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Dielectric properties of LCTO ceramics with various sintering temperature

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ABSTRACT

In this research, $La_{2/3}Cu_3Ti_4O_{12}$ (LCTO) ceramics were prepared by the solid-state mixed oxide method. The optimum calcinations temperature for obtaining the pure phase was 950 ^{o}C for 4 h. The calcined powders were ground and pressed into cylindrical pellets with 10 mm in diameter and 2-3 mm in thickness under a pressure of 50 MPa. The pellets were then sintered at 1000, 1025, 1050 and 1075 ^{o}C for 6 h with a heating rate of 5 ^{o}C/min. Phase evolution of the ceramics samples after sintered at various temperatures were investigated by X-ray diffraction technique (XRD). The microstructural evolution of the sintered samples was examined by scanning electron microscopy (SEM). Density of the sintered samples was measured by Archimedes's method with distilled water as the fluid medium. And dielectric properties were examined using a LCR meter at 1, 10, 100, 500 kHz and 1 MHz. It was found that, all of XRD patterns showed pure phase. The microstructure indicates a monophase constitution with uniformly packed parallelogram shape in grain. The density increased with increasing sintering temperature. The high dielectric constant and the lowest loss of dielectric were found in LCTO ceramic sintered at 1075 ^{o}C when monitored at frequency 100 kHz.

Keywords: LCTO ceramic, Sintering temperature, Dielectric properties

INTRODUCTION

The typical high dielectric materials use today are normal ferroelectric oxides such as $BaTiO_3$ or relaxor ferroelectrics like $Pb(Mg_{1/3}Nb_{2/3})O_3$ (Bender and Pan, 2005). Recently, synthesized giant dielectric constant material $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much attention because of its potential technological applications. It shows extremely high dielectric constant ($> 10^4$) at room temperature (Subramanian *et al*, 2000; Ramirez *et al*, 2000; Homes *et al*, 2001).

In this work, we report the details pertaining to the effect of sintering temperature on the microstructural features of $La_{2/3}Cu_3Ti_4O_{12}$ (LCTO) ceramics because LCTO is the member of $ACu_3M_4O_{12}$ (A = alkali, alkaline-earth metal, rare-earth metal or vacancy, M = transition metal) family of oxides (Prakash and Varma, 2006). The experimental results of the preparation of LCTO powders and ceramics by a conventional solid state mixed oxide method are presented. We selected the calcined LCTO powders from calculation perovskite phase and lattice parameters of this powder agree well with the value from the report of Subramanian and Sleight (2002). The effect of sintering temperature on microstructure, physical properties and dielectric properties were also studied.

EXPERIMENTAL PROCEDURE

In this research, $La_{2/3}Cu_3Ti_4O_{12}$ (LCTO) ceramic powders were prepared by the conventional solid-state mixed oxide method. Reagent grade La_2O_3 (99.99%, Aldrich), CuO (99%, Fluka) and TiO_2 (99%, Riedel-de Häen) powders were used as starting materials. The mixture of these powders was thoroughly mixed in an ethanol medium using yittria stabilized zirconia balls mill for 24 h with La:Cu:Ti ratio 2/3:3:4. The suspension was dried and subsequently calcined at 700-1025 ^{o}C for 4 h with heating rate of 5^{o}C/min. Formation of pure phase compound was confirmed via X-ray diffraction (XRD) using $Cu_{K\alpha}$ radiation. Perovskite phase and lattice parameters of all powders were calculated using equation (1) (Swart and Shrout, 1982) and X-ray program (Calligaris and Geremia, X-ray powder program version 1.20A, University of Trieste, Italy).

$$\%\text{perovskite phase} = \left(\frac{I_{perov}}{I_{perov} + I_{CaCO_3} + I_{CuO} + I_{TiO_2}} \right) \times 100 \qquad (1)$$

The results of perovskite phase and calculated lattice parameters determined the optimum calcinations temperature in this research. The calcinations of the LCTO powder was ball milled with 1% PVA in ethanol for 12 h using the same method as mentioned earlier. The slurry was dried, sieved and pressed into a disc shape and sintered at 1000, 1025, 1050 and 1075 ^{o}C for 6 h with heating of 5 ^{o}C/min. Density of the sintered samples was measured by Archimedes's method with distilled water as the fluid medium. The microstructural feature of sintered samples was characterized using a scanning electron microscope. The average grain sizes distribution was checked by linear interception method from SEM micrograph. For the electrical measurement, silver paste was applied to the both sides of circular faces of the ceramics, then dried at 600 ^{o}C for 15 min and cooled naturally to room temperature. Dielectric constant and dielectric loss were measured using a LCZ meter at 1, 10, 100, 500 kHz and 1 MHz.

RESULTS AND DISCUSSION

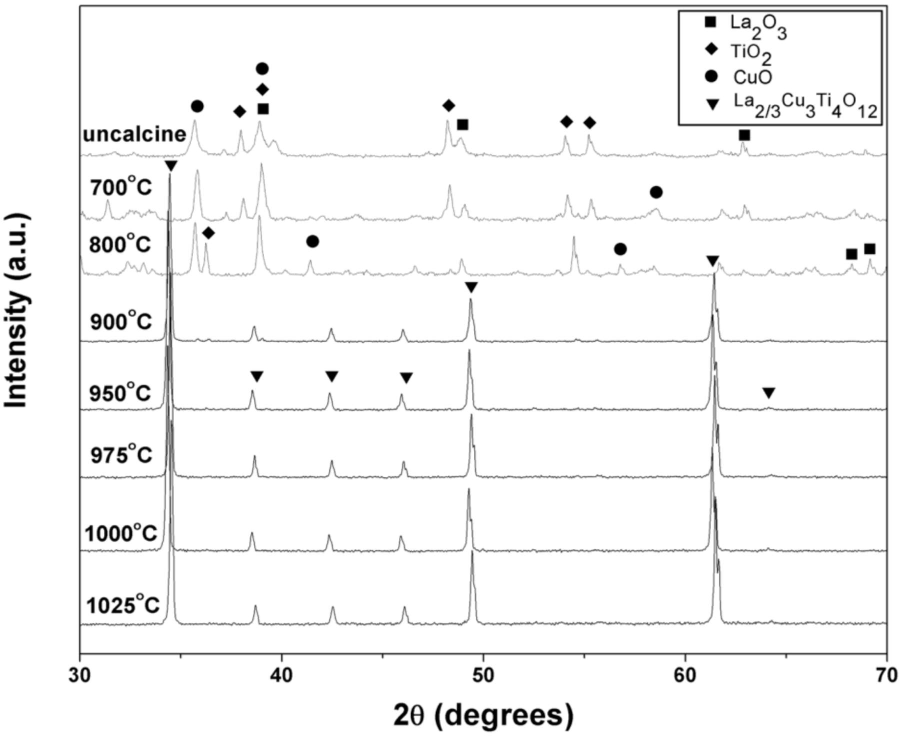


Figure 1. XRD patterns of LCTO powders uncalcined and calcined at 900-1025 ^{o}C for 4 h**.**

X-ray diffraction patterns LCTO powders uncalcined and calcined at 700-1025 ^{o}C for 4 h are illustrated in Fig. 1. LCTO powders with calcinations temperature from 700-800 ^{o}C for 4 h were found remain as precursor phases and small amount of the other phases compared with the patterns of uncalcined LCTO powders. Phase perovskite with 100% yielding was found when temperature exceeded 950 ^{o}C as shown in Fig. 2. The lattice parameters “a” of LCTO unit cell after calcinations at 950, 975, 1000 and 1025 ^{o}C for 4 h are 7.387(2) Ǻ, 7.373(5) Ǻ, 7.386(5) Ǻ and 7.372(0) Ǻ, respectively. We have found that powder sample that calcined at 950 ^{o}C for 4 h presents as pure phase and shows lattice parameter “a” of 7.387(2) Å which is closed to that of reported by M.A. Subramanian et al for LCTO (2002). Figure 3 shows XRD patterns of LCTO ceramics sintered at 1000, 1025, 1050 and 1075 ^{o}C for 6 h. All XRD patterns could be matched with that reported by Subramanian and Sleight (2002).

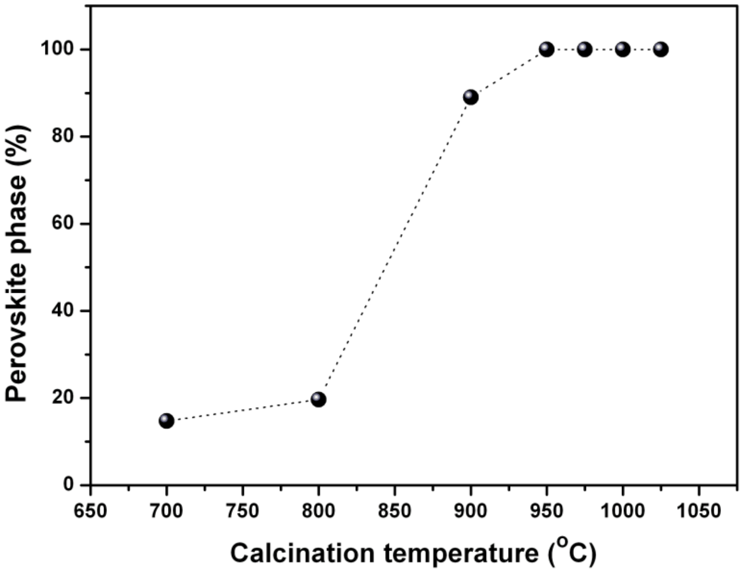


Figure 2. Perovskite phase of LCTO powders calcined at 900-1025 °C for 4 h**.**

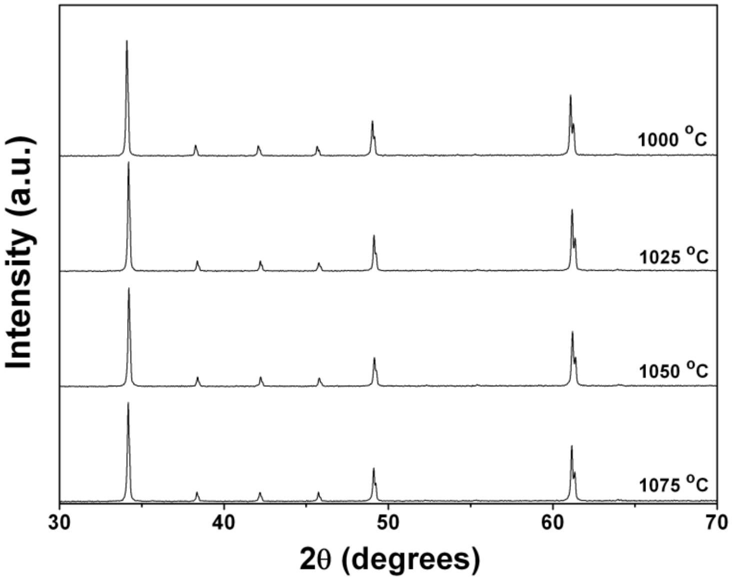


Figure 3. XRD patterns of LCTO ceramics sintered at 1000-1075 °C for 6 h**.**

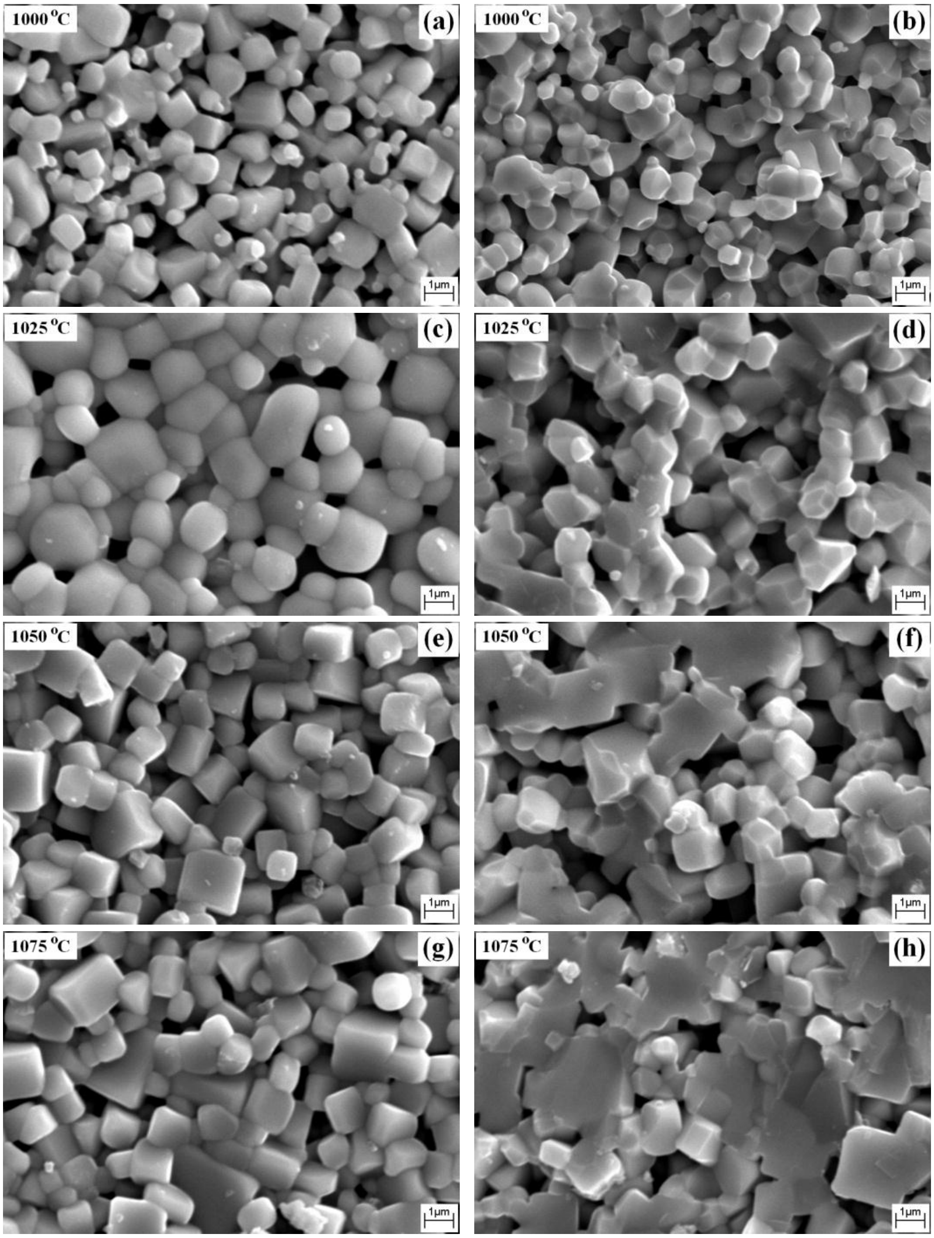


Figure 4. SEM photographs of top and fracture surface of LCTO ceramics sintered at: 1000 (a,b), 1025 (c,d), 1050 (e,f) and 1075 ^{o}C (g,h).

For LCTO ceramics sintered at 1000, 1025, 1050 and 1075 ^{o}C for 6 h, their microstructure reveal a monophase constitution with uniformly packed parallelogram shape in grain as shown in Fig. 4. LCTO ceramic sintered at 1000 ^{o}C for 6 h showed the smaller grains with the average size of 1.27 μm. While at higher sintering temperature (1025, 1050 and 1075 ^{o}C for 6 h) the LCTO ceramics showed larger grains with the mean grain size of 1.65, 1.69 and 1.74 μm, respectively. Fracture surfaces of the LCTO samples are shown in Figure 4 (b, d, f, h). The LCTO ceramics sintered at 1000 °C has a partially intergranular fracture as shown in Fig. 4 (a). The fracture mode changed to mainly intragranular for the sample with higher sintering temperature as shown in Fig. 4 (d, f, h), indicating that the sintering temperature effect to the reinforced of LCTO grain boundaries and size of grain (Ni *et al*, 2006). An intragranular mode of fracture can be associated with a strengthening of the grain boundaries, which encourages the crack to pass through the grain rather than along the grain boundary (Wang *et al*, 2008). The value of density is in the range of 3.85-4.81 g/cm^3. The densification of LCTO ceramics was improved significantly by increasing the sintering temperature. The average large grain size of LCTO ceramics were increased with increasing sintering temperature. Plots of density and average grain size of LCTO ceramics versus sintering temperature are shown in Fig. 5.

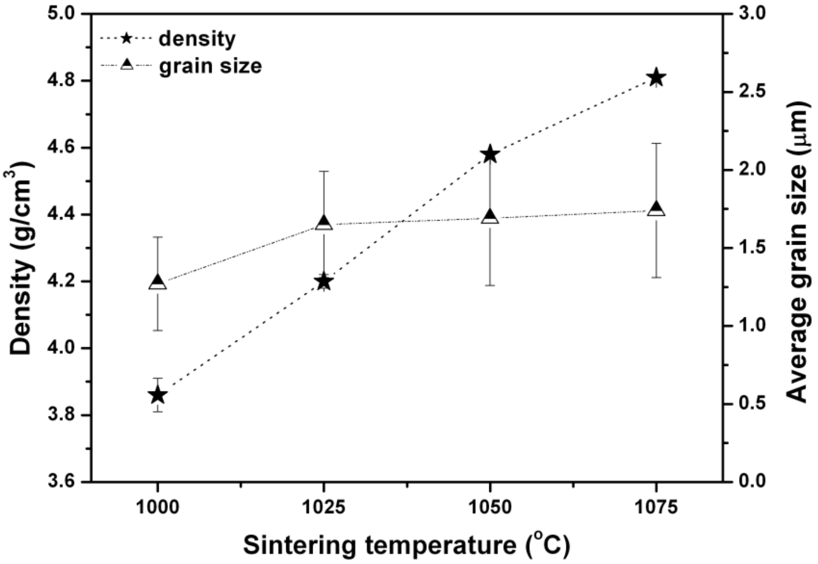
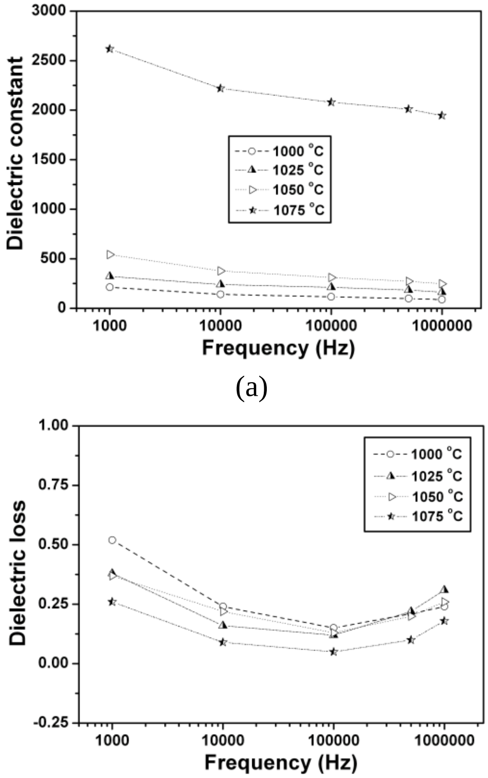


Figure 5. Average density and average grain size of LCTO ceramics sintered at 1000-1075 °C.

The dielectric constant and dielectric loss with different frequencies (1, 10, 100, 500 kHz and 1 MHz) at room temperature for LCTO ceramics sintered at 1000, 1025, 1050 and 1075 °C for 6 h are shown in Fig. 6 (a) and 6 (b), respectively. For all the samples, the dielectric constants slightly decrease with increasing the measurement frequencies. The dielectric constant for all samples increases with increasing sintering temperature. The dielectric losses for all sintered samples in the all frequency are lower than 0.52 (Fig. 6 (b)). The LCTO ceramic sintered at 1075 °C showed the highest dielectric constant of 2618 (measurement at 1 kHz, room temperature) but dielectric loss of this frequency was 0.26. The lowest loss of dielectric (0.05) was found in LCTO ceramic sintered at 1075 °C when monitored at frequency 100 kHz. The optimum dielectric properties condition for LCTO ceramics was found at 1075 °C measurement at 100 kHz (dielectric constant = 2080, dielectric loss = 0.05).



(a)

(b)

Figure 6. Variation of dielectric constant and dielectric loss with 1, 10, 100, 500 kHz and 1 MHz frequency at room temperature for the LCTO ceramics sintered at 1000-1075 °C.

CONCLUSION

The LCTO powders and ceramics were preparation by a conventional solid state mixed oxide method. The pure phase of LCTO powder as found at temperature higher than 900 °C with dwell time 4 h. The optimum condition for calcinations temperature was found at 950 °C for 4 h, the calculated lattice parameter “a” of unit cell is 7.387(2) Å. The microstructure of LCTO ceramics indicates a monophase constitution with uniformly packed parallelogram shape. The fracture surface of LCTO ceramics showed a change from intergranular to intragranular mode with increased sintering temperature. The density, average grain size and dielectric constant were increased with increasing the sintering temperature. The optimum dielectric properties condition for LCTO ceramics was found in the sample sintered at 1075 °C (measurement at 100 kHz).

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