Supporting Information

Superior Energy Storage Properties in Lead-free $NaNbO_3$-based Relaxor Antiferroelectric Ceramics via Combined Optimization Strategy

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Material and methods

The (1-*x*)$NaNbO_3$-*x*(0.58($Bi_{0.5}Na_{0.5}$)TiO_3-0.06$BaTiO_3$-0.2$SrTiO_3$-0.16Bi($Mg_{0.5}Zr_{0.5}$)O_3) (NN-*x*) (x = 0.20, 0.25, 0.30, 0.35) ceramics were fabricated using a conventional solid-state reaction approach. The raw materials of Na_2CO_3 (99.8%, Aladdin, Shanghai, China), Nb_2O_5 (99.9%, Aladdin, Shanghai, China), Bi_2O_3 (99.0%, Aladdin, Shanghai, China)，TiO_2 (99.0%, Aladdin, Shanghai, China), $BaCO_3$ (99.0%, Aladdin, Shanghai, China), $SrCO_3$ (99.0%, Aladdin, Shanghai, China), MgO (98.0%, Aladdin, Shanghai, China), ZrO_2 (99.0%, Aladdin, Shanghai, China) were weighted in accordance with their stoichiometries. After mixing with ethanol solvent and ZrO_2 balls, the powders were uniformly mixed in a plastic bottle and ball-milled at 220 rpm for 12 h in a planetary ball miller. Afterwards, the slurry was dried at 80 °C for 10 h. The powder was calcined at 850 °C for 3 h and then ball-milled again for 12 h. Then, 5% polyvinyl butyral (PVB) was used as a binder and the granulated powders were pressed into disks with 10 mm in diameter and ~ 1 mm in thickness under an axial pressure of 6 MPa. Whereafter, isostatic pressing at 200 MPa was carried out for further pre-densification of the green ceramic. Finally, the disks were sintered in the temperature range from 1080 °C to 1120 °C for 10 h after burnout of PVB at 600 °C for 1 h.

The best composition (*x* = 0.30) was selected and the tape-casting method was used to prepare the thick film ceramics. The tape-casting slurry consisted of the second ball-milled NN matrix powders, solvent (butanone and ethanol), binder and plasticizer ball milled for 24 h, then the slurry was tape-cast into a green belt and dried. Then the green belt was screen printed, cut into pieces, and sintered for 6 h to get the thick film ceramics.

The polycrystalline structure of the NN-*x* was characterized using an X-ray diffractometer (XRD, Rigaku Ultima IV diffractometer) with the Cu Kα radiation. The surface morphologies of various specimens were characterized using a scanning electron microscope (SEM, Hitachi S-3400N) and the grain size distributions were statistically analyzed using an ImageJ software. Raman spectra were collected at room temperature on polished pellets by 532-nm excitation using a Raman spectrometer (LabRam HR Evolution, HORIBA JOBIN YVON, Longjumeau Cedex, France). Temperature-dependent dielectric properties and impedances were procured using a dielectric property measurement system

(DMS-500, Partulab, Wuhan, China) at 1, 5,10, 50, and 100 kHz from -120 °C to 150 °C with a heating rate of 3 °C /min. A transmission electron microscope (TEM, Talos F200S) was used to obtain the electron diffraction patterns. For ESP measurements, the bulk samples were polished to ~100 μm in thickness, while the thickness of sintered thick film samples were ~12 μm. Both sides of specimens were covered by gold electrodes with a diameter of 2 mm. The polarization-electric field (*P*-*E*) hysteresis loops were recorded by a Sawyer-Tower circuit (RADIANT Multiferroic Test System). The sintered ceramics were ground to powder for ultraviolet-visible (UV-vis) absorbance spectra (UV3600 Plus, Shimadzu). The surface morphology and domain structure were characterized by AFM and PFM, respectively, which were performed on an integrated scanning probe microscope (Asylum Research MFP-3D) with Pt-coated silicon tips (Nanoworld EFM Arrow).

Figures

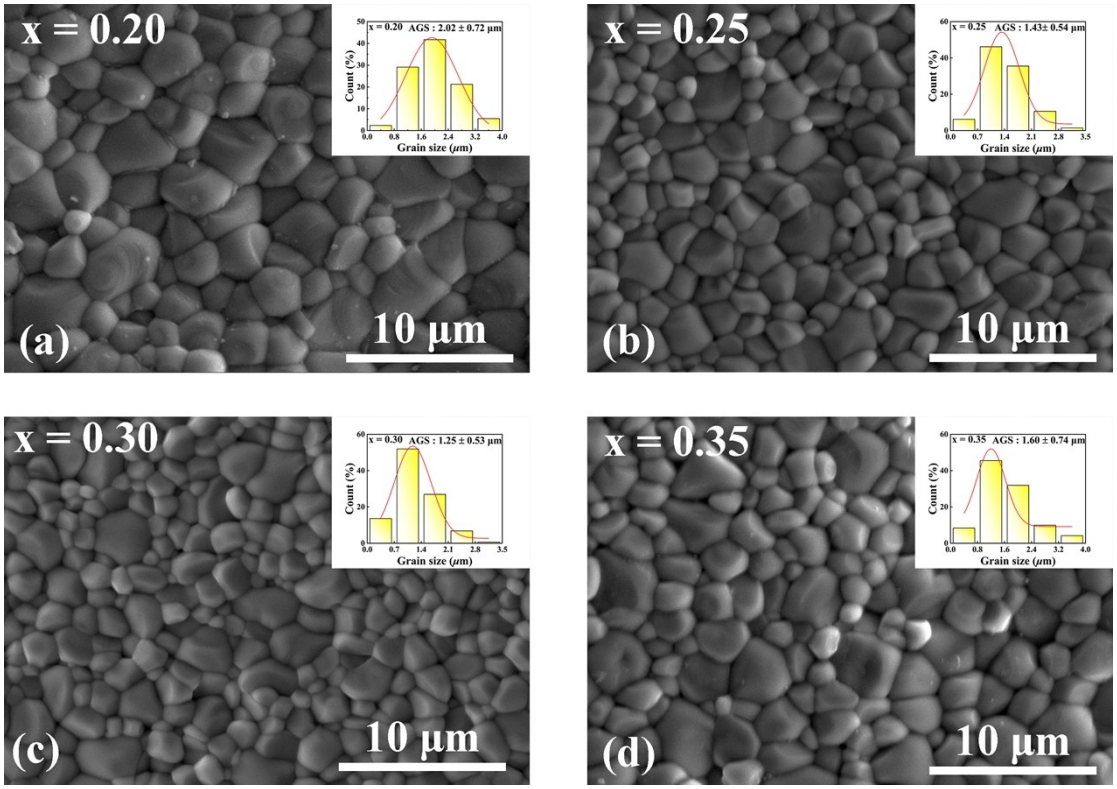

Figure S1 (a)-(d) Scanning electron microscope (SEM) images of various compositions. The inset of each figure corresponds to the statistical analysis of grain size distribution for each sample.

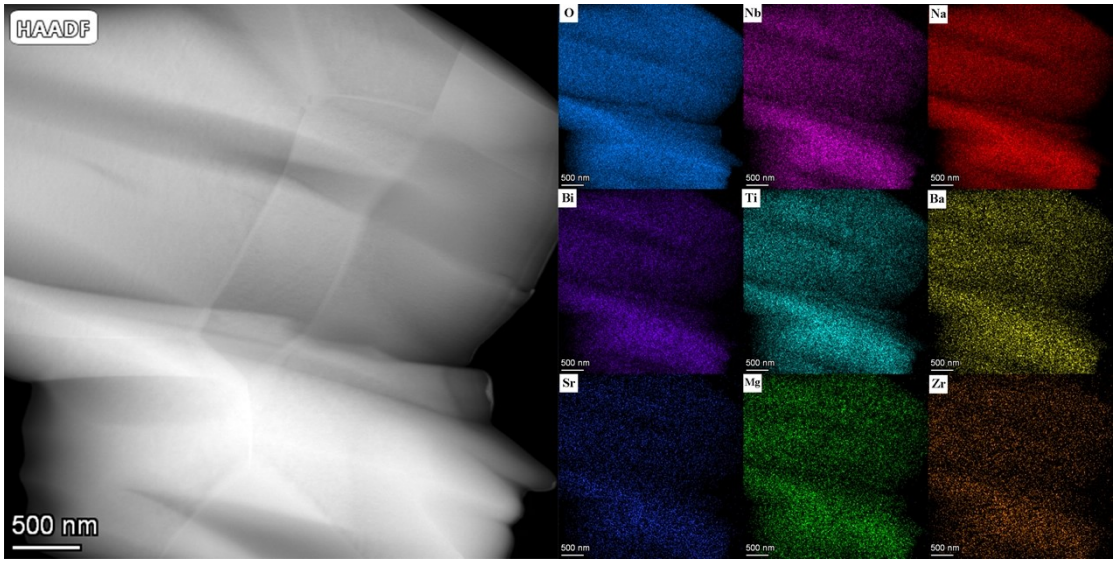

Figure S2 Bright-field TEM image and EDS mappings of each element for x =0.30 ceramic.