

Journal of Materials Chemistry C

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ARTICLE

Piezoelectricity of Lead-Free (K, Na)NbO₃ Nanoscale Single Crystals

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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(K, Na)NbO₃ (KNN) is a promising lead-free compound that is more suitable for piezoelectric applications requiring environmental or even biological compatibility than the traditional lead-based Pb(Zr,Ti)O₃ system. In this work, we synthesized single crystalline KNN nanorods (NRs) with various K/Na ratios, which were used as ideal specimens for investigating the compositional dependence of piezoelectricity. Piezoresponse force microscopy (PFM) was utilized to characterize three-dimensional (3-D) morphology and piezoelectric properties of single crystalline KNN NRs. A phase boundary was confirmed around K/Na ratio of ~45/55 based on local switching behavior, whereby enhanced piezoresponse in KNN single crystals was obtained with specific domain structures. The methodology demonstrated in this work can also be applied for further fundamental studies on KNN as well as other lead-free piezoelectric materials.

1 Introduction

Piezoelectric materials, which can interconvert electrical and mechanical energy, are crucial in medical imaging, ultrasonic, telecommunication, and even personal electronic devices.¹⁻⁵ Among the piezoelectric oxides with high piezoelectric performance, Pb(Zr, Ti)O₃ (PZT) is the most representative one; however, its use will be gradually prohibited even in the traditional applications because of the notorious toxicity of Pb element.^{6, 7} As a result, lead-free piezoelectric materials are highly desired due to the environment protection and human health concern.⁷ (K, Na)NbO₃ (KNN) material, the ceramics of which exhibit d_{33} over 400 pC/N comparable to its PZT counterparts, is a promising candidate,⁸⁻¹⁰ though the exact microscopic mechanism responsible for such excellent piezoelectricity is not well understood yet. So far, some studies showed that there exists a phase boundary in KNN whereby the piezoelectricity shows a peak in sintered ceramic materials,¹¹⁻¹⁷ but inconsistent results were also reported by several groups.¹⁸ Single crystals are highly desired as ideal specimens for the related studies, by which the effects of density and grain boundary and even compositional inhomogeneity in sintered polycrystalline materials can be reduced to a minimum so that one can get a clearer understanding of intrinsic compositional dependence of phase structure and hence piezoelectricity. However, due to the complexity of the KNN phase diagram and the lack of single crystalline materials with a wide range of compositions, the existence of the phase boundary and the relationship between the K/Na ratio and piezoelectricity is still not clear.

Recent investigations demonstrated that KNN single crystalline nanorods (NRs) can be synthesized by a relatively

simple method based on molten-salt reaction, as established by previous works.^{10, 19} This makes it possible to synthesize KNN single crystalline NRs with various K/Na ratios as a reliable and convenient approach to address the issue. And it also makes KNN more attractive than PZT due to the complicate synthesis process of nanostructured PZT.²⁰ It is worth mentioning that flexible and stretchable piezo-devices, which consist of nanoscale piezoelectric materials, are able to scavenge inappreciable energy effectively, such as rolling, bending, or even movement from human beings.²¹ High output electric signal from good piezoelectricity is required in such kind of energy harvesting applications,^{10, 22} and single crystalline KNN NR would be the ideal choice.

However, KNN NRs possess nanoscale size when compared to KNN bulk ceramics, making it extremely challenge to measure piezoelectric properties quantitatively.²³ Piezoresponse force microscopy (PFM) could be a promising method, which has emerged as a primary and effective technique for imaging, as well as conducting nondestructive characterization of piezoelectric and ferroelectric materials at the nanoscale.²⁴⁻²⁸ For instance, Kalinin's group developed the switching spectroscopy piezoresponse force microscopy (SS-PFM) to address quantitatively local switching characteristics of PZT materials.²⁹ And piezoelectric properties of monocrystalline PZT nanowires and polycrystalline BiFeO₃ nanofibers were also investigated using PFM, respectively.^{23, 30} Even soft biological tissues were proved to be electromechanically coupled in porcine aortic walls, demonstrating the PFM as a sensitive testing method.²⁵

In this work, the compositional dependent piezoelectric responses of KNN NRs were carried out by switching spectroscopy piezoresponse force microscopy. In particular,

quantitative measurement of the local electromechanical switching behavior was carried out. An MPB region induced by O_I and O_{II} phases was revealed in single-crystal KNN NRs, whereby an enhanced piezoresponse was observed. The current work demonstrates that the piezo-active nanostructures are not only promising for energy harvesting applications, but also effective to shed light on complex microscopic mechanisms in perovskite systems.

2 Experimental

Synthesis of KNN NRs

KNN NRs were synthesized according to a step-by-step procedure, which mainly consisted of four steps.¹⁹ The K/Na ratios of KNN NRs were effectively controlled by adjusting K_2CO_3/Na_2CO_3 in reactants, and the KCl was employed as the molten salt during the synthesis. Finally, (K, Na)NbO₃ NRs with controlled K/Na compositions were obtained after a series of structure transformations.¹⁰

Fabrication of TEM Samples

In order to obtain the clear observation of morphology and domain structure, the NRs were first mixed with resin, and a poly resin matrix with NRs well embedded in was obtained after solidifying process. After that, the matrix was sliced into thin wafer with thickness of $\sim 10\ \mu\text{m}$. Then, the thin sprayed area with thickness of less than 10 nm was achieved using ion spray machine. (see Figure S3 in Supporting Information)

Structure Characterization

The morphology and nanostructure of the synthesized KNN NRs were observed by scanning electron microscopy (SEM, JEOL JSM-7001F, Tokyo, Japan) and transmission electron microscopy (TEM, Tecnai G20, FEI, USA), respectively. The phase structure of KNN NRs was examined in a wide temperature range from room temperature (25 °C) to 500 °C by Raman spectrum (LabRAM HR, HORIBA Jobin Yvon, France) with an excitation wavelength of 488 nm.

SPM Characterization

The piezoelectricity of KNN NRs was carried out by Asylum Research MPF-3D atomic force microscope (AFM) with a Cr/Pt coated tip. The resonance frequency of the cantilever is 75 kHz in air, and the spring constant is 3 N/m (Budgetsensors probes, Multi75E-G, Innovative Solutions Bulgaria Ltd., Sofia, Bulgaria). Tapping mode was employed for all the topography mappings, while the piezoelectric responses were addressed using SS-PFM. During the switching test, the tip was fixed at a certain position, and a DC voltage with a superposition of triangular wave and sawtooth characteristic was applied, and an AC signal was simultaneously applied to measure the amplitudes.

3 Results and Discussions

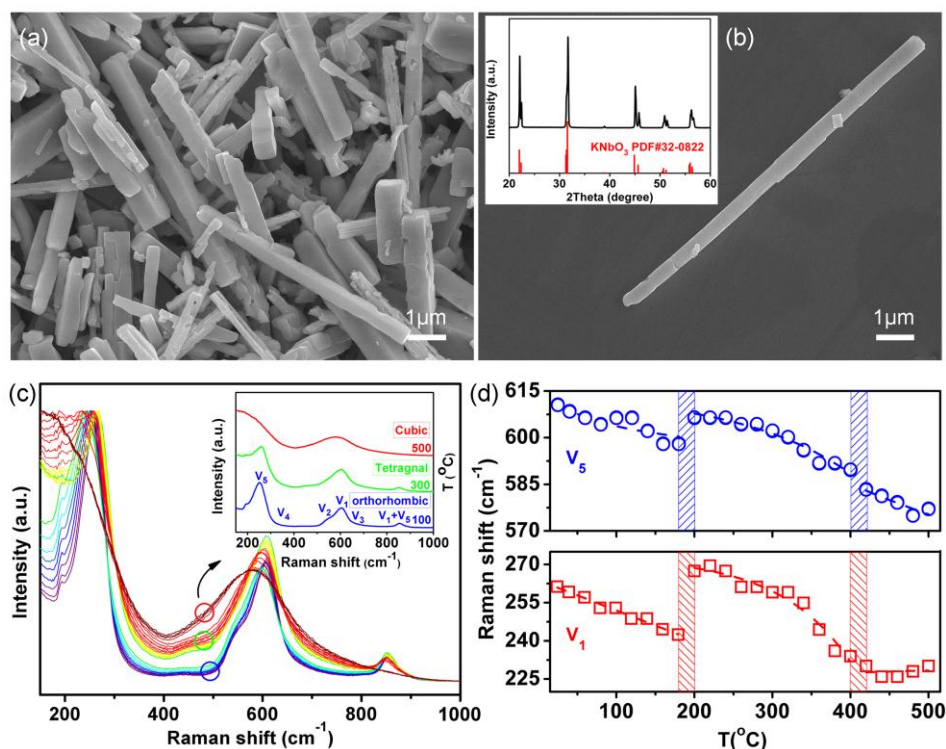


Fig. 1 (a) SEM images of (K, Na)NbO₃ NRs with the K/Na ratio of 49/51. (b) XRD patterns of KNN NRs and morphology of one individual NR. (c) Raman spectra from 25 °C to 500 °C, with three representatives shown in inset. (d) Typical Raman peak variations as a function of temperature.

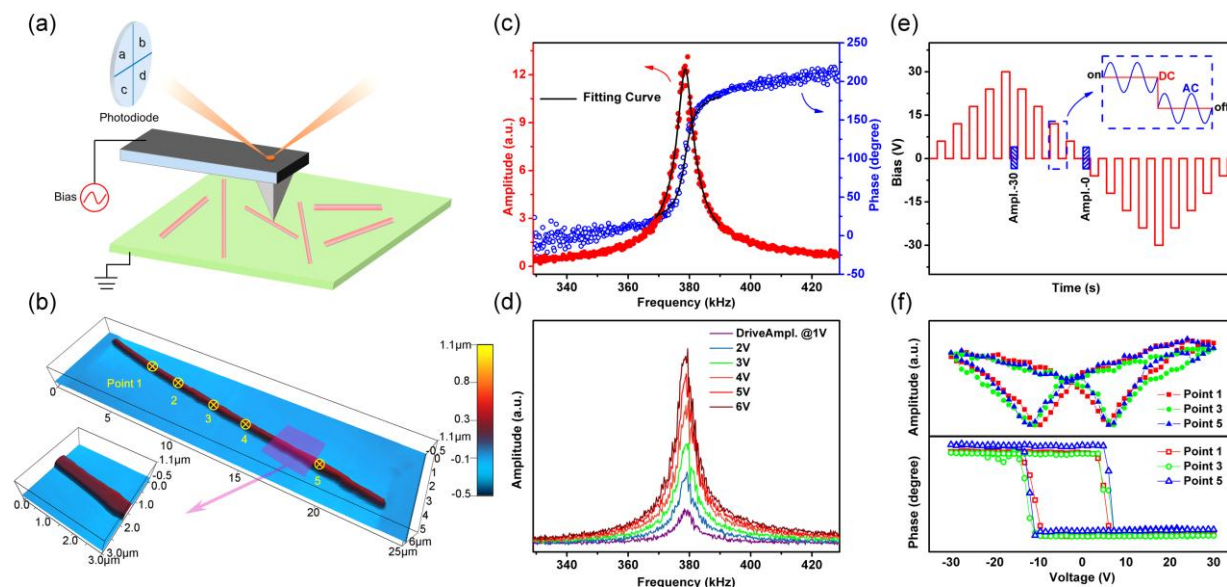


Fig. 2 (a) Schematic illustration of PFM measurement. (b) AFM image of an individual NR with the K/Na ratio of $\sim 49/51$. (c) PFM amplitude and phase versus excitation frequency near resonance. (d) Voltage-dependent vibration response. (e) Sketch of applied bias consisting of both AC and DC signals; the “on” and “off” states refer to the DC status, while the AC bias was applied throughout the measurement. (f) Piezoresponses and phases information gathered from Points 1, 3, and 5, as marked in (b).

An overview image shown in Fig. 1(a) illustrates that most KNN NRs are straight with relatively smooth surfaces, although some are rough due to slight dissolution of Nb_2O_5 NRs in the molten salt.^{31, 32} In addition, the cross section of KNN NRs appears to be square.¹⁰ The NR shown in Fig. 1(b) is up to $\sim 10 \mu\text{m}$ in length, and well crystallized, distinctive from that of the polycrystalline nanostructures fabricated via electrospinning method.³³ Furthermore, a representative XRD pattern of the as-synthesized KNN NRs is presented in the inset of Fig. 1(b). All the diffraction peaks can be assigned to an orthorhombic phase, which is in good agreement with KNbO_3 (PDF#32-0822). However, there is a small shift of diffraction peaks to higher angle due to the incorporation of Na^+ (1.39 \AA , CN=12), which is smaller than K^+ (1.64 \AA , CN=12). Figure 1(c) shows the temperature dependent Raman spectra from $25 \text{ }^\circ\text{C}$ to $500 \text{ }^\circ\text{C}$, where each spectrum was acquired at a temperature step of $20 \text{ }^\circ\text{C}$. Note that these spectra could be divided into three groups as indicated by the three circles. The representative spectra are presented in the inset, which correspond to the orthorhombic (O), tetragonal (T) and cubic (C) perovskite structures, respectively. Additionally, the dependence of the characteristic wavenumbers of ν_1 and ν_5 on temperature is shown in Fig. 1(d), and both data groups exhibit discontinuity at $\sim 200 \text{ }^\circ\text{C}$ and $400 \text{ }^\circ\text{C}$, indicating phase transition from O to T, and T to C, respectively. Thus, the temperature dependent Raman spectra confirm the structure consistency between KNN single crystalline NRs and polycrystalline bulks with the composition around $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$.³⁴ Furthermore, the size miniaturization of current KNN NRs does not affect the phase transition temperatures, *i.e.* $T_{\text{O-T}}$, T_{C} .

Atomic force microscopy (AFM) with tapping mode was used to map the topography of the KNN NRs, while the switching spectroscopy piezoresponse force microscopy (SS-PFM), as schematically shown in Fig. 2(a), was employed to determine the piezoelectric response of KNN NRs. It should be noted that the piezoelectric responses are considered to be along the $\langle 001 \rangle$ direction of KNN NRs, according to the previous work.^{17, 19} An electrical input signal was applied through the conductive tip to excite the piezoelectric vibration when the PFM mode was applied. Meanwhile, the laser reflection was gathered by the photodiode. The AFM image of one individual NR is presented in Fig. 2(b), together with the details revealed in the enlarged image. The NR is $\sim 25 \mu\text{m}$ in length, and $\sim 500\text{-}700 \text{ nm}$ in width, although the width of the NR varies to some extents. In addition, the surface is relatively smooth as indicated in the detailed segment of NR. After the morphology mapping by AFM, SS-PFM was employed to measure the piezoelectric effect, and the measurement points as marked in Fig. 2(b) were arranged along the length direction of NR. More than three NRs with the same K/Na composition were tested to make sure that the results are reliable. The resonance frequency of the cantilever-sample system (as indicated in Fig. 2(c)) was measured as the initial step according to the vibration amplitude, and the phase lag is confirmed to change steeply in the vicinity of this resonance. More importantly, the damped harmonic oscillator model was used to fit the resonance curve and calculate quality factor Q , which was introduced to quantify the sharpness of the resonance.³⁵ Furthermore, the vibration amplitude gradually increases with the drive amplitude increasing from 1 to 6 V, as

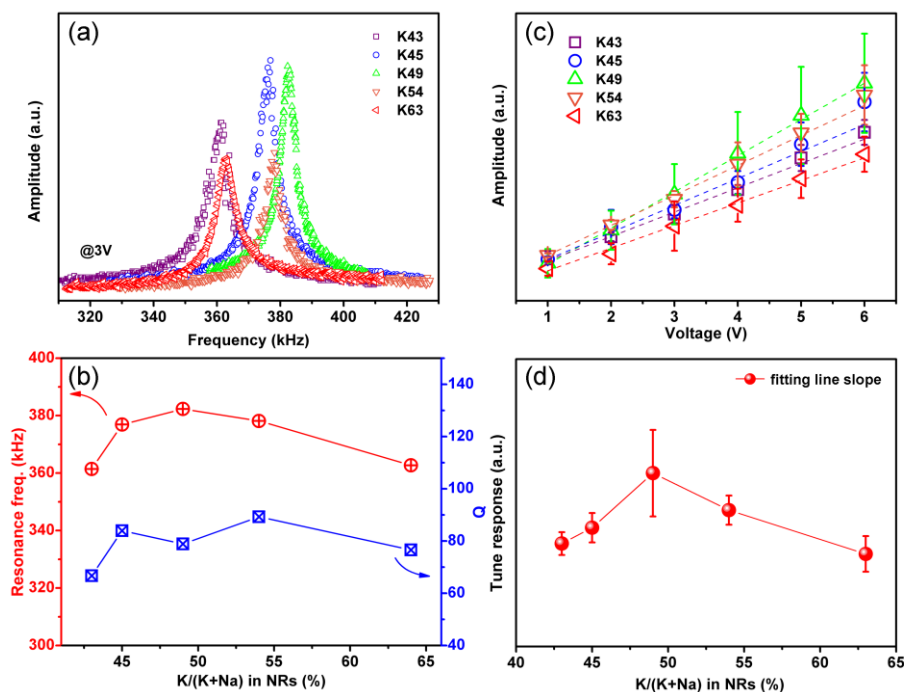


Fig. 3 (a) Vibration amplitude versus frequency near resonance gathered from KNN NRs with different compositions. (b) Variation of resonance frequency and calculated quality factor Q . (c) Tuning amplitudes and the linear fittings versus the applied AC voltage. (d) Dependence of vibration responses on $K/(K+Na)$ in NRs.

shown in Fig. 2(d), which confirms the linear piezoelectric effect of KNN NRs. In order to investigate the piezoelectric responses in association with polarization, a sequence of DC voltage signals with “on” and “off” state in periodic triangle wave were applied as shown in Fig. 2(e), and an AC signal with amplitude of 3 V was simultaneously applied to measure the corresponding piezoelectric vibration. It should be emphasized that the piezoelectric response was acquired during the “off” state in order to minimize the effects of electrostatic interactions.²⁵ The amplitude butterfly curves and phase hysteresis loops were concurrently acquired, while the results for the testing points 1, 3 and 5 are shown in Fig. 2(f). These results represent the typical amplitude-voltage and phase-voltage hysteresis loops, respectively. It is also observed that the piezoresponse along the NR is consistent, indicating the uniformity of NRs.

The cantilever-NR system, which is considered as a driven harmonic oscillator with damping, possesses the resonance frequency as shown in Fig. 2(c), and the electric signal should be driven near the resonance to enhance the sensitivity of output signals.²⁶ The resonance frequencies of NRs with various K/Na ratios were measured, and a sharp peak is observed in the vibration amplitude for each K/Na ratio, as shown in Fig. 3(a). The distinction of the resonance frequencies ranging from 361 to 382 kHz might attribute to the variation of contact stiffness,²³ which is confirmed by the stiffness estimated from the force curve, as shown in Figure 1S (see Supporting Information). The quality factor Q , as a useful

dimensionless parameter, can be approximately determined from the ratio of resonance frequency divided by the full width of the amplitude peak at $\sim 70\%$ of the peak value.³⁵ The composition dependences of resonance peaks, together with calculated Q values, are displayed in Fig. 3(b). A variation in quality factor Q ranging between 67 and 89 is observed when the driven bias is @3V, which highlights the importance of eliminating the influence of Q factor on the obtained amplitude data.²³ As a result, a qualitative comparison of responses in the tuning process for the KNN NRs with different K/Na ratios could be obtained. The linear fittings of the amplitude corrected by Q under different applied voltages, as shown in Fig. 3(c), indicate the piezoelectric nature of an individual NR, and the amplitude increases linearly while the drive amplitude increases from 1 to 6 V at a step of 1 V. More than fifteen sets of amplitude/ Q values were acquired for each data point in Fig. 3(c), indicating that the results represent the characteristics of the samples and are statistically meaningful. Further comparison was gained by calculating the slope of fitting lines in Fig. 3(c), and the result shown in Fig. 3(d) reveals that the KNN NRs with K/Na ratio locating at $\sim 49/51$ achieve the highest average values of piezoresponse with the applied AC bias, which is consistent with the optimum alkaline composition in the KNN bulk materials according to the previous work.¹⁵

Further experiment was carried out by switching the polarization to verify the ferroelectricity of NRs. The composition dependence of piezoelectric displacement and

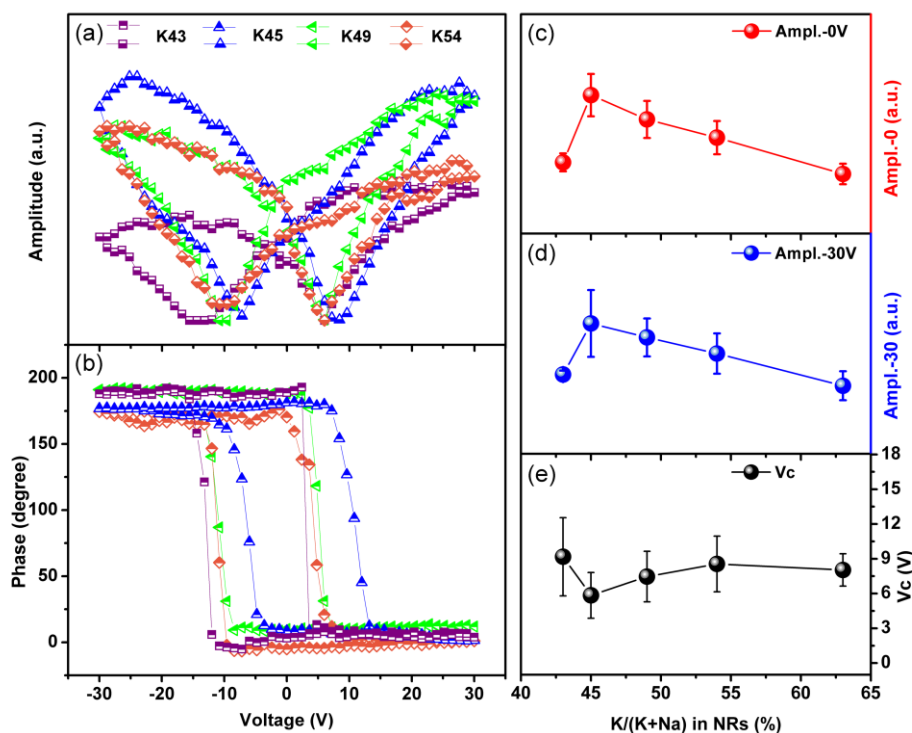


Fig. 4 Composition-dependent piezoelectricity measured by PFM switching test when K^+ locates at 43, 45, 49, 54 mol% in (K^+Na^+), respectively: (a) displacement-voltage butterfly loops and (b) phase-voltage hysteresis loops, and the dependent of (c) Amplitude-@0V off state, (d) Amplitude-@30V off state and (e) the coercive voltage on $K/(K+Na)$ in NRs.

phase loops, Amplitude @0 V “off” state, Amplitude @30 V “off” state, together with coercive voltage (V_c) of KNN NRs are shown in Fig. 4. Piezoelectric amplitudes of KNN NRs with K/Na of 43/57, 45/55, 49/51 and 54/46 are revealed in Fig. 4(a), respectively. Concurrently, phase reversal is observed in Fig. 4(b) when a coercive voltage is exceeded, and the phase contrast is approximately 180° , indicating a clear polarization switching process.²⁶ Figs. 4(c) and 4(d) compare the piezoelectric amplitudes, which are obtained as depicted in Fig. 2(e). The NRs with $K/(K+Na)$ around 45 mol% exhibit peak values at both conditions of @0V and 30V off states. Moreover, the variation of V_c versus $K/(K+Na)$ in the NRs is presented in Fig. 4(e). It can be revealed that the phase reversal occurs at approximately average voltage of 6.1 V with $K \sim 45$ mol%, reaching the lowest V_c value, which works in concert with the peak value of Ampl.-0V, Ampl.-30V piezoresponse shown in Figs. 4(c) and 4(d).

The correspondence of the variation trend between piezoelectric amplitudes and V_c , together the observed discontinuity of lattice parameters previously reported,¹⁰ suggests that the existence of an MPB in KNN single crystal is highly possible.^{12,36} It is assumed that the MPB locates at K/Na of $\sim 45/55$ in NRs, attributing to possible coexistence of orthorhombic_I and orthorhombic_{II} (O_I and O_{II}) phases in the $KNbO_3$ - $NaNbO_3$ system.¹⁶ This kind of O_I - O_{II} phase constitution, which does not strictly follow the typical morphotropic phase boundary (MPB) in PZT and BZT-BCT

materials,^{37,38} was considered as O_I - O_{II} induced MPB in the community.^{14,16} However, the piezoresponse amplitudes vary much less with composition than in PZT system, and the peak at K/Na of 45/55 is not very sharp. As is known, the O_I - O_{II} boundary exhibits octahedral tilting and discontinuity of lattice parameters rather than symmetry change,³⁹ while the MPB in PZT system is associated with a big change in polarization anisotropy due to the symmetry variation from rhombohedral (R) to tetragonal (T) structures.^{17,40} Thus, the enhancement of piezoresponse in KNN NRs with K/Na of 45/55 is less prominent than the MPB region in PZT. It should be emphasized the single crystalline nature eliminates the influence of densification and grain boundaries, which are inevitable in polycrystalline ceramics and may affect the macroscopic piezoelectric properties a lot.¹⁸ Therefore, this result reveals the existence of the MPB in the KNN single crystal, drawing a conclusion that the O_I - O_{II} induced MPB does exist in KNN bulk materials.¹⁶

In general, the composition-induced phase transition in the vicinity of the MPB engenders the instability of the polarization state due to the anisotropic flattening of the Gibbs free energy.⁴¹ The polarization direction can be easily rotated by electric field or external stress, thus a high piezoelectric response is reasonably expected.^{1,2,42,43} For the KNN NRs with K/Na of $\sim 45/55$, the existing MPB enables optimum polarization reorientation when the DC exceeds V_c , which could be considered as a “poling process”.⁴⁴ Therefore, when a DC

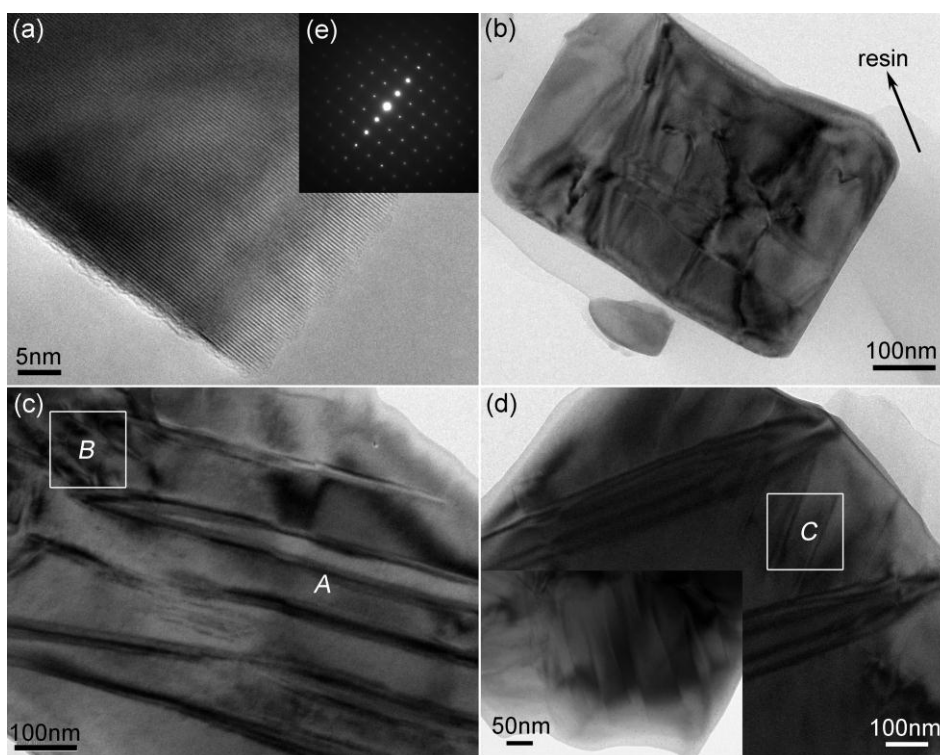


Fig. 5 (a) HRTEM images of an individual KNN NR with K/Na at the MPB region and (e) its corresponding SEAD pattern, and (b) cross-section of an individual NR embedded in the polymer matrix holder, accompanying with different domain configurations in (c) and (d). The capital letter labelling indicates three areas with representative domain features.

voltage of 30 V was applied, domains in a NR with the composition near MPB were supposed to be switched facily, and aligned almost along the electric field, and the superimposed AC bias of 3 V simultaneously measured the piezo-displacement after the domain switching process.^{25, 45} Moreover, the Ampl.-0V obtained at the zero-voltage, the variation trend of which is similar to that of Ampl.-30V, also confirms the MPB effect in KNN NRs.

However, cautions should be made for locating the MPB. Note that the considered with K/Na of 45/55 at MPB composition slightly deviates from the optimum composition of vibration where K/Na equals 49/51, as presented in Fig. 3(d). As is known, the piezo-amplitudes measured in Figs. 4(c) and 4(d) include the extrinsic responses originating from domain switching due to prior applied DC. However, the vibration amplitude does not rely on any DC signal. In other words, the bias ranging from 1 to 6 V was applied in order to acquire the resonance of cantilever-KNN NR system, and no switching effect existed, perhaps leading to the distinction of the optimum values.

It was reported that the domain size of PZT was reduced to nanometer dimensions around the MPB region.³⁷ Nano-domains was found in the vicinity of MPB, while micro-domain was revealed off the morphotropic region as reported by Theissmann *et al.*⁴⁶ Moreover, the miniaturized domains with a hierarchy structure also existed in BZT-BCT ceramics due to the phase coexistence at around MPB.³⁸ Similarly, nano-domains were observed in KNN NRs with composition located

around MPB, and detailed TEM results of the morphology and domain structures of KNN NRs are shown in Fig. 5. The high resolution TEM (HRTEM) image, together with the selected area electron diffraction (SEAD) pattern, as shown in Fig. 5(a), reveals the single crystalline nature of KNN NRs.^{19, 47} The strip-like domains with width of ~100 nm as marked with A are presented in Fig. 5(c), while some featureless/irregular-shaped domains coexist as marked in area B.^{48, 49} It should be noted that the nano-domains with an average size of <100 nm as indicated by C developed between the wider strip-like domains, and the angle is approximately 45° next to the *a* domains.³⁷ Meanwhile, nano-domains were also shown in the inset in Fig. 5(d), the width of which is around 50 nm. Besides, nano-domains with several tens of nanometers were rarely observed in KNN NRs with other composition, such as K/Na of 54/46, which were off the phase coexistence zone. (see Figure S2 in Supporting Information)

As is known, the reduction of domain dimensions (domain thickness *d*) in PZT material can be attributed to the decrease in the domain wall energy coefficient (*W*), following the classical theory:^{37, 50}

$$d \propto W^{1/2} \quad (1)$$

As a result, the existence of nano-domains might be considered as an evidence for the observed MPB region, since the energy equilibrium at phase boundary is considered to reduce the domain size. Besides, it is well known that both intrinsic and extrinsic components contribute to piezoelectric

effect in ferroelectric single crystals.⁴¹ The domain miniaturization enables itself respond facilely to external excitations, known as the extrinsic effect, leading to an enhanced piezoelectric property.^{46, 50}

Conclusions

In summary, composition-dependent piezoelectricity in single-crystalline (K, Na)NbO₃ nanorods (KNN NRs) with typical perovskite structure were investigated by PFM technique. It was demonstrated that the piezoelectric response of KNN NRs was dependent on the K/Na ratios, and a phase boundary induced by two orthorhombic phases was located in KNN monocrystals with K/Na of ~45/55. Meanwhile, the nano-domain structures revealed by TEM study are also consistent with the existence of this phase coexistence region, which would be also beneficial to the enhancement of piezoelectric response. It is suggested that KNN NRs with the compositions near K/Na of ~45/55 could be utilized for further fabrication of flexible energy harvesting devices, while promising electromechanical coupling can be expected.

Acknowledgements

This work is supported by the National Nature Science Foundation of China (Grants Nos. 51332002, 51221291), the Ministry of Science and Technology of China under the Grant 2009CB623304, and US NSF (CMMI-1100339).

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Electronic Supplementary Information (ESI) available: Materials stiffness calculated from the force curves for KNN NRs with various compositions, domain structures in KNN NR with K/Na ratio of 54/46, and graphical illustration of preparation of KNN NRs TEM samples. See DOI: 10.1039/b000000x/

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Piezoelectricity of Lead-Free (K, Na)NbO₃ Nanoscale Single Crystals

PFM characterization of (K, Na)NbO₃ nanoscale single crystal reveals the piezoelectric composition dependence and the existence of a phase boundary.

