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Microwave synthesis and sintering characteristics of $CaCu_3Ti_4O_{12}$

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Abstract. **$CaCu_3Ti_4O_{12}$ (CCTO) was synthesized and sintered by microwave processing at 2·45 GHz, 1·1 kW. The optimum calcination temperature using microwave heating was determined to be 950°C for 20 min to obtain cubic CCTO powders. The microwave processed powders were sintered to 94% density at 1000°C/60 min. The microstructural studies carried out on these ceramics revealed the grain size to be in the range 1–7 μm. The dielectric constants for the microwave sintered (1000°C/60 min) ceramics were found to vary from 11000–7700 in the 100 Hz–100 kHz frequency range. Interestingly the dielectric loss had lower values than those sintered by conventional sintering routes and decreases with increase in frequency.**

Keywords. **Microwave processing; sintering; giant dielectrics; microstructure.**

1. Introduction

Electroceramics associated with giant dielectric constants have been in increasing demand owing to the miniaturization of electronic devices. Recently, $CaCu_3Ti_4O_{12}$ (CCTO), a perovskite based centrosymmetric material, has received much attention because of its high dielectric constant over a wide range of frequencies and temperatures (Subramanian *et al* 2000) and has a potential for internal barrier layer capacitor applications. The processing conditions were found to affect the dielectric behaviour of CCTO to a great extent (Subramanian *et al* 2000; Homes *et al* 2001; Adams *et al* 2002; Sinclaire *et al* 2002; Lunkenheimer *et al* 2004; Bender and Pan 2005; Sriprakash and Varma 2006). CCTO was generally prepared via conventional solid-state reaction route using $CaCO_3$, TiO_2 and CuO as starting materials in stoichiometric ratio. The mixture of these was calcined at high temperature (>1000°C) for prolonged periods (24–48 h) with repeated intermediate grindings (Subramanian *et al* 2000; Lunkenheimer *et al* 2002, 2004; Sinclair *et al* 2002; Sriprakash and Varma 2006).

It was known in the literature that chemical reactions could be accelerated by microwave irradiation of reactants (Sutton 1989; Katz 1992; Landry *et al* 1995). Microwave heating is a novel technique for processing ceramic materials with many advantages such as uniform heating, rapid heating rate, considerably reduced processing time and temperature, improved material properties and performance. Many researchers have reported the enhancement in the solid state reaction rate or the solid state diffusion rate in a microwave dielectric field (Rao *et al* 1999; Thakur *et al* 2002; Vaidhyanathan *et al* 2002; Satapathy *et al* 2005). Complex oxides such as cuprates (Baghurst *et al* 1988), vanadates (Vaidhyanathan *et al* 1995), tungstates (Baghurst and Mingos 1988), ferrites (Krage 1981), niobates and titanates (Vaidhyanathan *et al* 1997) were prepared by microwave assisted solid state synthesis.

Electromagnetic waves interact with the ceramic materials, leading to volumetric heating by the dielectric loss mechanism. There are two main physical loss mechanisms: the flow of conductive current (in particular, ionic conduction), and dipolar reorientation. Mathematically, both these losses may be included in an effective dielectric loss factor,

$$\varepsilon''_{\mathrm{e}} = \varepsilon'' + \frac{\sigma}{\omega\varepsilon_0}, \tag{1}$$

where ε'' is the dielectric loss factor, σ the conductivity, ε_0 the permittivity of free space, ω the frequency, $\sigma/\omega\varepsilon_0$ represents the conductivity related losses. The power dissipated in the ceramics is given by

$$P = \omega\varepsilon_0\varepsilon''_{\mathrm{e}} \mid E \mid^2 = \omega\varepsilon_0\left(\varepsilon'' + \frac{\sigma}{\omega\varepsilon_0}\right) \mid E \mid^2, \tag{2}$$

where E is the electric field within the dielectric (Zhipeng *et al* 1999).

We thought that it was worth extending this technique for making ceramic powders of commercially important CCTO as this has moderately high dielectric loss which is one of the desired characteristics for efficient coupling.

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To the best of our knowledge, there exists no report so far on the microwave assisted solid-state synthesis of CCTO powders in the literature. A simple, relatively fast microwave assisted procedure for the synthesis of CCTO powders, their sintering behaviour along with preliminary dielectric data are reported in this communication.

2. Experimental

Stoichiometric amounts of high pure $CaCO_3$, TiO_2 and CuO were weighed and ball-milled using zirconia balls in an acetone medium for 2 h. The resultant mixture was oven dried and subjected to microwave processing. The microwave equipment that was used was a modified kitchen microwave oven (2·45 GHz, 1·1 kW) capable of generating temperatures up to 1600°C (Indian patent no. 1016/del/2001). The starting mixture of reactants (10 g) was heated at 900°C and 950°C for various durations using the microwave oven. For this, the mixture was taken in a recrystallized alumina crucible and in turn kept inside the alumina–silicon carbide crucible covered with a microwave compatible casket which was made up of alumino-silicate blanket. Sheathed Pt/Rh thermocouple was placed on the sample to monitor the temperature. The schematic of the casket used for calcinations is shown in figure 1. The microwave oven was switched off immediately after the specified soaking time and the calcined powder was removed from the oven after 2 h of experiment. The powders prepared via the microwave heating was cold pressed into pellets of 12 mm in diameter and 3 mm in thickness using 3% poly vinyl alcohol (PVA) and 1% polyethylene glycol as binders. The green pellets were then sintered using microwave oven at 1000°C for two different durations (30 and 60 min). For comparison, the CCTO was also synthesized via the conventional solid-state reaction route by calcining the starting mixture at 950 and 1000°C, respectively.

The formation of the monophasic compounds was confirmed via X-ray powder diffraction (XRD) studies. The densities of the sintered pellets were measured by the Archimedes principle using xylene as the liquid medium. Scanning electron microscope (SEM) (Cambridge Stereoscan S-360) was employed to study the microstructure of the sintered pellets. The capacitance measurements of the electroded pellets were carried out as a function of frequency (100 Hz–1 MHz) using an impedance gain-phase analyser (HP4194A).

3. Results and discussion

The XRD powder patterns for the microwave synthesized (at 900 and 950°C for different durations) are depicted in figure 2(a–e). The XRD patterns corresponding to the powders that are microwave processed at 900°C (figure 2(a–c)) show the presence of unreacted phases irrespective of the processing duration, whereas the XRD patterns corresponding to the powders processed at 950°C for 20 min (figure 2(e)) established the formation of single phasic CCTO. The X-ray diffraction patterns obtained for the powder processed by conventional heating at 950°C for different durations are shown in figure 3(a–d). It is evident that the peaks corresponding to unreacted phases are present even after 10 h of calcination (figure 3(c)) and phase-pure CCTO could be obtained only at 1000°C/5 h (figure 3(d)). Thus, the microwave method of synthesizing CCTO is more favourable for obtaining phase pure powders of CCTO as this is found to be fast and energy efficient.

Figure 4(a and b) shows the scanning electron micrograph of the fractured surfaces obtained for the pellets

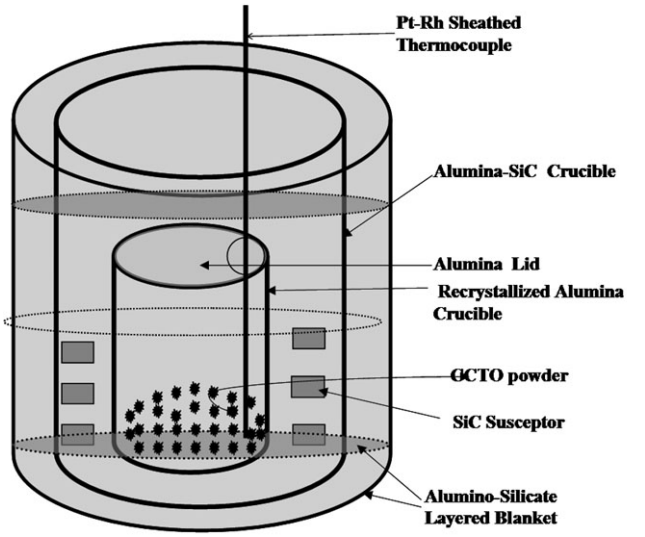

Figure 1. Schematic of set up used for calcining and sintering CCTO ceramic in this study.

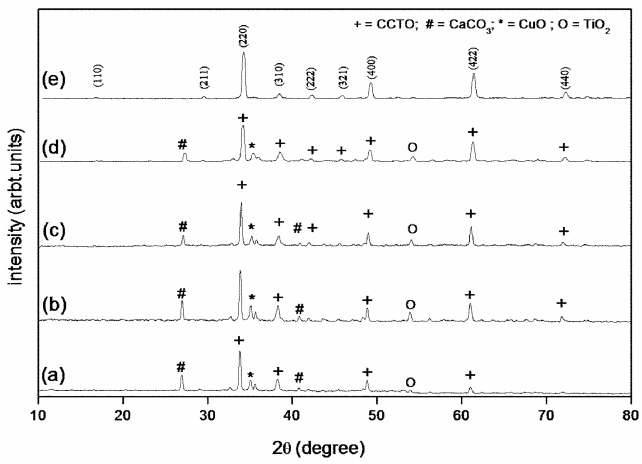

Figure 2. X-ray diffraction patterns for the powders synthesized in microwave furnace at (a) 900°C/20 min, (b) 900°C/30 min, (c) 900°C/60 min, (d) 950°C/10 min and (e) 950°C/20 min.

sintered at 30 and 60 min. It is observed that there is no significant difference in the grain sizes between the pellets sintered at 30 and 60 min. It establishes the presence of the grains with sizes lying in 2–7 μm range in both the cases. As seen from the microstructure, the ceramic sintered at 60 min is denser than the 30 min sintered one and the density increased from 92–94%.

Figure 5(a) shows the frequency (100 Hz–100 kHz) dependence of room-temperature dielectric constant for the microwave sintered pellets at 1000°C for 30 and 60 min. As seen from figure 5(a), the dielectric constant shows an increasing trend as the sintering duration increased from 30 min to 60 min, whereas the dielectric loss shows a decreasing trend at any frequency under study. The dielectric constants for the microwave processed CCTO decrease with increase in frequency. Typically, it decreases from 11,000 (100 Hz) to 7700 (100 kHz) in the case of 1000°C/60 min sintered pellets while dielectric loss decreased from 0·58–0·081 as the frequency increased from 100 Hz–100 kHz (figure 5(b)). Adams *et al* (2002) proposed a direct link between grain size and permittivity based on two sets of samples obtained by varying the sintering time. In contrast to these results, the dielectric constants obtained in this work are not directly correlated to the grain size, which is in agreement with the results obtained by Seymen *et al* (2005). The observed higher value of dielectric constant for the pellet sintered at 1000°C/60 min is ascribed to the enhanced density. The dielectric constants for CCTO ceramics obtained by the microwave sintering (1000°C/60 min) is higher than that of CCTO ceramics that were fabricated from the powders obtained by (i) solid state reaction route (Jha *et al* 2003; Seymen *et al* 2005; Ni *et al* 2006; Sriprakash and Varma 2006), (ii) polymer precursor route (Jha *et al* 2003) and (iii) modified glycine nitrate process (GNP) (Ren *et al* 2004). It is worth noting that the dielectric loss value in the whole frequency range of 1 kHz–100 kHz is below 0·17, which is lower than that of the results reported by Jha *et al* (2003) and Ren *et al* (2004). Further, the dielectric properties reported in this work are for the pellets that

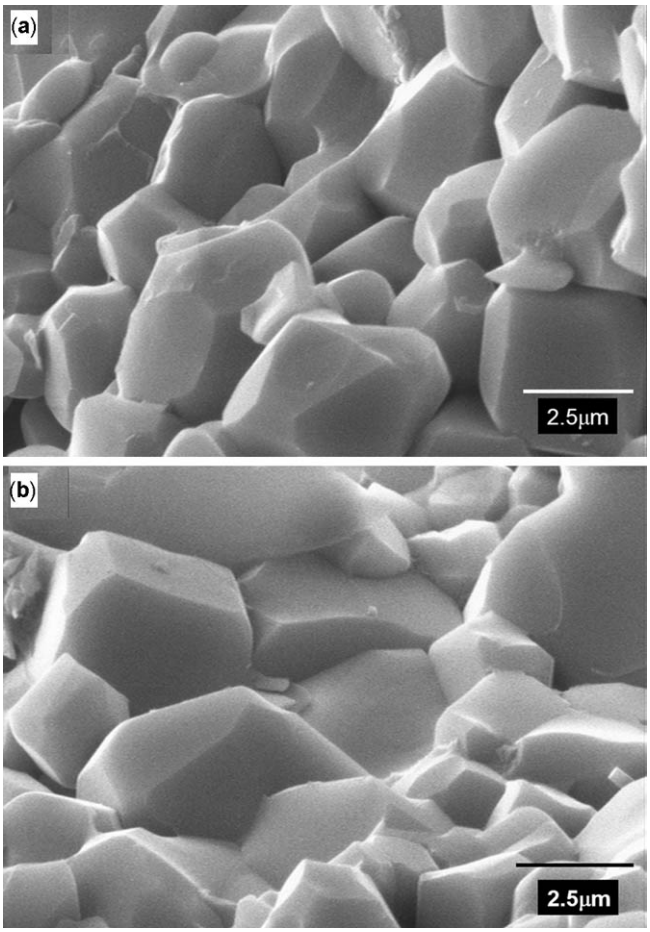

Figure 4. Scanning electron micrographs for microwave sintered pellets: (**a**) 1000°C/30 min and (**b**) 1000°C/60 min.

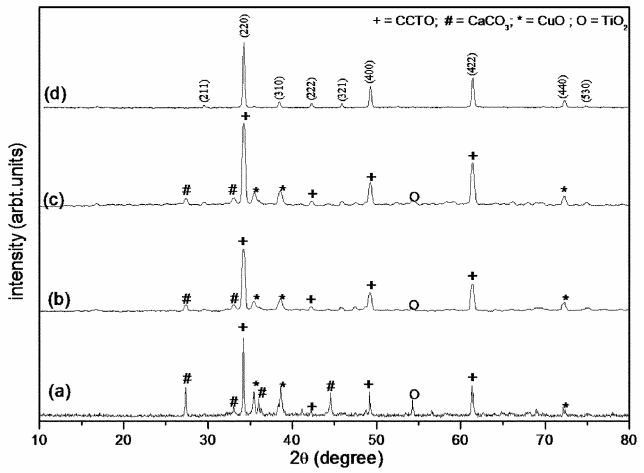

Figure 3. X-ray diffraction patterns for the conventional synthesized powder at: (a) 950°C/60 min, (b) 950°C/6 h, (c) 950°C/10 h and (d) 1000°C/5 h.

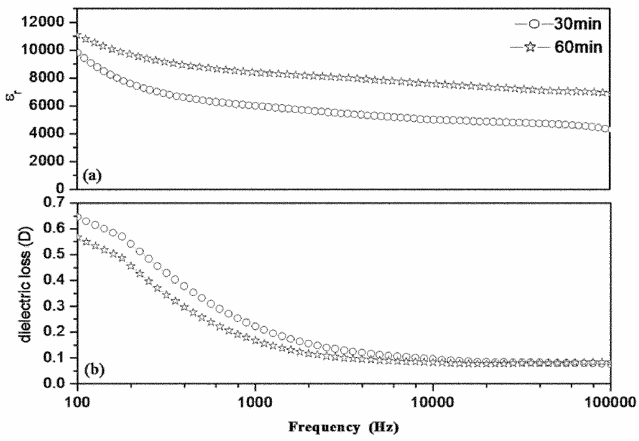

Figure 5. Frequency dependence of room-temperature dielectric properties for the microwave sintered pellet at 1000°C for 30 and 60 min.

were sintered in microwave oven for a much shorter duration (60 min) than those reported earlier (Jha *et al* 2003; Ren *et al* 2004; Seymen *et al* 2005; Ni *et al* 2006; Sriprakash and Varma 2006).

The incidence of giant dielectric constants in CCTO have been attributed to (i) the barrier layer capacitance arising at twin boundaries (Subramanian *et al* 2000), (ii) the interfaces between the sample and the electrode (Lunkenheimer *et al* 2002), (iii) grain boundary effects (Sinclair *et al* 2002; Liezhang 2005; Liu *et al* 2005), (iv) the lattice distortions (Chung 2005), (v) the internal domains (Fang and Liu 2005) and (vi) the oxygen vacancies (Li *et al* 2004; Pires *et al* 2006). Though different explanations for the origin of high dielectric constant have been proposed, the real mechanism is still debatable as to whether it is intrinsic or extrinsic in nature. Since the electrical properties of ceramics are mainly dependent on the bulk as well as on the microstructure vis-à-vis processing conditions, which include sintering temperatures and atmospheres (Subramanian *et al* 2000; Homes *et al* 2001; Adams *et al* 2002; Sinclair *et al* 2002; Lunkenheimer *et al* 2004; Ren *et al* 2004; Bender and Pan 2005; Seymen *et al* 2005; Ni *et al* 2006; Sriprakash and Varma 2006), systematic work has been in progress to visualize the dielectric properties of the CCTO pellets sintered under various microwave sintering conditions.

4. Conclusions

The microwave method of synthesizing CCTO powders has been demonstrated. This is found to be fast and energy efficient as compared to that of the conventional methods. Indeed CCTO powders could easily be synthesized by using 2·45 GHz, 1·1 kW modified kitchen microwave oven at 950°C for 20 min. The dielectric maximum of 11,000 at 100 Hz accompanied by lower loss was obtained for the pellets sintered at 1000°C for 60 min.

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