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Effect of Cu powder addition on thermoelectric properties of Cu/TiO_{2-x} composites

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Abstract

Spark plasma sintering was used to fabricate Cu/TiO_{2-x} composites by adding Cu powder to nonstoichiometric titanium dioxide, TiO_{2-x}. The composition and crystal forms of the composites were examined. The thermoelectric properties of the composites were measured and the effects of composite formation on these properties were discussed. The rule of mixture (ROM) of composite and general effective medium theory (GEM) were used to investigate the composite effects of the Cu/TiO_{2-x} composites. The results revealed that the electrical resistivities of the composites was much lower than that of TiO_{2-x}. As the added amount of Cu powder increased, the electrical properties of the composites shifted from semiconductor behavior to metallic behavior. The thermoelectric performances of the composites improved as a result of composition formation. The thermoelectric performance can be improved by adjusting the balance among electrical resistivity, thermal conductivity and the Seebeck coefficient, based on the composite effects.

Keywords: A. Sintering; B. Composites; D. TiO_2; E. Functional applications

1. Introduction

In recent years, thermoelectric materials have attracted increasing attention because of 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 major research topics in this field as they show many advantages such as non-toxicity, thermal stability, and high oxidation resistance [2–4]. Generally, the performance of a thermoelectric material 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 the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, and T is the absolute temperature. Conventionally, the power factor P is used to evaluate the performance of thermoelectric materials from the following relation:

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

From the above analysis, the Seebeck coefficient S should be increased, and the electrical resistivity ρ and the thermal conductivity κ should be decreased, to improve the performance of thermoelectric materials. Compounding by adding metal powders to ceramics or plastic materials has been used to decrease the electrical resistivity and increase the thermal conductivity of matrix materials. Numerous efforts have been carried out [5–7]. Recently, there has been a great increase in the number of attempts to produce materials with improved thermoelectric performances by adding metal powders such as Au and Ag to oxide thermoelectric materials [8–11]. These investigations have revealed that composite formation effectively decreases the electrical resistivity and increases the Seebeck coefficient, and thereby improving the thermoelectric performance. However, composite technology always has

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some negative effects, including an increase in thermal conductivity. It seems therefore necessary to investigate the effects of composites and their influence on thermoelectric properties.

In this work, Cu/TiO_{2-x} composite was fabricated using spark plasma sintering (SPS), by adding Cu powder to nonstoichiometric titanium dioxide, TiO_{2-x}. The compositions and crystal forms of the composites were examined. The thermoelectric properties of the composites were also investigated. Rule of mixture (ROM) and general effective medium theory (GEM) were used to investigate the effects of composite formation on the thermoelectric properties.

2. Materials and methods

2.1. Fabrication and characterization of Cu/TiO_{2-x} composites

Rutile TiO_2 powder of purity 99.0% and average diameter 300 nm was used as the matrix. Cu powder of purity 99.7% and average diameter 900 nm was used as the metal powder additive. The volume fractions of Cu added to the composite varied from 0% to 35%. Although the volume fractions changed at high temperatures, the change was confirmed to be trifling in that its effect on thermoelectric properties can be neglected. Therefore, the volume fractions at room temperature were adopted. The source materials, tungsten carbide balls, and acetone were placed in a bowl made of alumina. Blending was performed using 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 blending, compacts of the mixed powder were fabricated as follows. First, the mixed powder was charged into a graphite die (diameter 40 mm) as dense as possible. Second, the die was fixed in the SPS system (SPS-1030, Sumitomo), and then compacts of dimension Φ 40 mm × 1.5 mm were fabricated by SPS at 1273 K and holding for 5 min under a pressure of 27.3 MPa. After fabrication, bulk samples of dimension 40 mm × 5 mm × 1.5 mm were cut from the compacts for thermoelectric property measurement. The surfaces of the bulk samples were polished to remove contaminations. The compositions and crystal forms of the composite were examined by X-ray diffraction (XRD). The microstructures of the composites were observed using scanning electron microscopy (SEM).

2.2. Measurement of thermoelectric properties

To obtain a uniform temperature gradient along the length of the bulk samples for Seebeck coefficient measurement, 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 study, the temperature differences between 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. A negative temperature difference provided a reverse temperature gradient. The Seebeck coefficient was calculated from ΔT–ΔV curve. The electrical resistivities of the bulk samples were measured by the four-probe method at a temperature difference of 0 K. The measurements were performed up to approximately 973 K. Thermal conductivities were measured using the 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 produced using SPS. The gray areas were confirmed to be nonstoichiometric titanium dioxide, TiO_{2-x}, as discussed in our earlier work [12]. In that work, the introduction of oxygen vacancy was confirmed by thermogravimeric analysis (TGA) although the amount of oxygen vacancy was tiny. Here, the characterization was

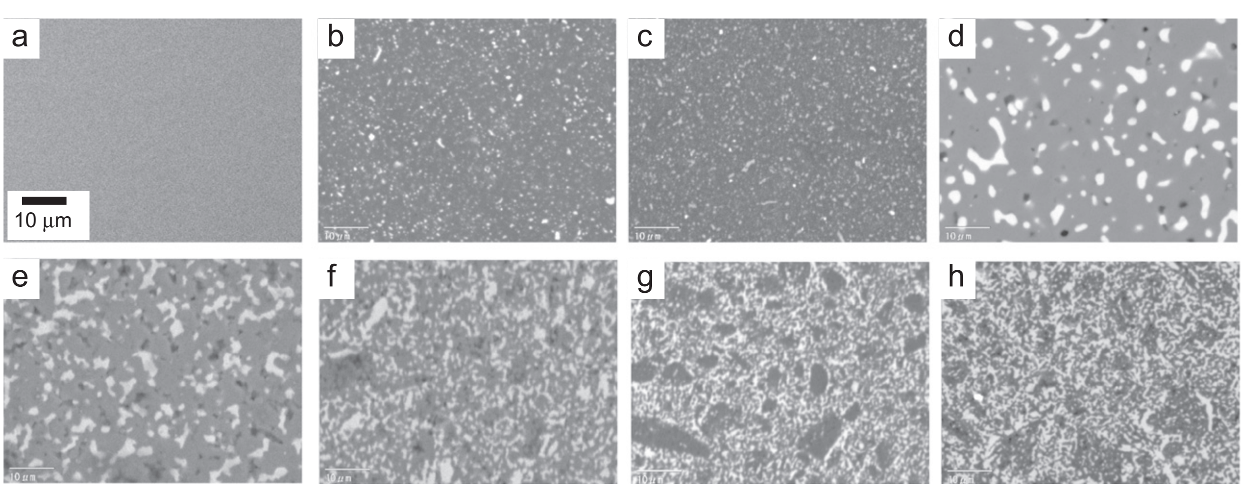

Fig. 1. SEM images of Cu/TiO_{2-x} composites with different volume fractions of Cu powder: (a) 0%, (b) 5%, (c) 10%, (d) 12%, (e) 15%, (f) 20%, (g) 25% and (h) 30%.

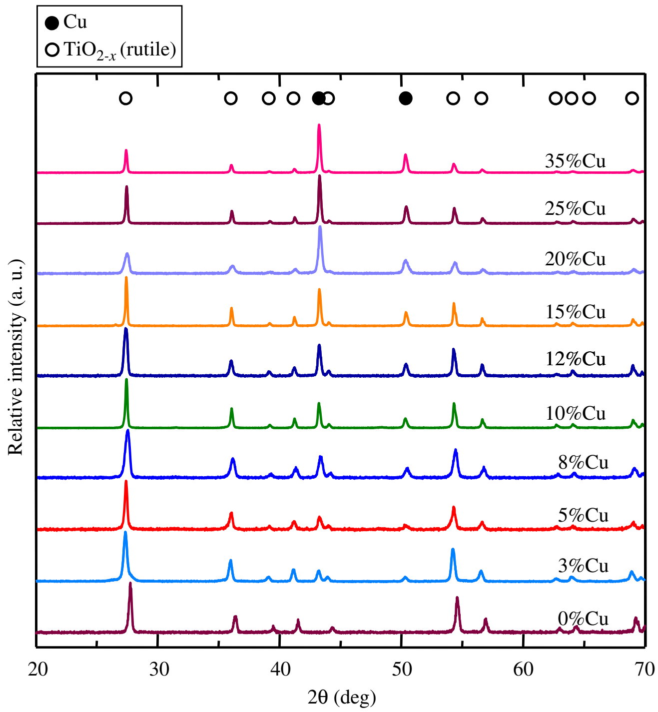

Fig. 2. XRD patterns of Cu/TiO_{2-x} composites with different volume fractions of Cu powder.

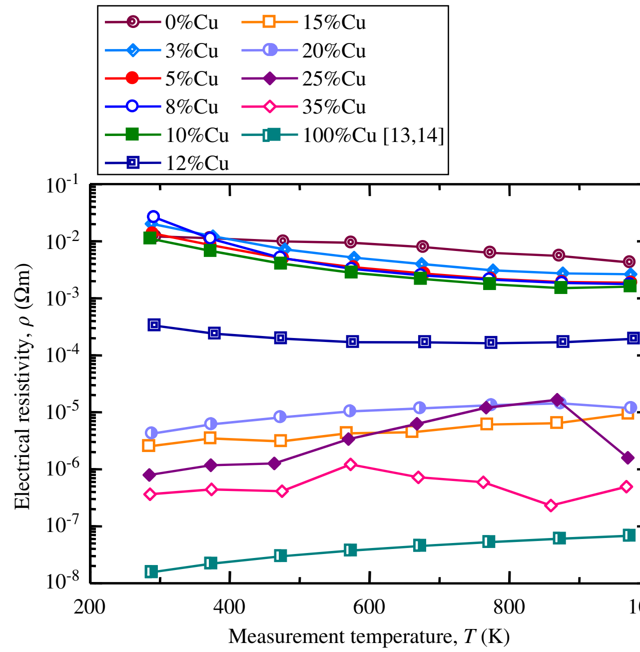

Fig. 3. Electrical resistivities of Cu/TiO_{2-x} composites with different volume fractions of Cu powder as a function of measurement temperature.

not involved and the result was directly cited. The white areas correspond to Cu powder, which was added to the matrix. It can be seen from the images that Cu powder particles were distributed evenly and discretely in the matrix when the added volume fraction of Cu powder was no more than 10% (Fig. 1(b) and (c)). As the volume fraction of Cu powder increased to 15%, Cu powder particles aggregated (Fig. 1(d) and (e)). When the volume fraction was increased to over 20%, Cu particles connected with each other and formed a network microstructure (Fig. 1(f)–(h)). Fig. 2 shows the XRD patterns of Cu/TiO_{2-x} composites with different added volume fractions of Cu powder. The diffraction peaks of Cu and TiO_{2-x} were detected when the added volume fraction of Cu powder was not 0%. As the added volume fraction of Cu powder increased, the Cu peaks became more intense, and those of TiO_{2-x} became less intense. The results confirm that the composites consisted of Cu and TiO_{2-x}.

3.2. Thermoelectric properties of Cu/TiO_{2-x} composites

The electrical resistivities of the Cu/TiO_{2-x} composites with different added volume fractions of Cu powder as a function of measurement temperature are shown in Fig. 3. When the added volume fraction of Cu powder was no more than 12%, the electrical resistivities of the composite decreased with increasing measurement temperature. It is typical semiconductor behavior. However, the electrical resistivities increased with increasing temperature when the added volume fraction of Cu powder was more than 12%. This is behavior typical of metallic Cu, as reported in the literatures [13,14]. The transition in the electrical behavior of the Cu/TiO_{2-x} composites from semiconductor to metal can be controlled by adjusting the added volume fraction of Cu powder. In addition, the electrical resistivities of the composites decreased with increasing added volume fraction of Cu powder in all temperature ranges.

ROM and GET have been used to evaluate and analyze electrical conductivity/resistivity and thermal conductivity [5–7,15]. ROM for parallel and series models, and the general effective medium equation (a GEM equation) [15,16] for particulate composites are shown as follows:

ROM for parallel model

$$\sigma_m = \phi\sigma_h + (1-\phi)\sigma_l \quad (3)$$

ROM for series model

$$1/\sigma_m = \phi/\sigma_h + (1-\phi)/\sigma_l \quad (4)$$

GEM

$$(1-\phi)(\sigma_l^{1/t} - \omega_m^{1/t})/\{\sigma_l^{1/t} + ((1-\phi_c)/\phi_c)\sigma_h^{1/t}\} + \phi(\sigma_h^{1/t} - \sigma_m^{1/t})/\{\sigma_h^{1/t} + [(1-\phi_c)/\phi_c]\sigma_h^{1/t}\} = 0 \quad (5)$$

where σ is the electrical conductivity, and the subscripts m, h, and l mean composite, high, and low electrical conductivities, respectively. ϕ is the added volume fraction, the subscript c means the critical condition and t is an exponent with a value from 1 to 3, and determines the effective percolation slope [16]. The electrical conductivity σ can be replaced with $1/\rho$ in Eqs. (3)–(5), where ρ is the electrical resistivity. Eqs. (3)–(5) can also be used to investigate the thermal conductivity [16].

The experimental electrical resistivities of the Cu/TiO_{2-x} composite at 289 K and 873 K, and those calculated from

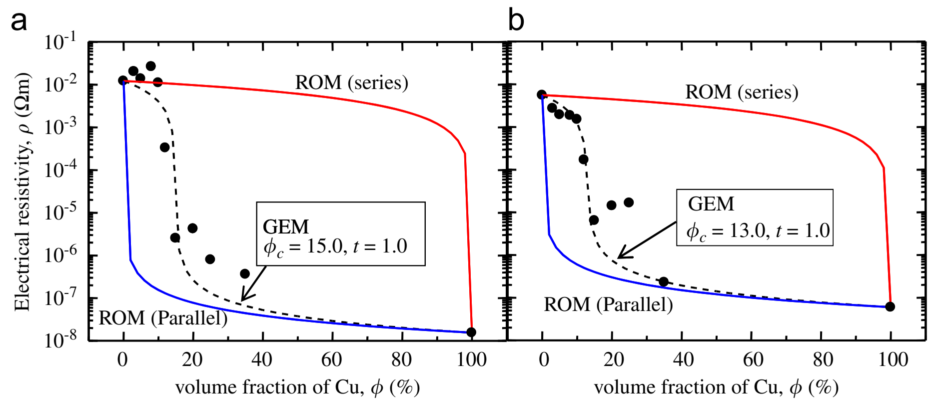

Fig. 4. Electrical resistivities of Cu/TiO_{2-x} composites, obtained experimentally and calculated using ROM and GEM at (a) 289 K and (b) 873 K.

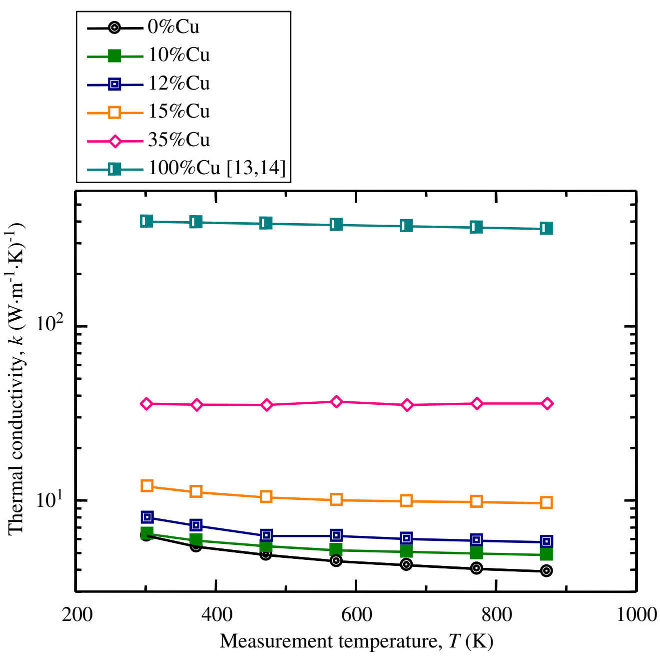

Fig. 5. Thermal conductivities of Cu/TiO_{2-x} composites with different volume fractions of Cu powder as a function of measurement temperature.

ROM and GEM, are shown in Fig. 4. From the figure, it can be seen that the experimental values fell between the theoretical values for the parallel and series models. In addition, they were generally in agreement with the values calculated using GEM. When the exponent t was 1, the critical volume fractions were 15% and 13% at 289 K and 873 K, respectively.

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

A comparison of the experimental thermal conductivities of the Cu/TiO_{2-x} composites at 289 K and 873 K and those calculated from ROM and GEM is shown in Fig. 6. As in the case of the electrical resistivity, shown in Fig. 4, the experimental thermal conductivities were located between the theoretical values calculated using the parallel and series models. The experimental values were also consistent with the theoretical values calculated using GEM. When the exponent t was 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 used to enhance the thermoelectric performance.

Fig. 7 shows the Seebeck coefficients of the Cu/TiO_{2-x} composites. Fig. 7(a) shows that the absolute values of Seebeck coefficient decreased with increasing added volume fraction of Cu powder in all temperature ranges. When the volume fraction was above 12%, the Seebeck coefficients were relatively small and near the value of pure Cu [13,14]. For the composites with the same added volume fraction of Cu powder, the Seebeck coefficient increased with increasing measurement temperature, but the increase was less significant when the added volume fraction of Cu powder addition was above 12%. In Fig. 7(b), changes in the Seebeck coefficient with added volume fraction of Cu powder addition can be clearly seen. When the volume fraction was above 10%, the Seebeck coefficient decreased quickly. However, when the volume fraction was 15% and above, further changes in the Seebeck coefficient were hardly seen.

3.3. Thermoelectric performance

Fig. 8 shows the power factors of the Cu/TiO_{2-x} composites. Fig. 8(a) shows that the power factors increased with increasing measurement temperature for the composites with the same added volume fraction of Cu powder. The maximum power factor was obtained when

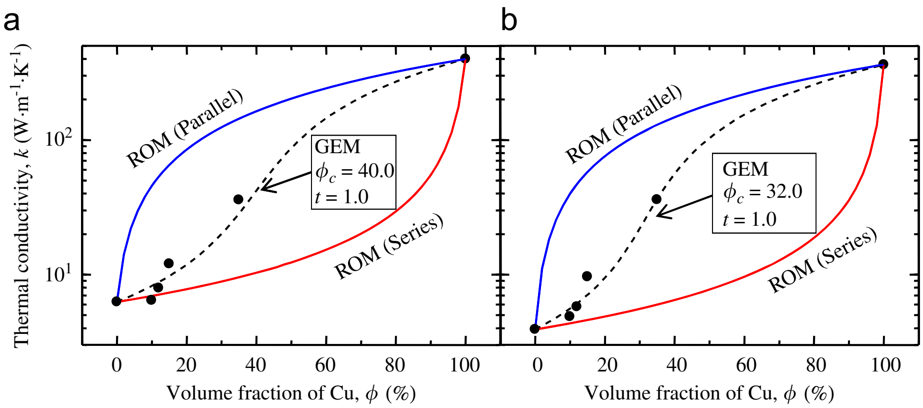

Fig. 6. Thermal conductivities of Cu/TiO_{2-x} composites with different volume fractions of Cu powder, obtained experimentally and calculated using ROM and GEM at: (a) 289 K and (b) 873 K.

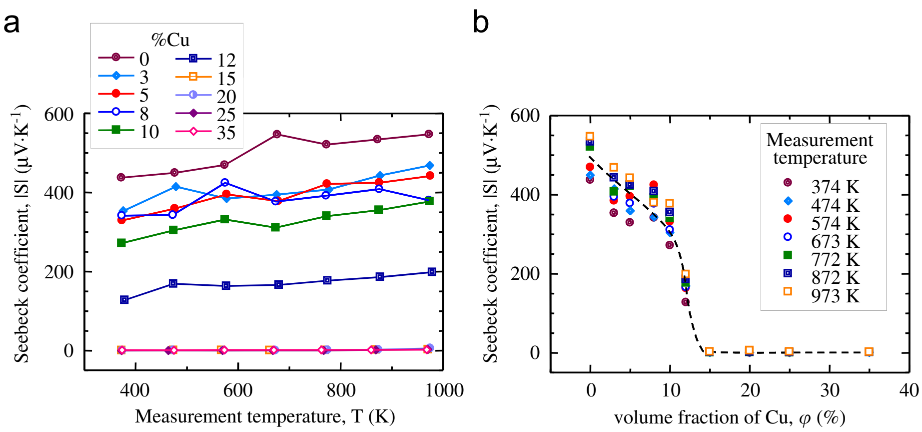

Fig. 7. Seebeck coefficients of Cu/TiO_{2-x} composites as a function of (a) measurement temperature and (b) added volume fraction of Cu powder.

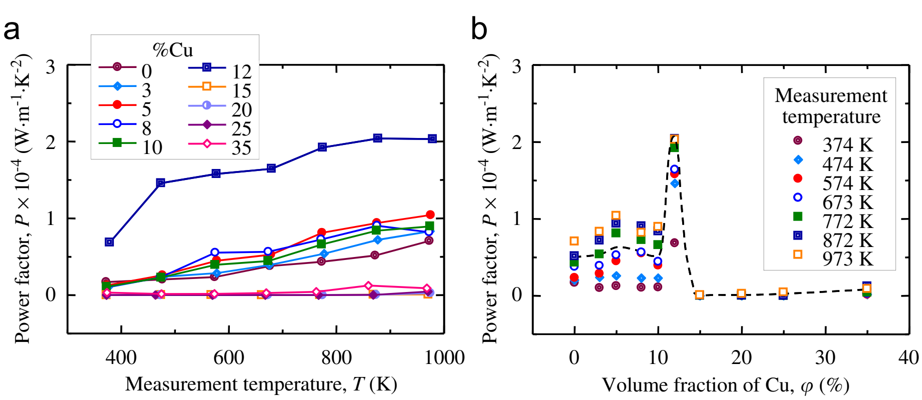

Fig. 8. Power factors of Cu/TiO_{2-x} composites as a function of (a) measurement temperature and (b) added volume fraction of Cu powder.

the volume fraction was 12%. When the volume fraction was above 12%, the power factors decreased significantly. Fig. 8(b) shows the power factor changes with changes in the added volume fraction of Cu powder. When the measurement temperature was 973 K, the composite with a volume fraction of 12% gave the highest power factor, above 2×10^{-4} Wm^{-1} K^{-2}.

The evolution of the dimensionless figure of merit ZT with measurement temperature is shown in Fig. 9. It can be seen that ZT had the greatest values when the added volume fraction of Cu powder was 12%. It means that the composite with 12 vol% Cu addition showed the best thermoelectric performance. It also indicates that thermoelectric performance can be improved by adjusting the

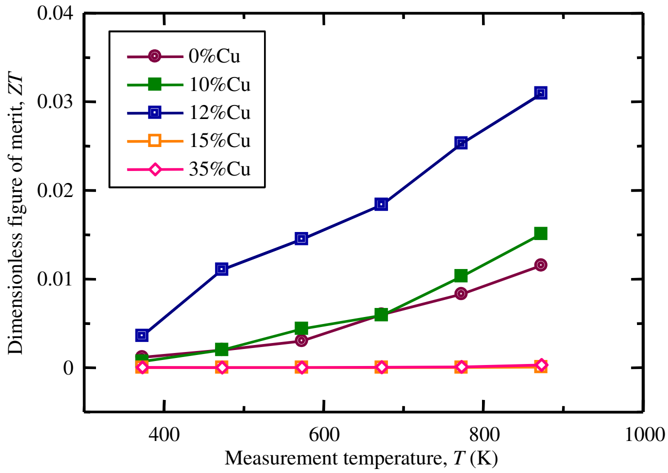

Fig. 9. Dimensionless figure of merit, ZT, of Cu/TiO_{2-x} composites with different volume fractions of Cu powder as a function of measurement temperature.

balance among electrical resistivity, thermal conductivity and the Seebeck coefficient, based on the composite theory.

4. Conclusions

Cu/TiO_{2-x} composites were fabricated using SPS, by adding Cu powder to nonstoichiometric titanium dioxide, TiO_{2-x} powder. The electrical resistivities of the composites were decreased, whereas the thermal conductivities increased, with increasing added volume fraction of Cu powder. The thermoelectric properties and the transition of the composites from semiconductor to metal behavior can be controlled by adjusting the added volume fraction of Cu powder. There was also a critical volume fraction of Cu powder for the Seebeck coefficient. The thermoelectric performance can be improved by adjusting the balance among electrical resistivity, thermal conductivity and the Seebeck coefficient, based on the composite effects. The highest power factor of the composites exceeded 2×10^{-4} $Wm^{-1} K^{-2}$, when the added volume fraction of Cu powder and the temperature were 12% and 973 K, respectively.

References

[1] D.M. Rowe, Thermoelectrics Handbook: Macro to Nano, CRC Press, London, 2006.
[2] I. Tsuyumoto, T. Hosono, M. Murata, Thermoelectric power in nonstoichiometric orthorhombic titanium oxides, Journal of the American Ceramic Society 89 (2006) 2301–2303.
[3] S. Harada, K. Tanaka, H. Inui, Thermoelectric properties and crystallographic shear structures in titanium oxides of the Magneli phases, Journal of Applied Physics 108 (2010) 083703.
[4] J.W. Fergus, Oxide materials for high temperature thermoelectric energy conversion, Journal of the European Ceramic Society 32 (2012) 525–540.
[5] J.K. Carson, S.J. Lovatt, D.J. Tanner, A.C. Cleland, Predicting the effective thermal conductivity of unfrozen, porous foods, Journal of Food Engineering 75 (2006) 297–307.
[6] P. Mamunya, V.V. Davydenko, P. Pissis, E.V. Lebedev, Electrical and thermal conductivity of polymers filled with metal powders, European Polymer Journal 38 (2002) 1887–1897.
[7] M. Taya, Electronic Composites: Modeling, Characterization, Processing, and MEMS Applications, Cambridge University Press, Cambridge, 2005.
[8] Y. Lu, H. Yoshida, M. Hirohashi, Fabrication of Cu_p/TiO_{2-x} thermoelectric composite by SPS and its thermoelectric properties, Journal of Japan Institute of Copper 48 (2009) 92–95.
[9] P.H. Xiang, Y. Kinemuchi, H. Kaga, K. Watari, Fabrication and thermoelectric properties of $Ca_3Co_4O_9/Ag$ composites, Journal of Alloys and Compounds 454 (2008) 364–369.
[10] M. Mikami, N. Ando, R. Funahashi, The effect of Ag addition on electrical properties of the thermoelectric compound $Ca_3Co_4O_9$, Journal of Solid State Chemistry 178 (2005) 2186–2190.
[11] M. Ito, D. Furumoto, Microstructure and thermoelectric properties of $Na_xCo_2O_4/Ag$ composite synthesized by the polymerized complex method, Journal of Alloys and Compounds 450 (2008) 517–520.
[12] Y. Lu, K. Sagara, L. Hao, Z.W. Ji, H. Yoshida, Fabrication of non-stoichiometric titanium dioxide by spark plasma sintering and its thermoelectric properties, Materials Transactions 53 (2012) 1208–1211.
[13] T. Hyodo, H. Nishihara, National Astronomical Observatory of Japan, Chronological Scientific Tables, Maruzen Publishing, Tokyo, 2012.
[14] Y. Yamashita, T. Yagi, T. Baba, Development of network database system for thermophysical property data of thin films, Japanese Journal of Applied Physics 50 (2011) 11RH03.
[15] D.G. Han, G.M. Choi, Computer simulation of the electrical conductivity of composites: the effect of geometrical arrangement, Solid State Ionics 106 (1998) 71–87.
[16] D.S. McLachlan, M. Blaszkiewicz, R.E. Newnham, Electrical resistivity of composites, Journal of the American Ceramic Society 73 (1990) 2187–2203.