Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Evidence of phase coexistence in hydrothermally synthesized $K_{0.5}Na_{0.5}NbO_3$ Nanofibers

Mohammad B. Ghasemian,[1] Aditya Rawal,[2] Zahra Shahrbabaki,[3] Qi Zhang,[1] Teng Lu,[4] Yun Liu [4] and Danyang Wang[1]*

[1]*School of Materials Science and Engineering, UNSW Sydney, Sydney, NSW 2052, Australia*
[2]*Nuclear Magnetic Resonance Facility, Mark Wainwright Analytical Center, UNSW Sydney, Sydney, NSW 2052, Australia*
[3]*School of Chemical and Biomolecular Engineering, University of Sydney, Sydney, NSW 2006 Australia*
[4]*Research School of Chemistry, The Australian National University, ACT 0200, Australia*

$K_{1-x}Na_xNbO_3$ The analytical grade Nb_2O_5, NaOH and KOH from *Sigma-Aldrich* were used for hydrothermal synthesis of KNN nanostructures in this work. NaOH and KOH acted not only as alkali element sources in A-sites but also mineralizers to control the morphology and size of KNN nanostructures in the process of hydrothermal reaction. As shown in **Figure S1A**, a 30 ml Nb_2O_5 water suspension with a concentration of 0.1 mol/l was first prepared. Mineralizers with different concentrations and different ratios of KOH/NaOH were added to this solution and stirred for one hour at room temperature. The autoclave was then transferred into an oven where it was held at different temperatures for hydrothermal reaction. Upon completion of the hydrothermal reaction, the autoclave was cooled down naturally to room temperature. The as-synthesized productions were filtered and washed with distilled water to the natural pH before drying at 80 ˚C overnight.

The flowchart in **Figure S1B** describes the steps of hydrothermal process of synthesising $K_{1-x}Na_xNbO_3$ nanostructures under different conditions and the resulted products. As demonstrated, $K_{0.5}Na_{0.5}NbO_3$ nanostructures were obtained when an approximate mineralizer ratio of KOH/NaOH=5 was used during the hydrothermal process. Higher and lower ratios of mineralizers resulted in KN-rich and NN-rich $K_xNa_{1-x}NbO_3$ nanostructures, respectively. Furthermore, the temperature of hydrothermal reaction determined the morphology of products, i.e. KNN nanofibers were formed at 160 °C whereas KNN microcubes were produced at temperatures $\geq$200 °C.

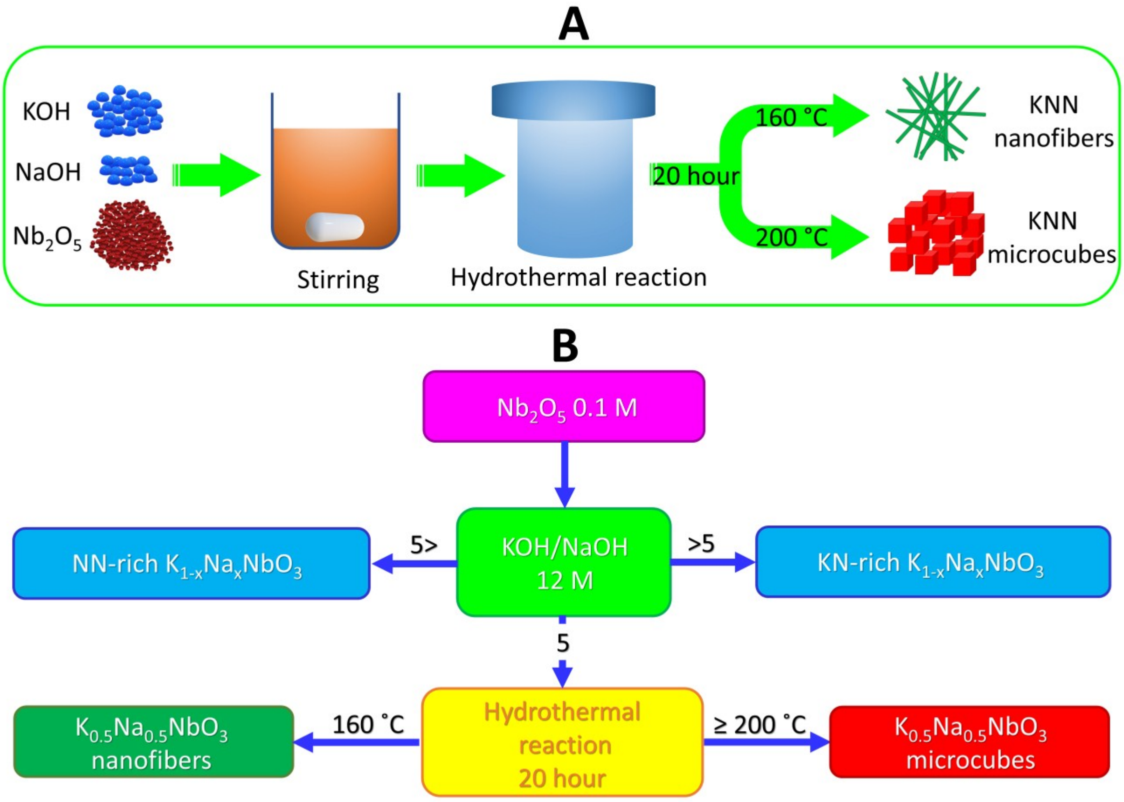

Figure S1. (A) Hydrothermal steps and procedure of synthesising KNN nanofibers and microcubes. (B) Flowchart of hydrothermal synthesis of $K_{1-x}Na_xNbO_3$ nanostructures. Products with different morphologies were resulted through tuning the processing conditions.

Chemical compositions of the hydrothermally-synthesized KNN nanostructures were determined by XRF. Lattice parameters and phase structures were acquired through the Rietveld refinements on the XRD patterns of KNN nanostructures, as listed in **Table S1**. All of the KNN nanostructures exhibited an overall orthorhombic symmetry and their lattice parameters were in good agreement with the reported data on KNN nanostructures.[13] The lattice parameters in **Table S1** were slightly larger than those of the corresponding KNN ceramics, presumably due to the presence of hydroxyl groups in the hydrothermally-synthesized KNN nanostructures.[19, 28]

Solid state NMR

The solid-state nuclear magnetic resonance (NMR) spectra were acquired using a Bruker Biospin Avance III solids-700 spectrometer with a 16.4 T superconducting magnet operating at frequency of 171, 185, and 700 MHz for the ^{93}Nb, ^{23}Na, and ^{1}H nuclei, respectively. Approximately 80 mg of powder was packed into 4 mm zirconia rotors fitted with Kel-f® caps and spun in a double resonance H-X probe head at 14 kHz MAS. The 1D ^{23}Na spectra were acquired with a hard 1 μs pulse and the ^{23}Na chemical shifts were referenced to solid NaCl at 0 ppm (corresponding to 1M aq. NaCl at -7.2 ppm) following Koller et al. [1] The 1D ^{93}Nb spectra were acquired with a 1 μs hard pulse and referenced to $K[NbCl_6]$ in acetonitrile using $NaNbO_3$ as a secondary reference. The 2D ^{23}Na multiple quantum magic angle spinning (MQMAS) spectra, which were acquired using a three-pulse triple quantum pulse sequence with pulse lengths of 8.5 μs for excitation pulse, 2.5 μs for conversion pulse and a 60 μs selective pulse; a repetition time of 200 ms and 256 rotation synchronized t_1 increments of 71.42 μs each. The spectra were simulated using with the DMFIT [2] software to extract the NMR parameters.

Table S1. Rietveld-refined lattice parameters of hydrothermally-synthesised $K_{1-x}Na_xNbO_3$ nanostructures. The KNN nanostructures were prepared at 200 ˚C for 20 hours with a fixed mineralizer concentration of 12M while a varying KOH/NaOH ratios.

	KOH/NaOH	Chemical composition [a]	Lattice parameters [b]		
			a **(Å)**	***b*** **(Å)**	***c*** **(Å)**
1	∞	$KNbO_3$	3.9739	5.6947	5.7197
2	6	$K_{0.761}Na_{0.239}NbO_3$	3.9707	5.6795	5.7052
3	5	$K_{0.522}Na_{0.478}NbO_3$	3.9659	5.6735	5.6819
4	4	$K_{0.333}Na_{0.667}NbO_3$	7.7673	5.5210	5.5735
5	0	$NaNbO_3$	7.7729	5.5139	5.5692

[a] K:Na:Nb atomic ratios were obtained from XRF analysis.

[b] The lattice parameters of samples were calculated according to the orthorhombic phase.

Table S2. ^{93}Nb NMR parameters extracted from simulating the 1D ^{93}Nb MAS NMR spectra.

^{93}Nb	δ_{iso} (ppm)	δ_{CSA} (ppm)	η_{CSA}	C_Q (MHz)	η_Q	α	β	γ
NN	-1069	-190	0.4(5)	21.9(2)	0.6(3)	70	66	62
KN	-1020	-159	0.4(3)	25.8(5)	0.6(0)	104	47	116
KNN C	-1022	-281	0.8(6)	26.8(6)	0.6(6)	79	148	124
KNN F	-1012	-272	0.9(3)	29.3(0)	0.6(6)	102	66	68

Table S3. Components of ^{23}Na NMR parameters determined from simulating the 1D Na slices extracted from the MAS dimension of the 2D ^{23}Na MQMAS experiments for (a) NN, (b) KNN microcubes, (c) KNN nanofibers.

(a) NN	δ_{iso}(ppm)	C_Q (MHz)	η_Q
i	-8.7	2.0(6)	0.7(6)
ii	-9.9	1.7(4)	0.6(6)
iii	-12.1	1.0(6)	0.5(7)

(b) KNN microcubes	δ_{iso} (ppm)	C_Q (MHz)	η_Q
i	-17.4	1.2(4)	0.4(3)
ii	-18.4	0.8(9)	1.0
iii	-20.9	0.07(8)	1.0

(c) KNN nanofibres	δ_{iso} (ppm)	C_Q (MHz)	η_Q
iv	-20.6	0.5(9)	0.0
iiia	-17.4	1.4(3)	1.0
iiib	-17.8	0.9(3)	0.5(7)
ii	-15.6	1.5(1)	0.3(5)
i	-14.1	1.6(6)	0.3(9)

The PFM measurements were carried out on multiple KNN nanofibers under different DC voltages to ascertain the reliability and reproducibility of the piezoresponse. The amplitude and phase hysteresis loops of KNN nanofibers were reasonably reproducible as exhibited in **Figure S2**. **Figure S3** shows the negligible amplitude and phase loops of the silicon wafer, implying that obtained piezoresponses in **Figures 11d** arise from KNN nanofibers instead of the substrate.

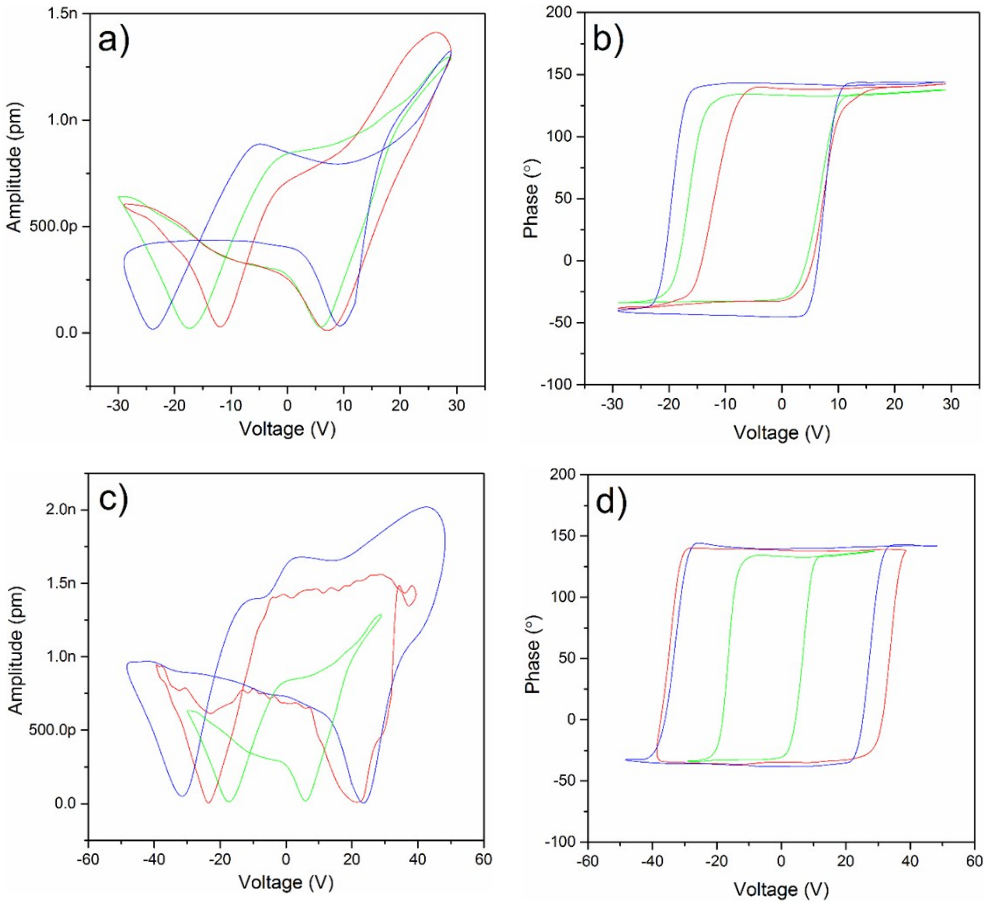

Figure S2. PFM (a) amplitude and (b) phase loops of different KNN nanofibers measured at 30V. (c) Amplitude and (d) phase loops of KNN nanofibers measured at different voltages.

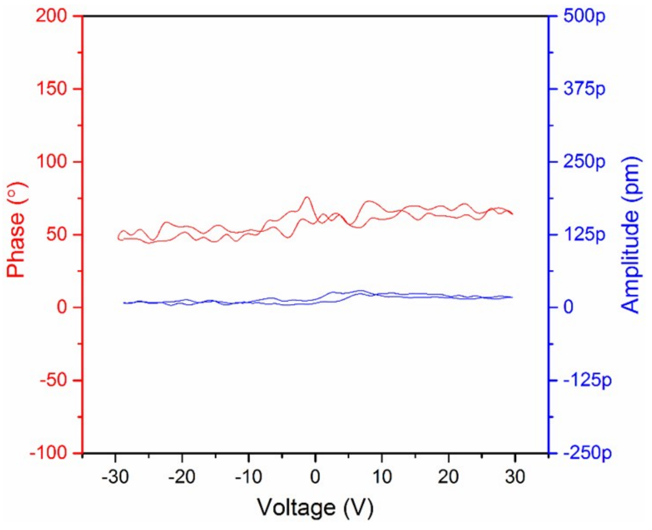

Figure S3. PFM amplitude and phase hysteresis of silicon substrate as reference.

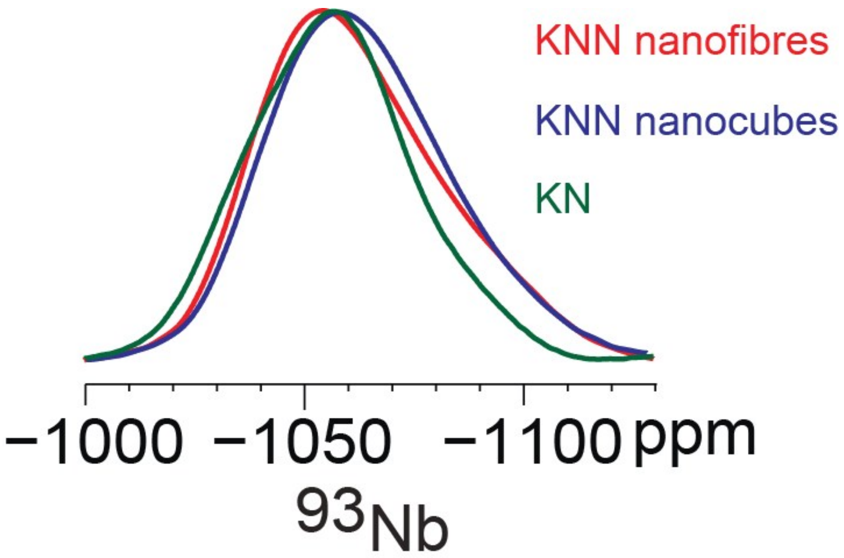

Figure S4. Zoomed in overlay of the ^{93}Nb MAS NMR spectra of KN, KNN microcubes and KNN nanofibres.

References:

[1] Koller H, Engelhardt G, Kentgens APM and Sauer J, ^{23}Na NMR Spectroscopy of Solids: Interpretation of Quadrupole Interaction Parameters and Chemical Shifts. J. Phys. Chem **1994**, 98, 1544-1551.

[2] Massiot D, Fayon F, Capron M, King I, Le Calvé S, Alonso B, Durand JO, Bujoli B, Gan Z and Hoatson G, Modelling one- and two-dimensional solid-state NMR spectra, Magnetic Resonance in Chemistry, **2002**, 40, 70-76