Electronic supplementary material

Ultrawide Bandgap $CaHfO_3$ as a Linear Dielectric Filler for Superior Energy Storage in $0.7Bi_{0.5}Na_{0.5}TiO_3$-$0.3Sr_{0.7}Nd_{0.2}TiO_3$ Ceramics

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Experimental section

Material preparation:

In this work, the $CaHfO_3$ component with an ultra-wide bandgap was introduced, incorporating Ca and Hf elements at the A-site and B-site, respectively. A series of $(1-x)$ $(0.7Bi_{0.5}Na_{0.5}TiO_3\text{-}0.3Sr_{0.7}Nd_{0.2}TiO_3)\text{-}xCaHfO_3$(BNT-0.3SNT-$x$CH) lead-free dielectric ceramic solid solutions, abbreviated as BNT-0.3SNT-xCH (x = 0, 0.02, 0.03, 0.04, 0.05, 0.06), were synthesized via the conventional solid-state reaction method. Using and drying Bi_2O_3 (≥99.0%), Na_2CO_3 (≥99.8%), TiO_2 (≥99.0%), $SrCO_3$ (≥99.0%), Nd_2O_3 (≥99.9%), $CaCO_3$ (≥99.0%) and HfO_2 (≥99.9%) (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) as raw materials. Firstly, the powders were weighed and milled 12 h with ZrO_2 balls and ethanol. After drying at 85°C, the mixed powders were calcined for 3h at 850°C in air, re-milled and dried again. Next, the calcined powders were blended with a 5wt% polyvinyl alcohol (PVA) binder. While the sintering temperature ranged from 1125 to 1150 °C. Among these, 1136 °C was identified as the optimal sintering temperature for BNT-0.3SNT-0.05CH, which exhibited the best performance. All subsequent structural characterization and property evaluations were conducted on samples sintered at their respective optimal temperatures. Before sintered, the green body needed to remove PVA at 600 °C for 2 h. This study systematically investigates the influence of CH doping content on the phase structure, ferroelectric properties, dielectric performance, and stability of the system.

Characterization:

The measurement of phase structure was used an X-ray powder diffraction with Cu K-α radiation (SmartLab-3 kW, Rigaku Ltd., Tokyo, Japan) and a micro-Raman spectrometry with an excitation source of 532 nm (LabRAM HR Evolution, HORIBA Jobin Yvon, Palaiseau, France). The analysis of phase information was used GSAS-II software with Rietveld refinement of XRD powder patterns. X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi, Thermo Fisher Scientific, USA) was performed on polished ceramic samples to examine the chemical states of atoms in the ceramic samples. The observation of microstructure of the ceramics was used field emission scanning electron microscope (FESEM, SU8020, Hitachi Co., Tokyo, Japan). The calculation of grain size was used Nano Measure software. Electrochemical impedance spectroscopy (EIS) was performed using an impedance analyzer (TH2829C, Changzhou, China). The complex impedance spectra of the ceramics were fitted using ZView software. Based on the fitting results, the activation energy of the samples was calculated employing the Arrhenius equation, to assess the vacancy defect characteristics of the materials. The microscopic morphology of nanometer scale and selected area electron diffraction (SAED) images were measured by field emission transmission electron microscope (FE-TEM, JEM-2100, JEOL, Tokyo, Japan). The curves of temperature-changing dielectric permittivity (ε_r) and dielectric loss (tan δ) was used by the impedance analyzer (E4990A, Keysight, Santa Rosa, CA, USA) to measure after polishing and gauging in Ag electrode-plated samples. Prior to ferroelectric measurements, the samples were polished, coated with Ag electrodes (1 mm in diameter), and annealed at 600 °C for 2 h. Polarization–electric field (*P–E*) hysteresis loops and current–electric field (*I–E*) characteristics were measured using a ferroelectric tester (TF Analyzer 3000, aixACCT Systems GmbH, Aachen, Germany). The measurement of charge–discharge characteristics was used a perfect charge–discharge apparatus at 10260 Ω (PK-CPR1801-10015, Polyk Technologies, Philipsburg, PA, USA).

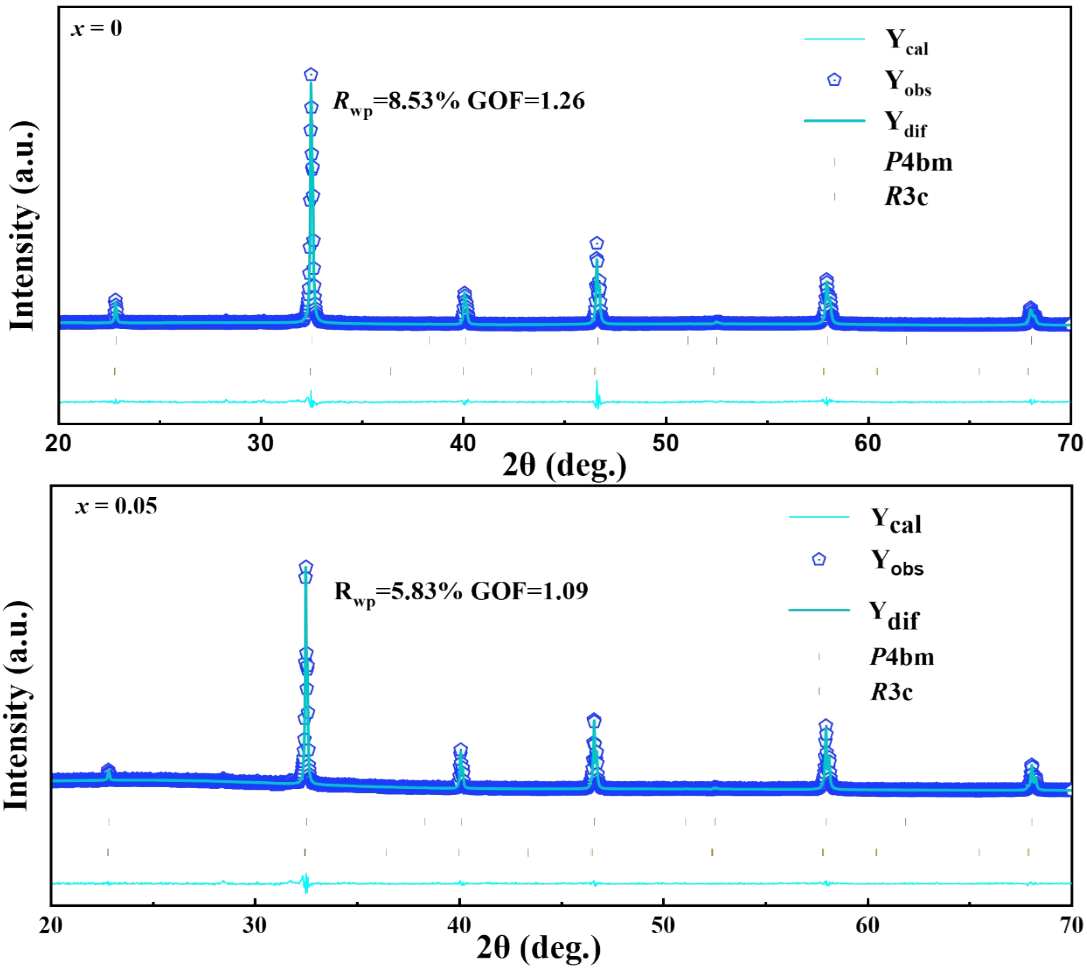

Fig. S1. Rietveld refinement XRD pattern of BNT-0.3SNT-*x*CH ceramics (a) $x = 0$, (b) $x = 0.05$.

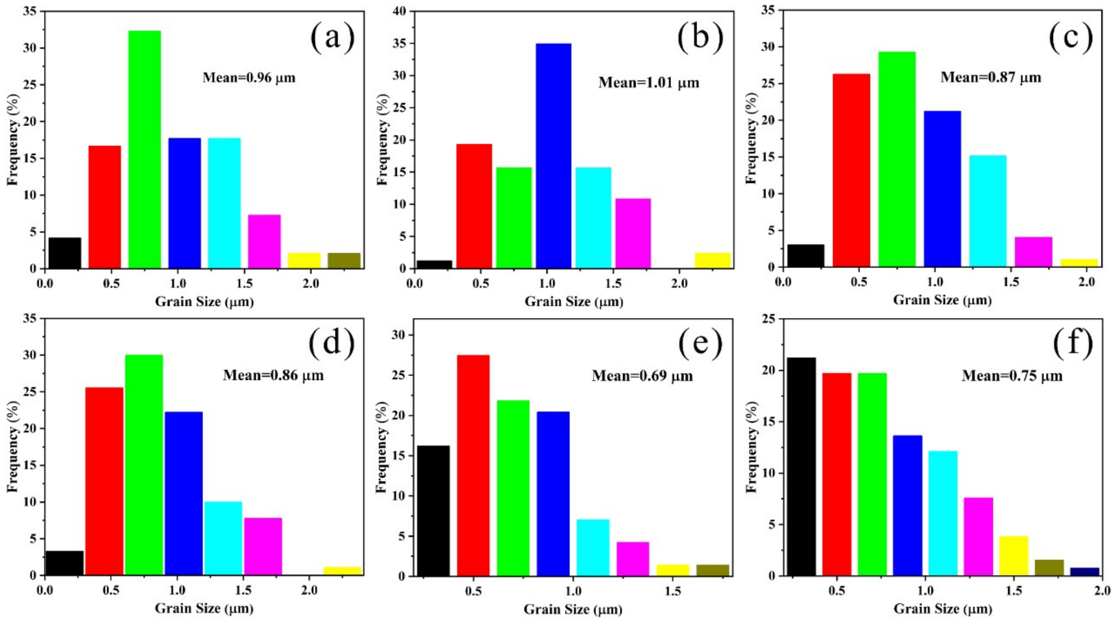

Fig. S2. Grain size distributions of BNT-0.3SNT-*x*CH ceramics: (a) $x = 0$, (b) $x =$

0.02, (c) $x = 0.03$, (d) $x = 0.04$, (e) $x = 0.05$, (f) $x = 0.06$.

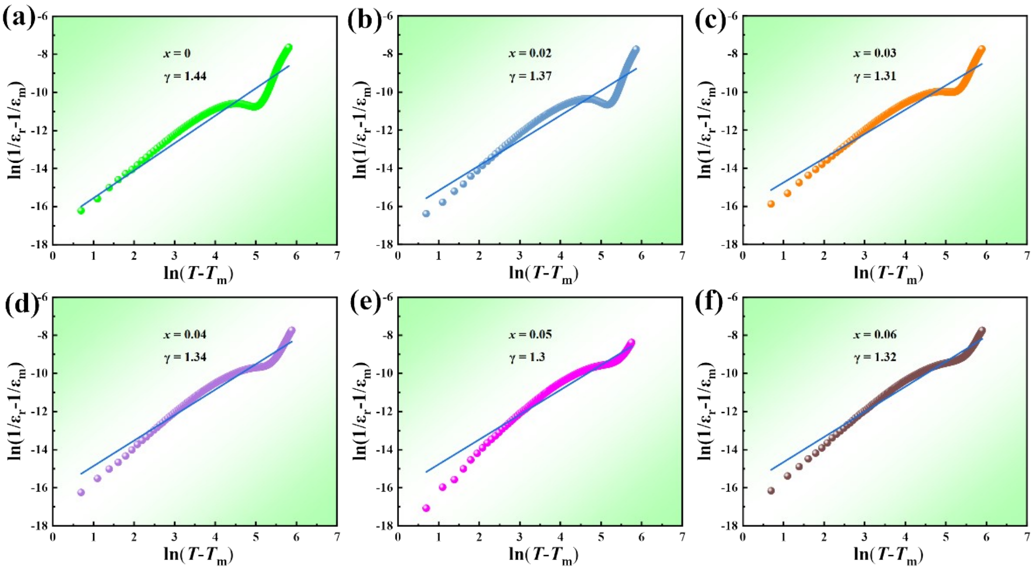

Fig. S3. The variation of $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ with $\ln(T - T_m)$ of BNT-0.3SNT-xCH ceramics ($x = 0$, 0.02, 0.03, 0.04, 0.05,0.06).