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The role of oxygen vacancies on DC lifetime and TSDC in $Bi(Zn,Ti)O_3$-$BaTiO_3$ (BZT-BT)

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The DC lifetime and thermally stimulated depolarization current (TSDC) of $(Bi_{0.22}Ba_{0.78})(Zn_{0.1}Ti_{0.9})O_3$ are shown to be signicantly impacted by thermal annealing in air. DC lifetime increases from ~1 day to 1 week at 30 kV/cm and 250 ºC by annealing as-sintered samples in air at 800 ºC for about one day. TSDC response is also decreased dramatically by annealing, and the resistivity increases orders of magnitude to expected values (~$10^{10.4}$ Ωcm at 250 ºC) after annealing. Oxygen vacancies induced during sintering and removed by lower temperature annealing are suggested to be the source of observed behavior.
Key words: relaxor, TSDC, lifetime, oxygen vacancies, bismuth

1. INTRODUCTION

$BaTiO_3$-$xBi(Zn_{0.5}Ti_{0.5})O_3$ (BT-xBZT) solid solutions exhibit attractive dielectric properties for high temperature and electric field capacitors. The x = 0.2 composition was previously shown to have a relatively temperature stable dielectric constant (ε_r ~ 1500) with low loss tangent (tanδ < 0.01) up to high temperatures (T < 400 ºC), overcoming the steep change in dielectric properties associated with the Curie temperature in $BaTiO_3$ [1]. The high field DC resistance, or insulation resistance, has been shown to be significantly improved with increasing x [2], with ~10^{10} Ωcm at 350 ºC reported for x = 0.2 [3]. Lastly, BZT-BT has been successfully fabricated in a multilayered ceramic capacitor (MLCC) using Ag-Pd electrodes [4].

While BT-BZT has shown attractive properties, there have not been any studies of its susceptibility to long-term degradation in resistance under high electric field (DC lifetime). Oxygen vacancies unintentionally added by impurities or formed from cation vacancy formation during high temperature sintering are often suggested to limit DC lifetime [5]. Since oxygen vacancies are typically a minority charge carrier, they are difficult to probe with conventional DC or AC electrical measurement techniques. Thermally stimulated depolarization current (TSDC) has been used to probe the relaxation current from mobile oxygen vacancies after an applied polarizing DC field has been released [6].

In this paper, the DC lifetime is examined on BT-0.2BZT and the role of oxygen vacancies is explored with TSDC. The material is effectively donor doped by partially substituting Ba^{2+} with Bi^{3+} to assist in decreasing oxygen vacancy content. The batched composition examined is $(Bi_{0.22}Ba_{0.78})(Zn_{0.1}Ti_{0.9})O_3$.

2. EXPERIMENTAL

$BaCO_3$, Bi_2O_3, TiO_2, and ZnO were ball milled in ethanol and dried to mix the precursor oxides. The material was then calcined at 1050 ºC for 6 h in air using dense alumina crucibles that were previously seasoned under the same calcining conditions with sacrificial BT-BZT powder. The powders were then mixed with 1.5 wt% polyvinyl butyral (PVB) binder with ethanol using a mortar and pestle, dried, and then pressed uniaxially, and then isostatically at 30 ksi. The pellet was then sintered on top of the same calcined powder using the same alumina crucibles as described above. The sintering conditions were 1150 ºC for 4h and the final pellet dimensions are about 22 mm diameter and 7 mm thick.

Phase analysis was performed using x-ray diffraction (XRD) with a Cu kα source. The dielectric constant was measured using an LCR meter with 1 V amplitude at 100kHz. Resistivity measurements were performed using an Ametek Modulab XM. TSDC was performed using a picoammeter to source voltage and measure current. DC lifetime measurements were performed using a high voltage power supply coupled with a picoammeter for current measurement. All temperature dependent electrical measurements were performed in temperature controlled ovens in air. Electrodes consisting of a Cr adhesion layer, followed by a Pt diffusion barrier, and a final Au contact layer were deposited using sputtering.

3. RESULTS AND DISCUSSION

The BT-BZT after calcination is single phase as shown by the XRD pattern in Figure 1. The pattern matches the expected P4mm structure of BT-BZT [7].

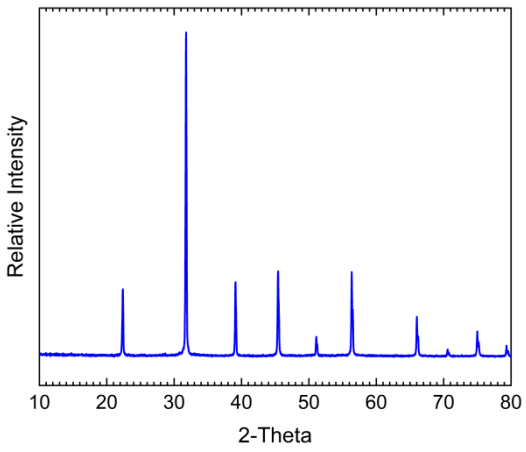

Figure 1: XRD of calcined BZT-BT

With increasing temperature, the dielectric constant (solid circles) first rises and then gently decreases

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following the expected relaxor behavior with increasing temperature as shown in Figure 2. A $BaTiO_3$ formulation for the X7R specification (AD302L from Degussa) shows a steep drop off above 150 °C for comparison (solid squares).

Impedance spectroscopy was used to estimate the resistivity of samples at the testing temperature of 250 °C reported here. An example of the impedance spectra is shown in Figure 3. A single semi-circular arc was typically observed with a low frequency tail in some cases. The low frequency contributions may be related to electrode and is not discussed further here. The large, high frequency contribution was fit with an equivalent circuit consisting of a resistor in parallel with a constant phase element (CPE). The CPE represents non-ideal capacitive behavior that may arise from, e.g., microstructural inhomogeneities. The equivalent circuit fit was performed using Zview (Scribner Associates) and matches the behavior of the data well, as shown in the figure. The n values were typically 0.99 – 1 which indicates a very small deviation from ideal capacitive behavior ($n \sim 1$).

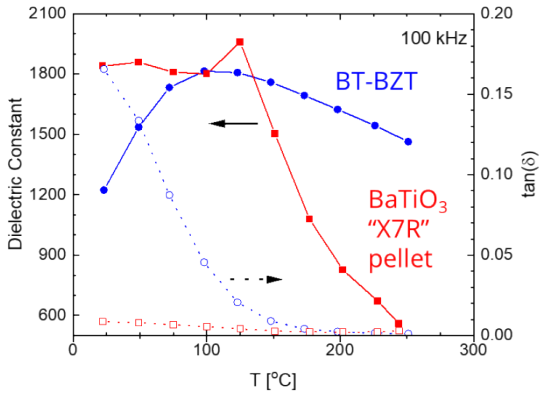

Figure 2: Dielectric constant and tanδ of BT-BZT and a $BaTiO_3$ X7R formulation as a function of temperature.

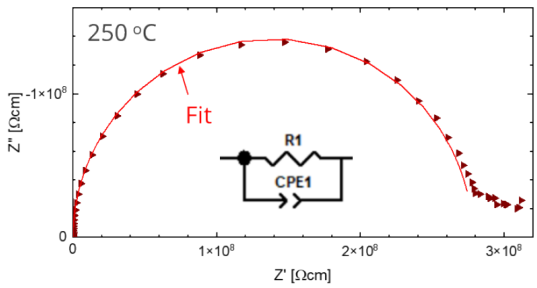

Figure 3: Example of impedance spectra measured at 250 °C with a fit of the equivalent circuit in the diagram also shown.

The pellet was sliced into sections ~0.5 – 1 mm thick and the resistivity, determined from impedance measurements, was found to exhibit orders of magnitude lower values at the center of the pellet, as shown in Figure 4. The large variation in resistivity is suspected to be from either inadequate oxidation of defects created from high temperature sintering during cooling, or from reduction due to residual binder burnout. In both cases, a larger oxygen vacancy content is expected at the center of the sample, which as shown below, leads to a significantly greater TSDC response, as well as a dramatically reduced DC lifetime. Another point to note is the sample exhibits very high resistivity (~10^{11} Ωcm) at the surface.

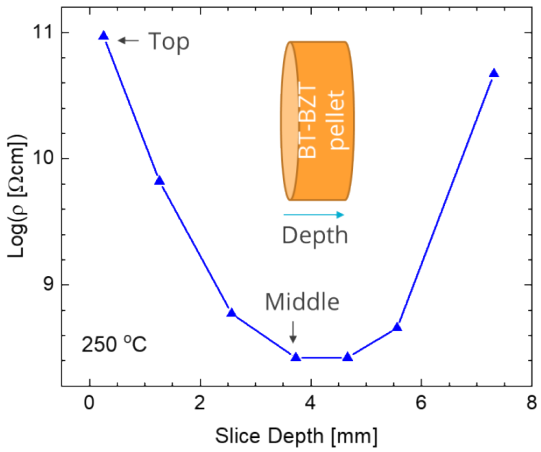

Figure 4: Resistivity of slices of pellet measured at 250 °C.

For TSDC, samples were first polarized at 5 kV/cm during heating at 10 °C/min to the polarization temperature and for an additional 3 min at the same temperature, then followed by quenching to freeze in the polarized carriers (e.g., oxygen vacancies swept to one electrode). After polarization, the samples were heated at 4 °C/min under a short circuit condition with the depolarization current (i.e., TSDC) recorded. The center sample shows a significantly larger TSDC response than the top sample, as shown in Figure 5. The significantly larger TSDC response of the center sample is consistent with a much larger concentration of oxygen vacancies.

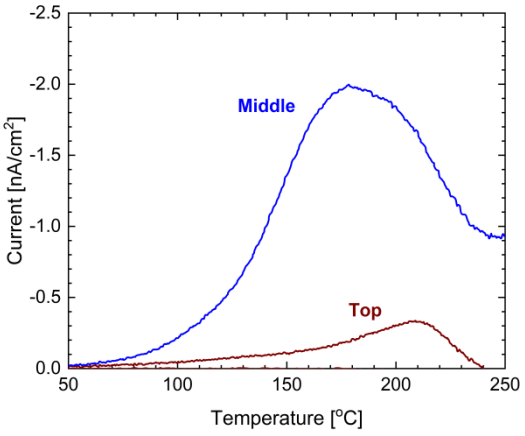

Figure 5: TSDC response for the top and center samples. Samples were polarized at 200 °C under 5 kV/cm.

Since oxygen vacancies created from thermal or residual binder induced reduction are suspected as the source for low resistivity and large TSDC, removing them by annealing the sample in an oxidizing

atmosphere is expected to increase resistivity and reduce the TSDC response. Indeed, the TSDC response is reduced significantly following an anneal in air conditions at 800 ºC for approximately one day for the middle sample, as shown by Figure 6. TSDC also decreased significantly for the top sample after annealing, indicating even the top sample was slightly reduced. Additionally, the resistivity after annealing increased slightly for the top sample and by orders of magnitude for the middle sample to ~$10^{10.4}$ Ωcm. It is worth noting that for annealing measurements, the original pellet was cut in half to enable measurements on both an as prepared and an annealed sample.

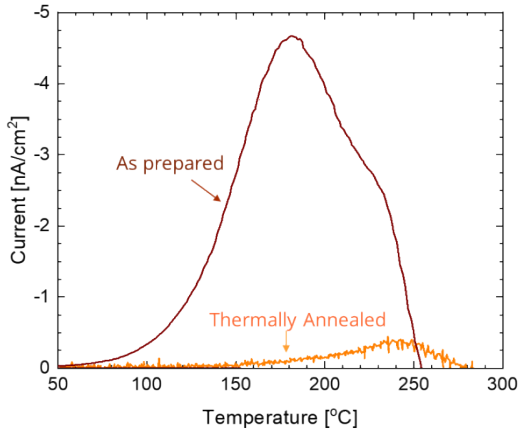

Figure 6: TSDC response of the middle sample before and after annealing in air at 800 ºC for ~ 1 day (TSDC using a 260 ºC polarization temperature).

The resistivity as a function of time (i.e., DC lifetime) under 30 kV/cm at 250 ºC is shown in Figure 7 for the middle sample. Both samples show the resistivity first increases with time, followed by a slow decrease and ultimately a fast decrease. Defining the point of failure as when ρ = 10^8 Ωcm, the as prepared sample exhibits failure at ~3 days, while the annealed sample exhibits failure at ~6 days Annealing has increased DC lifetime, indicating that oxygen vacancies play a significant role in degradation for this material. The initial rise in resistivity in DC lifetime data is believed to arise from polarization of charge carrying oxygen vacancies across the sample, followed by a switch from predominantly ionic to electronic conductivity. Analysis of activation energies and diffusion coefficients (not reported here) suggests this is a reasonable interpretation and will be discussed further in a future publication.

The sensitivity of BT-BZT to sintering conditions and post-annealing described here indicates that this material may have difficulty in integration with low-cost base metal electrodes (BME; e.g., Ni or Cu) where firing in reducing conditions to fabricate MLCCs is necessary. However, doping strategies similar to those used in $BaTiO_3$ may be useful to mitigate the impact oxygen vacancies may have [8]. Additionally, shorter oxidizing anneals than those used here, which, for example, may not oxidize BMEs but oxidize BT-BZT grain boundaries, may suffice.

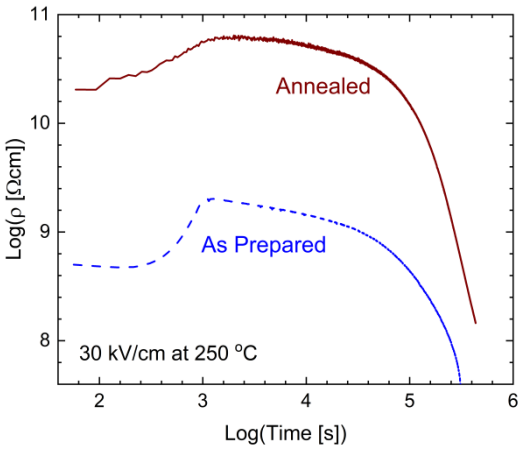

Figure 7: DC lifetime of the middle sample before and after annealing in air at 800 ºC for ~1 day.

4. SUMMARY

The DC lifetime of BT-BZT was shown to be improved significantly (from ~1 day to 1 week) by thermally annealing the material in oxidizing conditions. The source of the short lifetime of as prepared samples is likely from a large oxygen vacancy concentration, as supported by the large TSDC response and low resistivity. The low resistivity is dramatically increased to expected high values and the TSDC response is dramatically reduced after thermal annealing, consistent with oxidation of the sample. Challenges in integration with low-cost BME electrodes in MLCCs may be difficult due to the sensitivity to reducing environments, however, mitigation strategies through doping or shorter thermal anneals remain to be explored.

5. ACKNOWLEDGEMENTS

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