Journal of Alloys and Compounds 682 (2016) 594–600

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Dielectric nonlinearity and electric breakdown behaviors of $Ba_{0.95}Ca_{0.05}Zr_{0.3}Ti_{0.7}O_3$ ceramics for energy storage utilizations

Di Zhan, Qing Xu*, Duan-Ping Huang, Han-Xing Liu, Wen Chen, Feng Zhang

School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, People's Republic of China

ARTICLE INFO

Article history:
Received 29 February 2016
Received in revised form
27 April 2016
Accepted 28 April 2016
Available online 6 May 2016

Keywords:
Ceramics
Energy storage materials
Ferroelectrics
Oxide materials
Dielectric response

ABSTRACT

$Ba_{0.95}Ca_{0.05}Zr_{0.3}Ti_{0.7}O_3$ ceramics were prepared by a citrate method. The dielectric properties of the specimens were examined as a function of temperature, frequency and electric field. Moreover, the energy storage properties and electric breakdown behaviors of the specimens were inspected. Fitting of the dielectric constants under bias electric field to a multipolarization mechanism model resolved the contributions of involved polarization mechanisms. The result indicated that the intrinsic lattice polarization dominated the dielectric constants under strong electric field while the extrinsic contribution of polar nano-regions (PNRs) was basically faded. At the maximum applicable electric field of 160 kV/cm, the specimens achieved an energy storage density of 0.59 J/cm^3 and an energy storage efficiency of 72.8%. It was detected that the electric breakdown of the specimens initially occurred on the surfaces immediately adjacent to electrodes, followed by development of an electronic conduction pathway in the bulks. Complex impedance spectroscopy analysis determined that oxygen vacancies were the mobile charge carriers in the specimens. The occurrence of the initial breakdown was explained with respect to accumulation of oxygen vacancies in the specimens induced by strong electric field.

1. Introduction

In the past decades, lead-free ferroelectric $BaTiO_3$-based solid solutions have attracted much attention due to their scientific and technological importance. Conveying critical information concerning the basic physics of polar dielectrics, the polarization responses of $BaTiO_3$-based solid solutions relative to various external fields, such as temperature, frequency, electric field and pressure, have been the subject of intensive research. These dielectric characteristics, in turn, have rendered $BaTiO_3$-based solid solutions versatile for a variety of device applications, including ceramic capacitors [1], piezoelectric actuators [2], electrically tunable microwave components [3], dynamic random access memories [4] and pyroelectric detectors [5].

Storing electric charges and energies is the fundamental function of dielectrics. Recently, the utilization of $BaTiO_3$-based dielectrics in energy storage ceramic capacitors has evoked growing interest [6–10]. For polar dielectrics like $BaTiO_3$-based solid solutions, the energy storage density, U_{vol}, can be given by Ref. [11]:

$$U_{vol} = \int EdP = \int \varepsilon_0 \varepsilon_{r(E)} EdE \tag{1}$$

where E is the external electric field, P is the polarization, ε_0 is the permittivity of free space and $\varepsilon_{r(E)}$ is the dielectric constant at electric field E. According to the formula, breakdown strength and dielectric constant can be viewed as the elemental factors of energy storage density, with a high breakdown field and a large dielectric constant under working field favoring a high energy storage density.

Decrease of dielectric constant under external electric field is the essential attribute of ferroelectric solids, no matter in which state (i.e. ferroelectric or paraelectric) they are. This peculiarity, known as dielectric nonlinearity, is determined by the responses of involved polarization mechanisms under applied electric field [12]. In this sense, it is necessary to make clear the contributions of various polarization species in $BaTiO_3$-based solid solutions under strong electric field, so as to better understand their energy storage properties.

On the other hand, breakdown strengths of dielectric ceramics appear to be more dominant in determining their energy storage densities [11]. Theoretical calculations have predicted breakdown strengths up to a few 10^3 kV/cm for titanium-based perovskite-type

* Corresponding author.
E-mail address: xuqing@whut.edu.cn (Q. Xu).

http://dx.doi.org/10.1016/j.jallcom.2016.04.317

dielectrics [11,13]. Nonetheless, the practically accessible electric fields of these dielectrics in bulk form are usually much lower than the predicted level. As an example, for the $BaTiO_3$-based ceramics with reasonable thicknesses of 0.2–0.5 mm to withstand operations of electric test, the maximum applicable electric fields are typically in the range of 100–400 kV/cm [8,9,14–16].

Bonding between cations and oxygen ions plays as the intrinsic factor to breakdown strength for oxide dielectrics [13]. As for dielectric ceramics, many extrinsic factors are also highly contributive to their breakdown fields, such as porosity, grain size, geometrical parameter and electrode configuration [15]. Extensive efforts have been made to improve the breakdown field of $BaTiO_3$-based ceramics by employing various material strategies. The majority of these efforts have been concentrated on improving the densification and reducing the grain size of the ceramics [7,17,18]. Despite impressive progresses resulting from these attempts, several basic issues as to where and how an electric breakdown arises are still under debate [19,20]. Gaining a deeper insight into these open issues would offer valuable guideline for improving the breakdown field of $BaTiO_3$-based ceramics.

Employing ferroelectric compositions with Curie temperatures well below working temperature (e.g. room temperature) have been demonstrated to be preferred for achieving optimal energy storage properties [11]. In this work, we investigate the dielectric properties of $Ba_{0.95}Ca_{0.05}Zr_{0.3}Ti_{0.7}O_3$ ceramics in view of the energy storage utilization. The emphasis is placed on the dielectric nonlinearity and breakdown behaviors of the ceramics under strong electric field. The purpose is to achieve a better understanding on the energy storage properties of the ceramics.

2. Experimental

$Ba_{0.95}Ca_{0.05}Zr_{0.3}Ti_{0.7}O_3$ (abbreviated as BCZT hereafter) powder was synthesized by a citrate method. The synthetic process was basically identical to our previous procedures for preparing $BaZr_xTi_{1-x}O_3$ (x = 0.2–0.3) and $Ba_{0.6}Sr_{0.4}TiO_3$ powders [21,22]. In the present work, the powder was calcined at 650 °C for 2 h in air. X-ray diffraction (XRD) analysis identified a single perovskite phase for the powder. Field emission scanning electron microscopy (FESEM) observation illustrated that the powder consisted of fine and uniform particles around 100 nm. These results are not shown here. The powder was uniaxially pressed into discs of 13 mm in diameter and 1 mm in thickness under a pressure of 300 MPa. Then the compacted discs were sintered at 1280 °C for 2 h in air.

The crystal structure of the ceramic specimens was examined by a Philips X'pert PBO X-ray diffractometer using Cu Kα radiation. The measured data were analyzed using the Jade 6.0 software. The microstructure of the ceramic specimens was observed using a Jeol JSM-5610LV scanning electron microscope (SEM). The microstructural parameters of the ceramic specimens were estimated by image analysis using the Image-Pro Plus 6.0 software.

The density of the ceramic specimens was measured by the Archimedes method using alcohol as the medium. The ceramic specimens used for electric measurement were polished and painted with silver electrode on both surfaces. The dielectric constant (ε_r) and the loss (tan δ) were measured as a function of temperature and frequency using a TH2828 precision LCR meter (20 Hz–1 MHz) and a SSC-M10 environment chamber (C4 controller). The dielectric nonlinearity under bias electric field was examined at room temperature and 10 kHz using a TH2818 automatic component analyzer. A blocking circuit was adopted to protect the analyzer from applied bias voltages. The bias electric field was applied in an interval of 1 kV/cm. The dielectric constant data were recorded after holding at each applied field for 10 s. The plots of electric polarization (P) and current (I) vs. electric field (E) were measured at room temperature using a Radiant precision workstation based on the Sawyer-Tower circuit at 1 Hz. The leakage current was also recorded as a function of applied bias electric field using the workstation. The tested specimens were immersed into a silicon oil bath to avoid surface flashover. The ceramic specimens used for the dielectric nonlinearity, P–E, I–E and leakage current measurements were polished into thickness of ~0.5 mm. The complex impedance spectra were measured in the range of 460–540 °C using the TH2828 meter and a program-controlled oven (home-made). The measured data were analyzed using the Zview 3.1a software.

3. Results and discussion

3.1. Dielectric responses to ac testing signals

Fig. 1 shows the XRD pattern of BCZT ceramic specimen. A cubic perovskite structure was identified for the specimen, indicating that the specimen is macroscopically in the prarelectric state at room temperature. The inset in Fig. 1 shows the SEM image of the specimen. Polished and thermally etched surface of the specimen was used for the SEM observation. The SEM image illustrated a dense microstructure with uniform grains around 1 μm. The Archimedes measurement showed that the specimen attained more than 95% of the theoretical density.

Fig. 2 shows the dielectric constant and the loss of BCZT ceramic specimen at room temperature as a function of frequency. The dielectric constant was slightly declined with frequency within the measurement frequency range, while the loss kept almost invariant until 10^4 Hz and then was steadily increased with higher frequencies. The anomaly of the dielectric loss implies a relaxation process above the upper limit of the measurement frequencies (10^6 Hz), suggesting presence of dipole polarizations in the specimen [23,24].

Fig. 3a shows the temperature dependence of the dielectric constant and the loss of BCZT ceramic specimen at different frequencies. The ferroelectric-paraelectric phase transition of the specimen was characterized by a relaxor-like behavior. The temperature for the maximum of dielectric constant (T_m) was increased with higher frequencies, changing from 208 K at 1 kHz to 226 K at 1 MHz. The T_m values are consistent with a macroscopically prarelectric state of the specimen at room temperature. Similar relaxor-like behavior has been found for $BaZr_{0.3}Ti_{07}O_3$ ceramics, which has

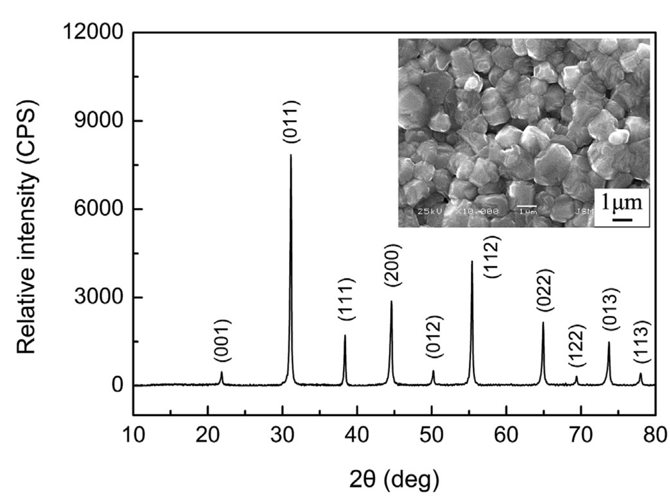

Fig. 1. XRD pattern of BCZT ceramic specimen. The inset shows the SEM image of the specimen.