ELSEVIER

Ceramics International 31 (2005) 129–133

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Preparation and thermoelectric properties of $Cd_{3-x}A_xTeO_6$ (A = In, La, and Bi) ceramics

Weiling Luan[a], Yue Jin Shan[b,*], Mitsuru Itoh[c], Hideo Imoto[b]

[a]*Department of Mechanical Engineering, East China University of Science and Technology, Shanghai 200237, PR China*
[b]*Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya 321-8585, Japan*
[c]*Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan*

Received 15 September 2003; received in revised form 4 March 2004; accepted 17 March 2004

Abstract

Due to its close-shelled electron configuration, perovskite structured oxide Cd_3TeO_6 was originally regarded as an electric insulator. When Cd_3TeO_6 was electron-doped by the substitution of trivalent cations (In^{3+}, La^{3+} and Bi^{3+}) and the introduction of oxygen vacancies, all samples showed bright changes on thermoelectric properties. A substantial negative temperature dependence of resistivity was observed in non-substituted Cd_3TeO_6, while substituted samples showed a slight dependence on temperature. Obviously resistivity degradation was found on air-sintered samples after nitrogen treatment. The negative Seebeck coefficient and Hall coefficient obtained indicated that electrons were the charge carriers. Among the three types of substituted cations, indium exerted the largest effect on the decrease of resistivity down to 1.3 mΩ cm at room temperature. The best thermoelectric power factor of 1.35×10^{-4} W m^{-1} K^{-2} was obtained for $Cd_{2.97}In_{0.03}TeO_6$ at 300 K.

Keywords: Thermoelectric properties; Cadmium tellurate; Perovskite oxide

1. Introduction

Cd_3TeO_6 is a 1:1 ordered perovskite oxide that has two types of octahedron—[CdO_6] and [TeO_6] alternatively appeared at B sites. The crystal structure of Cd_3TeO_6 is monoclinic with space group of $P2_1/n$, no phase transition of Cd_3TeO_6 above room temperature was found up to 1320 K. An important character of Cd_3TeO_6 is that Cd^{2+} and Te^{6+} have the same close-shelled electron configurations as $4d^{10}$. Pure Cd_3TeO_6 is thus regarded as an insulator, and its dielectric properties were reported 20 years ago. However, not much work has been concentrated on this material during the recent 10 years. In our laboratory, we accidentally found that the electrical resistivity of Cd_3TeO_6 could be changed by a few orders of magnitude through varying the temperature. Furthermore, a high negative Seebeck coefficient of nearly −200 μV/K was shown in this material. These observations suggested that by increasing the electron concentration, Cd_3TeO_6 would become a promising n-type thermoelectric material.

A thermoelectric material possesses the ability of converting heat into electricity or electricity into heat. In a certain temperature gradient, the thermoelectric power factor, which is given by S^2/ρ is a key factor of the thermoelectric property. Here S is the Seebeck coefficient, and ρ is the electric resistivity. Therefore, a good thermoelectric material should possess large S and low ρ. However, a high value of thermoelectric power factor is difficult to realize because S and ρ cannot be changed independently for both of them are factors of carrier concentration.

Till now a number of works [1–6] have been done on thermoelectric materials. Now this task is focused on the seeking of good n-type thermoelectric candidates. Because a pair of n- and p-type thermoelectric materials is required for the structure of a loop. Nevertheless, only p-type materials (e.g. $NaCo_2O_4$ [7] with power factor of 5×10^{-4} W m^{-1} K^{-2} at room temperature) have been fabricated with fine

---

* Corresponding author. Tel.: +81 28 689 6174; fax: +81 28 689 6009.
E-mail address: shan@cc.utsunomiya-u.ac.jp (Y.J. Shan).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2004.03.045

properties by now, while a comparable n-type oxide material is still on seeking. Up to now, researches have found some new kind of thermoelectric materials that show high performances [8–10], but the searching of n-type materials is still in urgent need for application. Cd_3TeO_6 has therefore aroused our interests on optimizing its thermoelectric properties by way of electron state modification.

In this paper, the thermoelectric property was studied on electron-doped Cd_3TeO_6. Normally, it is difficult to modify the electron state of such a material that owns full orbital structure for some impurities are easily to appear caused by the unbalance of electrovalence. However, if only one electron can be successfully introduced into Cd_3TeO_6 and a pure solid solution is formed, its band gap can be greatly changed and the electrical behavior will be largely modified. In this paper, three kinds of trivalent cations—In^{3+}, La^{3+} and Bi^{3+} were introduced into Cd_3TeO_6 in order to decrease its electric resistivity. Then to extensively increase electron concentration, parts of air-sintered samples were annealed in nitrogen atmosphere and the effect was compared with non-annealed samples. Thermoelectric properties were investigated on these modified samples and comparisons of thermoelectric power factors were made with literature data.

2. Experimental procedure

$Cd_{3-x}A_xTeO_6$ (A = In, La, and Bi, x = 0.01, 0.02, 0.03 or 0.04) powders were synthesized by conventional solid-state reactions. Reagent grade CdO, TeO_2, In_2O_3, La_2O_3, and Bi_2O_3 were used as starting materials. After weighing and liquid mixing, the mixture was calcined at 973–1073 K for 11 h in air. XRD patterns (Rint2100, Rigaku Co., Japan) from 20 to 80° were measured to confirm the purity of the calcined powders. Then the powders were made into pellets under 390 MPa isostatic pressure with water as liquid medium, and then sintered at 1353 K for 4 h in air. Parts of the air-sintered samples were annealed at 1073 K for 12 h in N_2 for comparison. Phase structure of sintered sample was checked by XRD and chemical constitution was determined by ICP (ICPS-7500, Shimadzu Co., Japan) using 1% HCl liquid medium. Electrical resistivities were measured by a dc four-probe technique using Pt line as a current lead. For Seebeck coefficients measurement, the temperature difference between both ends was given by a strain gage and measured by thermocouple. Strain gage was originally used as transducer production and experimental stress analysis. Here we used it as a small heat source by adding input current on its legs. Measurements of the concentration and mobility of charge carriers was performed by using the Hall effect and the standard Van der Pauw methods at room temperature in a magnetic field from 5 to 9 T. As a comparison, non-substituted Cd_3TeO_6 was also prepared. Besides, all measured samples here were compact pellets with relative density of more than 90%.

3. Results and discussion

The XRD results of samples substituted with In^{3+}, La^{3+}, Bi^{3+} showed same perovskite structure as pure Cd_3TeO_6. There was no change of the X-ray diffraction pattern for these samples in the temperature range of 295 to 1300 K, identifying thermal stability of the compound.

The chemical constitution of sintered samples was analyzed by Inductively Coupled Plasma (ICP), the mole amount of Te being taken as unit. Table 1 shows that the final sintered samples maintained nearly the same mole ratio as the starting composition.

The resistivities of air-sintered and N_2-annealed $Cd_{3-x}A_xTeO_6$ (A = In, La, and Bi) as a function of temperature are shown in Fig. 1(a) and (b), separately. Obviously the resistivity of the non-substituted semiconductive Cd_3TeO_6 sample sintered in air showed negative temperature dependence. After annealed in nitrogen, a positive temperature dependence of resistivity above 150 K was observed, which suggested a metallic-like property be generated (see Fig. 1(b)). On the contrary, all substituted samples of both air-sintered and nitrogen annealed showed very small temperature dependence of the resistivity. Moreover, after treated in nitrogen,

Table 1
The results of ICP analysis for $Cd_{3-x}A_xTeO_6$ (A = In, La, and Bi), here the mole amount of Te is taken as the unit

Substitution amount (x)	Element	Starting composition	Analysis composition		
			$Cd_{3-x}In_xTeO_6$	$Cd_{3-x}La_xTeO_6$	$Cd_{3-x}Bi_xTeO_6$
0	Cd	3.00	3.00(8)		
0.01	Cd	2.99	2.99(0)	2.98(6)	2.98(8)
	A	0.01	0.01(0)	0.00(8)	0.01(0)
0.02	Cd	2.98	2.98(6)	2.97(3)	2.97(7)
	A	0.02	0.01(9)	0.01(7)	0.01(8)
0.03	Cd	2.97	2.97(6)	2.96(5)	2.96(2)
	A	0.03	0.02(9)	0.02(4)	0.02(4)
0.04	Cd	2.96	2.95(6)	–	–
	A	0.04	0.03(9)	–	–

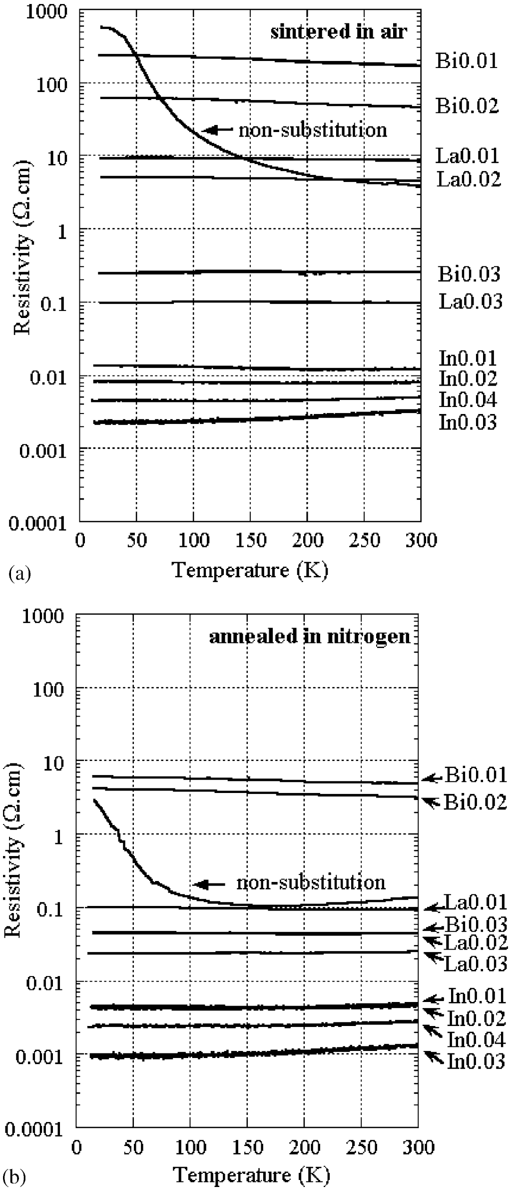

Fig. 1. Temperature dependence of the electrical resistivity of $Cd_{3-x}A_xTeO_6$ (A = In, La, and Bi).

all samples showed much smaller resistivity compared with their corresponding air-sintered ones.

With the aim of avoiding the generation of oxygen vacancies during the sintering process, samples were sintered under oxygen flow. However, high densified samples could not be obtained, the densities of all oxygen-sintered pellets being <70%. Because of some oxygen vacancies introduced in the air-sintered pellets, non-substituted samples changed from insulator of pure close-shelled Cd_3TeO_6 into semiconductor, accompanied with some degrees of degradation on resistivity. The treatment in nitrogen atmosphere enhanced the concentration of oxygen vacancy, that is increased the electron concentrations and then resulted in a decrease of resistivity.

Among the three elements introduced into the Cd_3TeO_6, indium gave the best effect on the degradation of resistivity. Comparing with the non-substituted sample, sharp decrease of more than three orders of magnitude at room temperature was found in $Cd_{3-x}In_xTeO_6$ ($0.01 \leq x \leq 0.04$), and $Cd_{2.97}In_{0.03}TeO_6$ gave the lowest value as 1.3 mΩ cm at room temperature.

It is interesting that a low amount of bismuth substitution ($x = 0.01$ and 0.02) gave the increase of resistivity instead of decrease, compared with other non-substituted samples. When the bismuth-substitution amount was increased to $x = 0.03$, a sharp decrease of resistivity was observed. Similar phenomena were found in the lanthanum-substituted samples. By X-ray refinement analysis, we tentatively found that the angles between neighbor octahedrons changed with the type of substituted ions and the substitution amount.

The Seebeck coefficients of all samples showed negative values, which indicated that electrons were the charge carriers. Fig. 2 shows a typical curve of Seebeck coefficient of indium-doped samples as a function of temperature. It can be seen that the absolute value of Seebeck coefficients changed by several times with the temperature during the measuring range from 20 to 320 K. Comparing with the corresponding nitrogen-treated samples, air-sintered ones showed higher absolute value.

Table 2 concludes resistivity (ρ), Seebeck coefficient (S), calculated thermoelectric power factor, Hall coefficient (R_H), as well as carrier concentration (n) and carrier mobility (μ) of all samples at 300 K. It is clearly shown that besides Seebeck coefficient, Hall coefficient was also negative in all samples, which indicated electrons to be the charge carriers. Substituted and non-substituted materials are quite different for their carrier concentration. The n value increased from 10^{17} up to 10^{19} by the introduction of trivalent cations, which suggested that a change from insulator to semiconductor occurred. Among the three kinds of substitution, indium

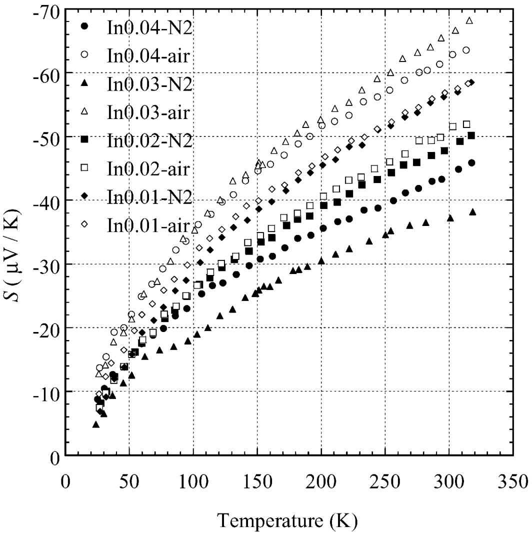

Fig. 2. Temperature dependence of the Seebeck coefficient of $Cd_{3-x}In_xTeO_6$ (x = 0.01, 0.02, 0.03 or 0.04).

Table 2
Comparison of thermoelectric properties of $Cd_{3-x}A_xTeO_6$ (A = In, La, and Bi) at 300 K

Sample			ρ (mΩ cm)	S (μV/K)	P (μW m^{-1} K^{-2})	R_H (cm^3 C^{-1})	$n \times 10^{17}$ (cm^{-3})	μ (cm^2 V^{-1} s^{-1})
Non-substituted		Air	3.73×10^3	−297	2.37	−10.93	5.72	2.93
		N_2	1.38×10^2	−283	58.0	−11.53	5.42	83.5
In	0.01	Air	1.19×10	−57.1	27.4	−0.3114	200.7	26.2
		N_2	4.88	−56.6	65.3	−0.3542	176.5	72.3
	0.02	Air	7.80	−51.6	34.1	−0.2036	307.0	26.1
		N_2	4.41	−48.4	53.1	−0.4999	125.0	114
	0.03	Air	3.22	−65.9	136	−0.2878	217.2	89.9
		N_2	1.30	−37.2	106	−0.3428	182.3	264
	0.04	Air	4.94	−62.8	80.6	−0.2642	236.6	53.9
		N_2	2.68	−43.9	71.4	−0.2008	311.2	74.4
La	0.01	Air	4.63×10^3	−69.6	0.101	−5.201	12.02	1.12
		N_2	9.91×10	−69.8	4.92	−0.6364	98.21	6.41
	0.02	Air	4.52×10^3	−45.6	0.052	–	–	–
		N_2	4.23×10	−50.3	5.97	−0.9573	65.30	22.6
	0.03	Air	9.88×10	−42.4	1.82	−2.082	30.02	21.1
		N_2	2.58×10	−39.6	6.09	−3.425	18.25	133
Bi	0.01	Air	4.68×10^4	−55.5	0.013	−2.778	22.50	0.061
		N_2	4.82×10^4	−61.9	0.081	−1.3931	44.86	0.29
	0.02	Air	8.78×10^2	−46.3	0.020	−2.486	25.14	0.28
		N_2	3.12×10^3	−45.3	0.068	−3.942	15.85	1.26
	0.03	Air	2.63×10^2	−39.9	0.614	−0.8220	76.04	3.13
		N_2	4.63×10	−45.9	4.56	−0.5861	106.6	12.7

presented the highest effect on the increase of carrier concentration from 5×10^{17} cm^{-3} to (1–3) $\times 10^{19}$ cm^{-3}, which is considered as the optimum figure for thermoelectric materials. Nitrogen treatment did not affect carrier concentration, but had a strong effect on carrier mobility. For example, the carrier concentration of non-substituted samples remained nearly the same of 5×10^{17} cm^{-3} after annealing, but mobility increased by some 10 times with the reducing treatment. As a result of the large increase of carrier mobility, a large reduction of resistivity was attained, which finally contributed to the thermoelectric power factor.

Our result of 1.35×10^{-4} W m^{-1} K^{-2} is comparable to that of best n-type perovskite thermoelectric material of $Ba_{0.4}Sr_{0.6}PbO_3$ [11], whose higher thermoelectric power factor was reported to be 1.8×10^{-4} W m^{-1} K^{-2} at 300 K. Same exciting results were got on single crystals by our group [12], here thermoelectric power factor at 300 K of non-substituted and indium-substituted single crystals were 0.36 and 4.0×10^{-4} W m^{-1} K^{-2}, respectively. Moreover, both the thermal conductivity of polycrystals and single crystals of our samples are almost the same and as low as 2–3 W m^{-1} K^{-1}. Therefore, Cd_3TeO_6 may become a valuable thermoelectric oxide material.

4. Conclusions

In order to increase the electron concentration of Cd_3TeO_6, oxygen vacancies and electrons were purposely introduced by heat-treatment in N_2 and doping with In^{3+}, $La^{3+}$and Bi^{3+}. The substituted samples displayed a very small temperature dependence of the resistivity. Annealing treatment increased the carrier mobility, resulting in the enhanced decrease of resistivity. The negative Seebeck coefficients and Hall coefficient showed that electrons were the charge carriers. Among the three kinds of substitution cations, indium ion showed a superior effect on the improvement of thermoelectric performance. The maximum thermoelectric power factor of 1.35×10^{-4} W m^{-1} K^{-2} was obtained on $Cd_{2.97}In_{0.03}TeO_3$ samples at 300 K.

Acknowledgement

We would like to thank for the Satellite Venture Business Laboratory of Utsunomiya University, Japan, for its financial supports.

References

[1] D. Hicks, M.S. Dresselhaus, Effect of quantum-well structures on the thermoelectric figure of merit, Phys. Rev. B47 (1993) 12727–12731.

[2] T.M. Tritt, Thermoelectric materials: holey and unholey semiconductors, Science 283 (1999) 804–805.

[3] F.J. DiSalvo, Thermoelectric cooling and power generation, Science 285 (1999) 703–706.

[4] R.T. Littleton IV, T.M. Tritt, J.W. Kollis, D.R. Ketchum, Transition-metal pentatellurides as potential low-temperature thermoelectric refrigeration materials, Phys. Rev. B 60 (1999) 13453–13457.

[5] B.C. Sales, Thermoelectric materials: smaller is cooler, Science 295 (2002) 1248–1249.

[6] V. Rama, S. Edward, C. Thomas, O. Brooks, Thin-film thermoelectric devices with high room-temperature figures of merit, Nature 413 (2001) 597–602.

[7] I. Terasaki, Y. Sasago, K. Uchinokura, Large thermoelectric power in $NaCo_2O_4$ single crystals, Phys. Rev. B 56 (1997) R12685–R12687.

[8] W. Shin, N. Murayama, High performance p-type thermoelectric oxide based on NiO, Mater. Lett. 45 (2000) 302–306.

[9] D. Chung, T. Hogan, P. Brazis, M. Rocci-Lane, et al., $CsBi_4Te_6$: a high-performance thermoelectric material for low-temperature applications, Science (2000) 287.

[10] S. Hirano, S. Isobe, T. Tani, N. Kitamura, et al., Electrical and thermal transport properties in layer-structured $(ZnO)_mIn_2O_3$ (m = 5 and 9) ceramics, Jpn. J. Appl. Phys. 41 (2002) 6430–6435.

[11] M. Yasukawa, N. Murayama, High-temperature thermoelectric properties of the oxide material: $Ba_{1-x}Sr_xPbO_3$ (x = 0–0.6), J. Mater. Sci. Lett. 16 (21) (1997/1998) 1731–1734.

[12] Y. Shan, K. Sasaki, K. Sudo, et al., New n-type thermoelectric oxide, Cd_3TeO_6, Jpn. J. Appl. Phys. 41 (2002) L780–L782.