Supplemental Data

Influence of temperature-induced A-site cations redistribution on the functional properties of A-site complex polar perovskite $K_{1/2}Bi_{1/2}TiO_3$

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1. **Temperature-dependent dielectric permittivity for samples cooled with different cooling rates from the Tmax of 900 °C**

Temperature-dependent dielectric permittivity measured up to 600 °C during heating for KBT samples cooled with different cooling rates from the Tmax of 900 °C. The room temperature permittivity value increases with decreasing cooling rate.

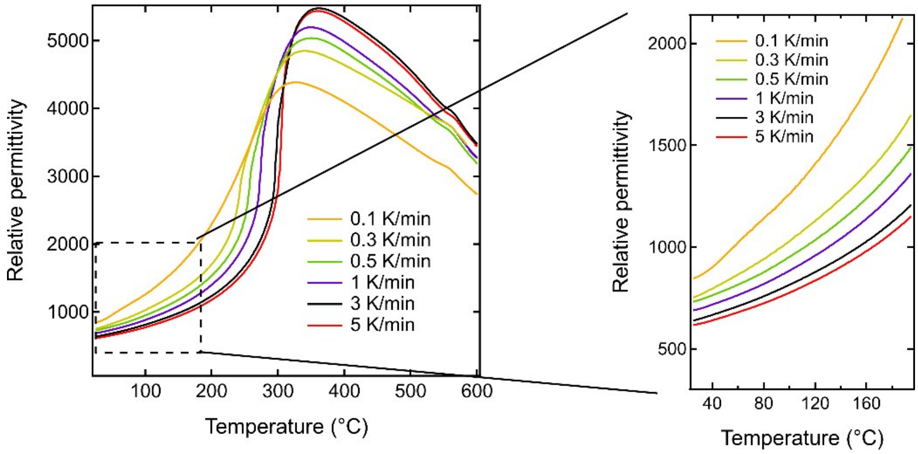

Figure S 1 Temperature-dependent dielectric permittivity of KBT samples treated with different cooling rates from the Tmax of 900 °C.

2. **Temperature-dependent dielectric permittivity of slow-cooled KBT from different $T_{\mathbf{max}}$**

Temperature-dependent dielectric peramittivity measured upto 600 °C during heating and cooling for maximum annealing temperature-dependent slow cooled KBT. Change in thermal hysteresis during heating and cooling found to be changed with increasing annealing T_{max}.

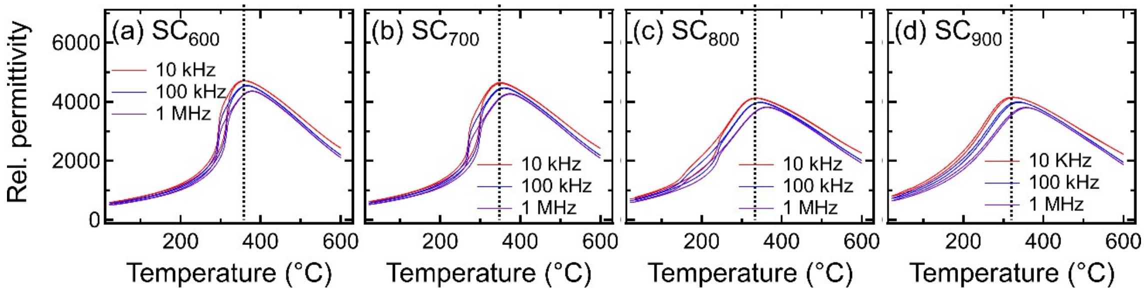

Figure S 2 Temperature-dependent dielectric permittivity of KBT samples treated with different T_{max} with a cooling rate of 0.1 K/min.

3. Analysis of TF-R from dielectric permittivity data

Inverse of permittivity data[25] was used to identify the transition temperature during heating and cooling. The $\Delta T_{F\text{-}R}$ indicates the difference in F-R and R-F transition.

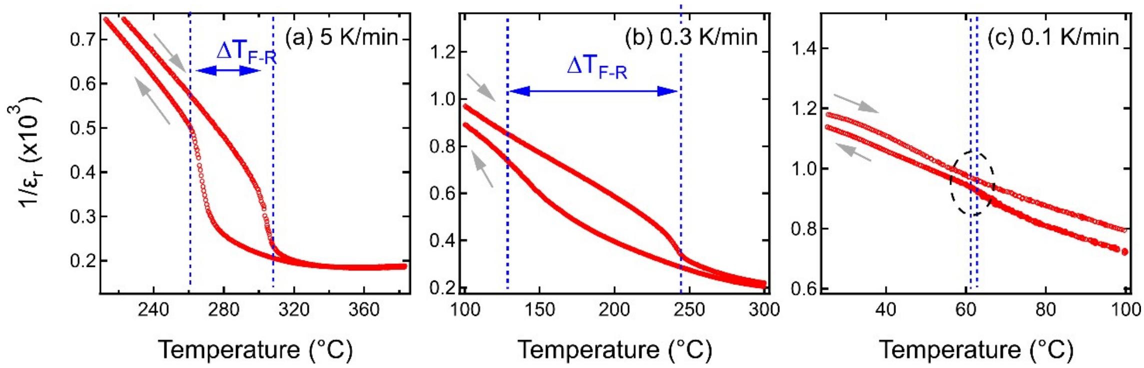

Figure S 3 Inverse dielectric permittivity for samples annealed with cooling rate (a) 5 K/min, (b) 0.3 K/min, and (c) 0.1 K/min from the T_{max} of 900 °C

4. Temperature-dependent dielectric permittivity of quenched KBT from different T_{max}

Dielectric permittivity of KBT ceramics measured after quenching at different T_{max}. A significant increase in T_{F-R} is observed for Q_{900} KBT.

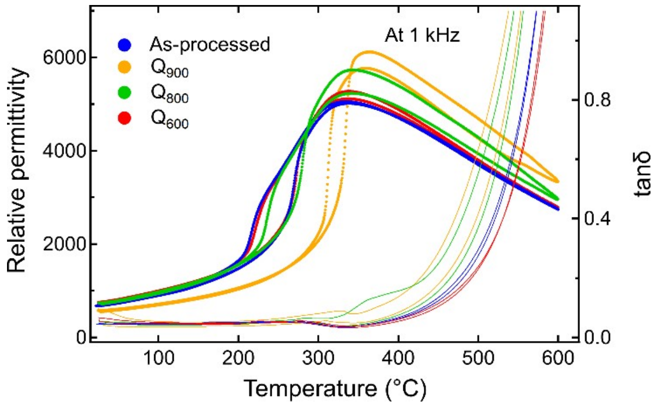

Figure S 4 Variation in dielectric permittivity for samples quenched at different T_{max}

5. **Reversible FE-RE-FE state change in KBT**

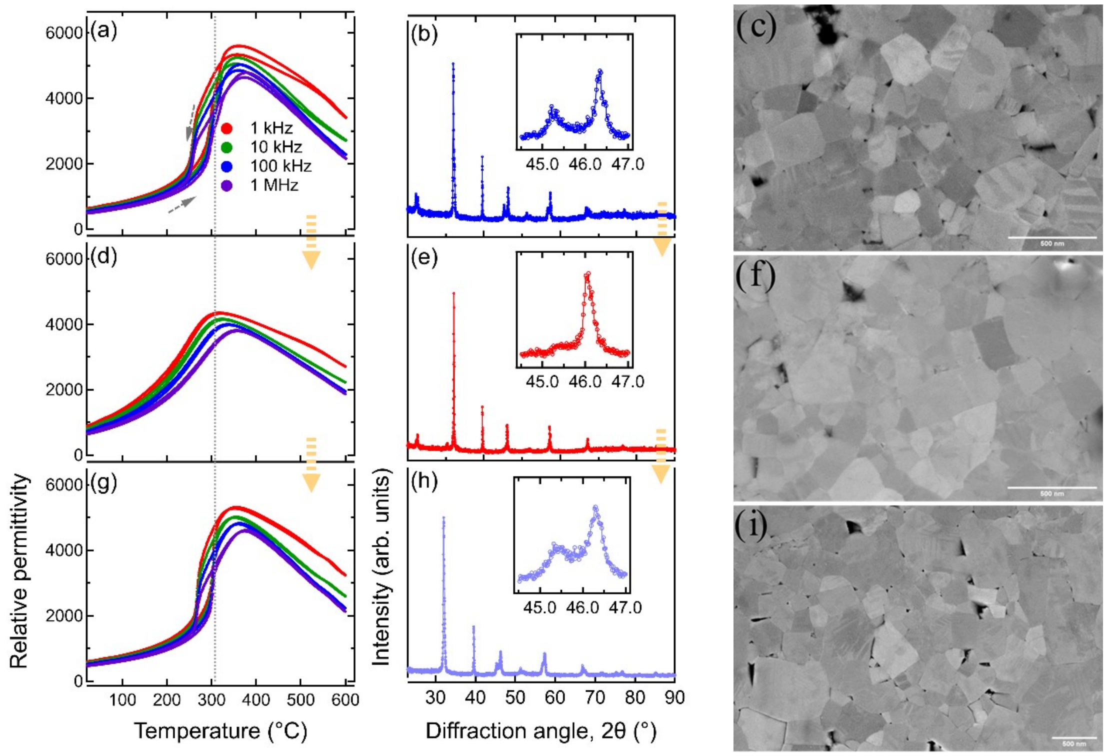

Figure S 5 Temperature-dependent permittivity, x-ray diffraction patterns, and microstructure for a single KBT sample after subsequent treatment with 5 K/min (a-c) NC_{900}, (d-f) SC_{900}, and (g-i) NC_{900} indicating the slow cooling induced change can be reverted to the original state.

6. **Simulation of NMR spectrum for TiO_2**

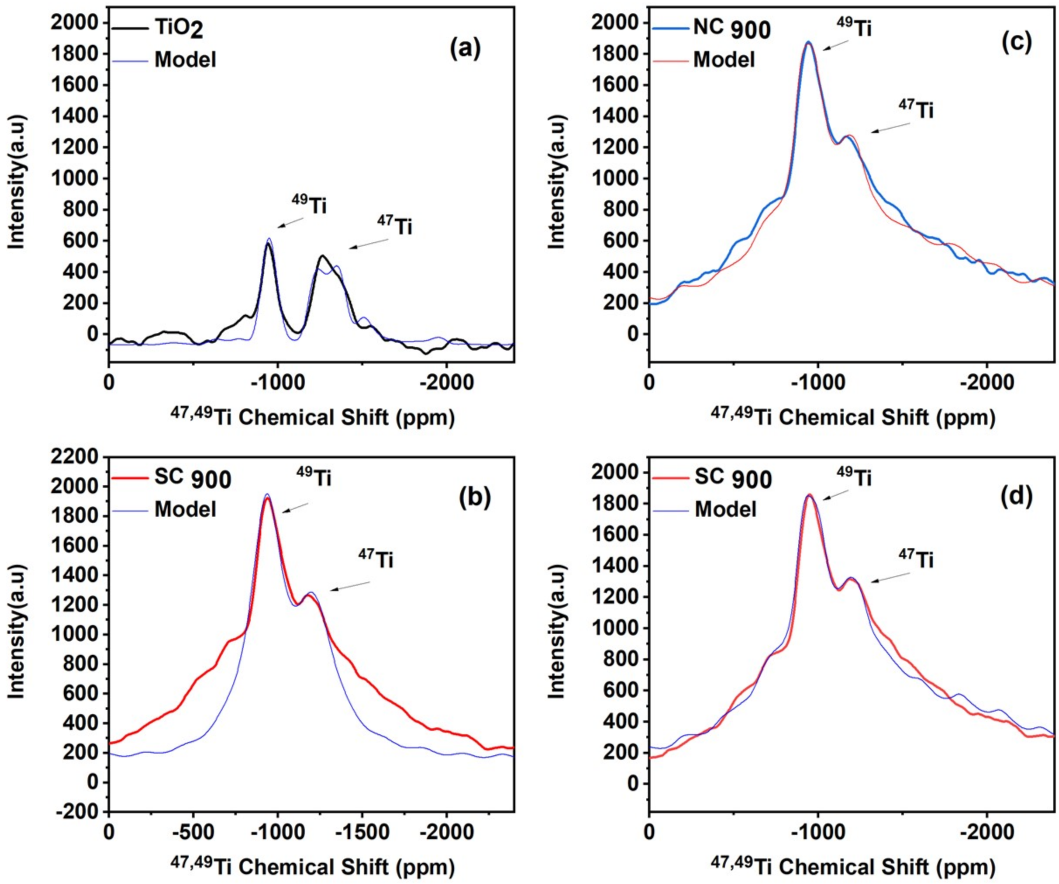

Figure S 6 Simulation of ^{47,49}Ti NMR spectra with different models (a) TiO_2 with int2QUAD, (b) SC_{900} KBT with int2QUAD, (c) NC_{900} KBT with Czjzek, and (d) SC_{900} KBT with Czjzek.

Simulation parameters are listed in Table S 1.

Table S 1 Simulation parameters for ^{47,49}Ti NMR spectra, simulated with DMfit.[51]

	model	chemical shift (ppm)	Quadrupolar Coupling C_Q (kHz)	eta	Window function (Hz)	MAS frequency (Hz)
TiO_2	int2QUAD	-907	4481	0	-3000	10000
NC_{900}	Czjzek	-870	3750* (7500)	-	3500	8000
SC_{900}	Czjzek	-880	4000* (8000)	-	3500	8000
SC_{900}	int2QUAD	-911	3122	0	8000	8000

*average CQ value computed from the Czjzek model (value in parenthesis represents CQ_max used as input for the distribution in dmfit) (Ref:10.1002/mrc.984)

7. **Internal residual stress measurement using synchrotron x-ray diffraction.**

The azimuth angle-dependent diffraction data were collected at the Spring8 using a monochromatic x-ray beam with an energy of 24 keV (λ = 0.5166 Å) and with an area detector Rigaku Hypix-9000HE. A beam size of 300 µm × 300 µm was used. Azimuth angle-dependent variation in d-spacings, i.e., 2θ position of selected individual reflections, can reveal the extent of internal residual stress in a material. Analysis of peak positions of 110 $_{pc}$, 111 $_{pc}$, and 200$_{pc}$ reflections did not show any significant variation in internal residual stress within the sensitivity of the measurement.

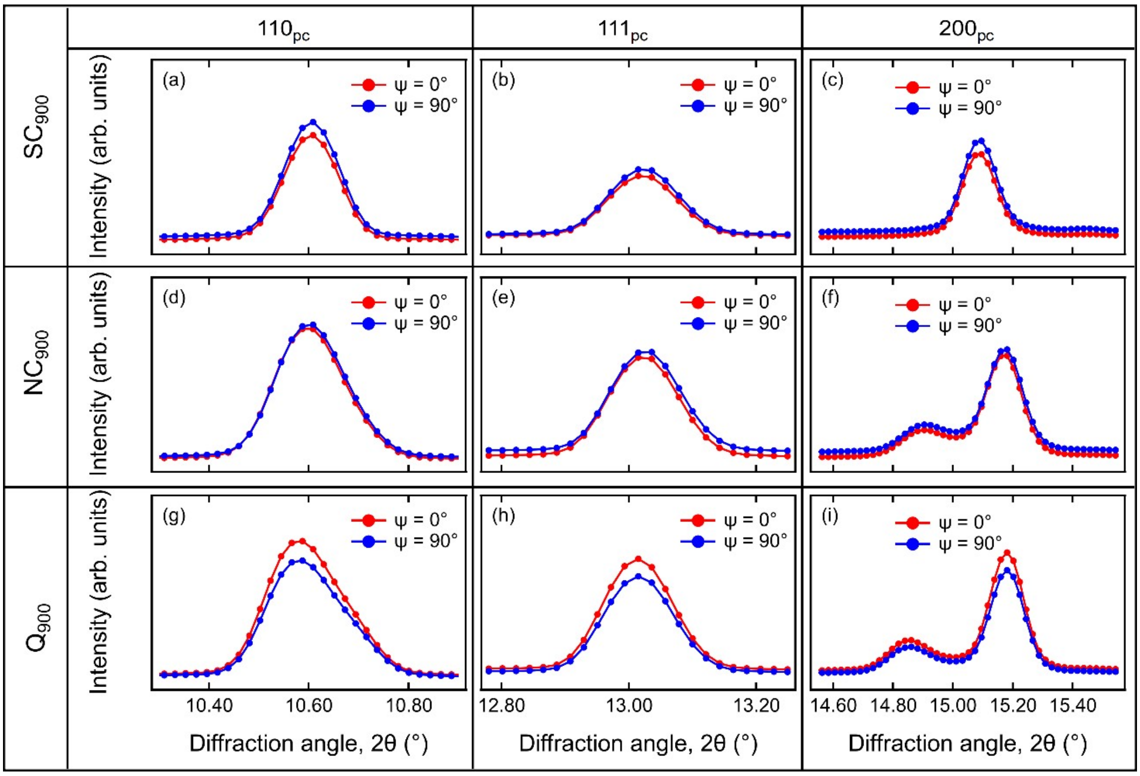

Figure S 7 Diffraction patterns of slow cooled (SC$_{900}$), normal cooled (NC$_{900}$), and quenched (Q$_{900}$) KBT for azimuth angle, ψ = 0°, 90°. No significant variation in peak position with azimuth angle is evident from the diffraction data.