The Effect of Sintering Temperature on The Properties of $CaCu_3Mn_4O_{12}$ (CCMO) Synthesized Via Solid State Reaction

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Intisari: Sintesis $CaCu_3Mn_4O_{12}$ (CCMO) telah berhasil dilakukan dengan metode reaksi fasa solid . Senyawa oksida komersial yaitu kalsium karbonat, tembaga oksida dan mangan oksida digunakan untuk preparasi CCMO. Karbonat dan oksida ditimbang berdasarkan rasio stoikiometri dan dicampur menggunakan ball milling selama satu jam. Campuran kemudian dikalsinasi pada suhu 850°C selama 12 jam dan disintering pada suhu 1000°C, 1050°C, 1070°C dan 1090°C selama 24 jam. Pembentukan CCMO ditunjukkan melalui difraksi sinar-X (XRD). Analisis mikrostruktur dilakukan dengan menggunakan Scanning Electron Microscope (SEM), sedangkan kerapatan dan porositas bulk diukur menggunakan teknik Archimedes. Efek suhu selama sintering pada mikrostruktur dan sifat listrik juga dilakukan. Campuran bereaksi seluruhnya dan membentuk CCMO pada suhu 850°C. Hasil ini menunjukkan peran penting suhu sintering pada sifat fisik dan listrik pada CCMO. Analisis mikrostruktur menunjukkan adanya hubungan penggabungan yang kuat antar bulir yang jelas terlihat pada suhu 1090°C selama 24 jam. Proses ini meningkatkan kepadatan pellet yang disinter dan menunjukkan pembentukan aliran konduksi baru dan pengurangan daerah efektif antar bulir untuk arus transport melalui sifat resistivitas. Pengamatan dengan SEM juga menunjukkan adanya pengurangan porositas mikrostruktur ketika suhu dinaikkan bervariasi dari 36,6% menjadi 0,5%. Sementara resitivitas CCMO menurun dari $18,1 \times 103\ \Omega{\cdot}m$ menjadi $7,96 \times 103\ \Omega{\cdot}m$ dengan adanya peningkatan suhu sintering.

Kata kunci: CCMO, reaksi fasa solid, suhu sintering, resitivitas

Abstract: The synthesis of $CaCu_3Mn_4O_{12}$ (CCMO) has been accomplished via solid-state reaction. Commercial oxides namely calcium carbonate, copper oxide and manganese oxide were used to prepare CCMO. The carbonate and oxides were weighed accordingly to stoichiometric ratios and mixed thoroughly via ball milling for 1 hour. The mixture was calcined at 850°C for 12 hours and then sintered at 1000°C, 1050°C, 1070°C and 10900C for 24 hours, respectively. The CCMO formation was confirmed using X-ray diffraction (XRD). The microstructure analysis was carried out using scanning electron microscopy (SEM), while bulk density and porosity were measured by Archimedes technique. The effects of sintering temperature on microstructure and electrical properties are reported here. The mixture is fully reacted to form CCMO at 850°C. The results confirmed that the crucial role of sintering temperature on physical and electrical transport properties of CCMO. Microstructural analysis revealed the presence of clean and clear intergrain strong connectivity at 10900C for the period of 24 hours. This process enhances the physical densification of the sintered pellets promotes the creation of new conduction channels and reduction of intergrain effective area for transport current under resistivity properties. SEM observation also revealed that the microstructure becomes less porous when sintering temperature increased which varied from 36.6% to 0.5%. Meanwhile resistivity of CCMO will decreased from $18.1 \times 103\ \Omega{\cdot}m$ to $7.96 \times 103\ \Omega{\cdot}m$ with the increasing sintering temperature.

Keywords: CCMO, solid state reaction, sintering temperature, resistivity

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1 INTRODUCTION

Recently, the complex perovskite $CaCu_3Mn_4O_{12}$ [1] has attracted the attention of researches. The crystal structure of $CaCu_3Mn_4O_{12}$ [2] has the rare feature of containing Cu^{2+} (or other Jahn-Teller transition metal cations, such as Mn^{3+}) at the A positions of the ABO3 perovskite. This Jahn-Teller cation and Ca^{2+} are 1:3 ordered in a $2a_0$x $2a_0$x $2a_0$ cubic cell of *Im3* symmetry (a_0: unit cell of the anistotype).

Perovskite-type (ABO3) doped manganese oxide have generated a considerable interest because of their many electronic, magnetic and structural properties and potential applications. Extensive theoretical and experimental efforts have been made to understand their complicated mechanism [3]. The mixed-valence oxides can be regarded as solid solutions between end members such as $LaMnO_3$ with formal valence states La^{3+} Mn^{3+} O_3^{2-} and Ca^{2+} Mn^{4+} O_3^{2-}.

In this paper, the synthesis of $CaCu_3Mn_4O_{12}$ was

reported state reaction and effect of different sintering temperature. The characterization of physical properties like density, porosity and microstructure observation and also transport current under resistivity properties are also given.

2 MATERIAL AND METHODS

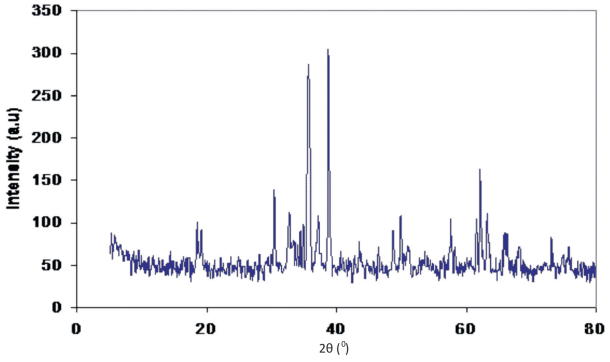
$CaCu_3Mn_4O_{12}$ (CCMO) was prepared by mixing stoichiometric proportions of $CaCO_3$ (99 + % Aldrich), CuO (99 + % Aldrich) and MnO_2 (90-95 %, Merck). The mixed powders were ball milled and then calcined in air at 850°C with soaking time 12 hours. After calcination, the sample were ground to fine powder and pressed into pellets with pressure of 300 MPa and then sintered in air at 1000°C, 1050°C, 1070°C and 1090°C for 24 hours, respectively.

After calcinations, the sample was ground to fine powder and was determined by X-Ray diffraction (XRD) using a Siemen D5000 X-ray diffractometer with a CuKα radiation. The surfaces of the sintered samples were investigated by scanning electron microscopy (SEM) was using on a Leo Supra 35VP system. Density and porosity of the sintered sample were measured by the Archimedes method. The resistivity was measured by the conventional four-probe technique on sintered pellets with silver paste as the electrical contact.

3 RESULTS AND DISCUSSION

3.1 X-Ray analysis

The diffractograms of CCMO was obtained as shown in Fig. 1. The mixture is fully reacted to form CCMO at 850°C. The diffractograms shows the presence of CCMO (ICSD 01-072-0401) with the compound crystallizes in a body-centered cubic perovskite-related structure (groups: *Im3*). The peaks are formed at positions which agree quiet well the values given in ICDS (01-072-0401) data (see Table 1).



GAMBAR 1: XRD pattern on $CaCu_3Mn_4O_{12}$ at calcinations temperature of 850°C

3.2 Scanning electron microscope

Microstructure is reported to play a vital role in determining the properties of electroceramics such CCMO and $BaTiO_3$ (BTO). There has been misperception that sintering parameters is the only factor that has major influence on the microstructure development. However, in actual fact, every single precessing step, from as early as starting raw materials selection will contribute to the final microstructure developed. These process (e.g. synthesis method, mixing and forming) are indirectly involved compared to sintering, but it is equally important in post sintering microstructural development.

Fig. 2 shows the SEM micrographs of CCMO fracture surfaces ceramics sintered at different temperatures. Obviously, porous microstructure is observed in all these sintering temperature except for sintering temperature at 1090°C. In Fig.2(a,b), extremely high porosity microstructures are shown in sintered pellet at 1000°C and 1050°C, respectively. It can be observed that sintering had just begun in the compacted pellets.

The temperature of 1070°C used for sintering is rather high to caused densification (Fig.2(c)). The increase of sintering temperature significantly promotes the grain growth and microstructural densification. High sintering temperature facilitate grain growth and therefore produced sharp shrinkage in the specimen sintered at 1090°C show in Fig.2(d).

3.3 Bulk density and porosity analysis

The influence of sintering temperature on the density and porosity value shows in Figs.3 and 4, respectively. Density of the CCMO was increased with increasing sintering temperatures. Theoretically, the density of CCMO is 5.62 g/cm^3. The highest density was recorded for sample sintered at 1090°C with 4.99 g/cm^3 and the lowest is at 1000°C with 3.43 g/cm^3.

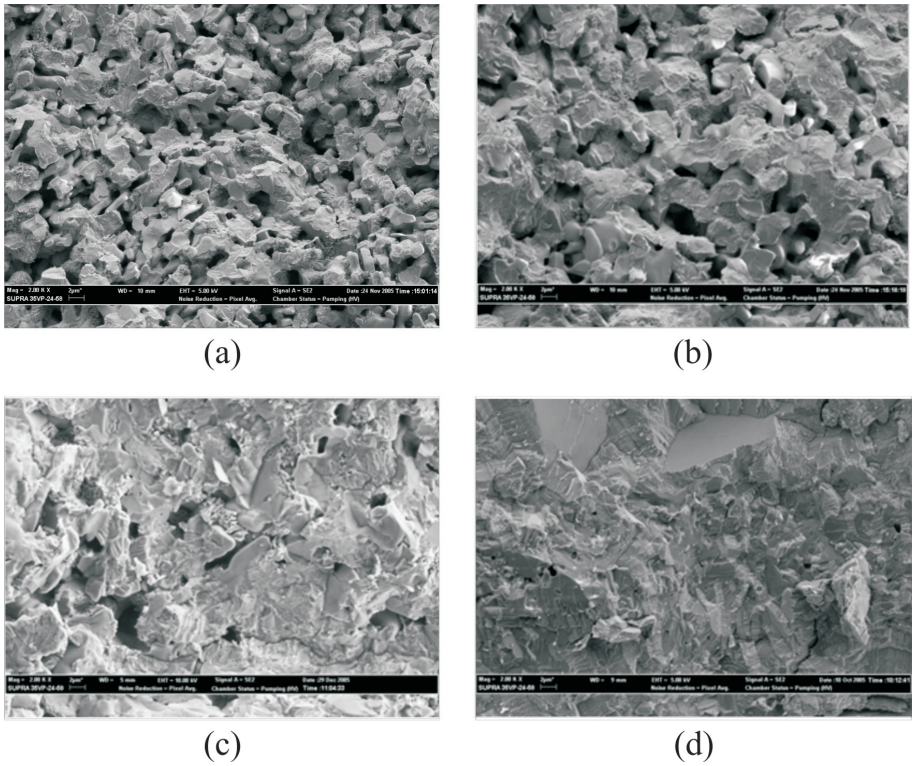
In theory, the porosity was inversely proportion to bulk density value. Effect of sintering temperature to porosity of CCMO is shown in Fig.4 Sample sintered at 10900C gave the lowest porosity i.e 0.5% compare to the sample sintered at 1000°C with 36.6%. These observations are confirmed by SEM analysis as given in Fig.2.

3.4 Linear expansion

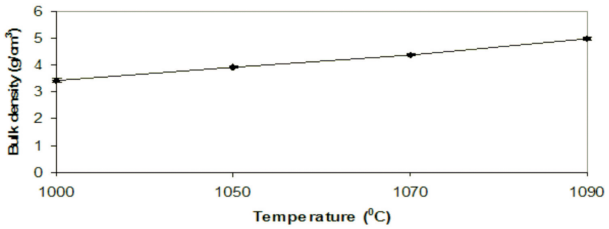
Since the samples have been sintered in normal atmosphere, it is observed that the thickness and diameter of the samples of CCMO quiet homogenous. Linear expansion test is a measurement of the dimension change before and after sintering. Comparison of the change in thickness and diameter (mm) for different sintering

TABEL 1: XRD pattern for $CaCu_3Mn_4O_{12}$ from ICSD (01-072-0401)

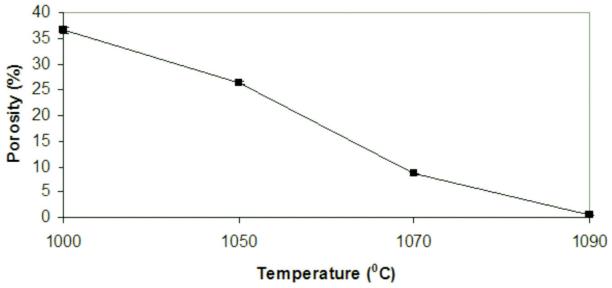
	2θ							
ICSD (01-072-0401) data	17.3	30.2	35.0	39.3	43.2	46.9	50.4	62.8
Present work (8500C)	18.9	30.4	35.6	38.8	43.1	48.7	49.9	63.2



GAMBAR 2: SEM micrograph showing fracture of CCMO in different sintering temperature (a) 1000°C, (b) 1050°C (c) 1070°C and (d) 1090°C



GAMBAR 3: Effect of sintering temperature on density



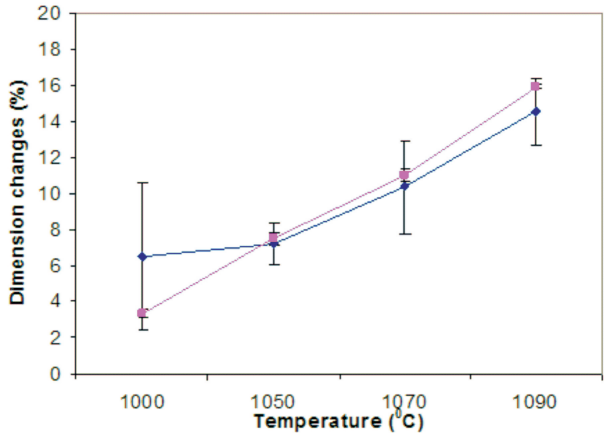
GAMBAR 4: Effect of sintering temperature on porosity

temperatures of CCMO is shown in Fig.5. The thickness expended 6.54% to 14.54%. While, for diameter, 3.34% to 15.93%. It can be explained that during sintering the pores tended to spheroidise. Hence on heating, the pores shrank in the direction perpendicular to the pressing direction, leading to a different dimensional change for both directions.

3.5 Electrical characterization

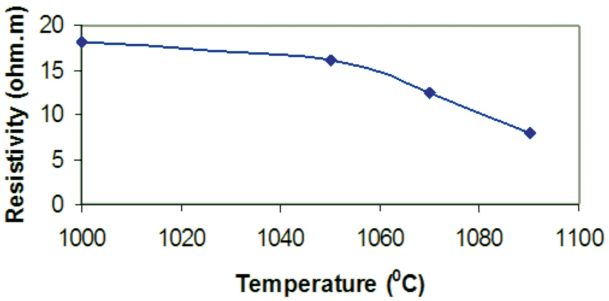
The resistivity (ρ) was calculated using the formula $\rho = RA/l$ (where, R is resistance , A is sample cross sectional area and l is the sample length). It is observed that the resistivity measured at four different sintering temperatures for CCMO sample.

The resistivity decreased with increasing of sintering temperature. It is notable that the microstruc-



GAMBAR 5: Effect of different sintering time on thickness and diameter change

tural evolution with sintering temperatures corresponds well to the variations of the conduction properties of CCMO or other ceramic [4]. The increase of sintering temperature promotes the microstructural densification. It benefits the conduction of electric carriers and is thus responsible for the improvement of the conductivity. With the increasing of sintering temperature, the grain size and mechanical connection between grains are expected to play an important role in the electronic conduction. It is known that the resistivity is mostly influenced by the presence of grain boundary which acts as region of enhanced scattering for the conduction electrons. The higher sintering temperature will effecting to more shrinkage and hence leads to the increasing of density. This is because sintering reduces the total pore surface and pore volume. However the fact remained that for $CaCu_3Mn_4O_{12}$ (CCMO) sintered at 1000°C, 1050°C, 1070°C and 1090°C the resistivity is higher than previous reported [5].



GAMBAR 6: Sintering temperature dependence of the resistivity for $CaCu_3Mn_4O_{12}$

4 CONCLUSION

Single phase $CaCu_3Mn_4O_{12}$ (CCMO) with a perovskite -related structure was synthesized by solid-state reaction at calcinations temperature of 8500C. This process enhances the physical densification of the sintered pellets promotes the creation of new conduction channels and reduction of intergrain effective area for transport current under resistivity properties. SEM observation also revealed that the microstructure becomes less porous when sintering temperature increased which varied from 36.6% to 0.5%. Meanwhile resistivity of CCMO will decreased from 18.1 × 103 Ω·m to 7.96 × 103 Ω·with the increasing sintering temperature. For this reason, the physical and electrical properties are greatly affected by sintering temperature. It is important to adjust the sintering temperature to get appropriate properties for room temperature applications.

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