Mechanosynthesis and Spark Plasma Sintering of Fine-Grained $Na_{1/2}Bi_{1/2}Cu_3Ti_4O_{12}$ Ceramics with Giant Dielectric Response

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Abstract

Materials with high values of the dielectric constant are technologically important for their use in various microelectronics applications, such as the components involved in charge storage capacitors. Giant dielectric constant (GDC) was discovered in the $ACu_3Ti_4O_{12}$ (ACTO) family of materials, where A = Ca, $La_{2/3}$, $Y_{2/3}$, $Bi_{2/3}$, $Na_{0.5}Bi_{0.5}$, etc, with $CaCu_3Ti_4O_{12}$ (CCTO) is the most studied example material [1-3]. These materials, with the perovskite structure, exhibit dielectric values up to $\varepsilon' \sim 10^4$-10^5 that is almost independent of temperatures and frequencies over wide ranges [1-3]. The observed (GDC) is due to internal barrier layer capacitance (IBLC) effects that originate from the presence of semiconducting grains separated by resistive grain boundaries [2,3]. The GDC oxide materials are usually prepared by solid state reaction followed by conventional sintering, leading to coarse grained ceramics. It is widely accepted that the dielectric permittivity will increase with increasing the grain size from few to hundreds μm [4]. However, we have reported recently that CCTO nanoceramics with grain size in the 100 – 200 nm exhibit GDC similar to the coarse grained ceramics [5]. In the current work we study the dielectric response of fine-grained $Na_{0.5}Bi_{0.5}Cu_3Ti_4O_{12}$ (NBCT) ceramics.

NBCT was synthesized by mechanosynthesis at RT using stoichiometric proportions of Na_2CO_3, Bi_2O_3, CuO and TiO_2. The milling process was performed in Fritsch P-7 machine using tungsten carbide pots and balls, where the balls to powder mass ratio was 8:1. The milling process continued for 30 h with a rotation speed of 450 rpm. NBCT ceramics were obtained by SPS at 800, 850 and 900 °C using SPS 4-10 system (Thermal Technology LLC). The SPS experiments were performed in a 20 mm graphite die under 60 MPa pressure with a heating rate of 150 °C/min and the dwelling time was fixed to 10 min followed by rapid cooling. The product materials were characterized by XRD and FE-SEM techniques. Impedance measurements were conducted in the 120 – 400 K temperature range over the 1 Hz – 40 MHz frequency range using Novocontrol concept 50 system.

XRD patterns of the SPS ceramics in Fig. 1(e) show the formation of the perovskite structure of the NBCT ceramics. SEM micrograph [Fig. 1(a-d)] of the mechanosynthesized powder shows that nanopowder with particle size < 50 nm was obtained. The grain size of the SPS ceramics increased to 250-450 nm with increasing the SPS temperature from 800 to 900 °C. The grain size of the current ceramics is one order of magnitude smaller than that obtained by conventional sintering. The frequency dependence of the dielectric constant of SPS-900 ceramics is shown in Fig. 2(a). At low frequencies, a plateau region exists with a dielectric value of ~ 3.0×10^4. At high frequencies the dielectric constant drops to a value of ~ 200, which represent the bulk response. The frequency dependence of the dielectric constant of SPS-800, SPS-850 and SPS-900 ceramics at 300 K is shown in Fig. 2(b). We notice that all the NBCT fine-grained ceramics hive very similar dielectric values. This is a result of the close grain size of the investigated materials. The transport properties of the current ceramics are studied though impedance spectroscopy. The impedance diagrams for SPS-900 ceramics are shown in Fig. 3(a). In this figure two semicircles are observed; a large one at the low frequency side, which is due to grain boundary contributions and a high frequency semicircle which is assigned to the bulk response. The temperature dependence of the grain and grain boundary conductivity is presented in Fig. 3(b). We notice that the grain conductivity is much larger than the grain boundary conductivity, supporting the IBLC model. However, the grain boundary conductivity in the SPS NBCT ceramics is very high (~ 2.7×10^{-3} S/cm at 300 K) compared to the ceramics prepared by conventional sintering with a value of ~ 5×10^{-6} S/cm [6]. The activation energy of the grain conduction is 0.089 eV, which agrees with the other ACTO GDC materials. However, the activation energy of the grain boundary contribution is 0.192 eV, which is much smaller than the value of ~ 0.5 – 0.6 eV that usually reported for GDC materials.

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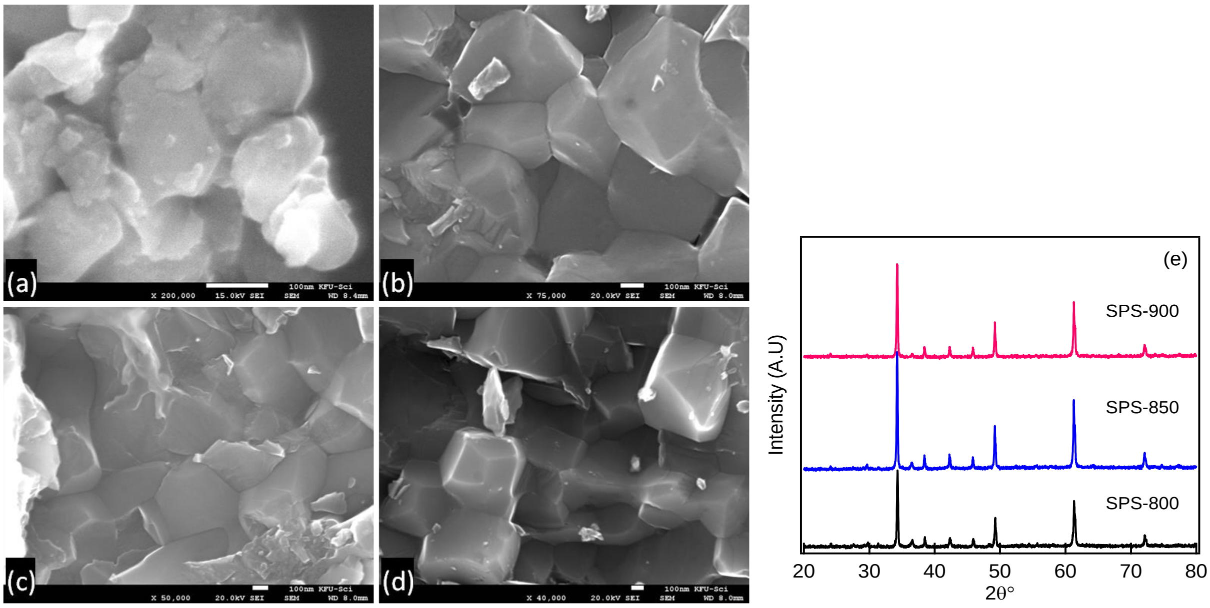

Figure 1. SEM micrographs of (a) NBCT nanopowder and (b-d) SPS-800, SPS-850 and SPS-900, respectively. (e) XRD patterns of SPS NBCT ceramics.

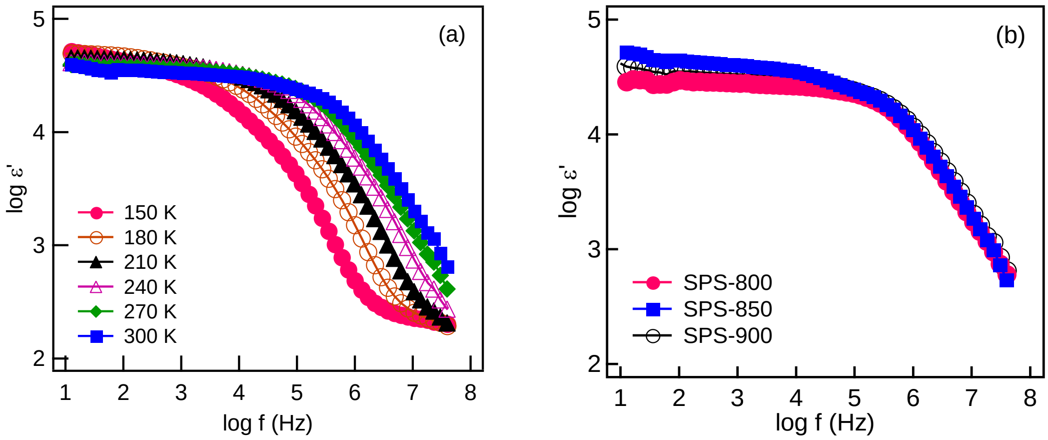

Figure 3. (a) frequency dependence of the dielectric constant for (a) SPS-900 sample and (b) for all ceramics at 300 K.

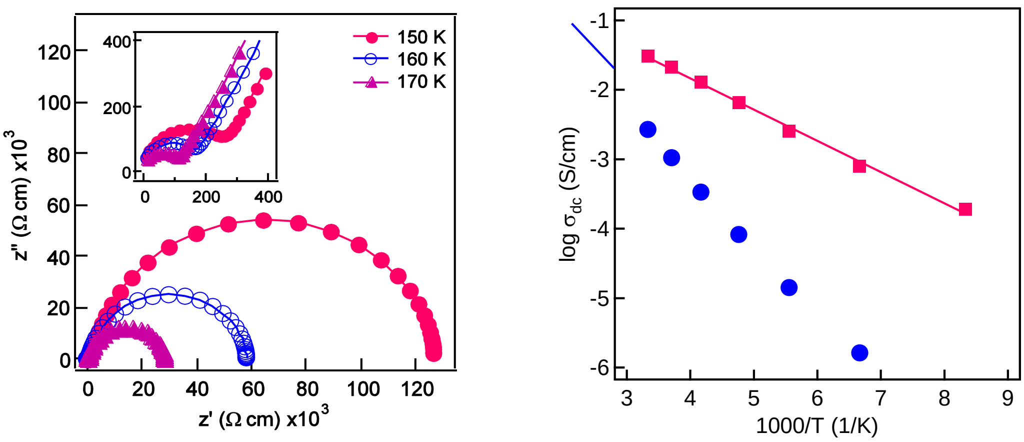

Figure 4. (Left graph) Complex impedance diagrams for SPS-900 ceramics at different temperatures. The inset shows the impedance of the grains at high frequencies. (Right graph)) The temperature dependence of the grain (closed squares) and grain boundary (closed circles) conductivities of SPS-900 ceramics.