Absence of piezoelectric enhancement around the morphotropic phase boundaries for Bi$_{1-x}$Nd$_x$FeO$_3$ ceramics

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ABSTRACT
BiFeO$_3$ has been receiving continuous attention for its excellent ferroelectric and multiferroic properties. Nevertheless, the piezoelectricity as a complementary property of ferroelectricity remains less addressed for BiFeO$_3$ at least in a single phase form. In this work, we investigate the piezoelectric behaviors of bulk Bi$_{1-x}$Nd$_x$FeO$_3$ ceramics, given that the Nd-substitution may trigger structural phase transitions from the R3c phase to the Pna2$_1$ phase and eventually toward the non-polar Pnma phase. It is revealed that the piezoelectric coefficient $d_{33}$ does increase with the increasing Nd content $x$ inside the R3c phase region. However, no $d_{33}$-enhancement across the R3c–Pna$_2$$_1$ boundary region and the Pna$_2$$_1$–Pnma boundary region is identified, suggesting no positive correlation between the piezoelectric coefficient and the possible morphotropic phase boundaries. The observed $d_{33}$-enhancement inside the R3c phase region should be attributed to the remarkably reduced domain size and release of pinned domain wall motion by defects.

I. INTRODUCTION
Piezoelectric effect refers to the accumulation of electric charges in materials in response to induced mechanical strain and has been extensively employed for a vast range of sensing and actuation applications in various industries. Materials with a large piezoelectric effect are thus highly desirable, driving substantial and continuous efforts in the past decades. A ferroelectric must be a piezoelectric, while the reverse is not necessarily true, and almost all the best piezoelectrics are ferroelectrics since the spontaneous electric polarization of a ferroelectric may provide a favorable source for generating large electromechanical response. In the past decades, extensive investigations have been performed along this line, launching a number of good ferroelectric and relaxor materials with super piezoelectric properties.

Usually, two major structure-based scenarios have been proposed. One scenario is associated with the ferroelectric domain structure and the other is that a properly developed domain structure will benefit the piezoelectric enhancement. On the one hand, the more the degenerate polarization states, the easier and thus larger the piezoelectric response. This implies rich domain patterns as a consequence of combination of all these degenerate polarization states. On the other hand, the coherent domain structure and ultra-small domain size benefit the piezoelectric properties to some extent. One of the simplified arguments is relevant to the fully satisfied ergodicity of the ferroelectric order parameter in such a small-size domain structure. Therefore, the whole ensemble of polarization states can be easily visited and re-aligned by small electric field, generating large piezoelectric response. In fact, the motion of domain walls, if available, can contribute largely to the
piezoelectric response, and thus, the domain wall density can have a profound effect too. Along this line, any pinning of domain wall motion would damage the piezoelectric response, while small domain size would be benefiting the piezoelectric response. The other scenario is related to the structural phase transitions, possibly developing the morphotropic phase boundary (MPB) between two adjacent phases. The intrinsic correlation between such a MPB and anomaly of some properties has been reported in a lot of ferroelectric systems and thus becomes one of the central issues. Specifically, such a MPB-based scenario puts the case that two ferroelectric phases with different symmetry will enhance the polarization rotation, while a third phase with non-polar symmetry may enhance the polarization extension. Note that both polarization paths may contribute to the flattening of a free energy profile. Therefore, the phase symmetry could be important, with each expected to perform a different role in the potential property enhancement. Anyway, exploration of MPB-based emergent phenomena has become an appreciated topic in the community of ferroelectrics, not only due to the fact that multiphase coexistence around the MPB allows more active polarization states but also due to the small domain size.

A comprehensive discussion on the two scenarios, which are summarized as the reduced domain size and more active polarization states, triggers more possibilities. Indeed, in some cases, one can identify such structural phase transitions in response to various stimuli such as chemical substitution and electric field. However, such anomaly of piezoelectric property around the MPB may not be observed in many cases. The possible reason may be relevant to the absence of sufficiently active polarization states and inter-switching between them. In addition, it may also be modulated by the movement of domain walls suppressed by various defects inevitably, thus searching for more ferroelectrics with which either of the two scenarios or both works would be highly appreciated.

Along this line, we may discuss one of the most known ferroelectrics, BiFeO₃ (BFO). First, BFO exhibits the largest spontaneous polarization among almost all known ferroelectrics. Second, BFO in the rhombohedral R₃c phase has eight equivalent polarization states, enabling rich domain structures including the 71°, 109°, and 180° domain walls. This character provides us opportunities to utilize the first scenario so that the piezoelectric behavior can be modulated to some extent. Furthermore, there are likely several technical approaches by which the domain size can be largely modulated. Third, recent reports did reveal rich structural phase transitions. For example, it was reported that rare-earth (Nd) substitution of Bi with BFO does drive such structural transitions, although no conclusive evidence is available. There have been also additional reports claiming the coexistence of these phases over a broad window of substitution. Nevertheless, the most striking feature is the possible existence of one MPB between the R₃c/Pna₂₁ phases or one MPB between the Pna₂₁/Pnm₃ phases.

In this work, it is our intention to investigate the BFO-based systems by proper R° substitution of Bi, in order to address the two major issues associated with the piezoelectric properties. One is the consequence of the domain size and domain structure, and the other is the piezoelectric response to gradual structure variation from the R₃c phase to the Pna₂₁ phase and eventually to the Pnm₃ phase. Based on these considerations, we shall perform a systematic investigation of the lattice structure, ferroelectric and piezoelectric properties, and domain structure of Nd-substituted BFO, in order to check these issues.

II. EXPERIMENTAL DETAILS

We focus on Biₓ−₀.₃NdₓFeO₃ (BNFO) ceramics with x from 0.0 to 0.3, and the rapid sintering as an effective technique has been widely demonstrated, and we utilized it for synthesizing our samples. BₓOₓ3, Nd₂O₃ (99.99%, Alfa Aesar), and Fe₂O₃ (99.9%, Aladdin) as the starting materials were used. These dried reagent oxides were pre-heated at 100 °C (1000 °C for Nd₂O₃) for 4.0 h, and then a thorough mixing plus ball-milling in the roughly stoichiometric ratio (Bi exceeds ~6%) inside agate media with ethyl alcohol for 24 h was carried out. The powder precursor was then dried in a static drying oven followed by sufficient grinding operation in agate mortar. The resulting powder samples were sintered, respectively, at 800 °C for x = 0.0, 820 °C for x = 0.02–0.04, 860 °C for x = 0.06–0.12, 900 °C for x = 0.16–0.20, and 920 °C for x = 0.24–0.30 for 3.0 h with the heating and cooling rates of 5 °C/min in a muffle furnace.

Given these well-prepared powder samples, the rapid hot-press sintering was used with a graphite cylinder mold and hydrostatic pressure of 90 MPa for 5.0 min. For the sintering temperature, a huge number of optimization procedures were tested and the optimized sintering temperature was 820 °C. After the sintering, the samples were submitted to 400 °C in the oxygen atmosphere for 4.0 h so that graphite possibly penetrated into the sample’s surfaces can be sufficiently removed by oxidation. Finally, the cylinder-like samples were each cut into thin pellets and then polished for subsequent characterizations.

All the samples were checked by the high-resolution x-ray diffraction (XRD) in the θ–2θ mode using the Bruker D8 Advance x-ray diffractometer with Cu Kα radiation (wavelength λ = 1.5418 Å). The standard GAXS program was used for the Rietveld refinement. The microstructure and chemical composition of the samples were checked using the scanning electron microscopy (SEM) and the associated energy dispersive x-ray spectroscopy (EDX) on the fresh and cracked surface. The samples used for electric measurements were well-prepared thin plates that are 3.0 mm in diameter and 0.2 mm in thickness. The Au electrodes were sputtered on both surfaces using the ion sputtering technique. The ferroelectric hysteresis (P–E loop) was measured using the integrated ferroelectric testing system (TF2000, AixACCT, Germany) at a frequency of 10 Hz. The piezoelectric coefficient d₃₃ was measured using the quasi-static d₃₃ piezometer (ZJ-3A, IACAS, Beijing, China) after the poling process of 120 °C silicone oil bath with a dc electric field of ~80 kV/cm. The PEM imaging was performed using the advanced piezoelectric force microscope (PFM) (Asylum Research Cypher ES, UK) in the vector PFM mode by using a conductive probe. The Dual AC Resonance-Tracking (DART, Asylum Research) technique was also used to obtain highly reliable signals.

III. RESULTS AND DISCUSSIONS

A. Phase and microstructure

The R₃c phase of BFO is characterized by the anti-phase α−α−α octahedral tilting (in the Glazer notationα) and off-center...
cation displacements along the [111]p direction; here, the subscript p refers to the pseudocubic structure. The Nd-substitution does induce successive phase transitions from the R3c phase to a bridging intermediate phase and finally to the orthorhombic Pnma phase. The Pnma symmetry possesses the \( a' a c' \) octahedral tilting and in-plane (IP) anti-polar displacement and in-plane anti-polar displacement along the [110]p and [1-10]p directions. More interesting is the bridging intermediate phase, which is normally believed to exhibit the anti-polar cation displacement along the [110]p/[1-10]p directions. It was claimed that the NaNbO3-like \( (a' a c')/\left(a' a c'\right) \) octahedral tilting exists likely for the La-, Sm-, and Gd-substituted systems, resulting in a MPB-like region. So far, various studies based on the reflection conditions in electron diffraction patterns assigned the bridging phase to the Pbam space group or its subgroup Pna2₁, while the former is nonpolar, but the latter is polar with a Z-axis aligned polarization.

The highly anisotropic atom displacements for the oxygen and Bi/R positions may cause deviation of the actual structure from the Pbam symmetry, making the polar Pna2₁ phase more favorable as the intermediate phase.

Based on the discussion, we look at the structural evolution upon the Nd-substitution, and the XRD 0–2θ spectra for several selected samples are plotted in Fig. 1. The appearance of the R3c phase in the low-x range \( (x < 0.12) \) and the Pnma phase in the high-x range \( (x > 0.20) \) can be reliably identified by properly indexing all the reflections of the two phases, respectively. All the samples show no well-identified impurity phase such as Bi₂Fe₄O₉ or Bi₁₂FeO₉₉, which are often reported to exist, although we did observe nearly invisible peaks in-between \( 2\theta = 20^\circ \) and \( 30^\circ \). However, in this work, we do not discuss any magnetism-related issue, and these impurity phases if any have no influence on the conclusion of this work. For the bridging and intermediate Pna2₁ phase, we check the data for samples with \( 0.12 < x < 0.24 \) and can clearly identify the peaks from this phase, marked by the star symbol “*”.

The reflections from the R3c phase for the low-x samples and from the Pnma phase for the high-x samples can be identified too in these samples with intermediate \( x \), a strong indication of the three-phase coexistence. It should be mentioned that the phase boundary is most likely morphotropic, referring to our observed consequence of phase appearance as a function of composition. Consequently, we can perform the structure refinement from the XRD data to evaluate the volume fractions of these phases as a function of \( x \) if possible.

Furthermore, we performed the lattice structure refinement using the Rietveld refinement program with the R3c and Pnma phases as the two end phases \( (x = 0.0 \) and \( x = 0.3) \). We choose both the Pbam and Pna2₁ phases to serve as the bridging phases to fit the measured data. The Pna2₁ space group seems to be much more favorable, and subsequently, our fitting strategy tracks the three phases in different volume fractions. Here, it should be mentioned that the fitting reliability (reliability factors as small as possible) may be a well-acceptable criterion and followed in the present work. The refined results show that the samples with \( x < 0.08 \) show the pure R3c phase. As shown in Fig. 2(a) for samples with \( x = 0.12 \), the data cannot be well fitted unless both the R3c phase and Pna2₁ phase are considered simultaneously, giving rise to the best reliability with factors \( R_{wp} \sim 6.38\% \), \( R_p \sim 4.48\% \), and \( \chi^2 = 1.745 \), noting that the R3c phase is still dominant. For \( x = 0.16 \), a consideration of only the R3c phase and Pna2₁ phase is yet insufficient and a proper combination of the three phases simultaneously is needed, giving the best reliability with factors \( R_{wp} \sim 7.20\% \), \( R_p \sim 5.42\% \), and \( \chi^2 = 2.186 \). It is noted here that the intermediate Pna2₁ phase becomes the dominant phase and the Pnma phase is minor but non-negligible.

Based on the refined data, we can present the fitted volume fractions \( f_{\text{jul}} \) of the three phases as a function of \( x \), respectively, which are plotted in Fig. 2(b). For \( x < 0.06 \), only the R3c phase is available. The bridging Pna2₁ phase begins to appear then and increases rapidly with increasing \( x \). The Pnma phase does not appear until \( x > 0.12 \), while its rapid growth begins at \( x \sim 0.20 \) and beyond. The three-phase coexistence becomes clear within \( 0.16 < x < 0.24 \), while the bridging Pna2₁ phase occupies \( \sim 60\% \) and is the dominant phase. As \( x > 0.24 \), the R3c phase becomes negligible and the Pnma phase occupies over 50%, entering again the two-phase coexistence region. The \( x \)-dependences of the three phases suggest the possible existence of two MPBs at \( x \sim 0.12 \) (MPB₁) and \( x \sim 0.24 \) (MPB₂), respectively.

Certainly, it is necessary to check how the microstructural qualities of the as-prepared samples are and whether the substituting Nd species are spatially homogeneous. It is shown that all these samples exhibit high microstructural quality with well-developed grains and highly dense grain-packing, as seen in Fig. 3 (left corner) with the SEM image of the cracked surface for the sample with \( x = 0.06 \) as an example. It is thus demonstrated that the rapid
FIG. 2. XRD θ–2θ spectra and corresponding Rietveld best refining data for the sample with $x = 0.12$ (a). The coexisting $R3c$ phase and $Pna2_1$ phase are used for the data fitting. The as-extracted volume fractions ($f_{vol}$) of the three phases as a function of $x$, respectively, are plotted in (b), noting that the data may not be quantitatively reliable but sufficient for a guide of eyes.

B. Ferroelectric and piezoelectric behaviors

For the ferroelectric and piezoelectric behaviors, we first discuss the measured ferroelectric hysteresis ($P–E$ loops, where $P$ is ferroelectric polarization), as shown in Fig. 4 for a set of samples. The pure BFO cannot exhibit a well-developed loop, as shown in Fig. 4(a). The shrinking effect is attributed to the domain-pinning by charged defects. This pinning can be largely removed once rare-earth substitution is done. The Nd-substitution does improve remarkably the $P–E$ loop quality, as shown in Figs. 4(b) and 4(c). The largest $P_r$ value $\sim 50 \mu C/cm^2$ is reached in the sample at $x \sim 0.06$. It is seen that $P_r$ begins to decay gradually as $x > 0.06$, although $E_c$ continues to grow slightly. The ferroelectricity seems to be largely suppressed once $x > 0.12$, around the first MPB (MPB$_1$). No saturated $P–E$ loop can be measured experimentally as $x > 0.12$ although the thin loop can be seen for the sample at $x = 0.16$, as shown in Fig. 4(g). Finally, nearly no identifiable $P–E$ loop can be obtained as $x > 0.20$, very close to the second MPB (MPB$_2$) at $x \sim 0.24$, beyond which the system enters the paraelectric $Pnma$ phase. The coercive electric-field ($E_c$) and remanent polarization ($P_r$) data extracted from the loops are plotted in Figs. 5(a) and 5(b). While the $P_r(x)$ data show some scattering from point to point, both $P_r(x)$ and $E_c(x)$ first increase with increasing $x$ and reach the maxima roughly at $x = 0.06–0.08$, beyond which they begin to fall rapidly at $x \sim 0.12$ (around MPB$_1$). At $x \sim 0.16$ and up to 0.24 around MPB$_2$, one sees that $P_r$ is down to almost zero and $E_c$, if definable, becomes small too.

The rapid decay of $P_r$ once $x$ passes across MPB$_1$ is certainly an unfavorable signal for any enhancement of piezoelectricity at the MPB for the present BNFO systems. In order to check this prediction, the measured out-of-plane (OP) piezoelectric coefficient $d_{33}$ as a function of $x$ and the results are plotted in Fig. 5(c). It is seen clearly that $d_{33}(x)$ surprisingly exhibits the tendency very similar to that of

hot-press sintering is highly favored for preparing the BFO-based ceramics. In fact, the samples’ density was measured using the standard Archimedes method, and the measured density is as high as $\sim 0.97$. In addition, the chemical homogeneity of these samples was checked using the EDX mapping of the cracked surfaces, and one set of data for species Bi, Fe, and Nd is presented in Fig. 3 too. While the special distribution over each grain is homogeneous for all the three species, the contrast difference was generated due to the cracked surface that is macroscopically rugged. It is noted that the in-plane contrast of Nd distribution in those grains is highly uniform although the substitution level is only $x = 0.06$. 

FIG. 3. SEM image of the fresh and cracked surface for the sample with $x = 0.06$ and the corresponding EDX mapping of elements Bi, Fe, and Nd in the same region. Similar microstructures and chemical homogeneity are shown for other samples prepared in this work.
FIG. 4. Measured ferroelectric $P$–$E$ loops for a series of BNFO samples with the $x$ values inserted in each plot. The shrinking effect for pure BFO samples is shown in (a), the remarkably improved $P$–$E$ loops for $x = 0.02$–$0.12$ are plotted in (b)–(f), thin loops for $x = 0.16$ are plotted in (g), and nearly no identifiable $P$–$E$ loops for $x > 0.20$ are plotted in (h) and (i).

$E_c(x)$ and $P_r(x)$: the piezoelectric response is largely enhanced by the Nd-substitution in the polar $R3c$ phase region and $d_{33}$ reaches the largest value $\sim 48$ pC/N at $x \sim 0.06$ from 30 pC/N for the pure BFO sample, a 60% enhancement. Afterward, $d_{33}$ shows a slow decay but remains to be 38 pC/N around MPB$_1$. Unfortunately, we have not yet observed any enhancement of $d_{33}$ around MPB$_1$ upon testing on a number of samples synthesized under the identical conditions. Passing across MPB$_1$ results in a rapid decay of $d_{33}$ down to 10 pC/N at $x \sim 0.16$, and $\sim 2$ pC/N at $x \sim 0.24$, indicating again that no anomaly of $d_{33}$ occurring around MPB$_2$ has been yet observed.

The absence of expected $d_{33}$ anomaly or enhancement around MPB seems to be usual if one compares $d_{33}(x)$ with $P_r(x)$ and finds their similarity. This absence suggests that the proposed ergodicity of polarization $P$ seems not operational for this case. In other words, one may argue that MPB$_1$ and MPB$_2$ do not provide additional polarization states for flip and switch so that the piezoelectric response can be further enhanced. In fact, no remarkable piezoelectric enhancement can be found in a number of ferroelectrics with the so-called MPB character. More discussion will be given later.
C. Domain structures

While no anomaly of $d_{33}$ around MPB$_1$ and MPB$_2$, unfortunately, is identified, we did observe remarkably enhanced $d_{33}$ in the $R3c$ phase region due to the Nd-substitution. It seems that this enhancement is most likely due to the extrinsic contribution. There is no evidence for intrinsic enhancement of $d_{33}$ in the $R3c$ phase due to Nd doping, and thus, the change in $d_{33}$ is most likely an extrinsic effect, for instance, domain structure evolution. In order to check the domain structure evolution, extensive PFM imaging of the domain structures was performed, including the out-of-plane (OP) and in-plane (IP) imaging. The representative images [only OP-amplitude (OP-amp) and OP-phase (OP-pha)] are collected in Fig. 6 for six samples. It is also noted that for samples $x > 0.20$, no clear domain signals can be reliably measured.

Since the samples are polycrystalline in nature, it may not be possible to construct the three-dimensional (3D) configuration of the domain structure. Here, we mainly focus on the domain pattern and size. First, the pure BFO sample shows the most sufficiently developed domain structure with large size (>7 µm–10 µm) and stripe-like pattern. Such a large domain size and strong shape anisotropy are unfavorable for domain switching, and thus, remanent polarization $P_r$ and piezoelectric coefficient $d_{33}$ would be small. Indeed, we see the measured $P_r \sim 15$ µC/cm$^2$ and $d_{33} \sim 30$ pC/N for our pure BFO samples. Second, a tiny Nd-substitution would be sufficient to slow-down the domain growth; consequently, the domain size becomes smaller and the shape anisotropy is also seriously weakened upon a substitution as low as $x = 0.02$, and the polytropic-like shape is preferred. The corresponding $P_r \sim 40$ µC/cm$^2$ and $d_{33} \sim 40$ pC/N. Third, the Nd-substitution induced effect continues and the maximal $P_r$ and $d_{33}$ are obtained for the sample at $x \sim 0.06$, giving rise to $P_r \sim 50$ µC/cm$^2$ and $d_{33} \sim 50$ pC/N, beyond which one observes slight degradation of $P_r$ and $d_{33}$, although the domain size decreases further with increasing $x$.

Upon the Nd-substitution, the domains prefer the stripe-like shape for $x = 0.0$, the polytropic-like shape for $x = 0.02$, and the fine branched shape for $x = 0.04$–0.08, respectively. This fine branched domain becomes very popular. As $x > 0.12$, the domains become even smaller and the branched domains are replaced by particle-like small domains, while the ferroelectric polarization is seriously degraded. The gradual disappearance of ferroelectric polarization upon entering the $Pna_2_1$-phase dominant region implies the gradual disappearance of the piezoelectric response. Here, the domain pattern is fine and branched, likely benefitting the $d_{33}$-enhancement.

Here, it should be mentioned that the $d_{33}$-enhancement as a function of increasing $x$ near MPB$_1$ can be explained by the doping process reducing domain-pinning, improving poling, and thus increasing $P_r$ and $d_{33}$, which is supported by the $P$–$E$ loops in Figs. 4(a)–4(c) and almost all related reports.$^{21,35}$ On the one hand, the Nd doping reduces the lattice defects, which seem to be of relatively high density, leading to the remarkable pinched loop of the pure BFO sample. This effect allows the domain-pinning by these defects to be largely suppressed, and thus, the $d_{33}$-enhancement can be expected. On the other hand, the domain size reduction would be believed to help the domain reversal kinetics, thus benefitting the $d_{33}$-enhancement. The two factors, both as extrinsic effects for the piezoelectric response enhancement, likely play important roles in the present work.

D. Discussion

Before concluding this work, some more discussion on the lattice structure of the intermediate phase could be informative. In fact, we were aware of the possibility of the anti-polar $Pbam$ phase as the intermediate, since we did measure no apparently saturated ferroelectric hysteresis at $x \sim 0.16$, as shown in Fig. 4(g). Eventually, we favor the intermediate phase to be the polar $Pna_2_1$ phase rather than the anti-polar $Pbam$ phase, although we admit that this issue remains open for further clarification. The reason includes two aspects: (1) On the one hand, the method for sintering the samples in this work is different from that used by Damjanovic et al. but similar to that used in another recent work by Chen’s group.$^{20}$ In the latter case, the intermediate phase was assigned as the polar $Pna_2_1$ phase based on various ways of identification, and our results such as the $P$–$E$ loops seem to be consistent with it. (2) On the other hand,
the absence of apparently ferroelectric hysteresis at $x \sim 0.16$ may be ascribed to the coexistence of the three phases, as shown in Fig. 2(b). Such a coexistence makes a clear identification of the ferroelectric domain structure complicated. It is very likely that these domains are very small and dispersed (the tendency can be seen in Fig. 6 but not shown), making the hysteresis weak and thin. However, the measured hysteresis shows no trace of anti-polar structure. Some researchers attributed the peak value with respect to the overall tendency of $d_{33}$-enhancement to the MPB-related behavior, while others obtained the maximum in the pure $R3c$ phase.\textsuperscript{21,34,36} Our result is obviously consistent with the latter case. Based on the structure symmetry discussion in the literature, it is clear that the underline result depends on the type of MPB. As the intrinsic mechanism, the MPB of two polar phases, which is generally accepted in the piezoelectric transducer (PZT) case, is more likely to observe enhanced $d_{33}$ due to polarization rotation. Unfortunately, here the polar phase is proposed and the above-mentioned polarization path seems also out of operation or dispersed by dispersed domains. Hence, the underlying reason may deserve additional exploration in the future, and further discussion of this issue is beyond the scope of this work.

To this stage, our experiments unveiled two aspects of the main results. On the one hand, we have not yet observed well-identifiable anomaly or enhancement of either $d_{33}$ or $P_e$ around the two MPBs. The absence of such anomaly does not necessarily exclude the MPB-related scenario, while the multi-phase coexistence over the whole $Pnma$-phase region can be the reason. This broad-region coexistence may smear the anomaly feature, and if any, the anomaly absence would be misleading. So far, the displayed demonstrations of the MPB scenario usually referred to those systems with a sharp MPB, suggesting that additional work should be done to suppress the phase coexistence over such a broad compositional range but maintaining the phase transitions. On the other hand, the domain structure scenario has been approved in the present experiment, at least qualitatively, although the $d_{33}$-enhancement is not so remarkable. We not only confirm that the substitution-induced domain refinement may benefit the piezoelectric enhancement but also unveil that the samples with small and fine branched domain patterns show the large $d_{33}$ values, at least in our BNFO samples. This scenario is certainly worthy of additional investigation.

IV. CONCLUSION

In conclusion, we have presented a comprehensive investigation of the ferroelectric and piezoelectric properties of bulk $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ (BNFO) ceramics. The structural phase transitions from the polar $R3c$ phase ($x < 0.12$) to the polar $Pnma$ phase ($0.12 < x < 0.24$) and eventually toward the non-polar $Pnma$ three-phase coexistence across the intermediate range ($0.12 < x < 0.24$). Unfortunately, no piezoelectric enhancement has been identified at the two nominal MPBs. However, the Nd-substitution of Bi in the $R3c$ phase region ($x < 0.12$) does result in the $d_{33}$-enhancement, contributed by the domain refinement from the coarse and stripe-like domains to the small-size branched domain patterns. The largest $d_{33}$ value reaches $\sim 50$ pC/N for $x = 0.06–0.08$ from $\sim 30$ pC/N for pure BFO ceramics. The present work has unveiled the role of domain structures in modulating the piezoelectric properties of BFO ceramics, while the morphotropic phase boundary scenario needs furthermore consideration.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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