Journal of Alloys and Compounds 747 (2018) 495–504

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Improvement of energy storage density with trace amounts of ZrO_2 additives fabricated by wet-chemical method

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ARTICLE INFO

Article history:
Received 30 November 2017
Received in revised form
2 March 2018
Accepted 5 March 2018
Available online 7 March 2018

Keywords:
Ceramics
Breakdown strength
Recoverable energy density
Non-polar phase

ABSTRACT

Lead-free (1-*x*)[0.6$SrTiO_3$-0.4$Na_{0.5}Bi_{0.5}TiO_3$]-*x*ZrO_2 ceramics (STNBT-*x*Zr) were synthesized in single perovskite phase. The average grain size decreased from 3.2 μm ($x = 0.1$ mol%) to 1.6 μm ($x = 0.6$ mol%) related to the addition of ZrO_2 powders prepared by microwave hydrothermal method. With the increasing of ZrO_2 content, the permittivity decreased gradually, and the breakdown strength (E_b) was remarkably improved due to composition induced disturbing of long range ferroelectric order. The increase of E_b led to the improvement of the recoverable energy storage density (W_{re}) from 1.80 J/cm^3 ($x = 0.1$ mol%) to 2.84 J/cm^3 ($x = 0.5$ mol%). However, when Zr^{4+} content was more than 0.5 mol%, the W_{re} decreased from 2.84 J/cm^3 to 2.26 J/cm^3 ($x = 0.6$ mol%) due to the reduction of the maximum polarization. The best energy storage properties were achieved in STNBT-*x*Zr ceramic with Zr^{4+} content of $x = 0.5$ mol %, which exhibited the W_{re} of 2.77–2.84 J/cm^3 in the range of 4–40 Hz, revealing an excellent frequency stability. All these results demonstrate the STNBT-*x*Zr ($x = 0.5$ mol%) ceramics are quite promising for frequency-stable energy storage applications.

1. Introduction

With the increasing requirement in pulsed power technology and power electronics [1,2], instantaneous charging can be achieved in energy storage capacitors within an extremely short time span, developing high-performance energy storage materials is becoming more and more imperative and important [3,4]. Although dielectric capacitors have fast charging/discharging rate and long lifetime, compared with fuel cells, Li-ion batteries and supercapacitors, the energy density of dielectrics is much lower [5–7]. Thus, as the main part of capacitors, enormous types of dielectrics have been developed and studied. In general, the recoverable energy storage density (W_{re}) can be estimated by integrating the area between the polarization axis and the discharge curve of the *P*-*E* hysteresis loops using equation [8]:

$$W_{re} = \int_{P_r}^{P_m} EdP \quad (1)$$

where P is the polarization, P_m is the maximum polarization with respect to the maximum applied electric field, P_r is the remnant polarization, E is the applied electric field which leads to a response in polarization dP. The required energy storage properties usually meet as follows: large P_m, small P_r, and high electric breakdown field strength (BDS) [9].

(1-*x*)$Na_{0.5}Bi_{0.5}TiO_3$-*x*$SrTiO_3$ (NBT-ST) ceramics are a solid solution system composed of ferroelectric sodium bismuth titanate and non-ferroelectric strontium stannate. Both of them are of perovskite structures with an ABO_3 formula. It was also determined that (1-*x*)$Na_{0.5}Bi_{0.5}TiO_3$-*x*$SrTiO_3$ solid solutions can from a morphotropic phase boundary (MPB) between the rhombohedral and pseudo-cubic phases at $x = 0.25–0.26$ https://www.sciencedirect.com/science/article/pii/S0955221917306593 [10]. Gomah-Pettry et al. [11] studied the structural and dielectric properties of NBT-ST systems and found the trigonal symmetry changed to cubic almost like a first order phase transition at $x > 30$. Most of the research on the system is focused on the piezoelectric properties [12,13]. Li et al. [14] reported that strains up to 0.2% could be achieved under a low driving fields ($E < 2$ kV/mm) in the 0.74NBT-0.26ST composition resulting in excellent actuating performance of S_{max}/E_{max}>1000 pm/V. A. R. Malathi et al. [15] studied the (1-*x*)NBT-*x*ST ($x = 0–1$) system and found that the P_r, P_r/P_m, BDS and piezoelectric coefficient (d_{33}) of 0.6$SrTiO_3$-0.4$Na_{0.5}Bi_{0.5}TiO_3$ sample

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https://doi.org/10.1016/j.jallcom.2018.03.058
0925-8388/

reached 0.52 μC/cm^2, 0.047 μC/cm^2, 32.807 kV/cm and 21 pC/N, respectively. In addition, Cao reported that the electrocaloric effect (ECE) in (1-*x*)NBT-*x*ST (*x* = 0.10, 0.25, 0.26, 0.30) ceramics and found that the maximum value of the recoverable energy density was 0.65 J/cm^3 obtained at 65 kV/cm in 0.7NBT-0.3ST ceramic [16]. However, recent research on the energy storage performance of the NBT-ST system is still scarce and their low BDS badly limits their application in energy storage devices. In order to improve the energy storage density, various attempts have been made. Adding metallic oxide in the matrix has drawn increasing interest because metallic oxide can significantly enhance the BDS. For example, the highest BDS of 21.2 kV/mm, the highest W_{re} (0.45 J/cm^3) were obtained in the glass ceramic with 2 mol% Sm_2O_3 [17]. Wang et al. [18] have successfully prepared ST/ZrO composites with an enhanced energy storage density of 1.62 J/cm^3. In addition to the adjustment of components, energy storage density can be further enhanced through the synthesis of core-shell ceramics [19], layered ceramics [20], film [21], nanofibers materials [22], etc. Furthermore, some powder synthesis methods such as wet chemical method [23] and sintering processes including liquid phase sintering [24] and spark plasma sintering (SPS) technique [25] have been carried out. However, these methods cannot be widely applied in actual industrial production because of their expensive cost, complex synthesis processes and less production compared with conventional solid-state method. Therefore, finding a balance between these methods and conventional solid-state method is crucial. Therefore, it is highly possible that higher energy storage density could be obtained by doping and synthesis methods. Thus, understanding how doping and synthesis methods change the structure and affect the energy storage properties are still critical problems to solve.

In our former work, we found the highest energy density of 1.70 J/cm^3 at ~21 kV/mm in $0.6SrTiO_3$-$0.4Na_{0.5}Bi_{0.5}TiO_3$ ceramic [26]. To further improve the energy storage density, in this work, we reported energy storage properties of (1-*x*)[$0.6SrTiO_3$-$0.4Na_{0.5}Bi_{0.5}TiO_3$]-*x*ZrO_2 (*x* = 0.1 mol%, 0.2 mol%, 0.3 mol%, 0.4 mol %, 0.5 mol%, 0.6 mol%) ceramics. The $0.6SrTiO_3$-$0.4Na_{0.5}Bi_{0.5}TiO_3$ and ZrO_2 powders were synthesized by conventional solid-state method (CSS) and microwave hydrothermal method (MH), respectively. The effects of trace ZrO_2 content on structure and energy storage properties of (1-*x*)[$0.6SrTiO_3$-$0.4Na_{0.5}Bi_{0.5}TiO_3$]-*x*ZrO_2 ceramics were investigated. As a result, our findings not only expand the spectrum of room-temperature lead-free energy storage materials for future applications but also may serve as a guide for revealing other energy storage material alternatives by the combination of CSS and wet-chemical method.

2. Experimental procedure

STNBT and ZrO_2 powders were synthesized by conventional solid-state method and microwave hydrothermal method, respectively. Then, STNBT-*x*Zr (*x* = 0.1 mol%, 0.2 mol%, 0.3 mol%, 0.4 mol%, 0.5 mol%, 0.6 mol%) ceramic samples were prepared using these two powder precursors.

2.1. Synthesis of $0.6SrTiO_3$-$0.4Na_{0.5}Bi_{0.5}TiO_3$ powders

Powders of analytical reagent grade, comprising Bi_2O_3 (99.0%), $SrCO_3$ (99.0%), TiO_2 (99.0%), Na_2CO_3 (99.0%), $BaCO_3$ (99.0%), were used as the starting materials and mixed according to the composition, $0.6SrTiO_3$-$0.4Na_{0.5}Bi_{0.5}TiO_3$. After ball-milled in alcohol for 24 h, the slurry was dried, then calcined in a closed environment at 1150 °C for 2 h. The calcined powder was ball-milled and dried again to obtain homogeneous powder.

2.2. Synthesis of ZrO_2 powders

ZrO_2 powders were synthesized by microwave hydrothermal method (Fig. 1). The raw materials $ZrOCl_2$ were dissolved in distilled water completely. $ZrOCl_2$ with a Zr^{4+} concentration of 0.05 mol/L was prepared as $ZrOCl_2 \cdot 8H_2O$ (purity 99%) aqueous solution. After that, 2 mol/L NaOH was added into $ZrOCl_2 \cdot 8H_2O$ prepared solution to adjust the solution pH to 13. Then, the white precursor generated and the process was accompanied by a large amount of heat release. After stirring for 20 min and ultrasonic dispersing for 30 min, the reaction mixture was sealed in a sealed vessel and heated to 220 °C for 30 min in a microwave hydrothermal reactor. The precipitate were filtered, washed and dried, then we obtained ZrO_2 powder. The reaction equation is as follows:

$$ZrOCl_2 \cdot 8H_2O + H_2O + 2OH^- \rightarrow Zr(OH)_4\downarrow + 2Cl^-$$

$$Zr(OH)_4 \rightarrow ZrO_2 + H_2O$$

2.3. Preparation of ceramic samples

STNBT and ZrO_2 powders were mixed according to the stoichiometric formula and ball milled in distilled water for 24 h. After dried, the powders were pressed into pellets of 10 mm in diameter and 1 mm in thickness by cold isostatic pressing under a pressure of 200 Mpa. The pellets were sintered by three stage heating at 1330 °C for 3 h. Among them, the three stage heating refers to the sintering process in three stages: heating, holding and cooling, is a common sintering method of ceramics.

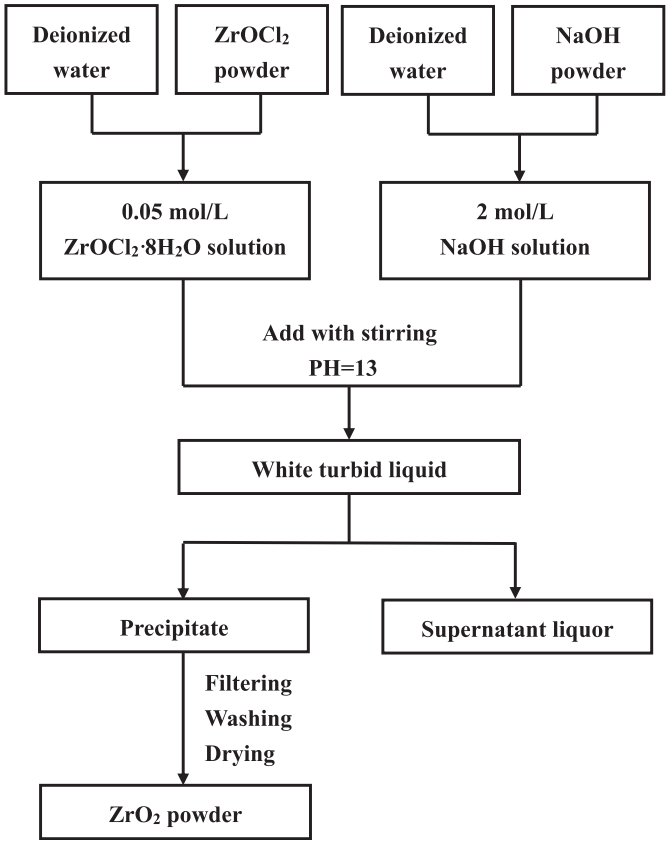

Fig. 1. The flow chart of microwave-hydrothermal synthesis for ZrO_2 powder.