Structural and ferroelectric phase evolution in [KNbO_{3}]_{1−x}[BaNi_{1/2}Nb_{1/2}O_{3−δ}]_{x} (x=0,0.1)

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Structural and ferroelectric phase evolution in $[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$ (x = 0, 0.1)

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The phase transition evolution for $[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$ (x=0, 0.1) is determined via complementary dielectric permittivity and Raman scattering measurements. Raman scattering by optical phonons over the range of 100-1000 cm^{-1} for 83 K $< T <$ 873 K reveals six discernible zone-center optical phonon modes. Mode behaviors are observed through structural and ferroelectric phases in the solid solution $x = 0.1$ and compared with those for end member $x = 0$ and with the results of temperature-dependent dielectric permittivity. Rigorous peak fitting analyses of spectra collected from the solid solution and end member indicate structural and ferroelectric phase transition temperatures that are close to those for the $KNbO_3$ end member despite the inclusion of 5 atomic % of ferroelectrically inactive Ni cations. Density functional theory calculations were performed in the solid solution and end member using both cation displacement and Berry phase-based methods. Differences in the electronic and polar properties between the solid solution and the end member highlights local and non-local characteristics, which are discussed in relation to the experimental data.

I. INTRODUCTION

Ferroelectrics have long been recognized as an interesting alternative to conventional semiconductor junctions for photo-excited carrier separation and photovoltaic solar energy conversion[1–18], exhibiting the bulk photovoltaic (PV) effect[19–22] and other ferroelectric polarization-induced or polarization-influenced carrier separation mechanisms, including those due to domain walls and Schottky barriers. The design and realization of visible wavelength-absorbing ferroelectric oxide perovskites poses special challenges for practical photovoltaic solar energy conversion due to the inherently large band gap ($\gtrsim$ 2.7 eV) associated typically with an O $2p$ valence and a transition metal d conduction band. Inclusion of other B-site cations (*e.g.*, Pd, Pt, etc.), substitutionally, within $PbTiO_3$[23] has been proposed as a strategy for band gap lowering[24–27]. Introduction of Ni onto B-site $KNbO_3$ in the solid solution $[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$ ($x = 0.1$) (KBNNO) was shown to result in significant decrease in band gap without loss of ferroelectric ordering[10], and relatively large shift currents in KBNNO (compared with $BiFeO_3$) have been predicted[28]. Recently, room-temperature Raman scattering spectra in bulk ceramic KBNNO have been reported[29] for several different values of x.

Incorporation of ferroelectrically inactive cations can be accomplished without complete suppression of ferroelectricity. However, concomitant decreases in ferroelectric phase transition temperature, T_c, with inactive cation concentration can be expected in accordance with well-known systems, *e.g.* Zr in $PbTiO_3$ (PZT)[30], and Sr in $BaTiO_3$ forming the well-known incipient ferroelectric solid solution $Ba_{1-x}Sr_xTiO_3$ (BST)[31]. Raman scattering spectroscopy is effective for probing the onset of a phase transition with local correlation lengths as short as several unit cells. The structural evolution and determination of T_c in $KNbO_3$ and related A-site (A = Na, Li, La) solid solutions $ANbO_3$ (KNNO and KLNO) has been reported via temperature-dependent dielectric, Raman scattering, and infrared spectroscopic analyses[32–40]. Other studies of T_c evolution in doped $KNbO_3$ have also been reported[41–45]. Unlike systems that involve isovalent substitutions, such as PZT, BST, KNNO, $KTa_{1-x}Nb_xO_3$, and $K_{1-x}Li_xNbO_3$, the aliovalent substitution of Ni^{2+} onto the B-site of $KNbO_3$ is accompanied by formation of a neighboring O vacancy, producing localized tensile strain near the cation-vacancy pair. Ferroelectric phase stability is a key consideration for potential optoelectronic applications including PV solar energy conversion, making it important to consider the extent to which the substitutional incorporation of Ni cations influences the structural and ferroelectric phase stability in the solid solution KBNNO.

As summarized in Tables I and II, end member $KNbO_3$ possesses fifteen modes, including three acoustic and twelve optical phonons. Of the optical phonons, by symmetry, 3 A_1 + 4 E are first-order Raman-active in the rhombohedral ($R3m$ or C_{3v}^5) phase with an A_2 phonon mode as Raman silent, 4 A_1 + A_2+ 4 B_1 + 3 B_2 in the orthorhombic ($Amm2$ or C_{2v}^{14}) phase, and 3 A_1 + B_1 + 4 E in the tetragonal ($P4mm$ or C_{4v}^1) phase. First-order Raman scattering of the 3 F_{1u} + F_{2u} modes is forbidden in the centrosymmetric cubic ($Pm3m$ or O_h^1) phase. Atomic site disorder lowers translational symmetry, effectively relaxing Raman selection rules. This increases phonon scattering rates, manifesting as broadened lineshapes, complicating determination of peak positions and mode assignments[42–44,46]. Nevertheless, Raman-active mode assignments and transition temperatures in solid solutions such as (K,A)NbO_3 have been made and can also be accomplished in B-site solid solution systems, based on comparison with end members. Here, we report temperature-dependent dielectric response in bulk ceramic $KNbO_3$ and KBNNO. Using rigorous lineshape and peak fitting analyses, we show temperature-dependent evolution of the structural and ferroelectric phases in bulk ceramic KBNNO from 100-1000 cm^{-1} for 83 K $< T <$ 873 K, comparing our results with bulk ceramic $KNbO_3$. Finally, we present the results of density functional theoretical analysis, calculating the structural relaxation and electric polarization and theoretically estimating the T_c in order to compare with our experimental data.

II. EXPERIMENTAL METHODS

Samples of $[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$ (x = 0 and 0.1) are synthesized by standard solid-state reaction followed by a sintering process. High purity powders, including K_2CO_3 (J.T. Baker, 99.9%), $BaCO_3$ (Cerac, 99.9%), Nb_2O_5 (Cerac, 99.95%), and NiO (Cerac, 99%) are dried at appropriate temperatures to remove absorbed moisture. Stoichiometric amounts of starting powders are mixed by ball milling for $\geq$ 2 hours in ethanol with yttrium-stabilized ZrO_2 grinding media. After evaporation of ethanol, the raw mixtures for samples with $x = 0.1$ are calcined at 1073 K for 6 hours in a muffle furnace, while for $x = 0$ samples, 873 K for 6 hours is used. The calcined powders are ball milled for 12 hours to minimize the particle size and then uniaxially pressed into pellets of 8 mm diameter and 2-4 mm thickness. In order to minimize the volatilization of K during sintering, all pellet samples are buried in calcined powders with the same composition and encapsulated with platinum foil. Pellets are sintered at temperatures which depend on compositions, with a dwell time of 1 hour and 5 K/min ramp rate. KNO pellets are sintered at 1253 K and $x = 0.1$ is sintered at 1418 K. The bulk densities of sintered pellets are calculated through the weights and dimensions of the samples; both the $x = 0$ and 0.1 samples show above 92% relative density.

Powder X-ray diffraction measurements of sintered ceramics are carried out on a Rigaku GiegerFlex D/Max-B diffractometer (40 kV, 30 mA). For dielectric property measurements, sample pellets are first rough polished with 400 grit polishing paper to obtain parallel top and bottom surfaces. Electrodes are then applied to the pellet by coating the polished surfaces with silver paint (Heraeus ST1601-14 type). Platinum lead wires are attached to the surfaces using the same silver paint. Paint is dried and sintered at 1023 K for 20 min. to provide a dense electrical contact. The dielectric data are collected with a high-precision impedance-capacitance-resistance meter (Hewlett-Packard, model 4284A) and a high-temperature thermal chamber. The ferroelectric transitions in dense $(K_{0.5}Na_{0.5})NbO_3$ are used to precisely calibrate the temperature (Supplemental Material[62]).

Temperature-dependent Raman spectra are collected in the backscattering configuration $z(x, x+y)\overline{z}$ using a single monochromator (XploRA, Horiba Jobin-Yvon, Edison NJ), 4 mW, 532-nm laser excitation, focused through a 10x objective to a spot diameter of ≈10 μm at an intensity of 1.6×10^3 W/cm^2. Light is dispersed using 2400 gr/mm gratings and collected using a thermoelectrically cooled array detector. The spectral resolution of this confocal micro-Raman instrument under these conditions is ≈1.2 cm^{-1}. The sample temperature is varied from 83 K to 873 K (Linkham THMS 600, instrumental precision ±0.1 K) in increments of 2.5 K (for $KNbO_3$) and 5 K (for KBNNO) at a heating ramp rate of 5 K/min. The sample is also allowed to equilibrate for one minute between consecutive Raman scans.

We use density functional theory (DFT) calculations to examine the local structure and polarization caused by substitution of 0.1 $Ba(Ni_{1/2}Nb_{1/2})O_{2.75}$ (BNNO) into KNO. To directly and accurately model the low concentration of Ba and Ni dopant atoms, we use a 4×4×2 159-atom supercell, with $x = 0.125$ BNNO content. This cell contains 2 Ni atoms and 4 Ba atoms substituting at 2 Nb and 4 K sites. To maintain charge balance, one O atom is removed, in two different configurations. For the first configuration, the O vacancy is placed between two Ni atoms located at nearest-neighbor B-sites along the z-direction, while for the second the vacancy is located between an Nb and an Ni, and the two Ni are separated by 7 Å. For computational efficiency, we performed all calculations at the $KNbO_3$ lattice constants. This choice is supported by the results of the XRD measurements that show that the lattice parameters of $KNbO_3$ and $x = 0.1$ KBNNO are essentially the same. The positions of the ions were fully relaxed at the DFT+U level of calculations, using Hubbard U values of 3.97 eV and 9.9 eV for Nb and Ni, respectively, as in previous KBNNO calculations[10]. Calculations with other values of U showed only slight dependence of the relaxed structure on the U value, supporting the reliability of our choice of U.

The relaxed structures are analyzed for cation displacements which can then be used to evaluate the effect of the $Ba(Ni,Nb)O_{2.75}$ substitution on the local structure and to estimate the polarization by multiplying the cation displacements by their respective Born effective charge (Z^*) values. We also used Berry phase calculations to rigorously evaluate the polarization, with good agreement obtained between the approximate displacement-based and the Berry phase polarization values. The decomposition of P into the contributions of individual cation sites enables analysis of trends in overall P in terms of local structure changes.

III. RESULTS AND DISCUSSION

The powder x-ray diffraction results show the formation of a stable perovskite for all compositions, while very small NiO impurity peaks are present in samples of $x = 0.1$ (Figure 1). Dielectric permittivities and losses are obtained as a function of temperature and frequency (Figure 2). Samples of composition $x = 0.1$ show dielectric anomalies which indicate phase transitions at 683 K and 533 K. The lack of frequency dependence indicates normal ferroelectric behavior, since frequency-dependent dielectric response is characteristic of a relaxor.

Since phonon linewidths are temperature-dependent, vibrational mode assignment is most straightforward in low-temperature spectra (Figure 3, rhombohedral phase). Neither the KNO nor KBNNO samples are single-crystalline, and therefore the signal measured is an average of many oblique angles not strictly associated with phonon wave vectors either parallel or perpendicular to the specific crystallographic axes that would allow for the proper assignment of transverse and longitudinal optical (TO, LO) phonon modes[47]. Due to this formalism, the modes will be referred to as ≈190 cm^{-1}, ≈290 cm^{-1}, ≈430 cm^{-1}, ≈529 cm^{-1}, ≈600 cm^{-1}, and ≈836 cm^{-1}; respectively, for both KNO and KBNNO polycrystalline samples with the primarily contributing modes denote in Figure 3. For simplicity, a single assignment will follow each mode through softening, stiffening, and any abrupt changes due to structural changes in the sample, with the understanding that there are often many modes with overlapping phonon frequency making up a spectral feature. Comparable peak energies are observed in the KBNNO sample and correspond well to reported mode assignments in $KNbO_3$[36,37,48–51]. The TO_1 mode, associated primarily with ferroelectricity and the polarization of the material, corresponds to the central B-site Nb atoms oscillating against the oxygen octahedra and is shown in Figure 4. This mode is particularly indicative of polarization in the material due to the parallel alignment of the polarization vector and the Nb-O bond. The TO_2 mode corresponds to the A-site K atoms vibrating counter to the greater NbO_6 octahedral structure. The TO_3 mode corresponds to the B-site Nb atoms and the apical oxygen atoms

moving parallel along the polarization vector, anti-parallel to the equatorial oxygen atoms. The *A*-site K atoms do not dynamically participate in the TO_3 mode. The TO_4 mode corresponds to stationary *A* and *B*-site atoms and apical O atoms, while the equatorial oxygen atoms vibrate out of phase along the polarization direction, with each equatorial oxygen atom moving anti-parallel to its nearest equatorial oxygen neighbors.

Temperature-dependent Raman spectra for $KNbO_3$ (KNO) and KBNNO are shown in Figure 5. Peak fitting analysis is performed to quantify the variation of each peak's intensity, width, and position with temperature (Supplemental Material[62]). Bose-Einstein correction has been performed before any data analysis of structural phase transitions; in addition, the contour plots and stacked plots are normalized for the convenience of the reader, as the low-temperature data has much greater signal and lower background than the high-temperature data. Transition temperatures are then extracted from the KNO and KBNNO samples based on reported mode assignments, as cited above.

Changes in Raman peak positions and intensities are seen at particular temperatures corresponding to first-order structural phase transitions: rhombohedral (R) → orthorhombic (O) → tetragonal (T) → cubic (C) (Figure 5). While determination of phase transition temperatures can be done by inspection for some modes, detailed analysis is required for others (Supplemental Material[62]). For example, the transition temperatures are clear in KNO modes of ≈190 cm^{-1}, ≈290 cm^{-1}, ≈529 cm^{-1}, and ≈600 cm^{-1}; Figure 5). By contrast, the peaks in the KBNNO solid solution sample are much broader, and specific modes (*e.g.* for ≈190 cm^{-1} and ≈836 cm^{-1}) which disappear in the end member upon reaching the cubic phase do not disappear at temperatures well above the expected transition temperature for the cubic phase in the solid solution. Although the temperature dependence of the relative intensities, peak widths, and position are not as distinct as in KNO, the end member's behaviors can be used as a reference for mode assignment and to extract the phase transition temperatures for KBNNO.

The R → O transition temperature for KNO was established using the relative intensity, mode linewidth, and frequency for the ≈190 cm^{-1}, ≈290 cm^{-1}, ≈430 cm^{-1}, ≈529 cm^{-1}, and ≈600 cm^{-1} modes (Supplemental Material[62]), yielding a R→O transition temperature $T_{\mathrm{R\rightarrow O,\ KNO}}$ of 272.0±0.1 K (Table III). For the KBNNO sample the ≈190 cm^{-1}, ≈290 cm^{-1}, and ≈430 cm^{-1} modes also exhibited abrupt changes, yielding $T_{\mathrm{R\rightarrow O,\ KBNNO}} \approx 275\pm8$ K. A particularly clear example is seen in Figure 6a where the degenerate ≈290 cm^{-1} modes' frequency undergoes a sharp discontinuity which can be clearly observed in the KNO sample. This combination of modes contributing to the peak at ≈290 cm^{-1} softens with higher temperatures. The frequency behavior of the ≈290 cm^{-1} modes in KBNNO exhibits a transition and softens, although the mode is much more difficult to resolve due to the various neighboring overlapping modes at those temperatures. While the initial frequency discontinuity in the KBNNO sample is more subtle, the softening with temperature is much more dramatic for the solid solution when compared to the end member.

The O → T transition temperature in KNO (512±1 K) is determined from the behavior of the ≈190 cm^{-1}, ≈290 cm^{-1}, ≈430 cm^{-1}, ≈529 cm^{-1}, and ≈600 cm^{-1} modes. The KBNNO transition is ascertained from the ≈430 cm^{-1}, ≈529 cm^{-1} and ≈600 cm^{-1} modes with $T_{\mathrm{O\rightarrow T,\ KBNNO}}$ of 523±6 K. Determination of this transition temperature in KBNNO based on other modes, such as the combination of vibrational modes at ≈290 cm^{-1}, could not be accomplished without unacceptably large error. Weighted error analysis is performed using standard expressions for the probability distribution and weighting factors (Supplemental Material[62]). This effectively removes the contributions of the ≈290 cm^{-1} modes by weighting them by the inverse of their variance such that they do not significantly affect the KBNNO transition temperature. Specifically, the ≈430 cm^{-1} modes are useful for both the KNO and KBNNO samples and are significant for determining the O → T transition (Figure 6b).

Changes in the mode frequency for ≈430 cm^{-1} phonons signal the onset of the orthorhombic phase at ≈273 K. For increasing temperature, the modes at ≈430 cm^{-1} stiffens until the O → T transition occurs, beyond which the modes soften slightly until the frequency stabilizes. A decrease in intensity to the background noise level prevents analysis at higher temperature. This stiffening and softening behavior around the O → T transition in KNO is used to discern the KBNNO transition temperature by identifying the same stiffening and softening in the much broader behavior of the ≈430 cm^{-1} modes. Without the context provided by the response of KNO, assigning the maximum frequency of these modes is, at best, challenging considering the various features that affect the relative intensities, linewidths, and frequencies of the Raman modes with temperature, including through structural phase transitions[52–55].

The highest-temperature tetragonal to cubic transition, corresponding to the ferroelectric to paraelectric transition, in the KNO sample occurs at 729.2±0.2 K, as is most easily seen in the ≈190 cm^{-1}, ≈529 cm^{-1}, ≈600 cm^{-1}, and ≈836 cm^{-1} modes. At this temperature, the ≈290 cm^{-1} modes have broadened to the point where the TO_1 and TO_4+LO_4 contributions are indistinguishable. Additionally, the modes at ≈290 cm^{-1} and ≈430 cm^{-1} that give signal above the background at lower temperatures have decreased or vanished as expected from previous studies of the mode evolution in KNO[36,37,48–51]. The ≈190 cm^{-1}, ≈529 cm^{-1}, and ≈600 cm^{-1} modes in the Raman spectra for the KBNNO sample yield $T_{\mathrm{T\rightarrow C,\ KBNNO}} \approx 736\pm7$ K. Through this transition temperature, the ≈600 cm^{-1} mode condenses into the ≈529 cm^{-1} mode to become a single mode at high temperatures[38] for both KNO and KBNNO (Figure 5). The temperature dependence of the Raman mode frequency for the ≈529 cm^{-1} mode can be traced until it becomes indistinguishable with the ≈600 cm^{-1} mode (Figure 7a). As expected with ≈529 cm^{-1}, there is a general

softening through the rhombohedral, orthorhombic, and tetragonal phases and transitions and significant changes to the mode linewidth through the various transitions as well (Figure 7b). Coalescing of ≈529 cm^{-1} and ≈600 cm^{-1} to degeneracy near ≈560 cm^{-1} is most clearly seen in Figure 7c. The amplitude of ≈600 cm^{-1} in KNO is seen to increase discontinuously at the transition temperature we assign to the merging of this mode with the ≈529 cm^{-1}. This justifies allowing the fitted amplitude of ≈600 cm^{-1} to decrease to zero as the two modes become degenerate (Supplemental Material)[52,54,62].

DFT calculations are performed for cation configurations where the vacancy is located between two Ni atoms and also where the vacancy is located between Ni and Nb atoms, with another Ni surrounded by 6 O atoms. We find that the configuration with the vacancy between the two Ni is lower in energy by 1.48 eV. Such a large energy difference suggests that KBNNO will mostly contain Ni-O_{vac}-Ni configurations.

In a 4×4×2 supercell, x and y are the long directions and z is the short direction. We place the two Ni along the x direction and relax all ions starting with the cations displaced along ⟨111⟩. Berry phase polarization calculations for the relaxed structure indicate that the values of the polarization components in the x, y and z directions are 0.142 C/m^2, 0.192 and 0.208 C/m^2, respectively. The polarization values in the y and z directions are slightly smaller than the 0.233 C/m^2 obtained for the x, y and z P components of the $KNbO_3$ parent material in the 0 K rhombohedral phase. The polarization component along the x direction is more significantly reduced to 0.142 C/m^2. Examination of the local displacements shows that the introduction of BNNO leads to a distribution of the local Nb displacements, with Nb off-centering magnitudes in a given Cartesian direction varying from 0 to 0.135 Å with the average Nb displacement magnitude of 0.16 Å. These average displacement values are smaller than the 0.103 Å displacements along the x, y and z direction found for $KNbO_3$ by our DFT calculations.

Using a previously established correlation between the experimentally observed T_c and the square of the 0 K DFT polarization[56–60], we estimate a decreased T_c for KBNNO of either ≈433 K based on the average total P, or ≈573 K based on the average magnitude of the Nb displacements related to the local polarization. While also predicting a stable room-temperature ferroelectricity in KBNNO, these values underestimate both the dielectric tetragonal to cubic (T-C) transition temperature of 683 K as well as the 736 K T-C transition temperature extracted from the Raman results. This discrepancy could be ascribed to the somewhat qualitative nature of the correlation between T_c and P^2 for materials with different local structures. The presence of Ni + O_{vac} introduces structural motifs into KBNNO that are entirely absent in KNO, diminishing the predictive accuracy of the $T_c - P^2$ correlation.

The DFT finding of a distribution of Nb displacement magnitudes and variation in the local structure is consistent with broadening in both the dielectric and Raman data, including the Raman linewidth. In particular, the temperature evolution of the Raman shift used to assign the T-C transition temperature changes from an abrupt drop at T_c observed for KNO to a gradual decrease to a constant value observed for KBNNO. It is likely that the distribution of local environments found in KBNNO leads to a broader distribution of Raman shifts, with the local environments displaying enhanced (relative to KNO) Nb displacements accounting for the higher temperature plateauing of the Raman shift that signifies the presence of the T-C transition. Such dependence of the Raman shift on the distribution of local structures (*i.e.* on the strong displacement contributions) is perhaps the explanation for the disagreement between the enhanced T_c found by Raman results and the decreased T_c found by the dielectric measurements. The dielectric results are given by the average structure of the material, where a decrease in the displacement and P is observed for KBNNO, corresponding to a less stable P and a lower FE-PE transition temperature. On the other hand, the Raman measurements are sensitive to the variation in the local structure, where some local environments exhibit enhanced 0 K displacements that are likely to persist to higher temperature than the FE structure in the parent KNO material.

IV. CONCLUSIONS

Dielectric permittivity measurements and Raman spectroscopy are used to probe temperature-dependent structural and ferroelectric phase evolution. Changes in the temperature-dependent Raman shifts are diffuse in KBNNO as compared with abrupt transitions observed in the end member KNO. Taken together with variations in DFT-calculated local atom displacements and local and averaged polarizations (the extent of applicability of $T_c - P^2$ scaling notwithstanding), and the absence of frequency dispersion in the dielectric permittivity, these results indicate persistence of ferroelectric ordering in KBNNO to temperatures that approach the T_c of the end member $KNbO_3$. This identification of structural and ferroelectric phases, combined with the ability to tune these solid-solution ceramic materials compositionally, highlights these oxides' promising application as semiconducting ferroelectric absorbers and carrier separating layers in novel photovoltaic devices.

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TABLE I. Twelve optical phonon modes of KNO, as predicted by Postnikov *et al.*[61] for the room temperature orthorhombic phase. Included are experimental values from this study.

Mode	Symm.	Calculated Frequency (cm^{-1})	Experimental Values (cm^{-1})
	B_2	soft	
TO_1	B_1	232	250
	A_1	257	296
	B_2	185	192
TO_2	B_1	146	a
	A_1	186	275
	B_2	467	532
TO_3	B_1	528	b
	A_1	593	596
	B_1	297	c
TO_4	A_1	307	c
	A_2	224	c

[a] indistinguishable with $B_2(TO_2)$
[b] indistinguishable with $B_2(TO_3)$
[c] indistinguishable with $A_1(TO_1)$

TABLE II. Summary of optical modes associated with the four structural phases in KNO and KBNNO.

Phase	Space Group	Point Group	Optical Modes
Rhombohedral	$R3m$	C_{3v}^5	3 $A_1(T_z,\alpha_{xx}+\alpha_{yy},\alpha_{zz})$ + A_2^* + 4 E $(T_x,T_y,\alpha_{xx}-\alpha_{yy},\alpha_{xy},\alpha_{xz},\alpha_{yz})$
Orthorhombic	$Amm2$	C_{4v}^{14}	4 $A_1(T_z,\alpha_{xx},\alpha_{yy},\alpha_{zz})$+ $A_2(\alpha_{xy})$+ 4 $B_1(T_x,\alpha_{xz})$ + 3 $B_2(T_y,\alpha_{yz})$
Tetragonal	$P4mm$	C_{4v}^1	3 A_1 $(T_z, \alpha_{xx}+\alpha_{yy},\alpha_{zz})$ + $B_1(\alpha_{xx}-\alpha_{yy})$ + 4 $E(T_x,T_y,\alpha_{xz},\alpha_{yz})$
Cubic	$Pm3m$	O_h^1	3 $F_{1u}^*(T_x, T_y, T_z)$ + F_{2u}^*

* mode is not Raman active

TABLE III. Summary of structural phase transition temperatures as determined from Raman.

	Rhombohedral → Orthorhombic (R→O)	Orthorhombic → Tetragonal (O→T)	Tetragonal → Cubic (T→C)
KNO	272.0±0.1 K	512±1 K	729.2±0.2 K
KBNNO	275±8 K	523±6 K	736±7 K

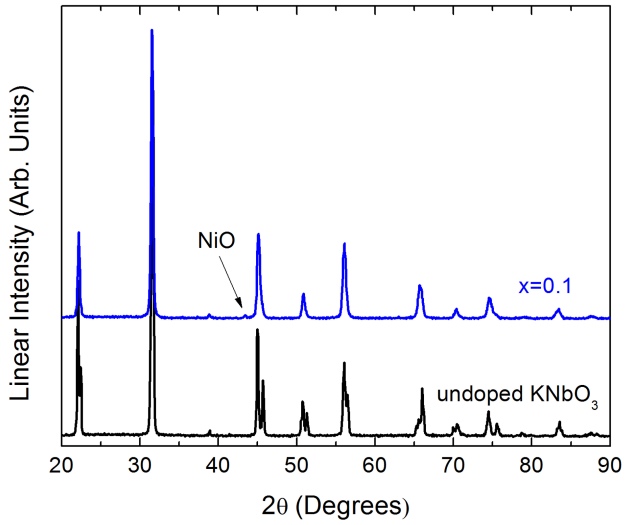

FIG. 1. X-ray diffraction spectra of end member KNO and $x = 0.1$ KBNNO stoichiometry. Arrows indicate the inclusion of NiO. Additional stoichiometries available in Supplemental Material[62].

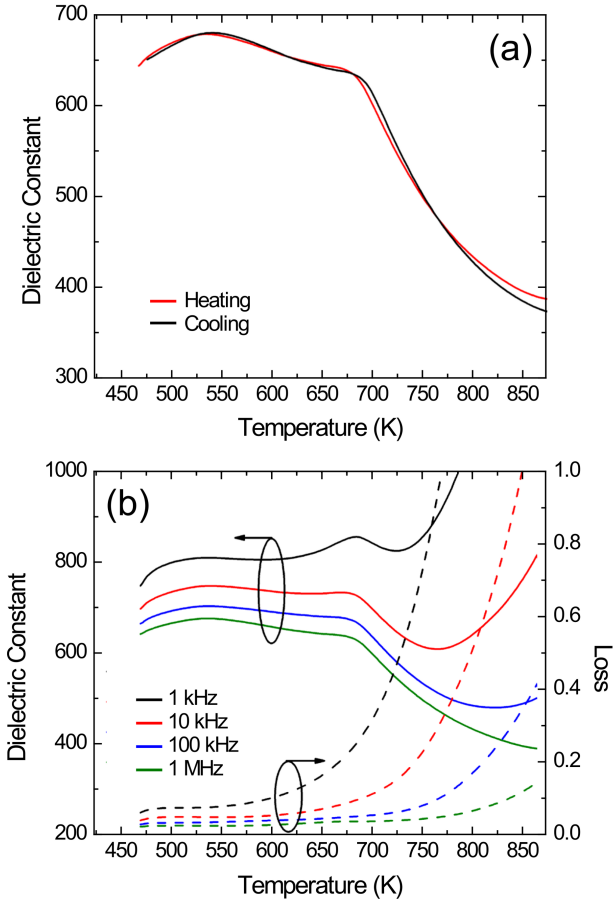

FIG. 2. Temperature dependence of dielectric permittivity measured at 1 MHz for (a) KBNNO $x = 0.1$; heating cycle and cooling cycle are red and black respectively. (b) Temperature-dependent dielectric permittivity and loss of KBNNO $x = 0.1$ for various E-field frequencies.

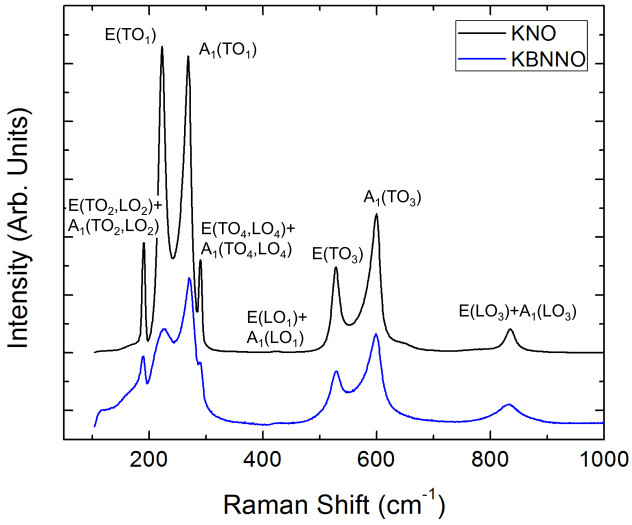

FIG. 3. Raman spectra of the KNO and KBNNO samples in the rhombohedral phase collected at 83 K with approximate mode assignments from bulk and polycrystalline litterature showing overall agreement between end member KNO and solid-solution KBNNO[36,37,48–51].

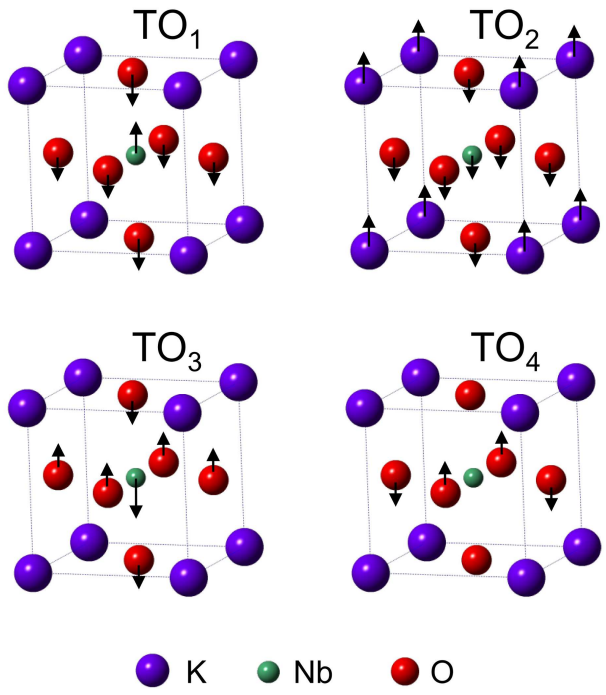

FIG. 4. Ionic displacements associated with the four transverse optical phonons from lattice dynamics calculations[37].

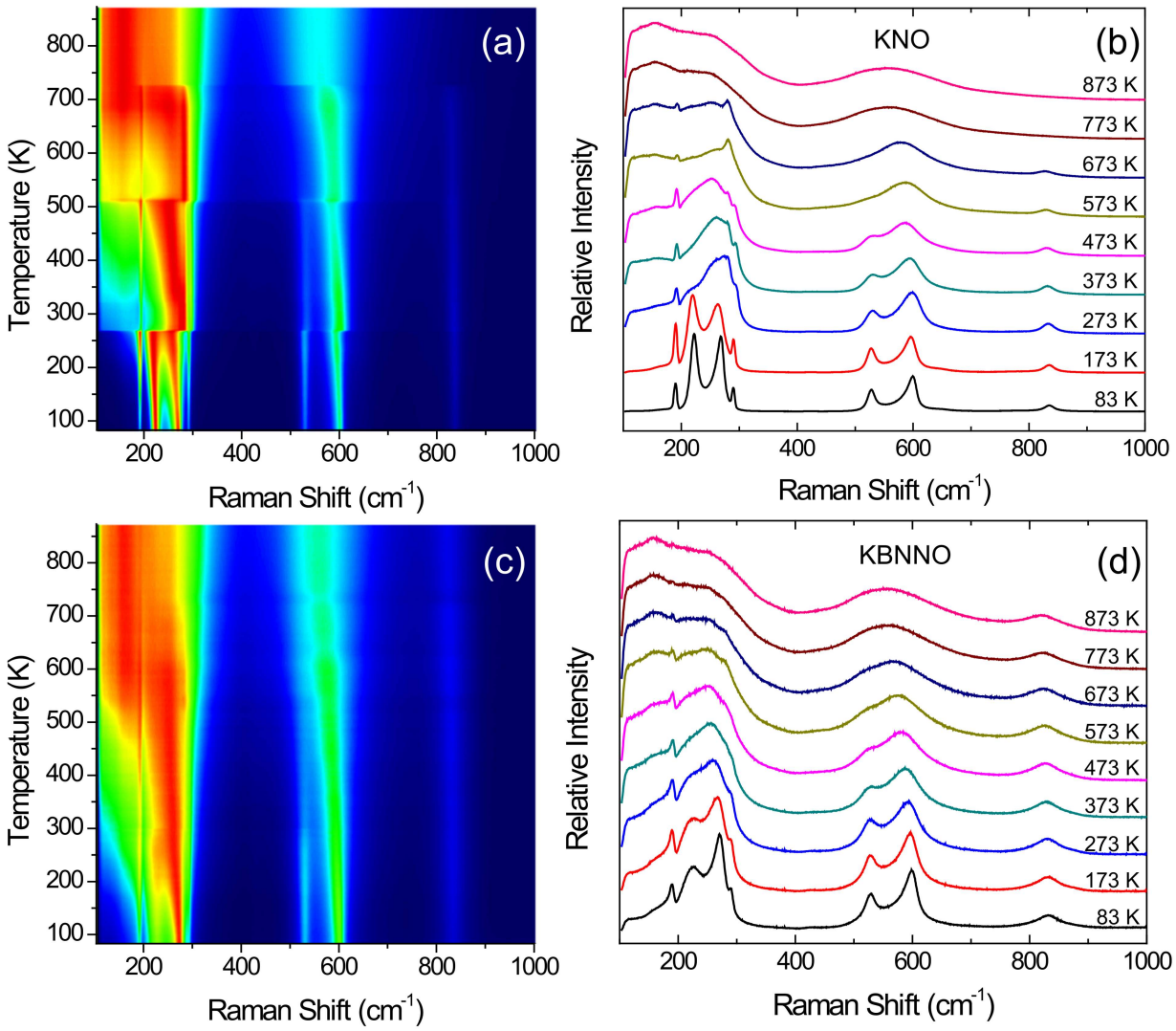

FIG. 5. Raman scattering spectra of KNO ceramic materials as a color map (a) and at selected temperatures (b). Raman spectra of KBNNO ceramic materials is shown as a color map (c) and at selected temperatures (d). Phase transitions more evident in KNO, but both ceramics show spectral characteristics revealing $R \rightarrow O \rightarrow T \rightarrow$ C phase transitions.

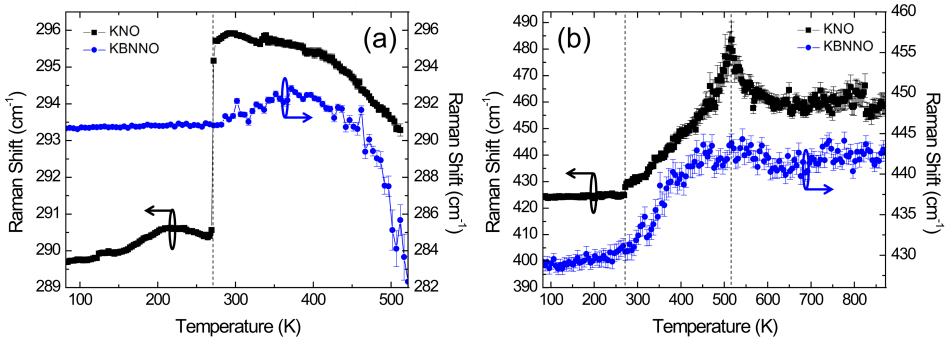

FIG. 6. (a) Temperature dependence of the overlapping phonon modes near 290 cm^{-1}. While a >4 cm^{-1} increase in peak energy is seen for KNO, signaling the R $\rightarrow$ O transition, a much smaller change is observed for KBNNO, as confirmed by analysis of the ≈430 cm^{-1} mode. (b) Temperature dependence of the ≈430 cm^{-1} modes shows a maximum stiffening which signals the O $\rightarrow$ T phase transition in KNO; a broader, weaker maximum is also seen at the same temperature in KBNNO. Vertical dashed lines correspond to determined phase transition temperatures in KNO.

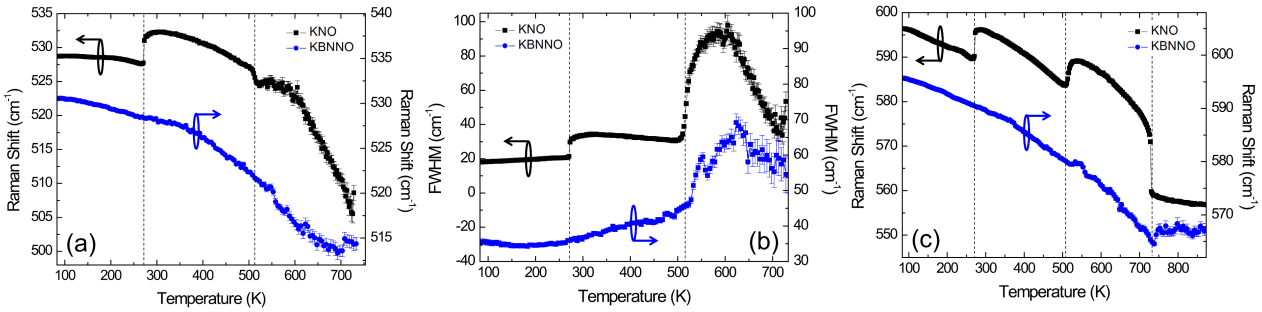

FIG. 7. Comparison of the fitted temperature dependences of the ≈529 cm^{-1} and ≈600 cm^{-1} modes (a) energy and (b) linewidth in KNO and KBNNO, enabling extraction of the O → T transition temperature; the ≈529 cm^{-1} modes become degenerate with the ≈600 cm^{-1} in the cubic phase and is only shown in (c). (c) Comparison of the ≈600 cm^{-1} mode softening in KNO and KBNNO. The behavior of the KNO and KBNNO modes here is qualitatively similar and, upon phase transition, the ≈600 cm^{-1} becomes degenerate with the ≈529 cm^{-1} modes to collect around 560 cm^{-1} enabling determination of T → C transition temperatures.