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Preparation and Characterization of High-K Dieletric Material of CCTO by Using Microwave Processing Technique

by

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SUMMARY

In this project, three different methods had been applied to synthesize high-k dielectric materials of $CaCu_3Ti_4O_{12}$ (CCTO). The methods are modified mechanical alloying, microwave assisted sintering and fully microwave processing techniques. The effects of calcination temperature, sintering temperature, duration and doping concentration to the phase formation, microstructure and electrical (dielectric constant, dielectric loss and resistance) properties of modified mechanical alloyed CCTO have been studied intensively. The results show that optimum parameter to synthesized CCTO via modified mechanical alloying technique are milling time 5 hours, calcination at 750 °C for 9 hours, and sintering at 950 °C for 12 hours. However, the effect Zn-doping concentration on the dielectric constant CCTO is not consistent, which was found that 5 % dopant give a lower dielectric constant value but shows the best dielectric loss properties if compared to others samples. Besides that, this sample also shows the highest resistance value. Therefore, it can be concluded that by doping with certain amount of zinc, the electrical and dielectric properties of CCTO can be improved. Meanwhile, denser single-phase CCTO can be via microwave assisted sintering on the pre-sintered CCTO pellet. The post-sintered CCTO using a domestic microwave oven possesses higher density and lower dielectric loss compared to those produced by conventional furnace. For fully microwave processing, it was found that the crucible used as susceptor is play an important role in preparation a single phase CCTO. Alumina or graphite crucible was gave incomplete microwave calcination process. The only by using SiC crucible has been successfully synthesized a single phase CCTO via microwave calcination for 30 minutes. Sintering for 90 minutes in microwave oven was produced denser CCTO pellet.

Keywords:
$CaCu_3Ti_4O_{12}$ (CCTO), electroceramic material, modified mechanical alloying, microwave assisted sintering, microwave calcination and sintering, high dielectric constant, low dielectric loss.

INTRODUCTION

High dielectric constant and ferroelectric materials are increasingly important for pushing the state of art in semiconductor integrated circuits. There are necessary in applications that require high capacitance values per lateral area. Ceramic materials are 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 are found to be 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 Chidelli et. al. [2] was reported the dielectric properties result of CCTO for single crystal, powders and thin films.

The electroceramic compound CCTO has been found as a material exhibit a giant dielectric constant with relatively temperature independent over a wide temperature range between 100 and 600 K. It was found the dielectric constant value up to 10^5. However, below 100 K its value drops abruptly almost three orders of magnitude. Local structural properties of CCTO system as a function of temperature was investigated within a range from 50 K up to room temperature [3,4]. The temperature dependence of the nearest neighbor Cu-O distance is very flat, supporting the idea that this is bracing the structures. However, unusual temperature dependence for the atomic displacement parameters of calcium and copper is observed. Temperature dependent modeling, suggests that the Ca atoms become under bonded at low temperature. This unique property makes CCTO a promising material for microelectronic and microwave device applications.

The dielectric properties of electroceramic materials are depends on the phase transition phenomena, and that is closely related to the crystal structure. On the other hand, the crystal structure is closely dependent on the thermal history and the fabrication method. Therefore, the properties of a certain electroceramic materials will finally affected by the sintering condition, including sintering temperature and time. Firing of electroceramic materials always is carried out by placing these materials in furnace. The mechanism of furnace heating methods is heat conduction from the material's surface inward, thus generate temperature gradient between outer and inner surface of the heated material. Furnace heating methods overcure the surface while undercuring the interior. Furnace heating is slow and inefficient for materials that conduct heat poorly. Furnace parameters that must be controlled include temperature, pressure, heating and cooling rates and atmosphere condition. High temperatures are required to achieve the desired strength and composition. During firing process, the material is soaked for few hours to get the desirable properties. The high temperature and longer processing time are some the disadvantages of conventional heating by using furnace. Therefore, an alternative method namely microwave processing has been developed in this research as a new tool for preparation of CCTO electroceramic materials.

Mechanical alloying technique has been used to produce CCTO by using two different experimental procedures [5]. The advantage of this procedure remains on the fact that melting is not necessary; the powders are nanocrystalline and exhibits extraordinary mechanical properties. It can also be easily shaped (injected, compacted, etc.) into any geometry or used in others procedures of film preparation. Although this technique is able to produce nanocrystalline powders of CCTO, but this process need a very long milling time up to 100 hours to obtain a single-phase of CCTO formation. On the other hand, a conventional ceramic solid state reaction technique is one of the promising technique to prepared CCTO, but again, this process need a relatively high calcination temperature, normally in the range of 1000-1100 °C. To solved these problems, in this work we try to reduce the milling time to 5 hours only and then following by calcination process at 600-900 °C for different soaking time to produce a single-phase CCTO formation. A novel technique that using in this work to prepare the $CaCu_3Ti_4O_{12}$ (CCTO) is called modified mechanical alloying technique. For comparison purpose, another technique namely solid state reaction method was employed to prepare CCTO.

Microwave heating is a quick and efficient method of heating materials that are difficult to heat by convection or infrared methods because the type of heating is volumetric heating, so production rates increase and product quality improves. Microwave heating is an electromagnetic spectrum with a frequency between 300 MHz to 300 GHz. Microwave heating have several properties as same as visible light that are may be reflected or absorbed by the material, may transmit through materials without any absorption and when traveling from one material to another, the microwaves may change direction. The radiation of microwave is non-ionizing and different from the ionizing radiation such as x-rays and gamma rays. Materials absorb microwave energy through relaxation mechanism like dipolar, ion jump and ohmic loses. Two important parameters for microwave processing are power absorbed and depth of microwave penetration. Unlike conventional heating, these parameters are highly dependent on the dielectric properties of the material and, in practice, can provide another degree of process flexibility. The factor to consider in microwave heating is the susceptor. Examples of the advantages associated with microwave processing are rapid and uniform heating, decreased sintering temperatures and reduce the long soaking time in conventional heating.

EXPERIMENTAL

The preparation of pure and doped $CaCu_3Ti_4O_{12}$ (CCTO) were carried out in two phases, i.e.: conventional process (calcination and sintering) via furnace and phase II, which is calcination and sintering via microwave processing.

Undoped and doped CCTO was prepared using materials of $Ca(OH)_2$ or $CaCO_3$, CuO, TiO_2 and dopant material. The raw materials were mixed via wet milling for 1 hour using zirconia ball as the medium. The mixed powder was calcined at 750-900 °C for 6-24 hours using furnace. Calcined powder was pressed to a pellet form and then sintered at 900-100 °C for 10-12 hrs. In the phase II, the mixed powder was calcined and sintered by using a domestic microwave oven (Panasonic, Model NN-S554WF/MF) for 30, 60, 90, 120, 150 or 180 minutes. This oven is able to generate a maximum microawve power of 1100 W at an operating frequency of 2.45 GHz.

The X-Ray Diffraction (XRD) analysis was done to the calcined powder and different duration sintered pellets by using D8 Bruker diffractometer machine. Density and porosity of the samples were obtained by Archimedes method. The microstructures were investigated on the fracture surface of the sintered specimens using SEM (FE-SEM, Zeiss SUPRA 35VP). The electrical and dielectric properties (resistivity, dielectric constant and dielectric loss) of the sintered pellets were measured by using Agilent 4284A Precision LCR meter at 1 kHz frequency in ambient temperature. The samples for measuring electrical and dielectric properties were polished to ensure surface flatness and then painted with silver paste on both surfaces as electrodes.

RESULTS AND DISCUSSION

Figure 1 show the color transformation from black color (mixed raw materials powder) to yellow-brown of calcined CCTO powder and then change to a grey color after sintering process.

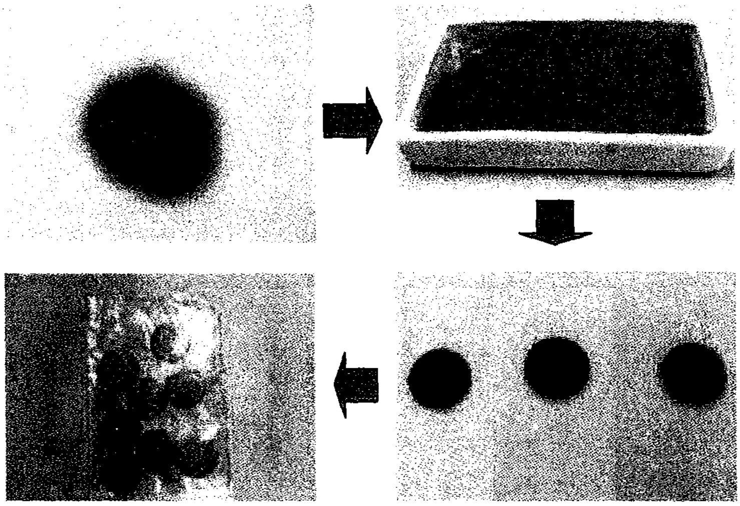

Figure 1. The color transformation from black color (mixed of raw materials powder) to yellow-brown (calcined CCTO powder) and then change to a grey color after completed sintering process.

Modified mechanical alloying

Electroceramic material of $CaCu_3Ti_4O_{12}$ was prepared using a modified mechanical alloying technique that covers several processes, which are preparation of raw material, mixing and ball milling for 5 hours, calcination, pellet forming and sintering. The objective of this modified technique is to enable the calcination and sintering processes to be carried out at a shorter time and lower temperature. The XRD analysis result shows that a single-phase of $CaCu_3Ti_4O_{12}$ was completely formed by calcination at 750 °C for 12 hours. Meanwhile, the grain size of a sample sintered at 1050 °C for 24 hours is extremely large which is in the range of 20-50 μm obtained from FESEM images. The dielectric constant value of 14,635 was obtained at 10 kHz by LCR meter in the sintered sample at 1050 °C. However, the dielectric constant value of samples sintered at 900 and 950 °C is quite low which is in the range of 52-119 [6].

Microwave-assisted sintering

Calcined and sintered powders were examined by XRD in order to investigate the phase formation of CCTO and the results are shown in Fig. 2. Fig. 2(b) shows XRD spectra of milled stoichiometric composition powder irradiated by microwave (MW) for 30 min. It was found that CCTO is not formed completely since only two small peaks 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. 2(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. 2(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. 2(e) and (f)). Almost all of the obtained peaks are coincided the reference pattern of CCTO (File no: 01-075-

2188, Fig. 2(a)). From this result, it can be seen that crystallinity and densification of CCTO pellet was improved by post-microwave sintering [7].

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 [8]. In this work, an alumina cup was used as susceptor might be not very good if compared to SiC [9]. 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. 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. Moreover, 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.

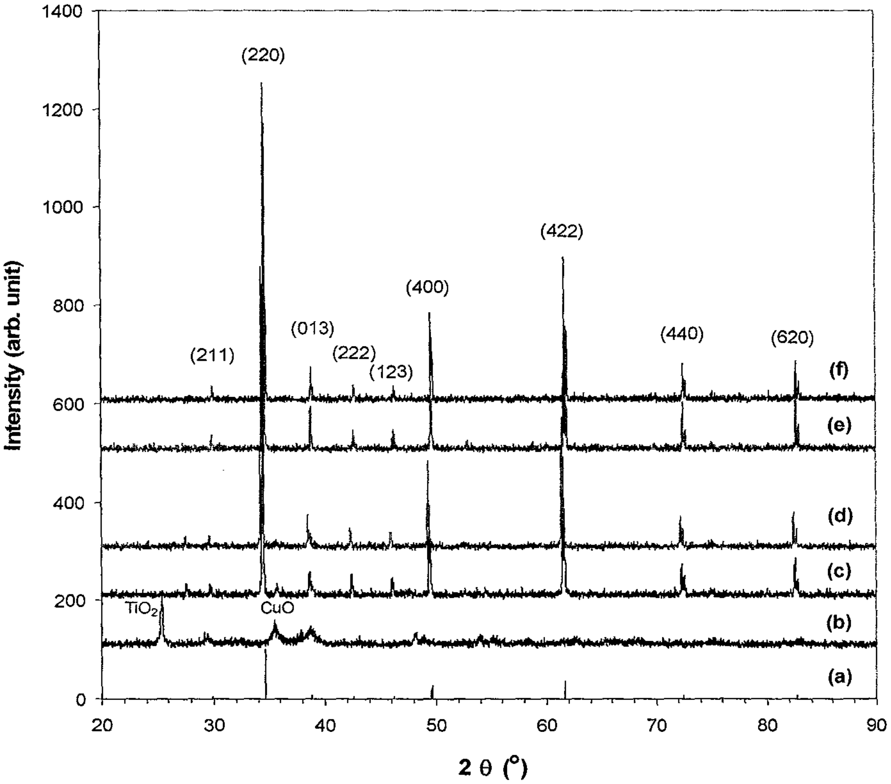

Fig. 2. XRD analysis results of (a) CCTO standard (File no: 01-075-2188), (b) milled stoichiometric raw materials and irradiated by full power MW for 30 min, (c) MW calcination for 90 min, (d) pressed pellet sintered by MW for 60 min, (e) furnace sintered 1000 °C/10 h, and (f) MW sintered for 30 min of pre-sintered pellet at 1000 °C/10 h.

Fig. 3 shows the effect of SnO_2 dopant concentrations on the dielectric constant and dielectric los higher dielectric constant values if compared to the samples without MW treatment.

These phenomena can be explained due to better densification and larger grain size of MW treated samples. Meanwhile, the SnO_2 addition gave strong effects on the dielectric constant of both without and with MW irradiated samples. The curve shown in Fig. 3(a) is indicating that dielectric constant decreased exponentially with increment of dopant concentration for both types of samples (MW treated and untreated).

The effect of MW treatment on the dielectric loss or dissipation factor of pure and SnO_2 doped CCTO are shown in Fig. 3(b). MW irradiated CCTOs have slightly better dielectric loss (lower dielectric value) if compared to samples without MW treatment. Fig. 3(b) also indicating an improvement on dielectric loss of CCTO by SnO_2 addition. Lower dielectric loss value is significant for samples doped with 4 and 6 mol% SnO_2. It is suggested that the optimum doping concentration to lower dielectric loss is at about 5 mol% for both untreated and MW treated samples. The lowest measured dielectric loss values were obtained as low as 0.06 for MW treated of 6 mol% SnO_2-doped CCTO and 0.10 for untreated of 4 mol% SnO_2-doped CCTO.

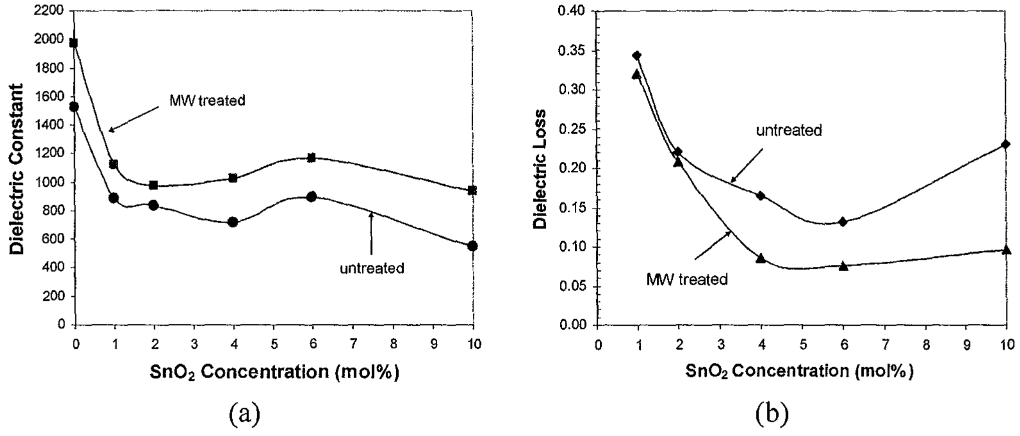

Fig. 3. Dielectric constant (a) and dielectric loss (b) versus SnO_2 dopant concentration of untreated and MW treated samples

Microwave processing (calcination and sintering)

Starting materials of $Ca(OH)_2$, CuO and TiO_2 have been weighted according to appendix A. The $Ca(OH)_2$-CuO-TiO_2 powders were mixtured and milled for 1 hour using alumina jar in ball milling process. Acetone had been added to ensure homogenous mixture were produced. The preparation of $CaCu_3Ti_4O_{12}$ continues with calcination process. Calcination had been done by microwave heating. Fig. 4 show the calcination process for 30 minutes in microwave. The microwave oven used in this study has power consumption of 1100 Watt with 2.45 GHz operation frequency. The power level chose in this study is high to ensure the susceptor has enough energy to heat the sample.

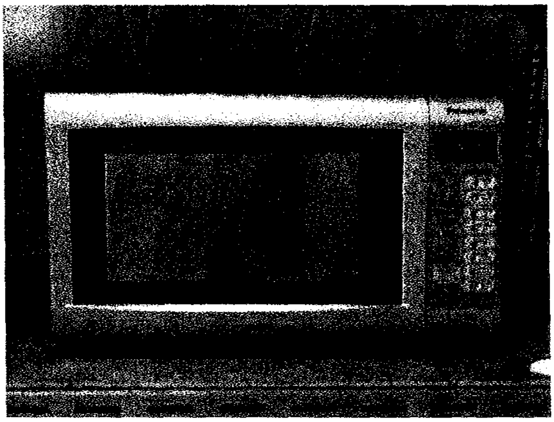

Fig. 4. Calcination process for 30 minutes in microwave processing

Since the alumina or graphite crucible produce incomplete calcinations process, it is important to find out another type of susceptor that able to absorb more microwave energy. Silicon carbide (SiC) was selected. Therefore, the next sample calcination was done by using SiC crucible as a susceptor. The crucible was placed in the middle of microwave cavity to ensure maximum exposure to the microwave radiation. The susceptor heats quickly, radiating heat to the sample and retain the heat. Radiant heat by the susceptor causes heating until the sample itself become absorber and heats.

XRD analysis had been done to a set of samples. Fig. 5 shows the combination of XRD patterns for $CaCu_3Ti_4O_{12}$ calcined powders in microwave oven using SiC susceptor. There are nine major belong to $CaCu_3Ti_4O_{12}$ appear in calcined powder. The calcined powder for 30 and 60 minutes did not shows any different peaks compared with the standard $CaCu_3Ti_4O_{12}$. Starting from calcination times of 90 to 180 minutes, the XRD patterns show additional peaks. This happened as a result of oxidation of SiC powders as the microwave heated to temperature above 1000 °C. The best time for calcination process in order to get single phase $CaCu_3Ti_4O_{12}$ calcined powders is 30 minutes because no secondary phase appear in the XRD result.

CONCLUSION

The modified mechanical alloying technique is enable the calcination and sintering process to be carried out in shorter time and lower temperature. Dielectric constant found increased by molarities percentage dopant of zinc. The increasing of dielectric constant is not consistent, as the $CaCu_3Ti_4O_{12}$ doped with 5 % Zn will give a lower dielectric constant value. However, the sample of $CaCu_3Ti_4O_{12}$ doped with 5 % Zn shows good dielectric loss properties, which is giving the lowest dissipation factor or the highest Q factor if compared to others doped CaCu3Ti4O12. Besides that, it also shows high resistance and low conductance value. Therefore, it can be concluded that by doping with certain amount of zinc dopant, the properties for dielectric and dielectric loss can be improved.

A denser single-phase CCTO product has been prepared by microwave-assisted sintering using a domestic microwave oven. Pellet obtained via this process possesses higher density and lower dielectric loss compared to those produced by the conventional route. A fully microwave processing CCTO using MW oven has also been produced.

The samples were calcined and then sintered in suitable susceptor using MW oven. Based on the phase analysis using XRD, single-phase $CaCu_3Ti_4O_{12}$ had been successfully synthesized at calcinations time of 30 minutes in microwave oven using SiC susceptor. Calcination also had been done at much higher time but the phase analysis using XRD shows secondary phases has been detected. Particle coarsening effect shown microwave heating led to wider particle size distribution; as a results, de-agglomeration stage must redone to the calcined powders. The dielectric constant is about 1387.321 at 1 kHz.

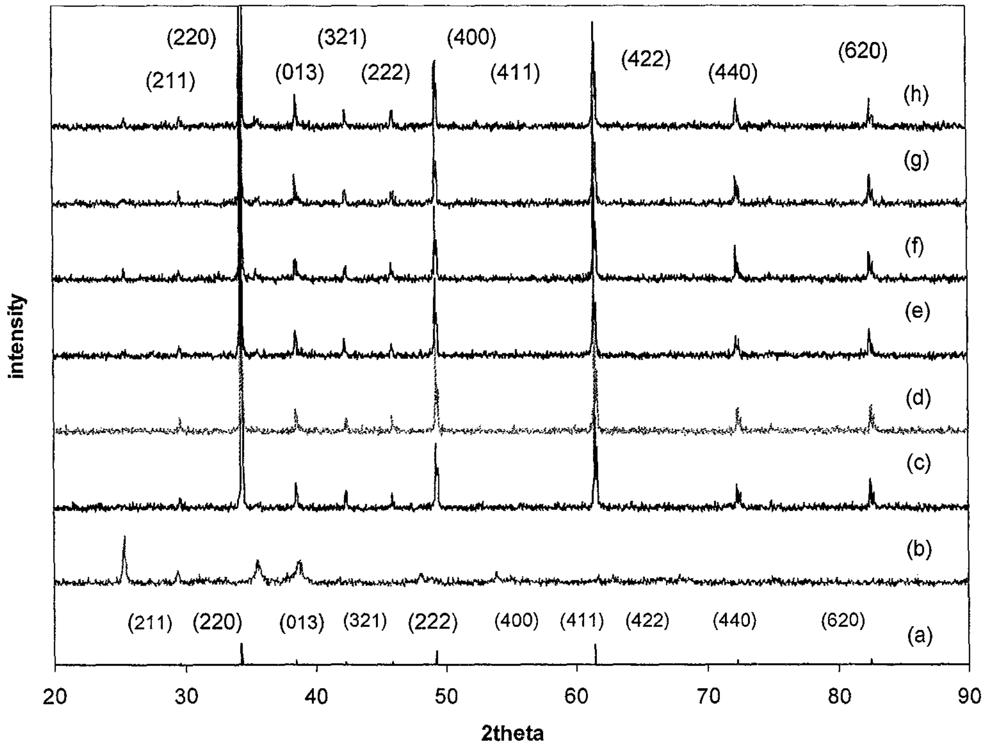

Figure 5. XRD patterns of $CaCu_3Ti_4O_{12}$ calcined using microwave oven with different time, (a) standard $CaCu_3Ti_4O_{12}$, (b) $Ca(OH)_2$-CuO-TiO_2 mixtures after milling, (c) MW heating for 30 min, (d) MW heating for 60 min, (e) MW heating for 90 min, (f) MW heating for 120 min, (g) MW heating for 150 min and (h) MW heating for 180 min.

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APPENDIX:

LIST OF PUBLICATIONS

1. S.D. Hutagalung, M.I.M. Ibrahim, Z.A. Ahmad, The role of tin oxide addition on the properties of microwave treated $CaCu_3Ti_4O_{12}$, Materials Chemistry and Physics (Elsevier), 2008 (in press).
2. S.D. Hutagalung, M.I.M. Ibrahim, Z.A. Ahmad, Microwave assisted sintering of $CaCu_3Ti_4O_{12}$, Ceramics International (Elsevier), 34 (2008) 939-942.
3. S.D. Hutagalung, Ooi L.Y, Z.A. Ahmad, Effect of sintering temperature on the properties of modified mechanical alloyed $CaCu_3Ti_4O_{12}$, IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control (IEEE, USA), 54 (2007) 2587-2591.
4. S.D. Hutagalung, J.J. Mohamed, Z.A. Ahmad, Lowering calcination temperature of $CaCu_3Ti_4O_{12}$ formation by modified mechanical alloying process, Emirates Journal for Engineering Research, 12 (2007) 61-64.
5. S.D. Hutagalung, M. Ikhwan M. Ibrahim, Z.A. Ahmad, Effect of Microwave treatment on the microstructure and dielectric properties of SnO_2-doped $CaCu_3Ti_4O_{12}$, Proceedings of the 16th IEEE International Symposium on Application of Ferroelectrics (ISAF 2007), Nara, Japan, 27-31 May (2007) 508-511.
6. S.D. Hutagalung, Ooi Li Ying, Z.A. Ahmad, Processing condition effects on the properties of $CaCu_3Ti_4O_{12}$ prepared by modified mechanical alloying technique, Proceedings of the 16th IEEE International Symposium on Application of Ferroelectrics (ISAF 2007), Nara, Japan, 27-31 May (2007) 512-515.

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The role of tin oxide addition on the properties of microwave treated $CaCu_3Ti_4O_{12}$

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ABSTRACT

A microwave (MW) irradiation process was performed to pre-sintered $CaCu_3Ti_4O_{12}$. A conventional furnace was used for calcination as well as for the sintering processes, whilst a domestic microwave oven was employed for MW irradiation in order to produce better morphology, improved phase structures and dielectric properties of $CaCu_3Ti_4O_{12}$ products. SEM analysis shows that the microstructures of MW irradiated samples are denser, with larger grain size if compared to the untreated samples. Dielectric properties also have been improved by MW treatment with higher dielectric constant and lower dielectric loss. Meanwhile, the addition of tin oxide (SnO_2) to $CaCu_3Ti_4O_{12}$ provides strong effects on the dielectric constant of both without and with MW irradiated samples. It was found that the dielectric constant of $CaCu_3Ti_4O_{12}$ decreases exponentially with mole percentages of SnO_2. However, the addition of SnO_2 shows better dielectric loss properties of $CaCu_3Ti_4O_{12}$.

1. Introduction

Some of ceramic compounds with perovskite structures are found to possess 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 [1]. CCTO is structurally similar to the more common perovskite, $CaTiO_3$. However, CCTO has attracted much interest because of its an anomalously large static dielectric constant, up to 10^5 at room temperature and remaining constant over a wide temperature range (100–350 K) [2] and also wide microwave (MW) frequency window [3,4]. The unique property of CCTO makes it a very promising material for applications in microelectronic and microwave device areas.

Although a lot of researches have been done to investigate the dielectric properties of CCTO, the nature of how CCTO represents such properties is still not well understood [5–8]. Some researchers claim that high value dielectric constant behavior comes from different factors, such as grain boundary, presence of twin boundaries or other planar defects, displacement of Ti ions, etc. [4,6]. But the real explanations of the phenomena are still under investigation.

There are many parameters that should be controlled to obtain CCTO electroceramics of good quality via conventional solid state reaction processing, i.e. calcination and sintering temperature, soaking time and atmosphere. It was stated by some researchers [9,10] that optimum sintering temperature and the time used to produce CCTO is 1100 °C for 24 h. However, it was found that microstructure and dielectric properties of CCTO are affected by sintering temperature and time. Sample sintered at 1050 °C for 24 h, results show the abnormal grain growth, the liquid phase and formation of large pores [11]. Therefore, it is important to apply a lower sintering temperature as well as a shorter soaking time, or to find out a new heat treatment technique to ensure procurement of the correct microstructure with better dielectric properties of CCTO.

Microwave irradiation is an attractive technique of material processing. Reasons for the growing interest in the use of microwave energy include rapid heating, enhanced densification rate, decreased sintering active energy and improved microstructure [12]. Microwave heating also has the potential for energy and cost savings when compared with conventional heating [13]. Electromagnetic waves interact with ceramic materials, leading to volumetric heating by dielectric loss. The power deposited in the ceramics is given by [14]

$$P = \omega\varepsilon_0\varepsilon_e''/E/^2 = \omega\varepsilon_0\left(\varepsilon'' + \frac{\sigma}{\omega\varepsilon_0}\right)/E/^2 \qquad (1)$$

where ε'' is the dielectric loss factor, representation of dipolar losses; σ the conductivity; ε_0 the permittivity of free space; ω the frequency; $\sigma/\omega\varepsilon_0$ presents conductive losses, E is the electric field. This technique has been employed by several researchers in order to produce dielectric ceramics [15–17], ferroelectrics [18,19], garnet, ferrite and spinel [20,21], semiconductor [22,23], superconductor

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[24], and solid oxide fuel cell (SOFC) materials [25] with very short processing time and high quality products.

In our previous work [26], it was found that the MW treated CCTO produces denser microstructures and slightly improved dielectric properties. In this study, tin oxide (SnO_2) was added as a doping agent with purpose to lower dielectric loss of CCTO.

2. Experimental procedures

The undoped and Sn-doped CCTO was prepared from starting materials of $CaCO_3$ (Aldrich, 99%), TiO_2 (Merck, 99%), CuO (Aldrich, 99%), and SnO_2 (Aldrich, 99%), as described in ref. [26]. Briefly, the raw materials were weighted according to the stoichiometric ratios and certain dopant concentration (1, 2, 4, 6, and 10 mol%) followed by wet ball milling in ethanol for 1 h. Milled powder was calcined at 900 °C for 12 h using a conventional electric furnace. Calcined powder was formed into pellet shapes of 12 mm in diameter and approximately 1.2 mm in thickness by applying a uniaxial pressure of 520 MPa using a stainless steel die. As-prepared green pellets were then sintered at 1000 °C and 1040 °C for 10 h in an ambient environment using a furnace. The samples doped with different concentrations of 1, 2, 4, 6, and 10 mol% SnO_2 were sintered at 1000 °C/10 h.

In order to study the effect of microwave (MW) treatment on the properties of CCTO, the pre-sintered pellets were irradiated by using a domestic microwave oven (Panasonic, Model NN-S554WF/MF). This oven is able to generate a maximum microwave power of 1100 W at an operating frequency of 2.45 GHz. In this process, the sample was put in a cup shaped alumina crucible and placed inside a quartz tube container, then positioned in the centre of the microwave cavity chamber. For the MW treatment process, the oven was operated at the full power condition for 60 min, followed by natural cooling in the oven. A shielded K-type thermocouple was attached to the sample for temperature sensing.

Phase formation of calcined powder was analyzed by XRD (Bruker D8). A field emission scanning electron microscopy (FESEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) (Zeiss SUPRA 35VP) was used for determination of microstructure and elemental composition of sintered samples. Dielectric properties (dielectric constant and loss) of pellets were measured using Agilent 4284A Precision LCR meter at a frequency of 1 kHz in ambient temperature.

3. Results and discussion

Heating profile generated inside the alumina crucible during MW irradiation is presented in Fig. 1. During the first 10 min, the heating rate of MW irradiation measured inside crucible is very high about 49 °C min^{-1}. However, after 20 min operation, the measured temperature is saturated at about 700 °C. It was suggested that alumina crucible has a limited capability to absorb MW power at certain level only due to its physical and electrical properties such as dielectric loss of material [17].

Fig. 2 shows XRD analysis result of calcined powder at 900 °C for 12 h. It was proved that the formation of single-phase structure of CCTO was completely formed. Five major peaks have been identified belonging to CCTO peaks, which overlapped with the reference pattern for standard CCTO file no. 01-075-2188.

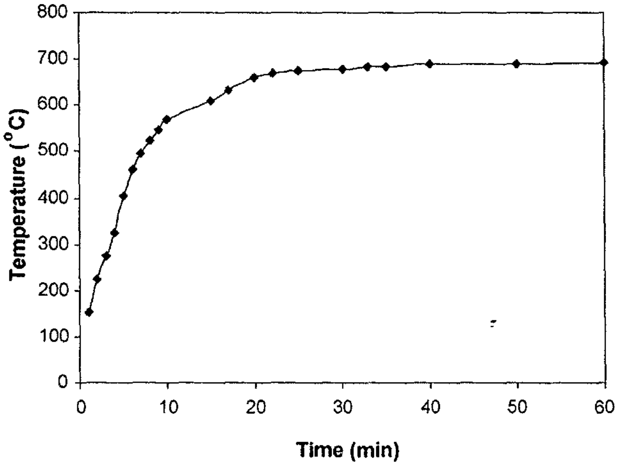

Fig. 1. Temperature profile recorded inside the crucible during MW irradiation.

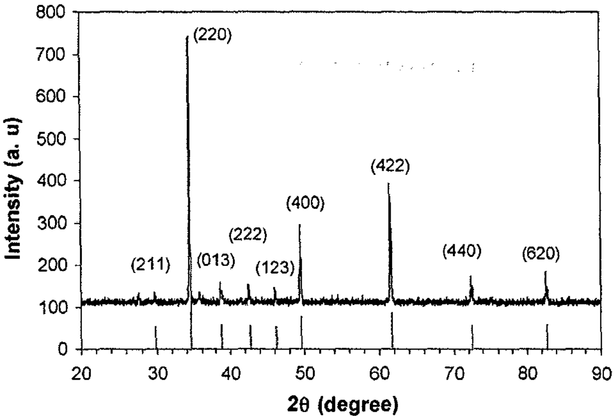

Fig. 2. XRD pattern of CCTO powder calcined at 900 °C for 12 h.

Fig. 3 shows FESEM images of surface and fracture of samples sintered at 1040 °C for 10 h using a conventional furnace. It was found that the grain boundary on the surface almost covered by melting component (Fig. 3(a)). The melting phase is expected belong to copper oxide compound as suggested in the previously reported [11]. However, there is no melting phase at the inside of microstructure (fracture) (Fig. 3(b)). Close observation on fracture

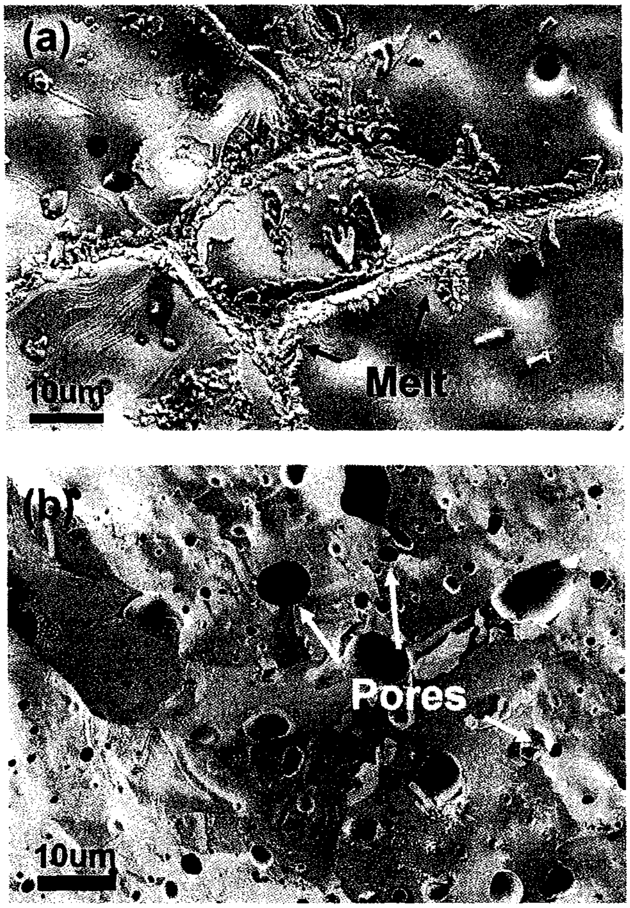

Fig. 3. FESEM images of surface (a) and fracture (b) of samples sintered at 1040 °C/10 h using a conventional furnace.

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found some pores. On the other hand, sample sintered at lower temperature (1000 °C for 10 h) shows a quite dense microstructure on surface as shown in Fig. 4(a). But, close observation to the interior (fracture) of sample revealed some porous area of microstructure as shown in Fig. 4(b). This is a disadvantage of conventional heating systems. In the conventional heating (i.e. furnace), the heating process starts from the outer surface towards the interior, which results in steep thermal gradients. The sample surface receives more heat than inside area of sample. That is a reason why a conventional furnace sometime produce melting component at the surface if sintered at high temperature, while interior of sample still having porous area.

The effect of MW treatment on the microstructure of undoped CCTO sample is shown in Fig. 5. The sample was pre-sintered at 1000 °C for 10 h using an electric furnace and followed by MW irradiation for 60 min. It was found that MW treated sample has larger grain size compared to the without MW treatment sample. The grain boundaries structure can be seen very clear on the MW treated sample as well as denser microstructure formation (Fig. 5(a)). Fracture (interior) image in Fig. 5(b) shows an improvement on density of sample. The porous area is significantly decreases when sample subjected to MW irradiation at the full power condition for 60 min. Therefore, it is suggested that the MW irradiation process can be used to assist uniformly growth of grains even at a deep level inside the bulk form of CCTO sample. The post-sintering by MW radiation also might be used as a thermal etching process to improve densification and grain boundary analysis. A reason why the MW process can be used to produce the uniform heating is because fundamentally it different from the conventional process in terms of its heating mechanism. In a MW oven, heat is generated within the sample volume itself by the interaction of microwaves with the material. MW energy heats the material on a molecular level, which leads to uniform heating, whereas, conventional heating systems heat the material from the outer surface towards the interior, which results in steep thermal gradients [16]. This is one of the advantages of the MW sintering process. However, in microwave processing, a suitable microwave cavity is needed to allow the transfer of microwave energy to the sample through the susceptor in an effective way [27].

Effects of SnO_2 addition on the microstructure of MW treated CCTO are shown in Fig. 6. A clear surface with relatively small grain size and some porous is observed in the sample doped 1 mol% as shown in the SEM micrograph of Fig. 6(a). There is no a significant additional phase of SnO_2 observed in this sample as the amount of dopant is very little. When the amount of dopant is increased to 4 and 6 mol%, some impurity particles randomly distributed at the grain boundary of CCTO as shown in Fig. 6(b) and (c), respectively. To investigate the elemental composition of CCTO, the EDX analysis was performed to the SnO_2 doped and MW treated samples. Fig. 7(a) shows EDX analysis on a grain of CCTO, whereas, Fig. 7(b) pointed on the impurity particle area. EDX analysis of grain CCTO shows only the raw material elements (Ca, Cu, Ti, and O) with

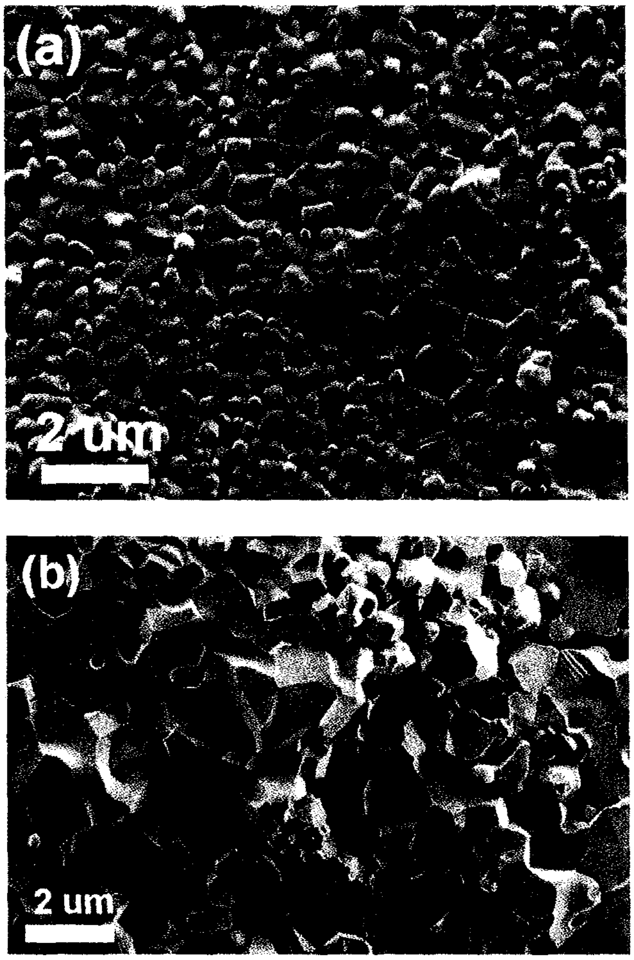

Fig. 4. FESEM images of surface (a) and fracture (b) of samples sintered at 1000 °C/10 h using a conventional furnace.

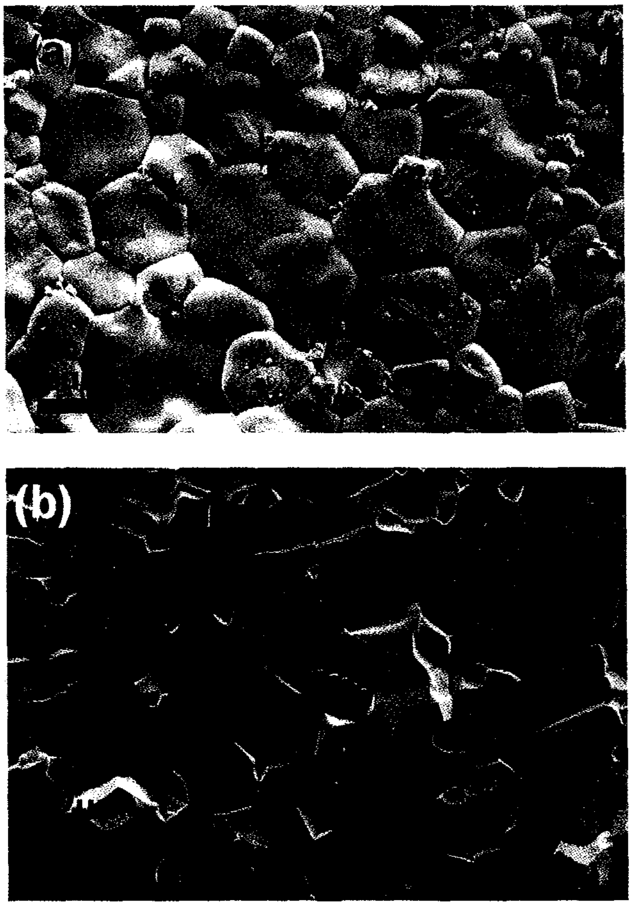

Fig. 5. FESEM images of surface (a) and fracture (b) of samples sintered at 1000 °C/10 h using a conventional furnace and followed by MW irradiation for 60 min.

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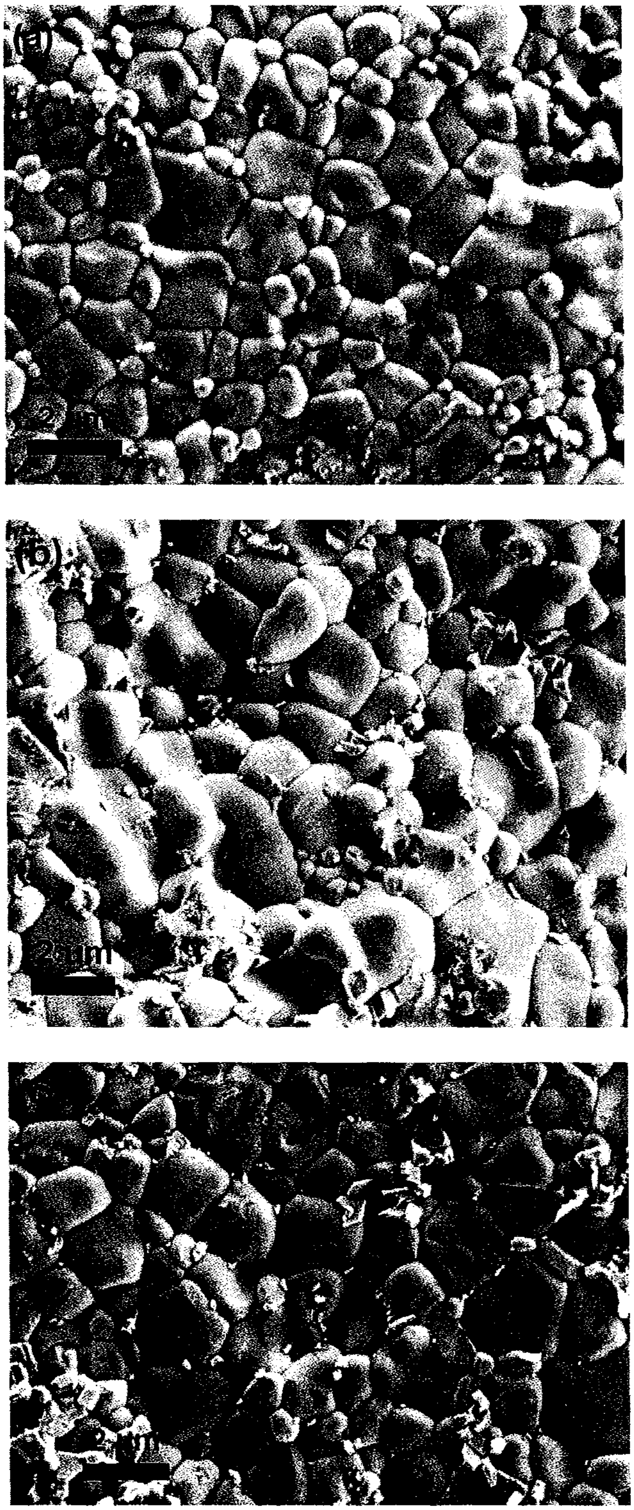

Fig. 6. SEM images of MW treated CCTO for 60 min with selected SnO$_2$ dopant concentrations of (a) 1 mol%, (b) 4 mol%, and (c) 6 mol%.

composition close to stoichiometric ratios (Fig. 7(a)). However, in the selected area of impurity, copper (46.40 at%) and oxygen (52.32 at%) were detected as the major components (Fig. 7(b)). Besides, a little amount of Ti (1.28 at%) was detected co-exist with copper and oxygen. Therefore, it is suggested that additional of SnO$_2$ to CCTO tends to stimulate the melting process of Cu component and formed secondary phase of CuO or Cu$_2$O.

Fig. 8 shows the effect of SnO$_2$ dopant concentrations on the dielectric constant of untreated and MW treated CCTO pellets. In this case, the samples were pre-sintered at 1000 °C for 10 h using a conventional furnace. The pre-sintered of CCTOs followed by MW treatment for 60 min have slightly higher dielectric constant values if compared to the samples without MW treatment. This phenomenon can be explained due to better densification and larger grain size of MW treated samples. Meanwhile, the SnO$_2$ addition gave a strong effect on the dielectric constant of both without and with MW irradiated samples. The curve shown in Fig. 8 is indicating that dielectric constant decreased exponentially with increment of dopant concentration for both types of samples (MW treated and untreated).

One of the main problems in CCTO is its high dielectric loss value. Therefore, some researchers have paid much attention to solve this problem and a lot of attempts have been done to produce low dielectric loss CCTO. The most approach is by doping process using a suitable element or compound such as La-doped CCTO [28]. That is a reason why, in this work, we attempt to lower dielectric loss value of CCTO by doping with SnO$_2$.

The effect of MW treatment on the dielectric loss or dissipation factor of pure and SnO$_2$ doped CCTO are shown in Fig. 9. MW

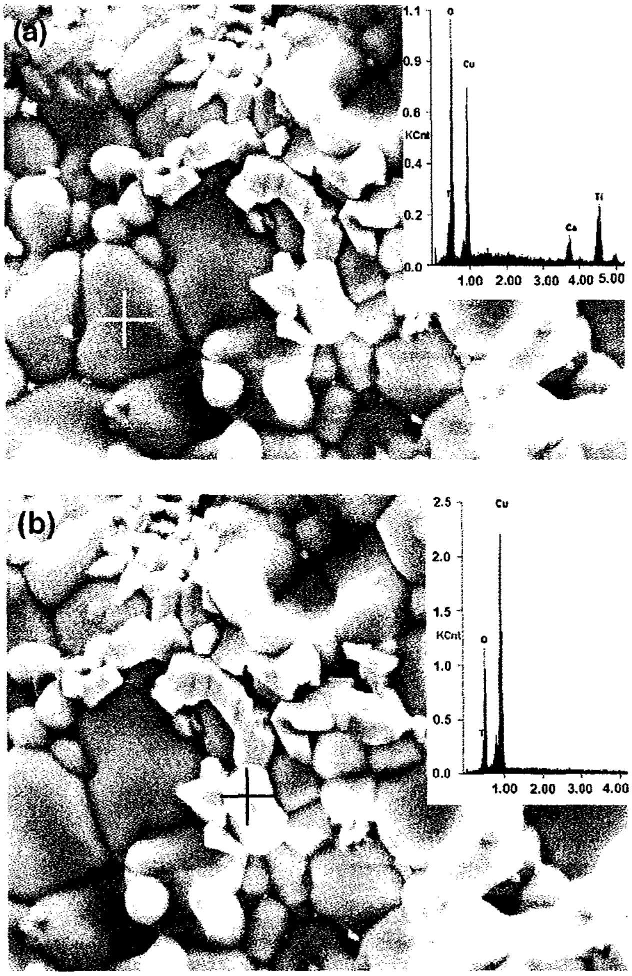

Fig. 7. EDX analysis of MW treated CCTO for 60 min with 2 mol% SnO$_2$ dopant. EDX was performed on the (a) grain area (O = 58.34, Cu = 14.95, Ca = 0.5, Ti = 20.91 at%), and (b) impurity particle area (O = 52.32, Cu = 46.40, Ti = 1.28 at%).

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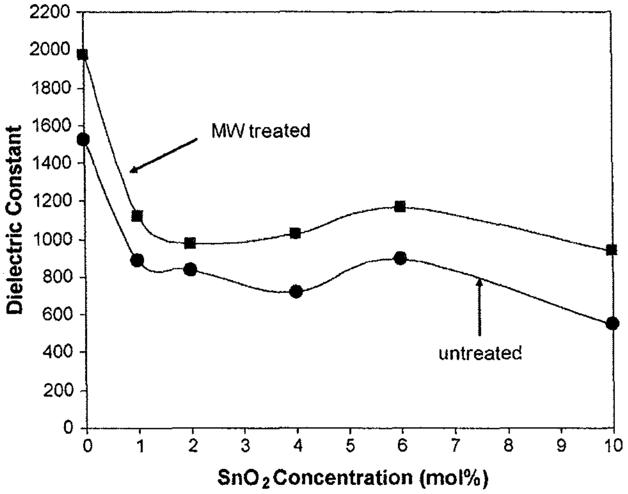

Fig. 8. Dielectric constant versus SnO_2 dopant concentration of untreated and MW treated samples.

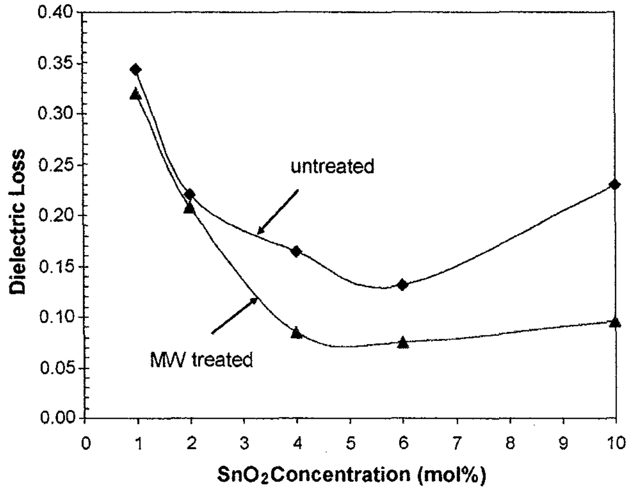

Fig. 9. Dielectric loss versus SnO_2 dopant concentration of untreated and MW treated samples.

irradiated CCTOs have slightly better dielectric loss (lower dielectric value) if compared to samples without MW treatment. Fig. 9 also indicating an improvement on dielectric loss of CCTO by SnO_2 addition. Lower dielectric loss value is significant for samples doped with 4 and 6 mol% SnO_2. It is suggested that the optimum doping concentration to lower dielectric loss is at about 5 mol% for both untreated and MW treated samples. The lowest measured dielectric loss values were obtained as low as 0.06 for MW treated of 6 mol% SnO_2-doped CCTO and 0.10 for untreated of 4 mol% SnO_2-doped CCTO.

From FESEM observation it was found that the MW treated CCTO produce bigger and denser microstructures (Fig. 5). The porous area of sample is significantly decreases when sample subjected to MW irradiation, which is uniformly growth of grains even at a deep level inside the bulk form of CCTO sample. Therefore, the MW irradiated CCTOs have lower dielectric loss if compared to untreated samples. Meanwhile, the role of Sn dopant on the dielectric loss behavior of CCTOs is suggested due to the increase of conductivity in the CCTO grain/subgrain. A similar phenomenon was found on La-doped CCTO [28].

4. Conclusion

A denser microstructure and better dielectric loss of CCTO can be produced by microwave treatment of pre-sintered sample using a domestic microwave oven irradiation. The results show the higher dielectric constant and lower dielectric loss have been obtained in the MW irradiated samples. Addition of SnO_2 dopant to CCTO was found tend to improve dielectric properties (lowering dielectric loss). Therefore, it is suggested that combination of the MW treatment and SnO_2 doping processes can be applied to improve the microstructures and dielectric properties of CCTO.

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Effect of Sintering Temperature on the Properties of Modified Mechanical Alloyed $CaCu_3Ti_4O_{12}$

Sabar D. Hutagalung, Ooi Li Ying, and Zainal Arifin Ahmad

***Abstract*—This paper presents the effects of calcination time and sintering temperature on the properties of $CaCu_3Ti_4O_{12}$. Electroceramic material of $CaCu_3Ti_4O_{12}$ was prepared using a modified mechanical alloying technique that covers several processes, which are preparation of raw material, mixing and ball milling for 5 hours, calcination, pellet forming and, sintering. The objective of this modified technique is to enable the calcination and sintering processes to be carried out at a shorter time and lower temperature. The x-ray diffraction (XRD) analysis result shows that a single-phase of $CaCu_3Ti_4O_{12}$ was completely formed by calcination at 750°C for 12 hours. Meanwhile, the grain size of a sample sintered at 1050°C for 24 hours is extremely large, in the range of 20–50 μm obtained from field emission scanning electron microscopy (FESEM) images. The dielectric constant value of 14,635 was obtained at 10 kHz by impedance (LCR) meter in the sintered sample at 1050°C. However, the dielectric constant value of samples sintered at 900 and 950°C is quite low, in the range of 52–119.**

I. Introduction

With the shrinking of dimensions of microelectronic devices, high dielectric constant materials have been playing a significant role in microelectronics because they can be used as important devices such as dynamic random access memory (DRAM) based on capacitive elements. The complex perovskite compound $CaCu_3Ti_4O_{12}$ (CCTO) has recently attracted considerable attention in view of its anomalously large dielectric response. Low-frequency studies uncovered dielectric constants up to 80,000 that are nearly constant over a wide temperature range (100–600 K) [1], [2]. This unique property makes CCTO a promising material for capacitor applications and certainly for microelectronics, microwave devices (cell mobile phones for example). Moreover, above a critical frequency that ranges between 10 Hz and 1 MH, the dielectric constant value depends on temperature [3]. The highest value of dielectric constant expected can be obtained during a phase transition as a function of temperature. Most of the CCTO studies have been performed on bulk materials (ceramics or single crystals) and focused on the identification of the mechanism responsible for unusual CCTO properties [4]-[6].

The mechanical alloying technique has been used t produce CCTO by using two different experimental procedures [1]. Although this technique is able to produc nanocrystalline powders of CCTO, the process needs very long milling time, up to 100 hours to obtain a single phase of CCTO formation. However, a conventional soli state reaction technique is one of the most promising techniques in preparing CCTO, but again, this process need a high calcination temperature, normally in the range o 900–1100°C. To solve these problems, in this work a combination of mechanical alloying and solid state reactio was used to produce a single-phase CCTO at lower temperature and shorter time of process.

II. Methodology

The starting materials of $Ca(OH)_2$ (Aldrich, 99%), Cu (Aldrich, 99%), and TiO_2 (Merck, 99%) powders wer weighed according to the stoichiometric ratios. Mixed powders were subjected to a fast ball milling (1500 rpm) i a sealed alumina vial using zirconia balls under ambien condition for 5 hours. The milled powder was put into a alumina crucible, then calcined at 750°C in air for 6, 9 12, 18, and 24 hours, respectively. The calcined powde was reground and pressed into pellets 12 mm in diamete and 1 mm in thickness using a stainless steel die set. Pellets were sintered in air at 900, 950, and 1050°C with soaking time of 24 hours, respectively.

Phase analysis was conducted on calcined powders b XRD analysis (Bruker D8, Germany). Surface and fractur morphology were investigated by field emission scannin electron microscopy (FESEM) (SUPRA 35VP, Zeiss, Germany), and dielectric properties measured using Agilen 4284A Precision LCR meter (Agilent Technologies, Inc. Santa Clara, CA) at a frequency of 100 Hz to 1 MHz i ambient temperature.

III. Results and Discussion

The calcined powder was examined by XRD in order t investigate the phase formation of $CaCu_3Ti_4O_{12}$ (CCTO) result is shown in Fig. 1. The CCTO compound was completely formed. There are three main and five small peak

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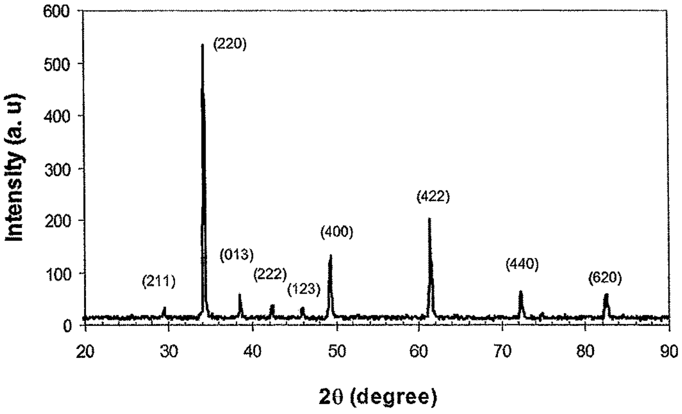

Fig. 1. XRD pattern of calcined powder at 750°C for 12 hours.

of (220), (400), (422), (211), (013), (222), (440), and (620) that overlap with the reference patter of CCTO. The result shows that calcination at 750°C for 12 hours, is enough to form single-phase CCTO via the modified mechanical alloying technique. It is very interesting, because this calcination temperature is much lower if compared to a conventional solid state reaction method. Finer particle size (about 200 nm) after the milling maybe contributes in lowering the calcination temperature. Mostly, calcination temperature used to form single-phase CCTO by a conventional solid state reaction technique is in the range of 900-1100°C [7]–[12].

The microstructure of sintered pellets was observed using a FESEM in order to understand the grain-boundary formation. Fig. 2 shows FESEM images on the surface of CCTO pellets sintered at 900, 950, and 1050°C for 24 hours, respectively. The sample sintered at 900°C is not dense. The microstructure consists of fine grain size and high porosity. The sample sintered at 950°C shows a quite dense microstructure, even though the grain size is still fine and some pores appear on the surface. However, the sample sintered at 1050°C experienced an over-grain growth, which starts to destroy the grain boundaries that may be due to the high sintering temperature. The similar overgrowth phenomenon due to a high temperature sintering process also was observed in the CCTO prepared by the conventional solid state reaction method [9].

Fig. 3 shows the SEM images on the fracture area of CCTO pellets sintered at 900, 950, and 1050°C for 24 hours, respectively. Fig. 3(a) shows very rough and high porosity inside the sample (fracture) sintered at 900°C. It can be suggested that a sintering process at 900°C is not enough to form a dense structure. For CCTO sintered at 950°C and 1050°C, very clear grain boundaries can be seen [Fig. 3(b) and (c)]. The grains of CCTO grow and connect with each other to form very dense structures [Fig. 3(c)]. There is a melting component on the surface and fracture as shown in Figs. 2(c) and 3(c).

Fig. 4 shows the elemental composition of sintered CCTO pellet, which are 4.05 atomic percent Ca, 15.2 atomic percent Cu, 17.69 atomic percent Ti, and 63.96 atomic percent O. Energy dispersive x-ray (EDX) anal-

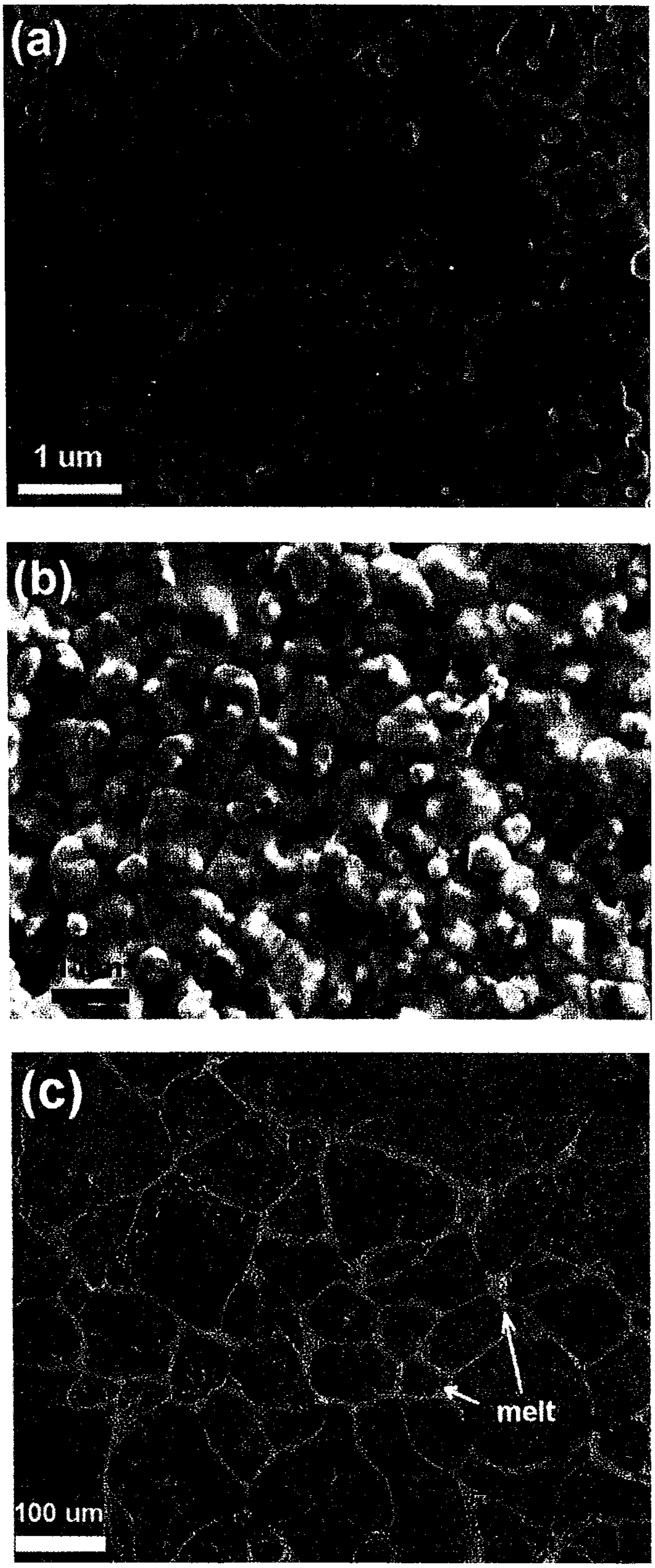

Fig. 2. FESEM images of sample surfaces sintered at (a) 900°C, (b) 950°C, and (c) 1050°C for 24 hours, respectively.

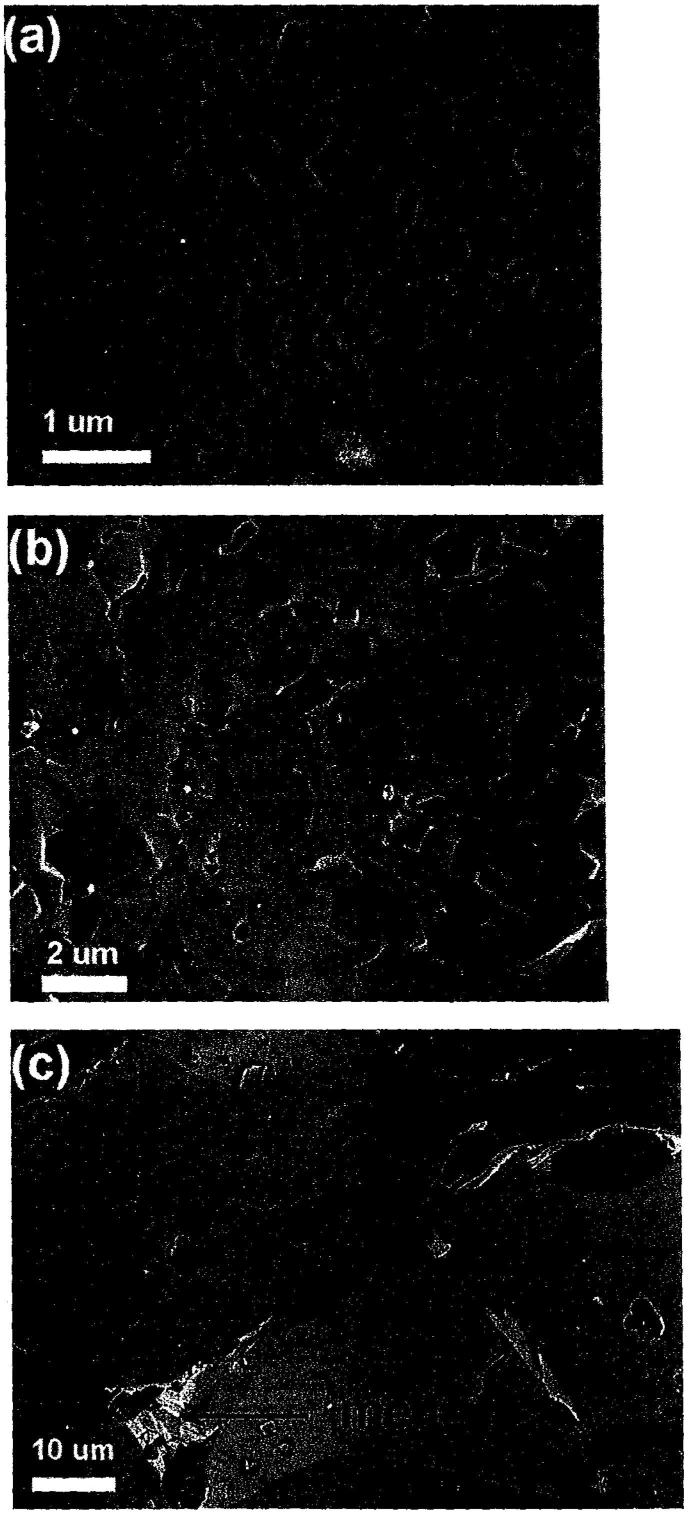

Fig. 3. FESEM micrographs of the fracture sintered pellets at (a) 900°C, (b) 950°C, and (c) 1050°C for 24 hours, respectively.

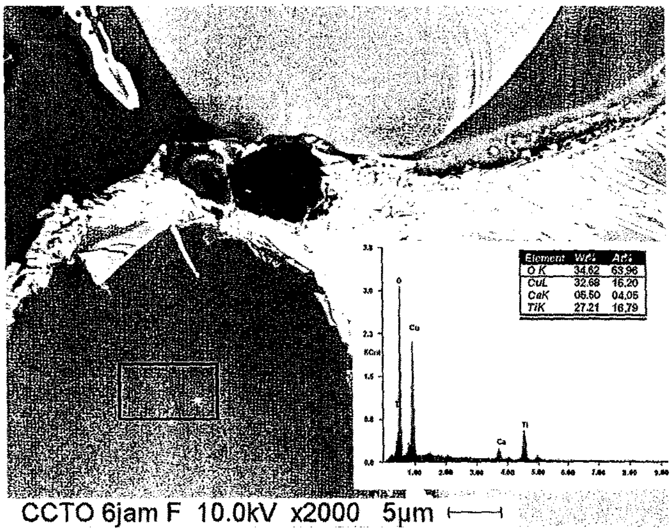

Fig. 4. EDX analysis of sintered pellet CCTO obtained elementa composition of 4.05 atomic percent Ca, 15.2 atomic percent Cu, 17.6 atomic percent Ti, and 63.96 atomic percent O.

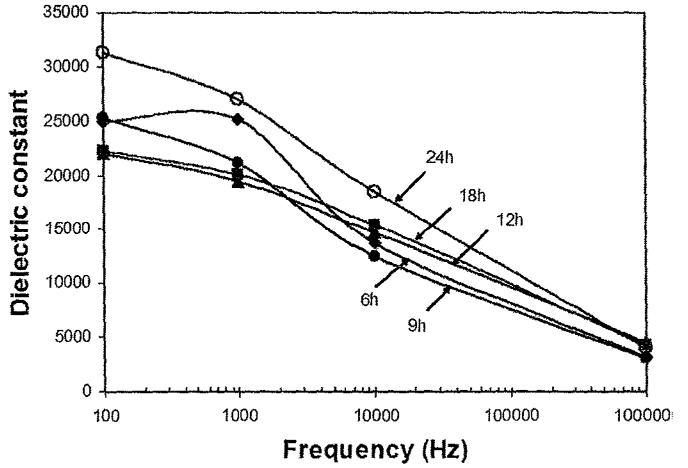

Fig. 5. Dielectric constant plotted against frequencies for differen calcination times of 6, 9, 12, 18, and 24 hours, respectively. Pellet were sintered at 1050°C for 24 hours.

ysis (Fig. 4) confirmed that the system is free from th contamination of alumina or zirconia.

The effects of calcination duration on the dielectri properties of sintered pellets at 1050°C for 24 hours wer investigated via capacitance measurement at different frequencies of 100 Hz, 1 kHz, 10 kHz, and 1 MHz. Fig. 4 show a graph for dielectric constant plotted against frequencie for sintered pellets formed from CCTO powders with different calcination times of 6, 9, 12, 18, and 24 hours. Th curves show that the dielectric constant slightly increase with prolonged calcination time in which the sample calcined for 24 hours is given the highest value. A very clea picture of the time dependent of dielectric constant valu measured at 10 kHz frequency is shown in Fig. 5. This phenomena is related to the microstructure condition of th sample in which higher calcination times exhibit dense microstructures.

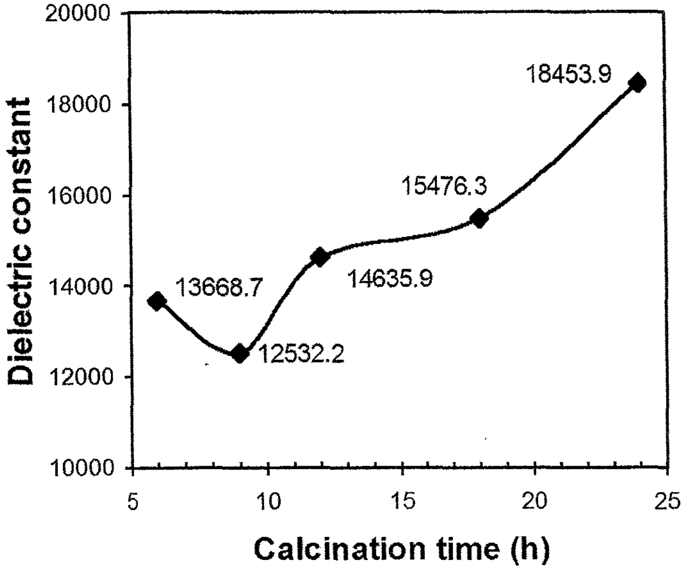

Fig. 6. Dielectric constant value as function calcination time measured at 10 kHz.

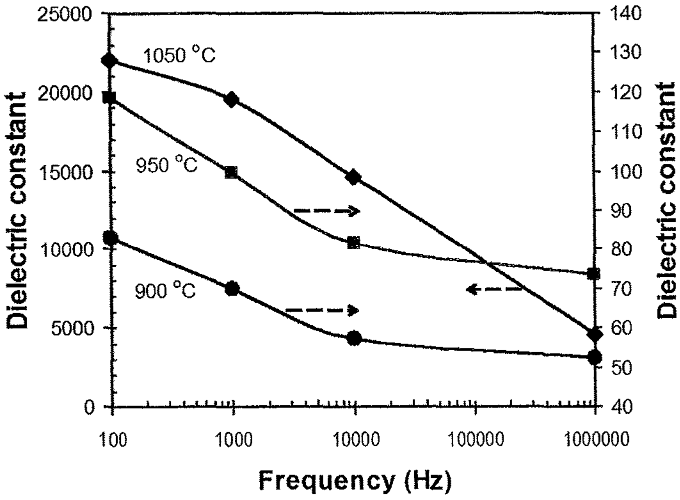

Fig. 7. Dielectric constant versus frequency of calcined samples at 750°C for 12 hours and sintered 24 hours at 900, 950, and 1050°C, respectively.

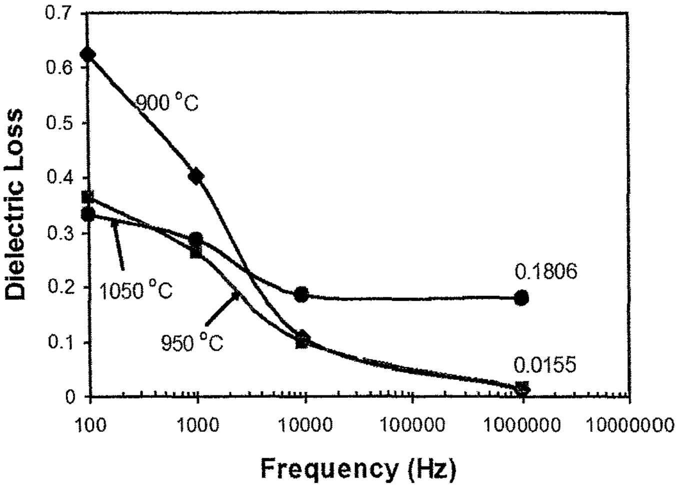

Fig. 8. Dielectric loss measured at different frequencies for samples sintered 24 hours at 900, 950, and 1050°C, respectively.

Fig. 4 shows the effect of frequency on the dielectric constant in which the dielectric constant decreases exponentially to higher frequency. This phenomena can be explained by mechanisms of polarization that have varying time response capabilities to an applied field frequency, and polarization contributes to the dielectric constant. Electronic displacement responds rapidly to the field reversals, and no lag of the polarization contribution occurs at a higher frequency. At a high frequency, the ionic displacement begins to lag the field reversals, increasing the loss factor and contributing less to the dielectric constant.

The effect of sintering temperature on dielectric properties of CCTO is shown in Figs. 6 and 7. It is found that the dielectric constant of a pellet sintered at 1050°C is much higher than both samples sintered at 900 and 950°C. At a frequency of 10 kHz, the dielectric constant value of 18,453 was obtained for the sample sintered at 1050°C. But for the sample sintered at 900 and 950°C, it is only about 57 to 81 (Fig. 6). As was mentioned earlier, this effect mostly came from the grain-boundary condition of the sample. It was found that the sample sintered at 900°C shows incomplete grain growth, but a dense microstructure with abnormal grain growth was observed on the sintered sample at 1050°C. The dielectric constant value for the sample sintered at 1050°C was in good agreement with those reported earlier [4], [5], [10].

The dielectric loss is closely related to the mechanism of the dielectric response. One of the most widely accepted models is the internal-barrier-layer-capacitance (IBLC) model. This model suggests that the dielectric loss mainly originates from the conductivity of the CCTO conducting crystalline grains/subgrains as well as that of the insulating barriers [4]. The conductance of the barriers leads to the leakage loss.

In general, CCTO exhibits a very high dielectric constant value, which is desirable for many microelectronic applications. However, the dielectric loss of this material is relatively high. Therefore, some attempts have been made by many researchers to produce CCTO with low dielectric loss value.

Fig. 8 shows the effects of sintering temperature on the dielectric loss of CCTO measured at different frequencies. At a lower frequency (100 Hz), the dielectric loss value is very high (0.3318 to 0.6246) and the sample sintered at 1050°C is the lowest. However, at a higher frequency (1 MHz), the value decreases to 0.181, 0.0155, and 0.0133 for samples sintered at 1050, 950, and 900°C, respectively. From Figs. 6 and 7, samples with low dielectric constant values (samples sintered at 900 and 950°C) gave better dielectric loss property at higher frequencies. Dielectric loss of CCTO can be reduced by doping with zinc [13] as well as La-doped CCTO [8].

IV. CONCLUSIONS

A modified mechanical alloying technique is a promising technique that enables the calcination process of CCTO formation carried out at shorter durations and lower temperatures (750°C for 12 hours). In this work, the highest dielectric constant value of about 15,000 at 10 kHz was obtained in the sample sintered at 1050°C. However, the dielectric loss of this sample is relatively high, about 0.186 compared to 0.099 for the lower sintered samples. At the higher measurement frequency (1 MHz), the sample sintered at 900°C for 24 hours gave a better dielectric loss value of 0.0133 followed by 0.0155 and 0.1806 for the samples sintered at 950°C and 1050°C, respectively.

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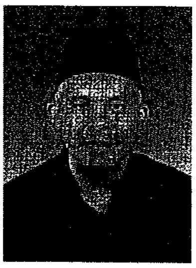

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Microwave assisted sintering of $CaCu_3Ti_4O_{12}$

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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

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-15], ferroelectrics [16,17], garnet and spinel [18–21], iconductor [22,23], superconductor [24], and solid oxide cell (SOFC) materials [25] with very short time processing high quality products. For example, a MW-assisted bustion synthesis has emerged as an attractive technique he production of homogeneous, high-purity, and crystalline l_2O_4 spinel oxide powders at significantly lower tem- tures, shorter time periods and using less amount of rnal energy as well [20].

ıs the MW sintering of CCTO has not been well explored, e is a possibility to apply this technique for the processing ı electroceramic materials. Therefore, in this work, an npt has been made to prepare CCTO by MW-assisted ering route using a modified domestic microwave oven. e importantly, a domestic microwave oven provides pensive multi-mode cavities that can be used for sintering ess of advanced materials with a simple procedure.

xperimental procedure

he CCTO was prepared from starting materials of $CaCO_3$ lrich, 99%), TiO_2 (Merck, 99%), CuO (Aldrich, 99%), and $)_2$ (Aldrich, 99%). The raw materials were weighed rding to the stoichiometric ratios to form pure CCTO. mixed powders were wet ball milled for 1 h using ethanol. milled powder was subjected to calcination process at °C with soaking time of 12 h using a furnace (Carbolite F 1300). Disc shaped specimens of 12 mm in diameter and roximately 1.2–1.5 mm in thickness were formed from ined powder by a uniaxial pressure of 520 MPa. Green ets were subjected to sintering process by electrical furnace 00 °C for 12 h and 1000 °C for 10 h in air (conventional ering). Meanwhile, MW-assisted sintering process was e by using a domestic microwave oven (Panasonic, Model -S554WF/MF). This oven is capable of generating rowave power from 0 to 1100 W at operating frequency .45 GHz. In this process, samples were put in alumina ible and placed inside a quartz container, and then itioned in the centre of microwave cavity chamber. For sintering processes, the oven was operated at full power for 60, 90, 120 and 150 min, respectively.

he samples were analyzed by XRD (Bruker D8), field ssion scanning electron microscopy (FESEM), and EDX iss SUPRA 35VP) for determination of phase structures, rostructures and elemental compositions, respectively. lectric properties (dielectric constant and loss) of the ered pellets were measured using an Agilent 4284A ision LCR meter at frequency of 1 MHz in ambient perature.

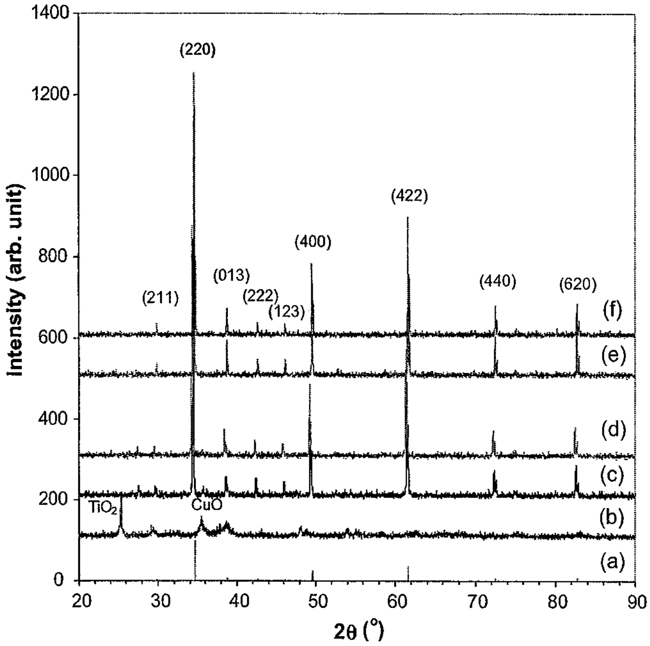

Fig. 1. XRD analysis results of (a) CCTO standard (File no: 01-075-2188), (b) milled stoichiometric raw materials and irradiated by full power MW for 30 min, (c) MW calcination for 90 min, (d) pressed pellet sintered by MW for 60 min, (e) furnace sintered 1000 °C/10 h, and (f) MW sintered for 30 min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

Results and discussion

alcined and sintered powders were examined by XRD in r to investigate the phase formation of CCTO and the ılts are shown in Fig. 1. Fig. 1(b) shows XRD spectra of led stoichiometric composition powder irradiated by rowave (MW) for 30 min. It was found that CCTO is not 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)).

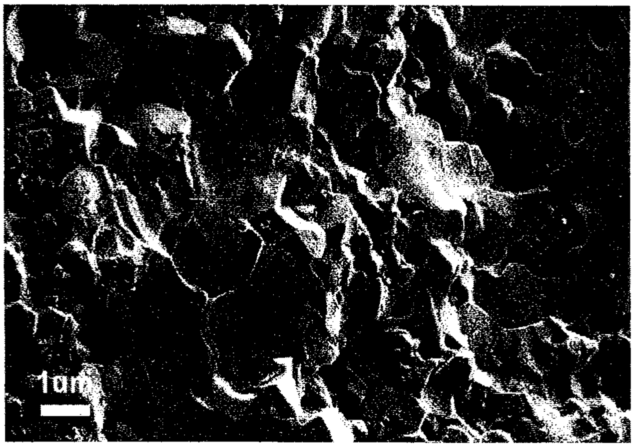

Fig. 2. FESEM image (fracture) of sample sintered at 1000 °C/10 h using a conventional furnace.

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.

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.

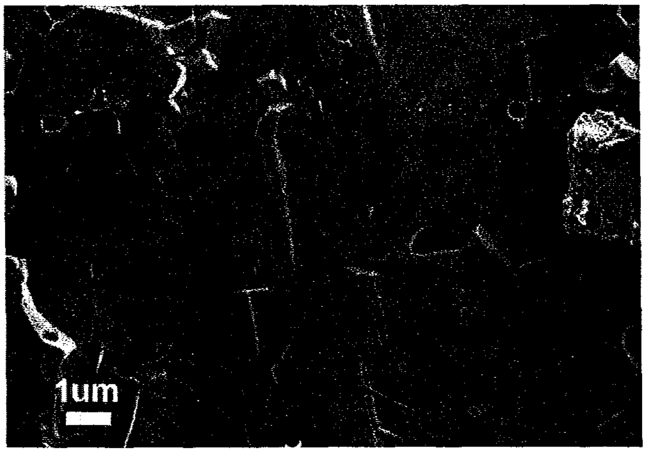

Fig. 4. FESEM image (fracture) of MW sintered of CCTO for 120 min.

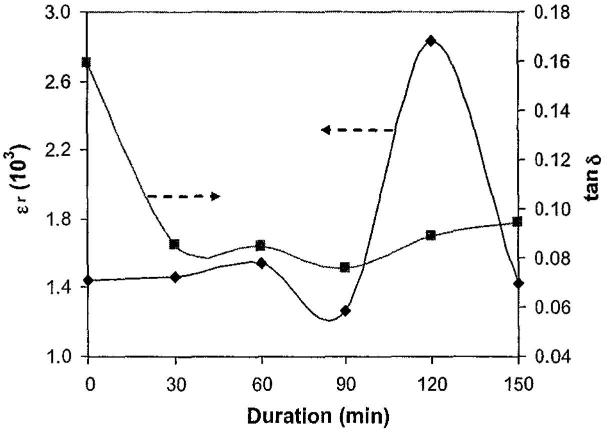

Fig. 5. Effect of MW sintering duration on the dielectric constant and dielectric loss of CCTO.

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.

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(Regular Paper)

LOWERING CALCINATION TEMPERATURE OF $CaCu_3Ti_4O_{12}$ FORMATION BY MODIFIED MECHANICAL ALLOYING PROCESS

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كثيراً من التقارير البحثية لباحثين كثيرين تمت عن مركبات الـ CCTO ذات بنية مجهريه من نوع Perovskite-type ليوضحوا قيمة معامل عزل كهربي عالي جداً وعدم اعتماد على درجة الحرارة خلال مجال واسع من درجات الحرارة. في هذا البحث تم إعداد الـ CCTO بواسطة تقنية خلط ميكانيكي معدلة وهى عبارة عن مزيج من إجرائيين. طحن وتفاعل حالة صلبة. مواد البداية عبارة عن مسحوق من هيدوكيسد الكالسيوم $Ca (OH)_2$ وأكسيد النحاس CuO وثاني أكسيد التيتانيوم $Ti O_2$ وزنت طبقاً لنسبة الـ Stoichiometric وخلطت معاً وتبع ذلك بطحن سريع في قارورة الومينا محكمة تحت ظروف جوية محيطة لمدة 5 ساعات. المساحيق المطحونة تم تعريضها لإجراء تكلس عند درجات حرارة 600, 700, 800 و 900 (درجة مئوية) في الهواء لمدة 12 ساعة على الترتيب. المساحيق البنية-الصفراء المكلسة تم ضغطها على شكل قرض كروي باستخدام قالب صلب فولازى. الحجم المتوسط للعينات بقطر 6 مم وسمك 1مم. الحبات الكروية المعدة تم تلبيدها في الهواء عند درجة حرارة 1050 C ووقت تشبع 24 ساعة. تحليلات الطور تم إجراؤها على المساحيق المكلسة والحبات الكروية الملبدة باستخدام تحليل XRD. نتائج XRD أوضحت أن CCTO طور مفرد تكون بنجاح في العينات المكلسة عند °C 700-900. البنية البلورية تحسنت بعد التكليس عن 1050 °C لمدة 24 ساعة. قيمة ثابت العدل الكهربائي لحبيبات الـ CCTO المكلسة تم الحصول عليها حتى 11,903.

$CaCu_3Ti_4O_{12}$ (CCTO) compounds with a perovskite-type structure have been reported by many researchers to show a very high dielectric constant value and temperature independence over a wide temperature range. In this work, the CCTO were prepared by modified mechanical alloying technique, which is a combination of a ball milling and solid state reaction processes. The starting materials of $Ca(OH)_2$, CuO and TiO_2 powder were weighed according to the stoichiometric ratio, mixed together and follow by fast ball milling in sealed alumina vial under ambient condition for 5 hours. The milled powders were subjected to calcination process at 600, 700, 800 and 900 °C in air for 12 hours, respectively. The yellow-brown calcined powders were then pressed into pellet disc shape using a stainless steel die set. Average size of the samples is 6 mm in diameter and 1 mm in thickness. The prepared pellets were sintered in air at 1050°C and soaking time of 24 hours. Phase analysis was conducted on the both calcined powders and sintered pellets by using XRD analysis. The XRD pattern results, showed, that a single phase CCTO was successfully formed in the samples that were calcined at 700-900 °C. The crystalline structure was improved after sintering at 1050 °C for 24 hours. Dielectric constant value of CCTO sintered pellets was obtained up to 11,903.

Keywords: CCTO, high-dielectric constant, modified mechanical alloying

1. INTRODUCTION

The complex perovskite compound $CaCu_3Ti_4O_{12}$ (CCTO) has recently attracted considerable attention in view of its anomalously large dielectric response. Low-frequency studies uncovered dielectric constant up to 10,000 for ceramics and 80,000 for single-crystal samples that are nearly constant over a wide temperature range (100-600 K). This unique property makes CCTO a promising material for capacitor applications and certainly for microelectronics, microwave devices (cell mobile phones for example)[1,2]. Moreover, above a critical frequency in the range between 10 Hz and 1 MH, dielectric constant value is dependent on temperature[3]. The highest value of dielectric constant expected is obtained during a phase transition as a function of temperature.

With the shrinking of dimensions of the microelectronic devices, high dielectric constant materials are playing a significant role in microelectronics, since they can be used as important devices such as DRAM based on capacitive elements. Most of the CCTO studies have been performed on bulk materials (ceramics or single crystals) and are focused on the identification of the mechanism responsible for unusual CCTO properties[4]. In order to apply CCTO in microelectronic devices and to determine a more fundamental understanding of its properties, the CCTO thin films can be prepared by pulsed laser deposition technique. Lasers can be used to fabricate thin extended films by condensing on a substrate surface the material that is ablated from a target under the action of laser light[5-7]. Recently, ceramic composite of $BaTiO_3$- $CaCu_3Ti_4O_{12}$ screen-printed thick films for high dielectric devices application in the medium frequency range have been studied extensively by Almeida et al.[8]. The composite of high dielectric constant and low loss films are very attractive for use in microwave devices like dielectric resonators and miniaturization of the microelectronic devices.

The unit cell of a cubic perovskite-related material $CaCu_3Ti_4O_{12}$ is shown in Figure 1. The Ti atoms sit at the center of canted TiO_6 octahedral (tilt angle is nominally 141°), with bridging Cu atoms and large Ca atoms sitting at the center and corners of the unit cell[9].

CCTO has been found as a material that exhibit a giant dielectric constant with relatively temperature independent over a wide temperature range between 100 and 600 K. However, below 100 K its value drops abruptly almost three orders of magnitude. Local structural properties of CCTO system as a function of temperature was investigated within a range from 50 K up to room temperature[8]. The temperature dependence of the nearest neighbor Cu-O distance is very flat, supporting the idea that this is bracing the structures. However, unusual temperature dependence for the atomic displacement parameters of calcium and copper is observed. Temperature dependent modeling, suggests that the Ca atoms become under bonded at low temperature.

Mechanical alloying technique has been used to produce CCTO by using two different experimental procedures[1]. Although this technique is able to produce nanocrystalline powders of CCTO, but this process need a very long milling time, up to 100 hours to obtain a single-phase of CCTO formation. On the other hand, a conventional ceramic solid state reaction technique is one of the promising technique to prepared CCTO, but again, this process need a relatively high calcination temperature, normally in the range of 900-1100 °C. To solved these problems, in this work we try to reduce the milling time to 5 hours only and then following by calcination process at 600-900 °C to produce a single-phase CCTO.

2. EXPERIMENTAL

$CaCu_3Ti_4O_{12}$ (CCTO) was prepared by a modified mechanical alloying technique. This technique is a modification of the original method that was reported by Almeida et al.[1]. The starting materials of $Ca(OH)_2$ (Aldrich, 99%), CuO (Aldrich, 99%) and TiO_2 (Merck, 99%) powders were weighed according to the stoichiometric ratio. Mixed powders were subject to a fast ball milling process (1500 rpm) in sealed alumina vial under ambient condition for 5 hours. The milled powders then were put in an alumina crucible and subjected to calcination process at temperature of 600, 700, 800 and 900 °C in air for 12 hours, respectively. The calcined powders were reground and pressed into a disc shape pellets with diameter of 6 mm and 1 mm in thickness using a stainless steel die set. The pellets were sintered in the presence of air at 1050 °C with soaking time of 24 hours. Phase analysis was conducted on the both calcined powders and sintered pellets by using XRD machine model D8 Bruker diffractometer with CuK_α radiation. Microstructure of samples was investigated by field emission scanning electron microscopy (FESEM) Zeiss Supra 35VP. Dielectric properties measurement (dielectric constant) was carried out on the pellets by using Philips PM6303 LCR meter at 1 kHz frequency in ambient temperature.

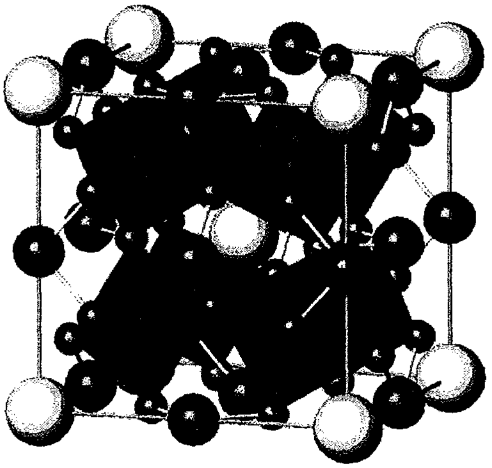

Figure 1. Schematic shows the unit cell of body-centered cubic of $CaCu_3Ti_4O_{12}$ [9].

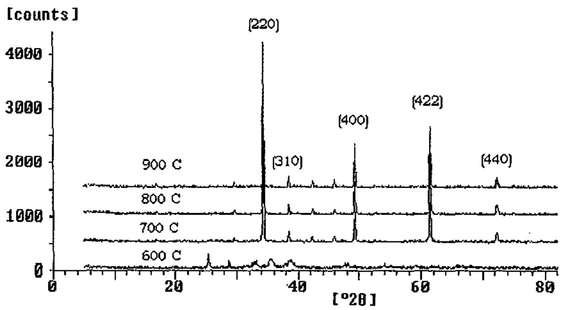

Figure 2. XRD patterns of the calcined powders at different temperature in the range of 600-900 oC for 12 hrs.

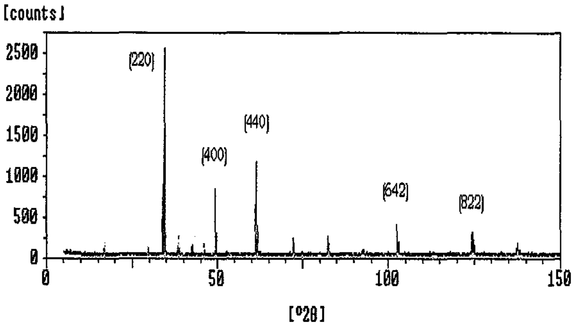

Figure 3. XRD pattern of sintered pallet at 1050 °C for 24 hours. Pellet was formed from the calcined powders at 900 °C for 12 hrs.

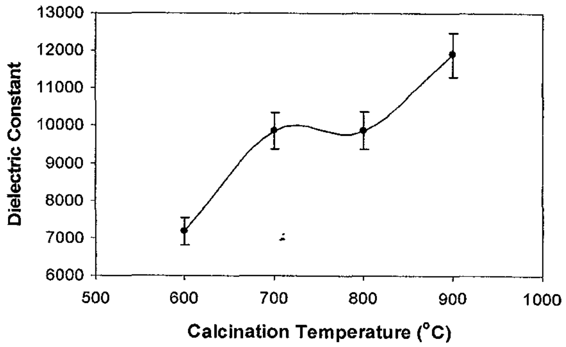

Figure 4. Dielectric constant of sintered pellets as a function of calcination temperatures.

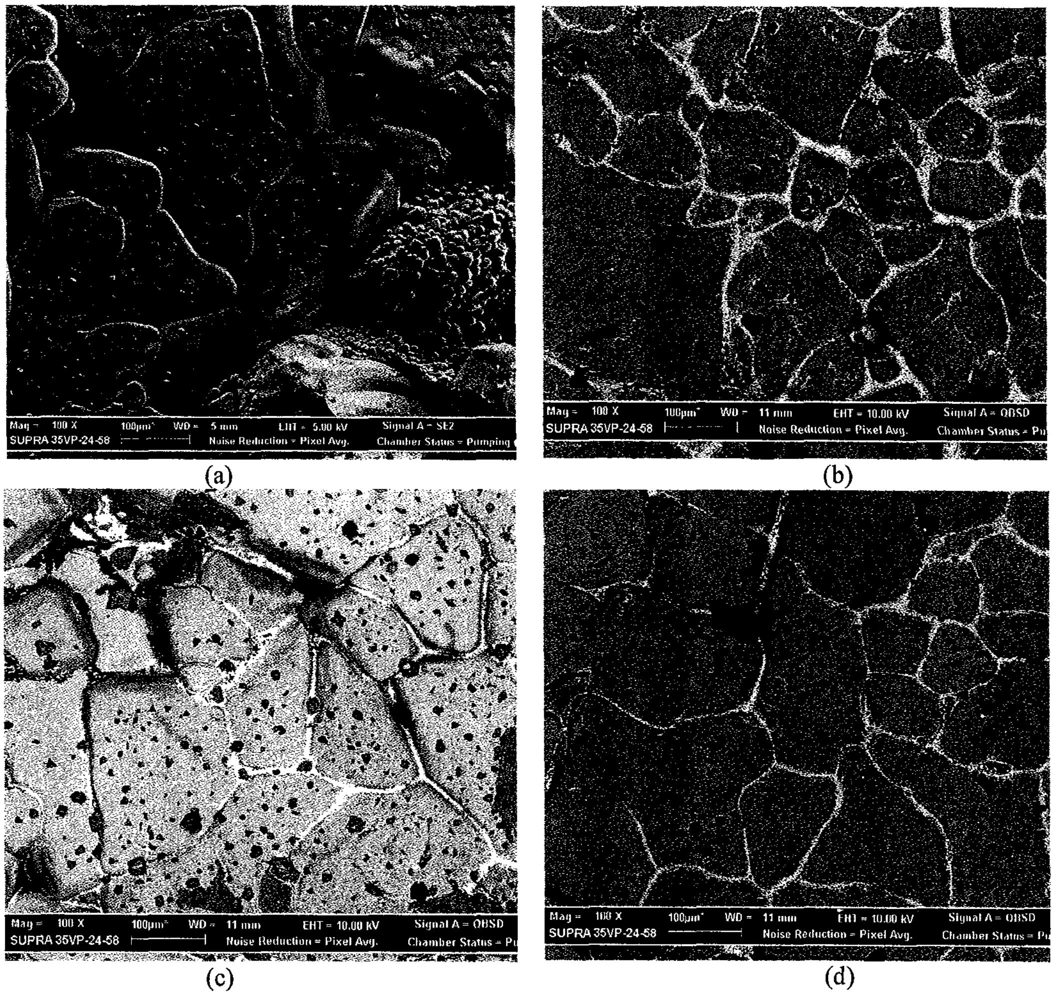

Figure 5. SEM images of the sintered pellets that formed from calcined powder at difference temperature of (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C for 12 hrs, respectively.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD analysis results for the calcined powders at different temperature of 600 °C, 700 °C, 800 °C and 900 °C for 12 hrs, respectively. The patterns show that the complete formation of single-phase polycrystalline CCTO occurred starting in the sample calcined at 700 °C. All of the detected peaks were identified and found to be corresponding to CCTO phase (JCPDS File No. 21-0140). This observation suggests that calcination temperature of 700 °C was enough to form CCTO single-phase by modified mechanical alloying technique. It is very interesting, because this calcination temperature is much lower when compared to the other methods. The calcination temperature of CCTO preparation by conventional solid state reaction technique is normally in the range of 900-1100 °C [1,8,10-12].

The XRD pattern result of sintered pellet is almost similar with those calcined powders. This indicates that the CCTO phase formed during the calcination processing was complete and very stable. See Figure 3 and compare to Figure 2. There is no additional major peak detected that would indicate the formation of secondary phases after the higher temperature sintering of 1050 °C.

Figure 4 shows the effect of calcination temperature on the dielectric constant of prepared CCTO. All the samples were sintered at 1050°C for 24 hrs after calcination processes. The dielectric constant measurements were performed three times for each sample and the average values were plotted. The dielectric constant value of CCTO pellets was found to be increase with the calcination temperature. The highest value of 11,903 was obtained on the sample of calcined at 900 °C. The increasing trend of the dielectric constant value was correlated to the relative density and microstructural features of the pellet where the density and grain size are also increases with calcination temperature (see Figure 5). At 600 °C (Figure 5a) it is obvious that the CCTO formation not completed and there is no dense microstructure. However, there is only a small difference between microstructure for samples calcined at 700 °C and 800 °C (Figure 5a & 5b). Therefore, both samples gave almost similar dielectric constant. Nevertheless, for sample calcined at 900 °C (Figure 5d), it has a denser microstructure with less and small amount of porosity which contribute to higher dielectric constant value.

4. CONCLUSION

The modified mechanical alloying by using combination of ball milling and solid state reaction method had proven to be another alternative processing method to produce a single-phase CCTO structures. CCTO has been formed completely at the sample calcined 700 °C for 12 hrs, which is much lower if compared to the other preparation techniques. The calcinations temperature of CCTO preparation by using conventional solid state reaction technique is normally in the range of 900 to 1100 °C for 24 hrs.

ACKNOWLEDGMENT

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Effect of Microwave Treatment on the Microstructure and Dielectric Properties of SnO_2-doped $CaCu_3Ti_4O_{12}$

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Abstract — A microwave (MW) treatment process was performed to pre-sintered of $CaCu_3Ti_4O_{12}$. Conventional furnace was used for calcinationd and sintered process, whereas a domestic microwave oven employed for treatment in order to produce the better phase structures, morphology and dielectric properties of $CaCu_3Ti_4O_{12}$ products. Analysis SEM show that the microstructures of MW treated sample is better densification, fine and larger grain size if compare to the untreated sample. Dielectric properties also have been improved by MW treatment, which is higher dielectric constant and lower dielectric loss. The effect of doping concentration of SnO_2 to dielectric properties of $CaCu_3Ti_4O_{12}$ had been studied. It was found that the dielectric constant of $CaCu_3Ti_4O_{12}$ decreased exponentially with molarities percentage of SnO_2. The lowest dielectric loss value has been obtained at sample with 6 mol% doping concentration.

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 are 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].

Some ceramic compounds with perovskite structures are found to be 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 [2]. CCTO has attracted much interest because of its high dielectric constant (up to 10^5) over a wide temperature range from 100 to 600 K and rather wide microwave frequency window [3,4]. This unique property makes CCTO a promising material for microelectronic and microwave device applications. However, the nature of how the CCTO represents such that properties are still not well understood [5-7]. Lately, researchers claim that this behavior comes from different factors, such as grain boundary, presence of twin boundaries or other planar defects, displacement of Ti ions and etc. [4,6]. But the real explanations of the phenomena are still under investigated.

There are many parameters that should be controlled to produce good quality of CCTO by conventional solid state technique, i.e. calcination and sintering temperature, and duration and atmosphere. It was stated by some researchers [9,10] that optimum sintering temperature and duration to produce CCTO is 1100 °C for 24 hours. However, in our previously work [11] was found that microstructure and dielectric properties of CCTO being affected by sintering temperature and time. The results show the abnormal grain growth, melting and formation of large pores found in the sintered sample at 1100 °C. Therefore, it is important to apply a lower sintering temperature to find out a new treatment technique to ensure obtaining the correct microstructure with better dielectric properties of CCTO.

Microwave (MW) irradiation is an attractive technique of material processing. This technique has been employed by several researchers in order to produce dielectric ceramics [12-15], ferroelectrics [16,17], garnet, ferrite 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.

As the MW treatment of CCTO has not been explored yet, there is obviously a wide breadth of technique that can be applied. Therefore, in this work, an attemption has been made to improve microstructure and dielectric properties of CCTO by microwave treatment of pre-sintered sample by using a modified domestic microwave oven. More importantly, a domestic microwave oven provides inexpensive multi-mode cavities that can be used for MW treatment as well as sintering process of advanced materials with a simple procedure.

METHODOLOGY

The undoped and SnO_2-doped 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 weighted according to the stoichiometric and dopant ratios followed by wet ball milling in ethanol for 1 hour. Milled powder was calcined at 900 °C with soaking time of 12 hours using furnace. The pellet shape of specimens with 12 mm diameter and approximately 1.2 mm thickness were formed by apply an uniaxial pressure of 520 MPa using stainless steel die. Green pellets were sintered at 1000 °C for 10 hours in air.

Meanwhile, microwave (MW) treatment process of sintered pellets were done by using a domestic microwave oven (Panasonic, Model NN-S554WF/MF).

This oven is able to generate a maximum microwave power of 1100 W at operating frequency of 2.45 GHz. In this process, samples were put in alumina crucible and placed inside of a quartz tube container, and then positioned in the centre of microwave cavity chamber. For MW treatment process, oven was operated at full power condition for 60 min.

Phase formation of calcined powder was analyzed by XRD (Bruker D8) and field emission scanning electron microscopy (FESEM) with EDX (Zeiss SUPRA 35VP) used for determination microstructure and elemental composition of sintered samples. Dielectric properties (dielectric constant and loss) of pellets were measured using Agilent 4284A Precision LCR meter at frequency of 1 MHz in ambient temperature.

RESULTS AND DISCUSSION

XRD analysis result of calcined powder was proven the formation of single-phase CCTO structure as shown in Fig. 1. The result shows that a single-phase structure of CCTO was completely formed. There are at least five major peaks have been identified as CCTO peaks that overlapping with reference patter of file no. 01-075-2188.

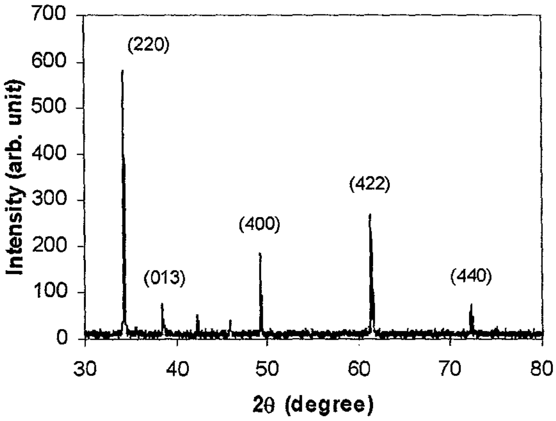

Fig. 1. XRD analysis result of calcined sample at 900 °C for 12h.

Fig. 2 shows the effect of MW treatment on the microstructure of undoped CCTO samples. We can see that sintered sample 1000 °C for 10 h using electric furnace and followed by microwave (MW) treatment for 60 min has larger grain size compare to sample without MW treatment. The grain-bondaries structure is very clear in MW treated sample as well as dense microstructure formation.

MW treatment process can be used to assist growth of uniform grains in bulk form sample. It is an advantages of MW sintering process. However, in microwave processing is needed a suitable microwave cavity to allows the transfer of microwave energy to the sample through susceptor [21]. The post-sintering by MW radiation also might be used as a thermal etching process to improve densification and grain boundary analysis.

MW process is fundamentally different from the conventional process in terms of its heating mechanism. In a MW oven, heat is generated within the sample volume itself by the interaction of microwaves with the material. MW energy heats the material on a molecular level, which leads to uniform heating, whereas, conventional heating systems heat the material from outer surface to interior, which results into steep thermal gradients [14].

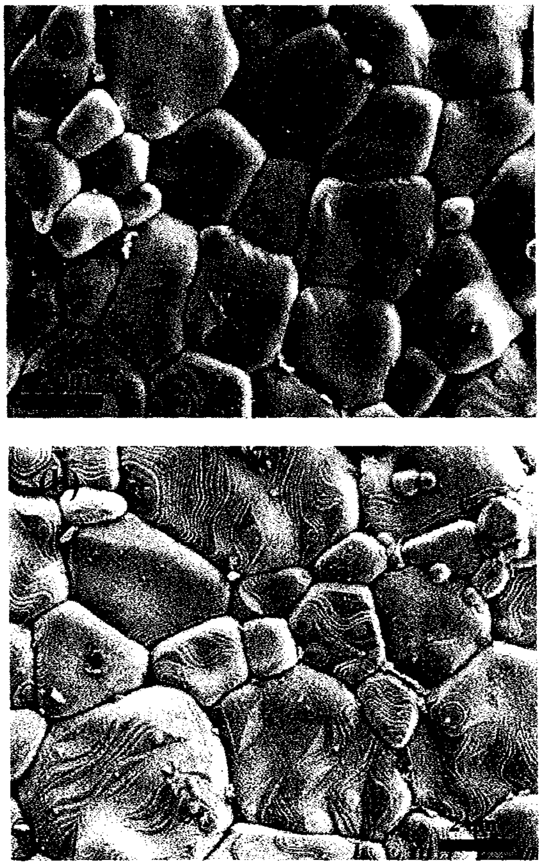

Fig. 2. Microstructure images of undoped sample without MW treatment (a) and with MW treatment for 60 min (b).

Effects of SnO_2 addition on the microstructure of MW treated CCTO are shown in Fig. 3. A smooth surface with relatively small grain size is observed in the sample doped 1 mol% as shown in the SEM micrograph of Fig. 3(a). There is no SnO_2 can be observed significanly as amount of dopant very litle. When amount of dopant is increase to 4 and 6 mol%, we found that some of small impurity particles ditributed randomly on CCTO surface as shown in Fig. 3b and 3c.

Fig. 4 show the effects of MW irradiation and SnO_2 dopant concentration on the dielectric constant value of pre-sintered pellets. From Fig. 4 we can see that pre-sintered and followed by MW treatment of CCTOs have the higher dielectric constant compare to without MW treatment samples. The samples were pre-sintered at 100 °C for 10 h using a conventional furnace. This phenomena can be explained due to better densification and larger grain size as shown in microstructure image of MW treated sample.

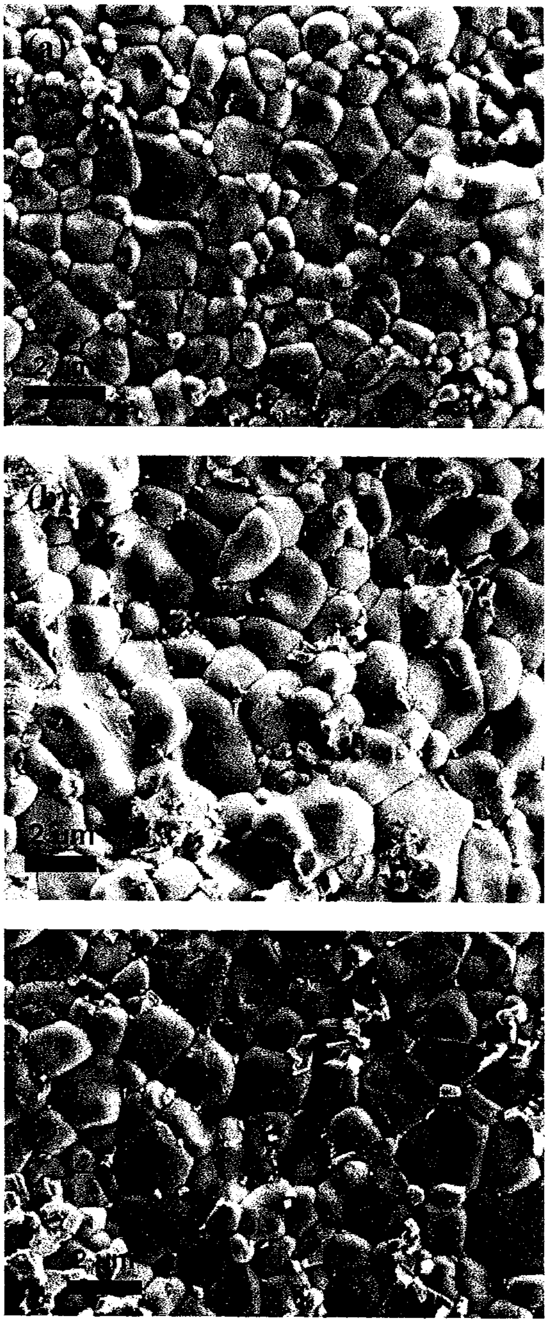

Fig. 3. SEM images of selected SnO_2-doped CCTO with MW treatment for 60 min: (a) 1 mol%, (b) 4 mol%, and (c) 6 mol%.

Meanwhile, SnO_2 dopant concentrations are strongly effects on the dielectric constant of without and with MW irradiated samples. The curve show that dielectric constant of both without and with MW irradiated samples are decrease exponentially with increment of dopant concentrat. It was found that at high dopant concentrations (2 mol% or above) the dielectric constant are stay at lower values of about 150.

One of the main problems in CCTO is its high dielectric loss value. This problem can be approached by doping process with suitable element or compound such as zinc [25] as well as La-doped CCTO [26]. In this work, we attempt to reduce dielectric loss of CCTO by doping with SnO_2.

The effects of MW treatment and SnO_2 dopant concentration on the dielectric loss or dissipation factor of pre-sintered pellets are shown in Fig. 5. We can see that MW irradiated of CCTOs have the better dielectric loss (lower dielectric value) if compare to without MW treatment samples. Fig. 5 also shows that dielectric loss of CCTO can be improved by SnO_2 addition. The optimum doping concentration to lower dielectric loss was found at about 6 mol% for both untreated and MW treated samples. The obtained dielectric loss values are decreased significantly from 0.359 to 0.131 for undoped and 6 mol% SnO_2-doped CCTO.

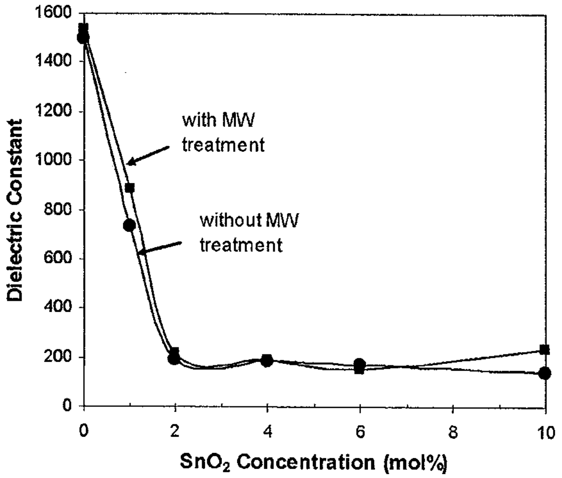

Fig. 4. Dielectric constant versus SnO_2 dopant concentration of sintered sample at 1000 °C for 12 h without and with MW treatment for 60 min.

CONCLUSION

A denser microstructure of CCTO can be produced by microwave treatment of pre-sintered sample using a domestic microwave oven irradiation. The results show that higher dielectric constant and better dielectric loss have been obtained in the MW irradiated samples. Additional SnO_2 dopant was found tend to reduce dielectric constant values of CCTO as well as dielectric loss. Therefore, the MW treatment and doping processes can be applied as alternative choice to improve dielectric properties of CCTO.

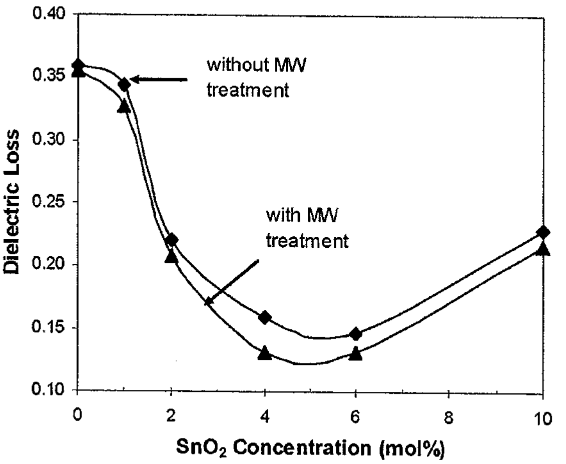

Fig. 5. Dielectric loss versus SnO_2 dopant concentration of sintered sample at 1000 °C for 12 h without and with MW treatment for 60 min.

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Processing Condition Effects on the Properties of $CaCu_3Ti_4O_{12}$ Prepared by Modified Mechanical Alloying Technique

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Abstract — In this paper presented the effects of calcination time and sintering temperature on the properties of $CaCu_3Ti_4O_{12}$. Electroceramic material of $CaCu_3Ti_4O_{12}$ was prepared by modified mechanical alloying technique that covers a several processes, which are preparation of raw material, mixing and ball milling for 5 hours, calcination, pellet forming and sintering. Objective of this modified technique is to enable the calcination and sintering processes in future carried out in shorter time and lower temperature. XRD analysis result shows that single-phase of $CaCu_3Ti_4O_{12}$ was completely formed by calcination at 750 °C for 12 hours. Meanwhile, grain size of sintered sample at 1050 °C for 24 hours is extremely large in the range of 20-50 μm obtained from FESEM images. The dielectric constant value of 14,635 was obtained at 10 kHz by LCR meter in the sintered sample at 1050 °C. However, dielectric constant value of sintered samples at 900 and 950 °C is quite low in the range of 52-119 only.

INTRODUCTION

With the shrinking of dimensions of the microelectronic devices, high dielectric constant materials have been playing a significant role in microelectronics, since they can be used as important devices such as DRAM based on capacitive elements. The complex perovskite compound $CaCu_3Ti_4O_{12}$ (CCTO) has recently attracted considerable attention in view of its anomalously large dielectric response. Low-frequency studies uncovered dielectric constant up to 80,000 that are nearly constant over a wide temperature range (100-600 K) [1,2]. This unique property make CCTO a promising material for capacitor applications and certainly for microelectronics, microwave devices (cell mobile phones for example). Moreover, above a critical frequency that ranges between 10 Hz and 1 MH, dielectric constant value depending on temperature [3]. The highest value of dielectric constant expected obtained during a phase transition as a function of temperature. Most of the CCTO studies have been performed on bulk materials (ceramics or single crystals) and focused on the identification of the mechanism responsible for unusual CCTO properties [4-6].

Mechanical alloying technique has been used to produce CCTO by using two different experimental procedures [1]. Although this technique is able to produce nanocrystalline powders of CCTO, but this process need a very long milling time up to 100 hours to obtain a single-phase of CCTO formation. On the other hand, a conventional solid state reaction technique is one of the promising technique to prepared CCTO, but again, this process apply high calcination temperature, normally in the range of 900-1100 °C. To solve these problems, in this work, we use a combination of mechanical alloying and solid state reaction to produce a single-phase CCTO formation at lower temperature and shorter time of process.

METHODOLOGY

The starting materials of $Ca(OH)_2$ (Aldrich, 99%), CuO (Aldrich, 99%) and TiO_2 (Merck, 99%) powders were weighed according to the stoichiometric ratios. Mixed powders were subjected to a fast ball milling process (1500 rpm) in sealed alumina vial using zirconia balls under ambient condition for 5 hours. The milled powder was put in an alumina crucible then calcined at 750 °C in air for 6, 9, 12, 18, and 24 hours, respectively. The calcined powder were reground and pressed into pellets with diameter of 12 mm and 1 mm in thickness using a stainless steel die set. Pellets were sintered in air at 900, 950 and 1050 °C with soaking time of 24 hours, respectively.

Phase analysis was conducted on calcined powders by XRD analysis. Surface and fracture morphology were investigated by field emission scanning electron microscopy (FESEM), and dielectric properties measured using Agilent 4284A Precision LCR meter at frequency of 100 Hz to 1 MHz in ambient temperature.

RESULTS AND DISCUSSION

The calcined powder was examined by XRD in order to investigate the phase formation of CCTO and result is shows in Fig. 1. It was found that CCTO completely formed where three main and five small peaks of (220), (400), (422), (211), (013), (222), (440), and (620) belong to CCTO. All of the obtained peaks are overlapping with reference patter of CCTO (File no: 01-075-2188). This observation shows that calcination temperature of 750 °C is enough to form CCTO single-phase by modified mechanical alloying technique. It is very interesting, because this calcination temperature is much lower if compared to the solid state method. The calcination temperature of CCTO preparation by conventional solid state reaction technique is mostly in the range of 900-1100 °C [7,9,10].

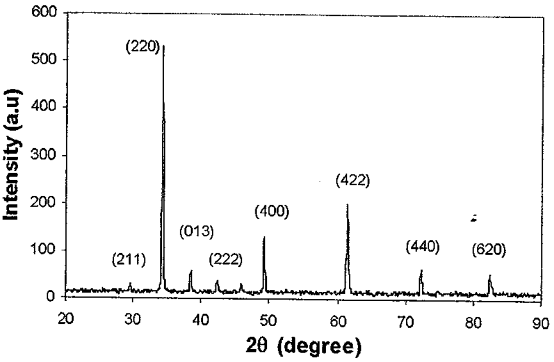

Fig. 1. XRD pattern of calcined powder at 750 °C for 12 hours.

Microstructural of sintered pellets were observed by using field emission scanning electron microscopy (FESEM) in order to understand the grain-boundary formation. Fig. 2 shows the surface micrograph of $CaCu_3Ti_4O_{12}$ pellets sintered at 900, 950, and 1050 °C for 24 hours, respectively. Sample sintered at 900 °C is not dense and we can see that the grain size is very small and high porosity. Meanwhile, sample sintered at 950 °C is show a quite dense pellet even though the grain size is still small and some porous structure appear on the surface. On the other hand, sample sintered at 1050 °C fort 24 hours show an over grow grain tends to starting be destroyed grain boundaries which may be due to the high sintering temperature and time. The similar over grow phenomenon due to high temperature sintering process also observed in the $CaCu_3Ti_4O_{12}$ prepared by conventional solid state method [9].

Fig. 3 shows the SEM images of sintered pellets at 900, 950, and 1050 °C for 24 hours, respectively on fracture areas. From these images, it is found that $CaCu_3Ti_4O_{12}$ sintered at 950 °C and 1050 °C show the very clear grain boundaries (Fig. 3(b) and (c)). The grain of CCTO was growing up and touches each others to form very dense structures (Fig. 3(c). Besides we can see some of the melting componen on surface and fracture as shown in Fig. 2(c) and Fig. 3(c).

The effect of calcination time on dielectric properties of sintered pellets at 1050 °C for 24 hours were investigated by capacitance measurement at different frequencies, of 100 Hz, 1 kHz, 10 kHz, 1 MHz. Fig. 4 shows dielectric contant plotted against frequencies for pellet formed from CCTO powders with different calcination time of 6, 9, 12, 18, and 24 hours. Pellets was sintered at 1050 °C for 24 hours. The curves show that dielectric constant is slightly increase with prolong calcination time, where is the calcined sample for 24 h gave the highest value. A very clear picture of the time dependent of dielectric constant value measured at 10 kHz frequency as shown in Fig. 5. This phenomena is related to the microstructure condition of the sample that the more calcination time exhibit denser microstructures.

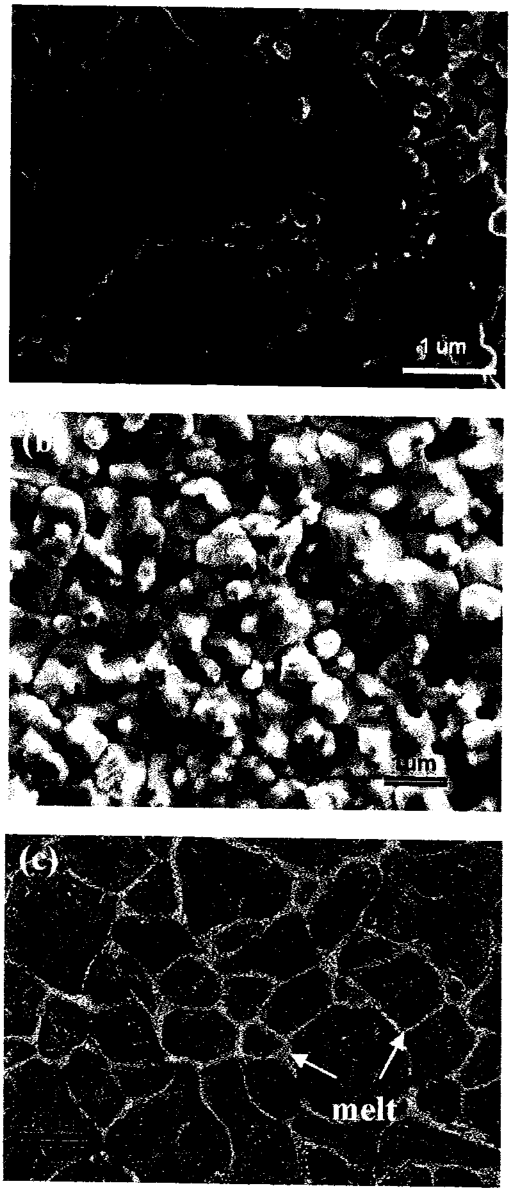

Fig. 2. FESEM image of sample surfaces: (a) 900 °C, (b) 950 °C, and (c) 1050 °C for 24 h, respectively.

The dielectric constant dependent of frequency is shown in Fig. 4, where the dielectric constant decrease exponentially to the higher frequency. These phenomena can be explained by mechanisms of polarization that have varying time response capability to an applied field frequency, and polarization contributes to the dielectric constant. Electronic displacement responds rapidly to the field reversals, and no lag of the polarization contribution occurs at higher frequency. At high frequency, the ionic displacement begins to lag the field reversals, increasing the loss factor and contributing less to the dielectric constant.

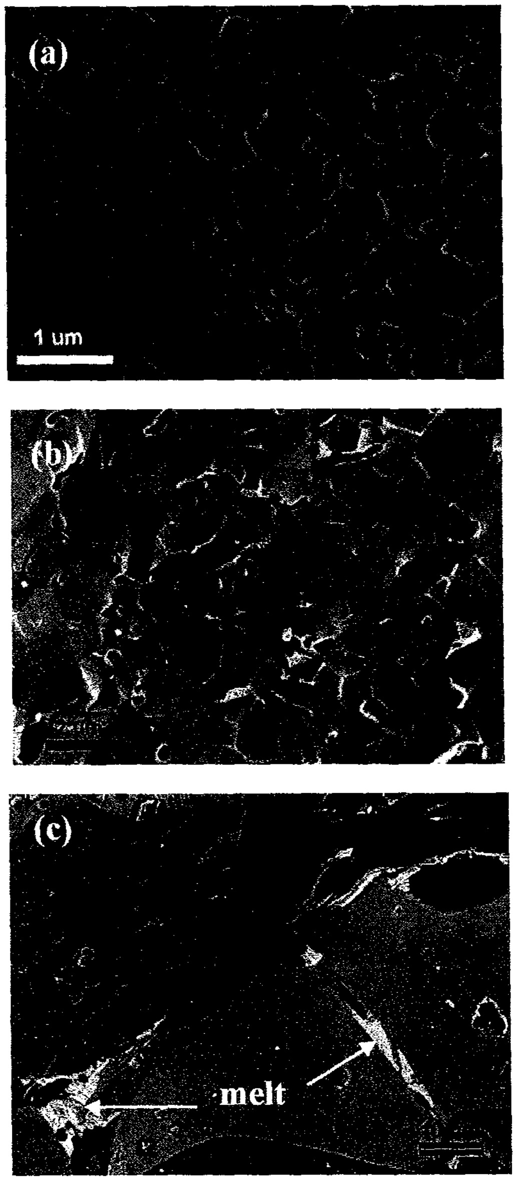

Fig. 3. FESEM micrograph of fractured pellets sintered at (a) 900 °C, (b) 950 °C, and (c) 1050 °C for 24 h, respectively.

The effect of sintering temperature on dielectric properties of CCTO, shown in Fig. 6 and 7. It is found that the dielectric constant of sintered pellet at 1050 °C is much higher than both samples sintered at 900 and 950 °C. At frequency 10 kHz, the dielectric constant value of 18,453 has been obtained for sintered sample at 1050 °C, whereas for sample sintered at 900 and 950 °C is about 57 to 81 only, see Fig. 6. As was mentioned early, this effect is mostly come from grain-boundary condition of sample. It was found that sample sintered at 900 °C show incomplete grain growth, while a dense microstructure with abnormal grain growth observed on the sintered sample at 1050 °C.

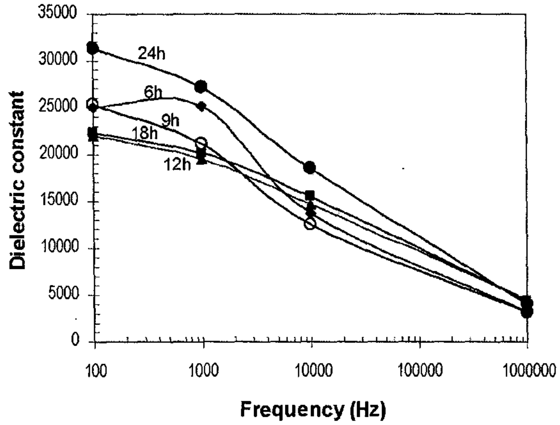

Fig. 4. Dielectric contant plotted against frequencies for different calcination time of 6, 9, 12, 18, and 24 hours, respectively. Pellets was sintered at 1050 °C for 24 hours.

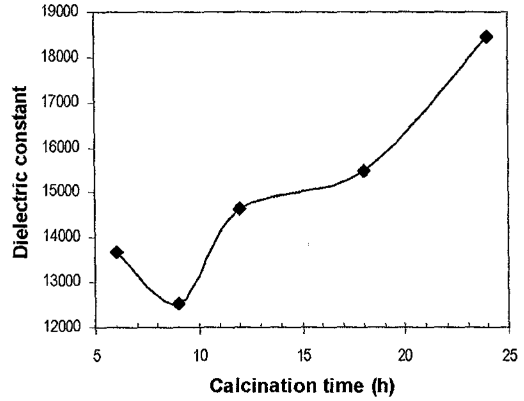

Fig. 5. Dielectric constant value as function calcination time measured at 10 kHz.

The dielectric loss is closely related with the mechanism of the dielectric response. Based on the widely accepted internal-barrier-layer-capacitance (IBLC) model, the dielectric loss mainly originates from the conductivity of the CCTO conducting crystalline grains/subgrains as well as that of the insulating barriers [4]. The conductance of the barriers leads to the leakage loss. In general, CCTO exhibits very high dielectric constant, which is desirable for many micro-electric applications. However, the dielectric loss of the material is relatively high.

Fig. 7 shows the effects of sintering temperature on the dielectric loss value of $CaCu_3Ti_4O_{12}$ measured at different frequencies. At lower frequency (100 Hz), the dielectric loss value is very high (0.3318 to 0.6246) and sintered sample at 1050 °C is the lowest. However, at high frequency (1 MHz), the value is decreased to 0.181, 0.0155 and 0.0133 for sintered samples at 1050, 950 and 900 °C, respectively. From Fig. 7 we can see that sample with low dielectric constant value give better dielectric loss property at high frequencies. Dielectric loss of

CCTO can be reduced by doped with zinc [13] as well as La-doped CCTO [8].

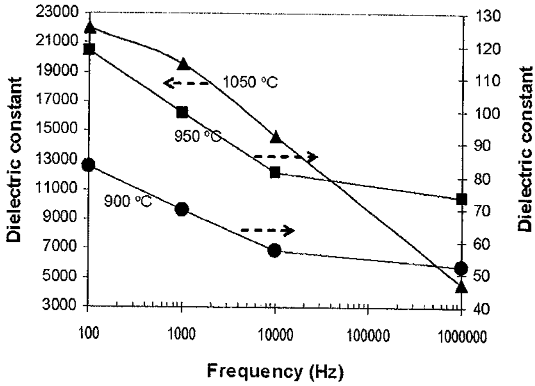

Fig. 6. Dielectric constant versus frequency of calcined samples at 750 °C for 12 h and sintered 24 h at 900, 950, and 1050 °C, respectively.

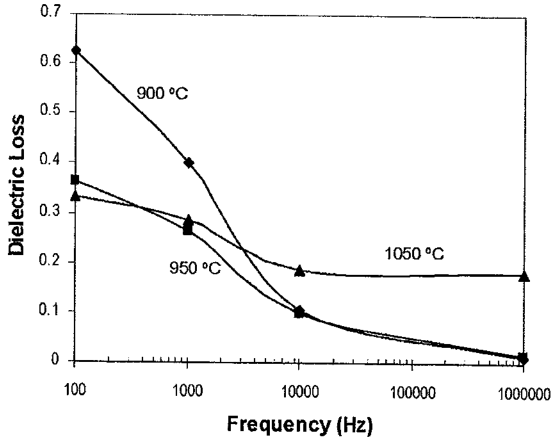

Fig. 7. Dielectric loss value of calcined samples at 750 °C for 12 h and sintered 24 hrs at 900, 950, and 1050 °C, respectively measured at different frequencies.

CONCLUSION

The modified mechanical alloying technique is a promising technique that enable the calcination and sintering process of CCTO carried out in shorter time and lower temperatures (750 °C for 12 h), so that can save energy. In this work, the highest dielectric constant value of about 15,000 at 10 kHz was obtained in the sample sintered at 1050 °C. However, the dielectric loss of this sample is relatively high about 0.2 compare to 0.1 for the lower sintered samples. At the higher measurement frequency (1 MHz), sintered sample at 900 °C for 24 h give better dielectric loss value of 0.0133 followed by 0.0155 for sample sintered at 950 °C.

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