

## DECREASED ELECTRICAL RESISTIVITY OF $\text{CaMnO}_3$ BY ADDED-CNTs

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### ABSTRACT

The powder of  $\text{MnO}_2$  and  $\text{CaCO}_3$  were mixed by ball milling to obtain the calcium manganese oxide compound. We investigate microstructures and thermoelectric properties of  $\text{CaMnO}_3$ -CNTs. The calcium manganese oxide compound was synthesized by solid state reaction technique. The compound was added the carbon nanotubes (CNTs) in  $\text{CaMnO}_3$ -CNTs 2% and  $\text{CaMnO}_3$ -CNTs 4% by molar ratio and following the calcinations and sintering process. X-ray diffraction analyses (XRD) indicated that the crystal orientation. The microstructures of the samples were observed with a scanning electron microscope (SEM) using both secondary electron. The electrical resistivity ( $\rho$ ) was analyzed by laser flash method. It results the electrical resistivity ( $\rho$ ) shown decreased the  $\text{CaMnO}_3$  by added-CNTs.

KEYWORDS: Thermoelectric properties;  $\text{CaMnO}_3$ ; Carbon nanotubes (CNTs); Electrical resistivity

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### INTRODUCTION

The performance of thermoelectric (TE) dimensionless figure of merit  $ZT$  giving by;

$$ZT = \frac{S^2 T}{\rho \kappa}$$

Where  $S$  is Seebeck coefficient,  $T$  is absolute temperature in K,  $\rho$  is electrical resistivity,  $\kappa$  is total thermal conductivity. Higher dimensionless figure of merit  $ZT$  values lead to thermoelectric devices of improved performance. In other words, good thermoelectric materials (TE), which depends on the high Seebeck coefficient ( $S$ ), low electrical resistivity ( $\rho$ ) and thermal conductivity ( $\kappa$ ), respectively [1].

The  $\text{CaMnO}_3$  is compound manganese perovskite oxides starting from stoichiometric mixtures powder of calcium carbonate and manganese oxide are mixed by ball milling to obtain the calcium manganese oxide compound. Crystallographic and microstructures are of primary importance in the technology and science of functional  $\text{CaMnO}_3$ -based materials [2]. The calcium manganese oxide with perovskite type crystal structure has received much interest in thermoelectric properties [3, 4, 5]. The manganite

exhibits both low total thermal conductivity ( $\kappa$ ) above room temperature [4] and relatively high Seebeck coefficient ( $S$ ). The calcium manganese oxide ( $\text{CaMnO}_3$ ) is crystal structure and temperature change induced phase transition [6, 7].

CNTs have properties a very high electrical conductivity [8] and exhibit a relatively high Seebeck coefficient in flexible materials [9]. Carbon nanotubes are being considered for energy production and storage. Graphite, carbonaceous materials and carbon fiber electrodes have been used for decades in fuel cells, battery and several other electrochemical applications [10]. Nanotubes are special because they have small dimensions, a smooth surface topology, and perfect surface specificity, since only the basal graphite planes are exposed in their structure.

In this paper, we were synthesized calcium manganese oxide by solid state reaction technique. The calcium manganese oxide compound was doped the carbon nanotubes (CNTs) 2% and 4% by molar ratio. It results the electrical resistivity ( $\rho$ ) shown decreased the  $\text{CaMnO}_3$  by added-CNTs.

## MATERIALS AND METHODS

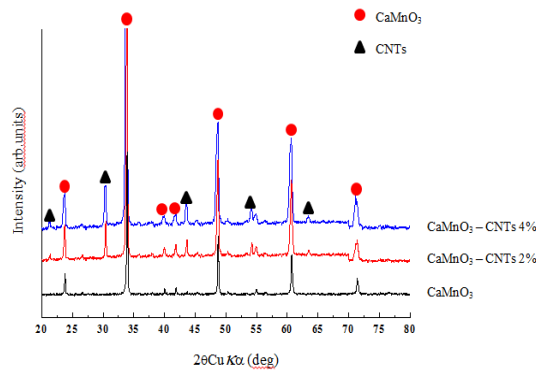
The compounds from powder of  $MnO_2$ , 90.00% (SIGMAALORICH) and  $CaCO_3$ , 99.99% (SIGMAALORICH) are mixed by ball milling technique to obtain  $CaMnO_3$  compound. Calcium manganese oxide compound is synthesized via solid state reaction in air. Then the calcium manganese oxide ( $CaMnO_3$ ) compound added the carbon nanotubes (CNTs), 90.00% SIGMAALORICH in  $CaMnO_3$ -CNTs 2% and  $CaMnO_3$ -CNTs 4% by molar ratio then calcinated at  $850^\circ C$  for 10 h in and sintering at  $1,150^\circ C$  for 36 h in air.

We were measure crystal structure samples of  $CaMnO_3$ ,  $CaMnO_3$ -CNTs 2% and  $CaMnO_3$ -CNTs 4% (XRD, Shimadzu). Electrical resistivity ( $\rho$ ) was measured in air in the temperature range of  $30\text{--}200^\circ C$  using a conventional four-probe DC technique.

## RESULTS AND DISCUSSION

### The structure of $CaMnO_3$ -CNTs

The structure of sintered  $CaMnO_3$ ,  $CaMnO_3$ -CNTs 2%, and  $CaMnO_3$ -CNTs 4% are shown in Figure 1.



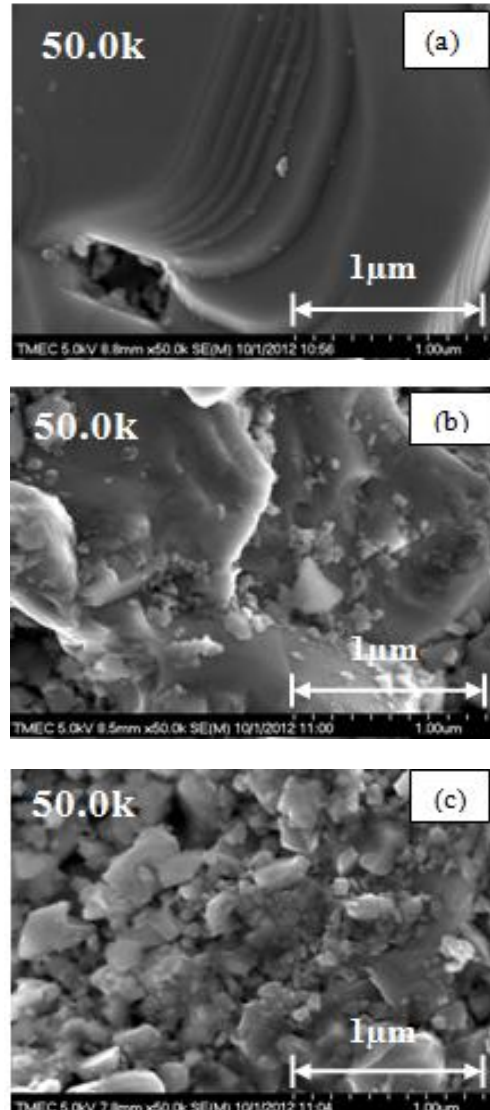
**Fig. 1** X-ray diffraction (XRD) analysis of  $CaMnO_3$ ,  $CaMnO_3$ -CNTs 2% and  $CaMnO_3$ -CNTs 4%

Figure 1. Shown  $CaMnO_3$ ,  $CaMnO_3$ -CNTs 2%, and  $CaMnO_3$ -CNTs 4% coarse grain appearing as the amount of CNTs increased. It also shown that the pore density of the prepared sample gets decreased gradually. In each case, it has shown the increase due to the additional amount of  $CaMnO_3$ -CNTs 2% and  $CaMnO_3$ -CNTs 4%. The grain growth was owing to the addition of CNTs.

The result of X-ray diffraction analysis of  $CaMnO_3$ -CNTs is shown in Figure 1. The

diffraction peak matches the previously reported data in the case of  $CaMnO_3$  (circles), and there have secondary phase caused by the additional amount of CNTs (triangles).

According to the X-ray diffraction peak in Figure 1. Thus, it has the orthorhombic perovskite structure of  $CaMnO_3$ -CNTs



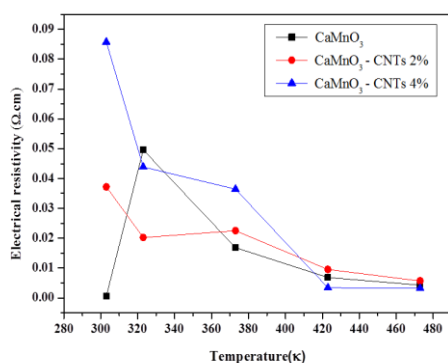
**Fig. 2** Scanning electron microscope (SEM) image of  $CaMnO_3$ -CNTs. (a)  $CaMnO_3$ , (b)  $CaMnO_3$ -CNTs 2% and (c)  $CaMnO_3$ -CNTs 4%

The crystallography and morphology of the calcium manganese oxide ( $CaMnO_3$ ) sample and  $CaMnO_3$ -CNTs sample were analyzed by the X-ray diffraction (XRD, LabX 6100, Shimadzu) analysis was carried out with a Rigaku diffractometer using  $CuK\alpha$  radiation. Lattice

parameters were obtained from the Rietveld analysis of the x-ray data. [11] The microstructures of the samples were observed with a scanning electron microscope (FE-SEM MODEL:HITACHI-S4700) using both secondary electron.

Electrical resistivity ( $\rho$ ) was measured in air in the temperature range of 30–200 °C using a conventional four-probe DC technique. Seebeck coefficient ( $S$ ) was calculated from a plot of thermoelectric voltage ( $\Delta V$ ) against temperature differential ( $\Delta T$ ) and  $S$  was deduced from the relation ( $\Delta V / \Delta T$ ) as measured in air at 30–200 °C using an instrument designed by our laboratory (TRC-ZTM1).

Two Pt–Pt/Rh (R-type) thermocouples were attached to both ends of the sample using Ag paste, and the Pt wires of the thermocouples were used as voltage terminals. Measured  $S$  values were reduced by those of the Pt wires alone to obtain the net  $S$  values of the samples. Thermal conductivity ( $\kappa$ ) is obtained from the thermal diffusivity. Thermal diffusivity was measured by a Laser Flash (TC7000) method in the room temperature to 700°C with steps of 100°C.



**Fig. 3** Temperature ( $T$ ) dependence of the electrical resistivity ( $\rho$ ) of  $\text{CaMnO}_3$ -CNTs samples  $\text{CaMnO}_3$ ,  $\text{CaMnO}_3$ -CNTs 2% and  $\text{CaMnO}_3$ -CNTs 4%

The temperature ( $T$ ) dependence of the electrical resistivity ( $\rho$ ) of the samples is shown in Fig. 3. The un-doped  $\text{CaMnO}_3$  is a  $n$ -type semiconductor which exhibits a electrical resistivity ( $\rho$ ) value around 0.3  $\Omega\text{cm}$  at room temperature. Whereas when CNTs are simultaneously substituted, it shows typical metallic resistivity, in which the electrical resistivity decreases with increasing temperature. It also decreases continuously with the amount of doped down to  $\text{CaMnO}_3$ -CNTs 4%. As the conduction is the hole-doped compounds, the resistivity decreases and Mn-O-Mn bond angles decrease for  $n$ -type

materials. [12] The electrical resistivity ( $\rho$ ) of  $\text{CaMnO}_3$ -CNTs 4% lower than un-doped  $\text{CaMnO}_3$  systems possessing. We obtained a value of 3.2  $\text{m}\Omega\text{cm}$  at 473 K in air for 4% of CNTs in  $\text{CaMnO}_3$  and 4.24  $\text{m}\Omega\text{cm}$  in  $\text{CaMnO}_3$  at 473 K.

## CONCLUSION

In summary, electrical resistivity ( $\rho$ ) were evaluated by simultaneously in  $\text{CaMnO}_3$ ,  $\text{CaMnO}_3$ -CNTs 2% and  $\text{CaMnO}_3$ -CNTs 4%. We found the electrical resistivity ( $\rho$ ) of  $\text{CaMnO}_3$ -CNTs 4% lower than un-doped  $\text{CaMnO}_3$  systems possessing. We obtained a value of 3.2  $\text{m}\Omega\text{cm}$  at 473 K in air for  $\text{CaMnO}_3$ -CNTs 4% and 4.24  $\text{m}\Omega\text{cm}$  in  $\text{CaMnO}_3$  at 473 K.

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