# EFFECT OF Cu POWDER ADDITION ON THERMOELECTRIC PROPERTIES OF Cu/TiO$_{2\text{-}x}$ COMPOSITE

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## Abstract

*In this work spark plasma sintering (SPS) was used to fabricate Cu/TiO$_{2\text{-}x}$ composites by adding Cu powder into nonstoichiometric titanium dioxide TiO$_{2\text{-}x}$. The composition and the crystal forms of the composites were examined. The thermoelectric properties of the composites and the composite effects were also measured and discussed. Rule of mixture (ROM) and effective medium theory (GET) were applied to discuss the composite effects for Cu/TiO$_{2\text{-}x}$ composites. The results revealed that the electrical resistivity of the composites was largely decreased compared with that of nonstoichiometric titanium dioxide TiO$_{2\text{-}x}$. With increase in addition content of Cu powder, the electrical properties of the composites were transferred from semiconductor behavior to metallic behavior. Thermoelectric performance of the composites was increased due to the composite effects.*

## 1 Introduction

In recent years, thermoelectric materials have attracted much attention due to their potential applications in conversion between heat and electrical power such as electrical power generation from waste heat [1]. Oxide thermoelectric materials have become one of the hot research topics in this field as they show many advantages such as non-toxicity, thermal stability, and high oxidation resistance, among others [2-4]. Generally, the performance of thermoelectric materials is evaluated by the figure of merit $Z$ or the dimensionless figure of merit $ZT$ as follows

$$ZT = S^2 \rho^{-1} \kappa^{-1} T \tag{1}$$

where $S$ is Seebeck coefficient, $\rho$ is electrical resistivity, $\kappa$ is thermal conductivity and $T$ is absolute temperature. Conventionally, power factor $P$ is always used to evaluate the performance of thermoelectric materials with the following relation

$$P = S^2 \rho^{-1} \tag{2}$$

From the above analysis, Seebeck coefficient $S$ should be increased and electrical resistivity $\rho$ and thermal conductivity $\kappa$ should be decreased in order to improve the performance of thermoelectric materials. Composite technology by adding metal powders into ceramics or plastic materials has been used to decrease electrical resistivity and increase thermal conductivity of matrix materials and numerous efforts have been made in the investigation [5-7]. Recently, the improvement of thermoelectric performance by adding metal powders such as Au and Ag into oxide thermoelectric materials is booming [8-11]. These investigations revealed that the composite technology was effective to decrease electrical resistivity and increase Seebeck coefficient and thereby improve thermoelectric performance. However, composite technology is always accompanied with some negative effects including the increase of thermal conductivity. It seems necessary to investigate the composite effects and their influence on thermoelectric properties.

In this work $Cu/TiO_{2-x}$ composite through adding Cu powder into nonstoichiometric titanium dioxide $TiO_{2-x}$ was fabricated by spark plasma sintering (SPS). The composition and crystal forms of the composite were examined. The thermoelectric properties of the composite were also investigated. Rule of mixture (ROM) and effective medium theory (GET) were introduced to discuss the influence of the composite effects on the thermoelectric properties.

## 2 Experimental

### *2.1 Fabrication and characterization of $Cu/TiO_{2-x}$ composites*

Rutile $TiO_2$ powder with a purity of 99.0% and an average diameter of 0.3 μm was used as the matrix. Cu powder with a purity of 99.7% and an average diameter of 0.9 μm was used as the addition metal. Volume fraction of Cu addition in the composite was from 0% to 35%. The source materials, tungsten carbide balls and acetone were put into a bowl made of alumina. The blending was performed by a planetary ball mill (Pulverisette 5/4, Fritsch) with a rotation speed of 300 rpm for 2 h and then the mixed powder was dried for 2 h. After the blending, compacts of the mixed powder were fabricated as follows. Firstly, the mixed powder charged into a graphite die (diameter: 40 mm) as dense as possible. Secondly, the die was fixed in the SPS system (SPS-1030, Sumitomo). Then, the compacts with the dimension of $\phi 40 \times 1.5$ mm were fabricated by SPS at 1273 K at which holding for 5 min under a pressure of 27.3 MPa. After the fabrication, bulk samples with the dimension of $40 \times 5 \times 1.5$ mm were cut from the compacts for measurements of thermoelectric properties. The surfaces of the bulk samples were polished to remove contaminations. The composition and crystal forms of the composite were examined by XRD. The microstructure of the composite was observed by SEM.

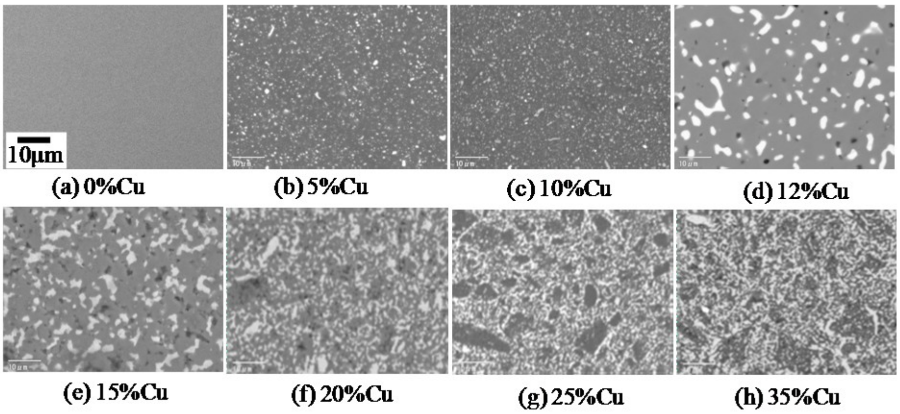
### *2.2 Measurement of thermoelectric properties*

To obtain a uniform temperature gradient along the length direction of the bulk samples for the measurement of Seebeck coefficient, a tubular electrical furnace with two heaters which can be controlled independently was used to maintain the required temperature and provide the desired temperature difference. In the work, temperature differences of the two sides of the samples were fixed at 6 K, 0 K and -6 K. A temperature difference of 0 K means that there was no temperature difference between the two sides. Negative temperature difference provided a reverse temperature gradient. Seebeck coefficient was calculated from $\triangle T$–$\triangle V$ curve. Electrical resistivity of the bulk samples was measured by the 4-probe method at a temperature difference of 0 K. The measurements were performed up to approximately 973 K. Thermal conductivity was measured by laser flash method (TC7000H, ULVAC-RIKO).

## 3 Results and discussion

### *3.1 Characterization of Cu/$TiO_{2-x}$ composites*

Fig. 1 shows the SEM micrographs of the Cu/$TiO_{2-x}$ composites by SPS. The gray areas were confirmed to be nonstoichiometric titanium dioxide $TiO_{2-x}$ in our published work [12]. The areas of white color correspond to copper powder that was added into $TiO_2$ powder. It can be seen from the figures that Cu powder particles distributed evenly and discretely in the matrix when the volume fraction of Cu powder addition was no more than 10% (Fig.1 (b) and (c)). With the volume fraction increase of Cu powder addition to 15%, Cu powder particles aggregated (Fig.1 (d) and (e)). When the volume fraction increased over 20%, Cu particles connected with each other and formed a network microstructure (Fig.1 (f)-(h)). Fig. 2 shows the XRD patterns of the Cu/$TiO_{2-x}$ composites fabricated by SPS. The diffraction peaks of Cu and $TiO_{2-x}$ were detected when the volume fraction of Cu powder addition was not 0%. With the increase of Cu powder addition, the peaks of Cu became higher and those of $TiO_{2-x}$ got lower. From the above analysis, it can be confirmed that the composites consisted of Cu and $TiO_{2-x}$ and the reaction between them did not take place.



**(a) 0%Cu** **(b) 5%Cu** **(c) 10%Cu** **(d) 12%Cu**

**(e) 15%Cu** **(f) 20%Cu** **(g) 25%Cu** **(h) 35%Cu**

**Figure 1.** SEM micrographs of the Cu/$TiO_{2-x}$ composites.

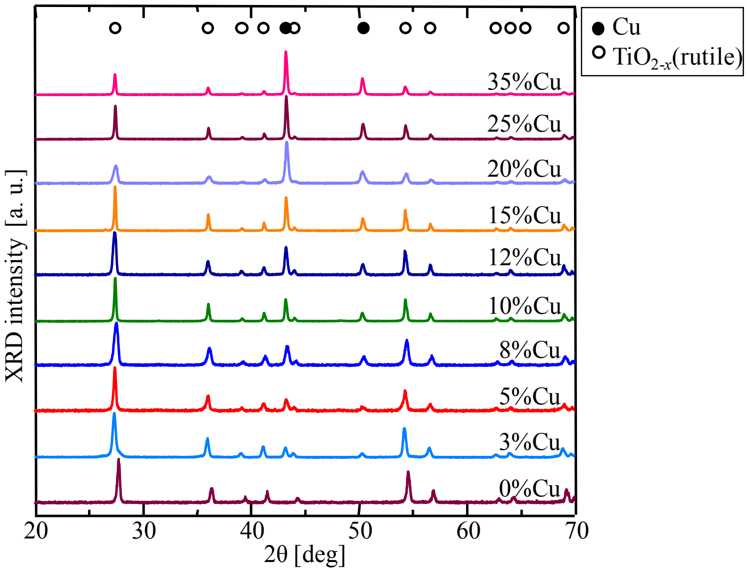


**Figure 2.** X-ray patterns of the Cu/$TiO_{2-x}$ composites.

### *2.2 Thermoelectric properties of Cu/TiO$_{2-x}$ composites*

Electrical resistivity of the Cu/TiO$_{2-x}$ composites as a function of measurement temperature is shown in Fig. 3. When the volume fraction of Cu powder addition was no more than 12%, the electrical resistivity of the composite showed a decrease evolution with the increase of measurement temperature. It is a typical semiconductor behavior. However, the electrical resistivity turned to increase with the increase of measurement temperature when the volume fraction of Cu powder addition was more than 12%. It is a typical metallic behavior as metal Cu reported by Ref. [13, 14]. The electrical behavior transition of the Cu/TiO$_{2-x}$ composites from semiconductor to metal can be controlled by adjusting the volume fraction of Cu powder addition. In addition, the electrical resistivity of the composites was decreased with volume fraction increase of Cu powder addition in all the temperature ranges.

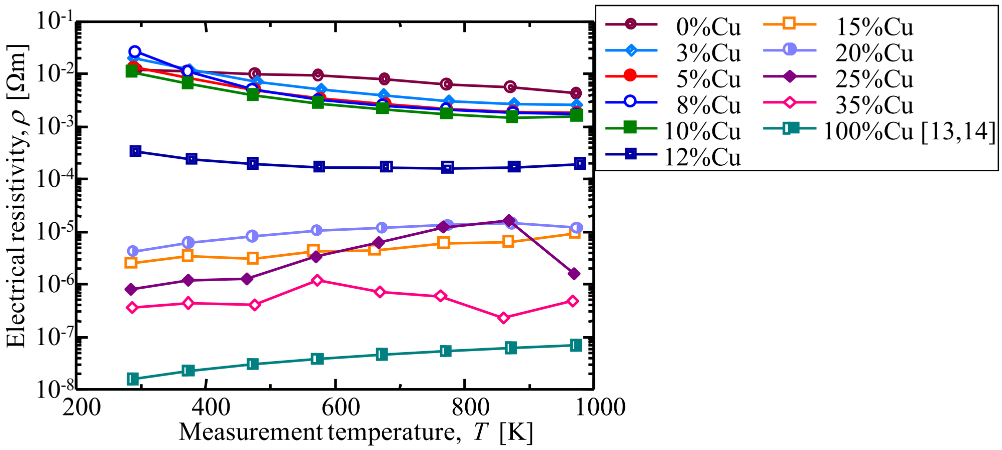


**Figure 3.** Electrical resistivity of the Cu/TiO$_{2-x}$ composites.

Rule of mixture (ROM) and effective medium theory (GET) have been used to evaluate and discuss electrical conductivity/resistivity and thermal conductivity [5-7, 15]. ROM for the parallel and series model, and general effective medium equation (GEM) proposed by McLachlan [16] for particulate composite (an equation of GET) are shown as following.

ROM for the parallel model:

$$\sigma_m = \phi\sigma_h + (1-\phi)\sigma_l \tag{1}$$

ROM for series model:

$$\frac{1}{\sigma_m} = \phi\frac{1}{\sigma_h} + (1-\phi)\frac{1}{\sigma_l} \tag{2}$$

GEM:

$$\frac{(1-\phi)(\sigma_l^{1/t}-\sigma_m^{1/t})}{\sigma_l^{1/t}+[(1-\phi_c)/\phi_c]\sigma_l^{1/t}} + \frac{\phi(\sigma_h^{1/t}-\sigma_m^{1/t})}{\sigma_h^{1/t}+[(1-\phi_c)/\phi_c]\sigma_h^{1/t}} = 0 \tag{3}$$

Where $\sigma$ represents electrical conductivity, the subscript $m$, $h$, and $l$ means composite, high and low electrical conductivity respectively. $\phi$ represents volume fraction of the filler and the subscript $c$ means the critical. $t$ is an exponent with the value from 1 to 3, and determines the effective percolation slope [16]. Electrical conductivity, $\sigma$ can be replaced with $1/\rho$ in Eqs.1~3. $\rho$ is electrical resistivity. Furthermore, Eqs.1~3 of ROM for the parallel and series model, and GEM can also be used to discuss thermal conductivity [16].

Electrical resistivity of the Cu/$TiO_{2-x}$ composite at 289 K and 873 K from the experiment, ROM and GEM is shown in Fig.4. From the figure, it can be seen that the experiment values located between theoretical values of parallel model and series model. In addition, they were generally in accord with those of GEM. When exponent $t$ was given by 1, the critical volume fractions were 15% and 13% at 289 K and 873 K respectively.

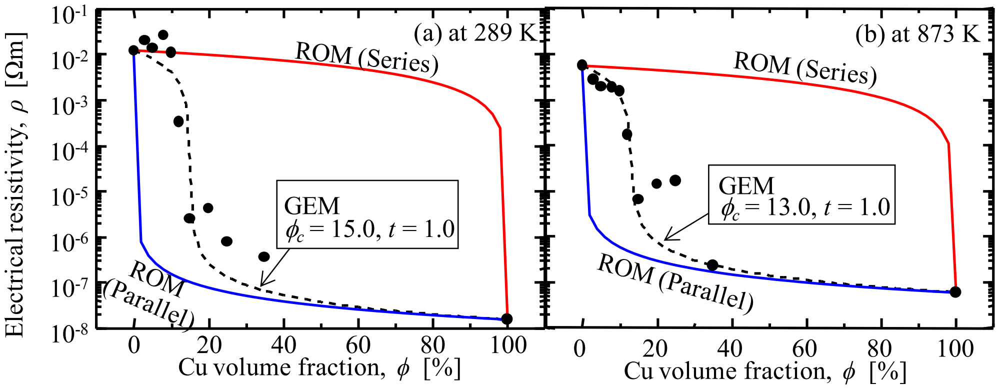


**Figure 4.** Electrical resistivity of the Cu/$TiO_{2-x}$ composites from the measurement, ROM and GEM at (a) 289 K and (b) 873 K.

Fig. 5 shows the thermal conductivity of the Cu/$TiO_{2-x}$ composites as a function of measurement temperature. When the volume fraction of Cu powder addition was no more than 15%, the thermal conductivity decreased with the increase of measurement temperature. However, when the volume fraction was more than 15%, the thermal conductivity hardly changed with the increase of measurement temperature. In addition, the thermal conductivity increased with the increase of the volume fraction of Cu powder addition in all the temperature ranges.

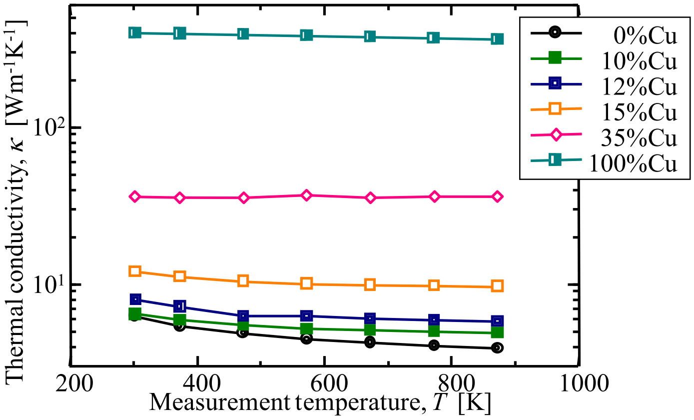


**Figure 5.** Thermal conductivity of the Cu/$TiO_{2-x}$ composites.

Thermal conductivity comparison of the Cu/$TiO_{2-x}$ composites at 289 K and 873 K from the experiment, ROM and GEM is shown in Fig. 6. As the electrical resistivity in Fig. 4, the thermal conductivity also located between the theoretical values of parallel model and series model. The experiment values also consisted with the theoretical values of GEM. When exponent $t$ was given by 1, the critical volume fractions were 40% and 32% at 289 K and 873 K respectively. It was noted that the critical volume fractions for the resistivity and the thermal conductivity showed evident difference. It can be applied to enhance thermoelectric performance.

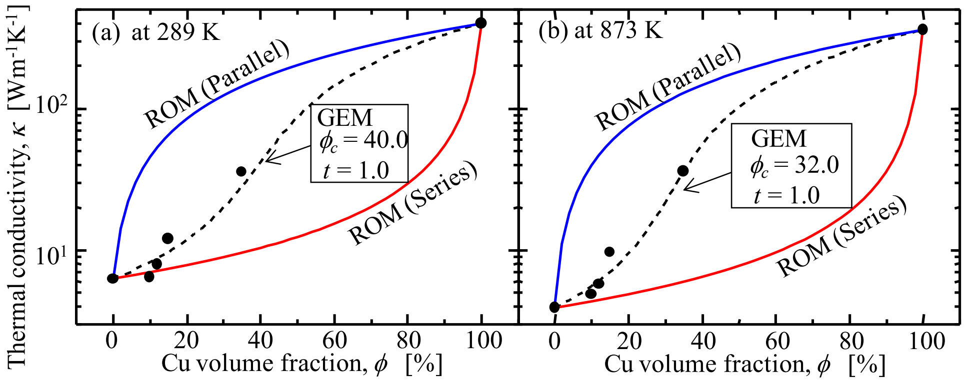
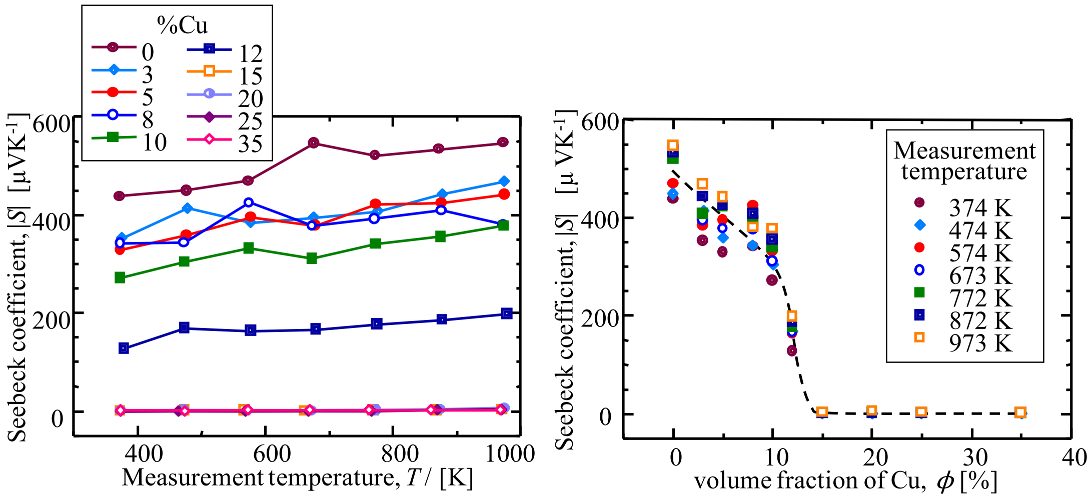


**Figure 6.** Thermal conductivity of the Cu/TiO$_{2-x}$ composite by measurement, ROM and GEM at (a) 289 K and (b) 873 K.

Fig. 7 shows Seebeck coefficient of the Cu/TiO$_{2-x}$ composites. From Fig. 7(a), Seebeck coefficient decreased with the increase of the volume fraction of Cu powder addition in all the temperature ranges. When the volume fraction was above 12%, it became relatively small which was near the value of pure Cu [13, 14]. For the composite with the same volume fraction of Cu powder addition, Seebeck coefficient was increased with the increase of the measurement temperature, but the increase became unconspicuous when the volume fraction of Cu powder addition was above 12%. From Fig. 7(b), Seebeck coefficient evolution as the volume fraction of Cu powder addition can be clearly seen. When the volume fraction was above 10%, Seebeck coefficient got smaller quickly. When the volume fraction was 15% and above, Seebeck coefficient hardly changed any more.

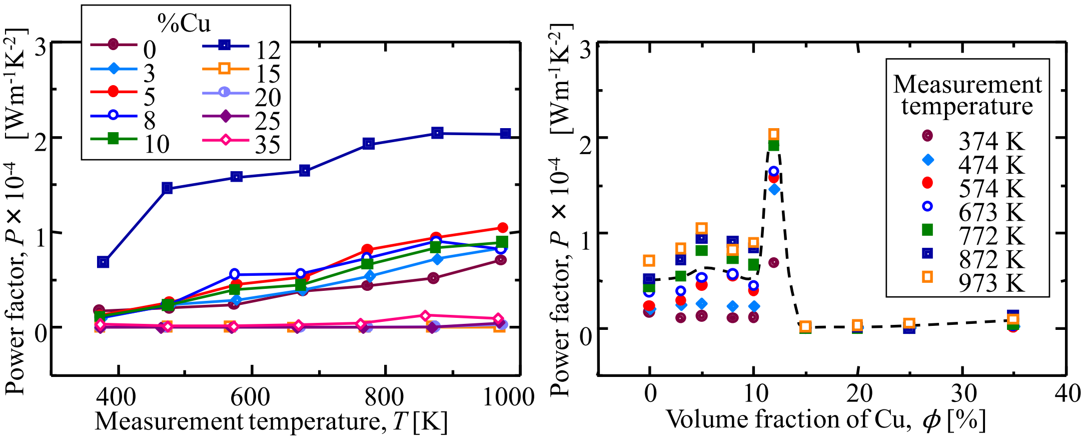


(a) Seebeck coefficient and temperature (b) Seebeck coefficient and volume fraction of Cu

**Figure 7.** Seebeck coefficient of the Cu/TiO$_{2-x}$ composites.

### *3.3 Thermoelectric performance*

Fig. 8 shows power of the Cu/TiO$_{2-x}$ composites. From Fig. 8 (a), power factor increased with the increase of measurement temperature for the composite with the same volume fraction of Cu powder addition. When the volume fraction was 12%, power factor obtained the maximum value. When the volume fraction was above 12%, power factor significantly decreased. From Fig. 8 (b), the evolution of power factor as the volume fraction of Cu powder addition can be seen.



(a) Power factor and temperature

(b) Power factor and volume fraction of Cu

**Figure 8.** Power factor of the Cu/$TiO_{2-x}$ composites.

The evolution of dimensionless figure of merit, *ZT* as measurement temperature is shown in Fig. 9. It can be seen that *ZT* had the largest values when the volume fraction of Cu powder addition was 12%. It means that the composite with 12%Cu addition showed the greatest thermoelectric performance in all the samples. It also indicates that thermoelectric performance can be improved by adjusting the balance among electrical resistivity, thermal conductivity and Seebeck coefficient with the composite theory.

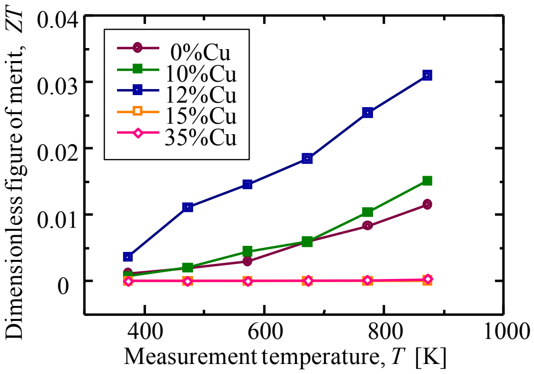


**Figure 9.** Dimensionless figure of merit, *ZT* of the Cu/$TiO_{2-x}$ composites.

## 4 Conclusions

Cu/$TiO_{2-x}$ composites were fabricated through adding Cu powder into nonstoichiometric titanium dioxide $TiO_{2-x}$ powder by SPS. The electrical resistivity of the composites was decreased and the thermal conductivity was increased with the volume fraction increase of Cu powder addition. The critical volume fractions of Cu powder addition for the electrical resistivity and the thermal conductivity of the composite showed evident different. The thermoelectric properties and the transition of the composites from semiconductor to metal can be controlled by adjusting the volume fraction of Cu powder addition. Seebeck coefficient also had a critical volume fraction of Cu powder addition. Thermoelectric performance can be improved by adjusting the balance among electrical resistivity, thermal conductivity and Seebeck coefficient with the composite effects.

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