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THERMOELECTRICITY BASED ON CUO AS A SEMICONDUCTING MATERIAL

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ABSTRACT

In this paper, thermoelectricity based on copper(II) oxide CuO as semiconducting material is explored. The electrical properties of the samples were studied under different temperature gradients and pressures. Moreover, the effect of baking temperature was also investigated. CuO prepared using decomposition of $Cu(NO_3)_2$ as well as CuO nanopowder prepared using microwave-assisted synthesis technique were investigated and their results were compared. It was found that the current density can be enhanced with increasing the pressing pressure of the sample and when the sample undergoes a baking process. Moreover, it was found that the current density can be considerably enhanced with increasing the temperature gradient between the two ends of the sample. The CuO prepared using microwave-assisted synthesis technique was found to exhibit much better results over those of the CuO prepared using decomposition of $Cu(NO_3)_2$.

Keywords: Thermoelectricity, Cuo, Seebeck coefficient.

Contribution/ Originality

This study is one of few studies which have investigated thermoelectricity based on copper(II) oxide CuO prepared using decomposition of $Cu(NO_3)_2$ as well as CuO nanopowder prepared using microwave-assisted synthesis technique.

1. INTRODUCTION

Thermoelectric field has been attracting increasing attention in recent years [1-12]. It is perhaps the simplest technology for direct thermal to electric energy conversion and can be used in both refrigeration and power generation devices. Thermoelectric materials can utilize heat difference between two terminals to produce electrical power. Moreover, they can provide active cooling as well as heating in which the electric power acts as heat pumps. In these energy converts, the conduction electrons behave as the working fluid.

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Thermoelectricity can be used to generate electricity, measure temperature or change the temperature of objects. Thermoelectric devices are considered competent temperature controllers because the direction of heating and cooling is controlled by the applied voltage polarity.

When a temperature difference is maintained between two electrical conductors a potential difference is produced between the two substances. This phenomenon is called Seebeck effect [1]. When heat is applied to one of the two conductors, heated electrons flow toward the cooler one. If the two conductors are connected through an electrical circuit, direct current flows through that circuit. The potential differences generated by Seebeck effect are usually small and measured in microvolts per kelvin (μV/k) of temperature difference at the junction between the two substances. Some Seebeck-effect devices can produce few millivolts if a large temperature difference is maintained between the pair. Such devices can be connected in series or in parallel to increase the generated voltage or current, respectively. The behavior of thermocouples, which are used to measure temperature differences or to actuate electronic switches that can turn large systems on and off, is attributed to the Seebeck effect.

Thermoelectric and optoelectronic properties of pure and doped Bi_2Te_3 with Se have been investigated [8]. It was shown that a huge thermoelectric effect can be observed by contacting a superconductor whose density of states is spin split by a Zeeman field with a ferromagnet with a nonzero polarization [9]. General expressions for the thermoelectric coefficients generated by two types of resonances were given and the thermoelectric properties of these systems were calculated, which encompass most nanoelectronics junctions [10]. Copper oxide can be used as a coloring dye in ceramics to produce shiny surfaces. It is also used to produce cup ammonium hydroxide solutions which are used to make rayon. Moreover, it is sometimes used as a nutritional enhancement in animals, against copper deficiency. Copper(II) oxide has a molar mass of 79.545 g/mol and a work function of 5.3eV [2]. One of the most important applications of Copper(II) oxide is p-type semiconductor due to its narrow band gap. Copper oxide can be used to produce dry cell batteries. It has also been used in wet cell batteries as the cathode, with lithium as an anode, and dioxalane mixed with lithium perchlorate as the electrolyte. Copper(II) oxide can be used to produce other copper salts. It is also used when welding with copper alloys.

In this work, the performance of CuO prepared using decomposition of $Cu(NO_3)_2$ as well as CuO nanopowder prepared using microwave-assisted synthesis technique was investigated in thermoelectricity generation. The CuO acts as a p-type semiconductor in the thermoelectric cell. The current density-voltage characteristic curves of the samples were studied under different temperature gradients and pressures. Moreover, the effect of baking temperature was also investigated.

2. EXPERIMENT

2.1. Preparing CuO Nanopowder

CuO nanopowder was prepared using microwave-assisted synthesis technique, which is generally quite fast, simple, and energy-efficient. The power, heating time, and on/off irradiation cycles are the main heating parameters of a microwave oven, and each of them may have a strong effect on the structure and properties of the products [7]. Cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and sodium hydroxide (NaOH) were used in the preparation of CuO nanoparticles. In a typical reaction, 6 g $CuSO_4 \cdot 5H_2O$ were dissolved in 80 mL of distilled water to form a homogeneous blue solution. Then, 140 mL 0.5 M, NaOH aqueous solution was added to the above solution, and stirred for 15 min [7]. The resulting solution was heated in a microwave oven at 900 Watt power for 7 min and cooled down to room temperature. The final product was washed with distilled water and absolute ethanol many times, and then dried at 40 °C for 24 h.

The CuO nanopowder was pressed in a hydraulic piston mold at three different pressures of 2000, 2500, and 3000 bar. Samples were formed in cylindrical shape of diameter 4.9 mm and height 2.09 mm. Samples prepared at a certain pressure were divided into three groups. One group was left without baking and the other two groups were baked at 300 °C and 500 °C.

2.2. Preparing CuO using Decomposition of Cu $(No_3)_2$

CuO was prepared by thermal decomposition of Copper(II) nitrate $Cu(NO_3)_2$ at 300 °C for 2 hrs according to the following equation

$$2\ Cu(No_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$$

The resulting CuO was pressed in a hydraulic piston mold at three different pressures of 2000, 2500, and 3000 bar. The pressed samples at a certain pressure were also divided into three groups in a manner similar to that mentioned in subsection 2.1.

2.3. Measurements

The experimental arrangement used in the measurements is shown in Fig. 1. The J-V characteristic curves were established using a National Instruments data acquisition card (USB NI 6251) in combination with the Lab VIEW program. The J-V curves were measured for all samples using the setup shown in Fig.1, after exposing the top surface of the sample to one of three temperatures of 150 °C, 200 °C, or 250 °C, and the lower surface to room temperature.

3. RESULTS AND DISCUSSIONS

3.1. Electro Thermal Properties of CuO Nanopowder

Figure 2 shows the current density versus the voltage for the samples prepared using the CuO nanopowder at three different pressures. The upper three panels show the results of samples pressed at P_1 = 2000 bar and baked T_1 = no baking, T_2 = 300 °C, and T_3 = 500 °C. The letters A, B, and C used in the legends denote the three different temperatures at which the upper surface of the sample was kept where A, B, and C denote 150 °C, 200 °C, 250 °C, respectively. The mid three

panels show the same for samples pressed at P_2 = 2500 bar whereas the lower three panels show the results of those pressed at P_3 = 3000 bar. All curves show the same behavior of the linear dependence of the current density on the voltage. The current density shows as obvious enhancement when the sample undergoes a baking process. Moreover, as the baking temperature increases, the current density increases. As the temperature gradient between the sample ends increases, the current density also increases. For example, samples pressed at P_1 gave 4.5 mA/cm², 15.8 mA/cm² and 50.7 mA/cm² at baking temperatures T_1, T_2, and T_3, respectively, at a temperature gradient of 125 ˚C. When the temperature gradient increases to 175 ˚C the same sample gave 9.8 mA/cm², 19.8 mA/cm², and 61.2 mA/cm², and for a gradient of 225 ˚C the current density increases to 17.2 mA/cm², 30.2 mA/cm², and 80.1 mA/cm². Similarly, the sample pressed at P_2 gave 6.2 mA/cm², 35.3 mA/cm², and 58.4 mA/cm² at baking temperatures T_1, T_2, and T_3 respectively, at a temperature gradient of 125 ˚C. When the temperature gradient increases to 175 ˚C the same sample gave 15.3 mA/cm², 45.5 mA/cm², and 60.4 mA/cm², and for a gradient of 225 ˚C the current density increases to 23.5 mA/cm², 48.4 mA/cm², and 75.3 mA/cm². On the other hand, the sample pressed at P_3 gave 29.3 mA/cm², 40.3 mA/cm², and 60.5 mA/cm² at baking temperatures T_1, T_2, and T_3 respectively, at a temperature gradient of 125 ˚C. For a gradient of 175 ˚C the same sample gave 35.4 mA/cm², 60.2 mA/cm², and 75.5 mA/cm². When the gradient becomes 225 ˚C the current density increases to 43.2 mA/cm², 62.7 mA/cm², and 104.2 mA/cm². Seebeck coefficient was calculated as $S = V/\Delta T$ for all samples. It ranged between 3.5 μV/k and 7.2 μV/k. All these values are listed in Table 1.

Table-1. Parameters of thermoelectric power using CuO nanopowder at different pressures, baking temperatures, and temperature gradients.

Baking Temp.		25 ˚C – 150 ˚C		25 ˚C – 200 ˚C		25 ˚C – 300 ˚C		
	Pressure (bar)	J_m (mA/cm²)	V_m (volt)	J_m (mA/cm²)	V_m (volt)	J_m (mA/cm²)	V_m (volt)	S (μV/k)
T_1 = no baking	2000	4.5	0.005	9.8	0.018	17.2	0.024	4.5
	2500	6.2	0.009	15.3	0.012	23.5	0.058	7.2
	3000	29.3	0.060	35.4	0.090	43.2	0.120	4.3
T_2 = 300 ˚C	2000	15.5	0.050	19.8	0.062	30.2	0.050	3.5
	2500	35.3	0.060	45.5	0.082	48.4	0.080	4.6
	3000	40.3	0.073	60.2	0.085	62.7	0.090	4.8
T_3 = 500 ˚C	2000	50.7	0.125	61.2	0.130	80.1	0.135	4.9
	2500	58.4	0.142	60.4	0.130	75.3	0.140	5.1
	3000	60.5	0.060	75.5	0.110	104.2	0.140	6.2

3.2. Electro Thermal Properties of CuO Prepared Using Decomposition of Cu $(NO_3)_2$

The J-V characteristic curves for the samples obtained using the CuO prepared using decomposition of $Cu(NO_3)_2$ are shown in Fig. 3. The upper three panels show the results obtained for the samples pressed at P_1 and baked T_1 = no baking, T_2 = 300 ˚C, and T_3 = 500 ˚C. The mid panels show J-V curves for samples pressed at P_2 and the lower panels show the results obtained for samples pressed at P_3.

The linear dependence of the current density on the voltage is still observed for samples prepared using CuO obtained from $Cu(NO_3)_2$. The effects of baking temperature and temperature

gradient between top and bottom surfaces of the sample are similar to those observed in Fig. 2 for samples prepared using CuO nanopowder.

Samples pressed at P_1 gave 1.8 mA/cm², 12.3 mA/cm², and 35.3 mA/cm² at baking temperatures T_1 ,T_2, and T_3, respectively, when the temperature gradient between the sample ends was 125 °C. When the temperature gradient increases to 175 °C, these samples gave 4.8 mA/cm², 18.5 mA/cm² and 46.2 mA/cm². For a gradient of 225 °C the current density increased to 8.25 mA/cm², 28.5 mA/cm² and 69.5 mA/cm². Samples pressed at P_2 gave 9.2 mA/cm², 25.3 mA/cm², and 50.3 mA/cm² at baking temperatures T_1, T_2, and T_3 respectively, at a temperature gradient of 125 °C. As the temperature gradient increases to 175 °C, the current densities were 12.5 mA/cm², 32.5 mA/cm², and 53.5 mA/cm². For a gradient of 225 °C the current density increased to 19.5 mA/cm², 35.5 mA/cm², and 60.2 mA/cm². On the other hand, sample pressed at P_3 gave the results 22.2 mA/cm², 25.7 mA/cm² and 55.5 mA/cm² at a temperature gradient of 125 °C, 28.2 mA/cm², 55.3 mA/cm², and 65.5 mA/cm² at a gradient of 175 °C, and for a gradient of 275 °C, it gave 35.3 mA/cm², 55.5 mA/cm², and 90.4 mA/cm². For these samples, Seebeck coefficient was found to range between 2.2 μV/k and 5.5 μV/k.All these current densities and the corresponding voltages are presented in Table 2.

Table-2. Parameters of thermoelectric power of samples prepared using CuO obtained from the decomposition of $Cu(NO_3)_2$ at different pressures, baking temperatures, and temperature gradients.

Baking Temp.		**25 °C – 150 °C**		**25 °C – 200 °C**		**25 °C – 300 °C**		
	Pressure (bar)	**J_m (mA/cm²)**	**V_m (volt)**	**J_m (mA/cm²)**	**V_m (volt)**	**J_m (mA/cm²)**	**V_m (volt)**	**S (μV/k)**
T_1 = no baking	2000	1.8	0.005	4.8	0.009	8.25	0.010	3.6
	2500	9.2	0.009	12.5	0.012	19.5	0.040	5.1
	3000	22.2	0.050	28.2	0.090	35.3	0.090	3.2
T_2 = 300 °C	2000	12.3	0.030	18.5	0.040	28.5	0.052	2.2
	2500	25.3	0.050	32.5	0.055	35.5	0.058	3.1
	3000	25.7	0.050	55.3	0.070	55.5	0.080	3.5
T_3 = 500 °C	2000	35.3	0.070	46.2	0.080	69.5	0.090	4.5
	2500	50.3	0.100	53.5	0.120	60.2	0.120	5.5
	3000	55.5	0.050	65.5	0.080	90.4	0.120	4.2

4. CONCLUSION

We have investigated the use of two different forms of CuO in thermoelectricity. CuO prepared using decomposition of $Cu(NO_3)_2$ and CuO nanopowder prepared using microwave-assisted synthesis technique were investigated at different pressing pressures, baking temperatures, and temperature gradients between the top and bottom surfaces of the sample. All samples exhibited the following features. First, the current density is enhanced with increasing the pressing pressure of the sample. Second, the current density is also enhanced when the sample undergoes a baking process. Third, as the baking temperature of the sample increases, the current density increases. Fourth, the current density can be considerably enhanced with increasing the temperature gradient between the two ends of the sample. Finally, the CuO prepared using microwave-assisted synthesis technique exhibited much better results over those of the CuO prepared using decomposition of $Cu(NO_3)_2$.

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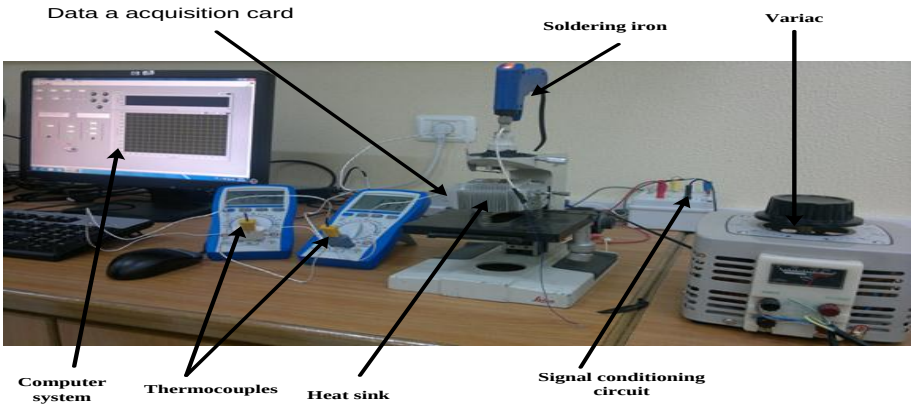

Fig-1. Experimental arrangement used in the measurement.

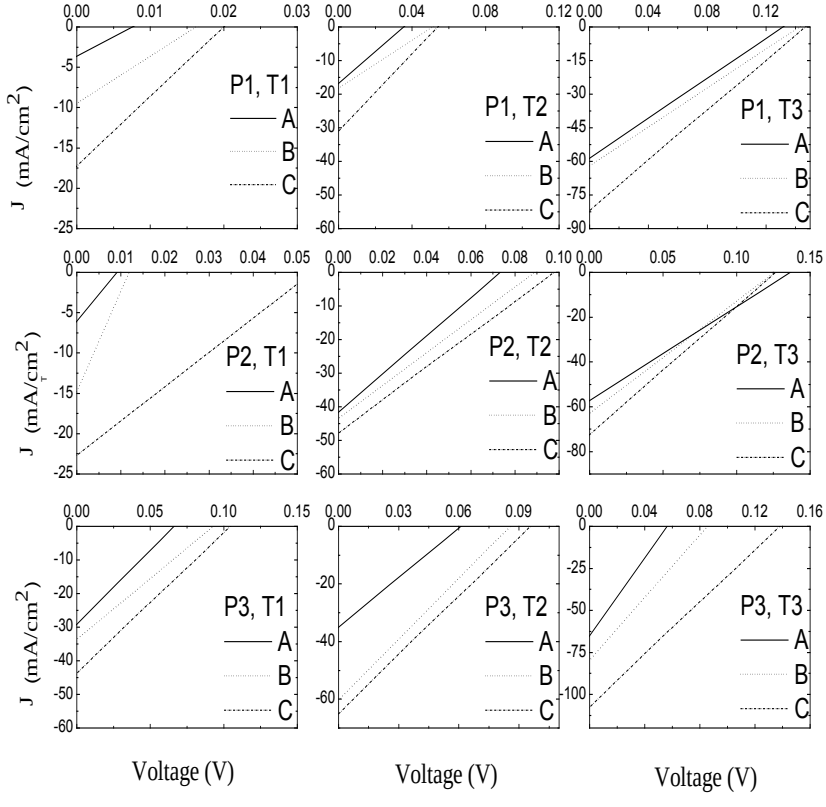

Fig-2. Thermoelectric current density–voltage curves for samples prepared using CuO nanopowder. The upper three panels show the results of samples pressed at P_1 = 2000 bar and baked T_1 = no baking, T_2 = 300 °C, and T_3 = 500 °C. The letters A, B, and C denote the three different temperatures at which the upper surface of the sample was kept where A, B, and C denote 150 °C, 200 °C, 250 °C, respectively. The mid three panels show the same for samples pressed at P_2 = 2500 bar whereas the lower three panels show the results of those pressed at P_3 = 3000 bar.

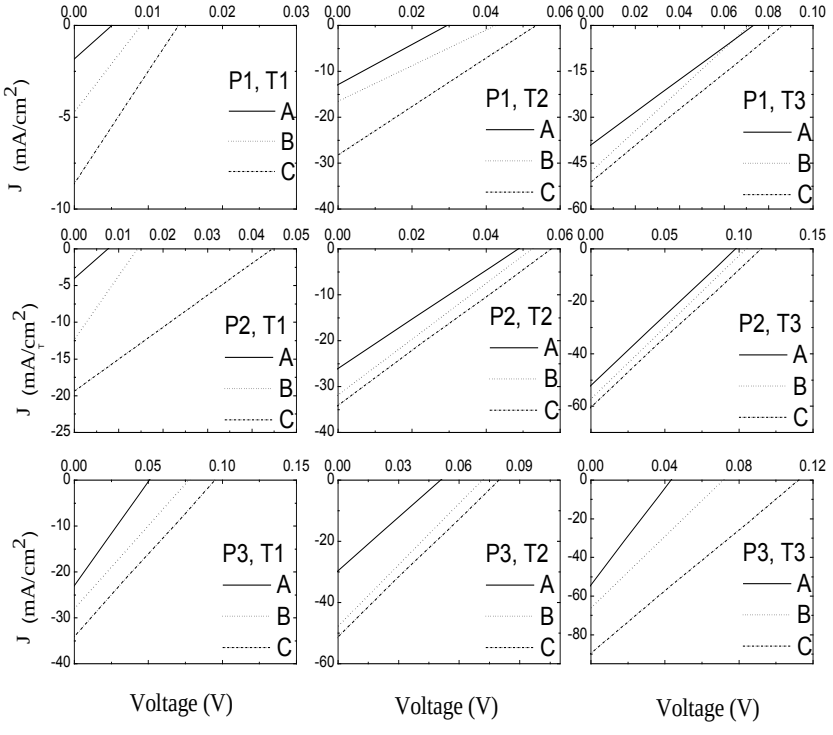

Fig-3. Thermoelectric current density–voltage curves for samples prepared using CuO obtained from the decomposition of $Cu(NO_3)_2$. The upper three panels show the results of samples pressed at P_1 = 2000 bar and baked T_1 = no baking, T_2 = 300 °C, and T_3 = 500 °C. The letters A, B, and C denote the three different temperatures at which the upper surface of the sample was kept where A, B, and C denote 150 °C, 200 °C, 250 °C, respectively.

The mid three panels show the same for samples pressed at P_2 = 2500 bar whereas the lower three panels show the results of those pressed at P_3 = 3000 bar.