# Local structural mechanism for phase transition and ferroelectric polarization in the mixed oxide K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>

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 $(K_x Na_{1-x})NbO_3$  (KNN) and its solid solutions are considered as potential alternatives to traditional Pb-based piezoelectric materials. Recent investigations indicated that the local structure in KNN is much more complex than its long-range average structure. Here, we have undertaken a systematic investigation of the temperaturedependent evolution of local and average structures of KNN5 [ $(K_x Na_{1-x})NbO_3, x = 0.5$ ] using time of flight neutron scattering. Rietveld analysis of neutron diffraction patterns indicated that the average structure of KNN5 changes from monoclinic to tetragonal to cubic upon heating from 100 to 773 K. In contrast, analysis of neutron pair distribution function (PDF) indicated that the local structure stays monoclinic within the above temperature range. Based on comparative analysis of local and average structures, it is proposed that the average structural phase transitions in KNN5 are partly derived from a local ordering of the polar units, which are correlated over a length of  $10 \sim 15$  Å. A clear indication of order-disorder type transition at 473 K is evident from the temperature-dependent PDF patterns. Additionally, based on local structural analysis, it is shown that large electrical polarization in KNN5 can be attributed to displacements of both *A*-site and *B*-site atoms. These structural insights may help in further optimization of electrical properties of Pb-free KNN piezoceramics.

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## I. INTRODUCTION

Piezoelectric ceramics, or piezoceramics in short, are widely used in sensors, actuators, ultrasonic transducers, and energy-harvesting devices, owing to their exceptional ability for electromechanical transduction [1]. Due to their large piezoelectric coefficient and high Curie temperatures  $(T_c)$ solid solution of  $PbZr_{1-x}Ti_xO_3$  (PZT) [2], and PZT-based ceramics are widely used in many electronic devices [1]. The peak piezoelectric properties in PZT are observed for x = 0.48, which constitutes a morphotropic phase boundary (MPB) [2]. However, since PZT ceramics contain up to 60% Pb by weight, which can cause environmental pollution and accumulate in the human body, various legislations have been passed since 2001 that encouraged research and development (R&D) of lead-free piezoelectric materials [3]. Among the Pb-free candidates,  $(K_x Na_{1-x})NbO_3$ -based ceramics are considered as a promising class of materials due to their large piezoelectric coefficients and high Curie temperatures  $T_c$  in the range of 400  $\sim$  500 °C. For pure (K<sub>x</sub>Na<sub>1-x</sub>)NbO<sub>3</sub>, maximum piezoelectric constant and high  $T_c$  are reported near x = 0.5 [4–8], although the underlying reason for such enhancements in properties remains unclear [9]. It was argued that the peak electrical properties for  $(K_r Na_{1-r})NbO_3$  near x = 0.5 can be attributed to the presence of an MPB [10–12], similar to what is observed for PZT. However, the structural changes across the MPB in  $(K_x Na_{1-x})NbO_3$  are very subtle, in contrast to those in PZT. Later, it has been suggested that the enhanced properties in  $(K_x Na_{1-x})NbO_3$ -based ceramics stem from a polymorphic phase transition from orthorhombic to tetragonal (O-T) phase near room temperature [13–15]. Although phase boundaries are considered to play an important role towards the high piezoelectric properties, the underlying structural complexities have made it difficult to unambiguously determine the microscopic mechanism for phase transitions in  $(K_x Na_{1-x})NbO_3$  and their exact role towards the enhanced properties.

The long-range crystallographic structure of  $(K_x Na_{1-x})NbO_3$  solid solutions have been extensively studied in the past. The phase diagram of  $(K_r Na_{1-r})NbO_3$ was reported by Jaffe et al. in 1971 [8], and by Ahtee and Glazer in 1976 [16], which included multiple phases with different oxygen octahedral tilting modes and cation displacements. In general, it was considered that upon heating,  $(K_x Na_{1-x})NbO_3$  transforms from rhombohedral (R) to orthorhombic (O) to tetragonal (T), and finally to a cubic (C) phase. Nevertheless, there exists a debate about the crystal structures of different phases in  $(K_rNa_{1-r})NbO_3$ . For example, recent works revealed that the crystal structure of  $K_{0.5}Na_{0.5}NbO_3$  at room temperature can be described as monoclinic with *Pm* space group, instead of the traditionally considered orthorhombic Amm2 space group [17–22]. Gupta et al. pointed out that the transformation from Amm2 to Pm

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suggests a loss of mirror plane and a twofold axis, which primarily arise due to a mismatch in the ionic radii of K<sup>+</sup> (1.64 Å) and Na<sup>+</sup> (1.39 Å) [23,24]. Since the *A* site is partially occupied by Na<sup>+</sup> and K<sup>+</sup>, the *A*–O bond distance is not homogeneous in (K<sub>x</sub>Na<sub>1-x</sub>)NbO<sub>3</sub> [25,26]. Consequently, the structure in (K<sub>x</sub>Na<sub>1-x</sub>)NbO<sub>3</sub> is more disordered as compared to the end members KNbO<sub>3</sub> and NaNbO<sub>3</sub>, with pronounced crystallographic distortions at short length scales ~10 Å [21,23].

Therefore, to understand the "structure-property" relationship for such mixed oxide compositions, characterization of the average structure from analysis of Bragg diffraction alone may not be sufficient. Instead, the pair distribution function (PDF), which informs about the pairwise atomic correlations as a function of interatomic distance, r, is a useful method for characterizing the local atomic structure [27]. Experimentally, PDF is obtained from Fourier transformation of x-ray/neutron total scattering patterns (containing information of both Bragg and diffuse scattering). Since no requirement for translational symmetry is imposed *a priori* in this method, PDF is particularly sensitive to the local-scale atomic correlations, which are not discernible from analysis of the Bragg diffraction peaks alone. In the past, the application of the PDF method revealed unique local structural information in many ferroelectric materials. For example, Egami et al. showed for Pb-based ferroelectrics, such as Pb(Zr, Ti)O<sub>3</sub>, Pb(Sc, Ta)O<sub>3</sub>, and Pb(Mg, Nb)O<sub>3</sub> [28-30], the local bonding environment of Pb<sup>2+</sup> remains unchanged up to 1000 K, even though there are multiple phase transitions characterizing changes in the average crystal structure [31]. Similar differences between local and average structures were also observed for Pb-free ferroelectrics, such as NaNbO<sub>3</sub>, Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>, and BaTiO<sub>3</sub> [32-34]. Recent PDF studies on KNN also indicated significant differences between the local and average atomic structures, which are caused due to difference in the ionic sizes of K<sup>+</sup> and Na<sup>+</sup> that leads to oxygen octahedral tilting disordering [21,26]. Especially, the local structure of KNN within 20 Å is different from the average crystal structure [21]. Nevertheless, a comparative analysis of the evolution of the average and local structures as a function of temperature in KNN is lacking, which is necessary to better elucidate the origin of enhanced properties at certain phase boundaries.

Here, we have systematically studied the structural evolution in KNN5 [( $K_x Na_{1-x}$ )NbO<sub>3</sub>, x = 0.5] at different length scales from 100 to 773 K. The average long-range structure, as a function of temperature, was analyzed by Rietveld refinement of neutron powder-diffraction patterns, while the local structure was analyzed from neutron total scattering patterns and PDF analysis. Our analysis indicates that although the long-range average structure undergoes three different phase transitions upon heating from 100 to 773 K (monoclinic to tetragonal to cubic), the local structure up to  $\sim 10$  Å length scale remains monoclinic at all temperatures. Furthermore, the local monoclinic structure retains a polar character due to octahedral distortions, and this local polarization acts as a driving force for long-range structural ordering. A structural evolution model is proposed in which the average long-range phase transitions in KNN5 are a consequence of increasing local-scale atomic (dis)order. Additionally, it is shown that large ferroelectric polarization in KNN5 results from displacements of both *A*-site and *B*-site ions. These results provide insights into the local atomistic mechanisms for multiple phase transitions in KNN5 and elucidate the origin of large functional properties near the different phase boundaries.

## **II. EXPERIMENT**

## A. Materials preparation

 $K_{0.5}Na_{0.5}NbO_3$  (KNN5) powders were prepared by a traditional solid-state reaction. K<sub>2</sub>CO<sub>3</sub> (Sigma-Aldrich, 99.7%),  $Na_2CO_3$  (Sigma-Aldrich, ~100%), and  $Nb_2O_5$  (Sigma Aldrich, 99.9%) were ball milled in ethanol for 24 h. The mixed powder slurry was dried and then calcined at 800 °C for 4 h. Then the calcined powder was ball milled for another 24 h, dried, and calcined again at the same condition. After a second ball milling, the dried powders were ground, mixed with polyvinyl alcohol, and sieved through  $100-\mu m$  mesh. Then the granulated powders were pressed into pellets of diameter 10 mm and thickness 1 mm with a pressure  $\sim$ 34.5 MPa. The pellets were placed in an alumina crucible and sintered in air at 1100 °C for 4 h. During sintering, the green pellets were covered with powders of the same composition KNN5, to compensate for the volatilization of certain elements. The sintered pellets were then ground, and the obtained powder was sieved through 100- $\mu$ m mesh to get fine uniformly sized powder for neutron diffraction and differential scanning calorimetry (DSC) experiments.

## B. Materials characterization

Time of flight neutron-scattering experiments were performed at the NOMAD BL1B instrument of the Spallation Neutron Source. The powdered sample was loaded into a vanadium can of diameter  $\sim 6$  mm for the data collection on the automatic shifter. A cobra cryostream was used to control the temperature from 100–290 K. Data at higher temperatures (373-773 K) were collected in an ILL furnace. Powder samples were filled into the standard NIST vanadium can with a diameter of 6 mm. Two ~24-min datasets were collected at each temperature, which were then summed together to improve the measurement statistics. For each temperature, background intensity measured from an empty vanadium can was subtracted from the neutron-scattering intensity of the sample. The background-corrected intensity was subsequently normalized against signal from a 6-mm vanadium rod to correct for detector efficiency. The thermal analysis of the powder samples was done on a differential scanning calorimetry instrument (DSC 404 F3, Netzsch) at a heating rate of 10 K/min.

## **III. RESULTS AND DISCUSSION**

## A. Average structure analysis of KNN5

Figure 1(a) shows the neutron diffraction patterns of KNN5 ceramic powders as a function of temperature from 100 to 773 K. All the diffraction peaks could be indexed using KNN5 perovskite phases, with the presence of a small amount of (<1%) undetermined secondary phase. The neutron diffraction patterns at 773 and 673 K were indexed based on an ideal cubic structure with the space group  $Pm\bar{3}m$ . At 573 K, the (220), (311), (320), (400), (420), and (422) peaks are



FIG. 1. (a) Evolution of the neutron diffraction patterns of  $K_{0.5}Na_{0.5}NbO_3$  (KNN5) as a function of temperature from 100 to 773 K. The *x* axis refers to the wave transfer vector **Q**. *h k l* reflections are indexed based on a cubic perovskite structure. The arrows mark changes in *h k l* peak profiles, which indicate phase transitions. (b) DSC profile for KNN5 powder from 400 to 800 K, showing endothermic peaks marking the onset of phase transitions behavior on heating. (c) Phase diagram for  $K_xNa_{1-x}NbO_3$ , showing phase evolution with temperature. KNN5 undergoes a monoclinic to tetragonal phase transition at  $T \sim 471-473$  K and a tetragonal to cubic phase transition at  $T \sim 673-674$  K.

split (marked with arrows), which indicates a noncubic phase at this temperature. Another change in the above *hkl* peak profiles is apparent at  $\sim$ 373 K, such as for the (220) peak, the shoulder at higher Q disappears and another shoulder appears at a lower Q value. This indicates a structural transition to a lower symmetry phase below 473 K. Figure 1(b) shows heat flow measured using DSC during heating of the powder samples over 400  $\sim$  800 K. The peaks in the DSC curve indicate phase transitions at  $T \sim 471$  K and  $T \sim 674$  K, which is consistent with the changes in different *hkl* diffraction peak profiles shown in Fig. 1(a) at these temperatures. The phase transition at  $T \sim 674$  K is consistent with the earlier reported phase diagram of KNN [8,19,20], which indicated a tetragonal to cubic phase transition upon heating at this temperature, as shown in Fig. 1(c). Based on earlier studies, the DSC peak at  $T \sim 471$  K can be attributed to a transition from tetragonal to either monoclinic [20,22] or orthorhombic [8] phase.

To resolve the average long-range structural phases in KNN5, the temperature-dependent neutron diffraction patterns were analyzed by Rietveld refinement using the software GENERAL STRUCTURE ANALYSIS SYSTEM (GSAS II) [35]. The structural parameters, viz., unit-cell constants, atomic coordinates, and atomic displacement parameters were refined against the experimental data. During refinement, the structural coordinates and atomic displacement parameters were constrained to be identical for K and Na atoms, since refining them separately resulted in unstable refinement. The quality of the fits was assessed based on weighted residuals  $R_{\rm w}$  [36]. To check the stoichiometry, after refining all the structural parameters, the occupancies for A-site cations, K<sup>+</sup> and Na<sup>+</sup>, were refined (given the constraint that the total occupancy should be 1), which provided values of 0.486(5) and 0.513(5), respectively. Since the deviation from the nominal composition was very small, the occupancies were subsequently fixed at 0.5 for refinement of other structural parameters.

A cubic  $Pm\bar{3}m$  structure model was used to refine the experimental data at 773 and 673 K, for which the obtained  $R_{\rm w}$  was 4.87 and 5.80%, respectively. The experimental and calculated diffraction profiles are shown in Figs. 2(a) and 2(b). At 573 K, a tetragonal P4mm structure model provides the best fit to the diffraction pattern, yielding an  $R_{\rm w}$  of 4.98% [Fig. 2(c)]. At the phase transition temperature of  $T \sim 473$  K, the measured diffraction pattern could not be satisfactorily fitted using a single-phase model, which is further addressed below. All the diffraction patterns measured at or below 373 K (shown in pink and red in Fig. 1) appear to be similar, which indicates no change in the average crystal structure occurs below this temperature. However, earlier studies variously described the room-temperature structure of KNN5 as either monoclinic (Pm space group) [20] or orthorhombic (Amm2 space group) [8]. To resolve this issue, we compared the Rietveld refinement fits using either Pm or Amm2 space group. The experimental and calculated profiles using the Pm space group are shown in Fig. 2(f); the corresponding fit using the Amm2 space group is shown in Supplemental Material, Fig. S1(a) [37]. The relatively lower  $R_w$  obtained for the *Pm* model ( $R_w$  of 4.48%) over that of the *Amm*<sup>2</sup> model ( $R_w$ of 4.94%) indicates the appropriateness of the former. More importantly, it was observed that the individual *hkl* peaks were better reproduced using the Pm space group, such as the (320) reflection shown in the inset of Fig. 2(f). This was also observed for the diffraction patterns measured at 373 and 100 K [Figs. 2(e) and 2(g)] (for Amm2 see Figs. S1(b) and S1(c) in the Supplementary Information [37]).

For the diffraction pattern measured at 473 K, the best fit was obtained using a two-phase "Pm+P4mm" model, as shown in Fig. 2(d). Instead, using only a single tetragonal phase P4mm space group led to a significantly worse fit with a correspondingly high  $R_w$  of ~7.52% (see Supplemental Material for details) [37]. It can therefore be concluded that



FIG. 2. Diffraction patterns of KNN5 powder at different temperatures showing measured (black symbol), refined (red line), difference (blue line) profiles, and Bragg positions (green ticks). The data shown are from BANK 5 of the NOMAD instrument. The Rietveld refinements were carried out using the software GSAS II. (a) Refinement using  $Pm\bar{3}m$  at 773 K; (b) Refinement using  $Pm\bar{3}m$  at 673 K; (c) Refinement using Pmm at 573 K; (d) Refinement using two phases P4mm and Pm at 473 K; (e) Refinement using Pm at 373 K; (f) Refinement using Pm at 290 K; (g) Refinement using Pm at 100 K. Weighted residuals  $R_w$  are shown for all the refinements. The insets in (e)–(g) show a comparison between experimental (symbols) and calculated (line) peak profiles for the 320 reflection.

both monoclinic and tetragonal phases coexist at 473 K, which may explain the enhanced piezoelectric properties at the phase transition temperature of  $T_{T-M} \sim 473$  K [3].

Note that the neutron diffraction patterns were recorded using all six banks of NOMAD. The diffraction data of the middle four banks ( $2\theta = 31^\circ, 67^\circ, 122^\circ, \text{ and } 154^\circ$ ) were fitted simultaneously. Figure 2 only shows the neutron diffraction patterns from BANK 5 of the instrument, which has the highest resolution. The diffraction data and corresponding fits from the other BANKs are shown in the Supplemental Material (Figs. S2, S3, and S4) [37]. The refined structural parameters such as unit-cell constants, atomic coordinates, and thermal factors at various temperatures are shown in Table I.The average structural parameters as a function of temperature are plotted in Figs. 3(a)-3(d). While the lattice constants a and c exhibit discontinuous changes at the tetragonal to monoclinic phase transition temperature  $T_{T-M}$ , b increases gradually with an increase in temperature from 100 to 773 K. Similarly, as shown in Fig. 3(d),  $\beta$  for the long-range average structure remains slightly higher than 90° below 473 K, but approaches 90° above 473 K. In the next section, we will compare the temperature-dependent changes in the long-range average structural parameters with that of local structural changes determined from analysis of neutron PDF.

#### B. Local structure analysis of KNN5

Since earlier works indicated a difference in local and average structures of KNN, we investigated the local structure using PDF analysis. The pair distribution function G(r) is calculated from the sine Fourier transformation of the timeof-flight neutron total scattering data. PDFs for KNN5 at 100 K~773 K in the range of  $r \sim 1.7-40$  Å are shown in Fig. 4(a). We analyzed G(r) at different temperatures for  $r \sim$ 1.7~40 Å using structural parameter from Rietveld refinement as a starting point, shown in Fig. S5. It was indicated that the local and average structure of KNN5 approach each other at a longer distance  $\sim 40$  Å (see Supplemental Material for details) [37]. Moreover, in Fig. 4(a), it is evident that the PDF peak profile changes most significantly within  $r \sim 1.7-3$  Å with temperature over the range of  $100 \sim 773$  K. Therefore, to further explore the length scale-dependent structural evolution, a "boxcar"-type refinement was carried out. This method was earlier used to characterize the lattice parameters variation at different length scales in Pb-free ferroelectrics such as Refs. [38,39]. All refinements were carried out using the software PDFGUI [40].

The boxcar fitting of KNN5 was done at 100 K since the amplitude of atomic thermal vibrations are small and thus the atomic positions could be determined more accurately at this temperature. The starting parameters for the boxcar fitting were obtained from the Rietveld refinement results of the long-range average structure at 100 K using the *Pm* space group, as discussed above. A size of 10 Å for fitting boxes and a step size of 2.5 Å were used for boxcar fitting of the *G*(*r*) patterns in the range from 1.7 to 40 Å. The lattice parameters *a*, *b*, *c*, and angle  $\beta$  of the monoclinic unit cell was adjusted, together with the thermal parameters, until the best possible fit to the experimental data was achieved. The quality of the fits was assessed visually and from the values



FIG. 3. Unit-cell parameters for KNN5 as a function of temperature from 100 to 773 K: (a) lattice parameter *a*; (b) lattice parameter *b*; (c) lattice parameter *c*; (d) interaxial angle  $\beta$ . Pink closed circles represent lattice parameters for the local structure from fits to *G*(*r*) of  $r \sim 1.7-10$  Å, while navy open circles represent lattice parameters for the average structure from Rietveld refinement of neutron diffraction patterns. Vertical dotted lines represent phase transition temperatures in average structure. The letters M, T, and C mark the temperature range with the average phases of monoclinic, tetragonal, and cubic, respectively.

of the weighted residuals  $R_w$ . Figures 4(b) and 4(c) show measured and calculated neutron G(r) profiles at 100 K in the range of  $r \sim 1.7-10$  Å and  $r \sim 30-40$  Å. The G(r) profiles for other r ranges are shown in Fig. S6, which shows that all

TABLE I. Structural parameters, fractional atomic coordinates, and equivalent isotropic displacement parameters ( $U_{iso}$ in A <sup>2</sup> ) from the
Rietveld refinement and 1.7–10-Å range PDF fit results of neutron data of KNN5 at various temperatures.

		R	ietveld and PD	F refinement o	f KNN5 at 773 K			
Rietvel	PDF refinement monoclinic phase ( <i>Pm</i> )							
Atoms	X	Y	Ζ	U <sub>iso</sub>	X	Y	Ζ	$U_{ m iso}$
K/Na	0	0	0	0.0338(3)	-0.0105(160)	0	0.0429(76)	0.0301(52)
Nb	0.5	0.5	0.5	0.0103(2)	0.5050(110)	0.5	0.5120(55)	0.0137(16)
01	0.5	0.5	0	0.0338(3)	0.5183(68)	0.5	-0.0034(83)	0.0117(30)
O2					0.0086(130)	0.5	0.4783(90)	0.0244(47)
03					0.4802(70)	0	0.4983(99)	0.0144(35)
Lattice parameter (Å) a = b = c = 3.9848(1) $\alpha = \beta = \gamma = 90^{\circ}$	attice parameter (Å)       Lattice parameter (Å) $= b = c = 3.9848(1)$ $a = 4.0215(69)$ $= \beta = \gamma = 90^{\circ}$ $b = 3.9511(59)$ $c = 4.0220(72)$				(Å)	$\alpha = \gamma = 90^{\circ}$ $\beta = 91.983(290)$		
		R	ietveld and PD	F refinement o	of KNN5 at 673 K			
Rietvel	ld refinement cub	ic phas	se $(Pm\bar{3}m)$		PDF refinement monoclinic phase ( <i>Pm</i> )			
Atoms	X	Y	Ζ	$U_{ m iso}$	X	Y	Ζ	$U_{ m iso}$
K/Na	0	0	0	0.0296(4)	-0.0252(140)	0	0.0476(75)	0.0275(44)
Nb	0.5	0.5	0.5	0.0097(2)	0.4917(62)	0.5	0.5277(31)	0.0115(14)
01	0.5	0.5	0	0.0170(2)	0.4998(68)	0.5	-0.0015(40)	0.0060(15)
02					0.0052(71)	0.5	0.4907(100)	0.0217(39)
03					0.4663(66)	0	0.5021(90)	0.0160(33)
Lattice parameter (A) a = b = c = 3.9795(1) $\alpha = \beta = \gamma = 90^{\circ}$ Rietveld and PDF refinement of					Lattice parameter (A) a = 4.01873(63) $b = 3.9487(55)$ $\alpha = \gamma = 90^{\circ}$ $c = 4.0199(69)$ $\beta = 91.8464(260)$ f KNN5 at 573 K			
Rietveld	refinement tetrag	onal pł	nase (P4mm)		PDF re	finemer	nt monoclinic ph	ase (Pm)
Atoms	X	Y	Ζ	$U_{ m iso}$	X	Y	Ζ	$U_{ m iso}$
K/Na	0	0	0.0152(10)	0.0281(3)	-0.0038(150)	0	0.0385(64)	0.0225(34)
Nb	0.5	0.5	0.5156(2)	0.0065(2)	0.4756(39)	0.5	0.5284(26)	0.0122(12)
01	0.5	0.5	0.0490(5)	0.0157(4)	0.4993(55)	0.5	-0.0012(32)	0.0055(10)
02	0.5	0	0.5571(2)	0.0115(2)	0.0005(40)	0.5	0.4922(68)	0.0148(19)
O3					0.4522(40)	0	0.5012(76)	0.0186(27)
Lattice parameter (Å) a = b = 3.9644(1) c = 4.0134(1) $\alpha = \beta = \gamma = 90^{\circ}$		R	ietveld and PD	F refinement o	Lattice parameter a = 3.9894(61) b = 3.9721(51) c = 4.0051(62) f KNN5 at 473 K	teter (Å) (i1) (i1) (i2) $\alpha = \gamma = 90^{\circ}$ $\beta = 91.2571(310)$ K		
Rietveld refiner	PDF refinement monoclinic phase (Pm)							
Atoms	X	Y	Ζ	$U_{\rm iso}$	X	Y	Ζ	$U_{ m iso}$
K/Na	-0.0003(29)	0	0.032(4)	0.0082(12)	-0.0001(100)	0	0.0597(42)	0.0151(35)
Nb	0.4754(13)	0.5	0.5515(13)	0.0049(9)	0.4769(23)	0.5	0.5317(20)	0.0095(12)
01	0.5328(10)	0.5	0.0391(21)	0.0157(16)	0.5091(55)	0.5	-0.0012(26)	0.0059(12)
02	-0.011(3)	0.5	0.5422(20)	0.0142(14)	0.0062(28)	0.5	0.5065(110)	0.0206(28)
O3	0.4869(14)	0	0.5080(8)	0.0054(11)	0.4897(58)	0	0.4933(56)	0.0100(18)
Lattice parameter (Å) a = 4.0019(3), b = 3.95 $\alpha = \gamma = 90^{\circ} \beta = 90.27$		Lattice parameter (Å) a = 3.9559(52) b = 3.9972(48) $\alpha = \gamma = 90$			$\alpha = \gamma = 90^{\circ}$			
phase fraction 0.47/7					c = 4	.0032(5	)))	$\beta = 91.023(270)$

			Rietveld and PD	F refinement of	KNN5 at 473 K			
Riet	veld refinement tw	o-phase	s coexistence phase 1 (	PDF refinement monoclinic phase ( <i>Pm</i> )				
Atoms	X	Y	Ζ	$U_{ m iso}$	X	Y	Ζ	$U_{ m iso}$
	pł	nase 2(F	24mm)					
Atoms	X	Y	Ζ	$U_{ m iso}$				
K/Na	0	0	0.0253(31)	0.0336(13)				
Nb	0.5	0.5	0.5137(4)	0.0056(6)				
01	0.5	0.5	0.0536(9)	0.0124(7)				
O2	0.5	0	0.5572(6)	0.0067(5)				
Lattic a = b = 3.958 c = 4.0205(2)	e parameter (Å) 88(2), )		$\alpha = \beta = \gamma = 90^{\circ}$ phase fraction 0.523					
			Rietveld and PD	F refinement of	KNN5 at 373 K			
	Rietveld refinen	nent mo	noclinic phase (Pm)	PDF refinement monoclinic phase (Pm)				
Atoms	X	Y	Ζ	$U_{ m iso}$	X	Y	Ζ	$U_{ m iso}$
K/Na	-0.0064(20)	0	0.0251(26)	0.0157(4)	-0.0383 (50)	0	0.0293(85)	0.0161(30)
Nb	0.4727(5)	0.5	0.5300(6)	0.0034(2)	0.4822(1)	0.5	0.5329(2)	0.0081(10)
01	0.5264(5)	0.5	0.0068(9)	0.0092(8)	0.5237(68)	0.5	-0.0029(27)	0.0183(23)
O2	-0.0026(10)	0.5	0.5167(12)	0.0107(7)	0.0154(1)	0.5	0.5089(2)	0.0061(10)
O3	0.4978(7)	0	0.4868(5)	0.0036(4)	0.5066(46)	0	0.4879(37)	0.0054(9)
Lattice parameters $a = 4.0003(2)$ b = 3.9465(2) c = 3.9905(2)	$\gamma = 90^{\circ}$ 90.301(1) Rietveld and PD	Lattice parameter a = 3.9776(1) b = 3.9714(42) c = 4.0047(44) KNN5 at 290 K	(Å)	$\alpha = \gamma = 90^{\circ}$ $\beta = 90.663(18)$				
	Rietveld refinen	nent mo	noclinic phase ( <i>Pm</i> )		PDF re	fineme	nt monoclinic phas	e ( <i>Pm</i> )
Atoms	X	Y	Z	Uiso	X	Y	Z	Uiso
K/Na	-0.0041(18)	0	0.0205(26)	0.0137(3)	-0.0282(41)	0	0.0229(60)	0.0160(19)
Nb	0.4803(4)	0.5	0.5284(5)	0.0028(2)	0.4840(1)	0.5	0.5315(12)	0.0058(6)
01	0.5334(5)	0.5	0.0010(8)	0.0083(7)	0.5269(38)	0.5	-0.0027(20)	0.0119(12)
02	0.0071(8)	0.5	0.5117(10)	0.0086(6)	0.0181(1)	0.5	0.5081(27)	0.0086(10)
O3	0.5076(6)	0	0.4838(5)	0.0037(3)	0.5104(30)	0	0.4837(25)	0.0051(6)
Lattice parameter (Å) a = 4.0024(2) b = 3.9698(29) c = 3.9930(2) $\alpha = \gamma = 90^{\circ}$ $\beta = 90.332(1)$ Rietveld and PDF refinement of					Lattice parameter a = 3.9631(1) b = 3.9698(29) c = 4.0181(30) KNN5 at 100 K	Ċ(Å)	$\alpha = \gamma = 90^{\circ}$ $\beta = 90.700(130)$	)
	noclinic phase ( <i>Pm</i> )	PDF refinement monoclinic phase ( <i>Pm</i> )						
Atoms	X	Y	Z	Uiso	X	Y	Z	Uiso
K/Na	-0.0036(16)	0	0.0301(19)	0.0082(4)	-0.0340(29)	0	0.0235(40)	0.0091(13)
Nh	0.0030(10) 0.4794(4)	0.5	0.5283(6)	0.0002(1) 0.0012(2)	0.0310(2)) 0.4820(1)	0.5	0.5328(9)	0.0051(5)
01	0.5326(7)	0.5	-0.0002(10)	0.0066(7)	0.5145(49)	0.5	-0.0051(19)	0.0131(10)
02	0.0101(9)	0.5	0.5097(11)	0.0060(7)	0.0145(1)	0.5	0.5029(15)	0.0053(6)
03	0.5101(7)	0	0.4844(6)	0.0022(3)	0.5098(25)	0	0.4829(18)	0.0029(4)
Lattice parameter (Å) a = 4.0004(2) $b = 3.9382(2)$ $\alpha = \gamma = 90^{\circ}$ $c = 3.9915(2)$ $\beta = 90.364(2)$					Lattice parameter a = 3.9685(10) b = 3.9569(23) c = 4.0166(23)	(Å)		$\alpha = \gamma = 90^{\circ}$ $\beta = 90.577(94)$

## TABLE I. (Continued).



FIG. 4. (a) Experimental G(r) with  $r \sim 1.7-40$  Å for KNN5 in the temperature range of  $100 \sim 773$  K, showing the evolution of local and average structures. Note that the peak profile changes most significantly within  $r \sim 1.7-3$  Å. (b), (c) The fits to the experimental G(r) patterns at 100 K using *Pm* space group for different *r* ranges: (b)  $r \sim 1.7-10$  Å, (c)  $r \sim 30-40$  Å. (d), (e) Evolution of structural parameters obtained from boxcar fitting as a function of *r*: (d) lattice parameters *a*, *b*, and *c*, (e) *a*-*c* interaxial angle  $\beta$  and unit-cell volume *V*. The markers correspond to the parameters obtained from boxcar refinements and the middle of the box, whereas the dotted lines correspond to the parameters.

the experimental G(r) could be fit well using the *Pm* space group. The residual factors  $R_w$  are in an acceptable range of 6 ~ 13%. Figures 4(d) and 4(e) show evolution of the structural parameters as a function of *r* at 100K in the range of  $r \sim 5$  to 35 Å, which are obtained from boxcar refinement. As shown in Fig. 4(d), the lattice parameters *a*, *b*, and *c* obtained from fitting of G(r) at low *r* (first box, 1.7 ~ 10 Å) are significantly different from those obtained from Rietveld refinement of the Bragg diffraction peaks, which demonstrates the difference between the local and average structures. However, the lattice parameters obtained from the analysis of G(r) and Rietveld refinement of Bragg diffraction patterns approach each other beyond  $r \sim 10-15$  Å, which indicates that the local structural distortions average out beyond this length scale. Additionally,



FIG. 5. Temperature-dependent evolution of G(r), showing nearest-neighbor pairwise atomic correlations. Peaks representing Nb-O, K/Na-O, and K/Na–Nb bond lengths are marked with arrows. Note that the profiles in red/pink (100–373 K) show a clear split in the nearest-neighbor A-O and B-O peaks, while for profiles shown in blue (473–773 K) the peaks appear asymmetric without a clear split.

as shown in Fig. 4(e), while the values of  $\beta$  obtained from fitting of the G(r) within  $r \sim 10$  Å are significantly higher than the average  $\beta$  value, they converge beyond r > 15 Å. The current results are consistent with the study of Petkov *et al.*, which indicated a convergence between local and average structures occurs beyond 2-nm length scales for KNN [21].

To characterize the local structural evolution with temperature, the temperature-dependent G(r) in the range of  $r \sim 1.7 - 10$  Å were next investigated. Figure 5 shows G(r)in the range of  $r \leq 4$  Å, as a function of temperature from 100 to 773 K. The  $r \leq 4$  Å region indicates the short-range correlations for nearest-neighbor and next-nearest neighbor interatomic distances. In Fig. 5, the first arrow represents Nb-O interatomic distance, and the next two arrows represent the K/Na-O interatomic distance for a typical perovskite structure. For the Nb-O bond, there exists a clear splitting below 473 K, which indicates that the local octahedra are more distorted below 473 K. To explore the local distortion evolution, we fitted the measured G(r) at different temperatures. Both Pm and Amm2 structural models were examined for the fitting of the G(r) measured at 100 K, as shown in Fig. 6(a) and Fig. S7. The *Pm* model ( $R_{\rm w} \sim 7.24\%$ ) provided a better fit to the data as compared to the Amm2 model ( $R_{\rm w} \sim 8.57\%$ ). Particularly, the peaks at  $r \sim 2.8$  and 4.9 Å were better reproduced using the Pm model. Similar results were obtained for G(r) at 290 and 373 K, as shown in Figs. 6(b) and 6(c) and Figs. S8 and S9. For temperatures at or above 473 K, for which the average long-range structure is transformed to tetragonal, the Nb-O peak appears broad and asymmetric in Fig. 5, indicating a breaking of the sixfold degeneracy of the Nb–O bond distance [25]. It is therefore apparent that the local structure of KNN5 for temperatures  $473 \sim 773$  K (blue line group) cannot be accurately described by a cubic model, even at the highest measurement temperature  $\sim$ 773 K. At the phase transition temperature  $T_{T-M} \sim 473$  K, the Pm space group could better reproduce the experimental G(r) as compared to Amm2 and P4mm structure models, especially with respect to the peaks at  $r \sim 2$  and 2.8 Å, as shown in Fig. 6(d) and Figs. S10(a)–S10(c). For the measured G(r) above 473 K, Pm yielded a superior fit compared to other models: P4mm or (and)  $Pm\bar{3}m$  [Figs. 6(e)–6(g)] and Figs. S11–S13). This was especially obvious for the peak at ~4 Å which was described satisfactorily by the Pm model as well as yielded lower  $R_w$  values compared to the other higher-symmetry models.

Based on the above analysis, it is therefore apparent that the local structure for r < 10 Å in KNN5 exhibits monoclinic distortion with *Pm* space group at all temperatures from 100 to 773 K, although the long-range average structure exhibits three different phase transitions from 100 to 773 K. The coexistence of a lower-symmetry local and a higher-symmetry average atomic arrangement is not an unusual picture and has been observed earlier in BaTiO<sub>3</sub> [34].

The refined structural parameters (unit-cell constants, atomic coordinates, and thermal factors) for the local structure within  $r \sim 1.7 - 10$  Å using *Pm* space group for temperatures  $100 \sim 773$  K are shown in Table I. A comparison of the temperature-dependent local and average structural parameters is provided in Fig. 3. Interestingly, in contrast to the average structure, b for the local structure reaches a maximum value, and the slope of the  $\beta$  significantly changes near the monoclinic-tetragonal phase transition,  $T_{T-M} \sim 473$  K. This result is similar to the proposed composition-dependent evolution of structural parameters in  $K_x Na_{1-x} NbO_3$ , whereby an abrupt change in slope of the  $\beta$  occurs at  $x \sim 0.20$ , which delineates regions with slightly different crystal structures [7]. Notably, in correlation to the inflection points for the local structural parameters [Figs. 3(b) and 3(d)], we note a distinct change in the G(r) profiles at  $T_{T-M}$ , as shown in Fig. 5. Specifically, for temperatures below 473 K, the peaks representing the Nb-O nearest-neighbor correlations become sharper, indicating that the structure becomes more ordered below this temperature. Therefore, the reversal in trends for temperature-dependent evolution in b and  $\beta$  (shown in Fig. 3) are likely correlated to an order-disorder type transition at this temperature, which is further discussed below.

### C. Discussion

#### 1. Nature of structural phase transitions in KNN5

Phase transitions in perovskite ferroelectrics, such as BaTiO<sub>3</sub> and KNbO<sub>3</sub>, have been shown to exhibit both displacive and order-disorder type characteristics [41–44]. As per the displacive model, the direction of the *B*-site atomic displacements changes at a phase transition point, such as from  $\langle 110 \rangle$ -type displacements in the orthorhombic phase to  $\langle 001 \rangle$ -type displacements in the tetragonal phase. In contrast, according to the order-disorder model, the *B*-site cation is always locally displaced along the  $\langle 111 \rangle$  directions, while the average structure changes are due to partial reordering of the local *B*-site displacements. To elucidate the characteristic of the phase transitions in KNN5, we analyze below the details of Nb displacements as a function of temperature.

Based on Rietveld refinement of the Bragg peaks as well as analysis of G(r), the fractional displacements of Nb at different temperatures from its high-symmetry position are shown in Figs. 7(a) and 7(b) (see Supplemental Material, Fig. S14 for details of calculation process) [37]. The components of Nb displacements along both the [ $\overline{1}00$ ]( $S_{\overline{1}00}$ ) and [001] ( $S_{001}$ )



FIG. 6. Experimental and fitted G(r) profiles of KNN5 for interatomic distance r < 10 Å, as a function of temperature: (a) 100, (b) 290, (c) 373, (d) 473, (e) 573, (f) 673, (g) 773 K. The calculated profiles correspond to the fit obtained using a *Pm* space group, with starting parameters obtained from Rietveld analysis of the Bragg diffraction patterns at corresponding temperatures.  $R_w$  corresponds to the goodness of the fit at each temperature.



FIG. 7. Atomic displacement and octahedral distortion as a function of temperature: (a) Nb fractional displacement along  $[\bar{1}00](S_{\bar{1}00})$  and  $[001](S_{001})$  directions, and (b) net Nb fractional displacement close to ~  $[\bar{1}01]$  or [001] direction, as a function of temperature from 100 to 773 K, where insets are schemes of NbO<sub>6</sub> at 100 and 773 K. Note that the Nb displacements are exaggerated for clarity. (c) Octahedral distortion parameter as a function of temperature from 100 and 773 K for the local and average structures. Note that open symbols represent parameters obtained from average Rietveld refinement, while the closed symbols represent parameters obtained from PDF refinement in the range  $r \sim 1.7 \sim 10$  Å. (d), (e) Illustration of the NbO<sub>6</sub> octahedron in the local structure at 100 K (left top) and 773 K (right top), respectively. (f), (g) Illustration of the NbO<sub>6</sub> octahedron in the average structure at 100 K (left bottom) and 773 K (right bottom), respectively. The indicated Nb-O bond lengths in (d)–(g) are in angstroms (Å).

directions are indicated in Fig. 7(a). The fractional displacements  $S_{001}$  are slightly higher than  $S_{\bar{1}00}$ , which is consistent with the Nb displacement direction reported by Petkov *et al.* [21]. The variation in net fractional displacements approximately parallel to the [ $\bar{1}01$ ] or [001] direction as a function of temperature is shown in Fig. 7(b). The inset in Fig. 7(b) illustrates the net displacements of Nb at 100 and 773 K, in which the Nb displacements are exaggerated for clarity. In the average structure, the Nb off-center displacements decrease in magnitude with increasing temperature on the whole, except for an abrupt change at  $T_{T-M} \sim 473$  K because of two-phase coexistence. In contrast, Nb displacements in the local structure decrease continuously with temperature.

Octahedral distortion due to Nb off-centering can be calculated from the Nb-O bond lengths determined from structural analysis, using the following equation:

$$D = \frac{1}{n} \left[ \sum_{i}^{n} \left( \frac{d_i - d}{d} \right)^2 \right],\tag{1}$$

where *n* is the coordination number (in this case n = 6), and  $d_i$  and d are the individuals and average values of the interatomic distances in polyhedral, respectively [45]. The calculated octahedral distortion parameters versus tempera-

ture are shown in Fig. 7(c). The navy line indicates the values of D calculated using Nb-O bond lengths that are determined from Rietveld analysis of the Bragg diffraction patterns, while the pink line indicates the same determined from analysis of G(r). A discontinuity in the average octahedral distortion is evident at  $T_{\rm T-M} \sim 473$  K, while the local octahedral distortion changes gradually as a function of temperature. Graphical representations of the Nb-O bond length within the oxygen octahedra are provided in Figs. 7(d)-7(g). The apical O atoms and the O atoms within the basal plane of the octahedra are marked as red O<sub>ap</sub> and pink O<sub>bas</sub>, respectively. In Figs. 7(d) and 7(f), at 100 K, there is an insignificant Nb displacement towards one of the Oap with an equal Nb-Oap bond length of  $\sim 1.98(9)$  Å. Instead, Nb is displaced towards one of the basal edges of the octahedron, which aligns with the direction of spontaneous polarization, leaving two groups of Nb-O<sub>bas</sub> bond lengths:  $\sim 1.85$  and  $\sim 2.14$  Å for the local structure [Fig. 7(d)], and 1.87 and 2.12 Å for the average structure [Fig. 7(f)]. Therefore, at 100 K, the apparent Nb off-centering is  $\sim 0.14$  Å for the local structure and  $\sim 0.12$  Å for the average structure. The octahedral distortion parameters in the local and average structures are shown in Fig. 7(c). At 773 K, for the local structure, there is a slight difference among the Nb displacements towards the Obas and Oap as depicted in Fig.



FIG. 8. The calculated spontaneous polarization of KNN5 as a function of temperature, based on atomic positions in (a) the average structure, and (b) the local structure. The polarization for the local structure changes continuously with temperature, while a discontinuous change in the polarization for the average structure can be noted at the phase transition temperatures. The local atomistic mechanism for order-disorder type transition in KNN5 is schematically illustrated in (c)–(e). In (c)–(e), the closed circle represents Nb displacement in the local structure, while the open circle represents resultant displacement in the average structure. The line with an arrow represents the direction of the average polarization vector. Note that the Nb displacements are exaggerated for clarity.

7(e), which results in a small but nonzero value of *D* at 773 K in Fig. 7(c). In contrast, for the average cubic structure at 773 K, all the Nb-O bonds length are ~1.99 Å as depicted in Fig. 7(g), and there is no off-centering of Nb within the oxygen octahedra, which leads to D = 0 in Fig. 7(c).

The spontaneous polarization  $(P_s)$  resulting from octahedral distortion is estimated from the following relation:

$$P_S = \frac{e}{V_C} \sum_i z''_i \,\Delta_i,\tag{2}$$

where  $V_c$  is the unit-cell volume,  $\Delta_i$  is the shifts of the *i*th atom along the ferroelectric axis,  $z''_i$  is the apparent charge [46,47]. Figures 8(a) and 8(b) show the calculated spontaneous polarization ( $P_s$ ) as a function of temperature for the average and local structure, respectively. The values calculated here for the polarization are consistent with those reported earlier [48]. In Fig. 8(a), the average  $P_s$  decreases discontinuously while local  $P_s$  decreases continuously with increasing temperature. This can be rationalized based on a change in the ordering of the local dipoles at the phase transition temperature of  $T_{T-M} \sim 473$  K. An order-disorder transition is also supported from the temperature-dependent G(*r*) profiles shown in Fig. 5. In Fig. 5, the Nb-O peak at  $T \leq 373$  K is split with peak centers at ~1.89 and ~2.13 Å, while for  $T \ge 473$  K, the Nb-O peak appears asymmetric but without a clear split within the experimental resolution, which indicates that the Nb displacements become more disordered above  $T_{T-M} \sim 473$  K. This is consistent with previous studies, which concluded orderdisorder characteristics of phase transition in ferroelectric perovskites [41,42].

In fact, an order-disorder type of transformation has been reported for the end members of KNbO<sub>3</sub> and NaNbO<sub>3</sub> [32,43,44]. For KNbO<sub>3</sub>, the sequence of phase transitions from rhombohedral to orthorhombic to tetragonal to cubic occurs due to incremental disordering of the Nb displacements [43,44]. In comparison, for NaNbO<sub>3</sub>, Nb always displaced along  $\langle 111 \rangle$  directions, while the different average phase transitions are due to the ordering of the oxygen octahedral tilts [32]. Based on a comparison of the temperature-dependent local and average structures of KNN5, the polarization within the local monoclinic units in KNN5 are all directed along the same  $[\bar{1}01]$  direction, which can be compared to the average orthorhombic phase of KNbO<sub>3</sub>. Therefore, the average phase transition sequence of monoclinic-tetragonal-cubic in KNN5 can be described as a disordering of the local monoclinic units by cooperative displacement of K/Na and Nb atoms relative to the oxygen network, similar to scenarios described in Refs. [43,49]. A scheme of order-disorder transition in KNN5 is shown in Figs. 8(c) and 8(e). As illustrated in Fig. 8(c), in the monoclinic phase, the local Nb displacements (solid circle) are oriented approximately along the  $[\bar{1}01]$  direction in the *a*-*c* plane with  $\phi \approx 45^{\circ}$ , where  $\phi$  is the angle between atom displacement and the [001] directions. Since the local polarization directions along  $[\bar{1}01]$  are highly ordered at low temperatures, the resultant atomic displacement (open circle) in the average structure is also along  $[\bar{1}01]$ . At higher temperatures, the Nb displacements become more disordered. As illustrated in Fig. 8(d), above 473 K, the Nb displacements are disordered along the [101] (position 1) and [101] directions (position 2) in the *a-c* plane, which results in an average Nb displacement along the [001] and therefore leads to an average tetragonal structure. With increasing temperature, the Nb atoms are displaced along four directions: [101](position 1), [101] (position 2), [101] (position 3), and [101](position 4) in the a-c plane, such as illustrated in Fig. 8(e), which results in a cubic average structure with no net polarization.

The driving force for long-range structural ordering in KNN5 is imparted by the polarizing force of the short-range polar units within  $\sim 15$  Å, similar to the situation that was reported for BaTiO<sub>3</sub> and Ba<sub>x</sub>Sr<sub>1-x</sub>O<sub>3</sub> [34]. With increasing temperature, the driving force provided by the local polar units becomes weaker because of decreasing octahedral distortion. At the same time, the required driving force for long-range structural ordering becomes higher due to increased thermal vibrations. At temperatures below 473 K, the driving force is strong enough for the ordering of the long-range structure to an average monoclinic Pm phase due to the large octahedral distortion, as shown in Fig. 7. However, for temperatures above 473 K, the driving force is not enough to transform the long-range structure into a monoclinic phase as compared to the polarizing force of the local polar units due to lower octahedral distortion, as shown in Fig. 7. In this situation, the KNN5 average structure transforms into a tetragonal P4mm space group above 473 K. For temperatures above  $\sim$ 673 K, the driving force provided by polar units is too weak due to a very low octahedral distortion and consequently, the longrange structure becomes cubic.

### 2. Origin of ferroelectric polarization in KNN5

The origin of the overall ferroelectric polarization in KNN5 can be characterized by the relative displacements of K/Na and Nb with respect to the oxygen polyhedral distortions. The polarization originating from Nb displacements are presented in Sec. III C 1. Here, we take a closer look at the K/Na displacements. As shown in Fig. 5, there appears an addi-

tional peak at ~2.5 Å and a shoulder at ~3.2 Å representing K/Na–O bond distances at low temperature, which can be explained as a result of the displacement of K/Na ions within the  $AO_{12}$  dodecahedron. The current observation is similar to that reported earlier by Jiang *et al.* [32], which also showed a three-way splitting of the Na-O at r = 2.4, 2.8, and 3.1 Å due to Na off-centering displacement in NaNbO<sub>3</sub>. For KNN5, the off-centering displacement of K/Na is difficult to characterize at high temperatures due to the higher thermal parameters. However, at 100 K, the amplitude of the thermal vibration of K/Na becomes relatively smaller, which leaves a window to determine K/Na off-centering more precisely based on the neutron total scattering data.

From the analysis of the G(r) profiles, the off-centered displacement of K/Na in KNN5 at 100 K is ~0.15 Å, which is  $\sim 0.25$  Å smaller than the  $\sim 0.4$  Å displacement of Na in NaNbO<sub>3</sub> [32]. It can be noted that the ionic radius of  $K^+$  is larger than that of Na<sup>+</sup> by  $\sim 0.25$  Å [24], which reduces the average off-centering of the A-site ions in KNN5 as compared to that in NaNbO<sub>3</sub>. According to Jiang *et al.*, the energy barrier for atomic motion between the off-centered positions is higher for Na<sup>+</sup> in NaNbO<sub>3</sub> due to the rather high displacement of  $\sim 0.4$  Å [32]. Since the average K/Na displacement of  $\sim 0.15$ Å is comparatively lower in KNN5, the energy barrier for atomic motion is also correspondingly reduced. This facilitates easier mobility of the A-site ions in KNN5 on average and therefore leads to greater ferroelectric switching. In other words, the origin of enhanced ferroelectricity in KNN5 as compared to NaNbO3 can be attributed to the improved mobility of the A-site alkali ions, which in turn is caused by partial replacement of Na<sup>+</sup> with K<sup>+</sup>. Therefore, the enhanced ferroelectric polarization in KNN5 originates from reorientable off-centered displacements of both A- and B-site atoms.

## **IV. CONCLUSION**

In summary, we have elucidated the local atomistic mechanism for phase transitions and ferroelectric polarization in KNN5 based on a detailed analysis of temperature-dependent neutron Bragg diffraction and pair distribution function patterns. Analysis of the neutron diffraction patterns indicated that the structure of KNN5 transformed from monoclinicto-tetragonal-to-cubic with increasing temperature from 100 to 773 K. In contrast, analysis of the neutron pair distribution function indicates that the local structure within  $\sim 10$  Å stays monoclinic over the same temperature range. We show evidence for an order-disorder type of transition at  $T_{\rm T-M} \sim$ 473 K, which stems from a competition between the polarizing force of the local monoclinic polar units and increased thermal vibrations at higher temperatures. Additionally, based on an analysis of the local atomic structure, we show that large ferroelectric polarization in KNN5 can be attributed to displacements of both A-site K/Na and B-site Nb ions relative to the oxygen polyhedra.

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