Origin of the high dielectric constant in Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics

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Abstract. The microstructure, crystalline structure, dielectric and electrical properties of polycrystalline Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics, prepared via conventional solid-state reaction were investigated. The structural evolution of these powders was analyzed by X-ray diffraction (XRD). Crystal structure investigated by Rietveld refinement was found to be cubic with space group Im$ar{3}$. It has been found that Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramic shows giant dielectric permittivity values with low frequency (1 kHz) larger than 30,000 at room temperature. In the temperature domain, a new dielectric relaxation was clearly observed beyond 200 K, in addition to the well-investigated dielectric relaxation close to 100 K. This Maxwell–Wagner type of relaxation was found to be originating from the formation of external depletion layers at the electrode-sample interface. The dielectric relaxation at high frequencies in the dielectric dispersion spectra of Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics is caused by an IBLC effect associated with the insulating grain boundaries and the other one at low frequencies originates from an electrode polarisation effect. The activation energy of semi conducting grain is found to be similar to that of CCTO (~0.06 eV). The observed giant value of the dielectric constant in the Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics originates due to polarisation at the electrode-sample interface and at the insulating grain boundary interface. The results suggest that the IBLC effect mechanism that was formerly proposed for CCTO ceramics is also valid in explaining the high dielectric constant in the compositionally and structurally CCTO-like, Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics.

1. Introduction

Materials that exhibit colossal dielectric constant (CDC) have attracted significant attention because of their potential applications in electronic devices, such as high dielectric capacitors, capacitor sensors, and random access memories. Miniaturization as well as the production of low cost, highly efficient electronic components can be achieved using these materials. The recent discovery$^1,^2$ of “colossal” values of the dielectric constant, $\varepsilon'$, up to about $10^5$ in CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has aroused tremendous interest. Recent research revealed that many compounds ACu$_3$Ti$_4$O$_{12}$ ($A =$ La$_{2/3}$, Y$_{2/3}$, etc.)
Na$_{1/2}$Bi$_{1/2}$, Na$_{1/2}$La$_{1/2}$) is isostructural to CCTO also shows giant dielectric constant accompanied by low dielectric loss at room temperature, and good temperature stability$^{3,6}$. But so far, there are only few literatures reporting the dielectric properties of the compound Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ (SCTO) which belongs to the ACu$_3$Ti$_4$O$_{12}$ family. Impedance spectroscopic studies demonstrated CCTO ceramics are electrically heterogeneous and large dielectric constant was attributed to grain boundary barrier layer capacitance effects$^{7,8}$. Polarization effects at insulating grain boundaries accompanied by a strong Maxwell-Wagner relaxation mode are the primary cause for non intrinsic colossal values of CCTO. There are some reports on the observation of two extrinsic relaxations in the dielectric spectrum of both single crystals and ceramics$^{9-12}$. These extrinsic relaxations were explained on the basis of a surface barrier layer capacitance (SBLC) effect due to the formation of Schottky barriers at the sample - electrode interfaces, and the giant value of permittivity was accounted for$^{9,11}$. Schottky barriers are interpreted to be formed due to the difference in the Fermi levels between the semi conducting ceramics and the metal electrode. The room temperature dielectric constant of SCTO ceramics reported by Subramanian et al. was only 1665 (measured at 100 kHz) [1]. It is reported that processing conditions such as calcinations temperatures$^{13}$, sintering times$^{14}$ and sintering temperatures$^{15}$ have great influence on the dielectric properties of CCTO ceramics. For higher sintering temperatures and/or longer sintering periods, the resistance of the grain boundary is found to decrease significantly to a level comparable to or smaller than the electrode. In this case electrode effects start to dominate and this results in two extrinsic responses and higher permittivity$^{16}$.

The present work is an attempt to enhance the dielectric properties of SCTO ceramics by varying the processing condition. SCTO ceramics were prepared by the solid-state reaction method. The phase structure, microstructure, and the dielectric properties of the prepared ceramics were analyzed. The complex impedance spectroscopy method is used to find the origin of giant dielectric constants of SCTO. The values of activation energy were obtained to reveal the differences of electric behaviors in SCTO ceramics.

2. Experimental section

Polycrystalline samples of Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ were prepared by solid-state reaction process using stoichiometric quantities of high purity Sm$_2$O$_3$, CuO, and TiO$_2$ (>99.9% purity). These reagents were mixed thoroughly using an agate mortar and pestle in an acetone medium. The calcinations of the mixed powder were done at 950 °C in a muffle furnace on Pt foil in successive cycles of 10 h. Cycles of regrinding and heat treatment were repeated until the phase compositions observed by XRD get stabilised. The calcined powder was reground and mixed uniformly with a few drops of 5 wt% polyvinyl alcohol as binder. The mixture was then uniaxially pressed under 5 tonnes and pellets of 13 mm diameter were yielded. These pellets were sintered for 24 hours in air at 1100 °C using heating and cooling rates 4 °C/min. The powder XRD data corresponding to 2θ values ranging from 10 to 120 ° at equal steps of 0.02 ° was collected using Cu-Kα radiation (λ=1.5418 Å) on a Bruker D8 Advance X-ray diffractometer. The Rietveld refinement of the data was done using FULLPROF program, assuming pseudo-Voigt profile for the peaks. The microstructure of the polished and thermally etched pellets was studied using scanning electron microscopy. The densities of the sintered pellets were determined by mass and volume measurements.

The pellet surfaces were fine polished with emery paper to make their faces flat and parallel. The low temperature dielectric measurements of the silver coated pellets were done using a NOVOCONTROL Alpha high-resolution dielectric analyzer (Alpha-S) in the temperature range 80 - 300 K and the frequency
range 1–10⁷ Hz. The complex impedance \( Z^* \) of the sample was then converted in to complex permittivity using the equation,

\[
\varepsilon^* = \varepsilon' - j\varepsilon'' = \frac{1}{j\omega C_0 \varepsilon'},
\]

In this equation \( \varepsilon' \), \( \varepsilon'' \) and \( \omega \) have their usual meaning and \( C_0 = \frac{\varepsilon_0 A}{d} \) is the empty cell capacitance, where \( A \) is the sample area and \( d \) is the sample thickness.

### 3. Results and discussion

![Figure 1. X- Rietveld refined XRD profiles of Sm\(_{2/3}\)Cu\(_3\)Ti\(_4\)O\(_{12}\)](image)

Structural refinement of the XRD data was carried out using the Rietveld’s refinement program ‘Full Prof’ and the refined profile is shown in Figure 1. Refined profile shows that the sample is mono-phased and the difference between the observed and calculated intensities is negligible. From structural refinement it is confirmed that SCTO ceramics belongs to cubic structure with space group \( I\bar{m}3 \) at room temperature. The refinement resulted satisfactory agreement factors and lattice parameters which are listed in Table 1. Refined lattice parameter, 7.3923 Å, is in conformity with the value, 7.394 Å, reported earlier.
Figure 2. SEM micrograph of the polished surface of Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramic.

Figure 2 shows the surface morphology of the polished and thermally etched SCTO sample. The sample is characterized by a dense microstructure of small and uniformly distributed grains with average grain size of 2-4 $\mu$m. A significant decrease in the grain size is observed on substituting A-site by Sm than that of pure CCTO sintered at 1100 °C (50-60 $\mu$m)\(^3\). Lower porosity and more uniform grain resulted in the formation of a dense ceramics with relative density value calculated to be within 94.9% of the theoretical value.

Figure 3. Frequency dependence of (a) dielectric constants $\varepsilon'$ for Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramic in the temperature range (90-295 K)

Variation of real part of dielectric constant $\varepsilon'$ as a function of frequency for SCTO samples at different temperature (90-290 K) is shown in Figure 3. It is clear from Figure 3 that below 200 K the dielectric
constant is considerably high and its variation is strictly in accordance with the typical Maxwell-Wagner relaxation process reported in ACu$_3$Ti$_4$O$_{12}$ ceramics$^5$. It has been found that Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramic shows giant dielectric permittivity values with low frequency larger than 30,000 at room temperature, which is much higher than that reported by Subramanian et al$^1$. It is clear from Figure 3, that an additional relaxation is observed in the low frequency region (below 100 kHz) when the temperature is increased beyond 200 K. The magnitude of the low frequency plateau of ($\sim 10^5$) is approximately one order greater than that of the intermediate frequency plateau ($\sim 10^4$). This type of an additional low frequency plateau, reported in CCTO ceramics with relatively low (grain boundary resistivity) values had been attributed to electrode polarisation$^{18}$.

![Figure 4. Temperature dependence of $\varepsilon'$ at different selected frequencies.](image1)

![Figure 5. Effect of dc bias on the $C'$ spectroscopic plot of Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramic at 300 K](image2)
The temperature dependence of dielectric constant at selected frequency values is shown in Figure 4, which shows the bulk contribution to dielectric constant at low temperature and the grain boundary contribution at higher temperature, which is in accordance with the IBLC model. To check the polarisation at the sample –electrode interface, a dc voltage is superimposed with the applied ac signal. The effect of dc bias on the dielectric properties of the sample at room temperature is shown graphically in Figure 5. With increasing dc bias the capacitance value steadily decreases in the low frequency region and remains almost unaltered in the intermediate and high frequency regions. Since $R_e \gg R_{DB}$, dc bias drops almost totally across the electrode/sample interface resulting in the decrease of $R_e$ (resistivity of the electrode sample interface) with increasing voltage. This result confirms the existence of a Schottky barrier at the sample electrode interfaces and an electrode effect in the low frequency response.

Figure 6. Variation of $\varepsilon'$ with frequency in the temperature range (90-295 K)

Figure 7. Arrhenius plots of relaxation frequency ($f$) data for Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics
The values of $f$, the relaxation frequency at any temperature obey Arrhenius law $f = f_0 \exp (-E_a / k_B T)$, where $f_0$ is the relaxation frequency at infinitely high temperature, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $E_a$ is the activation energy. The values of $f$ corresponding to the relaxation peak frequencies in Figure 6 due to the grains when fitted using Arrhenius law (Figure. 7) resulted in an activation energy, $E_a = 0.06$ eV. This value is comparable to reported value of the activation energy for relaxation due to grains in CCTO.

4. Conclusion

A compositionally and structurally CaCu$_3$Ti$_4$O$_{12}$-like oxide, Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics were prepared and investigated to obtain a systematical understanding about the dielectric behaviours and the underlying related mechanism. A single phase Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics with a cubic crystal structure in space group Im$ar{3}$ is obtained by solid-state reaction. A high density and fine grained microstructure is obtained for the Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramic. Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ ceramics sintered at 1100°C for 24 h exhibited a giant dielectric constant (30,000) around room temperature. The colossal dielectric constant Sm$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ was explained based on Maxwell-Wagner type contribution of depletion layers between the sample –electrode interface and at the grain boundaries.

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