Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 939–942
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Microwave assisted sintering of $CaCu_3Ti_4O_{12}$

Sabar D. Hutagalung *, M. Ikhwan M. Ibrahim, Zainal A. Ahmad

School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

Available online 2 October 2007

Abstract

$CaCu_3Ti_4O_{12}$ electroceramic was prepared by a microwave assisted solid-state reaction technique from $CaCO_3$, CuO and TiO_2 powders. Processing involved the preparation of raw material, mixing and milling, calcination, pellet forming and sintering processes. Conventional furnace and microwave assisted sintering processes were employed in order to improve phase structures, morphology and dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics. Surface and fracture FESEM analysis showed that the microwave assisted sintered $CaCu_3Ti_4O_{12}$ produced better densification and more uniform grain size compared to the conventional sintered sample.

Keywords: A. Microwave processing; B. Grain boundaries; C. Dielectric properties; D. Perovskites

1. Introduction

High dielectric constant materials are increasingly important for pushing the state of art in semiconductor integrated circuits. It is necessary in applications that require high capacitance values per lateral area. Ceramic materials also can be used in the microelectronic industries as dielectric substrates, due to their high reliability, high integration potential, good dielectric properties, excellent thermal conductivity and their thermal expansion coefficient close to silicon [1]. It is known that some ceramic compounds with perovskite structures were found to have very interesting dielectric properties. In particular, one of the members, $CaCu_3Ti_4O_{12}$ (CCTO), was recently studied to investigate the origin of the so-called colossal permittivity, and Chiodelli et al. [2] reported on the dielectric properties of CCTO for single crystal, powders and thin films.

The electroceramic compound CCTO had attracted much interest due to its high dielectric constant (up to 10^5) over a broad temperature range extending from 100 to 600 K [3,4]. This unique property makes CCTO a promising material for microelectronic and microwave device applications. However, the nature of how the CCTO possess such properties is still not well-understood [5–8]. Lately, researchers claim that this behavior comes from different factors, e.g., grain boundary, presence of twin boundaries or other planar defects, displacement of Ti ions, etc [4,6]. However, complete explanations of the phenomena have been not yet finalized.

There are four major sintering parameters that should be controlled to produce good quality single-phase of CCTO, i.e., temperature, heating rate, duration and atmosphere. It was stated by some researchers [9,10] that optimum sintering temperature and duration to produce CCTO is 1050 °C for 24 h. However, our previous work [11] has found that microstructure and dielectric properties of CCTO are affected by sintering parameters. The results showed that there was abnormal grain growth, and melting and formation of large pores. Therefore, it is important to investigate new sintering parameters as well as to find out a new sintering technique to ensure that the correct microstructure with better dielectric properties of CCTO is obtained. Meanwhile, making such a single-phase CCTO body from a powder obtained by conventional solid-state reaction routes is very difficult, since this technique requires calcination and sintering steps at high temperature and long duration to get the desired properties. Methods such as hydrothermal synthesis, plasma spray decomposition of oxides, sol–gel, etc., could be used to produce high-purity oxide powders; however, these techniques have not received much commercial importance because of the use of expensive raw materials and various steps of processing.

Microwave (MW) sintering is an attractive technique for material processing. This technique has been employed by several researchers in order to produce dielectric ceramics

* Corresponding author.
E-mail address: derita@eng.usm.my (S.D. Hutagalung).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.09.074

[12–15], ferroelectrics [16,17], garnet and spinel [18–21], semiconductor [22,23], superconductor [24], and solid oxide fuel cell (SOFC) materials [25] with very short time processing and high quality products. For example, a MW-assisted combustion synthesis has emerged as an attractive technique for the production of homogeneous, high-purity, and crystalline $MgAl_2O_4$ spinel oxide powders at significantly lower temperatures, shorter time periods and using less amount of external energy as well [20].

As the MW sintering of CCTO has not been well explored, there is a possibility to apply this technique for the processing such electroceramic materials. Therefore, in this work, an attempt has been made to prepare CCTO by MW-assisted sintering route using a modified domestic microwave oven. More importantly, a domestic microwave oven provides inexpensive multi-mode cavities that can be used for sintering process of advanced materials with a simple procedure.

2. Experimental procedure

The CCTO was prepared from starting materials of $CaCO_3$ (Aldrich, 99%), TiO_2 (Merck, 99%), CuO (Aldrich, 99%), and SnO_2 (Aldrich, 99%). The raw materials were weighed according to the stoichiometric ratios to form pure CCTO. The mixed powders were wet ball milled for 1 h using ethanol. The milled powder was subjected to calcination process at 900 °C with soaking time of 12 h using a furnace (Carbolite CWF 1300). Disc shaped specimens of 12 mm in diameter and approximately 1.2–1.5 mm in thickness were formed from calcined powder by a uniaxial pressure of 520 MPa. Green pellets were subjected to sintering process by electrical furnace at 900 °C for 12 h and 1000 °C for 10 h in air (conventional sintering). Meanwhile, MW-assisted sintering process was done by using a domestic microwave oven (Panasonic, Model NN-S554WF/MF). This oven is capable of generating microwave power from 0 to 1100 W at operating frequency of 2.45 GHz. In this process, samples were put in alumina crucible and placed inside a quartz container, and then positioned in the centre of microwave cavity chamber. For the sintering processes, the oven was operated at full power for 30, 60, 90, 120 and 150 min, respectively.

The samples were analyzed by XRD (Bruker D8), field emission scanning electron microscopy (FESEM), and EDX (Zeiss SUPRA 35VP) for determination of phase structures, microstructures and elemental compositions, respectively. Dielectric properties (dielectric constant and loss) of the sintered pellets were measured using an Agilent 4284A Precision LCR meter at frequency of 1 MHz in ambient temperature.

3. Results and discussion

Calcined and sintered powders were examined by XRD in order to investigate the phase formation of CCTO and the results are shown in Fig. 1. Fig. 1(b) shows XRD spectra of milled stoichiometric composition powder irradiated by microwave (MW) for 30 min. It was found that CCTO is not

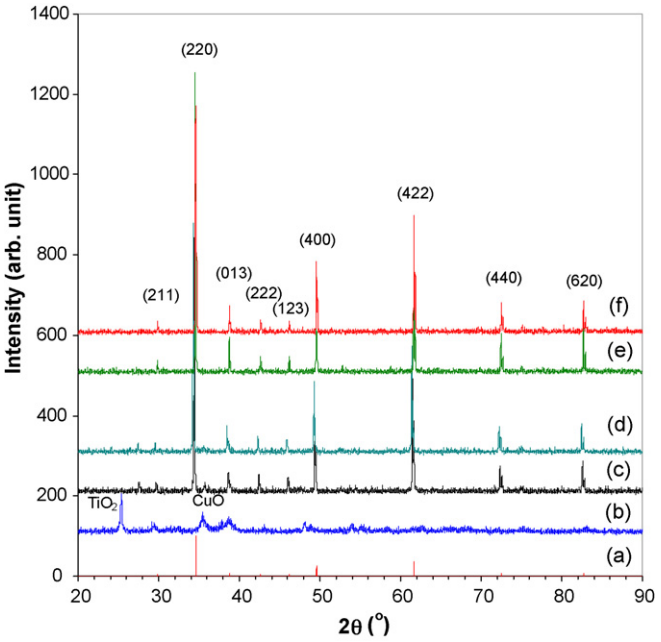

Fig. 1. XRD analysis results of (a) CCTO standard (File no: 01-075-2188), (b) milled stoichiometric raw materials and irradiated by full power MW for 30 min, (c) MW calcination for 90 min, (d) pressed pellet sintered by MW for 60 min, (e) furnace sintered 1000 °C/10 h, and (f) MW sintered for 30 min of pre-sintered pellet at 1000 °C/10 h.

formed completely since only two small peaks of (2 1 1) and (1 0 3) belonged to CCTO, and the other peaks are due to the raw materials of TiO_2 and CuO. By prolonging the MW exposure to 90 min, it was found that the CCTO phase formed significantly from the milled raw material powders (Fig. 1(c)). The MW calcined CCTO powder was pressed into pellet form and this was followed by MW sintered at full power for another 60 min. The result shows complete formation of single-phase CCTO structure (Fig. 1(d)), but pellets are still not fully dense. To overcome this problem, pressed pellet was pre-sintered using a conventional process (furnace) at 1000 °C for 10 h and this was then followed by MW irradiation for 30 min (Fig. 1(e) and (f)). Almost all of the obtained peaks are coincided the reference pattern of CCTO (File no: 01-075-2188, Fig. 1(a)).

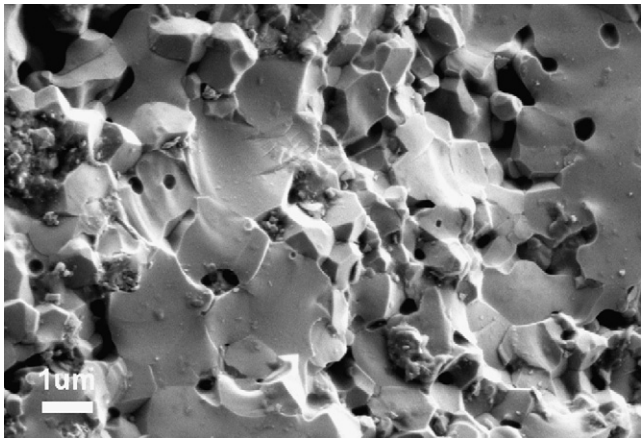

Fig. 2. FESEM image (fracture) of sample sintered at 1000 °C/10 h using a conventional furnace.

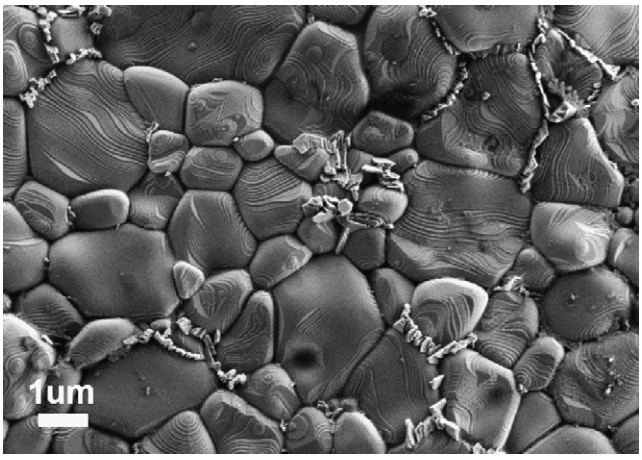

Fig. 3. FESEM image (surface) of MW sintered of CCTO for 120 min. Sample was pre-sintered at 1000 °C/10 h using a conventional furnace.

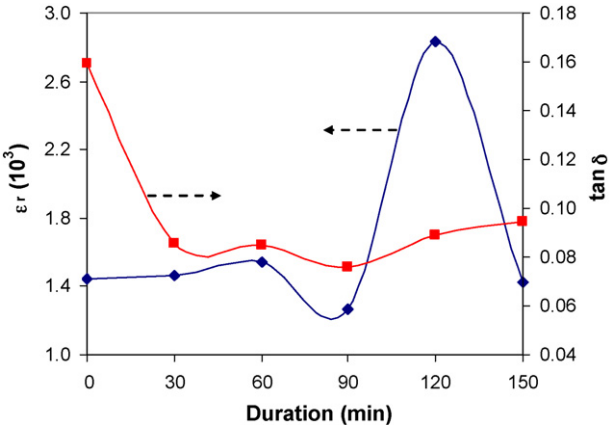

Fig. 5. Effect of MW sintering duration on the dielectric constant and dielectric loss of CCTO.

From this result, it can be seen that crystallinity and densification of CCTO pellet was improved by post-microwave sintering.

A porous microstructure with small grain size is observed in the sample sintered by MW for 60 min. In this case, the MW sintering process does not achieve the appropriate grain growth of the sample. This is the disadvantage of the MW sintering process. In microwave processing, a suitable microwave cavity to allow the transfer of MW energy to the sample through susceptor is needed [21]. In this work, an alumina cup was used as susceptor might be not very good if compared to SiC [16]. On the other hand, sample sintered at 1000 °C for 10 h is significantly promotes grain growth and dense microstructure. However, careful examination close to the fracture of sample revealed a porous area of microstructure as shown in Fig. 2.

Fig. 3 shows FESEM image of surface of MW sintered of CCTO for 120 min. Sample was pre-sintered at 1000 °C/10 h using a conventional furnace. The grain growth tends to decrease porosity as observed in the post-sintered specimens by MW irradiation. Further observation indicated that MW sintered for 120 min produced CCTO had very clear grain boundary (Fig. 3). From the results, one can propose that post-sintering by MW radiation might be used as a thermal etching process to improve densification and grain boundary analysis.

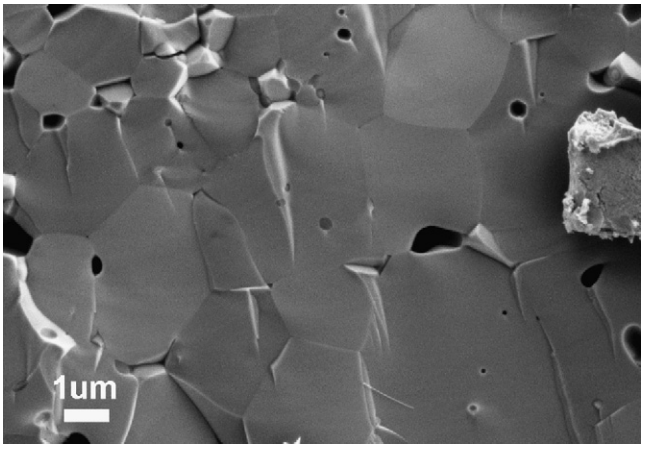

Fig. 4. FESEM image (fracture) of MW sintered of CCTO for 120 min.

Fig. 4 shows the FESEM micrograph of fracture of MW sintered of CCTO for 120 min. It was found that the microstructures of the pellet become denser or less porous if MW exposure time is increasing. The most promising microstructure was observed in the fracture of the post-sintered MW for 120 min sample (Fig. 4). EDX analysis result confirmed elemental compositions of Ca, Cu, Ti, and O that close to stoichiometric ratio of CCTO compound.

Microwave synthesis of materials is fundamentally different from the conventional process in terms of its heating mechanism. In a microwave oven, heat is generated within the sample volume itself by the interaction of microwaves with the material. Microwave energy heats the material on a molecular level, which leads to uniform heating, whereas, conventional heating systems heat the material from the outer surface to interior, which results in steep thermal gradients.

Fig. 5 shows the effect of MW sintering duration on the dielectric constant and dielectric loss of CCTO. The samples were pre-sintered at 1000 °C using conventional furnace. For dielectric constant, ε_r, as the exposure time increased, the curve has a fluctuated form with maximum value for the sample sintered at 120 min. The dielectric loss is slightly decreased with increasing sintering duration, even though a minimum value or better dielectric loss a property was found for sample sintered at 90 min. The highest ε_r value was obtained in this study and measured at room temperature was about 2800, whereas the lowest dielectric loss is about 0.08.

4. Conclusions

A dense single-phase CCTO product can be prepared by the post-sintering microwave-assisted combustion reaction using a domestic microwave oven. Pellet obtained by the post-sintering microwave-assisted irradiation possesses higher density and lower dielectric loss when compared to those produced by the conventional route.

Acknowledgement

This work was supported by Nippon Sheet Glass Foundation for Materials Science and Engineering Research Grant, Japan, 2006–2007.

References

[1] A. Stiegelschmitt, A. Roosen, C. Ziegler, S. Martius, L. Schmidt, Dielectric data of ceramic substrates at high frequencies, J. Eur. Ceram. Soc. 24 (2004) 1463–1466.
[2] G. Chiodelli, V. Massarotti, D. Capsoni, M. Bini, C.B. Azzoni, M.C. Mozzati, P. Lupotto, Electric and dielectric properties of pure and doped $CaCu_3Ti_4O_{12}$ perovskite materials, Solid State Commun. 132 (2004) 241–246.
[3] M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, A.W. Sleight, High dielectric constant in $ACu_3Ti_4O_{12}$ and $ACu_3Ti_3FeO_{12}$ phases, J. Solid State Chem. 151 (2000) 323–325.
[4] A.P. Litvinchuk, C.L. Chen, N. Kolev, V.N. Popov, V.G. Hadjiev, M.N. Iliev, R.P. Bontchev, A.J. Jacobson, Optical properties of high-dielectric-constant $CaCu_3Ti_4O_{12}$ films, Phys. Status Solidi (a) 195 (2003) 453–458.
[5] P. Jha, P. Arora, A.K. Ganguli, Polymeric citrate precursor route to the synthesis of the high dielectric constant oxide $CaCu_3Ti_4O_{12}$, Mater. Lett. 57 (2003) 2443–2446.
[6] L. Wu, Y. Zhu, S. Park, S. Shapiro, G. Shirane, Defect structure of the high-dielectric-constant perovskite $CaCu_3Ti_4O_{12}$, Phys. Rev. B 71 (2005) 014118.
[7] L. He, J.B. Neaton, D. Vanderbit, M.H. Cohen, Lattice dielectric response of $CdCu_3Ti_4O_{12}$ and of $CaCu_3Ti_4O_{12}$ from first principles, Phys. Rev. B 67 (2003) 012103.
[8] Y. Lin, Y.B. Chen, T. Garret, S.W. Liu, C.L. Chen, R.P. Bontchev, A. Jacobson, J.C. Jiang, E.I. Meletis, J. Hortwitz, H.D. Wu, Epitaxial growth of dielectric $CaCu_3Ti_4O_{12}$ thin films on (0 0 1) $LaAlO_3$ by pulsed laser deposition, Appl. Phys. Lett. 81 (2002) 631–633.
[9] A.F.L. Almeida, R.S. Oliveira, J.C. Goes, J.M. Sasaki, A.G. Filho, J.M. Filho, A.S.B. Sombra, Structural properties of $CaCu_3Ti_4O_{12}$ obtained by mechanical alloying, Mater. Sci. Eng. B96 (2002) 275–283.
[10] D. Valim, A.G.S. Filho, P.T.C. Freire, S.B. Fagan, A.P. Ayala, J.M. Filho, A.F.L. Almeida, P.B.A. Fechine, A.S.B. Sombra, J.S. Olsen, L. Gerward, Raman scattering and X-ray diffraction studies of polycrystalline $CaCu_3Ti_4O_{12}$ under high pressure, Phys. Rev. B 70 (2004) 132103.
[11] J.J. Mohamed, S.D. Hutagalung, M.F. Ain, K. Deraman, Z.A. Ahmad, Microstructure and dielectric properties of $CaCu_3Ti_4O_{12}$ ceramic, Mater. Lett. 61 (2007) 1835–1838.
[12] P. Boch, N. Lequeux, Do microwaves increase the sinterability of ceramic? Solid State Ionics 101–103 (1997) 1229–1233.
[13] Z. Xie, C. Wang, X. Fan, Y. Huang, Microwave processing and properties of Ce–Y–ZrO_2 ceramics with 2.45 GHz irradiation, Mater. Lett. 38 (1999) 190–196.
[14] D.E. Clark, D.C. Folz, J.K. West, Processing materials with microwave energy, Mater. Sci. Eng. A 287 (2000) 153–158.
[15] D.D. Upadhyaya, A. Ghosh, K.R. Gurumurthy, R. Prasad, Microwave sintering of cubic zirconia, Ceram. Int. 27 (2001) 415–418.
[16] Z. Xie, Z. Gui, L. Li, T. Su, Y. Huang, Microwave sintering of lead-based relaxor ferroelectric ceramics, Mater. Lett. 36 (1998) 191–194.
[17] A. Goldstein, M. Kravchik, Sintering of PZT powders in MW furnace at 2.45 GHz, J. Eur. Ceram. Soc. 19 (1999) 989–992.
[18] R.D. Peelamedu, R. Roy, D. Agrawal, Anisothermal reaction synthesis of garnets, ferrites, and spinels in microwave field, Mater. Res. Bull. 36 (2001) 2723–2739.
[19] P. Yadoji, R. Peelamedu, D. Agrawal, R. Roy, Microwave sintering of Ni–Zn ferrites: comparison with conventional sintering, Mater. Sci. Eng. B 98 (2003) 269–278.
[20] I. Ganesh, R. Johnson, G.V.N. Rao, Y.R. Mahajan, S.S. Madavendra, B.M. Reddy, Microwave-assisted combustion synthesis of nanocrystalline $MgAl_2O_4$ spinel powder, Ceram. Int. 31 (2005) 67–74.
[21] D. Grossin, S. Marinel, J.G. Noudem, Materials processed by indirect microwave heating in a single-mode cavity, Ceram. Int. 32 (2006) 911–915.
[22] G. Xu, H. Zhuang, W. Li, F. Wu, Microwave sintering of α/β-Si_3N_4, J. Eur. Ceram. Soc. 17 (1997) 977–981.
[23] I.N. Lin, W.C. Lee, K.S. Liu, H.F. Cheng, M.W. Wu, On the microwave sintering technology for improving the properties of semiconducting electronic ceramics, J. Eur. Ceram. Soc. 21 (2001) 2085–2088.
[24] Q.W. Qiao, J.S. Zhang, Y.J. Yang, L.H. Cao, Y.Z. Wang, Microwave processing of high T_c oxide superconductors at oxygen atmosphere, IEEE Trans. Appl. Supercond. 3 (1993) 1092–1093.
[25] D. Darcovich, P.S. Whitfield, G. Amow, K. Shinagawa, R.Y. Miyahara, A microstructure based numerical simulation of microwave sintering of specialized SOFC materials, J. Eur. Ceram. Soc. 25 (2005) 2235–2240.