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Dielectric breakdown of $BaO–B_2O_3–ZnO–[(BaZr_{0.2}Ti_{0.80})O_3]_{0.85}$ $[(Ba_{0.70}Ca_{0.30})TiO_3]_{0.15}$ glass-ceramic composites

Venkata Sreenivas Puli [a,*], Ashok Kumar [a], R.S. Katiyar [a,*], X. Su [b], C.M. Busta [b], D.B. Chrisey [b], M.Tomozawa [b]

[a] Department of Physics and Institute for Functional Nano Materials, University of Puerto Rico, San Juan, Puerto Rico, PR-00936, USA
[b] Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY-12180, USA

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ABSTRACT

We have successfully synthesized and characterized the alkali-free glass $0.3\ BaO + 0.6B_2O_3 + 0.1ZnO$ (BBZ) and electro ceramics $[(BaZr_{0.2}Ti_{0.80})O_3]_{0.85}–[(Ba_{0.70}Ca_{0.30})TiO_3]_{0.15}$ (BZT–BCT) composite for high energy density storage capacitor applications. First single phase BZT–BCT ceramic powders were prepared by conventional solid state reaction technique. X-ray diffraction studies of the sintered pellets revealed the pure perovskite phase with tetragonal to pseudocubic (rhombohedral phase). Raman spectroscopy results also confirmed the perovskite phase with tetragonal structure. These powders were mixed with 10–50 weight percentage of glass powder and were ground using low energy ball milling. The pellets of glass-ceramic composites with different amounts of glass were tested for ferroelectric at fixed frequency (50 Hz), dielectric, and breakdown field properties under a wide range of frequency. Pure ceramic BZT–BCT sample exhibits the well saturated hysteresis behavior, and as we increase the amount of glass composition with pure BZT–BCT, glass mixed ceramic hysteresis loops turn into linear behavior. Compositional enhancement in glass-ceramic composites indicates decrease in the room temperature permittivity and enhancement in breakdown field. The glass-ceramic composites have shown better dielectric breakdown field but low energy density compared to parent ceramics.

1. Introduction

High energy density capacitors can store more than ten times energy per unit volume than the common capacitor (device for storing electric charge), and the accumulated energy in dielectrics is determined by dielectric permittivity and breakdown strength, which depends linearly on the dielectric permittivity and quadratically on the electric field [1]. Polymers and ceramics are the primary dielectrics for solid-state capacitors; ceramic capacitors are more useful due to high operating temperatures when compared to polymer films. Glass and glass-ceramics are also two of the new promising materials for high temperature capacitor applications [2]. Lead-based glass ($PbO–Na_2O–Nb_2O_5–SiO_2$) materials are the most commonly used high permittivity materials in commercial dielectric components. However, with increasing concerns about lead toxicity which is harmful to health, research attention turned toward lead-free materials. Lead-free glasses: $BaO–B_2O_3–ZnO$ (BBZ), $Bi_2O_3–B_2O_3–ZnO–BaO–SiO_2$ are potential replacements for lead based ($PbO–B_2O_3–SiO_2–ZnO$, $PbO–Na_2O–Nb_2O_5–SiO_2$) glass frits. $BaO–B_2O_3–ZnO$ (BBZ) is one of the notable alkali free glass system with dielectric constants of 14–18 and a coefficient of thermal expansion of $8–9\times10^{-6}$/K [3,4]. These lead-free glass powders are widely used as dielectric layers in various types of plasma display panels (PDPs), ceramic capacitors and as well as in sealing glasses and enamels [3,5]. Glass-ceramic composites are first produced by obtaining a glass matrix using melt casting method [3]. Depending upon the sample dimensions and test protocol, glass synthesized by a bulk process can exhibit dielectric breakdown strengths in the range of 4–9 MV/cm [6]. Conventional ceramics show low breakdown strength of 10 kV/mm, despite having high dielectric permittivity values, during solid-state reaction process due to residual pores formed [7,22]. A glass-ceramic material is a composite created through controlled crystallization of an appropriate glass composition with pore-free structure and fine grains [8,9]. Glass-ceramics composites have the potential to serve as high-energy density capacitor materials for portable electronic or pulsed power applications and are also particularly useful in heart defibrillators and hybrid automotive vehicles, to name a few [10].

Higher electrical breakdown fields can be achieved in ceramics by optimizing, extrinsic material properties such as defect chemistry, microstructural development, reduced sample thickness, grain size, and electrode configuration, and these parameters play a crucial role in making high energy storage capacitors. Ceramic materials usually have large permittivity values, they are limited by their relative small breakdown strength and surprisingly maximum energy storage is not obtained in high dielectric constant materials but in those materials which display intermediate dielectric constant and highest

* Corresponding authors.
E-mail addresses: pvsri123@gmail.com (V.S. Puli), rkatiyar@uprrp.edu (R.S. Katiyar).

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ultimate breakdown voltage [11]. In the present work, we present dielectric breakdown measurements and the dielectric properties for composite mixtures of alkali-free glass and ceramics.

2. Experimental

Stoichiometric ratio of $BaCO_3$, $CaCO_3$,TiO_2, Zr_2O_3 powder were mixed for 2 h by adding isopropanol as milling media with zirconium ball in a low energy ball miller. Powders dried overnight were calcined at 1250 °C for 10 h. The alkali-free ($0.3BaO + 0.6\ B_2O_3 + 0.1$ ZnO) glass is prepared from precursor powders of $BaCO_3$, B_2O_3, and ZnO. The powder is melted in a platinum crucible at 1200 °C and allowed to fine for 1 h stirring every 10 min. The melt is then poured into a graphite mold heated to 500 °C. The mold is placed into a furnace at 500 °C for 1 h and subsequently furnace cooled.

Phase formation of the powder was checked by X-ray diffraction (XRD) technique, and later, crystallized powder was mixed with alkali-free $0.3BaO + 0.6\ B_2O_3 + 0.1$ ZnO glass powder (10–50 weight percentage of glass powder), and was again mixed for 2 h by adding Isopropanol as milling media in a low energy ball miller.

Glass ceramic composite powder was mixed with 4% PVA (polyvinyl alcohol) as an organic binder to increase the strength of green pellets and was formed into a pellet with13 mm diameter and 0.5 mm thickness. Pellets were kept at 500 °C for 30 min for binder removal and then sintered at 900 °C for 4 h in a Carbolite furnace. The structural and surface morphology of the sintered pellets were analyzed by XRD using $CuK_\alpha = 1.54$ Å radiation, Raman spectroscopy and scanning electron microscopy (SEM), respectively. Ferroelectric measurements were done with a Radiant Technologies (RT 6000 HVA-4000 V) amplifier by connecting copper cables on either side of the disks with silver paint. To measure dielectric properties, sintered disks were painted with silver on either side of the surfaces and were dried at 350 °C for 1 h for electrode formation.

Temperature-dependent dielectric properties were carried out with an Alfa impedance analyzer with fully computer interfaced Novocontrol thermal stage in the temperature range of 273–400 K in a frequency limit of 100 Hz–10 MHz. Electrical breakdown voltage of the ten samples of each composition was measured at room temperature using Trek high voltage amplifier.

3. Results

3.1. X-ray and scanning electron microscopy (SEM) characterization

The XRD patterns of the samples with pure BZT–BCT and different amounts (10–50 wt.%) of alkali free glass ($0.3BaO + 0.6\ B_2O_3 + 0.1$ ZnO) mixed BZT–BCT ceramics sintered at 900 °C for 2 h are shown in Fig. 1. Fig. 2 shows the SEM micrographs of BZT–BCT ceramics sintered at 1500 °C for 4 h and glass mixed BZT–BCT (BZCTG10–BZCTG50) sintered at 900 °C for 4 h. SEM micrographs of disks revealed pore-free and dense surfaces. The average grain size of the sintered BZT–BCT ceramic pellets is between ~200 and 250 μm. Whereas the average grain size of the glass mixed (BZCTG10–BZCTG50) ceramic pellets is between 5 and 10 μm.

3.2. Raman spectroscopy

Raman spectroscopy results can help to detect molecular vibrations directly and are very sensitive to non-uniform distortions of the crystal lattice in short-range ordering [12]. Raman spectra of the BZT–BCT ceramics and glass mixed ceramic BZT–BCT are shown in Fig. 3, in order to explore the phase structural transformation of the sintered pellets at room temperature. The shape of the Raman spectra resembles that of lead-free BZT–BCT ceramics [13,22]. The BZT–BCT has a basic matrix of $BaTiO_3$, with an ABO_3 type perovskite structure. For present BZT–BCT and glass mixed ceramics, the faint E(TO) mode

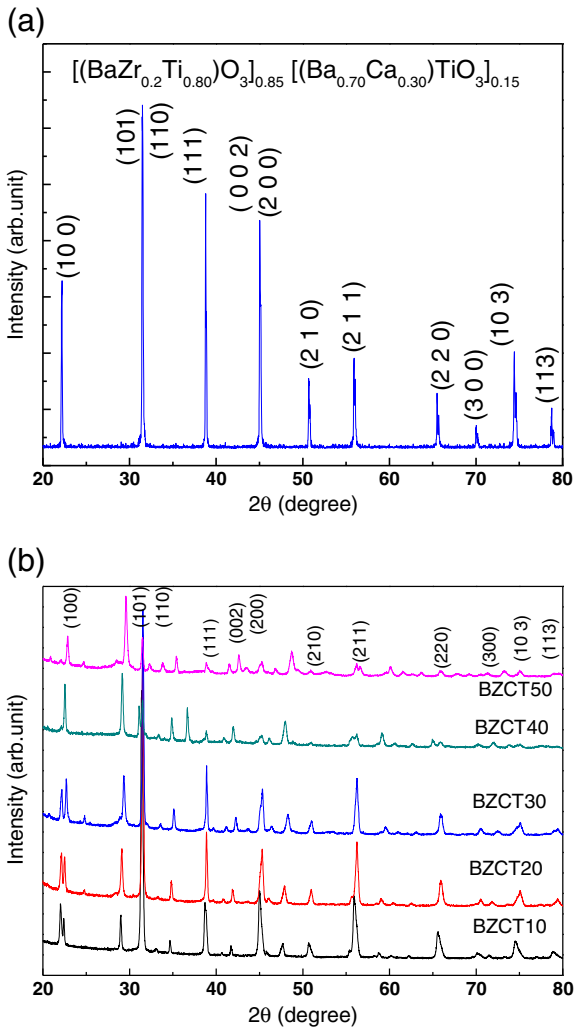

Fig. 1. Room temperature XRD patterns of (a) $(Ba_{0.955}Ca_{0.045})(Zr_{0.17}TiO_{0.83})O_3$ ceramics sintered at 1500 °C and (b) glass mixed ceramics (BZCTG10–BZCTG50) sintered at 900 °C, with 2θ angle ranging from 10 to 80°.

is observed at around ~37–40 cm^{-1}. The $A_1(TO_1)$ anti-symmetry mode detected at ~115–169 cm^{-1} shifted toward higher frequencies. The anti-symmetry mode $A_1(TO_2)$ between ~230–249 cm^{-1} is also shifted toward the higher frequency, while the A_1 $(TO_3)/B_1$ mode at around ~504–517 cm^{-1} is due to O–Ti–O symmetric stretching vibrations [16]. $A_1(LO_3)/E(LO)$ observed at around 708–721 cm^{-1} and for pure BZT–BCT, A_{1g} breathing mode is witnessed at ~792, where it is not found in glass mixed ceramics.

3.3. Ferroelectric and dielectric studies

P–E hysteresis loops for $[(BaZr_{0.2}Ti_{0.80})O_3]_{0.85}$ $[(Ba_{0.70}Ca_{0.30})TiO_3]_{0.15}$–(BZT–BCT) ceramics and glass ceramics composite (BZCTG10–BZCTG50) were presented in Fig. 4; well-saturated ferroelectric hysteresis P–E loop acquired under the maximum electric field before the breakdown is observed for BZT–BCT ceramic composition with polarization maxima 14 μC/cm^2, remanent Polarization (P_r)—5.40 μC/cm^2, coercive Field, (E_c)—1.71 kV/cm, respectively. Non-saturated ferroelectric hysteresis loops were recorded for BZCTG10–BZTCG30 and linear hysteresis behavior is observed both in BZCTG40 and BZCTG50 glass mixed ceramic compositions. As the glass composition increased from 10 wt.% to 40 wt.% remanent polarization (P_r) decreased from ~2.2 μC/cm^2 to 0.025 μC/cm^2 and the coercive field values also decreased from ~9.29 kV/cm to 3.06 kV/cm.