Supplementary Information

Large Electrocaloric Effect under Electric Field behavior in Potassium Sodium Niobate Ceramics with Incompletely Overlapped Phase Boundary

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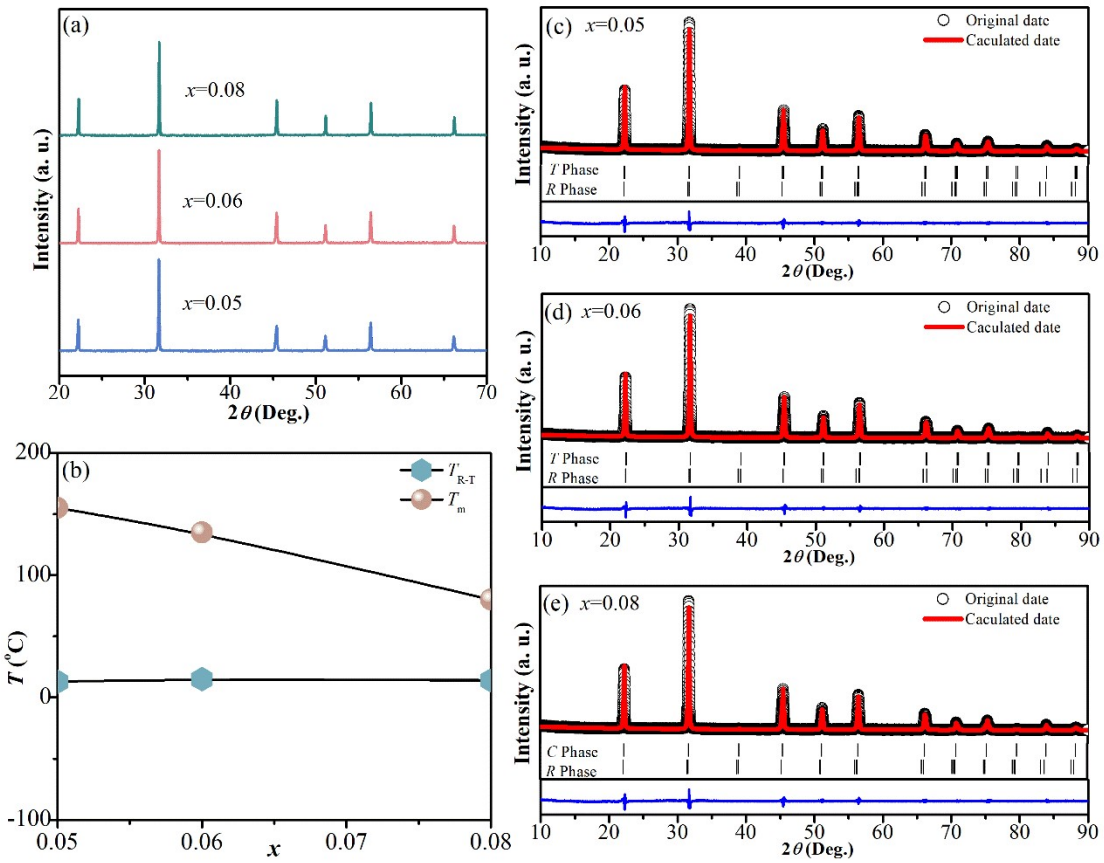

Figure S1. (a) XRD patterns for the ceramics with 2θ=20-70°, (b) phase diagram of the ceramics, Rietveld refinements of XRD patterns: (c) x=0.05, (d) x=0.05, (e) x=0.05.

Table S1. Parameters of refine result for the KNLNS-BZ-BNH-Fe ceramics with different phase boundary.

x	Sig	R_w (%)	Space group	a (Å)	b (Å)	c (Å)	Alpha(°)
0.05	1.89	4.7	R3m.R	4.0025	4.0025	4.0025	89.6491
			P4mm	3.9842	3.9842	3.9970	-
0.06	1.82	5.1	R3m.R	4.0030	4.0030	4.0030	89.6249
			P4mm	3.9854	3.9854	3.9948	-
0.08	1.85	5.39	R3m.R	4.0050	4.0050	4.0050	89.7732
			Pm-3m	3.9891	3.9891	3.9891	-

Figure S1(a) shows the XRD patterns of the ceramics measured at room temperature. Typical perovskite structure without impurity phase is found in all the samples. As shown in Fig. S1(b), the $T_{R\text{-}T}$ remain around room temperature with increasing x, while T_m gradually decreases. Specially, the phase transition temperature regions broaden for x=0.08. The T_m is strongly decreased near room temperature. Therefore, the phase structure can be determined as R-T for x=0.05 and 0.06, and R-C for x=0.08 at room temperature. The phase structures are further verified by well-matched Rietveld refine results, which contain low Sig and Rw values, as shown in Figs. S1(c)~(e) and Table S1. The relative structure parameters of different phases are also presented in Table S1.

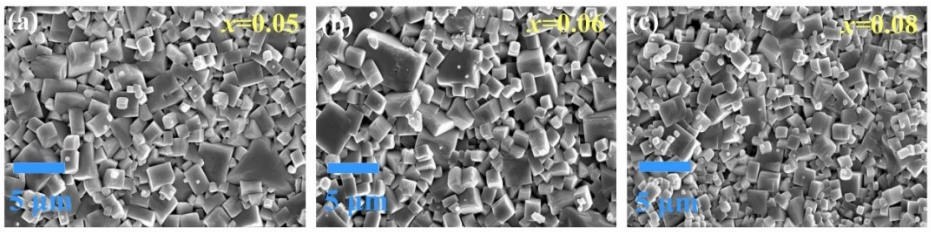

Figure S2. FE-SEM images of the ceramics: (a) x=0.05, (a) x=0.06 (a) x=0.08.

Figure S2 shows the FE-SEM images of the ceramics. It can be seen that all the samples are dense along with large and small grains, which is benefit of applying high electric field.

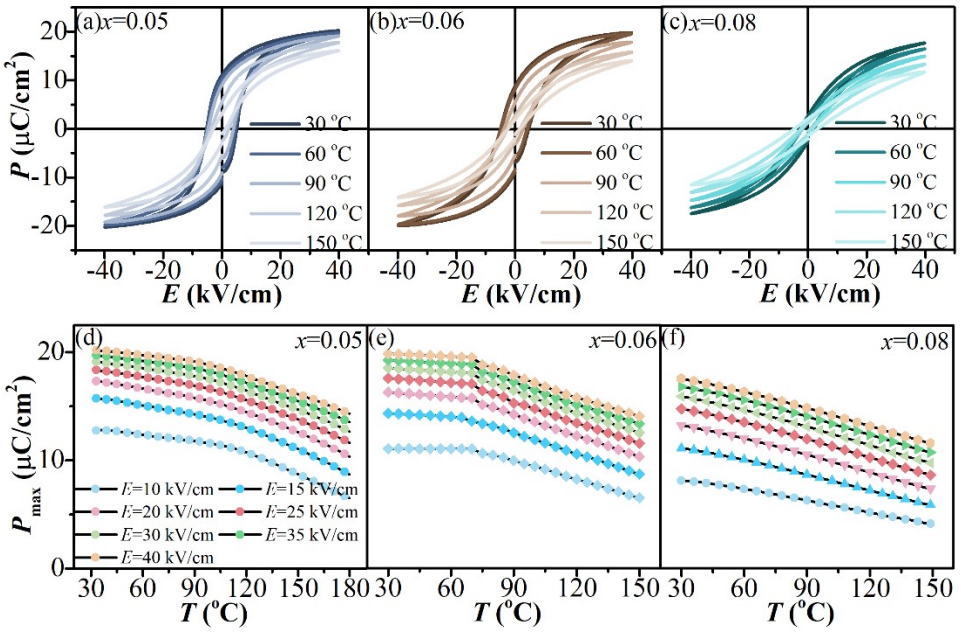

Figure S3. *P*-*E* loops of the ceramics under 40 kV/cm measured at different temperatures: (a) x=0.05, (b) x=0.06 (c) x=0.08, P_{max}-T curves: (d) x=0.05, (e) x=0.06 (f) x=0.08.

Figure S3 shows the temperature-dependent *P*-*E* loops of the ceramics when E=40 kV/cm. When $T>60$ °C, both P_{max} and P_r decreases obviously for x=0.05 and 0.06. When x=0.08, P_{max} and P_r decease with increasing temperature from 30 °C. All the *P*-*E* loops gradually becoming slim at high temperatures. The temperature dependence of P_{max} is shown in Figs. S3(d)~(f). Faster decrease of P_{max} is obtained around FE-PE phase transition regions with respect FE-FE phase boundary for x=0.05 and 0.06, while continuous decrease is found for x=0.08.

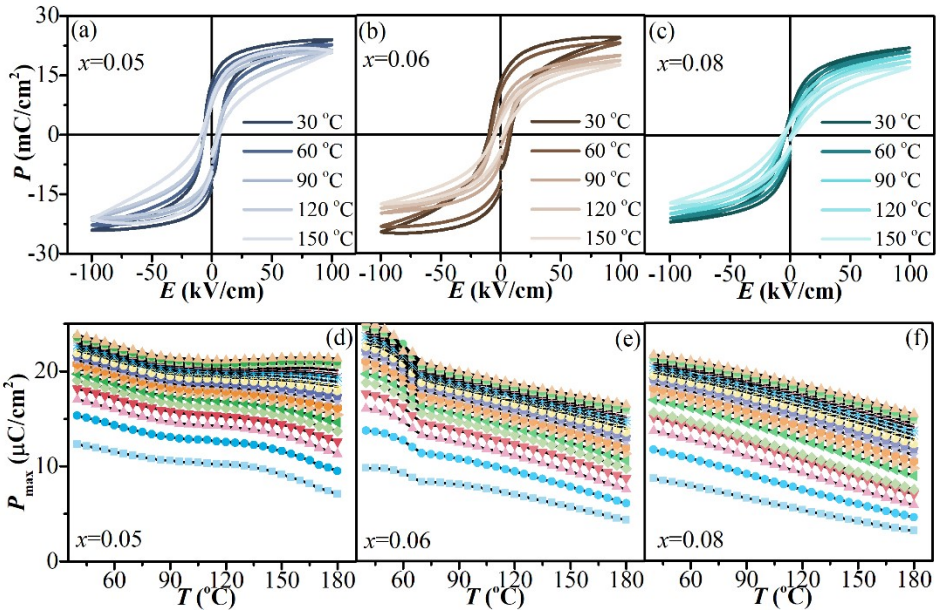

Figure S4. *P-E* loops of the ceramics measured at different temperatures under 100 kV/cm: (a) x=0.05, (b) x=0.06 (c) x=0.08, P_{max}-T curves: (d) x=0.05, (e) x=0.06 (f) x=0.08.

Figures S4(a)~(c) show the P-E loops at 100 kV/cm and different temperatures. Both P_{max} and P_r gradually decrease with increasing temperatures as well as lowered E_C, inducing slim *P-E* loops. The temperature dependence of P_{max} is presented at different E, as seen in Figs. S4(d) and (f). The decreasing tendency is similar to the phenomenon when E=40 kV/cm.

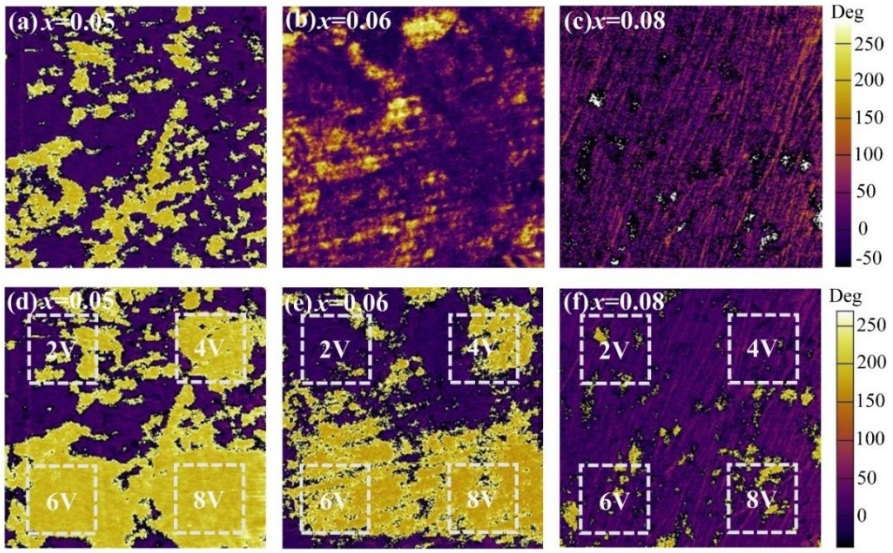

Figure S5. Phase images of virgin domain for the ceramics: (a) x=0.05, (b) x=0.06 (c) x=0.08, phase images after poled under 2V~8V: (d) x=0.05, (e) x=0.06 (f) x=0.08.

Figures S5(a)~(c) show the phase images of the virgin domain for the ceramics. Domain with both large and small size can be roughly gained for x=0.05 and 0.06, while refined domain occurs for x=0.08. Then, the phase images after poled under 2-8V, are presented in Figs. S5(d)~(e). Domain switching happens when V≥4V for x=0.05 and 0.06. Moreover, the reversion of switched domain is more for x=0.06 than that for x=0.05, while the reversion begins from the inside of domain. For x=0.08, the domain switching is poor because of the strong reversion behavior of the oriented domain after withdrawing V, which originates from the strong random field yielding to excess chemical/structure heterogeneity and PNRs.