Effect of sintering temperature on thermoelectric properties of CdO ceramics

Xinran ZHANG, Huiling LI, Jianglong WANG*

Hebei Key Lab of Optic-electronic Information and Materials, College of Physics Science and Technology, Hebei University, Baoding 071002, China

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Abstract: The effect of sintering temperature on thermoelectric properties of CdO ceramics was investigated by solid-state reaction method within the temperature range of 700–1000 °C. With the increase of sintering temperature, both the grain size and the carrier concentration of these samples increased, while the Seebeck coefficient decreased. The highest dimensionless figure of merit ZT , 0.34, was obtained at 1023 K for the sample sintered at 800 °C, suggesting the potential application of CdO ceramics in thermoelectric (TE) devices.

Keywords: thermoelectric (TE); CdO ceramics; sintering temperature; solid-state reaction

1 Introduction

Thermoelectric (TE) materials can directly convert heat into electricity through Seebeck effect and electricity into heat through Peltier effect, and therefore they have promising applications in power generation and cooling. The performance of a TE material is characterized by the dimensionless figure of merit, $ZT = (S^2 \sigma / \kappa) T$, where S , σ , κ , and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. The conventional thermoelectric materials are mainly intermetallic compounds and alloys. However, due to surface oxidation and sublimation at high temperature and toxic or scarce elements contained, the practical application of these materials is limited. Oxides can overcome these problems and therefore have attracted increasing attentions to the TE community, particularly to those

who are interested in high temperature applications in air [1–15]. Transparent conductive oxides (TCOs), mainly including ZnO-, In_2O_3 -, SnO_2 -, and TiO_2 -based oxides, have been extensively studied as a promising class of n-type TE materials for high temperature applications because of their low electrical resistivity and good stability at high temperature in air [9–15]. So far, the best ZT for above TCOs-based TE materials has been achieved in Al and Ga dually doped ZnO ceramics [10].

Cadmium oxide (CdO) is an n-type TCO with high carrier mobility. It has a simple cubic rock-salt crystal structure with direct band gap of 2.28 eV and indirect band gap of 0.84 eV [16]. Nonstoichiometric CdO usually exhibits low electrical resistivity due to native defects of oxygen vacancies and Cd interstitials [17]. Compared with ZnO, CdO has heavier constituting elements and lower Debye temperature ($\theta_D \approx 255$ K), and hence a relative lower phonon thermal conductivity [18]. These features suggest CdO might be a potential novel n-type oxide TE material despite its drawbacks of

* Corresponding author.
E-mail: jlwang@hbu.edu.cn

toxicity and volatility at high temperature. Very recently, a good TE performance has been demonstrated in CdO, and the effect of rare-earth elements doping on the TE properties of CdO ceramics has been investigated by our research group [19–21]. It is known that the carrier concentration and microstructure can greatly influence the carrier and phonon transport properties in TE materials, which are directly related with these three TE parameters, S , σ , and κ . Therefore, one common approach to improve the performance of a TE material is tuning its carrier concentration and microstructure. In this paper, the carrier concentration and microstructure of CdO ceramics were tuned via changing the sintering temperature of the samples, and the influence of sintering temperature on the thermoelectric properties of CdO ceramics was investigated. It was found that both the electrical resistivity and the Seebeck coefficient decrease while the thermal conductivity increases with increasing sintering temperature. We obtained a high ZT of 0.34 at 1023 K for the sample sintered at 800 °C. This value is comparable to that reported for the best n-type oxide ceramic thermoelectric materials.

2 Experimental

Polycrystalline CdO ceramic samples were prepared by the traditional solid-state reaction sintering method with the commercial high purity CdO powders (99.95%, Alfa Aesar) as the starting materials. After fully grinding, the powders of CdO were first presintered at 600 °C for about 3 h to decarbonate and then were compacted in pellets at 10 MPa. Finally, these pellets were sintered in air at temperatures of 700, 800, 900, and 1000 °C for about 20 h.

The crystal structure of the sintered CdO ceramics was examined by X-ray diffraction (XRD) with a Bruker D8 Advance X-ray powder diffractometer. The microstructure was measured using a Philips XL-30S scanning electron microscope (SEM). The room temperature carrier concentration n and mobility μ were determined by using the van der Pauw method with a Hall measurement system (ET-900, China). The electrical resistivity ρ and the Seebeck coefficient S were simultaneously measured by the standard DC four-probe technique with an LSR-3 measurement system (Linseis, Germany) from 300 to 1023 K under the low pressure helium atmosphere. The thermal

conductivity κ was calculated from the specific heat capacity C_p , thermal diffusivity D , and density d according to the equation $\kappa = DC_p d$, where D was measured using the laser flash technique with LFA1000 system (Linseis, Germany); C_p was measured by a differential scanning calorimeter (Netzsch DSC200F3); and d was determined by the Archimedes method. The density of CdO ceramics was found to increase with the sintering temperature and was about 7.81, 8.09, 8.16, and 8.22 g/cm³ for samples sintered at 700, 800, 900, and 1000 °C, respectively.

3 Results and discussion

Figure 1 presents the XRD θ - 2θ scans of these four samples sintered at different temperatures. All peaks in the XRD pattern of each sample can be indexed to CdO with space group $Fm\bar{3}m$ (PDF #780653). With increasing the sintering temperature, the width of XRD peaks becomes slightly narrower and the intensity of the peaks becomes stronger (as seen in the inset of Fig. 1), indicating that both the crystalline quality and grain size of the samples are increased at higher sintering temperatures. Figure 2 shows the SEM images from the fractured cross-sections of these four samples. It can be clearly seen that the average grain size of the samples becomes larger as the sintering temperature increases, which is about 1, 5, 10, and 15 μm for samples sintered at 700, 800, 900, and 1000 °C, respectively.

Fig. 1 XRD θ - 2θ patterns of CdO ceramics sintered at different temperatures of (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C. The inset is the magnified curves of CdO (200) peak for samples sintered at 700 °C and 1000 °C.

Fig. 2 SEM images of CdO ceramics sintered at different temperatures of (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C.

Figure 3 presents the room temperature carrier concentration n and mobility μ of these CdO ceramic samples sintered at different temperatures. With the increase of sintering temperature, n increases while μ decreases. The increase in the carrier concentration n with the sintering temperature is suggested to be caused by the increase of oxygen vacancies or cadmium interstitials. At higher sintering temperatures, more defects are thermally generated, resulting in more oxygen vacancies or cadmium interstitials. The variation of mobility μ with the sintering temperature can be explained by considering the following competing factors: (1) as the sintering temperature increases, both the bulk density and the grain size of the samples increase, increasing the time between electron scattering events of charge carriers at grain boundaries and thus increasing the mobility μ [22,23]; (2) the increase of sintering temperature leads to an increase in carrier concentration n , resulting in a decrease in

Fig. 3 Room temperature carrier concentration n and Hall mobility μ of CdO ceramics sintered at different temperatures.

mobility μ due to the enhanced scattering of carriers by more ionized impurities. From the above competing factors, it is suggested that the reduction in the mobility μ with the sintering temperature is mainly due to the ionized impurity scattering for these CdO ceramic samples [24].

Figure 4(a) displays the temperature dependence of electrical resistivity ρ for these four CdO ceramic samples. The room temperature electrical resistivity exhibits a rapid decrease when the sintering temperature increases from 700 to 900 °C, and further increasing the sintering temperature only results in a slight decrease in ρ . The decrease of ρ with the sintering temperature is mainly due to the increase of carrier concentration n since the mobility μ decreases at higher sintering temperatures. Moreover, Fig. 4(a) shows that the electrical resistivity of the samples sintered at 700 °C and 800 °C first increases with the temperature, reaches the maximum value at a certain temperature T^* , and then decreases. It should be mentioned here that T^* will be shifted to higher temperatures as the carrier concentration n is increased, and the T^* value for samples sintered at 900 °C and 1000 °C is out of our temperature measurement range. The above ρ – T behavior has been observed in many other semiconductors and can be explained in the following manner. In extrinsic temperature regime of a semiconductor ($T < T^*$), the number of thermally excited charge carriers is very small and the resistivity is primarily determined by the extrinsic carriers. As the temperature increases, the thermally excited intrinsic carriers across the energy gap of the semiconductor can not be ignored and thus begin to contribute to the resistivity, so the resistivity will decrease when the temperature is higher than T^* [25].

The temperature variation of the Seebeck coefficient S for these four CdO ceramic samples is shown in Fig. 4(b). The negative S values indicate the n-type conduction in these samples. The absolute value of the Seebeck coefficient, $|S|$, for all samples increases with the temperature T when T is lower than T^* , which is consistent with the characteristic behavior of an n-type degenerate semiconductor. The reduction of $|S|$ under the condition of $T > T^*$ is caused by the contribution of thermally excited charge carriers as we described above. In addition, Fig. 4(b) shows $|S|$ decreases with the increase of sintering temperature. The variation of $|S|$ of CdO ceramics with sintering temperature can be simply explained as follows. In the single parabolic band model,

Fig. 4 Temperature dependence of (a) electrical resistivity ρ , (b) Seebeck coefficient S , and (c) power factor S^2/ρ for CdO ceramics sintered at different temperatures.

the absolute value $|S|$ of an n-type degenerate semiconductor can be expressed by [26]

$$|S| = \frac{8\pi^2 k_B^2}{3eh^2} \left(\frac{\pi}{3n} \right)^{2/3} m^* T \quad (1)$$

where k_B , h , and m^* are the Boltzmann constant, Planck constant, and carrier effective mass, respectively. With the increase of sintering temperature, the carrier concentration n will increase and thus the $|S|$ will decrease according to Eq. (1). Based on the measured carrier concentration and the Seebeck coefficient at room temperature, the effective mass can be estimated from Eq. (1), which is 0.126, 0.185, 0.190, and 0.173 (in unit of free electron mass m_0) for samples sintered at 700 °C, 800 °C, 900 °C, and 1000 °C, respectively. It

can be seen that the effective mass of CdO samples sintered at 700 °C, 800 °C, and 900 °C increases with increasing carrier concentration, which is in agreement with the report from optical measurement [27]. The inconsistency for the 1000 °C sample might be due to the missed factors involving the non-parabolic band effect and the detailed scattering mechanism in Eq. (1). Figure 4(c) is the temperature dependence of the power factor S^2/ρ for these four CdO ceramic samples, and the power factor S^2/ρ of each sample is calculated with the corresponding ρ - T and S - T data shown in Fig. 4. The power factor of all samples increases with the increase of temperature. The sample sintered at 800 °C has the highest power factor of $1.1 \times 10^{-3} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 1023 K, which is comparable to that reported for other TCOs-based TE materials such as ZnO and In_2O_3 [13–15].

Figure 5(a) presents the thermal conductivity κ as a function of temperature for these four CdO samples. With the increase of sintering temperature, the thermal conductivity of the samples κ increases. To well understand this dependence of thermal conductivity on sintering temperature, we estimated the carrier thermal conductivity κ_e and the phonon thermal conductivity κ_{ph} of these four samples, which are displayed in Figs. 5(b) and 5(c), respectively. κ_e was estimated by the Wiedemann–Franz law $\kappa_e = LT\sigma$, and κ_{ph} was calculated from the equation $\kappa_{ph} = \kappa - \kappa_e$.

Here, the Lorentz number L of these four CdO samples at different temperatures is obtained by the calculations according to Ref. [28]. It can be seen that the carrier thermal conductivity κ_e of the samples increases with the sintering temperature because of the improvement of electrical conductivity at higher sintered temperatures. At the same time, the phonon thermal conductivity κ_{ph} of the samples is also found to increase with increasing the sintering temperature. As the sintering temperature increases, the grain size of the samples will become larger and thus the density of grain boundaries will decrease. Moreover, the increase of sintering temperature also results in a reduction in the porosity of the samples. In both cases, the phonon scattering will be suppressed, leading to an increase in κ_{ph} .

We calculated the ZT values of these samples, which are shown in Fig. 6. The sample sintered at 800 °C exhibits the best TE performance in the whole temperature range and its ZT reaches 0.34 at 1023 K.

Fig. 5 Temperature dependence of (a) thermal conductivity κ , (b) carrier thermal conductivity κ_e , and (c) phonon thermal conductivity κ_{ph} for CdO ceramics sintered at different temperatures.

Fig. 6 Temperature dependence of ZT for CdO ceramics sintered at different temperatures.

This value is comparable to that reported for the best n-type oxide ceramic TE materials [7,11,15,16], suggesting the potential applications of CdO in TE devices. Further improvement in ZT is possible by nano-engineering approach.

4 Conclusions

CdO ceramics were synthesized by the solid-state reaction sintering method, and the effect of sintering temperature on their thermoelectric properties was investigated. With the increase of sintering temperature, both the electrical resistivity and Seebeck coefficient of these samples decreased while the thermal conductivity increased. Detailed mechanisms were proposed to explain the experimental results. The sample sintered at 800 °C exhibited the best TE performance in the whole temperature range, and its ZT reached 0.34 at 1023 K. Our works demonstrated that the sintered CdO ceramics have potential application in oxide TE devices and their TE performance can be tuned by sintering temperature.

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References

- [1] Koumoto K, Wang Y, Zhang R, *et al.* Oxide thermoelectric materials: A nanostructuring approach. *Annu Rev Mater Res* 2010, **40**: 363–394.
- [2] Fergus JW. Oxide materials for high temperature thermoelectric energy conversion. *J Eur Ceram Soc* 2012, **32**: 525–540.
- [3] Terasaki I, Sasago Y, Uchinokura K. Large thermoelectric power in NaCo_2O_4 single crystals. *Phys Rev B* 1997, **56**: R12658.
- [4] Yin LH, Ang R, Huang ZH, *et al.* Exotic reinforcement of thermoelectric power driven by Ca doping in layered $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{Co}_2\text{O}_y$. *Appl Phys Lett* 2013, **102**: 141907.

- [5] Ohta H, Kim S, Mune Y, *et al.* Giant thermoelectric Seebeck coefficient of a two-dimensional electron gas in SrTiO₃. *Nat Mater* 2007, **6**: 129–134.
- [6] Wang HC, Wang CL, Su WB, *et al.* Doping effect of La and Dy on thermoelectric properties of SrTiO₃. *J Am Ceram Soc* 2011, **94**: 838–842.
- [7] Lee S, Bock JA, Trolier-McKinstry S, *et al.* Ferroelectric-thermoelectricity and Mott transition of ferroelectric oxides with high electronic conductivity. *J Eur Ceram Soc* 2012, **32**: 3971–3988.
- [8] Liu Y, Zhao L-D, Liu Y, *et al.* Remarkable enhancement in thermoelectric performance of BiCuSeO by Cu deficiencies. *J Am Chem Soc* 2012, **134**: 3312.
- [9] Kitagawa H, Kunisada T, Yamada Y, *et al.* Effect of boron-doping on thermoelectric properties of rutile-type titanium dioxide sintered materials. *J Alloys Compd* 2010, **508**: 582–586.
- [10] Ohtaki M, Araki K, Yamamoto K. High thermoelectric performance of dually doped ZnO ceramics. *J Electron Mater* 2009, **38**: 1234–1238.
- [11] Teranishi T, Mori Y, Hayashi H, *et al.* Thermoelectric property of polycrystalline aluminum-doped zinc oxide enhanced by micropore foaming. *J Am Ceram Soc* 2012, **95**: 690–695.
- [12] Jood P, Mehta RJ, Zhang Y, *et al.* Al-doped zinc oxide nanocomposites with enhanced thermoelectric properties. *Nano Lett* 2011, **11**: 4337–4342.
- [13] Park K, Seong JK, Kim GH. NiO added Zn_{1-x}Ni_xO ($0 \leq x \leq 0.05$) for thermoelectric power generation. *J Alloys Compd* 2009, **473**: 423–427.
- [14] Bérardan D, Guilmeau E, Maignan A, *et al.* In₂O₃:Ge, a promising n-type thermoelectric oxide composite. *Solid State Commun* 2008, **146**: 97–101.
- [15] Liu Y, Lin Y-H, Lan J, *et al.* Effect of transition-metal cobalt doping on the thermoelectric performance of In₂O₃ ceramics. *J Am Ceram Soc* 2010, **93**: 2938–2941.
- [16] Koffyberg FP. Thermoreflectance spectra of CdO: Band gaps and band-population effects. *Phys Rev B* 1976, **13**: 4470.
- [17] Koffyberg FP. Electron concentration and mobility in semimetallic CdO. *Can J Phys* 1971, **49**: 435–440.
- [18] Madelung O, Rössler U, Schulz M. *II–VI and I–VII Compounds; Semimagnetic Compounds*. Berlin Heidelberg: Springer-Verlag, 1999, **41B**: 1–5.
- [19] Wang S, Liu F, Lü Q, *et al.* The effect of Er³⁺ doping on the structure and thermoelectric properties of CdO ceramics. *J Eur Ceram Soc* 2013, **33**: 1763–1768.
- [20] Wang S, Lü Q, Li L, *et al.* High-temperature thermoelectric properties of Cd_{1-x}Pr_xO ceramics. *Scripta Mater* 2013, **69**: 533–536.
- [21] Lü Q, Wang SF, Li LJ, *et al.* Electrical and thermal transport properties of CdO ceramics. *Science China Physics, Mechanics & Astronomy* 2014, **57**: 1644–1647.
- [22] Park K, Ko KY, Kim J-G, *et al.* Microstructure and high-temperature thermoelectric properties of CuO and NiO co-substituted NaCo₂O₄. *Mat Sci Eng B* 2006, **129**: 200–206.
- [23] Park K, Kim KK, Seong JK, *et al.* Improved thermoelectric properties by adding Al for Zn in (ZnO)_mIn₂O₃. *Mater Lett* 2007, **61**: 4759–4762.
- [24] Yan M, Lane M, Kannewurf CR, *et al.* Highly conductive epitaxial CdO thin films prepared by pulsed laser deposition. *Appl Phys Lett* 2001, **78**: 2342.
- [25] Kuznetsova LA, Kuznetsov VL, Rowe DM. Thermoelectric properties and crystal structure of ternary compounds in the Ge(Sn,Pb)Te–Bi₂Te₃ systems. *J Phys Chem Solids* 2000, **61**: 1269–1274.
- [26] Jung K-H, Lee KH, Seo W-S, *et al.* An enhancement of a thermoelectric power factor in a Ga-doped ZnO system: A chemical compression by enlarged Ga solubility. *Appl Phys Lett* 2012, **100**: 253902.
- [27] Mendelsberg RJ, Zhu Y, Anders A. Determining the nonparabolicity factor of the CdO conduction band using indium doping and the Drude theory. *J Phys D: Appl Phys* 2012, **45**: 425302.
- [28] Zhao L-D, Lo S-H, He J, *et al.* High performance thermoelectrics from earth-abundant materials: Enhanced figure of merit in PbS by second phase nanostructures. *J Am Chem Soc* 2011, **133**: 20476–20487.