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Significantly Improved Energy Storage Performances of $K_{0.5}Na_{0.5}NbO_3$ Lead-Free Ceramics Via Composition Optimization Strategy

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Experimental

The (1-x) KNN-x BMT ceramics were synthesized by a traditional solid-state technique. The powders of K_2CO_3(99%), Na_2CO_3(99.8%), Nb_2O_5(99.5%), Bi_2O_3(99.9%), MgO (99%), Ta_2O_5(99.99%) were kept at 80℃ for 6 h to remove moisture. These raw materials were weighed based on the chemical formula and then mixed via zirconia balls using alcohol as a dispersion medium for 24 h. After drying, the mixture was pre-fired at 830°C for 4h and ball-milled for 24h again. The sieved powders were filled in a stainless-steel mold for a pre-compaction and then pressed into discs with a radius of 5 mm by a cold isostatic pressing facility at a pressure of 200 MPa for 3 min. Eventually, the samples could be obtained after densification at 1070-1100°C for 5 h.

Characterization

The X-ray diffraction (XRD) was carried out on the D8 Advanced Diffractometer (Cu Kα radiation) to get the phase structures of (1-*x*)KNN-*x*BMT ceramics. The scanning electron microscopy (SEM) images were obtained using SEM (S-4800, Hitachi, Japan) to study the microstructures of the samples. The Nano-Measure software describes the average grain sizes of all the samples. The dielectric characteristics of the samples coated with silver electrodes were measured by an LCR analyzer (E4980A, Agilent, USA) in a temperature range from -200°C to 500 °C with a heating rate of 3°C/min and a frequency range from 1kHz to 1MHz. The ferroelectric tester (Premier II, Radiant, USA) was adopted to indicate the ferroelectric performances of the samples with an Au electrode of 3.14 mm^2 (all

prepared samples were sanded and smoothed to the thickness of about 50~70μm). The forbidden band widths were acquired by the ultraviolet and visible (UV-vis) absorption spectra (Cary 5000, USA). The dynamic response of the domain to the external electric fields was investigated by piezoresponse force microscopy (PFM) (MFP-3D, Asylum Research, USA). The samples were well polished using diamond suspension before PFM measurements.

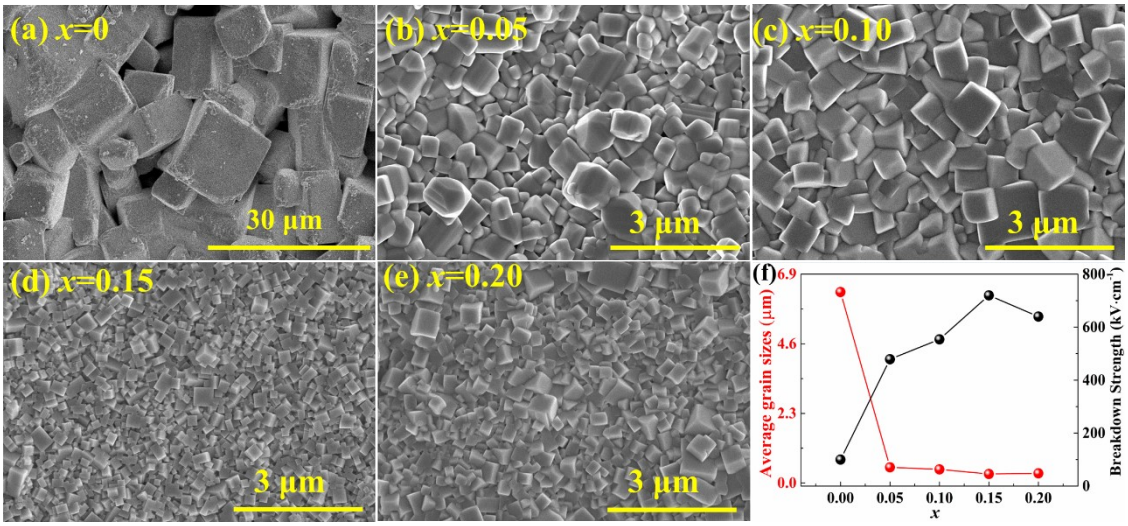

Fig. S1 SEM images of the (1-*x*)KNN-*x*BMT ceramics: (a) *x*=0; (b) *x*=0.05; (c) *x*=0.10; (d) *x*=0.15; (e) *x*=0.20; (f) Average grain sizes and BDS of (1-*x*)KNN-*x*BMT ceramics.

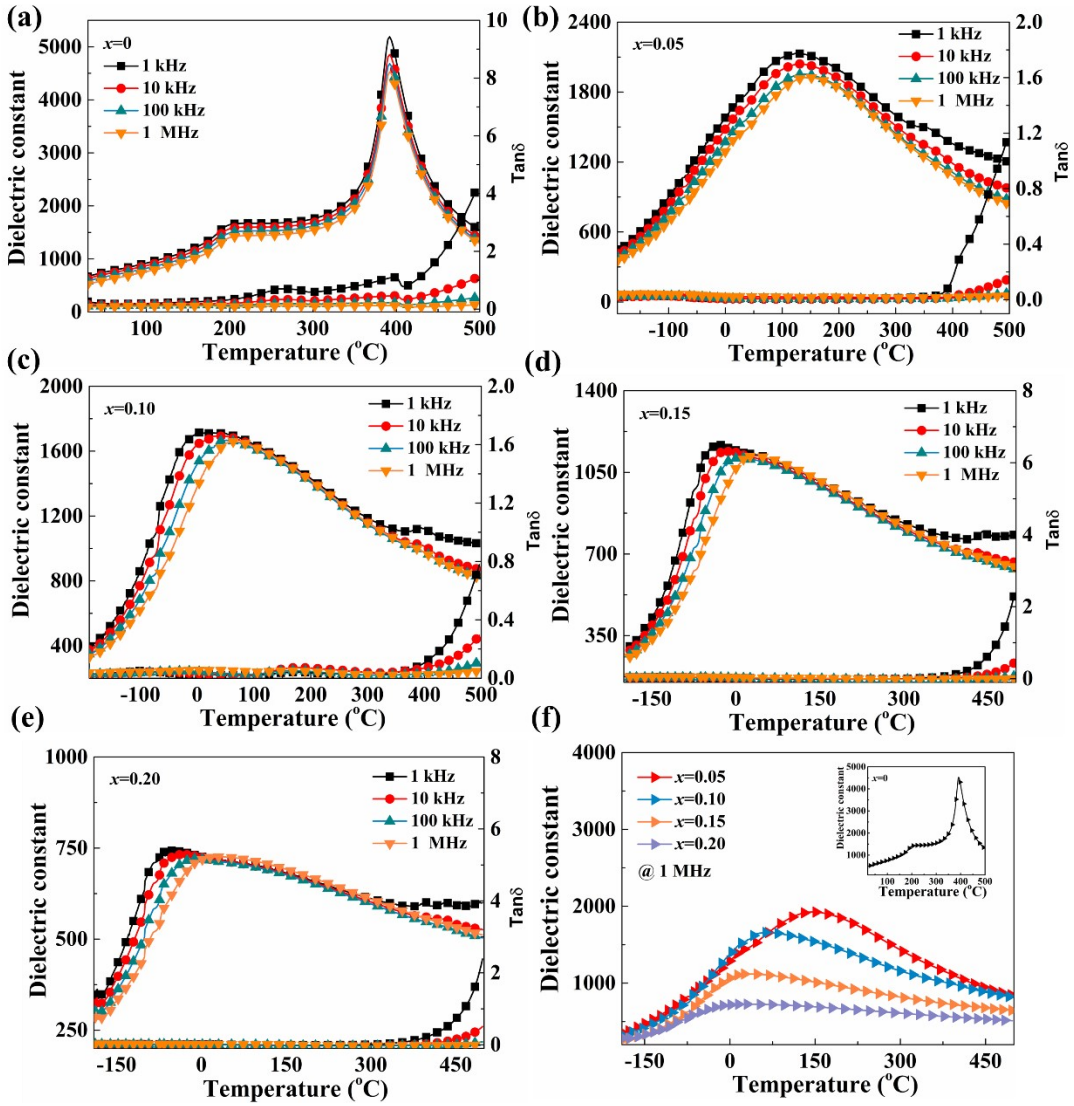

Fig. S2 Temperature dependence of the dielectric permittivity (ε′) and dielectric loss (tanδ) at 1 kHz-1MHz for the (1-*x*)KNN-*x*BMT ceramics from 25 ℃ to 500 ℃ and from -200 ℃ to 500 ℃: (a) *x*=0; (b) *x*=0.05; (c) *x*=0.10; (d) *x*=0.15; (e) *x*=0.20; (f) Temperature dependence of the dielectric permittivity (ε′) of (1-*x*)KNN-*x*BMT ceramics measured in the temperature range of -200 ℃ to 500 ℃ at 1 MHz.

According to the structural model that proposed by Randall et al. the dielectric constant of the grain and grain boundary can be calculated with the macroscopic dielectric constant of the ceramics by following formula:

$$\frac{1}{\varepsilon'} = \frac{1}{\varepsilon_g'} + \frac{1}{k\varepsilon_{gb}'} \tag{S1}$$

Where ε', ε_g' and ε_{gb}' represent the dielectric constant of the ceramics, grain and grain boundary, respectively. k is the ratio of grain size and grain boundary thickness. Based on the above formula and the measured macroscopic dielectric constant and average grain size of KNN and 0.85KNN-0.15BMT ceramics, the calculated dielectric constant of the ceramic grain is 908.876 for 0.85KNN-0.15BMT ceramic. Considering the fact that the KNN taking up a large proportion of 85% for 0.85KNN-0.15BMT ceramic, the grain boundary of them is perceived as non-crystallized KNN with the low dielectric constant of ~9.1 in simulation process for convenience.