Characterization and Studies on AC Conductivity of CaMnO$_3$ Material

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Abstract. Synthesis of CaMnO$_3$ has been performed by solid state reaction method using CaCO$_3$ and MnCO$_3$ powder as raw materials. The raw materials were weighed, milled, compacted into a pellet and then sintered at 1250°C. Phase of material, microstructure, and conductivity of the samples were observed. The refinement results of X-ray diffraction pattern shows that CaMnO$_3$ formed as a single phase, which has a structure orthorhombic (P n m a) with lattice parameters, $a = 5.277$ Å, $b = 7.452$ Å, and $c = 5.261$ Å. The atomic density of the refinement result is 4.591 gr.cm$^{-3}$. The morphology of CaMnO$_3$ sample has a good particle homogeneity with the particle size 1-2 μm. The value of AC conductivity on the CaMnO$_3$ is directly proportional with the increasing of the temperature. The highest value of the AC conductivity of the CaMnO$_3$ sample is 2.8 x 10$^{-3}$ S/cm at a temperature of 400°C.

1. Introduction

CaMnO$_3$ material has attracted the attention of researchers because CaMnO$_3$ is an oxide material which can be applied as thermoelectric[1]–[7]. J.W Park, et al has performed substitution of Bi on the Ca sites and Nb on the Mn sites and caused the thermoelectric properties increased due to electrical conductivity[8]. The indicator of the thermoelectric properties of the materials is the figure of merit ($Z$) value is relatively high. These $Z$ is defined as follow:

$$Z = \frac{\sigma S^2}{\kappa}$$

(1)

where $S$, $\sigma$, and $\kappa$ are respectively the Seebeck coefficient, the electrical conductivity and the thermal conductivity.

CaMnO$_3$ material can be synthesized through a solid-state reaction. J.W. Park, et al carried out synthesis of CaMnO$_3$ using solid-state reaction method[8]. The experiment was begun by mixing raw materials, followed by calcination, compaction and sintering at 1300°C for 12 hours.

Recently, several studies involving successful synthesis of CaMnO$_3$ have been reported, especially those performed at high temperatures ($\geq 1000$°C). The interesting features in the Ca-Mn-O system are the electrical and magnetic properties that are found in the Ca$_2$MnO$_4$, Ca$_3$Mn$_2$O$_7$, Ca$_3$Mn$_3$O$_{10}$, CaMnO$_3$, and Ca$_2$MnO$_4$ compounds[9]. The stable activity of the composition of CaO-MnO occurs in the temperature range of 1100-1300° C.

Based on the description that CaMnO$_3$ material can be applied as a thermoelectric device, so the aim of this study is to synthesize and characterize CaMnO$_3$ material.
2. Materials and Methods

CaMnO$_3$ was synthesized by solid-state reaction method. In this work, CaCO$_3$(Merck) and MnCO$_3$ (Aldrich) powders were used as the starting materials, by following equation of reaction:

$$\text{CaCO}_3(s) + \text{MnCO}_3(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaMnO}_3(s) + 2\text{CO}_2(g)$$

This experiment was started by weighing the raw materials in accordance with the stoichiometry. The starting materials were mixed and milled using planetary ball mill. After milling, the mixture was calcined at 800°C in order to eliminate the carbon content in CaCO$_3$ and MnCO$_3$. After calcinations, the mixture was pressed into a pellet with diameter of 25 mm and a thickness of 2 mm at 7 tons. The pellet was sintered at 1250°C for 6 hours in air atmosphere and then cooled to room temperature in furnace.

The phase formation was identified by the PHILIPS PW1710 X-ray diffractometer(XRD) with CoK$\alpha$ radiation ($\lambda = 1.7903$ Å), and the quantitative analysis of phases formed in the sample was carried out employing the GSAS software. Then the particle morphology was observed by using the JEOL-JSM 6390AScanning Electron Microscope (SEM), while alternating current (AC) conductivity was measured using the LCR meter instrument in the frequency range of 1 to $10^5$ Hz and the measurements were performed at room temperature, 100°C, 200°C, 300°C and 400°C.

3. Results and discussion

3.1. Analysis of X-ray diffraction

Figure 2 shows the results of X-ray diffraction pattern refinement of the sample CaMnO$_3$ using Rietveld method[10].

![Figure 1. CaMnO$_3$ diffraction pattern refinement using Rietveld method](image)

In the figure 2, the reliability factors $R_{wp}, R_p$ and $\chi^2$ (chi-squared) are relatively good, $R_{wp} = 4.74\%, R_p = 3.74\%$ and $\chi^2 = 1.099$, because here the curve of normalized error distribution just resembles the background intensity and its normal probability plot shows that the values of the observed and the calculated intensity seems to be in good agreement with each other. Qualitative analysis refers to the International Centre for Diffraction Data (ICDD), PDF-2, No. 89-0666[11]. The refinement results of x-ray diffraction pattern show that the sample consists of a single phase, which has an orthorhombic
(Pnma) structure with lattice parameters \( a = 5.277 \ \text{Å}, \ b = 7.452 \ \text{Å}, \ c = 5.261 \ \text{Å}, \ \alpha = \beta = \gamma = 90^\circ, \) and \( V = 206.88 \ \text{Å}^3. \) The atomic density of the refinement result is 4.591 gr.cm\(^{-3}\). From X-ray diffraction patterns the crystallite size estimation (L) by using Scherrer equation could also be determined with the L value is defined as follow:

\[
L = \frac{K \lambda}{\beta \cos \theta}
\]

(3)

Scherrer equation was developed to calculate the crystallite size of the sample powders by X-ray diffraction method using a specified wavelength \( \lambda \) (nm), by measuring the full width at half maximum of the peaks \( \beta \) (rad.) at an angle of \( 2\theta \).[12] The calculation results by this approach have yielded the estimated sample's crystallite size range of around 31 to 44 nm.

3.2. Observation by scanning electron microscope

The surface microstructure of the CaMnO\(_3\) sample that was sintered at 1250°C have been observed by using the scanning electron microscope (SEM), as shown in Figure 2. The SEM image in figure 2 shows that the particle morphology of CaMnO\(_3\) sample has a good particle homogeneity and particle diffusion is very uniform across the samples surface with the particle size varies from 1 - 2 μm. The SEM image also shows that samples sintered at temperatures of 1250°C is still visibly porous. This is presumably due to the reaction brought about by the release of CO\(_2\) from carbonate raw materials during the sintering process. Besides, it is suspected that air bubbles trapped during the compacting process would be the cause of pores formation after the heating process.

![Figure 2](image.png)

**Figure 2.** The particle morphology of the CaMnO\(_3\) sample sintered at 1250°C for 6 hours in air atmosphere. The sample was cooled in the furnace.

3.3. Analysis of AC conductivity

The result of conductance measurement (G) can be converted by a factor of sample geometry to obtain alternating current conductivity (\( \sigma \)) which is dependent on the frequency. In other words, if the value of the conductance of a material (G) is 1/R, while the resistivity (\( \rho \)) is 1/\( \sigma \), then the value of the conductivity of the material can be calculated based on the equation as follows:

\[
\sigma = G \frac{d}{A}
\]

(4)

where \( \sigma \), G, d, and A are respective the conductivity (S/cm), the conductance (Siemens), the thickness of the sample (cm), and the surface area of the sample (cm\(^2\)).
The alternating current conductivity of CaMnO$_3$ sample is shown in figure 3.

![Figure 3](image)

**Figure 3.** Curve of AC conductivity in the CaMnO$_3$ sample on the frequency as a function of temperature.

In figure 3 it appears that the value of AC conductivity on the CaMnO$_3$ is directly proportional to the increase in temperature. The convergence of conductivity values was seen in all conditions with varying treatment temperature. The convergence value of conductivity at room temperature occurs in the conductivity value of $6.6 \times 10^{-5}$ S/cm. While the convergence value of conductivity at 100°C, 200°C, 300°C and 400°C respectively are $1.6 \times 10^{-4}$ S/cm; $4.1 \times 10^{-4}$ S/cm; $8.2 \times 10^{-4}$ S/cm and $2.8 \times 10^{-3}$ S/cm.

![Figure 4](image)

**Figure 4.** Convergence curve of conductivity values as a function of temperature on the CaMnO$_3$.
The conductivity value experienced a different trend occurring at 400°C. The conductivity of CaMnO$_3$ increased from $2.5 - 2.7 \times 10^{-3}$ at a frequency of 1 Hz - 3 kHz, and then converged to the conductivity value of $2.8 \times 10^{-3}$ S/cm at a frequency of 5 kHz. This is different from the values of conductivity at room temperature, 100°C, 200°C and 300°C, where the convergence of conductivity value has occurred at a frequency of 1 Hz. Convergence curve of temperature conductivity values is shown in figure 4.

### 4. Conclusion

Synthesis of CaMnO$_3$ has been successfully carried out using solid state reaction method. The refinement results of X-ray diffraction pattern shows that CaMnO$_3$ was formed as a single phase, and has a good particle homogeneity and diffusion of particles is very uniform across the sample surface with the particle size varies from 1-2 μm. The value of AC conductivity on the CaMnO$_3$ is directly proportional to the increasing of the temperature. The highest value of the AC conductivity of the CaMnO$_3$ sample is $2.8 \times 10^{-3}$ S/cm at a temperature of 400°C.

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