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Energy-storage properties of $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$-$KNbO_3$ ceramics fabricated by wet-chemical method

Qi Xu[a,b], Juan Xie[a], Zichen He[a], Lin Zhang[a], Minghe Cao[a,*], Xindi Huang[a], Michael T. Lanagan[b], Hua Hao[a], Zhonghua Yao[a], Hanxing Liu[a,*]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China
[b] Materials Research Institute, Pennsylvania State University, University Park, PA, 16802, USA

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ABSTRACT

$0.93Bi_{0.5}Na_{0.5}TiO_3$-$0.07BaTiO_3$ (BNTBT) and $KNbO_3$ (KN) powders with average particle size of ~50 nm and ~300 nm were synthesized by sol-gel method and hydrothermal method, respectively. Then, $(1-x)$(BNTBT)-xKN (BNTBT-KN, x = 0, 0.01, 0.03, 0.05, 0.07) ceramic samples were prepared using these two powder precursors. The structure, dielectric and energy-storage properties of BNTBT-KN ceramics were comprehensively investigated. All the ceramic samples were in single perovskite structure, indicating that KN can completely dissolve into BNTBT within the studied composition range. BNTBT-KN ceramics exhibited a high dielectric constant at room temperature, being in the order of 1430–1550. Ferroelectric hysteresis loops at room temperature became more slim with the increase of KN content, which largely improved energy-storage density and efficiency. For the composition of x = 0.05, the maximum recoverable energy-storage density reached 1.72 J/cm^3 under 16.8 kV/mm, which is superior to linear dielectrics and even some Pb-based systems. All these results demonstrate that 0.95BNTBT-0.05KN fabricated by wet-chemical method is a promising lead-free dielectric material for energy-storage capacitors.

1. Introduction

A new energy-storage system based on $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) ceramics has received great attention in recent years. Various BNT-based solid solution and oxides-doped BNT-based systems were investigated, with a maximum energy-storage density of 0.6–1.4 J/cm^3, as shown in Table 1. In these reports, conventional solid-state reaction method is commonly adopted in the fabrication of ceramic samples. Actually, modification of technological process and parameters is also a good way to further improve the energy-storage properties. Ye [1] and Ding [2] compared the effects of different sintering methods on the structure and properties of BNT-based ceramics. They found that the energy-storage capacity of ceramics by two-step sintering method is three times larger than that by conventional single-step sintering method. Another strategy is about the powder fabrication techniques. Wet-chemical process exhibits considerable advantages, such as compositional homogeneity and excellent chemical stoichiometry [3,4]. It was found that BNT-based ceramics made from powders synthesized by wet-chemical method exhibit improved sinterability, poling process, and piezoelectric properties [5]. However, the effects of wet-chemical synthesis on the energy-storage properties for BNT-based dielectrics have been seldom reported.

Among the reported BNT-based energy-storage systems, $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xBaTiO_3$ (BNT-BT) near its morphotropic phase boundary (MPB) is the most widely used matrix. According to [6–8], x = 0.06–0.09 possess more pinched P-E loop, which is in favour of high energy-storage density. We investigated the ferroelectric properties of BNT-BT with x = 0.04–0.11 in earlier experiments. From the P-E loops (Supplementary Fig. S1), the composition with x = 0.07 exhibited large maximum polarization (P_m) and relatively small remnant polarization (P_r). Thus, 0.93BNT-0.07BT was selected as the matrix. Additionally, both niobium oxide and niobates have been reported to be good members to modify the ferroelectric properties of BNT-based ceramics [9–12]. Hiruma [13] found that the introduction of $KNbO_3$ (KN) into BNT could largely reduce the remnant polarization and coercive field, which is beneficial to energy storage. So, we chose KN as the third member. $(1-x)(Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3)$-$xKNbO_3$ (BNTBT-KN) ceramics were fabricated by wet-chemical method for the first time. The struc-

* Corresponding authors.
E-mail addresses: caominghe@whut.edu.cn (M. Cao), lhxhp@whut.edu.cn (H. Liu).

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Table 1
Energy-storage properties of BNT-based lead-free systems from literature and this work.

Process feature	Compound	Energy-storage density @ electric field	Ref.
Solid-state reaction method	BNT-BT-KNN	0.598 J/cm^3 @ 5.0 kV/mm	[14]
	BNT-BCTZ	0.665 J/cm^3 @ 7.0 kV/mm	[15]
	BNT-BKT-ST + LMN	0.70 J/cm^3 @ 5.5 kV/mm	[16]
	BNT-BKT-BZ	0.73 J/cm^3 @ 7.0 kV/mm	[17]
	BNT-BT-ST	0.98 J/cm^3 @ 9.0 kV/mm	[18]
	BNT-BCTZ + MgO	1.04 J/cm^3 @ 15.67 kV/mm	[19]
	BNT-BT-BZ + glass	1.05 J/cm^3 @ 11.0 kV/mm	[20]
	BNT-BKT-KNN	1.20 J/cm^3 @ 10.0 kV/mm	[21]
	BNT-BT + La + Zr	1.21 J/cm^3 @ 10.0 kV/mm	[22]
	BNT-BT-NBN	1.4 J/cm^3 @ 14.2 kV/mm	[23]
Two-step sintering method	BNT-BKT-ST	0.97 J/cm^3 @ 10.0 kV/mm	[1]
	BNT-BT-KNN	0.90 J/cm^3 @ 10.0 kV/mm	[2]
Wet-chemical method	BNT-BT-KN	1.72 J/cm^3 @ 16.8 kV/mm	This work

BNT: $Bi_{0.5}Na_{0.5}TiO_3$; BT: $BaTiO_3$; KNN: $K_{0.5}Na_{0.5}NbO_3$; BCTZ: $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$; ST: $SrTiO_3$; LMN: (Li, Mg, Nb); BKT: $Bi_{0.5}K_{0.5}TiO_3$; BZ: $BaZrO_3$; NBN: $Na_{0.73}Bi_{0.09}NbO_3$.

ture, dielectric and energy-storage properties of BNTBT-KN were comprehensively investigated.

2. Experimental procedure

BNTBT and KN powders were synthesized by sol-gel method and hydrothermal method, respectively. Then, (1 − x)BNTBT-xKN (x = 0, 0.01, 0.03, 0.05, 0.07) ceramic samples were prepared using these two powder precursors. They will be termed 0KN, 1KN, 3KN, 5KN, and 7KN in the following.

2.1. Synthesis of powder precursors

Fig. 1a shows the process of sol-gel method for the synthesis of BNTBT powder. Reagent grade $Ba(CH_3COO)_2$, $Na(CH_3COO)$, $Bi(NO_3)_3{\cdot}5H_2O$, $Ti(C_4H_9O)_4$, H_2NCONH_2, acetic acid and ammonium hydroxide were used as starting materials. First, $Ba(CH_3COO)_2$, $Na(CH_3COO)$ and $Bi(NO_3)_3{\cdot}5H_2O$ were weighted according to stoichiometry, H_2NCONH_2 was added as stabilizer. All these ingredients were dissolved in acetic acid at 90 °C. After adding ammonium hydroxide, clear concentrated Solution 1 was obtained. Then, stoichiometric $Ti(C_4H_9O)_4$ was dissolved in acetic acid at room temperature to form Solution 2. A certain amount of H_2NCONH_2 was added to avoid Ti^{4+} hydrolyzation. Solution 1 were dropwise added into Solution 2 to form a Bi-Na-Ba-Ti complex Solution 3 (sol). Stirring at 90 °C for 5 h, sol transformed into gel. The differential scanning calorimetric (DSC) and the thermo-gravimetric (TG) analysis were performed to determine the thermodynamic reaction of BNTBT gel. The measurement was conducted in the range of 25–850 °C under an air flow at a heating rate of 10 °C/min by TG-DSC analyzer (STA449c/3/G, NETZSCH, German). Dried gel was treated at different temperatures to obtain the desired single-phase BNTBT powder.

KN powder were synthesized by hydrothermal method (Fig. 1b). 1.5 g (0.006 mol) Nb_2O_5 was added into 100 mL 8 mol/L KOH solution. After stirring for 20 min and ultrasonic dispersing for 30 min, the reaction mixture was sealed in a 150 mL autoclave and heated to 180 °C for 24 h. The precipitate were filtered, washed and dried, then we obtained KN powder.

2.2. Preparation of ceramic samples

BNTBT and KN powders were mixed according to the stoichiometric formula and ball milled with zirconium media in ethanol for 24 h. After dried, the powders were pressed into pellets of 12 mm in diameter and 1 mm in thickness under a uniaxial pressure of 200 MPa. The pellets were sintered at 1050–1175 °C for 2 h.

2.3. Structure and property characterization

The bulk density of the ceramic pellets was determined by the Archimedes' immersion method. Phase purity was determined using X-ray powder diffraction (Cu Kα radiation, PANalytical X'Pert PRO, Holland). Microstructure was studied by scanning electron microscope (QUANTA FEG 450, USA). Fire-on silver paste was used to electrode all samples. The dielectric properties were measured using a precision LCR meter (E4980A, Agilent, USA) using a customer designed furnaces and computer-controlled data collection systems from 25 °C to 450 °C at a heating rate of 2 °C/min. To determine the polarization vs. electric field (P-E) curves, the sintered samples were polished to a thickness of 0.3 (±0.02) mm and then the test was performed using a ferroelectric material test system (HVI0403-239, Radiant Technology, USA) in a silicone oil bath.

3. Results and discussion

3.1. Powder properties

According to the TG − DSC analysis of dried BNTBT gel (Supplementary Fig. S2), the heat treatment temperature should be in the range of 400–600 °C. So, we calcined the gel for two hours at 400 °C, 500 °C, and 600 °C, respectively. The phase structure of the calcined powder at different temperature (Supplementary Fig. S3(a)) shows that pure BNTBT formed at 600 °C. Therefore, 600 °C was selected as the optimum heat treatment temperature. SEM image (Supplementary Fig. S3(b)) illustrates that fine grained BNTBT powder was obtained with an average particle size of 50 nm.

Single phase KN with orthorhombic structure was obtained by hydrothermal method (see Supplementary Fig. S4(a)). KN exhibited tabular crystal with angular texture (see Supplementary Fig. S4(b)). The particles were non-uniformly distributed with an average particle size of 300 nm.

3.2. Density and structure of BNTBT-KN ceramics

The relative densities of BNTBT-KN ceramics sintered at different temperatures were shown in Fig. 2. It can be found that the density varied with sintering temperature largely, suggesting that the sintering temperature range of this ceramic system is relatively narrow. The densities optimized at the sintering temperature of 1100 °C for 0KN–3KN and 1075 °C for 5KN–7KN, respectively. All the ceramic samples sintered at optimal temperature exhibited a relative density of more than 92%.

Fig. 3a displays the XRD patterns of BNTBT-KN ceramics with 2θ = 10–80°. As can be seen from the patterns, all the samples exhibited a pure perovskite phase with no secondary impurity. This indicates that KN has completely diffused into BNTBT lattice to form

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