

Effect of excess TiO_2 in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ on the microstructure and dielectric properties

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Dielectric material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) was prepared by a solid state technique. CaCO_3 , TiO_2 and CuO powders were mixed thoroughly in a ball mill for one hour. The reagent ratios were modified for TiO_2 contents (2–6 mol). The mixed powder were calcined at 900 °C for 12 hours and sintered at 1040 °C for 10 hours. The sintered samples were subjected to XRD phase analysis. The microstructures of sintered pellets were observed by SEM. The effects of TiO_2 content on the phase formation, density, microstructure and dielectric properties are reported. XRD results show that the different phase formation depends on the TiO_2 content. Increasing the TiO_2 content reduces the density. At the surface regions, clear grain boundaries and a dense microstructure were observed. The results show that a sample sintered at 1040 °C for 10 hours give a clearly uniform grain size with the highest dielectric constant (33, 210). The degree of nonstoichiometry of TiO_2 influenced the dielectric properties by reducing its dissipation factor.

Key words: TiO_2 Content, Microstructure, Dielectric, CCTO.

Introductions

Recently, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) was discovered to possess one of the largest static dielectric constant ever measured, reaching nearly $\epsilon_r \sim 80\,000$ for single crystal samples and 10,000 for bulk material at room temperature [1, 2, 3]. The higher the dielectric constant, the more charge it can store, and thus smaller electronic circuits can be designed. In addition, unlike most dielectric materials, CCTO retains its enormously high dielectric constant over a wide range of temperatures, from 100 to 600 K, or -173 to 327 °C, making it ideal for a wide range of applications [4, 5]. But the real explanations of the phenomena are still investigated.

Although having these unique properties, there was a limitation with CCTO, i.e. the dissipation factor is quite high (0.2–1.0). A low dissipation factor value was needed in microelectronic applications because the heat generated from a high tangent loss property will restrict its function. Lately, a few studies were made in order to investigate the effect of dopant elements to repair CCTO properties. Some of them have reported that CCTO doped with other elements can change the dielectric properties. A few approaches were done in order to reduce the dissipation factor, such as doping with other elements and controlling the processing parameters [6].

This study will highlight the reduction of the dissipation factor in CCTO by only varying its components stoichiometric, not by adding any dopants. The raw materials used for producing CCTO electroceramic are CaCO_3 , CuO and

TiO_2 . The effect of raw material contents might be one of the reasons why CCTO possess such properties has been argued among the researchers. Shao *et al.*, 2007 have reported that varying the CuO contents can influence the CCTO properties [7]. So, in this paper, we want to highlight the effect of another raw material, i.e. TiO_2 on CCTO formation. There are some reports on how TiO_2 can effect the properties of other electroceramics [8, 9, 10, 11, 12].

Experimental

CCTO samples were prepared by a conventional solid state method. High purity CaCO_3 (Aldrich, 99%), TiO_2 (Merck, 99%) and CuO (Aldrich, 99%) were used as starting materials. A stoichiometric and non-stoichiometric (2–6 mol of TiO_2) of the reagents were mechanically ball milled for 1 hour using zirconia balls. The samples were coded according to the content of TiO_2 . A powder exhibiting free flowing characteristics was then obtained by sieving the dried milled powders. The powders were calcined in air at 900 °C for 12 hours. Cylindrical specimens 5 mm in diameter and approximately 0.5–1 mm thick were pressed. The green pellets were sintered in air at 1040 °C for 10 hours, with a heating rate of $5^\circ\text{C}/\text{minute}^{-1}$, followed by the XRD analysis. Bulk density measurements were made using the Archimedes method. The microstructures were investigated on the surface of the sintered specimens using SEM (Zeiss SUPRA 35VP). The samples for measuring the dielectric constant were polished to ensure surface flatness and then painted with silver paste on both surfaces as electrodes. The measurement was done at room temperature by a Hewlett-Packard 4912 impedance spectrometer at a frequency range of 1 Hz to 10 GHz.

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Results and Discussion

Fig. 1 shows the result of XRD analysis for the CCTO sintered samples with different TiO_2 contents. The results were divided into two sections. The first figure (Fig. 1(a)) shows the arrangement of 2 M, 3 M and 3.3 M results. Its reveals that there was a raw material phase i.e. CuO and CaCO_3 that has not fully reacted to form a CCTO compound. This was caused by the smaller TiO_2 content in order to form a CCTO single phase. The second part of the Fig. 1(b) shows the results from 4 M, 4.3 M, 4.5 M, 5 M and 6 M samples. A single phase of CCTO was obtained with the stoichiometric ratios of reagents. As the amount of TiO_2 increased, the excess of TiO_2 content also increased (Fig. 1(b)). But the TiO_2 excess did not form other phases. The peaks from TiO_2 become higher with an increase of the TiO_2 content.

Fig. 2 shows the density result for all the samples. The density was decreased with the addition of TiO_2 . This was due to the low density of TiO_2 (3.90 g/cm^3). A drop off in density value with an increase of TiO_2 addition in other electroceramic systems was also reported by Zhang *et al.*, 2001 [8]. Overall, the porosity value was very low, mostly below than 1%.

Fig. 3 displays the surface observation for all the samples by SEM. The grain shape and boundaries were clearly seen for all the samples. By surface observations, no pores were noticed visually, due to the close packed grains. The grains become bigger with an enhancement of the TiO_2 content, up to 4.3 M sample. Addition of more than 4.3 mol TiO_2 reduces the grain size. The grain sizes for the 5 M and 6 M were smaller than the others. The 4.3 M sample

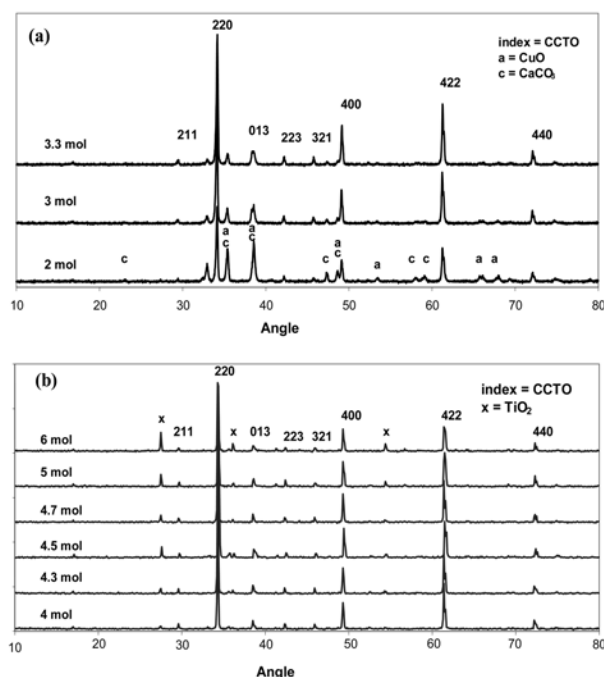


Fig. 1. XRD analysis for sintered samples with different TiO_2 content (a) 2-3.3 mol and (b) 4-6 mol.

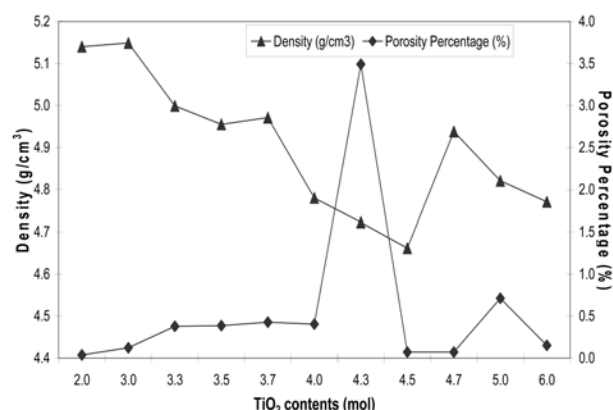


Fig. 2. The density and porosity percentage for different TiO_2 contents of CCTO samples.

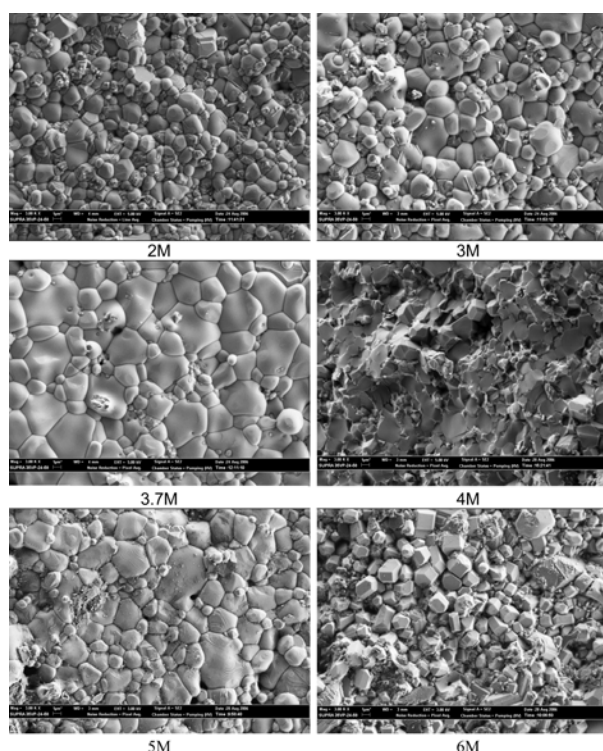


Fig. 3. The surface microstructures of CCTO samples with different TiO_2 contents.

shows the phenomena of melting and abnormal grain growth. Tsunooka *et al.*, 2003 [10] in their research about the effect of different amounts of TiO_2 in the forsterite system states that the increase of the TiO_2 content influenced the grain size. They reported that the addition of TiO_2 up to 5 wt% increased the grain size but adding TiO_2 more than that will reduce the grain size. The same trend was also reported by other researchers [12]. An excess of TiO_2 cannot be observed in SEM images. Fritsh *et al.*, 2006 [13] also reported that SEM cannot differentiate the CCTO and other phases formed because the grain formation was homogenous in size and shape.

Fig. 4 illustrates the dielectric constant and dissipation factor for all CCTO samples. The dielectric constant for samples 2 M to 3.7 M only show a slightly constant value

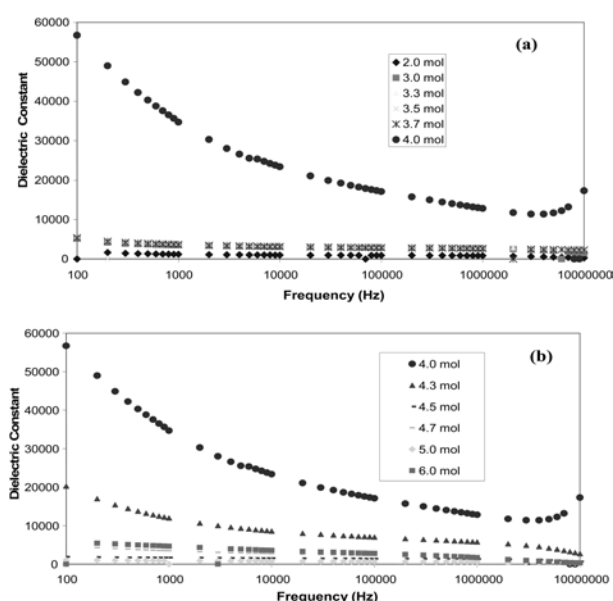


Fig. 4. The dielectric constant for CCTO samples with different TiO₂ contents (a) 2 M-4.0 M and (b) 4 M-6.0 M.

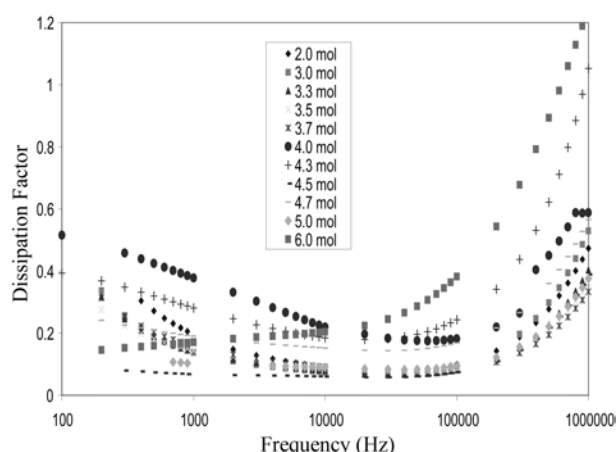


Fig. 5. The dissipation factor for CCTO samples with different TiO₂ contents (a) 2 M-4.0 M and (b) 4 M-6.0 M.

with the frequency. And the values are quite low, that is below 5,000. The stoichiometric CCTO shows a very high dielectric constant (33,210). The value decreases with increasing frequency. At a lower frequency, the dielectric constant is very high and drops drastically at 1 kHz, followed by slight declining trend until 10 MHz. The same trends were also reported by other researchers doing studies on the other electroceramic systems [3, 14, 15]. The dielectric constants for CCTO samples with extra TiO₂ content are much lower than with the stoichiometric ratios. The value decreases slightly with an increase in the frequency. Fig. 5 shows the value of the dissipation factor over the increasing frequency range for all the CCTO samples. The trends were almost same for all the samples. The value tends to decrease with an increase in the frequency, until a minimum value is reached at 10 MHz, before the value increases again. At 1 kHz, the dissipation factor value for all the

nonstoichiometric samples was lower than for the 4M sample. An alteration in the TiO₂ content can greatly affect the dissipation factor in a CCTO. The lowest value was in the 4.7 M sample, but the dielectric constant was low, hence a further investigation should be made to determine what appropriate amount of TiO₂ should be used to produce a CCTO with a high dielectric constant and a low dissipation factor without adding any dopants.

Conclusions

CCTO samples with different TiO₂ contents were fabricated and characterised by their phase formation, density, microstructure and dielectric properties. XRD results show a different phase formation, depends on the TiO₂ content. Increasing the TiO₂ content reduces the density. In the surface region, clear grain boundaries and a dense microstructure were observed. The grains are become bigger with the addition of more TiO₂ up to 4.3 mol, then the grains size tends to decrease. The dielectric constants for nonstoichiometric CCTO are much lower than for the stoichiometric case. The results show that the sample sintered at 1040 °C for 10 hours give a clearly uniform grain structure with the highest dielectric constant (33,210). At lower frequencies, the dissipation factor value for nonstoichiometric CCTO was much lower than for the 4.0 M sample. The variation in TiO₂ content influenced the CCTO properties.

Acknowledgement

This work was supported by the USM Short Term Grant No.6039001.

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