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Effect of CeO_2 on the thermoelectric properties of WO_3-based ceramics

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Abstract

The thermoelectric properties of tungsten trioxide (WO_3) ceramics doped with cerium dioxide (CeO_2) were investigated. The results demonstrated that the addition of CeO_2 to WO_3 could promote the grain growth and the densification. The magnitude of the electrical conductivity (σ) and the absolute value of the Seebeck coefficient ($|s|$) depended strongly on the CeO_2 content. The sample doped with 2.0 mol% CeO_2 yielded higher σ and $|s|$, resulting in a significant increase in the power factor (σs^2). In addition, the power factor value of all samples increased abruptly at high temperatures, which revealed that WO_3-based ceramics could have greater thermoelectric properties at high temperatures.

Keywords: C. Electrical conductivity; Seebeck coefficient; WO_3 ceramics; Power factor

1. Introduction

Since Seebeck [1] observed the thermoelectric effect for the first time in 1823, PbTe [2,3] and SiGe alloys [4,5] have been extensively studied as materials for high temperature thermoelectric power generation. However, the practical applications of these materials have been limited, because these materials are easily decomposed or oxidized at high temperatures. To overcome the foregoing problems, metal oxides have been exploited as candidates for applications in thermoelectric generation due to their great thermal and chemical stability at high temperatures [6–8].

The oxide thermoelectric materials have been investigated considerably from a discovery of some layered p-type cobalt oxides, which have a comparable figure of merit to the conventional materials [9]. In 1997, Japanese scientists [10] found that the porous Y_2O_3 ceramic exhibited huge Seebeck coefficient values up to −50 mV/K at 900–1000 K in vacuum. Since then, great attention has been focused on the metal oxides, and some oxides such as ZnO, $LaCoO_3$, $NaCo_2O_4$ and $SrTiO_3$ have been widely studied [6–9,11]. Because the physical and chemical properties of WO_3 and SnO_2 ceramics as metal oxide semiconductors are similar to ZnO, the applications of WO_3 in varistors and gas sensors are basically the same as ZnO [12–15]. Therefore, WO_3 ceramics could be utilized as thermoelectric materials. However, few studies on the thermoelectric properties of WO_3 have been reported. In the present study, the thermoelectric properties of WO_3-based ceramics doped with CeO_2 were investigated for the first time.

2. Experimental procedure

In this work, analytical-grade raw materials of WO_3 (purity ≥99.9%) and CeO_2 (≥99.99%) were used in compositions of $(100 - x)$ mol% $WO_3 + x$ mol% CeO_2, where $x = 0.0$, 0.5, 2.0 and 4.0. After milled with agate balls and ethanol for 10 h, the powders were then granulated with binder and pressed at 100 MPa to form discs 10 mm in diameter and 3 mm in thickness. The discs with the same concentration were sintered at 1000 °C in air for 2 h. The heating rate was maintained at 100 °C/h.

The microstructure of samples was examined using scanning electron microscopy (FEI QUANTA200 with an energy dispersive spectrometer). As for the SEM and EDX analysis, samples were cleaned in acetone, mounted, and gold-coated to prevent charging. Average grain sizes of the CeO_2-doped WO_3 ceramics have been estimated by the line-intersecting method, and the porosity of the specimens has been measured by the Archimedes principle. The crystalline phases of these sintered

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samples were identified by X-ray diffraction technologies (7602EA ALMELO) under the following experimental conditions: $\lambda(\mathrm{Cu\ K}\alpha) = 0.15406$ nm, 40 kV, 40 mA, $20 \leq 2\theta \leq 60^{\circ}$. The electrical conductivity from 323 K to 673 K was measured by means of a standard four-probe method using the KEITHLEY 2400. The thermoelectric power from 323 K to 673 K was calculated from the thermoelectric voltage collected with KEITHLEY 2400 and the temperature difference between the two ends of the sample.

3. Results and discussion

Fig. 1 shows the SEM micrographs of the sintered WO_3 ceramics with different amount of CeO_2. It can be seen that the grain size and the densification of the WO_3-based ceramics become greater with the increasing CeO_2 content. The rod-shaped structure can be evidently observed at the grain boundary regions as samples contain more than 0.5 mol% CeO_2. As shown in Fig. 2, the EDX spectra of the rod-shaped structure for WO_3 ceramics doped with 2.0 mol% CeO_2 indicates that the Ce-rich phase exists between WO_3 grains. The grain size and the porosity of the samples are given in Table 1. Previous studies [13–15] suggested that the grain size of WO_3-based ceramics remained almost constant with an average grain size about 10 μm and that the open porosity was about 14%. The grain size and the porosity in this research lie in the range 7.1–11.7 μm and 7.19–18.51%, respectively. Moreover, the grain size of the doped samples is obviously larger than the undoped one. Therefore, the addition of CeO_2 into WO_3 ceramics can improve the mass transfer during sintering process, leading to the grain growth and the increasing densification.

The densification of the SnO_2–CoO, SnO_2–MnO_2 and SnO_2–TiO_2 polycrystalline systems is attributed to the increased concentration of oxygen vacancies in the grain boundary region [16,17]. The densifying mechanism of the WO_3–CeO_2 ceramics may be similar to the one that occurs in the SnO_2-based ceramics, and the formation of oxygen vacancies could obey the following reactions:

$$\mathrm{CeO_2} \xrightarrow{\mathrm{WO_3}} \mathrm{Ce''_W} + \mathrm{V^{\bullet\bullet}_O} + 2O^{\mathrm{X}}_{\mathrm{O}} \quad (1)$$

Doping WO_3 with CeO_2 leads to the creation of additional oxygen vacancies that increase the flux of oxygen ions and promote WO_3 grain growth and densification. However, there is a Ce-rich phase existing between WO_3 grains in samples containing 2.0 and 4.0 mol% CeO_2, so the added CeO_2 does not fully dissolve in the WO_3 crystal lattice. As the content of CeO_2 in WO_3 is below its solubility limit in WO_3, the reaction that CeO_2 dissolves in WO_3 occurs. If the amount of CeO_2 exceeds the solubility in WO_3, the extra CeO_2 reacts with WO_3 to form $Ce_2O_3{\cdot}3WO_3$ [18], that is, $Ce_2W_3O_{12}$. The addition of CeO_2 can promote the grain growth and the densification of the WO_3-based ceramics, while the second phase $Ce_2W_3O_{12}$ lower the grain boundary mobility during sintering process and enable the pores to stay attached to the moving grain boundaries. Therefore, in spite of the slightly bigger grain size, the densification of the sample doped with 4.0 mol% CeO_2 is worse than that of the one with 2.0 mol% CeO_2.

The XRD patterns given in Fig. 3 reveal that there is an obvious second phase in the doped samples when the content of CeO_2 exceeds 0.5 mol%. The result is sharply different from the previous study [12]. Only monoclinic phase WO_3 (γ-WO_3) can be distinctly observed in the sample containing 0.5 mol% CeO_2, which is distinct from the co-existence of monoclinic and triclinic phases in undoped WO_3 ceramics [13], implying that the form of the triclinic phase WO_3 is effectively depressed by doping slightly CeO_2. Moreover, the rod-shaped intergranular phase present in specimens doped with 2.0 and

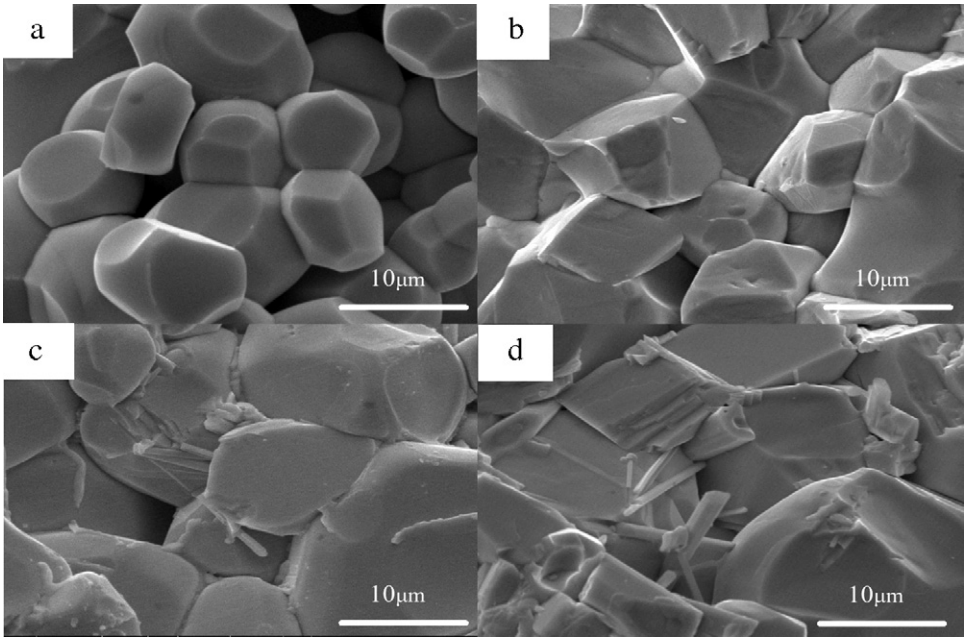

Fig. 1. SEM images of the samples $(100 - x)$ mol% $WO_3 + x$ mol% CeO_2: (a) $x = 0.0$; (b) $x = 0.5$; (c) $x = 2.0$; and (d) $x = 4.0$.

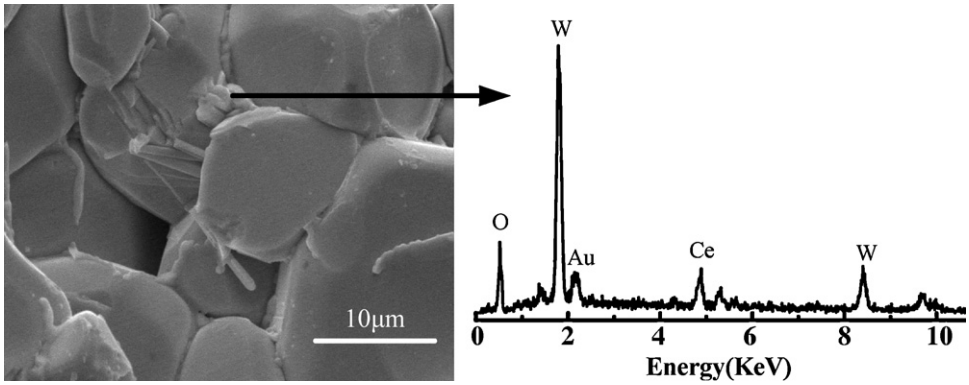

Fig. 2. EDX spectra of grain boundary regions for WO_3 ceramics doped with 2.0 mol% CeO_2 content.

4.0 mol% CeO_2 is identified as $Ce_2W_3O_{12}$ (JCPDS file card number 31-0340) through the XRD analysis.

The temperature dependence of the electrical conductivity (σ) for samples is shown in Fig. 4(a). It can be observed that the curves of $\log_{10}\sigma$ against $1000/T$ exhibit approximately a linear characteristic overall, showing a semiconducting behavior which obeys the Arrhenius low:

$$\sigma(T) = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

where σ is the electrical conductivity, σ_0 is a constant, k is the Boltzmann constant, and T is the absolute temperature. The activation energy of the samples has been evaluated and can be seen in Table 2. It can be noted that there are two activation energies one for low and the other for higher temperatures. This has been reported in Refs. [19,20], and the variation of the activation energy is due to the WO_3 phase transition at temperatures between 300 and 375 °C where $1000/T$ is between 1.5 and 1.7 K^{-1}. The result also demonstrates that the electrical conductivity of the doped WO_3 samples is lower than the pure one. The grain size and the porosity of the sample have notable effects on its thermoelectric properties. As the grain size is below 2 μm, the Seebeck coefficient sharply increases with the grain size decreasing, while the grain size is above 2 μm, the size effect of grain is not significant [21]. The grain size of all samples in this study is about 10 μm, and thus the grain size effect on the thermoelectric properties is not apparent. The additional scattering of phonons and electrons can happen at the pore sites or at the grain boundaries, so the porosity can degrade the electrical conductivity and the Seebeck coefficient [22]. The porosity of the doped samples is smaller than that of the undoped one, but the electrical conductivity of the doped ones is lower. This could be ascribed to the reduction of the electron concentration by adding Ce^{4+} for W^{6+}, which can be explained by the same mechanism as adding TiO_2 into WO_3 [23] and doping ZnO with Sb_2O_3 [24] and can have significant effects on the electrical conductivity. In the doped samples, the density and the grain size are greater with more CeO_2, so the time between electron scattering events of charge carriers increases, and thus the electrical conductivity of the doped ones rises with the increasing content of CeO_2.

Fig. 4(b) shows the Seebeck coefficients for all samples at different temperatures. The Seebeck coefficient values are all negative over the whole temperature range, indicating an n-type conduction. It is apparent that the absolute value of the Seebeck coefficient for the sample containing 2.0 mol% CeO_2 is larger than that of others. In general, the Seebeck coefficient decreases with increasing electrical conductivity [8,24]. Nevertheless, it can be seen in Fig. 4(b) that the absolute value of the Seebeck coefficient follows this rule except the specimen containing

Table 1
Grain size and porosity of the samples with different CeO_2 contents.

CeO_2 (mol%)	Grain size (μm)	Porosity (%)
0.0	7.1	18.51
0.5	9.4	10.47
2.0	11.5	7.19
4.0	11.7	7.95

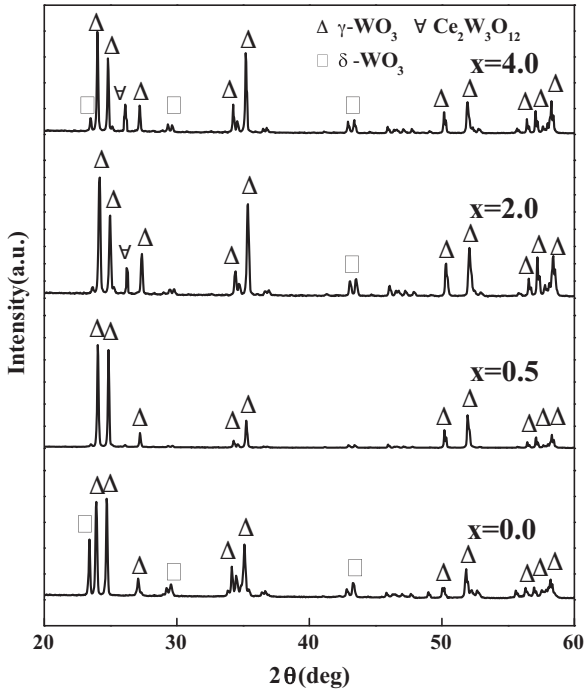

Fig. 3. XRD patterns of the $(100 - x)$ mol% $WO_3 + x$ mol% CeO_2 samples.

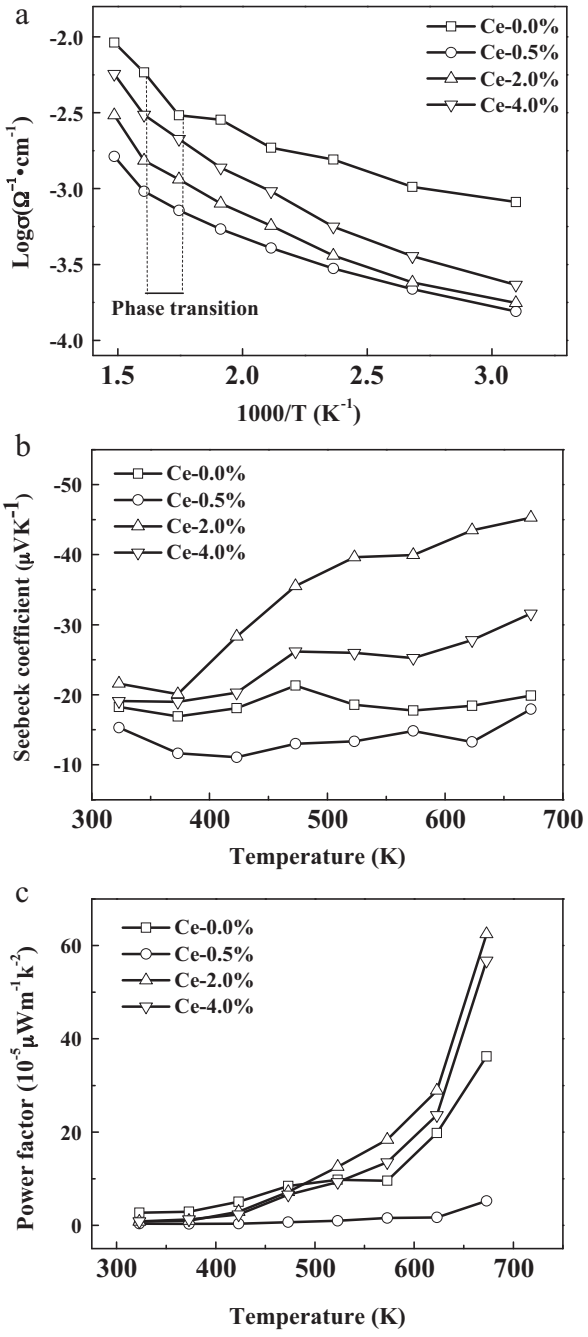

Fig. 4. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor of the samples with different amount of CeO_2.

0.5 mol% CeO_2. Moreover, when the temperature is under 573 K, the Seebeck coefficient is almost constant for the undoped sample and the one with 0.5 mol% addition of CeO_2. As the temperature is above 600 K, the Seebeck coefficient of them gradually goes up with the increasing temperature. According to the foregoing discussion, the grain size and the porosity of the sample have remarkable effects on its thermoelectric properties. The pure WO_3 ceramics is not densification and the porosity is tremendous, so the additional scattering of phonons and electrons occurs at the pore sites or at the grain boundaries, which degrades the Seebeck coefficient and makes it almost constant. For the sample with an addition of 0.5 mol% CeO_2, its Seebeck coefficient could be influenced by the following two factors. One is that the Ce ions dissolving in WO_3 block the migration of the carriers and thus slow down the mobility of the carriers even at high temperatures. The other is that the porosity of it is still large and the additional scattering of phonons and electrons occurs. Since the porosity of the specimens with 2.0 and 4.0 mol% CeO_2 is smaller, the Seebeck coefficient of them is better than that of others.

Table 2
Activation energy of the samples with different amount of CeO_2 before and after the phase transition.

CeO_2 (mol%)	E_a (eV) (before phase transition)	E_a (eV) (after phase transition)
0.0	0.063 ± 0.003	0.330 ± 0.005
0.5	0.108 ± 0.003	0.386 ± 0.005
2.0	0.158 ± 0.003	0.502 ± 0.005
4.0	0.187 ± 0.003	0.451 ± 0.005

The thermoelectric power factor (σs^2) of all specimens, calculated from the data in Fig. 4(a) and (b), as a function of temperature is illustrated in Fig. 4(c). The power factor of WO_3-based ceramics is improved by CeO_2 addition and increases with the temperature rising. The sample containing 2.0 mol% CeO_2 obtains the largest power factor with a value of 6.25×10^{-4} μW m^{-1} K^{-2} at 673 K. Although the Seebeck coefficient and the power factor of WO_3 are lower than that of ZnO [24], it is still attractive to research the thermoelectric properties of WO_3, because it could be improved in some ways. Previous study [15] revealed that the quenched WO_3 ceramics exhibited a very low resistivity with a value of 1.95 Ω cm at room temperature, that is to say, a very high conductivity. Moreover, it can be seen that the power factor of samples increases abruptly at the temperature above 600 K, implying a great performance at high temperatures.

4. Conclusions

The thermoelectric properties of WO_3-based ceramics have been investigated. The results demonstrate that doping CeO_2 can promote the grain growth and inhibit the porosity. The grain size and the porosity of samples have prominent effects on the thermoelectric characteristic. The Seebeck coefficient of the pure WO_3 ceramics is smaller than that of the ZnO-based ceramics, so it is important to densify the WO_3-based samples to obtain a better thermoelectric performance. The thermoelectric properties of WO_3-based ceramics at moderate temperatures are investigated for the first time, and thus the thermal diffusivity coefficients of samples have not measured in this work. However, the power factor of samples increases abruptly at the temperature above 600 K, indicating a better performance at high temperatures. The present results suggest that WO_3-based ceramics could be a candidate for high temperature thermoelectric power generation.

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