Atomistic origin of huge response functions at the morphotropic phase boundary of $(1 - x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $x\text{BaTiO}_3$

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The ferroelectric solid solution $(1 - x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $x\text{BaTiO}_3$ (NBT- x BT) is a promising material to substitute for the environmentally undesired Pb-based ferroelectrics. The strong enhancement of the dielectric permittivity and piezoelectric coefficients near the morphotropic phase boundary (MPB) in ferroelectric ABO_3 -type solid solutions is commonly related to the existence of a single or several long-range-ordered phases resulting in a complex nanodomain pattern. Here, NBT- x BT is studied by Raman scattering and complementary synchrotron x-ray total elastic scattering to follow the temperature evolution of the mesoscopic-scale structural transformations for x below, at, and slightly above x_{MPB} . The most remarkable result is that at $x \sim x_{\text{MPB}}$ the phonon mode involving vibrations of both off-centered A-site Bi and B-site Ti experiences strong softening and damping near the triple-point temperature in the phase diagram, in strong contrast to the compounds with $x < x_{\text{MPB}}$ or $x > x_{\text{MPB}}$. The chemically enhanced coupling between the Bi and Ti subsystems at x_{MPB} is facilitated by the subtle disturbance of the coupling processes within the Bi subsystem induced by Ba at x_{MPB} . These mesoscopic-scale structural and dynamic phenomena seem to be significant for the enhanced response functions at the MPB in NBT- x BT.

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I. INTRODUCTION

Perovskite-type (ABO_3) materials with transition elements on the B site are the best choice to produce multifunctional ferroelectrics (FEs) with tunable properties, due to the flexibility of the perovskite framework when accommodating various chemical elements on the cationic A and/or B sites. Lead-based FE solid solutions exhibit outstanding dielectric, piezoelectric, pyroelectric, and optoelectric properties, but they have become undesired for future exploration because their production and consequent waste storage are environmentally unfriendly. As a consequence, a huge amount of research is currently being dedicated to find alternatives to Pb-based systems with comparable properties. In this context, Bi-based systems have been anticipated as a suitable replacement, as A-site Bi^{3+} has a stereochemically active $6s^2$ lone pair similar to A-site Pb^{2+} . Thus, Bi-based FE solid solutions have the great potential to be used in high-performance ecologically friendly devices, which has inspired extensive structural studies of these materials in order to better understand the structure-property relations. In particular, the solid solution $(1 - x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $x\text{BaTiO}_3$ (NBT- x BT) has received much attention due to its similarities with $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ and $(1 - x)\text{PbB}'_{1/3}\text{B}''_{2/3}\text{O}_3$ - $x\text{PbTiO}_3$ in terms of the existence of morphotropic phase boundary (MPB) with weak temperature dependence and strong enhancement of the dielectric permittivity and piezoelectric response for $x \sim x_{\text{MPB}}$ [1,2]. Additionally, NBT- x BT exhibits a very rich phase diagram constructed on the basis of dielectric-permittivity anomalies and polarization hysteresis loop [1–3], which for low x and high T mismatches the observed changes in the average structure [4]. The nanodomain

structure near x_{MPB} deduced from electron diffraction has been controversially reported to be monoclinic [5] or tetragonal double-perovskite [6–8]. Furthermore, similar to $(1 - x)\text{PbB}'_{1/3}\text{B}''_{2/3}\text{O}_3$ - $x\text{PbTiO}_3$, NBT- x BT exhibits a relaxor behavior for $x \leq x_{\text{MPB}}$ [9–11], i.e. existence of nonstatic polar nanoregions with a size insufficient to be considered as long-range ordered FE domains. All this highlights the importance of ferroic coupling on the mesoscopic scale and calls for the application of nonconventional methods sensitive to the local structure and dynamics.

The considerable deviation of the short- and intermediate-range order in pure NBT from the long-range order of the average structure was demonstrated by recent x-ray absorption spectroscopy (XAS) [12] and neutron total elastic scattering (TES) [13,14]. Both methods revealed that (i) the off-centering of B-site Ti^{4+} cations is only slightly influenced by temperatures and persists in the high-temperature paraelectric phase at least up to 870 K, and (ii) the off-centering of A-site Bi^{3+} is considerably larger and less dispersed than that of A-site Na^+ cations. Neutron pair distribution function (PDF) analysis demonstrated that the B-site Ti^{4+} cations are rhombohedrally displaced at all studied temperatures between 766 and 10 K, while the A-site Bi^{3+} cations are tetrahedrally displaced at 766 K, form two distinct groups of monoclinically displaced cations between 473 and 298 K, and all are predominantly rhombohedrally off-centered at 10 K [14]. The complex temperature evolution of the off-centered Bi^{3+} displacements indicates that the Bi^{3+} coupling is the key factor for the multiple phase-transition sequence in pure NBT, and its disturbance by Ba^{2+} may be the main reason for the enhanced dielectric and piezoelectric properties at $x \sim x_{\text{MPB}}$ in NBT- x BT.

Raman spectroscopy is a method sensitive to local structural transformations and, thus, studies of the temperature dependence of phonon modes involving Bi vibrations can

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provide valuable information about the formation of the FE state near MPB in NBT- x BT. Bi^{3+} is similar to Pb^{2+} in mass and outermost electron shell and, therefore, Raman peaks generated by Bi-localized modes phonon modes (involving mainly Bi vibrations) in ABO_3 -type materials may appear near 50 cm^{-1} , like the phonon modes involving mainly Pb vibrations in Pb-based perovskite-type solid solutions [15–17] as well as like Bi-localized modes in complex bismuth oxides of other structure types [18,19]. Raman scattering near 50 cm^{-1} was indeed detected in pure NBT [20], but surprisingly, the majority of reported Raman spectroscopic studies of Bi-based perovskite-type ferroelectrics did not consider the important spectral range below 100 cm^{-1} [21–26]. Analyses on the behavior of the Raman scattering near 50 cm^{-1} in Bi-based ferroelectric solid solutions are scarce [27] and, to the best of our knowledge, no such studies were conducted on NBT-based solid solutions with variable content of Bi.

In this paper the temperature evolution of Raman-active phonon modes between 15 and 1200 cm^{-1} in three NBT- x BT compounds with $x = 0 < x_{\text{MPB}}$, $x = 0.06 \sim x_{\text{MPB}}$, and $x = 0.08 > x_{\text{MPB}}$ are comparatively analyzed to elucidate the differences between the mesoscopic-scale transformation processes at and aside from MPB. The Raman scattering data are complemented with temperature-dependent x-ray TES.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Ceramic samples of NBT- x BT were produced following the conventional solid-state synthesis route. Starting materials (Na_2CO_3 , Bi_2O_3 , TiO_2 , and BaCO_3) were first thoroughly mixed by wet ball-milling in ethanol media for about 24 h before the dried powders were heat processed. Three stages of heating with intermediate grinding were performed for each sample. Undoped NBT was first calcined at 1073 K for 6 h, then at 1273 K for 4 h, and finally sintered at 1373 K for 2.5 h. The doped samples were calcined at 1173 K for 6 h and at 1323 K for 4 h. They were finally sintered at 1423 K for 2.5 h. The chemical compositions of the sintered samples were verified by wavelength-dispersive spectroscopy (WDS) analysis, using an electron probe microanalyzer JEOL JXA-820, with an acceleration voltage of 15 kV and a probe current of 15 nA . Albite ($\text{NaAlSi}_3\text{O}_8$), rutile (TiO_2), metallic Bi, and BaO were used as standards for Na, Ti, Bi, and Ba, respectively.

B. Raman scattering

Raman spectra were collected with a Horiba Jobin-Yvon T64000 triple-grating spectrometer equipped with an Olympus BH41 microscope and a $50\times$ long-working distance objective. The measurements were conducted on plate-shaped pellets of pressed powders in a backscattering geometry. The 514.5-nm line of an Ar^+ laser (Coherent 90C FreD) with a power density on the sample surface of 1.4 kW/mm^2 was used to excite the Raman scattering. The achieved spectral resolution was approximately 2 cm^{-1} . At room temperature no polarization, orientation, or spatial dependence of the Raman spectra was detected, indicating that the average linear crystallite size is much smaller than the diameter of the laser spot on the sample

surface, which was $\sim 2\text{ }\mu\text{m}$. *In situ* temperature-dependent spectra were collected on cooling from 870 to 80 K using a Linkam THMS-E600 stage with a cooling rate of 10 K/min and a temperature accuracy of $\pm 0.1\text{ K}$. The reversibility of the observed temperature-induced structural changes was verified by measuring the room-temperature spectrum at the end of each run. The measured spectra were corrected by the Bose-Einstein phonon occupation factor to eliminate the effect of temperature on the peak intensities. The temperature-reduced spectra were then fitted with pseudo-Voigt peak-shape functions $\{PV = qL + (1 - q)G, q \in [0, 1], L \text{ and } G \text{ stand for Lorentzian and Gaussian, respectively}\}$ to determine the phonon wave numbers ω , full widths at half maximum (FWHMs), integrated intensities I normalized to the total spectrum profile areas, and the Lorentzian weight coefficients q . The choice of the peak shape function was justified by the fact that both local structural and chemical disorder are expected in solid solutions, which leads to phonon modes statistically dispersed in energy and results in a nonzero Gaussian contribution to the Raman peak shape.

C. X-ray total elastic scattering

Temperature-dependent powder diffraction data were collected on heating between 120 to 800 K at the BW5 beamline of the DORIS-III facility in Deutsches Elektronen-Synchrotron (DESY) using an incident beam energy of 100 keV ($\lambda = 0.12398\text{ }\text{\AA}$), which provided a maximum reciprocal-space Q value of $25\text{ }\text{\AA}^{-1}$. A flat panel detector (Perkin Elmer 1621) was used to record the two-dimensional (2D) powder rings. Powder samples were put in a quartz capillary of diameter $\sim 1.0\text{ mm}$ and then placed into a Linkam THMS600 cryofurnace. *In situ* 2D powder rings were collected on the fly with a temperature ramp of 2 K/min . The 2D images were integrated into typical one-dimensional (1D) powder patterns using the Fit2D software [28]. Final data corrections and Fourier transformations were performed using the PDFgetX3 software [29] to obtain the pair distribution functions.

III. RESULTS AND DISCUSSION

The temperature-reduced Raman spectra of NBT- x BT with $x = 0, 0.06$, and 0.08 collected at 80 and 870 K are shown in Fig. 1. As can be seen, all three compounds exhibit pronounced Raman scattering at 870 K , although they are all in a paraelectric state with symmetry of the average structure $Pm\bar{3}m$ [4], in which no Raman-active modes are allowed (see Table I) [30]. If the A-site Na^+ and Bi^{3+} cations form a NaCl-type chemical order, the crystallographic unit cell would double [20], and the symmetry of the paraelectric phase would be $Fm\bar{3}m$, in which one triply degenerate Raman-active mode localized in the B-site cations is allowed [20,30]. However, recent density functional theory calculations on pure NBT revealed that the most thermodynamically stable A-site cation configuration involves alternating planes of Bi and Na along one of the cubic $\langle 100 \rangle$ directions rather than 1:1 alternations of Bi and Na atoms along all $\langle 100 \rangle$ cubic directions [31], i.e. doubling of the perovskite structure due to NaCl-type chemical order is hardly plausible even on the mesoscopic scale. Therefore, we attribute the Raman

FIG. 1. (Color online) Raman spectra of NBT- x BT with $x = 0, 0.06$, and 0.08 measured at 80 and 870 K (solid black lines), the fitting pseudo-Voigt peak functions (thin lines), and the resultant spectrum profiles (dashed red lines). The blue thin lines mark the Raman peaks for which the temperature evolution is further discussed. Note that the Gaussian contribution to the shape of peaks 3, 4, and 5 was negligibly small within the entire temperature range 80–870 K.

scattering observed in the paraelectric state to local ferroic distortions, previously detected also by XAS [12] and neutron TES [13,14].

The Raman spectra measured at 870 K are essentially the same for $x = 0, 0.06$, and 0.08 , but at 80 K, the spectrum of NBT-0.08BT differs from the spectra of NBT and NBT-0.06BT in the shape of the scattering near 50, 290, and 570 cm^{-1} (see Fig. 1). To quantitatively evaluate the Raman data, we have fitted the spectrum profiles with pseudo-Voigt functions. For each compound, we first fitted the spectrum at 80 K, and the number of included peaks was chosen following the criterion that the obtained uncertainty in the intensity dI for each peak should be smaller than the corresponding intensity I . Then the same number of peaks was used as a starting model for the spectrum measured at the next higher temperature and, if for a certain peak, dI was larger than I , that peak was removed. We also tried to fit the spectra using only Lorentzians, but that yielded worse R^2 and χ^2 factors than fitting with pseudo-Voigt functions, indicating that for the majority of phonon modes, the Gaussian contribution to the peak shape due to the existence of structural and/or chemical disorder cannot be neglected. The Gaussian contribution was close to zero through the entire temperature range only for the peaks between 130–300 cm^{-1} (peaks 3–5 in Fig. 1). Such a strategy was entirely based on mathematical criteria as group-theory analysis was not very helpful because the resolved Raman peaks in the low-temperature spectra apparently mismatched the number of fundamental Raman-active modes in the possible ferroelectric phases: $R3c$, Cc , $P4bm$, for $x = 0$ [4,32,33], $R3c$, Cc , $P4bm$, $P4mm$ for $x = 0.06$ [4–8], and $P4mm$ for $x = 0.08$ [4,34]. Group-theory analysis of the phonon modes at the Brillouin-zone center of the corresponding phases is given in Table I. As can be seen in Table I, if possible two-mode behavior due to compositional disorder on the A site is neglected, the number

of expected Raman peaks in $R3c$, $P4bm$, Cc , and $P4mm$ are respectively 13, 16, 27, and 8, without taking into account the longitudinal optic (LO)–transverse optic (TO) effects, or 26, 24, 54, and 14, respectively, considering both the LO and TO components related to the polar modes. It should be underlined that the vibrational states in polar crystals that are arbitrarily oriented to the direction of the incident photon are quasi-LO and quasi-TO phonons with mixed symmetry and wave numbers depending on the angle between the phonon propagation and the crystallographic polar axis [35]. This further complicates the application of symmetry analysis to Raman spectra of polycrystalline multidomain samples. Stable fits with satisfactory dI/I could not be achieved using either of the predicted number of peaks for the range 15–950 cm^{-1} (the weak scattering near 1025 cm^{-1} labeled in Fig. 1 as peak 11 arises most probably from multiphonon scattering). Assuming two-mode behavior for the optical modes associated with A-site cations would lead to even larger number of expected peaks for $R3c$, $P4bm$, and Cc and would not influence the number of expected Raman peaks in $P4mm$ [see Table I and footnote (c)]. In fact, with the exception of the Raman scattering near 50 cm^{-1} , the low-temperature spectra of NBT, NBT-0.06BT, and NBT-0.08BT exhibit the same number of resolved peaks (see Fig. 1). The Raman peaks in the range 400–950 cm^{-1} most probably result from internal BO_6 vibrations, i.e. the corresponding phonon modes are comprised mainly of oxygen vibrations. This Raman scattering persists at elevated temperatures, indicating that the BO_6 are still ferroically deformed. The Raman scattering near 290 cm^{-1} (peaks 4 and 5 in Fig. 1) is also associated with distorted BO_6 octahedra [36], but due to the lower energy range, the generating phonon modes should considerably involve vibrations of off-centered B-site cations. The latter assumption is strongly supported by the fact that similar Raman scattering appears at lower

TABLE I. Crystal normal phonon modes in NBT-*x*BT in plausible space-symmetry groups, determined using the online available utilities on the Bilbao Crystallographic server (<http://www.cryst.ehu.es/>) [30].

Space group	Atom	Wyckoff position	Normal phonon modes at the Brillouin-zone center $\Gamma^{a,b,c}$
$Pm\bar{3}m$	Na/Bi/Ba	1b	$T_{1u}(ir)$
	Ti	1a	$T_{1u}(ir)$
	O	3d	$T_{2u}(ina) + 2T_{1u}(ir)$ $\Gamma_{\text{total}} = T_{2u}(ina) + 4T_{1u}(ir)$ $\Gamma_{\text{acoustic}} = T_{1u}$ $\Gamma_{\text{optical}} = T_{2u}(ina) + 3T_{1u}(ir)$
$R3c$	Na/Bi/Ba	2a	$A_1(r,ir) + A_2(ina) + 2E(r,ir)$
	Ti	2a	$A_1(r,ir) + A_2(ina) + 2E(r,ir)$
	O	6b	$3A_1(r,ir) + 3A_2(ina) + 6E(r,ir)$ $\Gamma_{\text{total}} = 5A_1(r,ir) + 5A_2(ina) + 10E(r,ir)$ $\Gamma_{\text{acoustic}} = A_1 + E$ $\Gamma_{\text{optical}} = 4A_1(r,ir) + 5A_2(ina) + 9E(r,ir)$
$P4bm$	Na/Bi/Ba	2b	$A_1(r,ir) + B_2(r) + 2E(r,ir)$
	Ti	2a	$A_1(r,ir) + A_2(ina) + 2E(r,ir)$
	O1	2a	$A_1(r,ir) + A_2(ina) + 2E(r,ir)$
	O2	4c	$2A_1(r,ir) + A_2(ina) + B_1(r) + 2B_2(r) + 3E(r,ir)$ $\Gamma_{\text{total}} = 5A_1(r,ir) + 3A_2(ina) + B_1(r) + 3B_2(r) + 9E(r,ir)$ $\Gamma_{\text{acoustic}} = A_1 + E$ $\Gamma_{\text{optical}} = 4A_1(r,ir) + 3A_2(ina) + B_1(r) + 3B_2(r) + 8E(r,ir)$
Cc	Na/Bi/Ba	4a	$3A'(r,ir) + 3A''(r,ir)$
	Ti	4a	$3A'(r,ir) + 3A''(r,ir)$
	O1	4a	$3A'(r,ir) + 3A''(r,ir)$
	O2	4a	$3A'(r,ir) + 3A''(r,ir)$
	O3	4a	$3A'(r,ir) + 3A''(r,ir)$ $\Gamma_{\text{total}} = 15A'(r,ir) + 15A''(r,ir)$ $\Gamma_{\text{acoustic}} = 2A'(r,ir) + A''(r,ir)$ $\Gamma_{\text{optical}} = 13A'(r,ir) + 14A''(r,ir)$
$P4mm$	Na/Bi/Ba	1a	$A_1(r,ir) + 2E(r,ir)$
	Ti	1b	$A_1(r,ir) + 2E(r,ir)$
	O1	1b	$A_1(r,ir) + 2E(r,ir)$
	O2	2c	$A_1(r,ir) + B_1(r) + 2E(r,ir)$ $\Gamma_{\text{total}} = 4A_1(r,ir) + B_1(r) + 5E(r,ir)$ $\Gamma_{\text{acoustic}} = A_1 + E$ $\Gamma_{\text{optical}} = 3A_1(r,ir) + B_1(r) + 4E(r,ir)$

^a*r*, Raman-active; *ir*, infrared-active; *ina*, inactive.^bOptical phonon modes which are simultaneously Raman and infrared active have longitudinal (LO) and transverse (TO) component and hence, they may give rise to two Raman peaks.^cAcoustic modes have a wave number approaching zero at the Γ point and therefore they are commonly attributed to the atoms with the largest mass and/or weakest bonding to the surrounding atoms, i.e., to the A-site cations in the case of NBT-*x*BT.

wave numbers in perovskite-type ferroelectrics with heavier cations on the B site, including Nb and Ta [15–17]. Thus, the persistence of the Raman peak near 290 cm^{-1} at high temperatures for all three NBT-*x*BT compounds indicates the presence of off-centered Ti even in the paraelectric state, in full accordance with previous XAS [12] and TES studies [14]. The Raman scattering near 140 cm^{-1} in NBT-based solid solutions was previously ascribed to vibrations of A-site alkali cations, as a result of two-mode behavior of the mode localized in the A-site cations [36]. The arguments for such a peak assignment were the smaller mass of alkali elements as compared to the mass of Bi, which may lead to a higher wave number component related to alkali-cation vibrations and a lower wave number component related to Bi vibrations, and the shift of

this peak toward lower wave numbers when K substitutes for Na [36]. The latter, however, can be due to chemically induced structural alteration rather than a direct chemical effect on the A-cation vibrations. For example, the addition of Ba to NBT causes a rhombohedral-to-tetragonal change in the average structure, and the position of the peak near 140 cm^{-1} stepwise drops at x_{MPB} instead of gradually decreasing with the increase in the content of Ba [21], which unambiguously speaks in favor of an indirect chemically driven structural effect rather than a direct chemical effect. Furthermore, a similar Raman peak near 140 cm^{-1} is observed in perovskite-type ferroelectric solid solutions with only Pb or with both Bi and Pb on the A-site [15–17,26], which also emphasizes that this peak cannot be related to a phonon mode localized in light alkali elements on

FIG. 2. Temperature evolution of the wave number ω and FWHM of Bi-localized mode in NBT- x BT for $x = 0, 0.06$, and 0.08 ; gray and black symbols represent the higher energy and lower energy component, respectively. The dashed lines in the bottom plots are polynomial baselines of the datasets, representing the conventional decrease of phonon mode widths on cooling in the absence of phase transition.

the A site. By analogy with complex Pb-based perovskite-type ferroelectrics [15–17], we assign the Raman scattering at $\sim 140 \text{ cm}^{-1}$ in NBT- x BT to an A- BO_3 translation mode involving vibrations of both A- and B-site cations. Previous studies of Pb-based relaxors and relaxor-ferroelectric solid solutions demonstrated that this Raman scattering mirrors the coupling processes between off-centered A- and B-site cations [15–17]. On the other hand, reverse Monte Carlo simulations of neutron TES of pure NBT [13] revealed that, due to the ionic type of Na-O interactions, Na^+ tends to position at the center of the 12 surrounding O^{2-} anions, in strong contrast to Bi^{3+} which shows affinity to off-center. This, along with the relatively high degree of covalency of Bi-O interactions and subsequently larger Raman cross section, implies that the Raman scattering near 140 cm^{-1} in NBT- x BT is dominated by Bi- TiO_3 vibrations and should be sensitive to coupling processes between off-centered Bi^{3+} and off-centered Ti^{4+} cations. The Raman scattering near 50 cm^{-1} of NBT- x BT is attributed to phonon modes localized in A-site cations [27] and again due to the mixed ionic-covalent character of Bi-O bonding versus the ionic type of Na-O and Ba-O interactions, it should be dominated by Bi vibrations. As expected, the wave number of this Raman scattering matches well that of Bi-localized modes in complex bismuth oxides [18,19] as well as of Pb-localized modes in perovskite-type relaxors and relaxor-ferroelectric solid solutions [15–17]. For all three compounds studied here, the Raman peak near 50 cm^{-1} persists at elevated temperatures (see Fig. 1), although it is not symmetry-allowed in $Pm\bar{3}m$, indicating the presence of off-centered Bi^{3+} cations in the paraelectric state, in agreement with XAS [12] and TES [13,14].

Thus, we have focused our analysis on the temperature evolution of the Raman scattering near $50, 290$, and 140 cm^{-1} , which respectively reflects the coupling processes within the

subsystem of off-centered Bi, within the subsystem of off-centered Ti, and between these two subsystems.

Figure 2 shows the temperature dependencies of the wave number ω and FWHM Γ of the Bi-localized mode near 50 cm^{-1} . For $x = 0$ and 0.06 , this mode exhibits splitting at $T_{\text{split}}^{\omega_1-\omega_2} \sim 450$ and $\sim 370 \text{ K}$, respectively. For $x = 0.08$, splitting of the Bi-localized mode near 50 cm^{-1} could not be resolved, but the Lorentzian contribution q becomes zero below 420 K , in contrast to the case of $x = 0$ and 0.06 for which the Lorentzian contribution of the higher energy components of the Bi-localized mode (peak 2 in Fig. 1) approaches unity in the temperature range where the mode exhibits splitting. This suggests that, if the content of Ba is above x_{MPB} , the compositional disorder on the A site is too high to allow for two distinct low-temperature dynamical states of Bi, at least down to 80 K . For all three compounds studied, $\omega_2(T)$ exhibits a minimum accompanied by an excess of FWHM, which is most pronounced for $x = 0$, indicating that the coupling processes within the subsystem of off-centered Bi are strongest in pure NBT. The temperature of the minimum of $\omega_2(T)$ $T_{\text{min}}^{\omega_2}$ is 580 K for $x = 0$, which coincides with the temperature of the maximum of $\Gamma_2(T)$. $T_{\text{min}}^{\omega_2}$ matches well the temperature of tetragonal-to-rhombohedral phase transition [4]. For $x = 0.06$ and 0.08 , $T_{\text{min}}^{\omega_2}$ is ~ 420 and $\sim 450 \text{ K}$, respectively, while the excess in $\Gamma_2(T)$ is spread out over a large temperature range without a well-pronounced maximum. Here, $T_{\text{min}}^{\omega_2}$ for $x = 0.06$ and 0.08 is close to the corresponding depolarization temperature T_d associated with the antiferroelectric-ferroelectric (AFE-FE) phase transition [1,2,4].

Figure 3 shows the temperature dependencies of ω , Γ , and the normalized integrated intensity I of the phonon mode near 290 cm^{-1} dominated by vibrations of off-centered Ti. This mode splits into two components for all three compounds, and

FIG. 3. Temperature evolution of the wave number ω , FWHM, and intensity of Ti-localized mode in NBT- x BT for $x = 0, 0.06$, and 0.08 ; gray and black symbols represent the higher energy and lower energy component, respectively.

the splitting temperature $T_{\text{split}}^{\omega_4-\omega_5}$ increases with the increase in the Ba content from 460 K for $x = 0$, to 630 K for $x = 0.06$, and 705 K for $x = 0.08$, which means that the addition of Ba stabilizes two distinct dynamic states of coupled off-centered Ti. However, the temperature evolution of the FWHMs and intensities of the two components of the Ti-localized mode reveals the turning point in this vibration state at $x = 0.06 \sim x_{\text{MPB}}$. For $x = 0 < x_{\text{MPB}}$, the higher energy component of the Ti mode (peak 5 in Fig. 1) has larger width and intensity than the lower energy component (peak 4 in Fig. 1) through the entire temperature range. For $x = 0.08 > x_{\text{MPB}}$, $I_4(T)$ and $I_5(T)$ as well as $\Gamma_4(T)$ and $\Gamma_5(T)$ cross each other at ~ 470 K, and at low temperatures, the lower energy state becomes dominant. For $x = 0.06 \sim x_{\text{MPB}}$, the two components of the Ti-localized mode are very close to each other in both width and intensity over a temperature range 380–240 K, but at low temperatures, the higher energy state remains dominant; note that the upper temperature limit of 380 K is approximately the same as the splitting temperature of the Bi-localized mode $T_{\text{split}}^{\omega_1-\omega_2}$ for $x = 0.06$.

Now let us consider the temperature dependencies of ω , Γ , and I of the Bi-TiO₃ translation mode near 140 cm⁻¹ (Fig. 4), which is composed of vibrations of both off-centered Ti and off-centered Bi. As can be seen in Fig. 4, there is a striking difference among the three compounds in the temperature behavior of this mode. For $x = 0.06 \sim x_{\text{MPB}}$, the Bi-TiO₃ translation mode shows a tremendous softening and damping between 290 and 650 K with an extremum at ~ 415 K, which is close to the triple $\text{FE}_{R3c} - \text{AFE} - \text{FE}_{P4mm}$ point in the x - T

diagram of NBT- x BT [1,2,4]. This is a classical soft-mode behavior at the ferroelectric phase transition, responsible for the enhancement of the macroscopic static dielectric permittivity [37], and it clearly indicates that the abundant coupling between the Bi- and Ti-subsystems drives the material into a ferroelectric state. In strong contrast, only a subtle hump near 420–450 K can be seen in the wave number, FWHM, and intensity of the Bi-TiO₃ mode for $x = 0$, which should correspond to the AFE-FE transition, and a kink in $\omega_3(T)$ at 580 K, which is close to the $P4bm - R3c$ phase-transition temperature [1,2,4]. For $x = 0.08$, $\Gamma_3(T)$ and $I_3(T)$ exhibit a maximum near 450 K, but it is not so well pronounced as for $x = 0.06$, and more importantly, $\omega_3(T)$ continues to soften down to 80 K, indicating instability in the system to the lowest temperature reached in our experiment. The gradual increase in the baseline of $\Gamma_3(T)$ on cooling, instead of the trivial decrease, is also indicative of significant instability induced by the temperature decrease for $x = 0.08$.

Likewise to the Raman data, our x-ray PDF data indicate a high degree of structural resemblance in NBT- x BT for x below, near, and slightly above MPB in terms of first-neighbor distances. Figure 5 shows the low- r range of PDFs of NBT- x BT for $x = 0, 0.06$, and 0.08 in the range 1–5 Å, calculated from x-ray TES measured at different temperatures. In this r range, the peaks can be assigned to specific A/B-O, A-B, and A/B-A/B atom-atom correlations. However, it should be emphasized that the x-ray data are greatly weighted by the heavy cations such as Bi³⁺, and hence, it is difficult to extract reliable information about A/B-O distances. In

FIG. 4. Temperature evolution of the wave number, FWHM, and intensity of Bi-TiO₃ mode comprising vibrations of both Bi and Ti atoms.

addition, these PDFs, which have been obtained from fast *in situ* powder diffraction data, are not suitable for any rigorous model-based refinements [38]. Nevertheless, some qualitative observations on the cation-cation correlations can be performed. For example, the peak at 3.3 Å, which represents mainly A-B coherent distances, i.e. Ti-Bi/Na/Ba distances,

remains nearly unchanged both as a function of composition and temperature. The incorporation of Ba affects the PDF around 3.8 Å measured at temperatures below the Curie temperature when x is above MPB. This PDF feature is in general related to A-A and B-B correlations. Since Bi and Ba have much higher atomic numbers Z than either Ti or

FIG. 5. (Color online) Temperature-dependent x-ray PDF patterns of NBT- x BT for $x = 0, 0.06$, and 0.08 . The short-dashed lines (3.3 Å) mark the feature corresponding to A-B distances; the dashed (3.7 Å) and dotted lines (3.9 Å) mark the two components in the feature related to A-A and B-B distances.

FIG. 6. (Color online) Temperature evolution of x-ray PDF intensities for NBT- x BT for $x = 0, 0.06$, and 0.08 ; the dashed rectangles mark the temperature ranges of the most pronounced changes in PDFs.

Na, this PDF peak should primarily reflect Bi-Bi, Bi-Ba, and Ba-Ba correlations. Furthermore, given the fact that the ratio between Ba content and Bi content is approximately 0.13 for NBT-0.06BT and 0.17 for NBT-0.08BT as well as that the Z number of Ba is smaller than that of Bi, it can be concluded that the dominant contribution to the PDF peak near 3.8 Å comes primarily from Bi-Bi coherent distances. Above 700 K , this particular PDF range shows a peak at 3.7 Å and a shoulder near 3.9 Å for all three compounds with x below, near, and above MPB. The shoulder near 3.9 Å progressively increases in intensity with the temperature decrease for all three compounds, while the intensity of the peak near 3.7 Å decreases. The change in the intensity ratio is, however, considerably less for $x > x_{\text{MPB}}$ than for $x < x_{\text{MPB}}$ and $x \sim x_{\text{MPB}}$. This firmly reveals that, for $x > x_{\text{MPB}}$, the incorporation of Ba prevents the vanishing of the shorter distanced Bi-Bi correlations ($\sim 3.7 \text{ Å}$) at temperatures below the Curie temperature, at least down to room temperature. For $x = 0$ and 0.06 , the peak at 3.9 Å continues to increase in relative intensity at temperatures below room temperature, suggesting diminishing dispersion in the off-centered Bi displacements on cooling. This result corroborates with the recent neutron PDF analysis of pure NBT [14] showing a strong dispersion of Bi displacements at 473 K , which gradually disappears on cooling to 10 K . Due to the limited beamtime for TES experiments, data below room temperature were not collected for $x = 0$.

The temperature evolution of the PDF intensities in the range $1\text{--}10 \text{ Å}$ for $x = 0, 0.06$, and 0.08 can also be compared from the plots in Fig. 6, which provides a bird's eye view of the PDF patterns. Again, qualitatively, a temperature range can be identified where notable changes occur in the Bi-Bi correlations, suggesting a temperature-induced displacive-type phase transition for each composition. The temperature-driven alteration of PDF near 3.8 Å is more gradual for $x = 0.08$ compared to $x = 0$ and 0.06 , which in fact follows the changes in the Raman scattering near 50 cm^{-1} , revealing a splitting of the Bi-localized mode for $x = 0$ and 0.06 , but not for $x = 0.08$. Finally, the variation of the temperature range of the

most pronounced PDF changes with x resembles the trend in the reported x - T phase diagram constructed by dielectric and polarization measurements [1,2,4]. This particular temperature range has been described as the crossover from antiferroelectric to ferroelectric order [1,2,39], and for pure NBT, it has been structurally characterized as the region of coexistence of several phases [9–11,32,33]. It is further important to note that, above this specific temperature range, the mesoscopic-scale ($1\text{--}10 \text{ Å}$) correlations are consistently maintained up to 800 K , which is in full accordance with the nonzero first-order Raman scattering of NBT- x BT in the paraelectric state.

IV. CONCLUSIONS

The temperature evolution of the Raman scattering near $50, 140$, and 290 cm^{-1} suggests the following scenario of chemically induced structural phenomena in NBT- x BT. The incorporation of Ba into the A site stabilizes the dynamical hopping of B-site Ti and thus enhances the ferroelectric coupling between off-centered B-site cations. At the same time, Ba doping disturbs the coupling between off-centered Bi, but for a certain value of Ba content, the delicate balance between coupled and uncoupled A-site cations allows for strong coupling between the Bi and Ti subsystems, i.e. dynamic coherence between the off-centered A- and B-site cations on the mesoscopic scale. This critical value x_c corresponds to the so-called morphotropic phase. These mesoscopic-scale structural and dynamic phenomena may turn out to be one of the major reasons for the enhanced response functions near the MPB in NBT- x BT.

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