Supplementary Information to Relaxor behavior and electrothermal properties of Sn and Nb modified (Ba,Ca)TiO3 Pb-free ferroelectric

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| **FIG. S1:** Logarithmic variations of the difference in the reciprocal values of the relative dielectric permittivity i.e, log(1/ɛ′-1/ɛ′m) as a function of log(T-Tm) for BCST-Nb0.04 ceramics. |
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**FIG. S2:** The logarithmic frequency variation with inverse transition temperature 1/Tmax (shown by hollow symbols) and the corresponding solid continuous lines are the best fits to the Arrhenius equation.

Arrhenius model can be expressed by:  where ω = 2π*f* (*f* is the measured frequency), ωo = 2π*f*o (*fo*is theattempt jump frequency), Ea is the activation energy and kB are the Boltzman constant. Figure S2 presents the ln ω versus 1/Tm plot fitted using the Arrhenius model. The values of *f*o and Ea are found to be ~1024 Hz and ~ 1.062 eV, respectively. Such high and unphysical values suggest that the electrical dipoles are not dynamic for all temperatures above absolute zero.

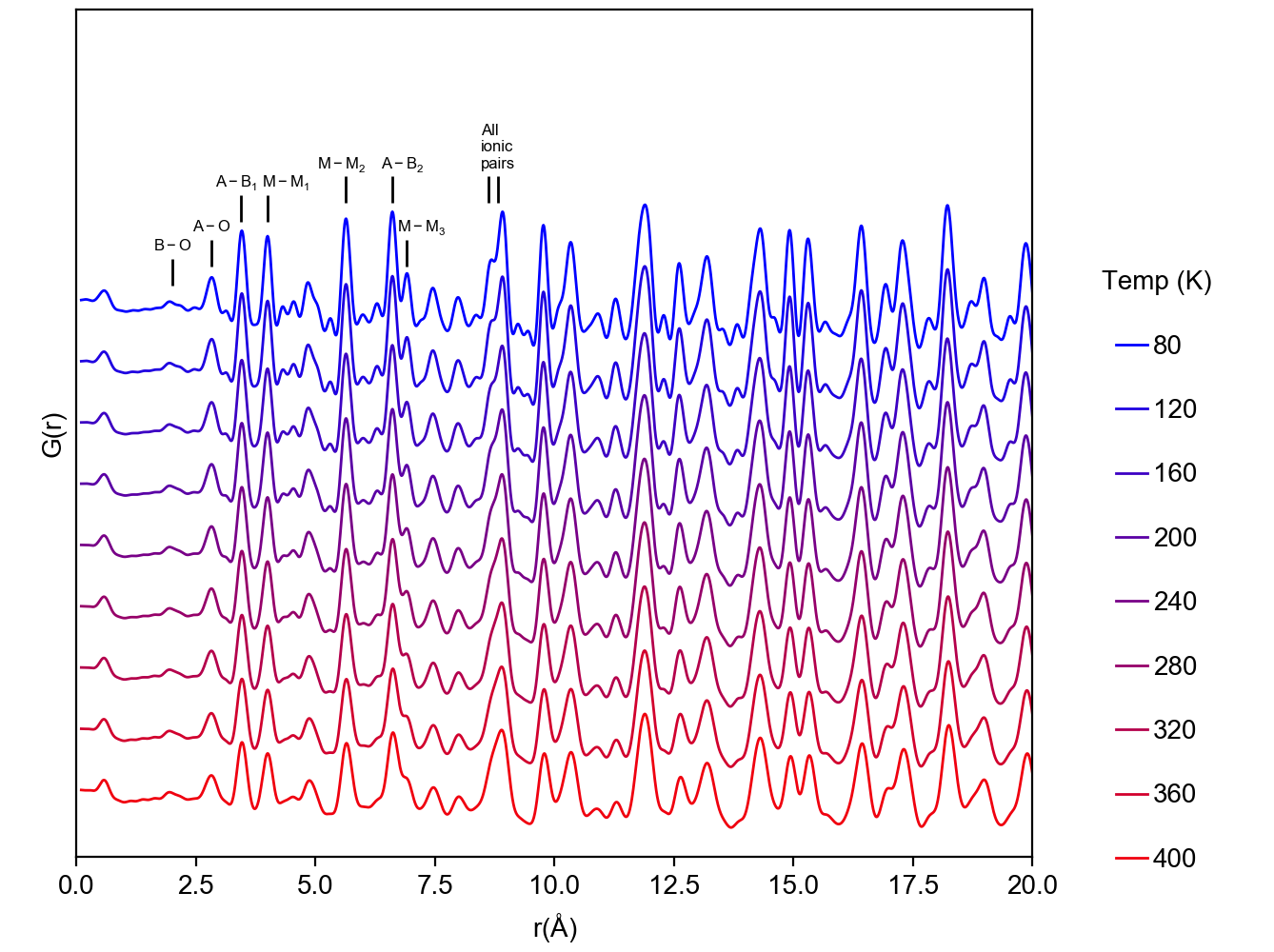
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**FiG. S3:** (a, b) Piezo force microscopy images, (a) amplitude and (b) phase, of Ba0.77Ca0.21Sn0.02(Ti0.94Nb0.04Sn0.02)O3(BCST-Nb0.04) ceramics showing presence of nanoscale domains**.** (c,d) Comparable images from ceramic sample of similar composition without Nb-doping shows presence of large domains.



**FIG. S3:** Comparison of XPS spectra of Ba0.77Ca0.21Sn0.02(Ti0.94Nb0.04Sn0.02)O3(BCST-Nb0.04) ceramics with those of pure SnO and SnO2 indicating presence of both Sn2+ and Sn4+ state in the synthesized ceramics.

The X-ray peak positions for Sn-3d5/2 and Sn-3d3/2 are identified based on refs. [1-2]. The relevant peak positions for Sn in Ba0.77Ca0.21Sn0.02(Ti0.94Nb0.04Sn0.02)O3(BCST-Nb0.04) are at lower binding energies as compared to Sn in SnO/SnO2, which is likely due to higher electron density around Sn in the ternary oxide.



**FIG. S4:** Temperature dependent PDF patterns over full scale extracted from X-ray total scattering patterns.

References:

[1] *Handbook of X-ray Photoelectron Spectroscopy* by J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, published by Perkin-Elemer Corporation, 1992

[2] National Institute of Standards and Technologies (NIST) XPS database (<https://srdata.nist.gov/xps/Default.aspx>).