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Supplementary Information

Synthesis of highly piezoelectric lead-free (K,Na)NbO₃ onedimensional perovskite nanostructures

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S1. Experimental Section

Materials

The raw materials used for the experiments were Na₂CO₃ (99.8 %, Sinopharm Chemical Reagent Co.(SCRC), Beijing, China), K₂CO₃ (99 %, SCRC), Nb₂O₅ (99.95 %, Conghua Tantalum & Niobate Smeltery, Guangzhou, China), KCl (99.5%, SCRC) and NaCl (99.5%, SCRC).

Synthesis procedure

The synthesis reaction of KNN consisted of the following four steps. In step 1, the mixture of Nb₂O₅, KCl and K₂CO₃ at a molar ratio of 1/10/x (*x*=1, 1.5, 2) was heated up to 1000 °C and soaked for 3 h, followed by washing the reaction products with hot deionized water to remove the excessive KCl. High-aspect-ratio NRs (which were identified to be K₆Nb_{10.8}O₃₀) were obtained. In step 2, the NRs obtained at Step 1 were transferred to H₃ONb₃O₈ by ion-exchange reaction in a 2 mol/L HNO₃ solution, which was stirred for 48 h at room temperature. In step 3, the dried H₃ONb₃O₈ NRs were heated at 550 °C for 1 h at a heating rate of 5 °C/min and cooled in air to produce Nb₂O₅ NRs. Finally (Step 4), the Nb₂O₅ NRs were mixed with Na₂CO₃ and K₂CO₃ at the molar ratio of 2/1/1 in the KCl and NaCl salt mixture of different compositions. Subsequently, the products were washed again with hot deionized water and dried to obtain the (K, Na)NbO₃ NRs.

Characterization

The crystal structure of the products was determined by X-ray diffraction (Rigaku, D/Max2500, Tokyo, Japan) using CuK α radiation ($\lambda = 1.5406$ Å). The morphology of the products was observed by scanning electron microscopy (SEM, JSM6460, Tokyo, Japan). The molar ratios of elements in the products in Step 1 were determined using Vista-MPX inductively coupled plasma spectroscopy (ICP) instrument. The microstructure of the as-synthesized KNN NRs was analyzed by transmission electron microscopy (TEM, Tecnai G20, FEI, USA). The phase structure and the composition of the KNN NRs were also examined by Raman spectrum (LabRAM HR, HORIBA Jobin Yvon, France) with an excitation wavelength of 488 nm. In order to obtain the converse piezoelectric coefficient d_{33}^* of an individual KNN NR, the products obtained in Step 4 were examined by scanning probe microscopy system (SPM, SPI 4000 & SPA 300HV, Seiko, Tokyo, Japan). The KNN NRs were first dispersed in alcohol, following by spreading the suspension on the Ptcoated silicon substrate. The location of an individual NR was detected by the conductive atomic force microscopy (AFM) probe tip with a conductive Rh-coated Si cantilever in the contact mode. After that a bias from 0 to 10 V was applied to the surface of the rod, and the information of the strains of the rod was gathered at the same time. The $d_{33}^* = \Delta l / \Delta V$.

S2. The ICP results of the products in Step 1 and the composition comparison.

Compound	$K_2Nb_8O_{21}$	KNb ₃ O ₈	K ₆ Nb _{10.8} O ₃₀	$K_4Nb_6O_{17}$
K/Nb (atom%)	25	33.3	55.6	66.7

Table S1. Different compounds which contain elements of K, Nb and O.

Table S2. The relative atomic ratios of the products in Step 1 with different K_2CO_3 molar ratio in the reactants.

K ₂ CO ₃ in the	1.0	1.5	2.0
reactants (mol%)			
K/Nb (atom%)	51.3	59.6	68.7

The ICP results of the products in Step 1 when the relative K_2CO_3 molar ratio varies in the reactants are listed in Table 2. The composition of the product is close to $K_6Nb_{10.8}O_{30}$ (PDF #70-5051) when the molar ratio of K_2CO_3 in the reactants is 1.5.

S3. SEM images of products obtained in Step1 by varying the molar ratio of K₂CO₃ in reactants.

After heating Nb₂O₅ and KCl salt, together with different molar ratios of K₂CO₃ at 1000 °C for 3 h, the rod-shaped products were obtained when the amount of K₂CO₃ was not too high. Figure S1a) shows that a large quantity of NRs with length of several tens of micrometers were obtained. Meanwhile, the NRs in Fig. S1b) are more straight with more smooth surface, and the diameter of an individual NR is uniform throughout its length. However, as shown in Fig. S1c), the predominant products are not NRs but cube-like particles which correspond to the phase of K₄Nb₆O₁₇ (PDF #31-1064) when the K₂CO₃ molar ratio is 2. The histogram in Fig. S1d) shows that most rods in Fig. S1a) vary from 300 nm to 1100 nm in diameter, while the rods in Fig. S1b) have a narrow diameter distribution with a peak around 400 nm to 500 nm when the K₂CO₃ molar ratio is adjusted to 1.5.



Figure S1. SEM images of products obtained in Step1 by varying the molar ratio of K_2CO_3 in reactants, a) $K_2CO_3/Nb_2O_5/KCl=1/3/10$, b) $K_2CO_3/Nb_2O_5/KCl=1.5/3/10$, c) $K_2CO_3/Nb_2O_5/KCl=2/3/10$, and d) counts distribution of the diameter of the NRs with K_2CO_3 molar

ratio is 1 and 1.5, respectively.



S4. X-ray diffraction and Raman spectrum analysis of the final KNN NRs.

Figure S2. a) XRD patterns of the KNN NRs with molten salt of (a) KCl/NaCl=60/40, (b) KCl/NaCl=70/30, (c) KCl/NaCl=80/20, (d) KCl/NaCl=90/10 and (e) KCl/NaCl=100/0. b) The calculated d_{111} of KNN NRs as a function of KCl molar ratio, and the d_{111} and d_{200} of single crystalline KNbO₃ and NaNbO₃ are also marked in the figure, respectively. c) Raman spectra of the KNN NRs

with different compositions of molten salt. The inset corresponds to the relative peak intensity ratios change (see S6 in SI).

It is confirmed that the KCl/NaCl ratios can affect the composition of the KNN NRs, as shown in Figure S2. The calculated d_{111} is the interplanar spacing of (111) crystalline planes of KNN NRs. In Figure S2a), all of the peaks are shifted to lower angles when increasing KCl amount in the molten salts, indicating that more K^+ cations occupy the A sites in the perovskite ABO₃ structure and the interplanar spacing becomes larger. It is considered that Na⁺ (1.39 Å, CN=12) may be easier to fill into the A sites in ABO₃ perovsktes than K⁺(1.64 Å, CN=12), which is attributed to the smaller cation radii of Na⁺.[SI-1] Figure S2b) also shows the d₁₁₁ of KNbO₃ (PDF#32-0822) and d₂₀₀ of NaNbO₃ (PDF#33-1270), with corresponding diffraction angles on the right axis as references. In addition, the d₁₁₁ (2.814 Å) of K_{0.5}Na_{0.5}NbO₃ from a solid state reaction is labeled with the dashed line for reference.[SI-2] It is clearly shown that the products are close to the composition of K_{0.5}Na_{0.5}NbO₃ when KCl/NaCl ratios locate ~90/10, and the K/Na ratio in the KNN NRs is ~52/48 calculated from the literature data reported in reference 18 Similar conclusions can also be drawn from the Raman results shown in Figure S2c). Raman spectroscopy is sensitive to phase structure and bond order of metal oxides, especially for metaloxygen stretching modes.[SI-3] It is observed that multiple and strong Raman peaks (v_5) exist in the region between 100 and 300 cm⁻¹, corresponding to the translational modes of K⁺ and Na⁺ cations and rotations of the NbO₆ octahedra. Meanwhile, the tiny peaks marked with arrows come from NaNbO3 or similar compositions. It should be noted that the peak observed at around 860 cm⁻¹ (v_1+v_5) is too weak to be obtained at room temperature for NaNbO₃ A factor α is defined to identify the relative intensity of this peak, which could be taken for estimation of K/Na ratios (see details in SI5).

S5. A defined factor *α* to estimate K/Na ratios in the A sites of ABO₃ structure.

The factor α is calculated by the following formula (1) to identify the ratio of K⁺ and Na⁺ filled in A sites of ABO₃ structures.

$$\alpha(iii) = \frac{I(iii)}{I(i) + I(ii) + I(iii)} \times 100\%$$
(1)

where I(i), I(ii) and I(iii) refer to the intensities of the peaks which corresponds to the vibrational modes v_5 , v_1 and v_1+v_5 , respectively. This equation follows the characterization of the work from Ruangchalermwong.[SI-4] As a result, the ratio of K/Na in the NRs increases when the amount of KCl increases in the molten salt, and it matches the XRD patterns in Figure S2a) well.

S6. KNN NRs measured by scanning probe microscopy (SPM) system.



Figure S3. a) Schematic illustration of the measurement of the piezoelectric response of an individual nanobar by SPM system [SI-5], **b)** Displacement-Voltage curve and calculated converse piezoelectric coefficient curve with different molten salt composition of KCl/NaCl=70/30, 80/20 and 90/10, respectively.

Typical well-shaped butterfly loops of electric-field-induced displacement are obtained for an individual KNN NR, and the converse piezoelectric coefficient are also calculated and labeled to the right axis. The loops with the salt composition of KCl/NaCl=70/30 reaches an average d_{33}^* value of 103 pm/V, and 123 pm/V for the higher KCl amount in the salt. Then, the d_{33}^* value increases significantly to ~230 pm/V when the KCl amount reaches 90 % in the salts.

Reference

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