Supporting information for

Synthesis and dielectric properties of nanocrystalline oxide perovskites, $[KNbO_3]_{1-x}[BaNi_{0.5}Nb_{0.5}O_{3-\delta}]_x$, derived from potassium niobate $KNbO_3$ by gel collection

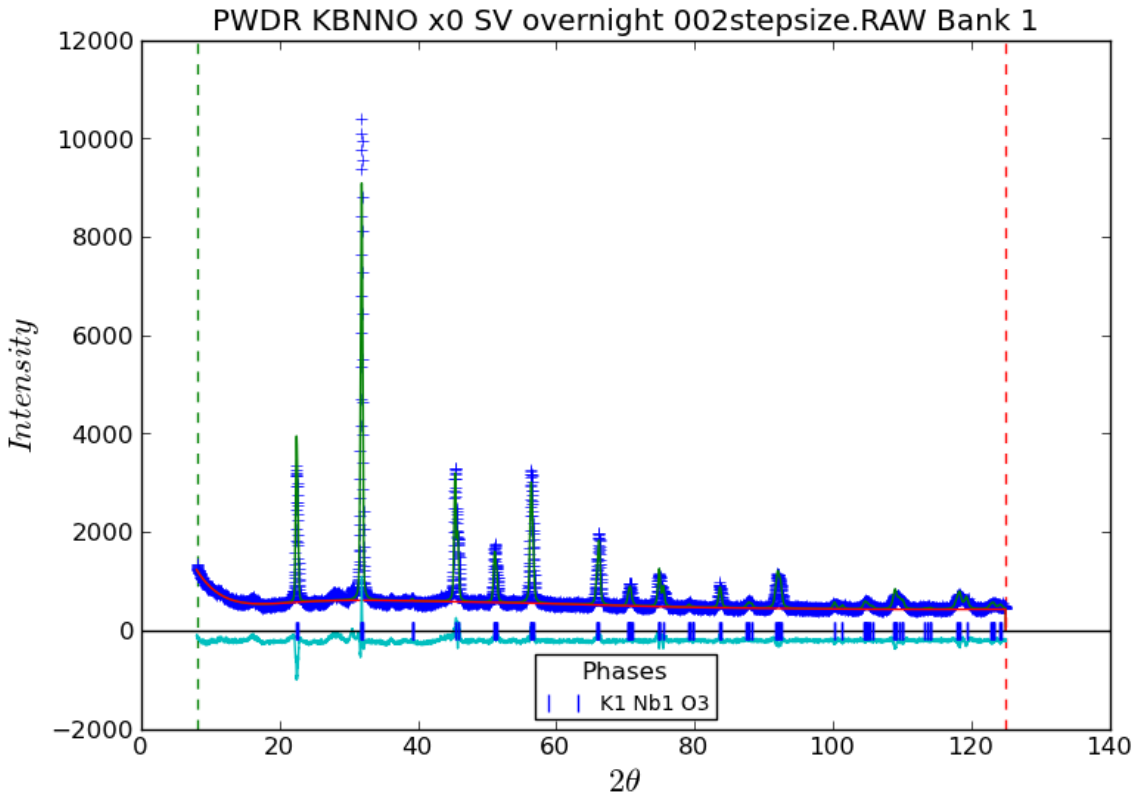


Fig S1: Rietveld refinement of $KNbO_3$ (KNO) heated to 525 ^{o}C. The refinement was performed on the program GSAS-II[1].

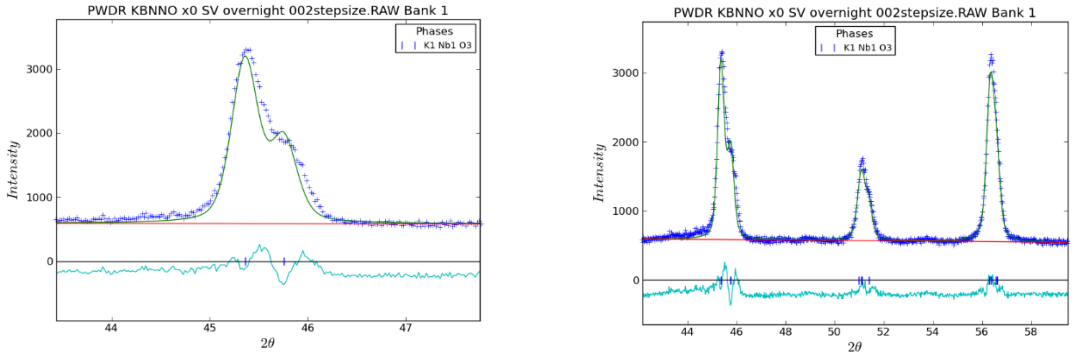


Fig S1.1: Rietveld refinement of $KNbO_3$ (KNO) heated to 525 ^{o}C regions 2q = 40-60 (left) and 2q = 40-50 (right) using GSAS-II[1,2].

Table S1: Unit cell parameters of KNbO3 (KNO) as calculated from Rietveld refinement using GSAS-II[1].

	$KNbO_3$ (KNO)		
Crystal Structure:	Orthorhombic		
Space Group:	*A m m 2*		
Unit Cell Dimensions			
a (Å)	3.99323		
b (Å)	5.68794		
c (Å)	5.70066		
Atomic Coordinates	*x*	*y*	*z*
Nb	0.00007	0	0.00977
K	0.5	0	0.51226
O1	0.5	0	0.06044
O2	0	0.24485	0.27374
Rwp	9.90 %		
Reduced C^2	3.2		

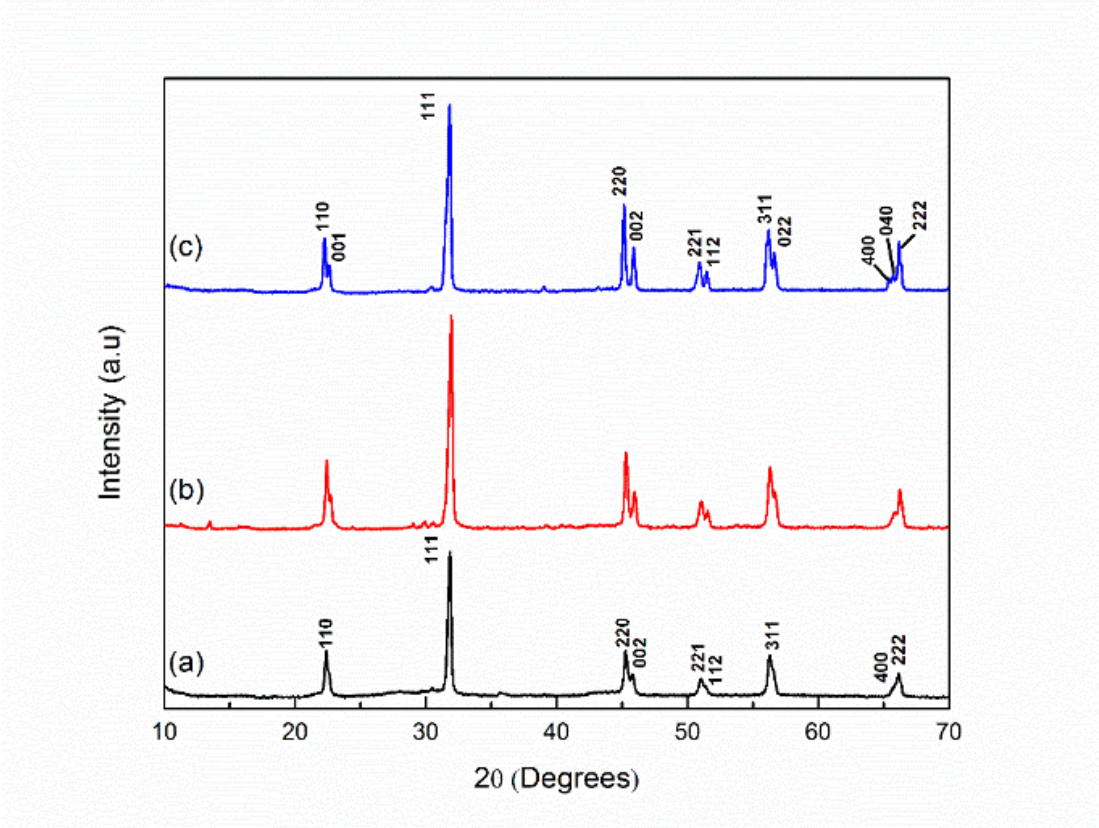
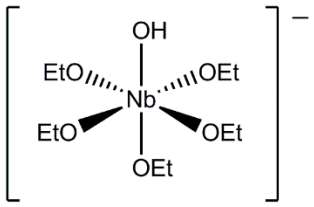
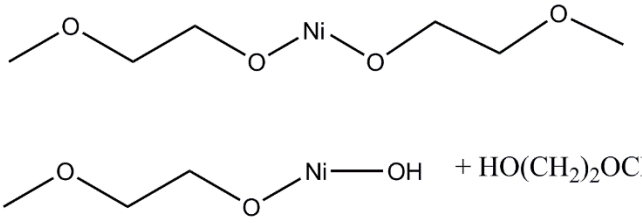


Fig S2: XRD of KNbO3 samples that were calcined at (a) 525 °C, (b) 700 °C, and (c) 900 °C.

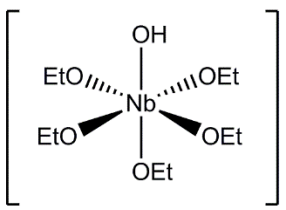
(1) $Nb(OCH_2CH_3)_5 + H_2O$ 

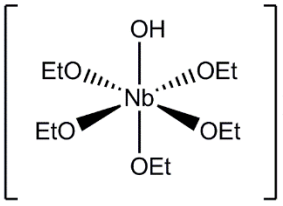
$+ H^+$



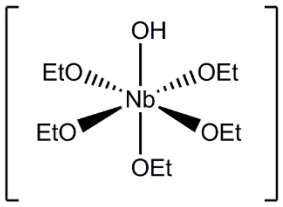
$+ H_2O$

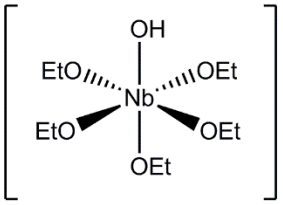
$+ HO(CH_2)_2OCH_3$

(2) 

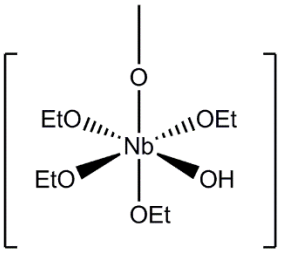
$+ KOCH_2CH_3 + H^+$ Charge Balancing, K coordination 

$K + CH_3CH_2OH$

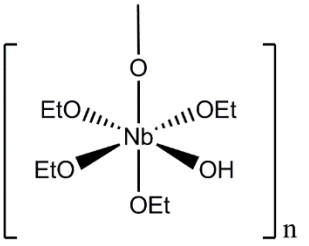
(3) 

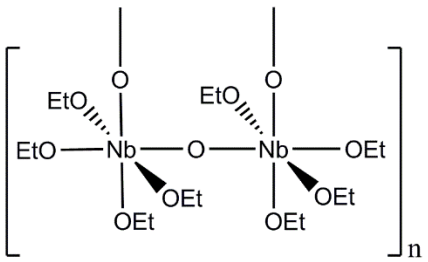
Polymerization, Partial Hydrolysis; Autoclave at 180 °C for 2d 

$+ nH_2O$

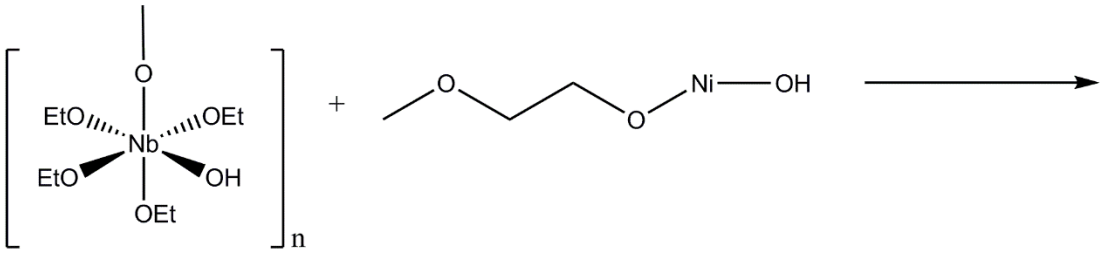


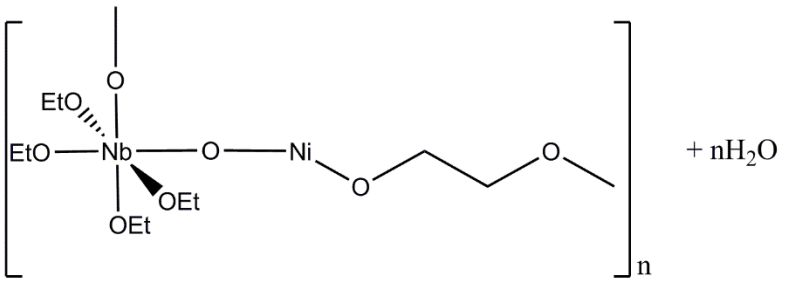
$+ nCH_3CH_2OH$

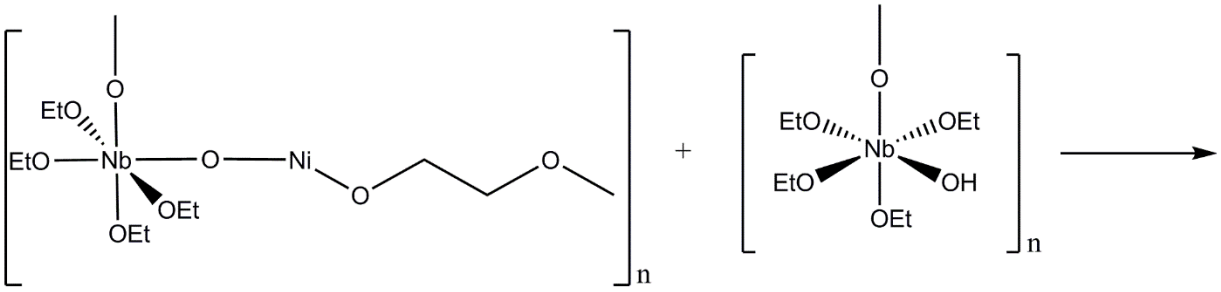
(4) 

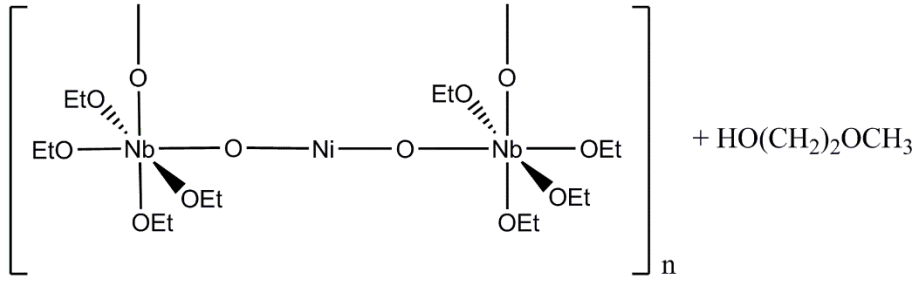


$+ nH_2O$

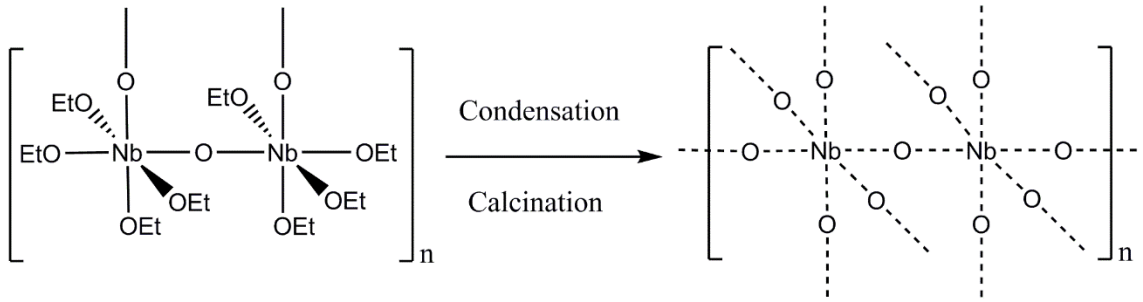

O
EtO
OEt
Nb
EtO
OH
OEt
n
+
O
Ni
OH
O


O
EtO
EtO
Nb
O
Ni
O
O
OEt
OEt
n
+ nH2O


O
EtO
EtO
Nb
O
Ni
O
O
OEt
OEt
n
+
O
EtO
OEt
Nb
EtO
OH
OEt
n


O
EtO
EtO
Nb
O
Ni
O
Nb
OEt
OEt
OEt
OEt
OEt
n
+ HO(CH2)2OCH3

(5)


O
EtO
EtO
Nb
O
Nb
OEt
OEt
OEt
OEt
OEt
n
Condensation
Calcination
O
Nb
n

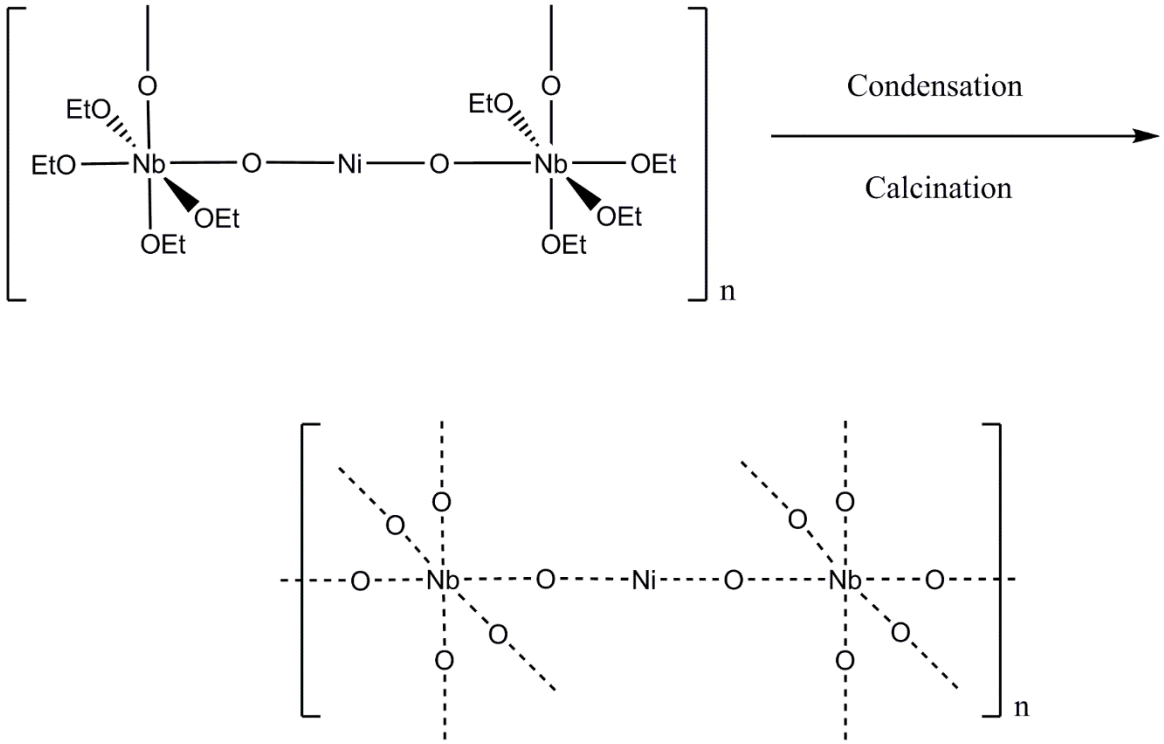


Fig S3: Schematic of the mechanism of the hydrolysis reaction producing nanocrystalline KBNNO and KNO through the gel collection method.

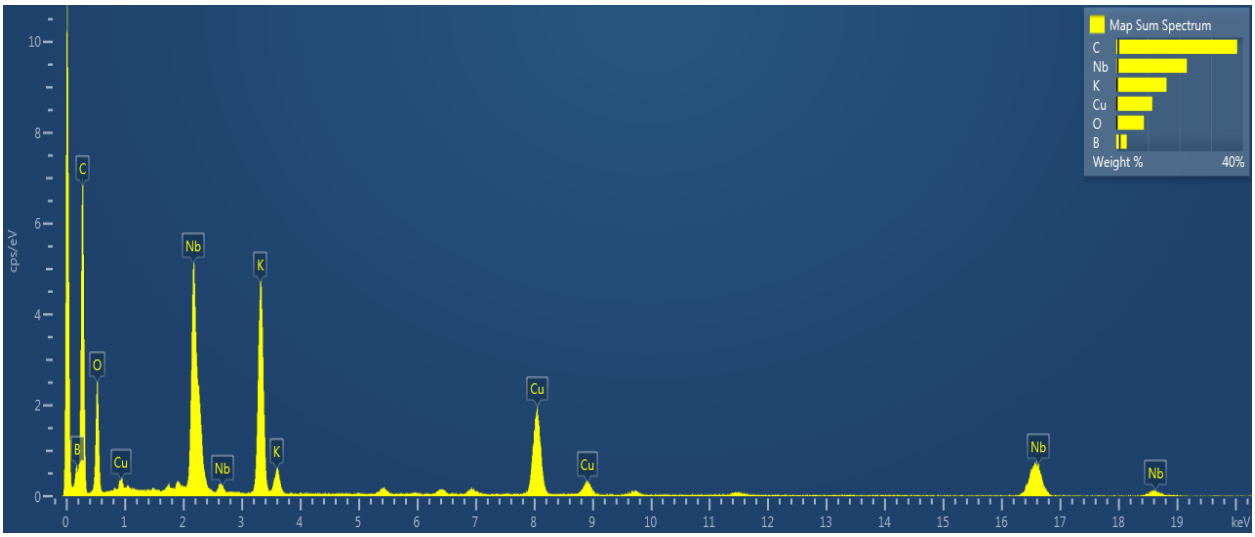


Fig S4: Elemental analysis EDS spectrum of $KNbO_3$ by TEM equipped with an EDS system.

Table S2: Elemental analysis weight % calculation of $KNbO_3$ by TEM equipped with an EDS system.

Element	Line Type	K Factor	Absorption Correction	Wt %	Wt % Sigma
C	K Series	2.76943	1.00	28.70	0.61
O	K Series	2.01995	1.00	19.43	0.34
K	K Series	1.00867	1.00	19.99	0.28
Nb	K Series	3.85651	1.00	31.89	0.53
Total:				100.00	

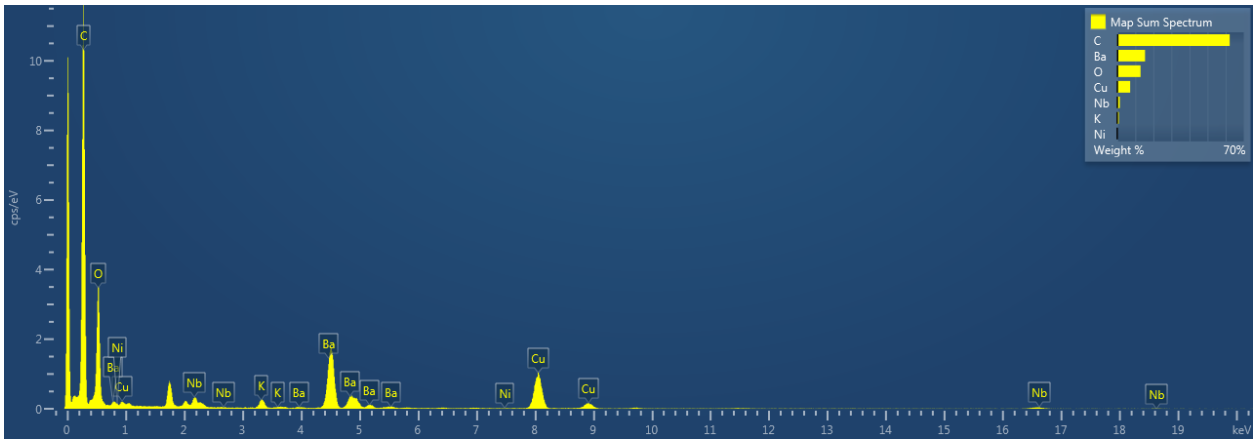


Fig S5: Elemental analysis EDS spectrum of KBNNO *x* = 0.1 by TEM equipped with an EDS system.

Table S3: Elemental analysis weight % calculation of KBNNO *x* = 0.1 by TEM equipped with an EDS system.

Element	Line Type	K Factor	Absorption Correction	Wt %	Wt % Sigma
C	K Series	2.76943	1.00	62.26	0.30
O	K Series	2.01995	1.00	12.89	0.17
K	K Series	1.00867	1.00	0.89	0.03
Ni	K Series	1.16381	1.00	0.02	0.02
Cu	K Series	1.24676	1.00	7.15	0.07
Nb	K Series	3.85651	1.00	1.40	0.09
Ba	K Series	2.05639	1.00	15.39	0.21
Total:				100.00	

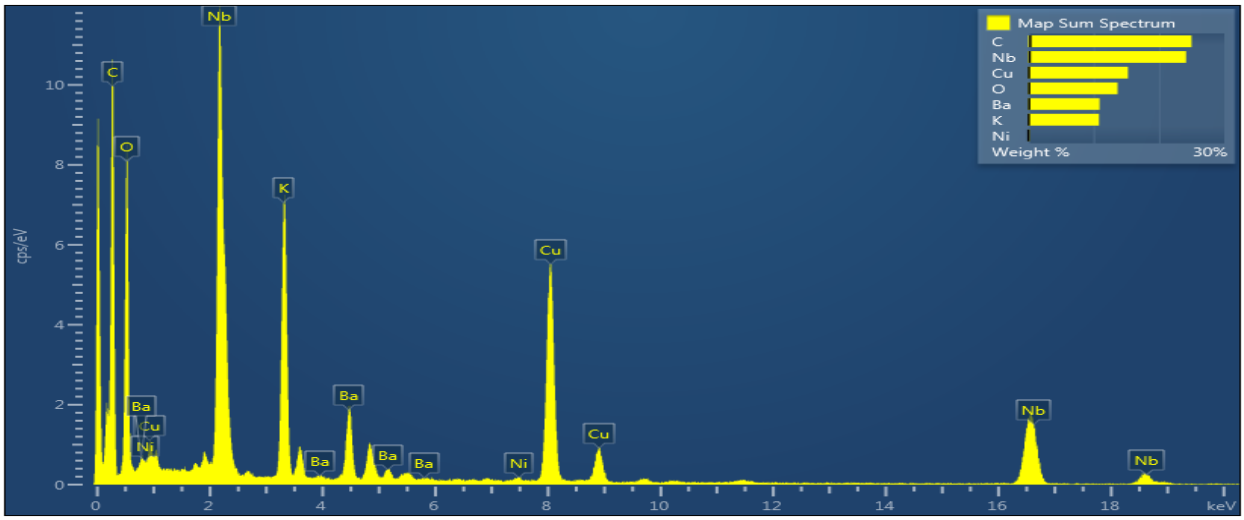


Fig S6: Elemental analysis EDS spectrum of KBNNO *x* = 0.2 by TEM equipped with an EDS system.

Table S4: Elemental analysis weight % calculation of KBNNO *x* = 0.2 by TEM equipped with an EDS system.

Element	Line Type	K Factor	Absorption Correction	Wt %	Wt % Sigma
C	K Series	2.76943	1.00	10.22	0.56
O	K Series	2.01995	1.00	14.97	0.30
K	K Series	1.00867	1.00	13.25	0.21
Ni	K Series	1.16381	1.00	0.79	0.07
Cu	K Series	1.24676	1.00	16.80	0.26
Nb	K Series	3.85651	1.00	30.86	0.51
Ba	L Series	2.05637	1.00	13.11	0.32
Total:				100.00	

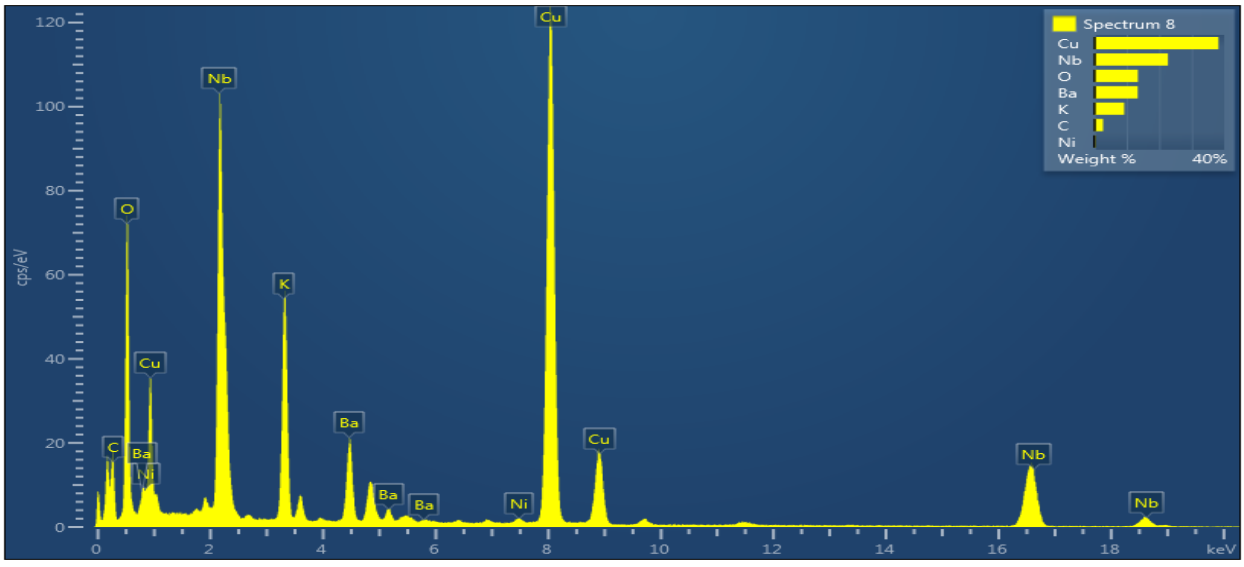


Fig S7: Elemental analysis EDS spectrum of KBNNO *x* = 0.3 by TEM equipped with an EDS system.

Table S5: Elemental analysis weight % calculation of KBNNO *x* = 0.3 by TEM equipped with an EDS system.

Element	Line Type	K Factor	Absorption Correction	Wt %	Wt % Sigma
C	K Series	2.76943	1.00	2.75	0.15
O	K Series	2.01995	1.00	13.42	0.11
K	K Series	1.00867	1.00	9.26	0.06
Ni	K Series	1.16381	1.00	0.30	0.02
Cu	K Series	1.24676	1.00	38.21	0.15
Nb	K Series	3.85651	1.00	22.71	0.17
Ba	L Series	2.05639	1.00	13.36	0.12
Total:				100.00	

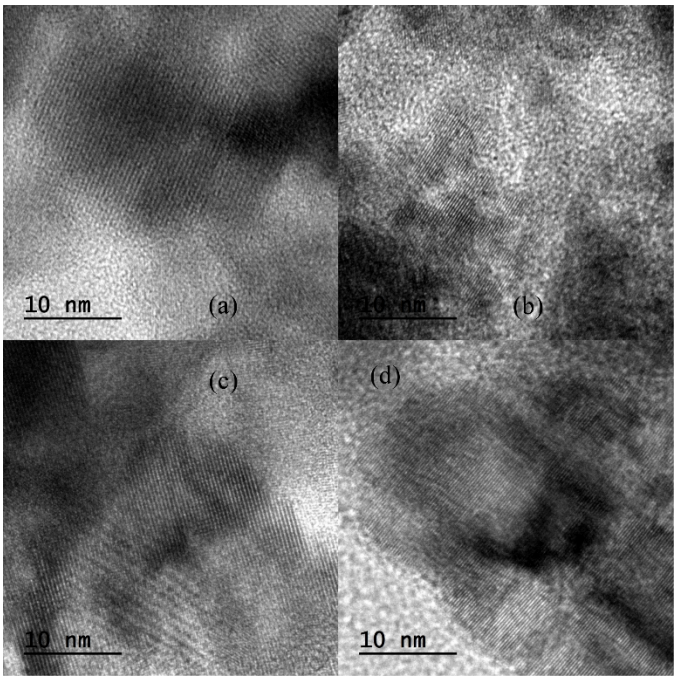


Fig S8: TEM micrograph of $KNbO_3$ and KBNNO *x* = 0.1-0.3. (a) $KNbO_3$, (b) KBNNO *x* = 0.1, (c) KBNNO *x* = 0.2, (d) KBNNO *x* = 0.3.

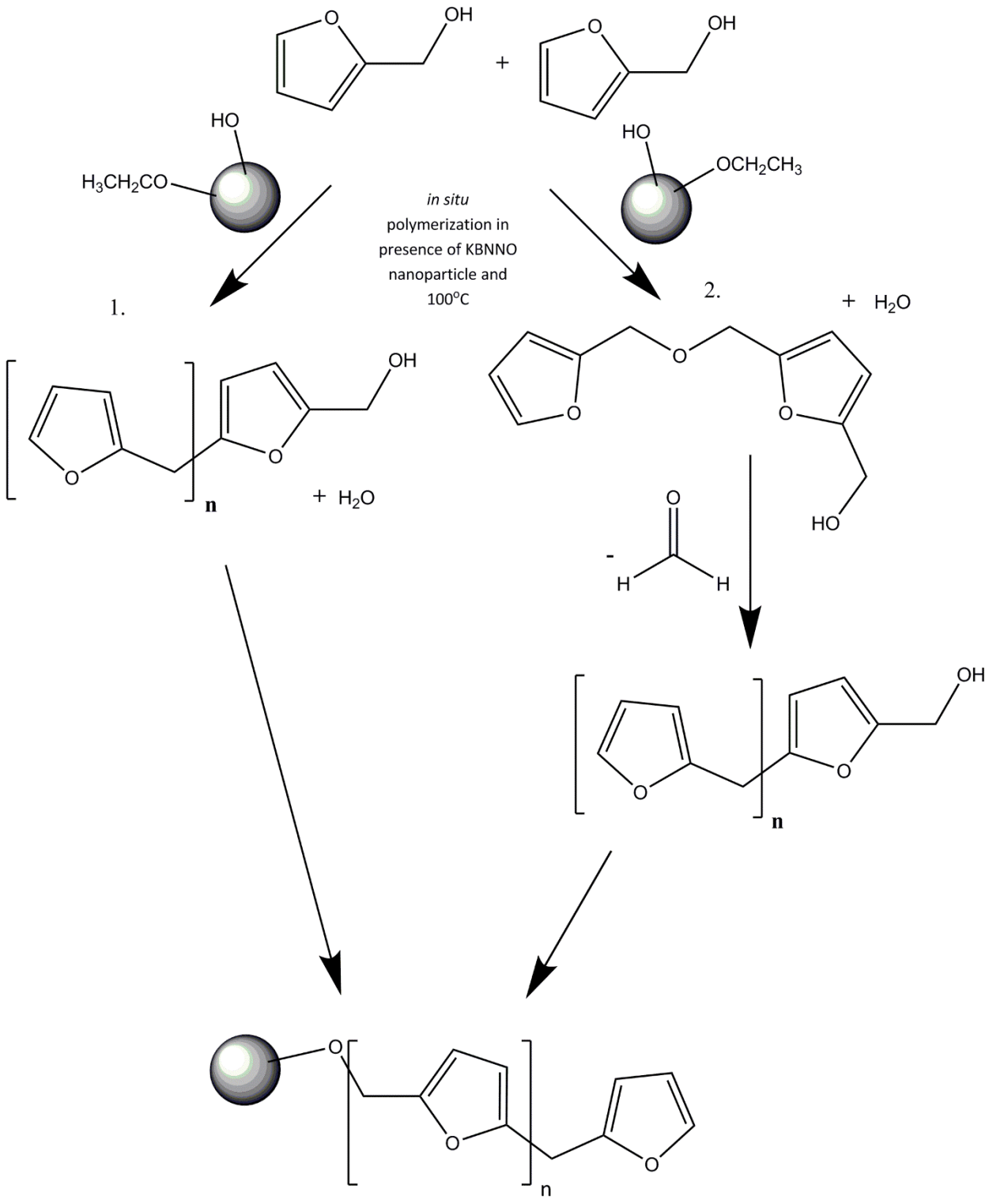


Fig S9: Proposed mechanism for the polymerization and chain extension of furfuryl alcohol resins in the presence of nanoparticle surface groups.

Discussion S10: Error analysis for dielectric measurements.

Error Propagation

Depending on whether addition/subtraction or multiplication/division of measured values with uncertainties is involved, separate formulas for error propagation must be used. In all cases uncertainty is rounded to **one significant** figure. For addition/subtraction:

$$z = x + y + \cdots$$

Where z is the calculated value, x, and y are the measured values with uncertainties. The ellipsis represents the possibility adding/subtracting more than only two measured values. The error in the calculated value can be determined using the following equation:

$$\Delta z = |\Delta x| + |\Delta y| + \cdots$$

Where Δz is the calculated error, Δx, Δy, are the uncertainties in measurement.

For mutliplication/division:

$$z = xy$$

and

$$z = \frac{x}{y}$$

Where again, z is the calculated value and x, y, are the measured values with certain uncertainties.

$$\frac{\Delta z}{z} = \frac{\Delta x}{x} + \frac{\Delta y}{y} + \cdots$$

The ellipsis here represents the possibility of multiplying/dividing more than only two measured values. Note that when calculating a value using multiplication by an **exact** number (i.e. a non-measured number) the uncertainty is multiplied by the **same** number.

Dielectric Calculations

In order to calculate the effective dielectric of a pellet or thin film capacitor, the rearranged capacitance formula can be used:

$$\varepsilon_{eff} = \frac{C * d}{(\varepsilon_0) * (A)}$$

Where C is the capacitance in farads, A is the area of overlap between capacitor electrodes, ε_{eff} is the effective dielectric, ε_0 is the electric constant (8.854E-12 F/m) and d is the separation between the plates.

The measured values here consist of C, d, and A. C is measured using the LCR impedance analyzer, while d and A are both measured using a caliper. The uncertainties can be written as follows:

$$\Delta d = 0.01mm$$

$$\Delta A = \frac{2\Delta r}{r} * (A)$$

$$\Delta r = 0.01mm$$

$$\Delta C = 0.05\%^{3}$$

For the samples measured in these experiments (pellet capacitors of KNO, KBNNO *x* = 0.1, *x* = 0.2, and *x* = 0.3) instrumental capacitance measurements from the LCR range on the order of pico-farads. Therefore, the instrument uncertainty in capacitance would range from 5E-4 to 5E-2 pico-farads. Averaged values for measurements of pellet capacitors are here listed:

Table S6: Average values for thickness (d) of pellet, radius (r) of top electrode, and area (A) of electrode for $KNbO_3$, and KBNNO *x* = 0.1-0.3 samples.

Sample	d (mm)	r (mm)	A (mm^2)
KNO	0.13	0.64	1.29
KBNNO *x* = 0.1	0.13	0.60	1.13
KBNNO *x* = 0.2	0.12	0.73	1.67
KBNNO *x* = 0.3	0.12	0.67	1.41

Since the average capacitance changes depending on frequency, and reporting an average capacitance from each frequency point is inordinate, instead it is here proposed that the capacitance ranges from 1 to 100 pico-farads. Using these averaged numbers for KNO as an example, it can be shown that even at 100 pico-farads, the uncertainty in capacitance measurement is negligible when calculating the error in ε_{eff}:

$$\frac{\Delta\varepsilon_{eff}}{\varepsilon_{eff}} = \frac{\Delta A}{A} + \frac{\Delta d}{d} + \frac{\Delta C}{C}$$

$$\frac{\Delta A}{A} = \frac{2\Delta r}{r} = 0.03$$

$$\frac{\Delta d}{d} = 0.076$$

$$\frac{\Delta C}{C} = 5\text{E-}4$$

The contribution of the uncertainty in capacitance is orders of magnitude smaller than even the second largest value (the area's contribution), even at the highest capacitance range (100 pico-farads). It is possible to neglect this capacitance contribution without significantly altering the calculated uncertainty in ε_{eff}. Therefore, the uncertainty in $\Delta\varepsilon_{eff}$ can be calculated as the sum of $\Delta A/A + \Delta d/d$:

$$\Delta\varepsilon_{eff} = (0.10) * (\varepsilon_{eff})$$

Note that the value of (0.10) is the error for KNO and this value changes per sample. Recall that uncertainties should have one significant figure and so the final calculation should reflect that.

The frequency dependent dielectric measurement can therefore be plotted for each sample with an accurate representation of the uncertainty of a capacitance derived calculation, due to the uncertainties in sample area and thickness. (See plot below)

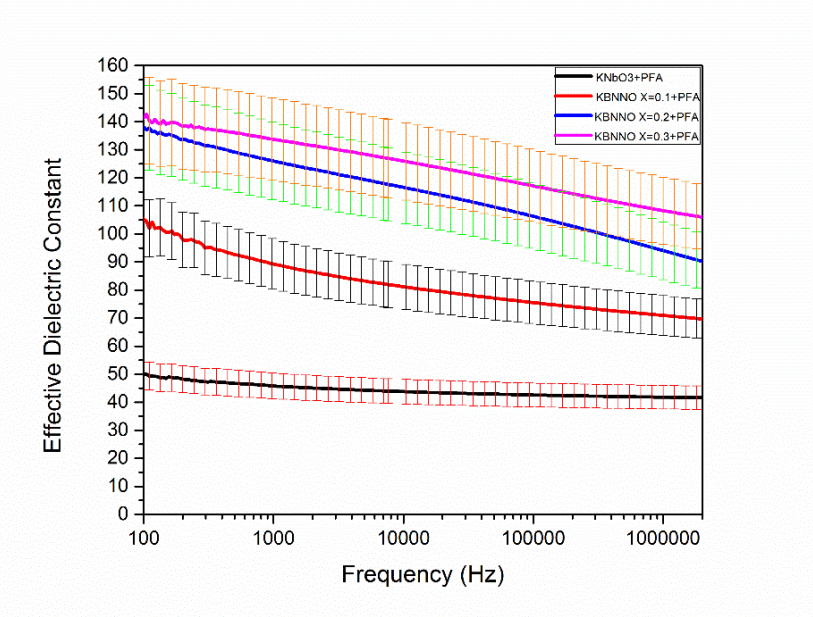


Fig. S10 Effective dielectric constant as a function of frequency for 0-3 nanocomposites of KNbO3/PFA, KBNNO *x* = 0.1/PFA, *x* = 0.2/PFA, and *x* = 0.3/PFA with error bars included.

Volume Fraction Calculations

In order to calculate the volume fraction, the effective density (ρ_{eff}) must be determined and compared to the theoretical density (ρ). The theoretical density changes on which material we are studying in question. The theoretical density was calculated by first taking the standard unit cell of KNO and calculating density, using atomic packing factor calculation. Since the precise unit cell of KBNNO (atomic coordinates, unit cell parameters etc.) is unknown, the theoretical densities of KBNNO (x= 0.1 to 0.3) were derived from the KNO unit cell, with substitutions for Ba and Ni at the K and Nb respectively, with solid solution cation substitution.

For KNO, KBNNO *x* = 0.1, *x* = 0.2, and *x* = 0.3:

Table S7: Densities of the unit cells of KNO, and KBNNO *x* = 0.1-0.3.

Sample	ρ (g/cm^3)
KNO	4.61
KBNNO *x* = 0.1	4.82
KBNNO *x* = 0.2	5.03
KBNNO *x* = 0.3	5.23

The formula for the effective density is as follows:

$$\rho_{eff} = \frac{m}{V}$$

Where m is the mass of the pellet, and V is the volume. These parameters are measured experimentally and have uncertainties:

$$\Delta m = 0.0001\ \mathrm{g}$$

$$\frac{\Delta V}{V} = \frac{2\Delta r}{r} + \frac{\Delta h}{h}$$

$$\Delta r = 0.01\ mm$$

$$\Delta h = 0.01\ mm$$

Where h is the thickness of the pellet. The uncertainty in ρ_{eff} can be calculated using:

$$\frac{\Delta\rho_{eff}}{\rho_{eff}} = \frac{\Delta V}{V} + \frac{\Delta m}{m}$$

With values for r and m:

$$r = 6.36\ mm$$

$$m \sim 0.0511\ g$$

Finally, this effective density is compared to the theoretical density to give the volume fraction of filler in any given pellet:

$$v_f = \frac{\rho_{eff}}{\rho}$$

If we treat the theoretical density as an exact number, the uncertainty in effective density is:

$$\Delta v_f = \frac{\Delta\rho_{eff}}{\rho}$$

Once the uncertainty in effective density is calculated, the Kerner model values can be calculated with an error margin adjustment to account for uncertainty in the combined volume fractions of host/filler. See main article for results.

Supporting information references

[1] B. H. Toby, *J. Appl. Cryst.*. 2001, **34**, 210-213

[2] B. H., Toby, R. B, Von Dreele,. 2013, **46**(2), 544-549.