Investigations on structure, ferroelectric, piezoelectric and energy storage properties of barium calcium titanate (BCT) ceramics

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Abstract

We investigated structural, aging induced ferroelectric, piezoelectric and energy density properties of ceramic (Ba0.70Ca0.30)TiO3 (BCT) capacitors that were prepared by the solid-state reaction method. According to X-ray (XRD) data, along with BaTiO3 tetragonal peaks, CaTiO3 rich orthorhombic peaks were also observed at room temperature. Raman scattering gives evidence for the formation of oxygen vacancies in BCT due to partial migration of Ca2+ into Ti4+ site. Abnormal double like hysteresis polarization-electric field (P–E) loops were observed at room temperature for naturally aged BCT ceramics. Strain-electric field (S–E) loops confirm piezoelectric behavior. Room temperature (300 K) charge and discharge curve energy densities [(|Ed|) ~ 0.35 (before aging) 0.39 J/cm3 (aged)], [(|Ed|) ~ 0.20 (before aging) 0.24 J/cm3 (aged)], respectively, at a maximum electric field ~50 kV/cm. The bulk BCT materials have shown interesting energy densities with good energy storage efficiency (~58% before aging, ~61% after aging) suggesting they might be strong candidates for high energy density capacitor applications.

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1. Introduction

Barium titanate (BaTiO3 or BT)-based materials have been extensively studied for their interesting electrical properties like high dielectric constant, low dielectric loss, ferroelectric, piezoelectric and pyroelectric behavior. Among the dielectric ferroelectric perovskite oxides, BT was used most for electrical and electronic applications, in the years immediately after its discovery. Perovskite oxides derived from BT have a wide range of applications in electronic devices [1,2]. Recently, research attention turned towards lead-free and environmentally-friendly dielectric BaTiO3 based piezoelectric materials because of its high dielectric constant, polarization and high piezoelectric properties [3]. BT based high dielectric constant materials with low dielectric loss and high dielectric breakdown field are useful in energy storage capacitors.

Doping is an effective way to improve the electrical performance of electroceramics [4,5]. For instance, barium zirconium titanate Ba(Zr, Ti)O3 [BZT], and barium calcium titanate (Ba,Ca)TiO3 [BCT] [4–6,8] are widely used in electrical material applications. Also, these materials are attracting attention as ceramic capacitors in which the temperature dependence and reliability of the dielectric properties of the BT are improved [6,7]. BCT solid solutions are specifically used in multilayer ceramic capacitor applications and in various other applications like: dielectric filters, antennas, resonators, duplexers and phase shifters, and piezoelectric actuators [8]. Ca2+ can occupy either Ba2+ site or Ti4+ site in BaTiO3 lattice. Ca2+ substitution in the Ti4+ site requires charge compensation by creating oxygen vacancies in Ba(Ca, Ti1–x)O3 [9,10]. Oxygen vacancies are created by charge compensation mechanism and this might be the reason for Ca2+ (ionic radius rca = 0.99 Å) occupancy at B-site (Ti4+ site, ionic radius of rTi = 0.60 Å) in perovskite BaTiO3. The solubility limit of Ca2+ occupying B-site (x ~ 0.04) in Ba(Ca,Ti1–x)O3 [11], is much lower when compared to that of A-site doping, due to the larger ionic radius of Ca2+ to that of Ti4+ [7].

Aging induced double P–E hysteresis behavior has been previously observed for lead-free perovskite BaTiO3/(Ba,Sr)TiO3 [12], BiFeO3 [13], KNbO3 [14], and (Na,Bi)TiO3-based ceramics [15]. However, not much was reported on BCT ceramics aging behavior and only a few reports were available on Ca2+ occupying Ti4+ in BCT oxides. So far, it has been reported that aging behavior [16–19]. Many studies are available on BCT based materials for capacitor applications; but none were found on energy density measurements to our knowledge. Many studies are available on BCT based materials for capacitor...
applications; but none were found on energy density measurements to our knowledge. Here in, we report structure, Raman spectra, ferroelectric, piezoelectric and energy density measurement of BCT ceramics for capacitor applications.

2. Experimental procedure

High-purity BaCO₃ [99.99%], CaCO₃ [99.99%], TiO₂ [99.99%] (Alfa Aesar, U.S.A) powders were used as the starting materials. (Ba₀.₇₀xCa₀.₃₀)TiO₃ ceramics were prepared by the conventional solid state reaction of BaCO₃, CaCO₃, and TiO₂. Stoichiometric quantities of starting materials were ball-milled in a polyethylene jar for 4 h using ZrO₂ balls with ethanol. The mixtures were heated at 800 °C in air for 3 h after drying and sieving. The mixture was calcined at 1250 °C for 10 h. The calcined powder was ball milled and dried again to obtain homogeneous powder. The granulated powders were pressed into disks of 13 mm in diameter and 0.5 mm in thickness using 5% PVA binder, binder burnt out by heating at 500 °C for 1 h and then sintered at 1500 °C in air for 6 h. X-ray diffraction (XRD) patterns at room temperature were obtained on an automated Rigaku D/max 2400 X-ray diffractometer with rotating anode using Cu Kα radiation. After polishing, the dimensions were measured before silver electrodes were deposited on the pellets, then the specimens were fired at 810 °C for 1 h. The Raman measurements were performed using an ISA T64000 triple monochromator. An optical microscope with an 80× objective was used to focus light with wave number 514.5 nm radiations from a Coherent Innova 99 argon ion laser on the sample. Laser power of ~10 mW was focused on a ~2 μm spot. The same microscope objective collected the backscattered radiation. The scattered light, dispersed by the spectrophotometer, was detected by a 1 inch charge-coupled device (CCD) detection system with 1800 grooves/mm grating and the spectral resolution was typically <1 cm⁻¹. Ferroelectric hysteresis loops were measured at 50 Hz, with pored disk-shaped samples under an electric field using Radiant Technologies high voltage amplifier (RT 6000 HVA-4000V). Dielectric breakdown voltage of the samples was measured at room temperature using a Trek high voltage amplifier (Trek Inc., Model 30K/20A).

3. Results and discussion

Fig. 1 shows the room temperature XRD patterns obtained from (Ba₀.₇₀xCa₀.₃₀)TiO₃ (BCT) ceramics with angle 2θ (degree) ranging from 10° to 80° with a scan rate of 1° per minute. Tetragonal peaks corresponding to perovskite BaTiO₃ and orthorhombic peaks corresponding to CaTiO₃ XRD patterns were observed for BCT ceramics with majority of tetragonal phase peaks as reported in previous investigations [20–24] and tetragonal BCT, XRD reflection peaks are isostructural with Ba₀.₃₀Ca₀.₇₀TiO₃ (JCPDS 81-1288). In addition to prominent indexed tetragonal diffraction peaks, orthorhombic peaks corresponding to CaTiO₃ were detected at 2θ = 32.94°, 47.43°, 58.87°, 69.07° and were indexed with (121), (202), (042) planes respectively. Detected peaks are isostructural with CaTiO₃ in complete agreement with JCPDS 75-2100 [24,25]. According to the phase diagram of BaTiO₃–CaTiO₃ solid solutions prepared by conventional dry route, the formation of CaTiO₃ is expected for x > 0.16 at the calcination temperature of 1150 °C [23,26]. In the present study, prolonged calcination (1250 °C/10 h) and sintering (1350 °C/4 h) could not suppress the orthorhombic phase for higher concentrations of calcium in BCT (not shown here). Whereas sintering at higher temperature ~1500 °C/6 h, drastically reduced orthorhombic peaks and whose lattice parameters [(a ~ 3.9519 Å, c ~ 3.94950 Å), tetragonal distortion (c/a ~ 0.99) and volume (~61.6817 Å³)] of the unit cell decreased from that of the lower sintering temperature 1350 °C/4 h, [(a ~ 3.958 Å, c ~ 4.066 Å), tetragonal distortion (c/a ~ 1.027) and volume (~63.7094 Å³)]. This decrease might be due to partial incorporation of calcium at barium site due to higher sintering temperature (1500 °C) with more dwelling time (6 h). The SEM micrographs of BCT ceramics are shown in Fig. 1 inset. It is found that the sintered ceramics are very dense, uniform void free. The average grain size of the ceramics calculated by line intercept method is around 40–65 μm.

Ferroelectric tetragonal BaTiO₃ contain 3A1 + B1 + 4E Raman active phonons; however cubic phase has no Raman active modes in BaTiO₃. In brief, room temperature tetragonal BaTiO₃ Raman mode were E(TO₁), A₁g(TO₁) [sharp mode], A₁g(TO₂) [asymmetric broad mode], B₁g(E(TO + LO)) [sharp mode], A₁g(TO₂)E(TO₂) [asymmetric broad mode], A₁g(LO)/E(LO) [asymmetric broad mode]. However much broader and symmetrical A₁g(TO₂), A₁g(TO₂)E(TO), A₁g(LO)/E(LO) modes are also present in cubic paraelectric phase, they were often attributed to second-order effects. More precisely, they relate to the disorder of Ti displacements in the TiO₆ octahedra [10]. Raman spectrum in Fig. 2, reveals spectral features at 146 cm⁻¹ [A₁g(TO₁)], 224 cm⁻¹ [A₁g(TO₂)], 297 cm⁻¹ [B₁g(E(TO + LO)], 473 cm⁻¹ A₁g(LO)/E(LO)], 524 cm⁻¹ A₁g(TO₂)E(TO₂), 734 cm⁻¹ A₁g(LO)/E(LO)], 863 cm⁻¹ A₁g. Similar results were observed in Ba₁₋ₓCaₓTiO₃, Ba₁₋ₓCaₓTiO₃, Ba₁₋ₓCaₓTiO₃ ceramic systems [16,27]. The shift of the modes namely A₁g(TO₂)/E(TO), A₁g(LO)/E(LO) to higher frequencies when compared to pure and Ca substituted BaTiO₃ [27], implies an increase in force constant which resulted from the presence of higher amount of calcium in reaction at the Ba sites. The shift of these bands to higher frequencies is attributed to the formation of CaO₃ defects, which is closely related to the phonon vibrations of the Ba-O bonds [27]. Both [A₁g(TO₂)], [B₁g(E(TO + LO)] modes at 224 cm⁻¹ and 297 cm⁻¹ respectively shifted towards lower wave number region, the shift in these two bands to lower wave number region might be caused by the phonon vibrations of Ti-O bonds [27]. These results are in agreement with previous reports on BaTiO₃, Ba₁₋ₓCaₓTiO₃ (BCT), Ba₁₋ₓCaₓTiO₃ (BCT) [16,17,27] and simulta-
neously substituted La\(^{3+}\), Yb\(^{3+}\) system in BaTiO\(_3\) [34]. In contrary to these results, Strathdee et al., reported that [A\(_i\)(TO\(_j\))] mode shifted to higher wave number region, when both Bi\(^{3+}\) and Yb\(^{3+}\) simultaneously incorporated into the BaTiO\(_3\) lattice [35]. This is attributed to the presence of lone pair electrons in Bi\(^{3+}\), which hardens the phonon vibrations in BaTiO\(_3\)-BiYbO\(_3\) system and as well as the bond bending in Ti-O bonds in TiO\(_6\) octahedra [17,35].

In general the presence of \(B_1\)/[E(TO + IO), A\(_i\)(TO\(_j\))/E(VO)] modes represents the tetragonal phase at room temperature. Strong A\(_{1g}\) octahedral breathing mode is only observed in BCT ceramics, which is Raman inactive for simple perovskite structured materials, and this mode is observed when Ca\(^{2+}\) is substituted for Ti\(^{4+}\) in BaTiO\(_3\) lattice [10]. This higher wave number Raman mode has resulted from the formation of Ca\(_4\) defects. Extended X-ray absorption fine structure (EXAFS) results on BaTi\(_{0.97}\)Ca\(_{0.03}\)O\(_2\) [BCT] solid solutions revealed that the Ca occupancy on the Ti site is only 2\% instead of 3\%. The remaining 1\% of Ca occupied Ba site [31].

Raman spectra of present BCT ceramics, revealed a well defined breathing mode (A\(_{1g}\)) peak at 863 cm\(^{-1}\) whereas this peak was absent in the spectra of BaTiO\(_3\), (Ba,Ca)TiO\(_3\) in earlier reports [10,32]. Presence of A\(_{1g}\) mode in BCT ceramics might be attributed to the greater amount of Ca\(^{2+}\) on the Ba\(^{2+}\) (A) site than its solid solubility limit and as well we predict that Ca\(^{2+}\) ions partially migrated into both Ba\(^{2+}\) and as well as Ti\(^{4+}\) sites due to solid solubility limit \(x < 0.25\) [31]. As well previous reports also supports that some of the Ca\(^{2+}\) ion have been substituted for the Ti\(^{4+}\) ions, even when the chemical composition of the starting materials with the ratio of A-site ions to B-site ions was one for BCT [16,33]. And as well presence of octahedral breathing mode (A\(_{1g}\)) is also attributed due to the formation of oxygen vacancies at both Ba\(^{2+}\) and Ti\(^{4+}\) sites due to partial migration of Ca\(^{2+}\) from Ba\(^{2+}\) to Ti\(^{4+}\) site. This may imply that, the Ca\(^{2+}\) ion is partially substituted for Ti\(^{4+}\) in BCT ceramics, and O\(^{2-}\) vacancies have formed to compensate for the charge imbalance [16,19,27]. Almost similar results were evidenced in Ca\(^{2+}\) ion substitution for B-site Ti\(^{4+}\) ions in Bi–BCT [16,27].

The P–E loops were examined using a computer controlled modified Sawyer–Tower circuit operating at a frequency of 50 Hz. BCT ceramics were poled overnight (~20 kV/cm) and then ferroelectric measurements were carried out. The ferroelectric nature of conventionally prepared BCT ceramics was confirmed by a hysteresis loop of polarization (\(P\)) as a function of applied electric field (\(E\)) with a maximum electric field of 50 kV/cm, before and after aging. Before aging BCT samples have shown normal ferroelectric hysteresis loops. Abnormal double hysteresis P–E loops were observed at room temperature for naturally aged (3 weeks) samples. P–E hysteresis loops of the conventionally prepared BCT ceramics were shown in Fig. 3(a). The saturation polarization (\(P_s\)) were ~16.78 \(\mu C/cm^2\) (before aging) and 17.53 \(\mu C/cm^2\) (after aging), remnant polarization (\(P_r\)) ~4.37 \(\mu C/cm^2\) (before aging) and 2.25 \(\mu C/cm^2\) (after aging), the coercive field (\(E_c\)) ~10.10 kV/cm (before aging) and 5.12 kV/cm (after aging) respectively for of the BCT ceramics were shown in Fig. 3(a) and Table 1.

Single hysteresis P–E loops become double-like in the P–E hysteresis behavior after natural aging for 3 weeks demonstrating antiferroelectric like behavior. However, such double hysteresis loop behavior is only found when Ca\(^{2+}\) ions occupies Ti\(^{4+}\) site in BCT ceramics [16,17]. The aging effect with double hysteresis P–E loop behavior in acceptor-doped ferroelectrics is generally considered to be caused by the migration of oxygen vacancies (which are highly mobile) during aging in Bi–BCT samples and as well the ground state of Bi-doped (Ba\(_{1-x}\)Ca\(_x\)Sr\(_{y}\))TiO\(_3\) (BCST) might be antiferroelectric at about 6 \(^\circ\)C [17–19]. The spontaneous polarization values for aged BCT are comparably higher than before aging; however the remnant polarization and coercive field values are behave in opposite manner and are less pronounced after aging. The present BCT ceramics exhibit comparatively improved values in both cases (before aging and after aging) than earlier reports [16,17]. Presence of such an antiferroelectric double hysteresis P–E loop behavior might be attributed to oxygen vacancies created during partial migration of Ca\(^{2+}\) from Ba\(^{2+}\) site to Ti\(^{4+}\) site in perovskite BaTiO\(_3\) as explained earlier. Asymmetric S–E piezoelectric butterfly hysteresis loops were observed in both cases (before aging and after aging) as shown in Fig. 3(b). Electric field dependent strain behavior in both cases (before and after aging) reveals that obvious nonlinear transition region is observed in bi-polar region of the measurement that corresponds to the possible steps of the reorientation of domains induced by external electric fields [4,28]. The aged BCT ceramics exhibited a little higher maximum percentage of strain (~3\%) than the normal samples (~2.8\%) at ~50 kV/cm). BCT ceramics have shown higher strain than pure BaTiO\(_3\) ceramics (~0.14\% at 50 kV/cm) [4], as well as Ba\(_{0.77}\)Ca\(_{0.23}\)-TiO\(_3\) ceramics (~0.22\% at 50 kV/cm) [21].

The energy density (\(E_d\)) of a capacitor is calculated from the P–E hysteresis loop, and is the integral area of the P–E loop (charge-

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>(P_s) ((\mu C/cm^2))</th>
<th>(P_r) ((\mu C/cm^2))</th>
<th>(E_c) (kV/cm)</th>
<th>(S_{max}) %</th>
<th>Degree of hysteresis ((\Delta x/x)) %</th>
</tr>
</thead>
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<td>Before aging</td>
<td>4.37</td>
<td>16.73</td>
<td>9.10</td>
<td>2.8</td>
<td>47</td>
</tr>
<tr>
<td>After aging</td>
<td>2.25</td>
<td>17.53</td>
<td>5.12</td>
<td>3.0</td>
<td>42</td>
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</table>
The calculated discharge and charge curve energy densities and energy density efficiencies were listed in Table 2. The BCT ceramics exhibited energy densities (~0.2–0.39 J/cm³) and with high energy efficiencies (η ~ 58–61%) in both before and after aging than BCT ceramics, due to enhanced non-linear behavior of ferroelectric hysteresis loops. Enhanced energy storage properties in aged samples were attributed to antiferroelectric behavior in BCT ceramics. These moderate values of the energy densities might be due to low electric field strength (~50 kV/cm). Electric field dependent discharge and charge curve energy densities before and after aging were shown in Fig. 4(a) and (b). As the electric field increased from ~10 kV/cm to ~50 kV/cm, both discharge and charge curve energy densities were increased and the energy efficiency of storage capacitor is drastically increased to 61%.

4. Conclusions

In conclusion, based on the experimental observations, the BCT ceramics have shown tetragonal perovskite crystal structure along with orthorhombic CaTiO₃ peaks at room temperature due to incomplete solid solubility of Ca²⁺ in BaTiO₃ lattice. The Raman spectrum at room temperature confirms the presence of tetragonal modes at room temperature. A strong A₁g octahedral breathing mode was observed in BCT ceramics, which may be due to formation of oxygen vacancies at both Ba³⁺ and Ti⁴⁺ sites due to partial migration of Ca²⁺ from Ba²⁺ to Ti⁴⁺ site. This may imply that the Ca²⁺ ion is partially substituted for Ti⁴⁺ in BCT ceramics and O²⁻ vacancies have formed to compensate for the charge imbalance. However, to completely understand the site occupancy mechanism further the compositional analysis studies as well as the temperature dependent phase transitional studies are needed. Interesting aging induced double hysteresis like P–E loops were observed with higher saturation polarizations, which is also attributed to migration of oxygen vacancies (which are highly mobile) during aging. Bulk BCT ceramics with ferroelectric and piezoelectric behavior might be useful in actuator applications. Higher energy densities with high energy storage efficiencies were obtained for aged BCT ceramics which is due to antiferroelectric behavior. Optimizing intrinsic and extrinsic parameters (composition, bulk structure defect chemistry, microstructural development, thickness, electrode configuration and grain size and) will further improve dielectric breakdown values and enhance energy densities in making commercially viable energy storage device capacitors for wide range of energy storage applications.

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Reference