CHAPTER 4

EFFECT OF PREPARING CONDITIONS ON THE DIELECTRIC PROPERTIES OF CaCu₃Ti₄O₁₂ CERAMICS

4.1. Introduction

The perovskite-type compound CaCu₃Ti₄O₁₂ (CCTO), was first discovered by Subramanian et al. [12]. Its extraordinary dielectric constant is almost temperature independent from 200 K to 400 K, with low frequency dielectric constant of CCTO which can be as high as 95,000 in the single crystal form, and 12,000 in the sintered pellets [12,44]. For the ceramic [12] and thin-film [43] samples at room temperature, the typical value of tan δ is about 0.2 at 10 kHz. The CCTO has various advantages as capacitive elements in microelectronic devices over other ferroelectric materials including BaTiO₃ [17]. This titanate oxide crystallizes in a cubic structure with Im3 space group. The TiO₆ octahedra are tilted, resulting in the doubling of the perovskitelike lattice parameter and involves a square planar arrangement of the oxygen around the Cu²⁺ cations [44].

The high dielectric constant of CCTO can then be understood based on a barrier layer mechanism. This is a well-known mechanism for titanates processed in such a way as to produce grains that are reduced and conducting when coupled with grain boundaries with much less conduction [12]. The CCTO has an electrically heterogeneous structure involving mobile charged species in terms of the MaxwellWagner relaxation [23], and the internal interfaces in polycrystalline CCTO give rise to the polarization in semiconducting grains and insulating grain boundaries based on the internal barrier layer capacitor (IBLC) model [28,21].

The phase stability of CCTO was examined by controlling various preparing conditions, there we used ball milling and vibratory milling techniques. Characterization of the samples was carried out using x-ray diffraction (XRD) and scanning electron microscopy (SEM). Other properties such as, density, dielectric constant and loss angle were intensively studied.

4.2. Experimental procedure

The CaCu₃Ti₄O₁₂ (CCTO) powder was prepared by the mixed-oxide route. High purity (> 99.9%) CaCO₃ (Riedel-de Haen), TiO₂ (Riedel-de Haen) and CuO (Aldrich) powders were weighed in the desired ratio. The first samples were mixed by ball milling for 24 h using yttria-stabilized zirconia balls in ethanol media. The second samples were mixed together and milled using a vibratory mill for 6 h. After being dried, the powders were calcined at 900°C for 2 h to form the CCTO powders. The distribution of the particles was observed using a particle analyzer (Malvern Instruments Limited Mastersizer S). The calcined powder was granulated using polyvinyl alcohol (PVA) 3% binder and formed under a uniaxial pressure of 1500 kg/cm² into discs, typically 12 mm in diameter and 2 mm in thickness. The discs were sintered in air at 1000 - 1100°C in a step size of 50°C (with soaking time of 4 h). The ramping and the cooling rates were 300° C/h. The polished CCTO pellets under the different mixing conditions were examined via an X-ray diffractometer (Bruker D8 Discover) for their phase evolution. The crystallite sizes and the strain of the powders prepared through both methods were calculated using the Scherrer equation and the formula derived from Bragg's equation, respectively. Density of the polished CCTO samples was measured by using the Archimedes method. Silver paste was used as the electrical contact. The painted samples were dried at 750 °C for 20 minutes, and the dielectric constant and the loss tangent were measured in terms of the frequency (f = $10^2 - 10^6$ Hz) with an Agilent 4284A LCR meter at room temperature. Microstructure of the polished ceramics and the calcined powders were studied using SEM (JEOL JSM-5910LV). The impedance spectroscopy measurements of the ceramics prepared via ball milling and vibro-milling were made at 500 kHz to 1 MHz (HP 4194A impedance analyzer).

4.3. Results and discussion

Figure 4.1 shows the X-ray diffraction patterns for the CCTO ceramic samples with prepared by ball milling and vibro-milling techniques at various temperatures (1000-1100°C). The XRD peaks obtained here are in agreement with that obtained by Yang *et al.* [58] and Brize et al [59]. All peaks can be matched exactly with the data in the Inorganic Crystal Structure Database (ICSD) file No.032002, which is according to the file. The density and lattice parameter (a) of CCTO are 5.053 g/cm³ and 7.371 Å respectively. The lattice constants and the densities of the ceramics of various conditions were determined and tabulated in Table 4.1.



Figure 4.1 XRD patterns of CCTO polished surface ceramics with two different milling methods and sintered at different temperatures. Sample A: Ball milling, sintered at 1000°C, B: Ball milling, sintered at 1050°C, C: Ball milling, sintered at 1100°C, D: Vibromilling, sintered at 1050°C, E: Vibro-milling, sintered at 1050°C, F: Vibro-milling, sintered at 1100°C.

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| Sintering | | Den | Lattice | Average grain |
|------------------|------|-----------|-------------------|---------------|
| temperature (°C) | | sity* (%) | parameter (a (Å)) | size (µm) |
| 2 | 1000 | 94.05 | 7.391 | 17 |
| Ba Il milling | 1050 | 95.97 | 7.391 | 18 |
| 22 | 1100 | 98.63 | 7.391 | 19 |
| Vi | 1000 | 92.85 | 7.391 | 5558 |
| bro-milling | 1050 | 93.94 | 7.391 | 9 |
| E | 1100 | 96.76 | 7.391 | 12 |

Table1 4.1 Relative density, lattice parameter (a) and average grain size of the prepared

CCTO ceramics at various conditions.

The lattice constants of all CCTO ceramic samples were obtained by the least-squares fit method, which have a very close value to that of the lattice parameter of CCTO recorded in ICSD No.032002 data. The density results of the sintered ceramics increased with increasing sintered temperature. The maximum density values of the samples prepared via ball milling and vibro-milling techniques, both sintered at 1100°C were 98.63% and 96.76% of the theoretical density recorded in ICSD data, respectively. This means that the milling technique has insignificant effect on the densification of the sintered CCTO at 1100 °C.



Figure 4.2 The particle distribution of the calcined CCTO powders prepared via ball-milling (A) and vibro-milling (B) techniques.

Figure 4.2 displays distribution of the CCTO particles prepared from ballmilling and vibro-milling methods. It can be seen that the particle sizes prepared via ball-milling are separated into 2 modes with the average sizes of 5 μ m and 50 μ m, (overall average value is 12.5 μ m) while that obtained from vibro-milling revealed only 1 mode with the average size of approximately 3 μ m. This confirms the better results of both particle distribution and small size of the vibro-milling assisted method for ceramic powder preparation.







Figure 4.3. Temperature dependence of the dielectric constant and loss tangent for CCTO samples, sintered at 1100°C/4h. A and B represent the samples prepared by ball milling technique while C and D prepared by vibro-milling technique at various frequencies.

The strain and the crystallite size of the calcined powders prepared through both methods (at 900°C) were calculated. The results show that the crystallite size and the strain of the calcined powders are 46 nm and 0.011 prepared via ball-milling and 48 nm and 0.0125 prepared via vibro-milling, respectively. It can be also seen that the powder obtained from the vibro-milling method yields smaller crystallite size. Thus, it is expected that the particle size of powder and grain size of the ceramic prepared by the vibro-milled powder could be finer than that obtained from ball-milling method (in Figure 4.4).

Figure 4.3 shows the dielectric constant and dielectric loss of CCTO which prepared by ball milling and vibro-milling techniques and sintered at 1100°C for 4h, against the temperature ranging from room temperature to 120°C in the frequency range of 1-500 kHz. As can be seen, at the room temperature and at the frequency of 10 kHz, the dielectric constant (ε_r) of the ball-milled sample is 9100, against 32,000 of the vibro-milled samples while their dielectric loss (tan δ) values are almost the same (~0.05) at room temperature to 70°C. At higher frequencies, the dielectric constants of the vibro-milled samples still show higher values than that of the ballmilled samples. Moreover, the dielectric loss increased but still remained lower than 0.5 in a range of room temperature to

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Figure 4.4 SEM pictures of CCTO powders calcined at 900°C for 2 h(A: prepared by ball milling technique, B: prepared by vibro-milling technique) and the crack surfaces of CCTO ceramics sintered at 1100°C for 4 h (C: prepared by ball milling technique, D: prepared by vibro-milling technique).

Figure 4.4 shows the SEM pictures of powders calcined at 900°C and the crack surface of CCTO samples sintered at 1100°C. As can be seen, the average size of the ball-milled powder, about 10 µm (Figure 4.4A) is larger than that obtained from the vibro-milled powders, about 2.0 µm (Figure 4.4B). These results are closely similar to that obtained from the particle size analysis (Figure 4.2). The average grain size of the CCTO the ball-milled ceramic (Figure 4.4C) are particularly larger (20µm) than that of the vibro-milled sample which has smaller grain size of $\sim 12 \,\mu m$ (Figure 4.4D). It often is the case that the distance between grains (from vibro-milled ceramics may be narrower than that of larger grain size in the ball-milled ceramic. The details of the grain size are shown in Table 4.1. The idea of the conductivity of the sample is prevented to percolate by the presence of insulating blocking layers at the surfaces or at internal domain boundaries. The insulating layers are thought to cause internal boundary layer capacitance (IBLC). Based on these possibilities, the higher grain boundary resistance (R_{gb}) could play major role to enhance the dielectric constant. The different morphological models were proposed to explain the unusual dielectric behaviour [60]. The IBLC model was recently supported by different observations of defects inside both single crystals [61] and grains of polycrystalline CCTO [62,63] and by complex impedance spectroscopy measurements on a CCTO crystal [64]. The dielectric properties of CCTO ceramics are very sensitive to processing parameters. Values between 500 and 20000 are usually reported [65,66]. In this work, the impedance plot of the CCTO samples prepared from both ballmilling and vibro-milling methods are revealed in Figure 4.5.



Figure 4.5 The impedance plots of the CCTO ceramics prepared via ballmilling and vibro-milling at 500 kHz to 1 MHz.

The inset is the plot of the impedance of CCTO. It can be seen that by extrapolation the resistance of the grain boundaries (R_{gb}) are 26 k Ω and 43 k Ω for the ball-milled and vibro-milled samples respectively. Based on the R_{gb} values in this experiment, the CCTO ceramics prepared by vibro-milling technique, with smaller average grain size, have both dielectric constant and dielectric loss more than that obtained from the ball-milled CCTO samples.

4.4. Conclusions

In conclusion, CCTO ceramics were prepared by vibro-milling technique, which sintered at 1100° C for 4h. The results show that the vibro-milled CCTO ceramics have excellent dielectric constant even at higher frequency (10 - 100 kHz) while the dielectric loss is still under 0.1 at temperature not over 100° C. In constrast to the CCTO ceramics prepared by ball-milling technique, sintered at 1100° C for 4h, the dielectric constant is much lower within the same temperature range. Therefore, CCTO ceramics prepared via vibro-milling technique are considered to be a promising candidate for high capacitance density applications, especially in the frequency range of 10-100 kHz.

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