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Multilayer ceramic capacitors based on relaxor $BaTiO_3$-$Bi(Zn_{1/2}Ti_{1/2})O_3$ for temperature stable and high energy density capacitor applications

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The need for miniaturization without compromising cost and performance continues to motivate research in advanced capacitor devices. In this report, multilayer ceramic capacitors based on relaxor $BaTiO_3$-$Bi(Zn_{1/2}Ti_{1/2})O_3$ (BT-BZT) were fabricated and characterized. In bulk ceramic embodiments, BT-BZT has been shown to exhibit relative permittivities greater than 1000, high resistivities ($\rho > 1$ GΩ-cm at 300 °C), and negligible saturation up to fields as high as 150 kV/cm. Multilayer capacitor embodiments were fabricated and found to exhibit similar dielectric and resistivity properties. The energy density for the multilayer ceramics reached values of ~2.8 J/cm^3 at room temperature at an applied electric field of ~330 kV/cm. This represents a significant improvement compared to commercially available multilayer capacitors. The dielectric properties were also found to be stable over a wide range of temperatures with a temperature coefficient of approximately −2000 ppm/K measured from 50 to 350 °C, an important criteria for high temperature applications. Finally, the compatibility of inexpensive Ag-Pd electrodes with these ceramics was also demonstrated, which can have implications on minimizing the device cost. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4922947]

Current state-of-the-art capacitors require a relatively large fraction of the total volume of the electronic components in power electronics systems. Multilayer ceramic capacitors (MLCCs) are an effective means for improving the volumetric efficiency of the capacitive components. With dielectric layers of small thicknesses arranged in parallel, higher capacitance levels can be achieved along with miniaturization of the electronic circuitry. However, manufacturing of high quality MLCCs is challenging and often faces problems such as inter-diffusion or chemical reaction between the metal electrode and ceramic, oxidation of electrodes during the co-firing step, residual stresses, and the need to add significant levels of dopants to lower the sintering temperature during co-firing which may affect the properties adversely.[1–7] The growing need for further miniaturization, higher volumetric efficiency, lower cost, and the need to resolve the issues associated with the current manufacturing technology motivates the current research activities in the field of MLCCs.[8–11]

Ceramic capacitors have the potential to achieve the requirements for high temperature power conversion and energy storage systems. Traditionally, MLCCs based on chemically inhomogeneous and doped $BaTiO_3$ (BT) (X7R specification, Electronic Industries Association standards) have been used to attain temperature-stable dielectric properties.[6,12–15] However, there is a constant effort to explore materials with better properties especially at higher temperatures and specifically designed for use at high fields (E > 100 kV/cm). Recently, MLCCs based on relaxor perovskites have shown great promise with improved properties compared to traditional X7R capacitors.[16–20] Previous research has shown that relaxor dielectrics based on compositions in the BT-$Bi(Zn_{1/2}Ti_{1/2})O_3$ (BT-BZT) system have unique properties including a high dielectric constant (>1000) which remains stable up to high temperatures (T > 300 °C) and that persists to high electric fields (E > 100 kV/cm).[21–23] They also maintain a high insulation resistance even at high temperatures which enables these materials to withstand large electric fields without breaking down. In addition, they exhibit negligible hysteresis due to the relaxor mechanism in compositions with greater than 8 mol. % BZT. This results in MLCC devices with low dielectric losses and potential for high energy densities.

In this study, high energy density multilayer ceramic capacitors based on the (1 − x)BT-xBZT system (where x = 15%, 20%) were fabricated. The MLCCs were fabricated with two internal electrode systems, an Ag-Pd alloy (70Ag-30Pd) and a Pt-Au-Pd alloy (40Pt-40Au-20Pd). The MLCC devices were characterized and the properties were compared to the bulk ceramic material.

Ceramic powders of the composition $(1-x)BaTiO_3$-$xBi(Zn_{1/2}Ti_{1/2})O_3$ (x = 15%, 20%) were prepared using conventional solid state synthesis following the methods described in Ref. 24. The calcined ceramic powders were mixed with various organic binders and solvents and cast to thin tapes for multilayer fabrication. Uniformly mixed slurry was passed through a doctor blade on a steel belt and was dried as the belt traveled through a heated cabinet. The internal electrodes for the multilayer capacitor were screen printed onto ceramic tapes. Lamination of the printed stack of 30 active layers was conducted under a hydraulic pressure of 21 MPa at 65 °C. The laminated stack was cut into

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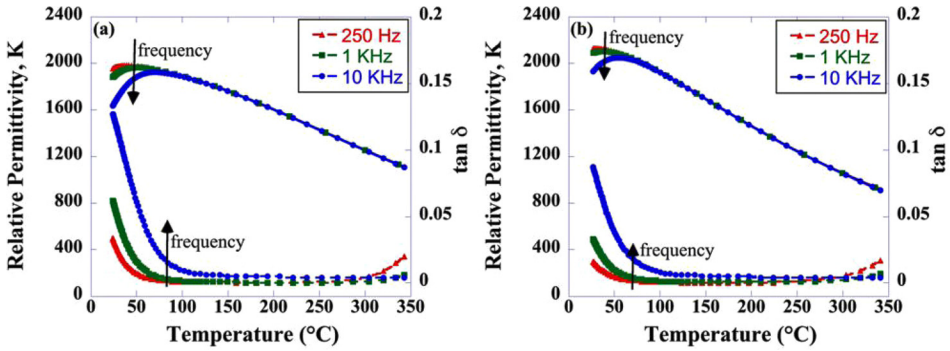

FIG. 1. Temperature dependence of relative permittivity and dielectric loss for (a) 80BT-20BZT and (b) 85BT-15BZT MLCCs from 250 Hz to 10 kHz. The arrows denote the direction of increasing frequencies.

individual multilayer capacitors. The cut multilayer capacitors went through a binder removal process that involved slow heating up to 550 °C. After burnout, the capacitors were sintered at 1200 °C for 1 h in a tube furnace with flowing oxygen and then hot isostatically pressed (HIP'ed) at 1100 °C and 5000 psi for 3 h. The HIP is effective in removing residual pores or defects after sintering. Capacitors were then tumbled to expose internal electrode for 30 min and then silver terminal electrodes were applied and the part was fired at 590 °C using a tunnel kiln. The dielectric properties of the MLCCs were measured using a high temperature measurement cell (NorECs AS ProbostatTM, Oslo, Norway) and an LCR meter (Agilent 4284A, Santa Clara, CA, USA) using an oscillating voltage of 0.1 V. The MLCCs had a parallel arrangement of layers of capacitor, which was taken into account while calculating permittivity from MLCC. The energy density was estimated from the polarization-electric field curves by calculating the area enclosed by the curve and polarization axis. An impedance analyzer (Solartron SI1260A) equipped with a dielectric interface (Solartron 1296A, Farnborough, UK) was used over the frequency range of 1 Hz to 1 MHz, in conjunction with SMaRT impedance measurement software program to collect the data. The DC resistances were measured using the Probostat and a High Voltage Source-Measure Unit (Keithley 237, Cleveland, OH, USA). For each measurement, a voltage of 100 V (~22 kV/cm for 20BZT and ~34 kV/cm for 15BZT) was applied and the current was measured after 30 s. Polarization hysteresis measurements were performed at 1 Hz using Radiant Technologies RT66A, Albuquerque, NM, USA. The ceramic-electrode interface was exposed with a focused ion beam (FIB) and imaged using a Scanning Electron Microscope (Quanta 3D Dual Beam SEM/FIB, FEI, Hillsboro, OR, USA).

Figures 1(a) and 1(b) show the dielectric properties as a function of temperature for MLCC devices of the compositions 80BT-20BZT and 85BT-15BZT with Pt-Au-Pd electrodes. The dielectric response shown in Figure 1 is characteristic of the relaxor mechanism with a large, weakly temperature dependent permittivity and a frequency dependent dielectric maximum. In relaxor materials, these dielectric characteristics are attributed to the presence of polar nanoregions (PNRs).[25–27] The PNRs exhibit a variation in size and dipolar strength and random interactions result in a broad distribution of relaxation times which gives rise to a broad dielectric peak.

The results in Figure 1 closely match the dielectric behavior of bulk ceramics in terms of temperature, stability, and dielectric loss values.[21,22] The room temperature dielectric constant for the MLCCs was found to be comparable (<10% different) to their bulk ceramic counterparts. Some of the disparity in the dielectric constant values can be attributed to uncertainties associated with the calculation of the layer thickness and internal electrode area. The close correspondence between the MLCC and ceramic properties is significant because the dielectric properties of MLCC devices are often inferior due to electrode interactions, low porosity, and other factors.

Low-field AC impedance measurements were performed on MLCCs of both compositions with Pt-Au-Pd internal electrodes and the data are shown in Figure 2. From the Nyquist plots, it appears that the 20BZT composition exhibited some degree of electrical heterogeneity with an apparent low frequency shoulder, while the 15BZT composition appeared more electrically homogeneous. The activation energies derived from the Arrhenius plots were approximately 1.6 eV which are close to half of their optical band gaps, which suggests intrinsic conduction as the dominant mechanism.[28] These data indicate that the transport behavior in the MLCC devices was similar to that obtained in the bulk ceramics. This implies that no significant defects were introduced during the multilayer fabrication process.[28,29] Figure

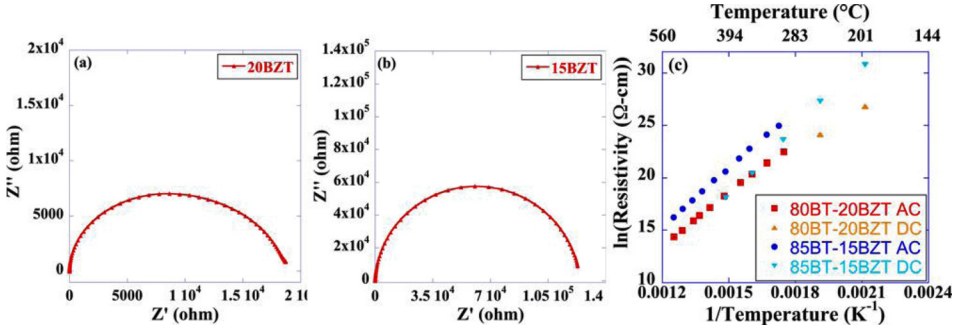

FIG. 2. Nyquist plots for (a) 80BT-20BZT and (b) 85BT-15BZT MLCCs at 400 °C and (c) Arrhenius plots for AC and DC resistivity.

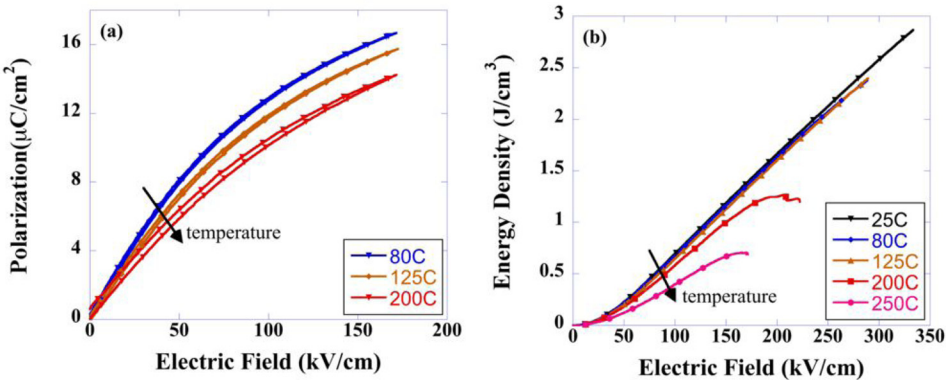

FIG. 3. (a) Polarization as a function of electric field for 85BT-15BZT MLCCs and (b) the energy density of 85BT-15BZT as a function of electric field at various temperatures. The arrows denote the direction of increasing temperatures.

2(c) shows the Arrhenius plots from the data obtained from high-field DC measurements superposed onto the Arrhenius data obtained from low-field AC measurements. In Figure 2(c), while the AC and DC behaviors were quite similar for the 20BZT composition, the resistivity calculated for the 15BZT composition was one order of magnitude lower for the high-field DC measurements as compared to the low-field AC measurement. The measurement of high resistivity values at high temperatures ($\sim 10^{10}$ Ω-cm at 300 °C) indicates that these devices can withstand high E-fields, which can extend the operational temperature range of these MLCCs. A detailed comparison between AC and DC resistivities of the bulk BT-BZT ceramic embodiments has been made elsewhere.[30]

Figure 3(a) displays an example of polarization data for a 15BZT MLCC with Pt-Au-Pd internal electrodes at various temperatures. The overall polarization decreased slightly as the temperature increased; however, there was minimal hysteresis up to 200 °C. The minimal hysteresis is important in order to maximize the energy storage capability of these devices. The low hysteresis is also indicative of low dielectric losses up to higher temperatures. Figure 3(b) shows the energy densities obtained at different temperatures. At room temperature, the energy density for the MLCC with thirty dielectric layers, where each dielectric layer had a thickness of ~29 μm, was calculated to be at least ~2.8 J/cm^3 at a field of ~330 kV/cm. This represents a significant improvement compared to several commercial X7R capacitors.[18,31,32] For example, an X7R capacitor with precious metal electrodes had energy density values of ~1.5 J/cm^3 at room temperature and at electric field levels of ~350 kV/cm.[18] The improved energy density values in these ceramics may be a combined consequence of minimal polarization-hysteresis owing to the relaxor mechanism, high dielectric strength, and high permittivities with negligible polarization-saturation even at these high fields.[29] The energy density curves also appeared relatively insensitive to temperature. This can be attributed to the high insulation resistances in these compositions even at high temperatures, as shown in Figure 2.

The results shown in Figures 1–3 were obtained for MLCCs fabricated with Pt-Au-Pd internal electrodes. The Pt-alloys have natural advantages over other internal electrode systems because of their low reactivity with dielectric layers and higher melting temperatures which can support higher co-firing temperatures. However, these advantages are accompanied with a higher cost for fabricating the MLCC devices. Research over the past two decades has explored the viability of inexpensive Ni internal electrodes. However, because of the thermochemistry of Ni/NiO, this requires the MLCCs to be co-fired in reducing atmospheres, which are incompatible with the stability of Bi/Bi_2O_3 in the BT-BZT system as well as the formation of oxygen vacancy-related defects.[10,33–37] The internal electrodes based on Ag-Pd alloys require lower co-firing temperatures, which may not be suitable for MLCC compositions without the addition of low-melting additives that may degrade the electrical properties. There can also be issues associated with Pd due to chemical reactions with Bi and also its characteristic volume expansion.[2,38] Nevertheless, Figure 4 shows the polarization and energy density behavior for the 20BZT composition with Ag-Pd internal electrodes. The results indicate that the properties of MLCCs were largely unaffected by the change in electrode chemistry and energy densities greater than 2 J/cm^3 could be obtained similar to MLCCs with Pt-Au-Pd internal electrodes. The polarization data show no hysteresis and the energy densities were high and

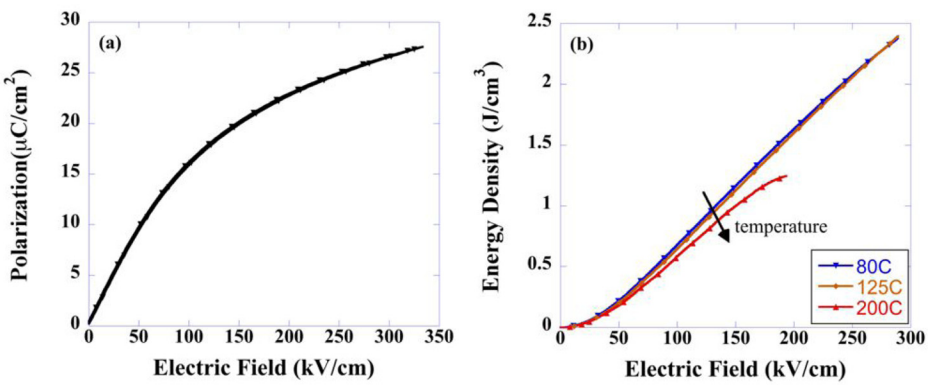

FIG. 4. (a) Polarization and (b) energy density as a function of electric field for 80BT-20BZT multi-layer capacitors with Ag-Pd electrodes. The arrow denotes the direction of increasing temperatures.

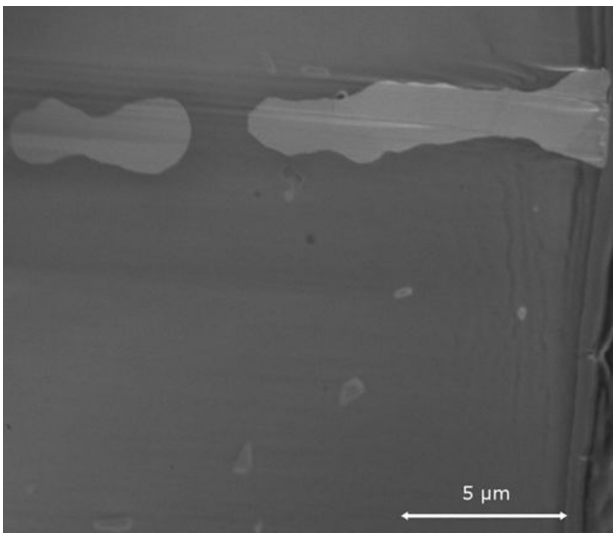

FIG. 5. SEM image of an internal cross-section of the MLCC with Ag-Pd internal electrodes.

essentially insensitive to temperature. While more detailed reliability tests are needed to assess the long-term stability of the Ag-Pd-alloy electrodes, these results show great potential for cost reduction.

Figure 5 shows an SEM cross-section of an MLCC with no evidence of electrode interactions at the electrode-ceramic interface or delamination. This demonstrates that MLCCs based on BT-BZT can be fabricated into dense embodiments without the need for sintering fluxes or other additives.

In summary, multilayer capacitors based on (1−x)BT-xBZT had high capacitance values greater than 1 μF at room temperature and a temperature stable capacitance up to 350 °C. Energy density values greater than $\sim$2.0 J/cm^3 were obtained at room temperature. The compatibility of Ag-Pd electrodes with BT-BZT-based MLCCs was also demonstrated, which is critical in reducing the cost. The electrical properties of the MLCC devices closely matched the properties of bulk ceramics, which is indicative of the high quality of the MLCC devices.

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