Improved dielectric properties of Na$_{1/2}$Y$_{1/2}$Cu$_3$Ti$_4$O$_{12}$ ceramics synthesized by ball-milling and reactive sintering

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Abstract

Na$_{1/2}$Y$_{1/2}$Cu$_3$Ti$_4$O$_{12}$ (NYCTO) ceramics with giant dielectric constant ($\varepsilon'$) were synthesized by simple reactive sintering. NYCTO nanopowder was first synthesized using high energy ball-mill. Then the pelletized powder was sintered in air at temperatures in the range 975 °C to 1050 °C for 10–20 h. The obtained ceramics showed pure CaCu$_3$Ti$_4$O$_{12}$ (CCTO)-like cubic phase as revealed by x-ray diffraction measurements. Field effect-SEM observations showed that the grain size increases from 2 μm to 5 μm with increasing sintering temperature. NYCTO samples sintered at temperatures higher than 975 °C showed giant dielectric constant (10$^3$–10$^4$) over most of the frequency range. The minimum dielectric loss (tanδ) of ~0.055 at 300 K has been approved for the ceramic sample sintered at 1050 °C. Impedance and modulus spectra of the current samples showed two relaxations related to semiconductor (grain) and high resistance (grain-boundaries) elements. The activation energy for conduction located in the range 0.1–0.5 eV highlighted the role of single ionized oxygen vacancies in the dielectric properties of the investigated NYCTO ceramics.

1. Introduction

CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has interesting dielectric properties in terms of giant dielectric constant (10$^3$–10$^4$) that is temperature and frequency independent over large temperature and frequency range [1, 2]. Nevertheless, most of studies on CCTO ceramics have reported room-temperature dielectric loss which is higher than the necessary for practical applications (tanδ < 0.05) [2–4]. Numerous possible sources for the unique dielectric properties of CCTO have been proposed and reported such as lattice vibrations, permanent dipoles, defects, charge polarization at grain/grain-boundaries and electrode polarization effect [5–8]. However, the internal barrier layer capacitance (IBLC) is the most widely accepted model [9]. According to this model, the apparent giant dielectric constant arises due to the Maxwell-Wagner polarization effects at internal resistive boundaries such as grain-boundaries and/or domain-boundaries. Recently, a great deal of studies on the effects of doping, powder synthesis and sintering techniques on the dielectric properties of CCTO has been carried out [2–4, 10–16]. Most of these studies used the solid state reaction (SSR) technique for the fabrication of ceramics. However, SSR has the disadvantages of being long process including several steps of calcination and sintering at high temperature (1050 °C–1110 °C). Moreover, SSR usually result in chemical composition inhomogeneity and overgrowth of the grain size (20 μm–50 μm) for the final ceramic product. Several studies aimed to replace SSR by lower temperature fabrication process without scarifying the giant dielectric properties of the ceramic. One strategy is to use rapid sintering techniques such as spark plasma sintering (SPS) [11, 17] and microwave sintering [18]. Another strategy is to use sol-gel process to prepare the precursor powder with nano-metric size which reduce the calcination and sintering temperature to prepare the dense ceramics [19]. In the present work we explore the structural and dielectric properties of Na$_{1/2}$Y$_{1/2}$Cu$_3$Ti$_4$O$_{12}$ (NYCTO) ceramics prepared by mechano-synthesis using high energy ball mill and conventional sintering. Na$_{1/2}$Y$_{1/2}$Cu$_3$Ti$_4$O$_{12}$ NYCTO ceramics prepared by standard SSR technique are reported to have giant dielectric constant but high dielectric loss [20, 21]. Somphan
used SSR process comprising two calcination steps at 950 °C for 15 h and 1000 °C for 10 h followed by conventional sintering at 1090 °C for 5 h. Resulting ceramics showed \( \varepsilon' \sim 2 \times 10^4 \) and \( \tan\delta \sim 0.112 \) at room temperature and 1 kHz. In the study of Liang et al [21], NYCTO ceramics prepared using calcination and sintering temperature in the range 910 °C–950 °C (15 h) and sintering 1050 °C–1080 °C (10–30 h), showed \( \varepsilon' \sim 10^3–10^4 \) and \( \tan\delta \sim > 0.2 \) at room temperature and 1 kHz [21]. In our previous work we prepared ceramics using mechanosynthesis and SPS for 10 min at temperatures in the range 900 °C–1000 °C [22]. Though all the samples showed giant dielectric constant \( (\varepsilon' = 10^3–10^4) \) at room temperature and 1.1 kHz, they showed high dielectric loss (\( \tan\delta > 3 \)). In the present work, the mechanosynthesis conditions were chosen to have nanopowder of the studied material. Then, the pelletized powder had been directly sintered in tubular furnace in air at temperatures in the range 975 °C–1150 °C. The dielectric properties of the prepared ceramics have been studied in wide range of frequencies (1 Hz–40 MHz) and temperatures (120 K–450 K).

2. Experiment

Synthesis of NYCTO powder was carried out by mechanochemical milling Fritsch P-7 premium line machine using stoichiometric amounts of high-purity Na₂CO₃, Y₂O₃, CuO and TiO₂. Details of the powder preparation process can be found elsewhere [22]. The XRD pattern of the as-prepared NYCTO powder confirmed the onset formation of the CCTO-like phase, i.e. body centered cubic structure [22]. Then, pelletized powder was sintered in air at 975 °C, 1000 °C, 1025 °C and 1050 °C for 10 h with the heating rate of 4 °C min⁻¹. An additional sample was prepared by sintering in air at 1050 °C for 20 h. The prepared samples are referred to as S975, S1000, S1025, S1050 and S1050–20h. The micro-structural characterization of the samples were carried out using field emission scanning electron microscope (FE-SEM) (Joel, SM7600F) technique. X-ray diffraction (XRD) data were collected over the 10° ≤ 2θ ≤ 90° range using a Bruker D8 Advance x-ray powder diffractometer, with CuKα-radiation. Impedance spectroscopy (IS) measurements were performed by the turnkey concept 50 system from Novocontrol over the 1 Hz–40 MHz frequency range. IS measurements were performed in dry nitrogen atmosphere in the 120–500 K temperature range, where the temperature was controlled by the Quatro Cryosystem. Sputtered gold electrodes were used for electrical measurements.

3. Results and discussion

Figure 1 depicts the XRD patterns of the current NYCTO ceramics. The main diffraction peaks for each sample are similar to that reported for CCTO (JCPDS card # 75–2188) with no evidence for secondary phases. The lattice parameter for the present ceramics was estimated using the least-square method and found to be 7.320 Å, 7.314 Å and 7.310 Å for the ceramics S975, S1025 and S1050, respectively, which is slightly smaller than the pure NYCTO prepared by SSR [20, 21].
The microstructure of the current ceramics is shown in figure 2. The sample S975 is seen to have porous microstructure with the smallest grain size of about ∼2 μm. The porosity of the samples decreased while the grain size increased with increasing the sintering temperature to reach ∼5 μm for the ceramics S1050 and S1050–20h. It is worthy to note that grain sizes of the current samples are considerably smaller than those reported for NYCTO ceramics prepared by standard solid state reaction (20–40 μm) [20, 21].

Figures 3(a)–(c) depicts the frequency dependence of ε′, tanδ and the conductivity (σ′) at room temperature for the current NYCTO ceramics. It can be seen in figures 3(a), (b) that NYCTO samples which were sintered at temperatures above 975 °C showed giant dielectric constant (103–104) over most of the frequency range. The S975 sample showed a lower dielectric constant and higher electrical resistivity than other samples. At 300 K, the S1050 sample showed the lowest tanδ of ∼0.055 which is considerably lower than the reported values for the NYCTO prepared by SSR [20, 21]. This result is thought to be related to the lower grain size of the current samples compared to those of SSR technique as evidenced by SEM measurements. The lower grain size may
result in more grain boundaries encountered by charge carriers in the sample which reduce the dielectric loss. Extending the sintering time at 1050 °C did not show significant effect on the dielectric properties where both of S1050 and S1050–20h samples showed nearly the same characteristics. Therefore, in the following we will focus only on the electrical and dielectric properties of S1025 and S1050 samples, which offered the best compromise of having high dielectric constant and low dielectric loss. Figures 4 and 5 depict the frequency dependencies of $\varepsilon'$ and $\tan \delta$ for the ceramics S1025 and S1050, respectively, at selected temperatures. Both of the samples showed step-like decrease in $\varepsilon'$ accompanied by a clear relaxation peak in the spectra of $\tan \delta$. The frequency corresponding to the maximum peak of $\tan \delta$ exhibited thermally activated behaviour where it shifts to higher frequencies with increasing temperature. It is worthy to note that at
comparatively higher temperatures (>240 K), $\tan \delta$ increases monotonically with decreasing frequency in the low frequency range which might be due to the increase of conductivity.

For a better understanding of the dielectric relaxation of the current ceramics the frequency dependence of imaginary parts of impedance $-Z''$ and modulus $M''$ are shown in figure 6. Both samples show two peaks in the spectra of $-Z''$ accompanied by two peaks in the spectra of $M''$. The height of the low frequency peak ($R_{LF}$) of $-Z''$ is about five orders of magnitude higher than its value for the high frequency peak ($R_{HF}$). It is worthy to remind that the height of $M''$ peak is inversely proportional to the capacitance $C$ as ($M''/\varepsilon_0 = 1/2C$) [23] where $\varepsilon_0$ is the permittivity of free space ($\varepsilon_0 = 8.854 \times 10^{-14} \text{ F cm}^{-1}$). It is seen that the capacitance of the LF peak of the $M''$ spectrum is considerably higher than that of the HF peak for both samples. These results then suggest that the prepared ceramics have an electrically inhomogeneous structure of semi-conductive grains surrounded by resistive grain-boundaries. Figure 7 shows the complex impedance plan for the investigated samples at 250 K. The inset of figure 7 shows an expanded view of the high frequency region of the complex plan plots. It is clearly seen that each impedance spectrum comprises two semicircular arcs coming from two entities with different electrical properties. It is widely accepted that the arc at high frequency and low temperature is typically attributed for the grain response while that at low frequency and high temperature is due to the electrical response of the grain-boundaries. This electrical behavior is comparable to previous reports on CCTO and its derived ceramics and fits to an equivalent circuit of two elements ($R_g||C_g$) and ($R_{gb,0,0}||C_{gb,0,0}$) connected in series.
Thus, the LF and HF relaxation peaks of both spectra of $M''$ and $-Z''$ are attributed to the responses of the grain-boundaries and grain responses, respectively.

Figures 8(a), (b) shows the evolution of the spectra of $-Z''$ with temperature for S1025 and S1050 ceramics, respectively. For both ceramics, the peak-maximum decreases and shifts towards high frequency range as the temperature increases. Considering the inter barrier layer capacitance (IBLC) which is based on the electrical heterogeneity of ceramics, the frequency dependence of $-Z''$ is given as [24]:

$$-Z''(\omega) = R_g \left[ \frac{\omega R_g C_g}{1 + (\omega R_g C_g)^2} \right] + R_{g,b} \left[ \frac{\omega R_{g,b} C_{g,b}}{1 + (\omega R_{g,b} C_{g,b})^2} \right]$$

(1)

Here $\omega$ is the angular frequency. For the case $R_g \ll R_{g,b}$, the grain-boundary resistance can be calculated as $R_{g,b} = -2Z''_{\text{max}}$ where $Z''_{\text{max}}$ is the value of $Z''$ peak maximum at low frequency. As shown in figure 8(c), the temperature dependency of the conductivity of grain and grain-boundaries followed the Arrhenius law:

$$\sigma = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right)$$

(2)

Here $\sigma_0$ is the pre-exponential factor, $k_B$ is Boltzmann constant and $E_a$ is the activation energy for conduction. The calculated values for the room temperature resistivity and the activation energy of conduction in grains and grain-boundaries were given in table 1. The values of activation energy are close to the widely reported values for the singly ionized oxygen vacancies which are in the range 0.1–0.5 eV [25, 26].

Figure 7. Complex impedance plan plots at 250 k for S1025 and S1050 ceramics.

Figure 8. Spectra of $Z''$ at selected temperatures for the (a) S1025 and (b) S1050 ceramics; insets show Arrhenius plots of grain and grain-boundaries for each sample.
Figure 9 depicts the dependence of ac conductivity \( \sigma' \) on frequency at selected temperatures for the S1025 and S1050 ceramics. The conductivity spectra shifted to higher values with increasing measuring temperature. Moreover, a plateau at low frequencies appears at comparatively high temperatures, which represents the dc conductivity of the sample at the measuring temperature. This behaviour is consistent with the dielectric universal law \[ (3) \] where \( \sigma_{dc} \) is the dc conductivity and \( s (0 < s < 1) \) is a constant.

The activation energy for DC conduction was found to be 0.52 and 0.58 eV for S1025 and S1050, respectively. These values are close to both of the conduction activation energy in grain-boundaries and the activation energy of single ionized oxygen vacancies. Figure 10 depicts the evolution of \( M'' \) spectra with increasing temperature.

It is known that the mean value of the relaxation time, \( \tau \), is related to the frequency of \( M'' \) peak as \[ \tau = \frac{1}{2\pi f_{\text{max}}} \] where \( \tau_0 \) is the pre-exponential factor, \( E_R \) is the activation energy for the relaxation process, and \( k_B \) is the Boltzmann constant. The calculated values of \( E_R \) are included in Table 1. The ensemble of the activation energy

Table 1. Room temperature resistivity \( \rho (\Omega \cdot \text{cm}) \) and activation energy for conduction \( E_g (\text{eV}) \) and for relaxation \( E_R (\text{eV}) \) for NYCTO ceramics.

| Sample   | \( \rho_g \) | \( \rho_{gb} \) | \( E_g \) | \( E_{gb} \) | \( E_{HF} \) | \( E_{RHF} \) |
|----------|--------------|----------------|---------|-------------|-------------|-------------|
| S1025    | 895          | \( 6.7 \times 10^7 \) | 0.183   | 0.516       | 0.148       | 0.489       |
| S1050    | 238          | \( 4 \times 10^7 \)   | 0.147   | 0.546       | 0.115       | 0.462       |

Figure 9. The frequency dependence of ac conductivity for NYCTO ceramics.

Figure 10. Spectra of \( M'' \) at selected temperatures for the (a) S1025 and (b) S1050 ceramics; insets show Arrhenius plots of grain and grain-boundaries for each sample.
values for relaxation and conduction are very close which may signifies that the same entities are responsible for the two processes. Besides, these activation energies locate in the range of single ionized oxygen vacancies.

4. Conclusions

\( \text{Na}_{1.2}\text{Y}_{1/2}\text{Cu}_{3}\text{Ti}_{4}\text{O}_{12} \) (NYCTO) ceramics were prepared by simple reactive sintering based on the mechanosynthesis of the powder using ball-milling and conventional sintering at temperatures in the range 975 °C to 1050 °C for 10–20 h. The prepared ceramics showed CCTO-like cubic phase with an average grain size in the range 2–5 \( \mu \text{m} \) which is lower than NYCTO ceramics prepared by standard solid state reaction (SSR) (>20 \( \mu \text{m} \)). Moreover, NYCTO ceramics sintered at temperatures higher than 975 °C showed giant dielectric constant (\( \varepsilon' > 10^3 \)) at 300 K and 10 kHz. A minimum dielectric loss (\( \text{tan}\delta \sim 0.055 \)) was obtained for the ceramics sintered at 1050 °C. Impedance spectroscopy analysis revealed an electrically heterogeneous structure for the investigated ceramics. Two types of dielectric relaxations were identified using the impedance and modulus formalisms as responses of the grains and grains-boundaries interfaces. The activation energy for conduction located in the range 0.1–0.5 eV highlighted the role of single ionized oxygen vacancies in the dielectric properties of the investigated NYCTO ceramics.

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