450\text{--}650\text{ cm}^{-1}$ separated into two relatively prominent peaks. The features clearly demonstrate a change in the phonon behavior in the NBT– x BT solid solution. **Figure 1(b)** shows the Raman spectra in a frequency range $50\text{--}700\text{ cm}^{-1}$ for various compositions. A significant change in the spectral signature is observed at the composition $x = 5.5$, as indicated by the dotted lines in the figure. For a closer inspection, the variations of the peak frequency, FWHM and intensity of individual peaks with composition are plotted in **Fig. 2**. The mode at 138 cm^{-1} assigned to A_1 symmetry, which is associated with the Na–O vibration, shifts to a lower frequency as the Ba concentration increases.¹⁷⁾

The low frequency shift can be attributed to the larger mass of Ba compared to Na. However, the mode reveals a sudden drop in the frequency around the composition of $x = 5.5$ and then remains mostly unchanged. The mode intensity and FWHM undergo a slope change around the same composition. The broad band centered at 256 cm^{-1} is assigned to the A_1 symmetry which is dominated by a Ti–O vibration.¹⁵⁾ The mode shows an anomaly at $x = 5.5$ and starts splitting into two bands that shift apart from each other with a further increase in x . At a higher composition the band appears to split into three peaks (the third peak is indicated by the arrow in **Fig. 1(b)** but is not included in **Fig. 2**). Similar observations are found in BaTiO_3 and PbTiO_3 compounds in earlier reports.^{18),19)} 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 two overlapping bands associated with the vibration of the TiO_6 octahedra in the frequency range of $450\text{--}650\text{ cm}^{-1}$ show a hard mode type behavior as the composition increases. However, the spectral signature of the bands show a change at a composition of $x = 5.5$ and then separate into two distinct bands at higher compositions.^{14),15)} The variations of the intensity and the FWHM of all peaks show a similar type of anomaly at a composition of $x \approx 5.5$. Therefore, it can be suggested that the MPB of the NBT– x BT in the present investigation lies at the composition of $x = 5.5$.

The NBT– x BT samples were further investigated by X-ray diffraction to give insight into the change in their crystal structure as the BT content increases and to provide subsequent verification of the Raman scattering results. The variations of the $\{100\}$, $\{111\}$ and $\{200\}$ peaks with the composition are shown separately in **Fig. 3**. The shift of the peaks to a lower angle indicates an increase in the lattice parameter with an increase in the BT content. This can be explained by the higher ionic radii of Ba^{2+} compared to Na^+ and Bi^{3+} . The pattern reveals the characteristic rhombohedral split in the $\{111\}$ peak at lower compositions and a tetragonal split in the $\{200\}$ peak at higher compositions. 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. The split in the $\{111\}$ peak gradually decreases to a composition of $x = 5.5$ and, then disappears. However, significant broadening is observed at $x = 5.5$. The broadening of the peaks decreases at $x \geq 5.5$. Conversely, a clear tetragonal split can be observed in $\{100\}$ and $\{200\}$ at $x \geq 5.5$ which indicates that the symmetry should be tetragonal above the stated composition.

Fig. 1. (a) Raman spectra of NBT and NBT–10BT. The grey lines are the experimental data and the solid lines are the fitting curves, (b) Raman spectra of 1) $x = 0.0$, 2) $x = 0.03$, 3) $x = 0.05$, 4) $x = 0.055$, 5) $x = 0.06$, 6) $x = 0.065$, 7) $x = 0.08$ and 8) $x = 0.1$.

Fig. 2. Variations of (a) the peak frequency, (b) FWHM, (c) the intensity of different modes in the Raman spectra with composition.

Fig. 3. Variation of (a) {100}, (b) {111} and (c) {200} reflections in XRD patterns of NBT-xBT: 1) $x = 0$, 2) $x = 3$, 3) $x = 5$, 4) $x = 5.5$, 5) $x = 6.5$, 6) $x = 8$ and 7) $x = 10$.

The results obtained from the Raman spectroscopy and X-ray diffraction are complimentary to each other. Therefore, in light of the present observations, it can be said that the MPB of the NBT-xBT solid solution lies at the composition of $x \approx 5.5$. The MPB compositions determined for this system using different experimental techniques by various other groups are mentioned in the introduction. Referring to the previously reported results, it is found that our results are in good agreement with the work of Chiang et al. ($x = 5.5$)⁴ and are very close to the results reported by Takenaka et al. ($x = 6-7$)³ and Hosono et al. ($x = 5-9$).¹² Nevertheless, Chu et al. reported higher values of piezoelectric properties at $x = 6$ ¹⁰ and Pengpat et al. observed the MPB at $x = 10$.¹¹

The discrepancies observed in determining the exact MPB composition of the NBT-BT solid solution system between our results and those previously reported may be related to different preparation methods or processing parameters employed by different groups. For example, Chiang et al. used single crystals of NBT-BT samples, whereas Takenaka et al.³ and Hosono et al.⁴ used ceramic samples prepared by the conventional method at different sintering temperatures. Moreover, Pengpat et al.¹¹ added 1.7% of La^{3+} at the A-site and Chu et al.¹⁰ used Nb_2O_5 and Co_2O_3 as additives for some selected compositions during the preparation of NBT-BT samples.

4. Conclusion

The rhombohedral-tetragonal morphotropic phase boundary in NBT-xBT solid solution ceramics was investigated by Raman spectroscopy in this study. The characteristic bands in the Raman spectra were analyzed in terms of the wave number, intensity and FWHM as the BT concentration increased. The low frequency mode at 138 cm^{-1} shows an anomaly at the composition of $x = 5.5$. The mode centered at 256 cm^{-1} associated with the structural phase transition starts splitting into two at $x = 5.5$ and later splits into three peaks, which is a clear demonstration of a rhombohedral to tetragonal phase change. The high frequency overlapping mode shows a hard mode like behavior. It also shows an anomaly at the same composition, of $x = 5.5$. These features allow us to propose that the MPB in the present system lies at the composition, of $x \approx 5.5$. This phenomenon is further verified thorough X-ray diffraction by a thorough inspection of the variations of the structure sensitive Bragg peaks of {111} and {200}.

Acknowledgement This research was supported by a grant from the Center for Advanced Materials Processing (CAMP) of the 21st Century Frontier R&D Program funded by the Ministry of Knowledge Economy (MKE), Republic of Korea under Grant No. PM007-8-01-01, and also by a Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-005-J09701).

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