Theoretical predictions of morphotropic phase boundary in \((1-x)\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3-x\text{BaTiO}_3\) by first-principle calculations

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Abstract A morphotropic phase boundary (MPB) in a solid solution of \((1-x)\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3-x\text{BaTiO}_3\) \((0 \leq x \leq 1.0)\) (NBT-BT) is directly demonstrated by first-principle calculations. The results show that in the NBT-BT system, a structural transition from rhombohedral to tetragonal occurs when \(x\) is changed from 0.06 to 0.12, and the MPB appears at compositions of around 0.05 \(\leq x \leq 0.07\). It can be verified by the stronger hybridization orbital of p-d based on the analysis of the partial density of states (PDOS) in the Ti–O atoms. The theoretical predictions agree well with experimental observations which indicate that the best ferroelectric properties can be attained in the vicinity of around 0.05 \(\leq x \leq 0.07\) in the MPB of the NBT-BT system. Another tetragonal-cubic phase transition which needs further experimental verification is also found from the system with compositions of 0.475 \(< x < 0.65\).

1 Introduction

Environmental friendly \(\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\) (NBT) and related materials which possess outstanding piezoelectric properties close to the morphotropic phase boundary similar to the PZT systems [1, 2] are promising substitutes for lead-based piezoelectric ceramics on account of their potential electromechanical properties [3]. It is well known that the best ferroelectric materials for piezoelectric applications are solid solutions with compositions in the vicinity of the morphotropic phase boundary (MPB) [4] where the crystal structure changes abruptly, and the electromechanical properties are optimal [5]. Consequently, it is necessary to investigate the MPB of the NBT-based solid solutions such as the dual system of \((1-x)\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3-x\text{BaTiO}_3\) (NBT-BT), which can reduce costs greatly and expand the utility of piezoelectric materials. A number of studies [3, 6, 7] have in fact been carried out to improve the properties of NBT-BT near the MPB compositions. Several studies have been conducted by using X-ray diffraction, dielectric measurements, and Raman spectroscopy, and the MPB is suggested to be between \(x = 0.055\) to 0.07 [3, 8]. However, few theoretical investigations have hitherto been performed on the MPB in the NBT-BT system. First-principle methods based on the density functional theory (DFT) have emerged to be a powerful tool in investigating the properties of ferroelectric system theoretically [9, 10], and in this letter, we theoretically confirm the existence of the MPB in the NBT-BT system to establish the theoretical framework to explain and corroborate the experimental observations [8, 11].

2 Computational model

The first-principle calculations are conducted using plane-wave pseudopotential method and density functional theory (DFT) [3, 12]. Since the virtual crystal approximation (VCA) [13] has been successfully applied to a number of materials from semiconductor alloys to perovskite...
solid solutions such as PZT [14], BST [15], or PSN [16] and LNTO [10], we have also adopted the VCA to simplify the structural model as shown in Fig. 1. In our calculations, we use the CASTEP computer code [17]. The generalized gradient approximation [18] (GGA) is used with the ultra-soft pseudopotential [19], and a plane-wave cutoff energy of 380 eV is adopted. The first Brillouin zone (FBZ) is sampled with a \( k \)-point mesh corresponding to (6, 6, 6) in the FBZ of the five-atom unit cell for the self-consistent calculation of the total energy and for the calculation of density of states. To check the accuracy of our results, we have increased the energy cutoff from 380 to 500 eV and increased the number of \( k \) points from (6, 6, 6) to (8, 8, 8). In the geometry relaxation, the total energy of the system was converged \(< 1 \times 10^{-4} \text{ eV} \), the displacement of atoms \(< 1 \times 10^{-3} \text{ Å} \), and the residual bulk stress \(< 0.05 \text{ GPa} \). The atomic positions have been relaxed until the maximum component of the force on any atom is smaller than 0.03 eV/Å.

3 Results and discussion

The original structure of the trigonal phase is optimized by calculation, and the lattice constant of NBT \((x = 0)\) is only 2.8% bigger than the experimental value [9]. The change in the lattice parameters with different compositions of BT in NBT-BT is calculated at first. As shown in the inset of Fig. 2, there are two distinct peaks in the curve when \(x\) is changed from 0 to 1. For the peak of \(x = 0.125\) in Fig. 2 which shows the composition range of \(0 < x < 0.125\), the volume (or lattice constant) increases monotonically with \(x\), which is related to the ion radius of \(\text{Ba}^{2+}\) of 0.135 nm [larger than the average radius \((0.0955 \text{ nm})\) of A-site ions \((\text{Na}^+ 0.095 \text{ nm}, \text{Bi}^{3+} 0.096 \text{ nm})\)]. The structure shows the tetragonal phase completely in the composition range of \(x > 0.125\). It is probably a consequence of phase transition (it has already be confirmed that the first peak is

\[
\Delta H = E_{\text{NBT-BT}} - xE_{\text{BT}} - (1 - x)E_{\text{NBT}},
\]

where \(E_{\text{NBT-BT}}, E_{\text{BT}},\) and \(E_{\text{NBT}}\) are the total energies of the relaxed systems NBT-BT, BT, and NBT, respectively.
In order to further support our conclusions of MPB at $0.05 < x < 0.07$, the structural properties of the tetragonal (P4mm) and cube (Pm3m) phases are also calculated by the same method as that of the rhombohedral (R3c/R3m) phases. It is clear in Fig. 4 that, when $x < 0.05$, the pseudocubic (rhombohedral) is the optimal structure; the total energy of rhombohedral structure is close to that of the tetragonal phase at $0.05 < x < 0.08$, and it may indicate that two phases coexist in MPB; the energy discrepancy between the rhombohedral and tetragonal phase structure is more obvious at $0.07 < x < 0.10$, while the rhombohedral structure is more stable (Minimum Energy); the tetragonal phase structure is in the highest flight when $x > 0.12$. These calculations further validate the previous analysis of MPB.

In order to further clarify the micro-mechanism of MPB, we plot the partial density of states (PDOS) of the Ti 3d and O 2p orbitals for the various $x$ values in the $(1 - x)$NBT-$x$BT system. As shown in Fig. 5, the O 2p and Ti 3d orbital electrons in the vicinity of the Fermi level move to the Fermi level for $x = 0, 0.05, 0.07$, and 0.15. The hybridization of the Ti 3d and O 2p states is weak, and these states mostly determine the nature of the available states around the Fermi level at which the Ti–O octahedral state gives rise to the regular octahedron at $x = 0$ [9]. The Ti–O band rises near the Fermi level as $x$ increases, and when $x = 0.15$, the LDOS of the O 2p state is clearly different from those in other compositions. This means that the configuration when $x = 0.15$ is composed of the tetragonal phase.

At an energy of about −3.0 eV, a resonant peak emerges from samples with $x = 0.05$ and 0.07. Hybridization of the Ti 3d and O 2p states is much greater at the composition around 5%–7% compared with other compositions. It forms the so-called p-d hybridization orbital. As a result of the p-d hybridization orbital, the Ti–O octahedral is tilted, and this is similar to that reported by Frantti [4]. A large hybridization orbital of p-d is one of the factors forming the MPB in piezoelectric perovskites. In addition, because of the difference in the A-site cations for various $x$ values, the relative position between the B-site (Ti) cation and O anions around the B-site has changed. Hence, displacement of the Ti cation occurs along the c-axis relative to the site of O ions, consequently increasing the TiO$_6$-octahedra distortion and producing a separation of core valence charge in the c-axis crystal direction. An electric dipole moment reflecting the characteristics of the excellent ferroelectric tetragonal phase is produced. At compositions of around 5%–7%, the O 2p and Ti 3d states represent stronger p-d hybridization, and it reduces the short-range repulsive force between the atoms and promotes formation of the ferroelectric tetragonal phase. The calculated results are in good agreement with those produced by Cohen [22].

Our analysis reveals more interesting results. Figure 2 (inset) shows an additional peak at $x = 0.475$ and Fig. 3...
shows another peak at \( x = 0.65 \), and the region of \( 0.475 < x < 0.65 \) may be another phase transition region. The results show that the phase structures tend to transform into the cubic phase at \( x > 0.475 \) and complete transform into the cubic phase at \( x > 0.65 \). Therefore the tetragonal-to-cubic phase transition occurs in the composition range of \( 0.475 < x < 0.65 \). Although similar experimental results have been reported \[23\] showing that the tetragonal-to-cubic phase transition occurs at \( x = 0.5 \) in the NBT-BT system, direct verification requires further experiments.

4 Conclusions

In conclusion, the morphotropic phase boundary (MPB) in the solid solution \((1-x)Na_{1/2}Bi_{1/2}TiO_3-xBaTiO_3 (0 \leq x \leq 1.0) \) (NBT-BT) system is predicted based on virtual crystal approximation (VCA) by first-principle calculations. The results show that in the NBT-BT system, a phase transition from rhombohedral to tetragonal occurs when \( x \) is changed from 0.06 to 0.12, and the MPB appears for \( x \) values between 0.05 and 0.07. It arises from the stronger hybridization orbital of p-d according to the analysis of the partial density of states (PDOS) in the Ti–O atoms. Our theoretical predictions are consistent with experimental results showing that the best ferroelectric properties can be attained when the \( x \) value is between 0.05 and 0.07 in the MPB of the NBT-BT system. Moreover, it is predicted that the tetragonal-to-cubic phase transition occurs in the composition range of \( 0.475 < x < 0.65 \), but more experiments are needed for verification.

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