UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

Production of $CaCu_3Ti_4O_{12}$ (CCTO) Electroniceramics via Plasma Spray Method

by

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Kod Projek :	FRGS/FASA1-2009/(BIDANG)/(NAMA IPT)/(NO.RUJ. KPT)

BORANG FRGS – P3(R)

FINAL REPORT
FUNDAMENTAL RESEARCH GRANT SCHEME (FRGS)

Laporan Akhir Skim Geran Penyelidikan Asas (FRGS) IPT
Pindaan 1/2009

A

RESEARCH TITLE : Production of $CaCu_3Ti_4O_{12}$ (CCTO) Electroceramics via Plasma Spray Method
Tajuk Penyelidikan

PROJECT LEADER : **Julie Juliewatty Mohamed**
Ketua Projek

PROJECT MEMBERS : **1. PM Dr Sabar Derita Hutagalung**
(including GRA) **2. Prof Dr Zainal Arifin Ahmad**
(including GRA)
Ahli Projek

PROJECT ACHIEVEMENT *(Prestasi Projek)*

B

ACHIEVEMENT PERCENTAGE			
Project progress according to milestones achieved up to this period	**0 - 50%**	**51 - 75%**	**76 - 100%**
Percentage			80%

RESEARCH FINDINGS		
Number of articles/ manuscripts/ books	**Indexed Journal**	***Non-Indexed Journal***
	1	6
Paper presentations	**International**	***National***
	1	2
Others (Please specify)		

HUMAN CAPITAL DEVELOPMENT

Human Capital	Number		Others (Please specify):
	On-going	Graduated	
PhD Student			
Masters Student		1	
Undergraduate Students		2	
Temporary Research Officer			
Temporary Research Assistant	2		
Total	5		

EXPENDITURE *(Perbelanjaan)*

C

Budget Approved *(Peruntukan diluluskan)*	:	RM 40,000
Amount Spent *(Jumlah Perbelanjaan)*	:	RM 34,464
Balance *(Baki)*	:	RM 5536
Percentage of Amount Spent *(Peratusan Belanja)*	:	86.16 %

ADDITIONAL RESEARCH ACTIVITIES THAT CONTRIBUTE TOWARDS DEVELOPING SOFT AND HARD SKILLS
(Aktiviti Penyelidikan Sampingan yang menyumbang kepada pembangunan kemahiran insaniah)

D

International

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)	International Conference on Xray and its Related Technique 2012 July, 2012	USM

National

Activity	Date (Month, Year)	Organizer
(e.g : Course/ Seminar/ Symposium/ Conference/ Workshop/ Site Visit)	Electron microscopy conference 2011, Dec 2011 The AUN/SEED-NET Regional Conference on Materials Engineering January, 2013	Electron microscope society malaysia USM

PROBLEMS / CONSTRAINTS IF ANY *(Masalah/ Kekangan sekiranya ada)*

E

- plasma spray (as proposed in the title) was not well fuction to fabricate the CCTO compound. So the reserach was change to study the $CaCu_3Ti_4O_{12}$ doped with MgO prepared by solid state technique.
- Submission of final report was late due to waiting for extension approval (the apllication was not approved, and the letter was attached)

RECOMMENDATION (*Cadangan Penambahbaikan*)

F

RESEARCH ABSTRACT – Not More Than 200 Words(*Abstrak Penyelidikan – Tidak Melebihi 200 patah perkataan*)	
G	Undoped $CaCu_3Ti_4O_{12}$ and Mg-doped $CaCu_3Ti_4O_{12}$ ($CaCu_{3-x}Mg_xTi_4O_{12}$ and $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$) have been prepared by solid state reaction method. Starting materials of $CaCO_3$, CuO, TiO_2 and MgO were wet milled for 1 hour. XRD analysis on calcined powders shows the formation of $CaCu_3Ti_4O_{12}$ (CCTO) phase with present of minor secondary phases (CuO and TiO_2). Mixing process in deionized water gave better mixing and produces higher intensity of CCTO phase after calcined at 900°C for 12 hours. Compacted pellet was sintered at 1020°C, 1030°C and 1040°C for 10 hours. The sintering profile of 1030°C/10 hours was identified as an optimum parameter in the formation of single phase of CCTO with fine grain growth, high density and low porosity. MgO dopant composition had been verified from 1 until 10 mol percent for Cu and Ca site of CCTO structure. SEM images show that the grain size becomes larger with increasing the concentration of dopant. Density and porosity of sintered samples were improved by dopant. The $CaCu_{3-x}Mg_xTi_4O_{12}$ samples with x = 0.01 exhibited the highest dielectric constant of 1821 at frequency 1 MHz and 85 at 1 GHz. Besides, the $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ samples with x = 0.05 exhibited highest dielectric constant of 1278 at 1 MHz. Meanwhile, the experimental shows a significant decrement in dielectric loss for the Mg-doped samples. Therefore, Mg dopant can be used to improve the dielectric behavior of CCTO.
Date : 9/5/2013 *Tarikh*	**Project Leader's Signature:** *Tandatangan Ketua Projek*
COMMENTS, IF ANY/ ENDORSEMENT BY RESEARCH MANAGEMENT CENTER (RMC) (*Komen, sekiranya ada/ Pengesahan oleh Pusat Pengurusan Penyelidikan*)	
H	Project Completed.
	Name: *Nama:*
	Signature: *Tandatangan:* PROF. MADYA LEE KEAT TEONG Pengarah Pejabat Pengurusan & Kreativiti Penyelidikan Universiti Sains Malaysia 11800 USM, Pulau Pinang.
	Date: 16/5/13 *Tarikh:*

Final Report:

Production of $CaCu_3Ti_4O_{12}$ (CCTO) Electroceramics via Plasma Spray Method

(203 / PBAHAN / 6071197)

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9 May 2013

Abstract

Undoped $CaCu_3Ti_4O_{12}$ and Mg-doped $CaCu_3Ti_4O_{12}$ ($CaCu_{3-x}Mg_xTi_4O_{12}$) have been prepared by solid state reaction method. Starting materials of $CaCO_3$, CuO, TiO_2 and MgO were wet milled for 1 hour by using three wetting agents which are acetone, deionized water and ethanol. XRD analysis on calcined powders shows the formation of $CaCu_3Ti_4O_{12}$ (CCTO) phase with present of minor secondary phases (CuO and TiO_2). Mixing process in deionized water gave better mixing and produces higher intensity of CCTO phase after calcined at 900°C for 12 hours. Compacted pellet was sintered at 1020°C, 1030°C and 1040°C for 10 hours. The sintering profile of 1030°C/10 hours was identified as an optimum parameter in the formation of single phase of CCTO with fine grain growth, high density and low porosity. MgO dopant composition had been verified from 1 until 10 mol percent for Cu and Ca site of CCTO structure. SEM images show that the grain size becomes larger with increasing the concentration of dopant. Density and porosity of sintered samples were improved by dopant. The $CaCu_{3-x}Mg_xTi_4O_{12}$ samples with x = 0.01 exhibited the highest dielectric constant of 1821 at frequency 1 MHz and 85 at 1 GHz. Besides, the $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ samples with x = 0.05 exhibited highest dielectric constant of 1278 at 1 MHz. Meanwhile, the experimental shows a significant decrement in dielectric loss for the Mg-doped samples. Therefore, Mg dopant can be used to improve the dielectric behavior of CCTO.

Keywords: CCTO, *Electroceramic, Solid State Technique, Dielectric*

KAJIAN KE ATAS BAHAN ELEKTROSERAMIK CALCIUM COPPER TITANATE ($CaCu_3Ti_4O_{12}$) DIDOP MAGNESIUM DISEDIAKAN MELALUI KAEDAH TINDAK BALAS PEPEJAL

ABSTRAK

$CaCu_3Ti_4O_{12}$ tulen dan $CaCu_3Ti_4O_{12}$ yang didop Mg ($CaCu_{3-x}Mg_xTi_4O_{12}$) telah disediakan melalui kaedah tindak balas keadaan pepejal. Bahan mentah $CaCO_3$, CuO, TiO_2 dan ZrO_2 telah dikisar basah menggunakan tiga agen pembasahan iaitu aseton, air ternyah ion dan etanol. Analisis XRD pada serbuk kalsin menunjukkan pembentukan fasa $CaCu_3Ti_4O_{12}$ (CCTO) dengan kehadiran sedikit fasa kedua (CuO dan TiO_2). Proses pencampuran menggunakan air ternyah ion memberikan campuran yang lebih baik dan menghasilkan fasa CCTO dengan keamatan yang lebih tinggi selepas dikalsin pada suhu 900°C selama 12 jam. Pelet yang ditekan telah disinter pada pada suhu 1020°C, 1030°C dan 1040°C selama 10 jam. Profil pensinteran pada 1030°C/10 jam telah dikenalpasti sebagai parameter yang optimum dalam pembentukan fasa tunggal CCTO dengan pertumbuhan butiran yang kecil, ketumpatan yang tinggi dan keliangan yang rendah. Komposisi dop MgO dipelbagai dari 1 hingga 10 peratus mol untuk kedudukan Cu dan Ca dalam struktur CCTO. Imej SEM menunjukkan saiz butiran semakin meningkat dengan peningkatan kepekatan bahan dop. Ketumpatan dan keliangan sampel yang disinter telah ditambah baik dengan pendopan. Sampel $CaCu_{3-x}Mg_xTi_4O_{12}$ dengan x = 0.01 menunjukkan pemalar dielektrik yang paling tinggi iaitu 1821 pada frekuensi 1 MHz dan 85 pada 1 GHz. Disamping itu, sampel $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ dengan x = 0.05 menunujukkan pemalar dielektrik yang paling tinggi iaitu 1278 pada 1 MHz. Sementara itu, ujikaji menunjukkan penurunan ketara dalam lesapan dielektrik pada sampel didop dengan Mg. Oleh itu, pendopan Mg boleh digunakan untuk menambah baik sifat dielektrik bagi CCTO.

Katakunci: CCTO, *Elektroseramik, Teknik Keadaan Pepejal, Dielektrik*

Introduction

Ceramics are classified as an inorganic materials and it is consisting of metallic and nonmetallic elements. Inorganic materials are compounds that most typically oxides, carbides, and nitrides. The 'ceramic' phrase comes from word Greek word, keramikos which is stand for "burnt stuff". It shows that a firing process or high temperature heat treatment is required in order to get the desirable properties of the ceramic materials (Callister, 2007). The common properties of ceramic materials are hard, brittle, high compression strength and low shearing strength. Besides, it is also able to withstand at high temperatures and harsh environment compared to the metal and polymers. Ceramic materials are mostly act as insulator because it cannot conduct heat and electricity.

The development of traditional ceramics to advanced ceramics has begun and expanded especially in our advanced technologies nowadays. Particularly, the electrical, optical, and magnetic properties of ceramic materials have been explored in order to develop a new product. Beginning year 1910 onwards, many ceramics materials have been synthesized for the development of electronic materials. The substances such as manganese zinc ferrites and nickel-zinc were used as choke and transformer core materials. The products were used for high frequencies application (beyond 1 MHz) due to high resistivity and low susceptibility to eddy currents (Moulson and Herbert, 2003).

Electroceramic is referring as ceramics materials that have been created for electrical, optical and magnetic properties. The electrical properties that were usually stressed are capacitance, conductivity, resistivity, dielectric constant and dielectric loss. The electroceramic materials can be used for the applications as capacitor, filter, resonator, sensor, actuator, etc. Capacitor is one of the main devices which are very important in electronic circuit because it can be use as AC-DC separation, coupling and decoupling, filtering, power factor correction and energy storage (Kao, 2004). The size of electronic devices can also be decrease since high dielectric constant allows smaller capacitive components to be made. The attempt to raise dielectric constant and minimize dielectric loss will increase the effectiveness of dielectric materials (Hutagalung et al., 2009).

Dielectric materials are an electrical insulator but it can support the electric field effectively. Most dielectric materials are solid but some liquids and gases also can be used as dielectric materials. The important property of dielectric material is that it can sustain the electric field with minimal dissipation of energy which in the form of heat (Kao, 2004). In practice, all dielectric exhibit some conductivity, generally proportional with temperature and applied field (McGraw-Hill, 2002). If the applied voltage across dielectric material is too large or applied field becomes too intense, the material will start to conduct current. This incident is called dielectric breakdown (Callister, 2007).

Calcium copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO) is known as one of the electroceramic materials. Subramanian et al. (2000) reported that CCTO exhibited high dielectric constant which is about ~10^4 and good temperature stability in a wide temperature range 100 to 400K. CCTO is different from other perovskite material that has ferroelectric properties such as $BaTiO_3$. Near its Curie point, $BaTiO_3$ shows a great enhancement in dielectric constant but it can also have unfavorable structural phase transition due to strong temperature dependence. Meanwhile, the permittivity of CCTO is stable at high value from 100 to 400 K. The dielectric constant of CCTO was found drops rapidly to a value around 100 when the temperature was below 100K but it is not accompanied by any structural phase transition.

Experimental procedure

$CaCu_{3-x}Mg_xTi_4O_{12}$ (x = 0, 0.01, 0.02, 0.03, 0.05 and 0.10) were prepared by conventional solid state reaction method. The starting materials of $CaCO_3$, CuO, TiO_2 and MgO were weighted according to form $CaCu_{3-x}Mg_xTi_4O_{12}$ and mechanically wet ball milled in deionized water using fast mill for 1 hour. The dried powder was calcined in air at 900°C for 12 hours using Carbolite Furnace. Calcined powders were pressed at 300 MPa to form pellets using hydraulic press. The pellets were then sintered in air at 1030°C for 10 hours using Lenton Tube Furnace. X-ray diffraction (XRD) (model: Bruker AXS D8 Diffractometer) analysis was carried out for both calcined powders and sintered pellets to investigate the phase formation and lattice distortion. The microstructures of the samples was observed by using Scanning Electron Microscopy (SEM) (model: Tabletop Microscope TM 3000) while the densities of sintered samples were measured using Archimedes principle. For electrical measurements, both sides of the sintered PZT ceramics were polished, the dielectric properties were measured using Impedance Analyzer (model: RF Impedance/Material Analyzer 4291B Hewlett Packard) at frequencies 1 MHz to 1 GHZ.

Results and Discussion

Fig. 1(a) shows the diffraction pattern of $CaCu_{3-x}Mg_xTi_4O_{12}$ pellets sintered at 1030°C for 10 hours. All samples produce single phase CCTO which match with ICDD Data File Card No. 01-075-2188. Although in calcined samples found minor secondary phases of TiO_2 and CuO (XRD results not shown), their completely eliminated by sintering process to form single phase CCTO. In Fig. 1(b) shown peak shifted phenomena which related to the lattice distortion of CCTO structure due to Mg dopants. A close observation on the most intense peak which is corresponding to (220) plane found that the peak shifted toward higher 2θ values at 1 mol% dopant. It indicates that the lattice constant was decreased. Ionic radius of Mg^{2+} is slightly smaller (0.72Å) than Cu^{2+} (0.73Å) [5]. When some of

Cu^{2+} ions were substituted by Mg^{2+} ions, a smaller lattice parameter will produce. However, as MgO concentration increased at x ≥ 0.02, the peak of (220) plane were shifted toward lower 2θ values that indicates of increasing in the lattice constant. It is because of some excessive Mg^{2+} ions might be replaced Ti^{4+} ions which is has smaller ionic radius of 0.605Å.

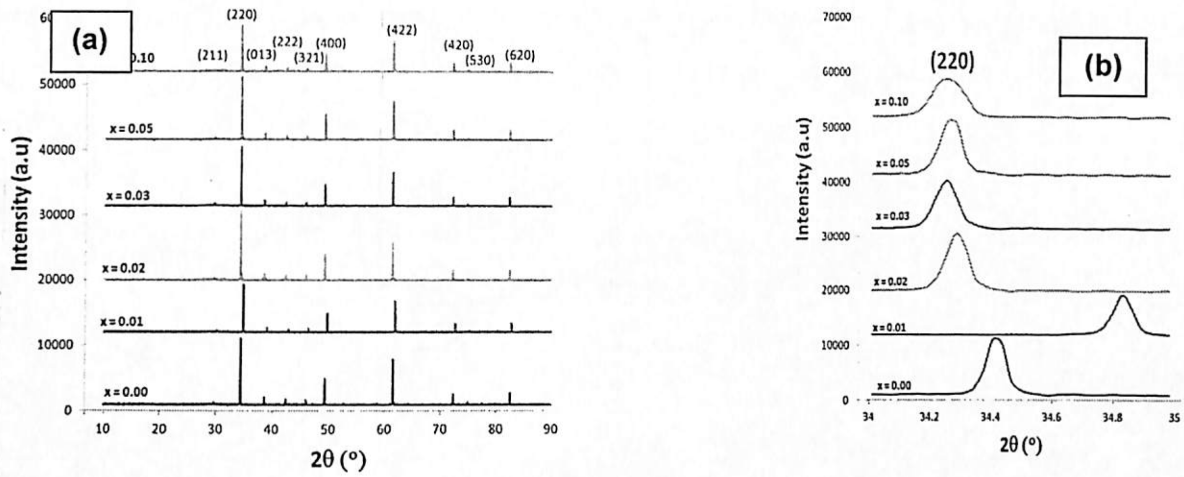

Fig. 1: XRD patterns of: (a) sintered $CaCu_{3-x}Mg_xTi_4O_{12}$, (b) (220) peak with different Mg concentration.

Fig. 2 shows SEM micrographs of $CaCu_{3-x}Mg_xTi_4O_{12}$. It can be seen that grain size is slightly increase with the addition of Mg dopant. The average grain size of undoped CCTO is about 2 μm, while sample with x = 0.10 is about 3 μm. Improved porosity can be observed on Mg-doped CCTO. On the other hand, sample with x = 0.10 found to be the highest density with relative density of 89.04%. It indicated that Mg dopants can be used to improve densification of CCTO ceramics. This result is well agreement with Zhang et al. [6] who found that MgO can improve the densification of $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics.

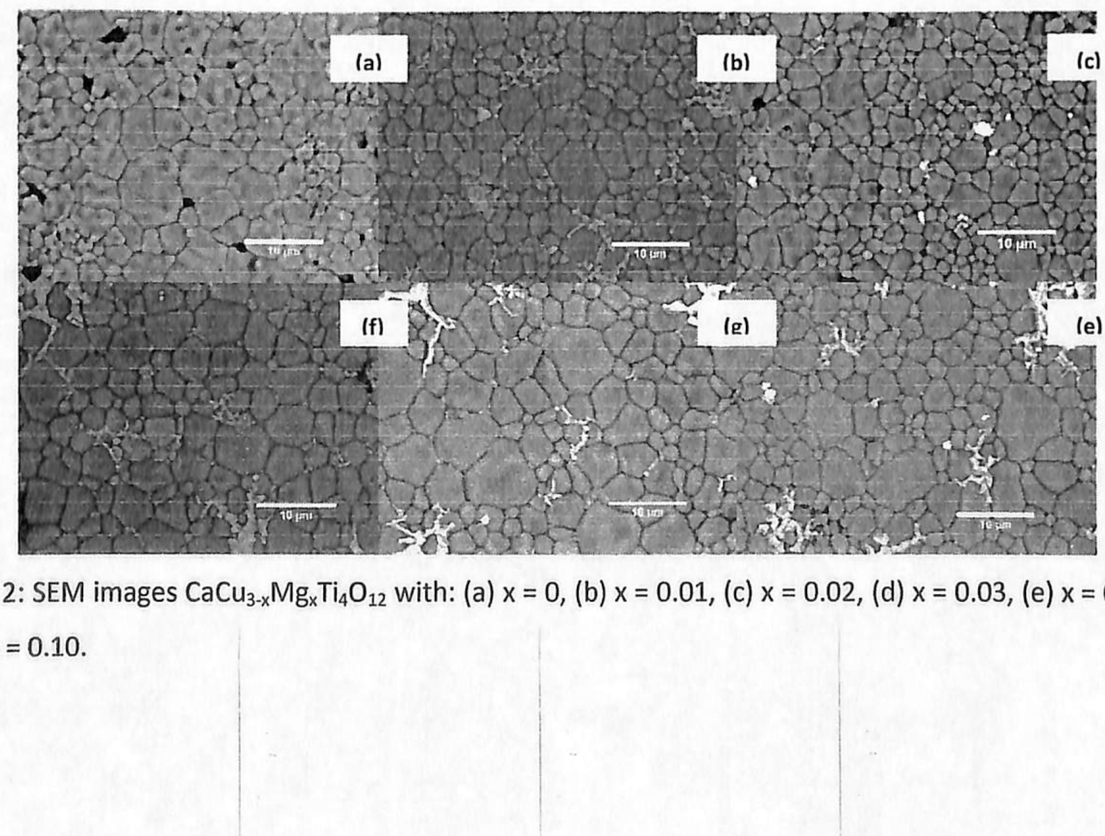

Fig. 2: SEM images $CaCu_{3-x}Mg_xTi_4O_{12}$ with: (a) x = 0, (b) x = 0.01, (c) x = 0.02, (d) x = 0.03, (e) x = 0.05, (f) x = 0.10.

Dielectric properties of $CaCu_{3-x}Mg_xTi_4O_{12}$ ceramics are shown in Figs. 3 and 4. Fig. 3(a) shows that the sample with x = 0.01 exhibited highest dielectric constant at all frequencies range from 1 MHz to 1GHz. Effect of Mg dopant on dielectric constant of CCTO can be seen in Fig. 4. All of the samples exhibited same relaxation trend of dielectric constant which sample with x = 0.01 shows the highest dielectric constant value. At 1 MHz, the undoped sample exhibited dielectric constant of 946, while the 1 mol% Mg-doped sample gave the highest dielectric constant of 1821. The dielectric constant is slowly decrease when increasing frequency from 1 MHz to 1 GHz. Dielectric constant of undoped and Mg-doped samples is only about 85 at 1 GHz. It is expected the grain size of samples correlated to the dielectric behaviour. The undoped sample which has smaller grain size exhibited lower dielectric constant than Mg-doped CCTO samples. The previous studied by Brizè et al. [7] stressed that larger grain size can increase dielectric constant of CCTO ceramics.

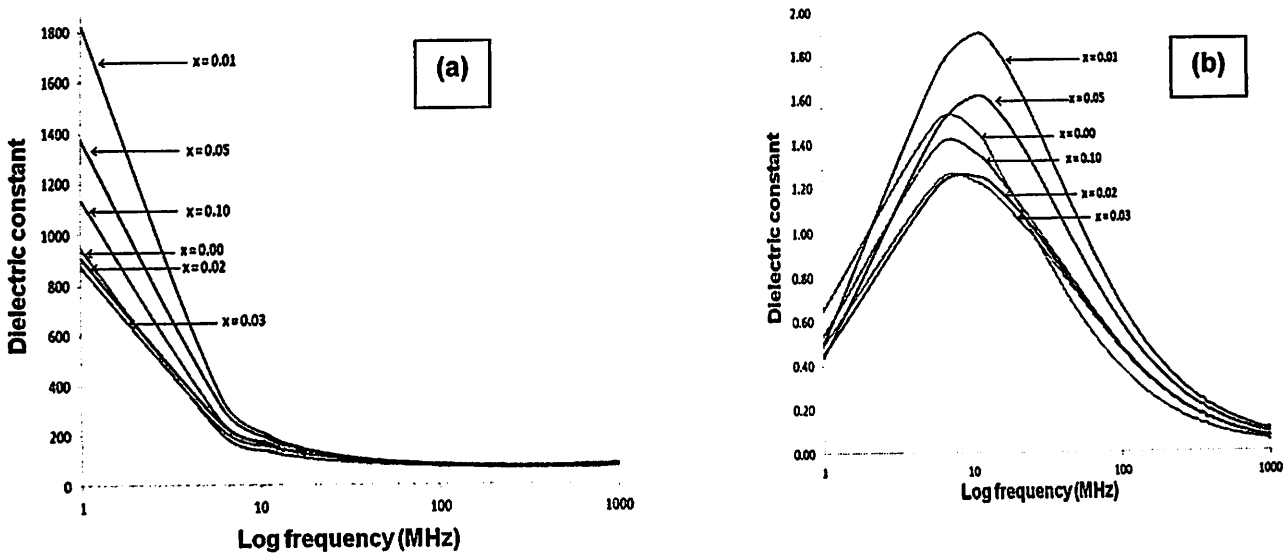

Fig. 3: Frequency dependence of (a) dielectric constant and (b) dielectric loss as a function of x value of $CaCu_{3-x}Mg_xTi_4O_{12}$.

On the other hand, the dielectric loss of Mg-doped CCTO samples is lower than the undoped CCTO especially at frequency 1 MHz to 10 MHz. The dielectric loss was reduced from 0.65 (x = 0.00) to 0.44 (x = 0.02) with the introduction of Mg dopant. It might be correlated to the porosity of samples that undoped CCTO sample has higher porosity. High porosity in ceramic body will obstruct more dielectric to penetrate and can dissipate more heat which related to high dielectric loss. Sulaiman et al. [4] also claimed that higher porosity on the sample can increase the dielectric loss of CCTO. So, MgO dopant can be used to improve dielectric properties of CCTO.

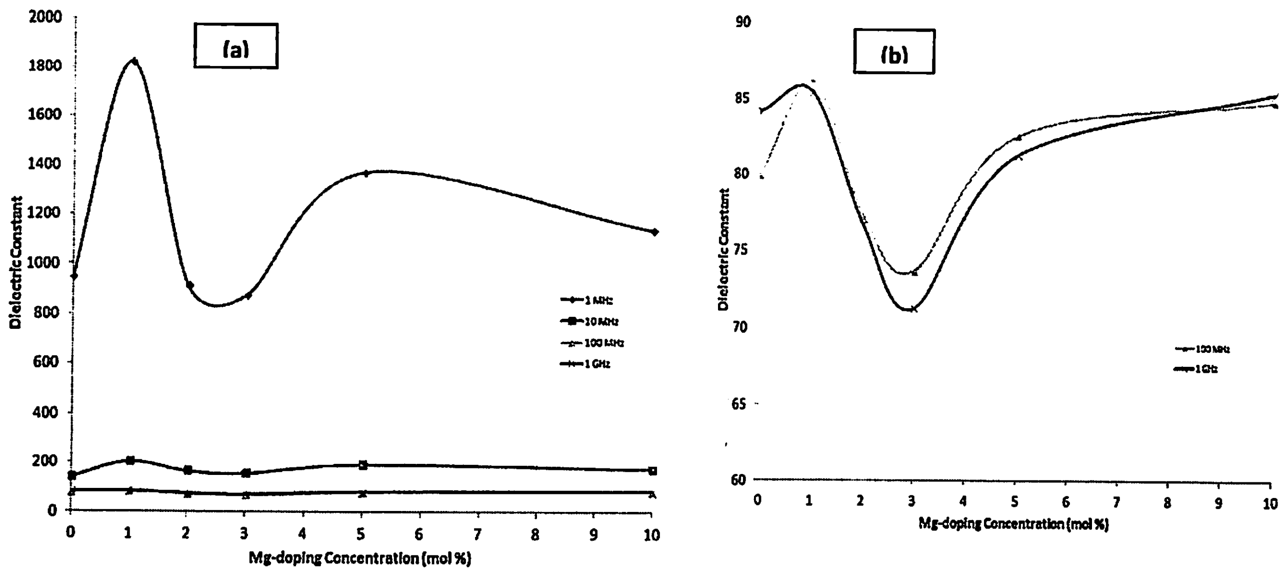

Fig. 4: Dielectric constant of $CaCu_{3-x}Mg_xTi_4O_{12}$ with different Mg concentrations at various frequencies (a) 1 MHz, 10 MHz, 100 MHz and 1 GHz, and (b) close up of dielectric constant at 100 MHz and 1 GHz.

CONCLUSION

$CaCu_{3-x}Mg_xTi_4O_{12}$ ceramics with x = 0, 0.01, 0.02, 0.03, 0.05 and 0.10 have been successfully prepared using solid state reaction method. From XRD analysis, the formation of single phase of CCTO was observed after sintering and the change in lattice constant indicate that Mg ions were completely substituted into the crystal lattice of CCTO structure. SEM micrographs show the grain size becomes larger and the density increased with the increment of Mg dopant concentration. Highest dielectric constant was observed in $CaCu_{3-x}Mg_xTi_4O_{12}$ sample when x = 0.01 at the frequency range from 1 MHz to 1 GHz. Meanwhile, the sample with x = 0.02 exhibited lowest dielectric loss at the frequencies range from 1 MHz to 10 MHz. Therefore, Mg-doped CCTO can be used to improve the dielectric properties of CCTO.

References

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Ceramic
Processing Research

Effect of excess TiO_2 in $CaCu_3Ti_4O_{12}$ on the microstructure and dielectric properties

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Dielectric material $CaCu_3Ti_4O_{12}$ (CCTO) was prepared by a solid state technique. $CaCO_3$, TiO_2 and CuO powders were mixed thoroughly in a ball mill for one hour. The reagent ratios were modified for TiO_2 contents (2-6 mol). The mixed powder were calcined at 900 °C for 12 hours and sintered at 1040 °C for 10 hours. The sintered samples were subjected to XRD phase analysis. The microstructures of sintered pellets were observed by SEM. The effects of TiO_2 content on the phase formation, density, microstructure and dielectric properties are reported. XRD results show that the different phase formation depends on the TiO_2 content. Increasing the TiO_2 content reduces the density. At the surface regions, clear grain boundaries and a dense microstructure were observed. The results show that a sample sintered at 1040 °C for 10 hours give a clearly uniform grain size with the highest dielectric constant (33, 210). The degree of nonstoichiometry of TiO_2 influenced the dielectric properties by reducing its dissipation factor.

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

Introductions

Recently, $CaCu_3Ti_4O_{12}$ (CCTO) was discovered to possess one of the largest static dielectric constant ever measured, reaching nearly ε_r ~80 000 for single crystal samples and 10, 000 for bulk material at room temperature [1, 2, 3]. The higher the dielectric constant, the more charge it can store, and thus smaller electronic circuits can be designed. In addition, unlike most dielectric materials, CCTO retains its enormously high dielectric constant over a wide range of temperatures, from 100 to 600 K, or −173 to 327 °C, making it ideal for a wide range of applications [4, 5]. But the real explanations of the phenomena are still investigated.

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

This study will highlight the reduction of the dissipation factor in CCTO by only varying its components stoichiometric, not by adding any dopants. The raw materials used for producing CCTO electroceramic are $CaCO_3$, CuO and TiO_2. The effect of raw material contents might be one of the reasons why CCTO possess such properties has been argued among the researchers. Shao *et al.*, 2007 have reported that varying the CuO contents can influence the CCTO properties [7]. So, in this paper, we want to highlight the effect of another raw material, i.e. TiO_2 on CCTO formation. There are some reports on how TiO_2 can effect the properties of other electroceramics [8, 9, 10, 11, 12].

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Experimental

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

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REVIEW

Influence of sintering parameters on melting CuO phase in $CaCu_3Ti_4O_{12}$

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Received 9 June 2011; accepted 10 October 2011

KEYWORDS

CuO melt phase;
Microstructure;
CCTO

Abstract Dielectric material $CaCu_3Ti_4O_{12}$ (CCTO) was prepared by solid state technique. $CaCO_3$, TiO_2, and CuO powders were mixed thoroughly in a ball mill for an hour and were calcined at 900 °C for 12 h. This is followed by sintering at a defined standard temperature for this work (1050 °C for 24 h). Other samples were prepared in a similar manner but with different sintering durations. Each of the sample's microstructure was observed by a Scanning Electron Microscope (SEM). Meanwhile, Energy-dispersive X-ray Spectroscopy (EDX) analysis was done on fracture surfaces in order to examine the elements present at grain boundaries. Microstructure observations show the melting and abnormal grain growth with large pores. The solidified liquid at grain boundaries was verified as Cu rich region, as confirmed by EDX analysis. By using the SEM, microstructure of small grains with clear grain boundaries were obtained when sintering was done at temperatures lower than 1050 °C. The microstructure of CCTO was very sensitive to sintering parameters.

Contents

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ELSEVIER Production and hosting by Elsevier

1. Introduction

It is known that some perovskite-structured ceramic compounds display interesting dielectric properties. One of the members, which was named as $CaCu_3Ti_4O_{12}$ (CCTO), was recently studied to investigate the origin of the so-called colossal permittivity, and results were published on single crystal, powders and thin film (Chiodelli et al., 2004). This insulating cubic compound CCTO has attracted much interest because of its high dielectric constant (up to 10^5) over a broad temperature range extending from 100 to 600 K. Furthermore, cubic compound CCTOs display a rather wide microwave frequency window (Subramanian et al., 2000; Litvinchuk et al., 2003). This unique property makes CCTO a promising material for microelectronic applications.

However, the nature on how the CCTO exhibits such high dielectric constant at 100 and 600 K is still not well understood (Lin et al., 2002). Many researchers claimed that factors such as grain boundary, presence of twin boundaries or other planar defects and displacement of Ti ions could be the reasons behind those high dielectric constant properties (Litvinchuk et al., 2003; Wu et al., 2005). More extensive research efforts are needed in order to provide a comprehensive explanation to the said phenomena.

The dielectric properties are very sensitive to processing, such as the mixing, calcination shaping and sintering (Brize et al.,

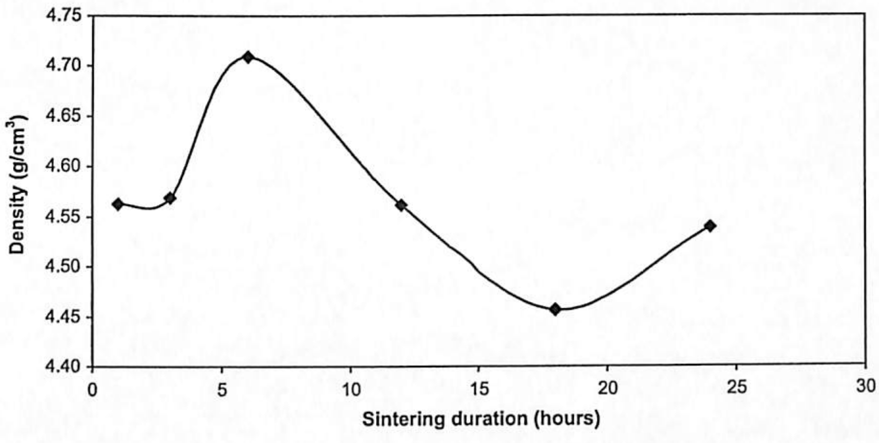


Figure 1 The density results for CCTO sample sintered at different sintering durations.

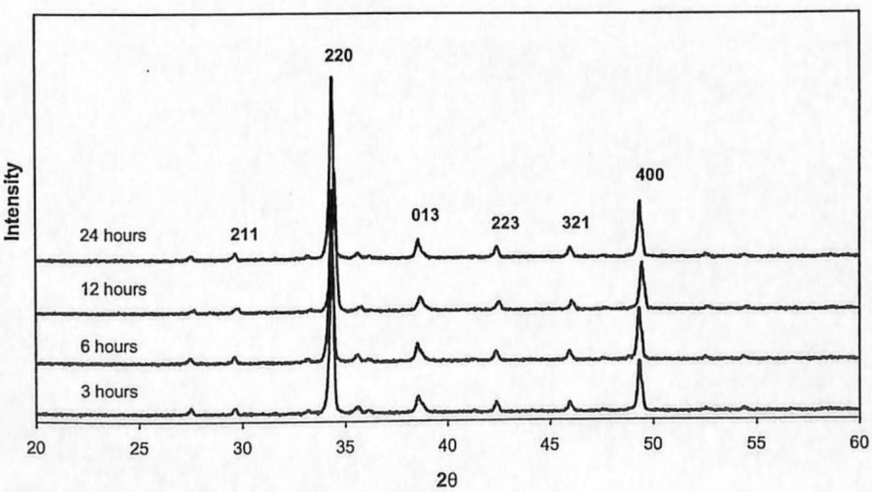


Figure 2 The XRD results for CCTO sample sintered at 1050 °C for different sintering durations.

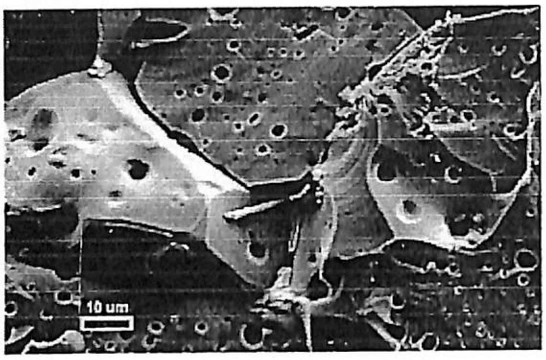


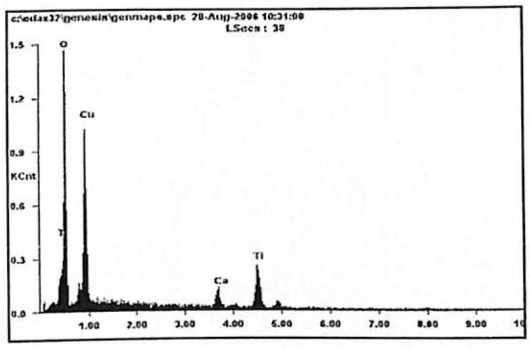
Figure 3 The microstructure of the melt and abnormal grain growth for sample sintered at 1050 °C for 24 h (mag.: 1000×).

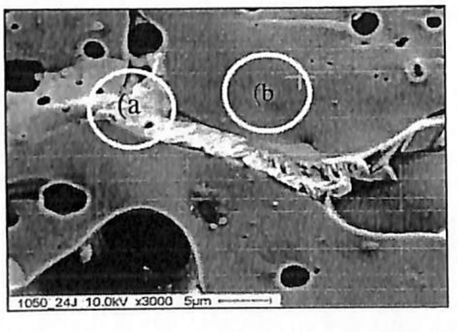
2006). Different parameters in each steps will contribute changes in CCTO properties. In this project, the CCTO was prepared by solid state technique. This involves mixing, calcination, compaction and sintering. Many researchers are concentrating on sintering process, because it is important to find the right sintering parameter such as the duration and temperature. The proper sintering parameter ensures that small grain formation (2–5 μm) with high dielectric constant will be obtained (Brize et al., 2006; Prakash and Varma, 2007). This paper will also be focusing on the sintering parameters. It was stated by some researchers (Valim et al., 2004; Almeida et al., 2002; Kolev et al., 2002) that sintering at 1050 °C for 24 h in the normal atmosphere will produce single phase of CCTO. However, earlier studies on the fabrication of CCTO failed to include microstructure observations. This paper highlights the microstructural observations obtained from this sintering parameter. The results show that there were abnormal grain growth and melting grain with very large pores. Therefore, it is important to investigate the new sintering parameter to ensure the correct microstructure with high dielectric constant property will be obtained. Based on the above facts, a study on the effects of sintering conditions to microstructure is presented in this paper.

2. Method and materials

CCTO samples were prepared by a conventional solid state method. $CaCO_3$ with mean particle size of 15.52 μm (Aldrich, 99%), TiO_2 (0.68 μm) (Merck, 99%) and CuO (6.85 μm) (Aldrich, 99%), respectively, were used as starting materials. Stoichiometric ratios of the reagents (i.e., $CaCO_3$, TiO_2,

(a)





Element	Wt%	At%
O K	35.13	64.49
CuL	32.72	15.12
CaK	05.64	04.13
TiK	26.51	16.25

(b)

Element	Wt%	At%
O K	22.31	53.28
CuL	77.69	46.72

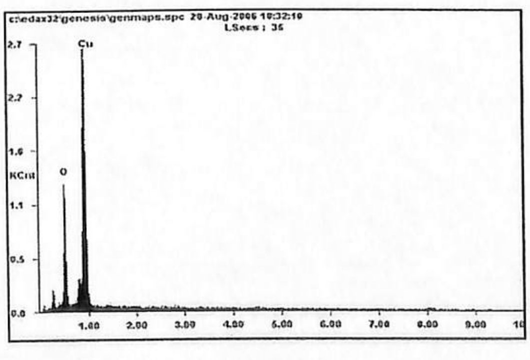


Figure 4 EDX analysis for the sample sintered at 1050 °C for 24 h.

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CuO: 1, 4, 3) were mechanically ball milled for 1 h, with a ball to powder ratio of 10:1. The milling process was done in inert atmosphere. A powder exhibiting free flowing characteristics was then obtained by sieving the dried milled powders. Subsequently, the powder was calcined in air at 900 °C for 12 h. Next, the powders are pressed at 300 MPa, to be made into cylindrical specimens (with dimensions of 5 mm in diameter and thickness of approximately 0.5–1 mm). These pressed specimens, or green pellets, were then sintered in air at 1050 °C for 1, 3, 6, 12, 18 and 24 h soaking time. Bulk density measurements were made using the Archimedes principle. The microstructures (on the fracture surface of the sintered specimens) were investigated using SEM (Zeiss SUPRA 35VP). EDX analysis was done to analyze the elements presence in CCTO grains and its boundary.

3. Results and discussions

Fig. 1 shows the densities of the CCTO samples that were sintered at various sintering durations. The graph shows that the density increases with sintering duration, up to a maximum relative density of 93% after 6 h of sintering. Beyond this sintering time, the density was found to drop. The same trend also was reported by previous researchers that have studied on other electroceramic systems (Guo et al., 2004; Wang et al., 2004; Zhang et al., 2004). Temperature, duration, heating rate and atmosphere are the main factors to be considered to obtain dense electroceramic materials (Wang et al., 2004).

Fig. 2 shows the XRD results for samples sintered at different sintering durations. The diffraction shows the formation of a single phase of CCTO (ICSD 01-075-2188) with peaks observed when 2θ angles are 29.2991°, 34.0233°, 38.3573°, 42.0577°, 45.6385°, 49.0135°, and 61.1392°, respectively. The same formation also was reported by Valim et al. (2004) and Almeida et al. (2002).

SEM observations were done to scrutinize the microstructure of the sintered samples. We have tried to keep our experimental parameters and conditions in similar to those reported for the same parameters of CCTO preparation (Almeida et al., 2002). Fig. 3 shows the fracture surface of the sample sintered at 1050 °C for 24 h. This figure shows the melt and abnormal grain growth (100 μm), with large pores. There were also solidified liquid regions assembled at grain boundaries, which are of brighter shade.

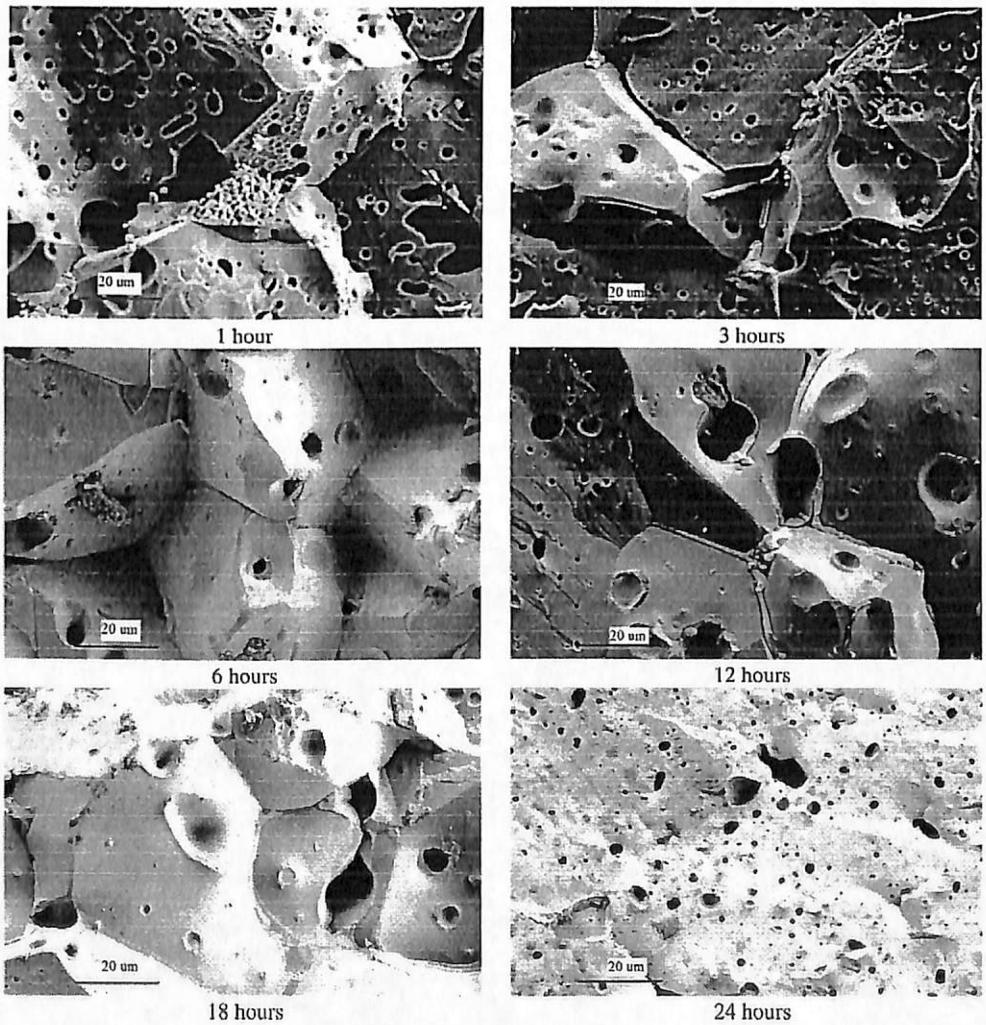

Figure 5 The microstructure observation for the samples sintered at 1050 °C for different durations (mag.: 1000×).

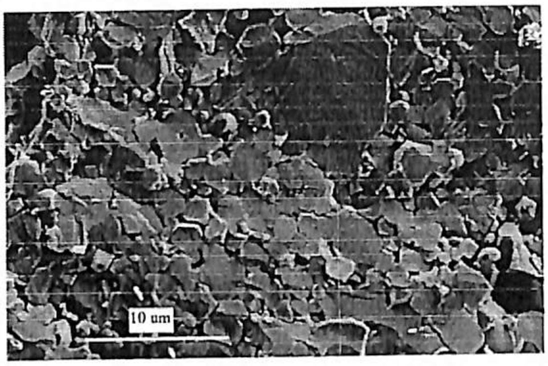

Figure 6 The micrograph of sample sintered at 1040 °C for 10 h (mag.: 3000×).

EDX analysis was done on the regions with brighter shades. This is to detect the present elements and the result is shown in Fig. 4. Bright zone (a) shows the existence of Ca, Cu, Ti and O elements, all correspond to CCTO compounds. Meanwhile, Cu and O elements were detected in the (b) region. This was not identified by XRD, may be due to its amorphous state.

Since the grain was melted, the experiment was carried on by sintering the CCTO samples at shorter times. Fig. 5 shows the microstructures obtained from the samples sintered at 1050 °C for different durations. The microstructures were similar to what was obtained for CCTO sintered for 24 h. It displays the abnormal grain growth with large pores, instead of melting phase wetting and assembling at grain boundaries region. When the soaking time was increased up to 18 h, the whole structure melts. There are obvious signs of grain growth in the sintered specimens at longer times, implying a considerable increase in the amount of liquid phase. This phenomenon may be caused by secondary recrystallization and possible vaporization of Cu during a very long sintering time. Fritsh et al. (2005) also reported that the huge grains observed for the CCTO that contain copper oxide are also probably related to the appearance of a liquid phase that wets the grain during the sintering. Small amounts of copper oxide are believed to be responsible for the abnormal grain growth.

From the microstructure viewpoint, the 6 h sintered sample was seen to be the most dense. This corresponds to the measured density, obtained by the Archimedes principle. Since the changes in sintering duration still cannot produce a fine and dense CCTO grain, the research was extended in order to investigate the right sintering parameters that should be used to get the desired CCTO grain. Finally, after several attempts, results showed that the samples sintered at lower temperatures and shorter times gave fine and dense grain, without solidified melting CuO phase at grain boundaries. Fig. 6 represents the microstructure observed from the sample sintered at 1040 °C for 10 h. The micrograph shows that the grains were squarish in shape with an average size of 1–3 μm.

4. Conclusion

The CCTO single phase compound was successfully produced by sintering the sample at 1050 °C for 24 h (defined standard temperature of this work). Nonetheless, the microstructures only showed abnormal grain growth and large pores reducing sintering times alone did not change the grain formation. The sintering should be done at lower temperatures (i.e., 1040 °C), plus reduced times (i.e., 10 h) in order to obtain a fine and dense grain, without solidified melting CuO. The sample sintered at 1040 °C for 10 h produces stacked grains of squarish shape with the average size of 1–3 μm.

Acknowledgements

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The Effect of MgO Dopant on the Dielectric Properties of $CaCu_3Ti_4O_{12}$ Ceramics

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Keywords: $CaCu_3Ti_4O_{12}$, Mg-doped, solid state processing, dielectric constant, dielectric loss.

Abstract. The properties of undoped and Mg-doped $CaCu_3Ti_4O_{12}$ (CCTO) ceramics have been studied. The samples were calcined at 900°C for 12 hours, and sintered at 1030°C for 10 hours. X-ray diffraction analysis on calcined samples shown the formation of CCTO phase with trace of secondary phases meanwhile completed formation of CCTO single phase obtained for sintered pellets. The peak positions of Mg-doped CCTO were slightly left-shifted from the undoped CCTO, attributed to the lattice expansion. Scanning electron microscopy analysis showed that the grains size becomes larger with the increment of dopant amount. Enhanced dielectric constant was observed in the $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ ceramics with x = 0.05 for the frequency range from 1 MHz to 1 GHz. The dielectric loss seem to be at lowest value when $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ ceramics with x = 0.10 at the same frequency range. The results indicate that Mg ions have effectively changed the properties of CCTO.

Introduction

Recently, the perovskite structure $CaCu_3Ti_4O_{12}$ (CCTO) has been attracted many researchers to give the attention due to an extraordinarily large dielectric constant (ε_r~10^4) at room temperature and have stability at low frequencies (<1 MHz). Subramanian and his teams [1] were first discovered these unique properties of CCTO. Meanwhile, Ramirez et al. [2] reported that the high-K CCTO has very small temperature dependence even though in a broad temperature range (100-400K). Higher ε_r means more charge can be stored and hence smaller electronic devices can be designed. However, the problem of high dielectric loss seems to inhibit this material to be commercialized. The typical value of dielectric loss of CCTO as reported by Fritsch et al. [3] is about 0.5 at 1 kHz at room temperature. The origin of the colossal dielectric permittivity of CCTO is still being discussed among the researchers. The extrinsic effect is believed to be responsible for this high dielectric constant and most attributed to an internal barrier layer capacitor (IBLC) [4]. A nature of Maxwell-Wagner relaxation is shows by IBLC model in CCTO ceramics. Hence, some methods have been introduced to decrease dielectric loss such as the substitutions and the insulating phase doping [5,6]. The dielectric properties of CCTO can be modified by using suitable dopants such as lanthanum oxide [7], niobium oxide [8] and mangan oxide [4].

Therefore, with the same objective, this research also seeks to improve the electrical properties of CCTO. P. Gao et al. [9] have stated magnesium oxide (MgO) can reduce dielectric loss $Ba_{0.6}Sr_{0.4}Ti_3$ (BST) material. So, MgO was used as dopant material to produce Mg-doped CCTO ($Ca_{1-x}Mg_xCu_3Ti_4O_{12}$). Even though many reports have been published about dielectric behavior of Mg-doped CCTO, most of the works focused on characterization in the low frequency range which is from 20 Hz to 1 MHz [10,11]. In this study, the dielectric properties of undoped and Mg-doped CCTO were characterized at high frequencies (1 MHz to 1 GHz).

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Effect of MgO additive on the properties of $CaCu_3Ti_4O_{12}$ electroceramics

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Keywords: $CaCu_3Ti_4O_{12}$, Substitution, Microstructure, Dielectric Responses, High Frequency.

Introduction

Materials with high dielectric constant are broadly used in technological applications such as capacitors, filters and resonators. $CaCu_3Ti_4O_{12}$ (CCTO) was known to have colossal dielectric constant (ε_r~10^4) at room temperature [1]. Besides, it was also reported that the high dielectric constant has small temperature dependence and stable in a wide temperature range (100-400K) [2].

In this study, MgO was used as dopant source to improve the electrical properties of CCTO. Mg^{2+} ions have same ionic valence with Ca^{2+} and Cu^{2+} ions. Thus, it can be used to modify the perovskite structure of CCTO to $CaCu_{3-x}Mg_xTi_4O_{12}$ and $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ ceramics. The structure of CCTO is body-centered cubic (bcc) with four perovskite type formula units of ABO_3 where Ca^{2+} and Cu^{2+} ions share A sites and Ti^{4+} is placed at B sites [3]. The Mg ions of additive that can be used to improve the dielectric properties of CCTO is known as isovalent substitution. It is the alteration of chemical formula to substitute the elements with other elements that have same ionic charge [4]. Therefore, in this work, study is focused on cation substitution on A-site CCTO by magnesium dopant. The dielectric properties of undoped and Mg-doped CCTO samples were measured at high frequency range of 1 MHz to 1 GHz.

Experimental

Undoped and Mg-doped CCTO with different mol % of dopant (x = 0, 0.01, 0.02, 0.03, and 0.05) were prepared by solid state processing. The raw materials of $CaCO_3$, CuO, TiO_2 and MgO were weighted accordingly to stoichiometric ratio. The samples were wet ball milled using zirconia balls and deionized water as wetting agent for 1 hour. The mixtures were dried, grinded and then calcined in air at 900°C for 12 h. The calcined powder was pressed at 300 MPa into pellet forms using hydraulic press. The pellets were then sintered in air at 1030°C for 10 h. XRD was used to identify phase and crystal structure of the calcined powder and sintered samples. Meanwhile, the microstructure of the samples was observed using SEM. The samples were polished and both surfaces were coated using silver paste for dielectric measurement. The dielectric properties of the samples were measured through Impedance Analyzer at frequency range from 1 MHz to 1 GHz.

Results and Discussion

Figure 1 illustrated XRD pattern for sintered CCTO samples. Single phase CCTO was obtained for all sintered samples (ICDD no: 01-075-2188). All of diffraction patterns can be indexed to a cubic unit cell with space group *Im*3.

The effect of Mg dopant on lattice parameter of CCTO was calculated from XRD results. It was found that lattice constant is initially decrease with Mg dopant concentrations

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THE EFFECT OF MgO DOPANT ON THE DIELECTRIC PROPERTIES OF $CaCu_3Ti_4O_{12}$ CERAMIC

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ABSTRACT
The properties of undoped and Mg-doped $CaCu_3Ti_4O_{12}$ (CCTO) ceramics have been studied. The samples were calcined at 900°C for 12 h, and sintered at 1030°C for 10 h. All calcined samples shown the formation of CCTO phase with trace of secondary phases meanwhile completed formation of CCTO single phase obtained for sintered pellets. The peak positions of Mg-doped CCTO were observed have slightly left-shifted from the undoped CCTO, attributed to the lattice expansion. The grains size becomes larger with the increment of dopant amount. Enhanced dielectric constant was observed in the $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ ceramics with x = 0.05 for the frequency range from 1 MHz to 1 GHz. The dielectric losses seem to be at lowest value when $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ ceramics with x = 0.10 at the same frequency range. The results indicate that Mg ions have effectively changed the properties of CCTO.

Keywords: $CaCu_3Ti_4O_{12}$, Mg-doped, grain growth, dielectric properties.

INTRODUCTION
Nowadays, many researches paid their attention to the huge dielectric constant of $CaCu_3Ti_4O_{12}$ (CCTO). It was first discovered by Subramanian et al. [1] and they claims that CCTO can exhibits a high dielectric constant over ~10,000 at room temperature. Ramirez et al. were also reported that its giant permittivity is temperature independence over the temperature range of 100-400K [2] and its dielectric constant is almost frequency independent below 10^6 Hz [3]. Some method has been introduced to decrease dielectric loss by using suitable dopants like lanthanum oxide [4] Therefore, with the same objective, this research also seeks to improve the electrical properties of CCTO. Hence, in this study, the dielectric properties of undoped and Mg-doped CCTO characterized at high frequencies (1 MHz to 1 GHz) were investigated.

EXPERIMENTAL PROCEDURE
$Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ (x = 0, 0.01, 0.02, 0.03, 0.05 and 0.10) were prepared using conventional solid state processing technique. Appropriate amount powders of $CaCO_3$, CuO, TiO_2 and MgO were firstly weighted and were mechanically wet ball milled using deionized water as wetting agent for 1 hour. Zirconia ball was used as milling medium with the mass ratio of balls to powder is 10:1. The mixtures were dried overnight in oven at 100°C. Dried powder then were grinded using agate mortar to form the fine free powders. The powder was placed in alumina crucible and calcined in air at 900°C for 12 hours using Carbolite Furnace. Then, the yellowish powder was characterized by X-ray Diffractometer (XRD) analysis to investigate the phase formation of calcined powder. The calcined powder was ground and pressed to form a pellet shape by using hydraulic press at 300 MPa. The pellets samples were sintered in air at 1030°C for 10 hours using High Temperature Tube Furnace, and then were subjected to XRD to identify phase purity and crystal structure of the samples. Microstructure of the samples was observed using Scanning Electron Microscopy (SEM). The dielectric properties of samples were measured using Impedance Analyzer at frequencies range from 1 MHz to 1 GHz.

RESULTS AND DISCUSSION

All calcined powder show the formation of CCTO phase with minor peaks of secondary phase and unreacted raw materials. The XRD analysis was also done for sintered samples. A completed formation of single phase CCTO was observed for all the samples as shown in Fig.1.

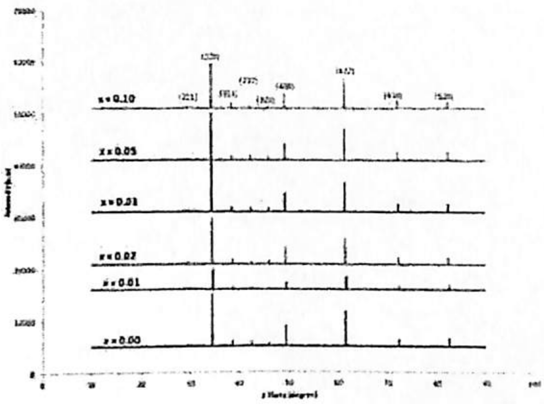

Figure 1: X-ray diffraction patterns of sintered samples.

Fig. 2 shows the SEM micrographs of undoped and Mg-doped CCTO. According to the Fig. 2, the undoped sample produced the smallest grain size and the grain size becomes larger with the increase of mole of Mg doping. The 10 mol % of Mg-doped CCTO produced highest grain size and also promotes abnormal grain growth. The abnormal grain growth might be caused by Cu_2O or CuO segregates at the grain boundaries [5].

CONCLUSIONS

The $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ (x = 0, 0.01, 0.02, 0.03, 0.05 and 0.10) ceramics samples have been prepared using solid state technique. From the XRD analysis, the formation of single phase of CCTO was seen after sintering process and the change in lattice constant indicate that Mg ion substitute into the lattice of CCTO. SEM micrograph shows the grain size becomes larger with the increment of mol % of dopant.

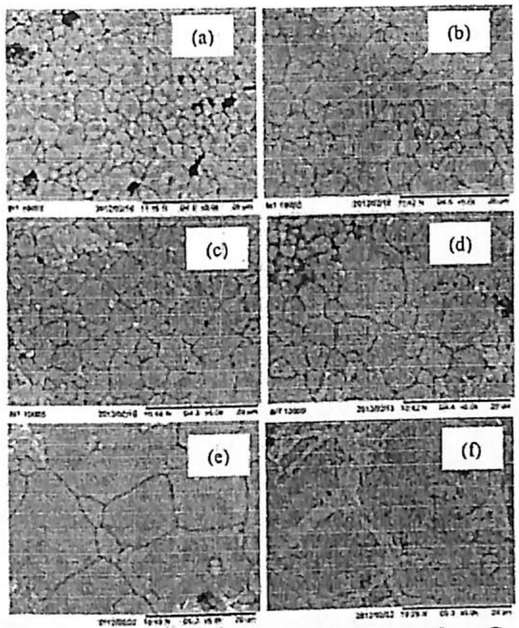

Figure 2. SEM images of $Ca_{1-x}Mg_xCu_3Ti_4O_{12}$ with: (a) x=0, (b) x=0.01, (c) x=0.02, (d) x=0.03, (e) x=0.05, (f) x=0.10

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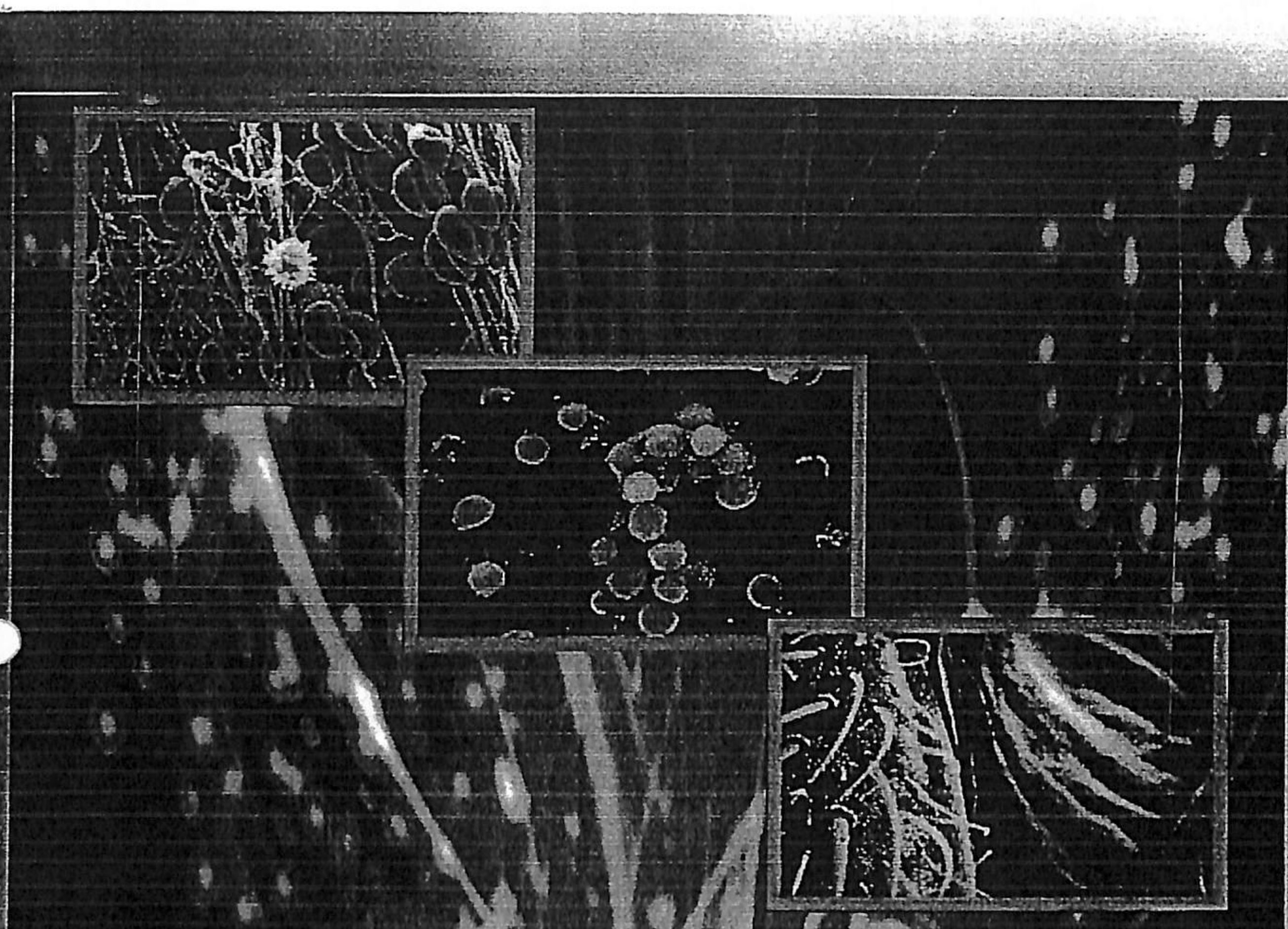

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Study of Dielectric Properties of $CaCu_3Ti_4O_{12}$ Doped with MgO

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Abstract

Pure and MgO doped dielectric material $CaCu_3Ti_4O_{12}$ (CCTO) was prepared by solid state technique. $CaCO_3$, TiO_2 and CuO powders were mixed thoroughly in a ball mill for an hour. The MgO was added into reagent for 0.1 – 1.0 mol%. The mixed powders were calcined at 900 °C for 12 hours and sintered at 1040 °C for 10 hours. The phase formation was identified by XRD and the microstructures of sintered pellets were observed by SEM. The surface polished sample was painted with silver paste to construct the dielectric measurement at different frequencies. CCTO ceramics exhibited a polycrystalline characteristic by XRD patterns and no obvious changes in crystal phase with various mol% of MgO dopant added. The secondary phase also detected, confirmed as CuO. All samples show the phenomena of abnormal grain growth, with solidified liquid phase at grain boundary region. Addition of dopant increases the dielectric constant and reduced the loss tangent. The optimum dielectric properties are obtained for sample CCTO-3MgO with highest dielectric constant value (40,120) and loss factor (0.071), measured at 10 kHz.

Keywords: MgO content, microstructure, dielectric, CCTO

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Tajuk Projek	:	***Production of CaCu3Ti4O12 (CCTO) Electroceramics via Plasma Spray Method.***
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Saya dengan hormatnya merujuk kepada perkara di atas dan surat daripada Kementerian Pengajian Tinggi (KPT) yang telah diterima pada 21 Mac 2013 adalah berkaitan.

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