

Role of mixing mediums in the synthesis of single phase $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO)

Rosyaini Afindi Zaman^{a,c}, Wan Fahmin Faiz Wan Ali^{a,b}, Mohamad Johari Abu^a, Julie Juliewatty Mohamed^a, Mohd Fadzil Ain^b, Zainal Arifin Ahmad^{a,*}

^aStructural Materials Niche Area, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

^bSchool of Electrical and Electronic Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

^cFaculty of Applied Sciences, Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia

The role of mixing mediums on synthesizing high purity CCTO as a function of calcination temperature was systematically investigated via solid state reaction (SSR) route. The efficacy of the mediums (ethanol, deionised water, distilled water, and dry mix) was primarily determined by X-ray diffraction (XRD) technique and FESEM, respectively. It is found that, a single phase CCTO was successfully synthesized in all mediums, with the deionised water showed the lowest reaction temperature (950 °C) to fully crystallize the powder mixtures compared to other mediums. No significant changes were seen in the grain shape since only a bimodal structure with grain size ranging from 0.5 μm to 2.57 μm was observed. The effect of media was also seen in their dielectric properties of the calcined powders. Dry mixing (DM) had the highest dielectric permittivity ($\epsilon_r = 118$) whereas others are only between 59-99. Therefore, this observation proved that mixing medium could influence the formation temperature and dielectric properties of CCTO.

Key words: Mixing medium, Calcination, XRD, CCTO, Dielectric properties.

Introduction

Recently, materials with colossal dielectric constant (CDC) become subject of interest due to the advancement in modern microelectronic devices such as capacitors, resonators and filters [1-3]. The ternary oxide compound of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has been considered for these applications due to its exceptionally giant dielectric permittivity values ($\epsilon \sim 120000$) and low dielectric loss ($\tan \delta \sim 0.0452$) [4, 5]. However, these characteristics can only be attained if single phase CCTO is produced. Various methods are employed such as sol-gel route [6], combustion techniques [7] and hydrothermal [8] process to fulfil this need. Unfortunately, these methods are rather complex and costly. For example, a slight pH change in sol-gel route (from pH 4 to pH 5) produces secondary phases (e.g. Cu-rich phase, Cu_2O) [9]. Therefore, solid state reaction (SSR) method is a better choice due to a straight-forward process besides the cost efficient starting raw materials [10]. These justify its being comprehensively adopted in many researches and industries to produce a single phase CCTO. The drawbacks of SSR method are high processing temperature (up to 1400 °C) and presence of unreacted

starting raw materials if the mixing and/or firing steps are not properly done. This method is always end up with undesired reaction that produces unnecessary secondary phase(s) [11].

These disadvantages have been investigated for years and various finding related to the CCTO formation were established. From literatures, the effect of sintering temperatures, soaking times, addition of glass additives and modification of the standard CCTO stoichiometry were investigated, yet the issue still found unresolved. For example, Sanjesh and Govindan [12] found that a single phase CCTO could be produced at 1100 °C for 10 h. However, Ab Rahman et al. [13] commented that the temperature was insufficient for the formation of single phase CCTO. Mazumder et al. [14] claimed that glass addition (e.g. V_2O_5 , TeO_2 , B_2O_3) of less than 2% could improve CCTO formation but the final product was seen to have exfoliated sheets of Cu-rich phase at CCTO grain boundaries. Non-stoichiometry formulation was suggested by Cao et al. [15] which also produced single phase CCTO. However, their findings contradicted Schmidh et al. [16], since both Ca_2CuO_3 and CaTiO_3 were also present in CCTO ceramics. Unlike Daumann et al. [17] work, they verified that the classical SSR parameters such as mixing speed, mixing duration, and type of mixing medium, also contributed the formation of a single phase product [17-19]. Nevertheless, so far, the role of mixing medium is not yet extensively investigated in the synthesis of CCTO.

*Corresponding author:
Tel : +6045996128
Fax: +6045946907
E-mail: srzainal@usm.my

The above mentioned SSR parameters also identified as one of the important operations to intermingling the solid particles so that, the uniform and homogeneous distribution of the ingredients can be attained in addition to overcoming the particles segregation [19, 20]. To ensure an occurrence of a complete reaction, the reactants must be in intimate contact with the molecular scale. Thus, it is necessary to understand the elementary processes involved during the operation. Literatures indicated that there are two forms of mixing processes i.e., dry and wet. However, compare to dry mixing, it is proven that wet mixing shows more significant effect on the mobility and dispersion of particles. This in fact, positively improve the reactant contact prior to the initiation solid-state reaction [20, 21]. Besides being able to enhance the reaction, wet mixing at different mediums (such as ethanol, methanol, distilled water, etc.) is found to be affecting the product microstructure. For example, when methanol is used for BaTiO_3 synthesis, the grain size obtained was approximately $2\ \mu\text{m}$. However, when methanol is replaced by distilled water the grain size increased by 96% (up to $50\ \mu\text{m}$) [22].

These findings have conceded that different mixing mediums would strongly affect the final product properties which related to the contact quality of particles of the starting raw materials. When the solid mixing is poorly done (inadequate selection of mixing medium), an incomplete reaction-diffusion also known as imperfect mixing between powder mixtures resulting from the poor particle contact may occur [17]. Thus, a systematic investigation has to be carried out on the effect of mixing medium on the CCTO phase(s) formation, which directly influences its microstructure and dielectric properties.

Therefore, an investigation to evaluate the effects of mixing medium efficiency for wet mixing (ethanol, deionized water and distilled water) on the formation of single phase CCTO has been carried out. The results are compared to the dry mixing process. The mixing performance has been qualitatively and quantitatively measured using X-ray diffraction (XRD) software (X'pert HighScore Plus, PANanalytical v.2.2). Thermal analysis, microstructure evaluations and dielectric properties are also conducted to further confirm and verify the mixing performance. Finally, a simple model for different mixing mediums has been proposed.

Experimental

Commercial powders of CaO (Sigma-Aldrich, $d_{50} \approx 5.25\ \mu\text{m}$, 99.9% purity), CuO (Sigma-Aldrich, $d_{50} \approx 10.24\ \mu\text{m}$, 99.9% purity) and TiO_2 (Sigma-Aldrich, $d_{50} 9.32\ \mu\text{m}$, 99.9% purity) were used as the starting raw materials. The raw materials were weighted according to the on-stoichiometry ratio of CCTO ($\text{CaO} + 3\text{CuO} + 4\text{TiO}_2$) and poured into four sets of 500 ml polyethylene (Super 90) bottle with zirconia balls

(weight ratio of mixture to ball is 10:1). For dry mixing, the sample was designated as DM. Meanwhile, for wet mixing; distilled water, deionized water and ethanol ($\text{C}_2\text{H}_5\text{O}$) were used separately as a medium (150 ml per bottle) and later labelled as WM-D, WM-W and WM-E, respectively. A rotary ball mill (Heidolph Overhead Shaker Reax 2) with 120 rpm rotation was used to form homogeneous slurry of the combined powders at different mediums for 8 h. The slurry was dried in an oven (Memmert Oven, UM 400) at $100\ ^\circ\text{C}$ for 24 h to form "dried-cake" before being ground using an agate mortar. Later, the dried mixtures were calcined from $650\ ^\circ\text{C}$ to $1000\ ^\circ\text{C}$ for 5 h, respectively.

The performance of each mixing has been evaluated based on the amount of CCTO formation observed through characterization by XRD (Bruker D8 Advanced). The patterns were obtained at a scan speed of $0.2\ ^\circ\text{s}^{-1}$ using Cu-K α radiation and analysed qualitatively and quantitatively using PANalytical X'Pert HighScore Plus software based on Young's refinement strategy method. The quality of refinement is evaluated based on (i) weighted residual profile, ($R_{\text{wp}} < 15$), and (ii) Goodness of fit, $\text{GOF} < 4$ [23] to ensure that the refinement is reasonable and acceptable. Meanwhile, a Linseas X81 machine was used to investigate the material properties with respect to temperature changes (TGA and DTA). The morphology of calcined powders was observed via field-emission scanning electron microscopy (FESEM, 35VP Supra Carl-Zeiss). The dielectric properties of compacted calcined powders were measured using an LCR meter (Agilent 4284A), at frequency range of 20 Hz - 10 MHz. The results at different mixing mediums were then compared as presented in the discussions.

Results and Discussion

The performance of the mixing process in synthesizing single phase CCTO is very much influenced by types of mixing medium. It can be proven by X-ray diffraction (XRD) analysis. Fig. 1 shows the XRD analysis of CCTO formation as a function of mixing mediums and their respective composition is given in Table 1. This phase determination is essential to investigate the amount of CCTO formation (%) for any given mixing medium. There are five main phases presence in all samples and best fitted with the ICSD database i.e., $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ /CCTO (#98-005-8087), TiO_2 (#98-005-1309), CuO (#98-002-8593), CaTiO_3 (#98-006-6626), and CaO (#98-005-8843), respectively.

It is found that different mixing mediums at various calcination temperatures have affected the amount (%) of single phase CCTO formation. It is seen WM-M as presented in Fig. 1(c) has produced 100% CCTO at $950\ ^\circ\text{C}$ followed by WM-D (Fig. 1(b)) at $980\ ^\circ\text{C}$. Therefore, WM-E (Fig. 1(a)) and DM (Fig. 1(d)) has produced 100% CCTO at $1000\ ^\circ\text{C}$ which $50\ ^\circ\text{C}$ later compared to WM-M. This 5% temperature differences

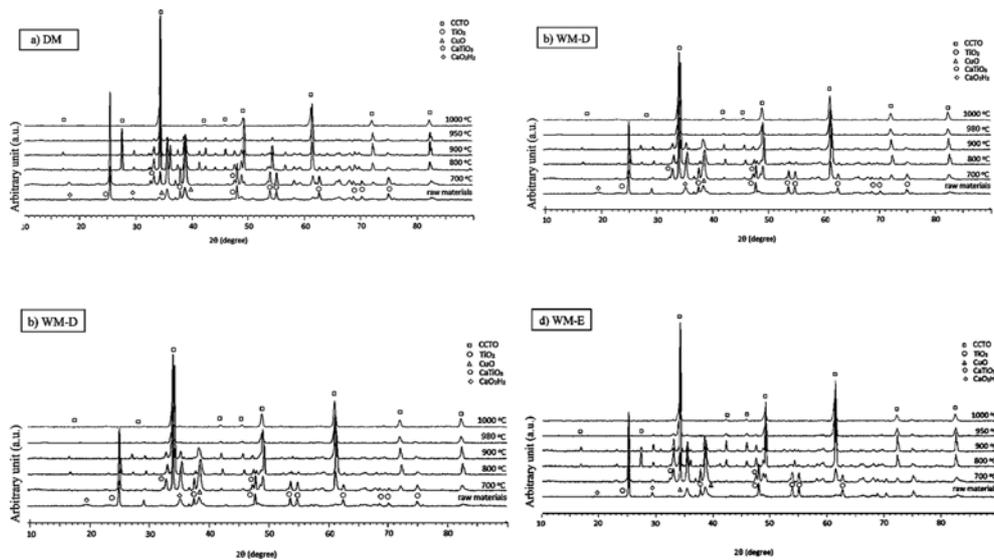


Fig. 1. The XRD pattern of the calcined CCTO powder synthesized with various mixing mediums; (a) dry mixing (DM), (b) distilled water (WM-W), (c) deionized water (WM-D) and (d) ethanol (WM-E), respectively.

Table 1. Results of Rietveld refinement of phase composition as a function of mixing medium and calcination temperature.

Mixing medium	Phase	Phase composition (wt%) at different calcination temperature (°C)				
		700	800	900	950	1000
Dry	CCTO	12	33	61	68	100
	CaTiO ₃	13	11	10	12	
	CuO	28	27	13	11	
	TiO ₂ (A)	47				
	TiO ₂ (R)		29	16	9	
Ethanol	CCTO	15	53	86	98	100
	CaTiO ₃	16	15	3	2	
	CuO	34	19	9		
	TiO ₂ (A)	35	5			
	TiO ₂ (R)		8	2		
Deionized water	CCTO	28	54	57	100	100
	CaTiO ₃	12	13	11		
	CuO	24	20	18		
	TiO ₂ (A)	36	7	5		
	TiO ₂ (R)		6	9		
Distilled water	CCTO	27	63	75		100
	CaTiO ₃	14	14	10		
	CuO	31	13	10		
	TiO ₂ (A)	29	10			
	TiO ₂ (R)			5		

implied that WM-M is able to provide a homogeneous and better surface contact; where the reactant are intimately being contacted at molecular level compared to WM-D, WM-E and DM.

However, at 1000 °C, the formation of 100% CCTO

is suggested not governed by surface contact (surface diffusion) but via cation diffusion (i.e., Ti⁴⁺, Cu²⁺, Ca²⁺) [16]. At this temperature, the mobility of these cations increases and able to produce 100% CCTO. However, the effect of the mixing process on cation diffusion is not explained further in this work. It is suggested that developing a reaction diffusion model via kinetic investigation is necessary to further explain the effect of mixing process at the micromixing scale [24]. Thus, the XRD results show that the conversion of starting raw materials to single phase CCTO with respect to type of mixing mediums are different at various calcination temperatures. The reasons are based on i) the amount (%) of CCTO yielded is varied at various calcination temperature, ii) different mixing mediums would affect the formation of single phase CCTO and iii) the mixing mediums may also affect the particle surface contact of precursor, respectively.

Besides qualitative and quantitative XRD analyses, the effect of mixing mediums on microstructure was also observed via FESEM and EDX analyses as depicted in Fig. 2. The samples particle sizes as a function of mixing mediums measured at respective calcination temperatures is shown in Fig. 3. FESEM micrograph shows that the particle sizes increased proportionally from 0.5 μm to 2.57 μm as the calcination temperature increase from 650 °C to 1000 °C besides exhibiting a spherical particle shape. The uniform particle shapes implied that the starting powders component are homogeneously disperse [25]. It is seen that DM has demonstrated the largest particle size (~ 2.57 μm) while WM-W shows otherwise (0.73 μm). These particle profile evolutions indicated that the mixing mediums exhibit interesting behaviour at reactant interfaces. These changes will be explained later based on various possible arrangements of particles and their

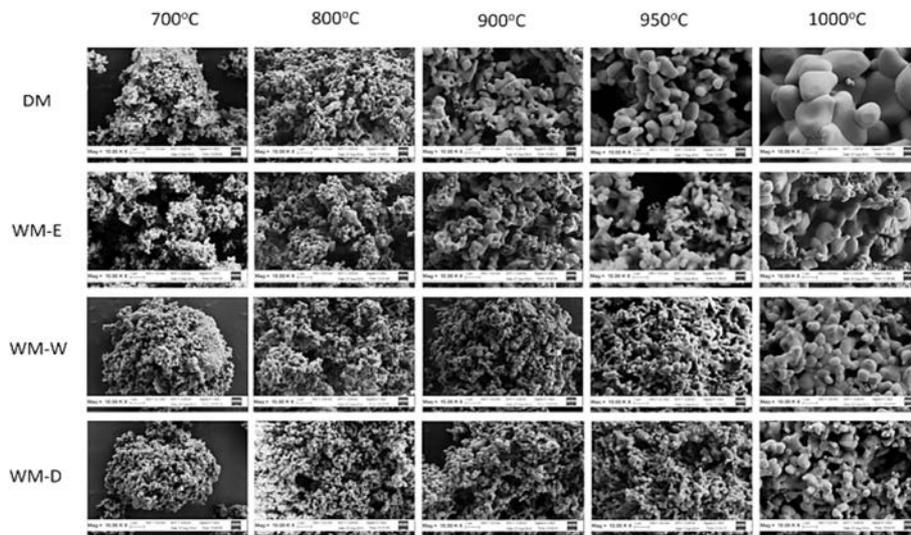


Fig. 2. FESEM micrograph of CCTO powders prepared at different mixing mediums and calcination temperatures.

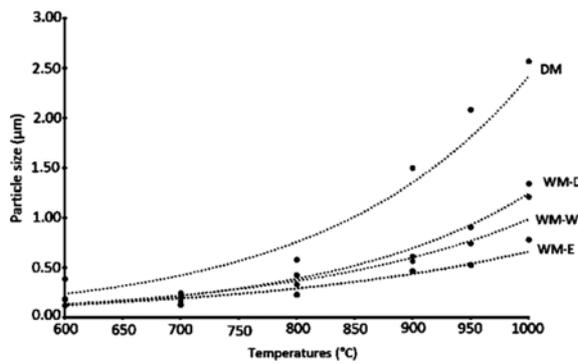


Fig. 3. Grain sizes of calcined CCTO powders at various mixing mediums.

shape.

Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) were employed to further analyse the effect of mixing medium on the CCTO formation. Fig. 4 shows the thermal analysis of CCTO powders synthesized via different mixing mediums measured from 25 °C to 950 °C, respectively. TGA graph shows the three significant weight loss curves during the CCTO formation. The first curve at around 390 °C is due to loss of moisture (H_2O) and organic solvent ($\text{C}_5\text{H}_4\text{O}_6$) because of their low boiling temperature (<120 °C). The second curve ranging from 390 °C to 470 °C describes the weight loss (average of 16%) of carbon monoxide from decomposition of ethanol. However, a significant loss seen at the third curve from 630 °C to 720 °C (~20%) suggested the evaporation of CO_2 from the powder mixture [26]. The formation of intermediate phase ($\text{CaO} + \text{TiO}_2 \rightarrow \text{CaTiO}_3$) took place between second and third curves were confirmed by DTA analysis. It is also found that the stable phase is started to form at 780 °C representing the CCTO formation as confirmed by XRD analysis (Fig. 1).

Different mixing mediums have caused several variations in particle sizes and shapes. These changes

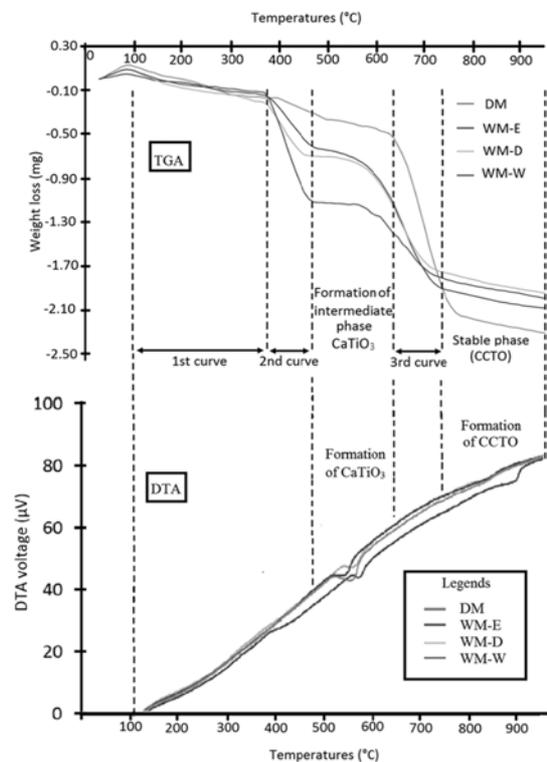


Fig. 4. TGA and DTA results of CCTO powders with different mixing mediums, respectively.

also may affect the dielectric properties of compacted calcined CCTO powders. Fig. 5 shows the average dielectric permittivity (ϵ_r) of compacted calcined CCTO powders at 1000 °C for 5 hours between 20 Hz - 10 MHz. It is found that ϵ_r for all samples synthesized using different mixing mediums are not the same. The highest ϵ_r shows by DM (118) followed by WM-W (99), WM-D (93) and WM-E (59). These differences are due to ILBC effect arose from particle boundaries and domain boundaries of CCTO structure [25-26].

According to the above mentioned scenario, the

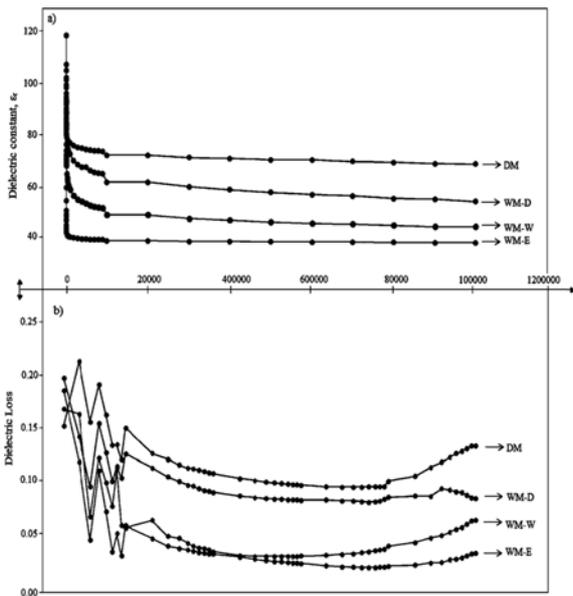


Fig. 5. (a) Dielectric constant and (b) dielectric loss of calcined CCTO powders synthesized using different mixing mediums.

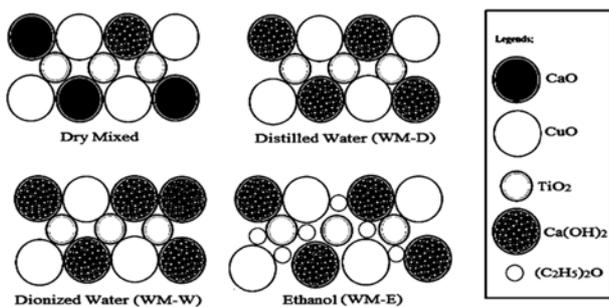


Fig. 6. Schematic diagram of reactant powders distribution at various mixing mediums.

following scene for the formation of CCTO at different mixing mediums is proposed. The explanation is not on the basis of mathematical fitting to the empirical data or comparison to any analytical mixing model, but, based on the XRD, FESEM, and TGA-DTA analyses, respectively. Fig. 6 illustrates the CCTO formation using 4 types of mixing mediums. For dry mixing, the conversion rate of reactant powders to CCTO ceramics is suggested to be low due to poor particle surface contact. A similar viewpoint in dry mixing also took place in ethanol mixing. The decomposition of ethanol created many empty spaces between particles (indicated by the small red circle in Fig. 6). Thus, the increment of diffusion distance of reactant particles made the CCTO conversion become slow down drastically. Meanwhile, CCTO mixing via deionized and distilled water is faster compared to dry and ethanol mixing. Since CaO is exothermally reactive to H₂O content ($\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$). This eventually increased the particles surface contact and led to the diffusivity enhancement.

Conclusions

Mixing medium played an important role in the formation of single phase CCTO. Based on qualitative and quantitative analysis of XRD, single phase CCTO was produced in all mediums after sintered at 1000 °C for 5 h. However, WM-W showed a faster reaction conversion to CCTO phase at 950 °C compared to other mixing mediums. Besides improving the CCTO formation, the efficiency of mixing medium was also seen in the grain size development. Various sizes of grains ranging between 0.5 μm to 2.57 μm were observed indicated that the particle surface contact between the reactants were influenced by the types of mixing medium. The dielectric properties of CCTO powder also were also different. DM has the highest ϵ_r (118) followed by WM-W, (99), WM-D (98) and WM-E (59), respectively. Thus, in all mediums, it is found that, wet mixing especially WM-W, showed a higher conversion rate of CCTO formation compared to dry mixing (DM). Therefore, it is conceded that, one should know the types of mixing mediums before synthesizing any ceramics materials.

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