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Electronic Supplementary Information

Ferroelectric and dielectric properties of Ca^{2+}-doped and Ca^{2+}-Ti^{4+} co-doped $K_{0.5}Na_{0.5}NbO_3$ thin films

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XRD curve fitting using the Pawley method

The Pawley method was used for curve fitting of the X-ray diffractograms from powders calcined at 700 and 850 °C for 4 h after calcination. The patterns were fitted to the monoclinic space group Pm, using a=c=4.000 Å, b=3.950 and β=90.33° as starting parameters. Calculated unit cell parameters and unit cell volumes from the Pawley fitting are presented in Table S.1 and plotted in Figure S.1. Pawley method fitted curves to powder X-ray diffractograms are given in Figure S.2.

Table S.1: Lattice parameters, unit cell volumes, crystallite sizes and weighted profile R-factors from Pawley method fitting of X-ray diffractograms from the KNN powders.

	a [Å]	b [Å]	c [Å]	β [°]	V [Å^3]	Crystallite size [nm]	R_{wp} [%]
KNN-700°C	4.005	3.949	3.989	90.19	63.089	26.3	10.04
KNN-850°C	4.004	3.943	3.998	90.22	63.119	56.5	13.48
KNN-Ca^{2+}-700°C	4.001	3.945	3.981	90.52	62.833	18.4	10.32
KNN-Ca^{2+}-850°C	3.997	3.944	3.981	90.42	62.755	23.6	10.66
KNN-$CaTiO_3$-700°C	4.000	3.943	3.977	90.78	62.712	21.4	14.48
KNN-$CaTiO_3$-850°C	3.998	3.945	3.979	90.53	62.755	23.1	10.76

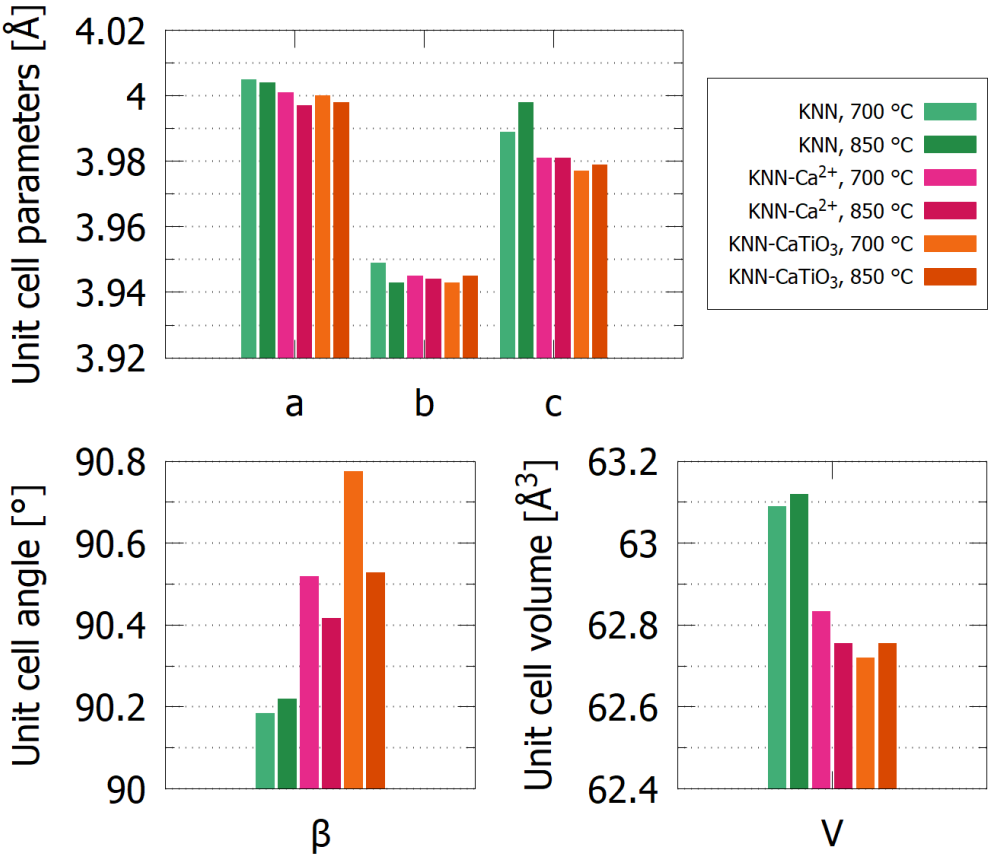

Figure S.1: Unit cell parameters and unit cell volumes from the Pawley method fitting of XRD patterns of the powder (values in Table A.1).

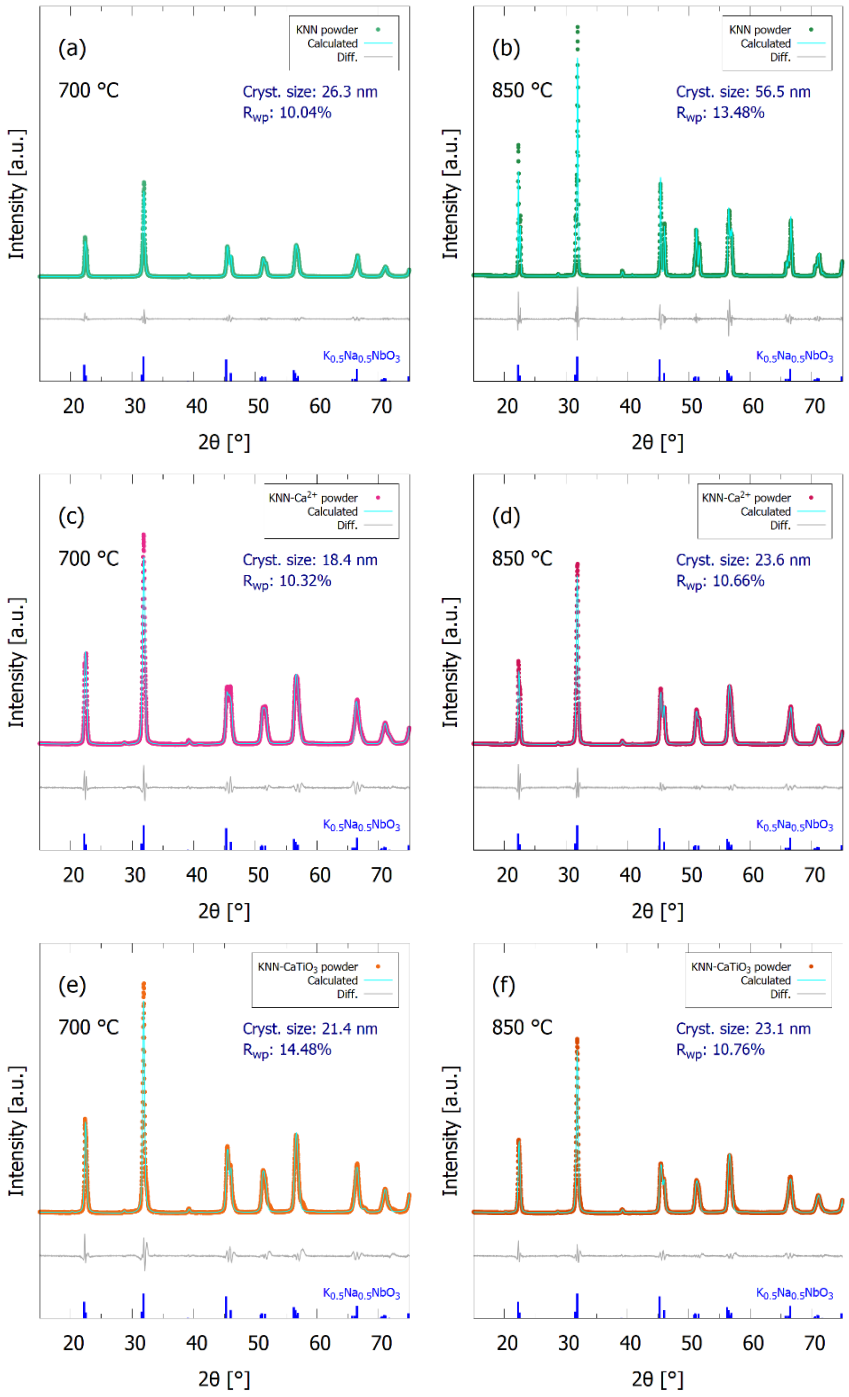

Figure S.2: Pawley method fitting of powder X-ray diffractograms from (a), (b) undoped, (c), (d) Ca^{2+}-doped and (e), (f) $CaTiO_3$-doped KNN powders. Figures (a), (c) and (e) are from powders heat treated at 700 °C and figures (b), (d) and (f) from powders heat treated at 850 °C. Crystallite sizes and weighted profile R-factors (R_{wp}) for the fits are given in each plot. Reference pattern for $K_{0.5}Na_{0.5}NbO_3$ (blue, PDF card 00-061-0315 (1)) is included.

Conventional XRD of KNN films

Conventional XRD diffraction patterns (θ-2θ mode) of the KNN films after pyrolysis (550 °C) and annealing (700 °C) are presented in Figure S.3. The intensities of the Bragg reflections of the annealed KNN films are comparable to those of the reference pattern of bulk KNN, demonstrating the films are polycrystalline and with no degree of texture. The pyrolyzed films have some (100) preferential orientation (inset) which might be caused by the film not being completely crystallized.

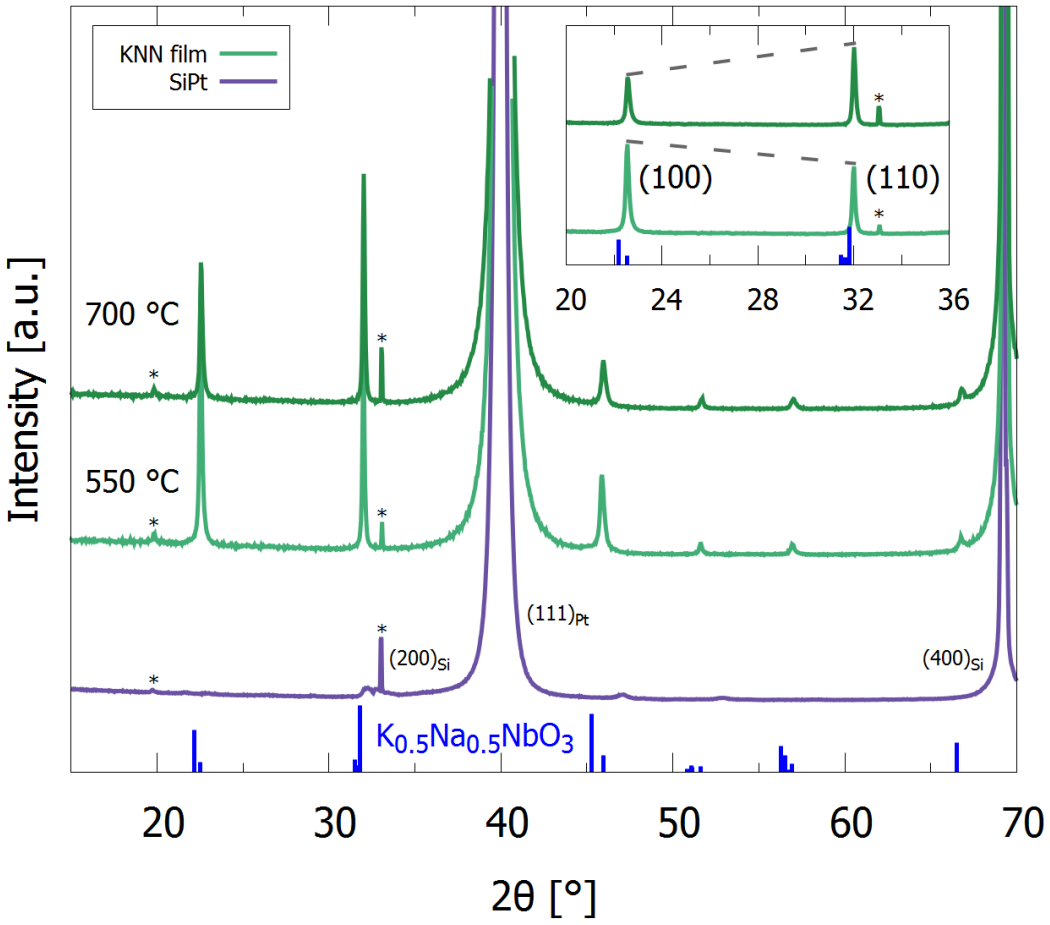

Figure S.3: Conventional XRD patterns of pyrolyzed (550 °C) and annealed (700 °C) KNN films on SiPt. The pattern of a blanc SiPt substrate is included for comparison. Reference pattern for $K_{0.5}Na_{0.5}NbO_3$ (blue, PDF card 00-061-0315 (1)) is included. The films were prepared by 30 repeating spin coatings.

P_r, P_{max} and E_c from polarization-electric field measurements

Remnant polarization (P_r), maximum polarization (P_{max}) and coercive field (E_c) from the polarization vs. electric field measurements of the films at 10 to 5000 Hz (Figure 4 and 5) are presented in Table S.2. The values at 10 Hz are measured using an electric field of 100 kV cm^{-1}. The values at 50 to 5000 Hz are measured using an electric field of 125 and 142 kV cm^{-1} for KNN-Ca^{2+} and KNN-$CaTiO_3$, respectively.

Table S.2: Remnant polarization (P_r), maximum polarization (P_{max}) and coercive field (E_c) of KNN-based films from 10 to 5000 Hz.

		10 Hz	**50 Hz**	**100 Hz**	**500 Hz**	**1000 Hz**	**5000Hz**
P_r [µC cm^{-2}]	KNN	5.47±2.25	-	-	-	-	-
	KNN-Ca^{2+}	4.24±0.47	6.37±0.94	5.69±0.37	4.90±0.05	4.69±0.07	4.90±0.46
	KNN-$CaTiO_3$	6.65±1.44	7.40±0.17	6.88±0.96	6.37±0.57	6.20±1.02	6.95±0.80
P_{max} [µC cm^{-2}]	KNN	13.80±2.00	-	-	-	-	-
	KNN-Ca^{2+}	18.20±0.00	21.45±0.50	20.70±0.20	19.70±0.00	19.00±0.00	17.85±0.30
	KNN-$CaTiO_3$	22.20±0.20	26.45±0.10	25.60±0.40	24.90±0.20	24.20±0.20	23.35±0.50
E_c [kV cm^{-1}]	KNN	47.08±12.83	-	-	-	-	-
	KNN-Ca^{2+}	18.42±4.17	22.00±8.67	22.58±3.50	24.08±0.17	23.00±0.67	26.58±1.83
	KNN-$CaTiO_3$	17.92±1.17	27.75±4.50	27.83±3.00	27.08±5.50	28.25±6.50	31.00±4.33

Frequency dependency of dielectric permittivity

The frequency dependency of the dielectric permittivity from 1 to 10^6 Hz is presented in Figure S.4. The measurements were performed at 150 °C (upon heating), using an AC amplitude of 50 mV. The dielectric loss tangent (tan δ) for the measurements is included in the figure.

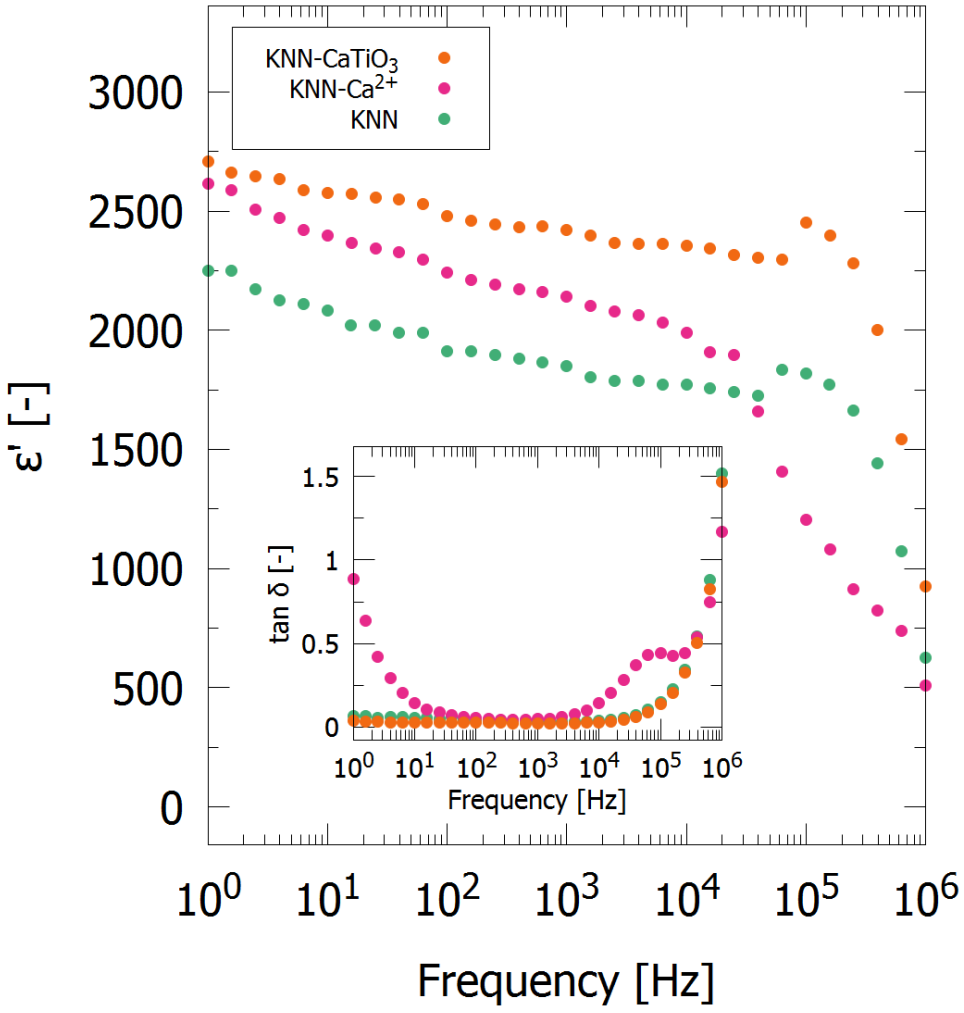

Figure S.4: Dielectric permittivity as a function of frequency for the three KNN-based films, measured at 150 °C and using an AC amplitude of 50 mV. Inset: The loss tangent recorded during the measurement.

References:

1. Tellier J, Malic B, Dkhil B, Jenko D, Cilensek J, Kosec M. Crystal structure and phase transitions of sodium potassium niobate perovskites. Solid State Sci. 2009;11(2):320–4.