Sol gel synthesis and characterization studies of Cupromanganite $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$

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Abstract. A single-phase $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ electroceramic had been prepared via sol gel method and fairly well densified at relative low temperature under atmospheric condition where the crystallization of $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ occurred due to amorphous polymeric mixture. The precursor was prepared by mixing the solutions with 0.6 M citric acid ($\text{C}_6\text{H}_8\text{O}_7$) as a chelating reagent with the mol ratio 1:2. The precursor gel formed was calcined and sintered at range 400 °C to 800°C by varying dwell time. Material formations under the reported conditions have been confirmed by X-ray diffraction (XRD). The results show that the formation of $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ started at 500 °C and was formed completely at 700 °C for 18 hours. The microstructure of all $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ was analysed using field emission scanning electron microscopy (FESEM). A smaller particle size with higher grain boundary was obtained at sintering 700°C to 800°C. FESEM results show the significant influence of calcinations and sintering parameter on the microstructure behaviour of $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$.

1. Introduction

The investigation of $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ (CCMO) electroceramic has attracted considerable attention recently due to its unusually high magnetoresistive property [1]. The good magnetoresistance of CCMO was reported at 20K and 5 tesla due to the special of double distorted of perovskite structure of CCMO [2]. These perovskite-like phase structures possess colossal magnetoresistance in a wide range temperature. Among various synthesis techniques, sol-gel method was proposed as the best method in producing CCMO and able to be an effective process in reducing the sintering temperature while achieving good properties. Sol-gel synthesis has been proven as a simple and effective method in precisely controlling the composition homogeneity of the complex oxide [3]. This method is based on the principle that the reactants are mixed in the molecular level where the low calcinations temperature is needed to produce fine powders with higher surface area and high purity [4]. The sol gel processing
also gives a better control in the stoichiometry and shorter reaction times with respect to the other synthesis routes, especially the solid state reaction method [5].

The new method development especially in wet chemistry processing involving improvement in synthesis condition where the properties of materials obtained are strongly dependent on the preparation method [5]. In our best knowledge, the CCMO material report up to now, obtained by the combination of sol gel with high oxygen pressure technique; at sintering temperature ~ 700 °C for 3days under 0.18kbar (2600Psi) [6]. As an alternative to the previously reported methods, we are proposed the synthesis of CCMO via sol gel under atmospheric pressuring condition with the lower optimum sintering temperature and minimum of dwelling time.

In the present study, a simple powder preparation method was developed where the citric acid was used to chelate metal ions, while ethylene glycol reacts as solvent for the polymerization between citric acid and ethylene glycol. On the other hands, we are also report the investigation of influence process parameter on the properties of CCMO. The effects of sintering temperature on the microstructure behaviour and phase formation of CCMO ceramic were investigated.

2. Experimental Procedure

Sol-gel method was used to produce CaCu$_3$Mn$_4$O$_{12}$ from the mixing of CaCO$_3$, CuO, Mn(NO$_3$)$_2$.4H$_2$O, citric acid (C$_6$H$_8$O$_7$), nitric acid (HNO$_3$,) and ethylene glycol (HOCH$_2$CH$_2$OH,). The copper citrate and calcium citrate solution was prepared by dissolving the stoichiometric amounts of CuO and CaCO$_3$ in 0.6M citric acid (CA) with molar ratio of [citrates/metallic ion] is 1:2. The stoichiometric of manganese nitrate tetrahydrate, Mn(NO$_3$)$_2$.4H$_2$O was dissolved in citric acid-ethylene glycol solutions which are counter as a chelating reagent. The copper and calcium citrate solution were directly mixed to the clear Mn solution. A small amount of nitric acid (HNO$_3$, 35%) was added in order to catalyze the esterification between citric acid and ethylene glycol [7]. Resultant of these mixtures was magnetically stirred on a hot plate and slowly increased the temperature up to ~ 90 °C for 5h to remove excess water and accelerate the polyesterification. The light blue and sticky gels formed were treated in oven at 140 °C for 18h to fully evaporate and promote polymerization. The resulting material had appearance of a dark brown resin which was slightly ground into agate mortar. The precursor then heat-treated at range 400 to 800°C for 12h. The powders were pressed under load 2.9 ton (369 Mpa) for 10s under Uniaxially Hydraulic Pressing machine. Pellets then sintered in high temperature furnace at relative low temperature (600, 700 and 800 °C) under atmospheric condition for 18, 24, 36 and 72h of dwelling time. The phase formation behavior and structure properties of CCMO sample at different calcinations and sintering condition were characterized by X-ray diffraction and FESEM.

3. Results and Discussion.

3.1. Phase and microstructure evolution of CCMO Powder

XRD analyses indicate the evolution of the CCMO phases on calcinations powder at different temperatures (Figure 1-2). All the peak positions were identifying by comparison with CCMO JCPDS file No. 01-072-0401. The result shows the formation of CCMO started at lowest temperature around 400 °C. At temperature between 400 to 500 °C, only a board peaks of CCMO appeared with certain trace amounts of CuO (ICSD: 44-0706), Cu$_2$O$_3$ (ICDD: 01-083-1665) and Mn$_2$O$_3$ (ICDD: 01-072-0401). Powder at 600 °C contained a higher amount of CCMO phase with lower number XRD peaks appear for unreacted element Mn$_2$O$_3$. The peaks is getting stronger and sharper as the calcinations temperature increased from 600 to 800 °C, which are effected by increasing in the degree of long-range order in the perovskite lattice [8].
Figure 1: X-ray diffraction pattern of CCMO calcined powder for 12h at 400 °C and 500 °C with the certain purity.

Corresponding to the result obtained, there are only significant different in peaks formation and x-ray diffraction showed only the nearly pure phase of CCMO when temperature increased between 600 to 800 °C. Since the near pure phase of CCMO formed after Cu$_4$O$_3$ and Mn$_2$O$_3$ disappeared, therefore, the temperature at ~ 600 °C is the best optimum lower temperature that needs to develop a near pure phase of CCMO.
Morphology and microstructure of CCMO powder for the differences calcinations temperature was analyzed. Some of agglomerates calcined powders were observed in Figure 3-4. The particles are increased in size by increasing the calcinations temperature which the lowest mean of particle sizes $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ are gained for sample calcined at 600 °C by 0.457 µm and the highest is 20.150 µm for 800 °C. The measurements of particle size were successfully conducted by particle analyzer testing machine as mention detail in other paper by authors. A comparison between micrograph Figure 3-4 revealed that the needles platelet-like particles were developed well after calcine between 500 to 600 °C. The particle size of powders then turned to be agglomerates at 700 °C due to high temperature atoms and molecules begin to migrate across the interface where particles touch each other. This happens at a certain elevated temperature. The FESEM micrograph also show a pretty good properties of CCMO powder at 600°C when come out with an uniformity of grain size distribution, fine particle size and uniform formation microstructure.

Figure 2: X-ray diffraction pattern of CCMO calcined powder for 12h at 600 °C, 700 °C and 800 °C.
**Figure 3:** FESEM micrograph of CCMO powder before calcinations.

**Figure 4:** FESEM morphology of CCMO powder calcined at 400 °C, 500 °C, 600 °C and 700 °C for 12h.
3.2. Phase and microstructure properties of CCMO ceramics

Figure 5 show the XRD profiles of the CCMO sample sintered at varying temperature. By observing closely, the diffraction peaks at 600 °C for 18h is initially broader which indicate a relatively small crystallite [9]. As temperature increased between 700 °C to 800 °C, the diffraction peaks becomes progressively narrower due to increasing of crystallite size and grain growth [10]. Starting at 700 °C, the amount of CCMO phases enhances but the significant peaks of CuO is disappear; suggesting that lowest temperature ~ 700 °C is needed for complexion of the reaction. The increasing of temperature is also examined as a caused to a relative strength of diffraction peaks. These fractions turned to become stronger due to the effect and beneficial of crystal growth.

![XRD pattern of CCMO ceramic after being sintered for 18h at 600 °C, 700 °C and 800 °C.](image)

Increasing in dwelling time also favours the densification of the samples as the higher grain growth reduced the porosity. This can be display by the narrow and sharp peaks of x-ray diffraction. By comparing the x-ray diffraction, results showed that the optimum lowest dwelling sintering time is at 18h. At this temperature, the maximum of CCMO phases are formed with minimum of CuO. The
increasing of the soaking time up to 24 and 36h only give the significant different in phase’s formation. The decomposition of CCMO phases are observed occurred when the sample sintered at 36 and 72h (3days). This phenomenon occurred caused by the atmospheric sintering condition where some of required phase are decomposed during the sintering due to absence of oxygen flow.

Figure 6: XRD pattern of CCMO after being sintered at varying soaking time for 700 °C.
Figure 7: FESEM micrograph of CaCu$_3$Mn$_4$O$_{12}$ ceramic sintered at 600 °C, 700 °C, and 800 °C for 18h.

The morphology of CCMO sample sintered at different temperature and soaking time are shown in Figure 7-8. Based on the microstructure study, a more uniform grain size distribution, a finer grain size and more homogenous microstructure are observed for the sample sintered at 700 °C for 18h. The increasing of sintering temperature from 600 to 800 °C promotes the grain growth in the microstructure. By comparing to the sample 600 °C, the needles-like phase of grain particles are clearly visible when sintered up to 700 and 800 °C. The microstructure morphology for sample sintered at 700 °C also show the more compact arrangement in grain structure compare to sample at 600 °C. This uniformity of grain formation will promotes the microstructural densification that will benefit in conduction of electrical carriers and thus responsible for improvement of conductivity properties.

There are only few pores were observed for the sample sinter at 18 and 24h (Figure 8). Further increase of soaking time between 36 and 72h will lead to grain grown of microstructure. The grain structure for the sample sintered for 72h (3days) displayed melting features which was caused the packing process between grains. From these results, it can be concluded that the sample CCMO sintered at 700 °C for 18h dwelling time is the optimum sintering parameter that causes the better spinel morphology than the other sintering parameter.
4. Conclusion.
The CaCu$_3$Mn$_4$O$_{12}$ electroceramic has been prepared by the sol-gel synthesis and successfully form at relative lower sintering calcine and sintering temperature under atmospheric pressure condition. The influences of the process parameter on the microstructure and phase formation were also studied using XRD and FESEM. Varying calcinations and sintering parameter in CaCu$_3$Mn$_4$O$_{12}$ processing also exhibit different in phase formation and microstructure behavior. The samples show good characteristic in optimum calcinations at ~ 600 C for 12h and promotes better properties at optimum lowest sintering temperature; 700 C in 18h of dwelling time.

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