High-temperature thermoelectric properties of the $Ca_{1-x}Bi_xMnO_3$ system

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Polycrystalline samples of $Ca_{1-x}Bi_xMnO_3$ (0.02 $\leq x \leq 0.20$) were studied by means of x-ray diffraction, electrical resistivity (ρ), thermoelectric power (*S*), and thermal conductivity (κ) at high temperature. Bi doping leads to the lattice parameters *a*, *b*, and *c* increasing. And the ρ and the absolute value of *S* decrease rapidly with Bi doping. The largest power factor, S^2/ρ , is obtained in the x = 0.04 sample, which is 3.6×10^{-4} W m⁻¹ K⁻² at 400 K. The figures of merit ($Z = S^2/\rho\kappa$) for this sample and 1.0×10^{-4} and 0.86×10^{-4} K⁻¹ at 600 and 1000 K, respectively.

I. INTRODUCTION

Thermoelectrics, namely energy conversion between heat and electricity via thermoelectric phenomena in solids, has long been a fundamental issue in condensed matter physics and is currently attracting a renewed interest as a promising energy-conversion technology that is not harmful to the environment. Performance of thermoelectric (TE) materials can be evaluated by a figure of merit defined as $Z = S^2 / \rho \kappa$ (or $ZT = S^2 T / \rho \kappa$; T, temperature), where S, ρ , and κ are the Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively. In comparison with conventional TE materials such as metal chalcogenides,^{1,2} transition metal disilicides,³⁻⁵ and Si–Ge alloys,^{6–8} metal oxides, due to their high thermal and chemical stability, have attracted more and more attentions. Among the oxide TE materials, cobalt oxides with layered structure [such as $NaCo_2O_4$ (Co-124), $Ca_3Co_4O_9$ (Co-349), and $Bi_2Sr_2Co_2O_y$ (BC-222)] have been found to be strong *p*-type candidates.^{9–13} For *n*-type TE materials, some candidates, including (ZnO)₅In₂O₃, $In_2O_3 \cdot MO$ (M = Cr, Mn, Ni, Zn, Y, Nb, Sn), (Zn, Al)O, and (Ba, Sr)PbO₃, have been systematically studied.14-17 As a member of the large family of perovskitetype oxides, the electron-doped CaMnO₃ system has also been suggested to be potential material for high-temperature thermoelectrics.^{18,19} Furthermore, the one oxide TE module had been fabricated using $Ca_{0.92}La_{0.08}MnO_3$ *n*-type legs and $Ca_{2.75}Gd_{0.25}Co_4O_9$ *p*type legs by our group²⁰ and has been proved to be operable for a few weeks in air showing high durability. However, for the electron-doped CaMnO₃ system, only a few systematical studies about carrier concentration dependence of high-temperature TE properties were reported.²¹ Since the parameters S, ρ , and κ are dependent

on each other, optimization of the TE performance always requires a compromise between them. The adjustment of carrier concentration by doping is a feasible route to optimizing the TE performance. Our experimental results indicate that the highest power factor (PF), S^2/ρ , and the figure of merit, Z, were reached at an optimal carrier density near x = 0.04 for Ca_{1-x}M_xMnO₃ (M: Bi³⁺, La³⁺, etc.).²² And also the Bi-doped CaMnO₃ system was found to show the best TE performance among these systems. In this paper, a series of samples of Ca_{1-x}Bi_xMnO₃ were synthesized and the compositiondependent thermoelectric properties at high temperature were investigated.

II. EXPERIMENTAL

Polycrystalline samples of $Ca_{1-x}Bi_xMnO_3$ ($0.02 \le x \le 0.2$) were synthesized by the conventional solid-state reaction using powders $CaCO_3$ (99.99%), Bi_2O_3 (99.9%), and Mn_2O_3 (99.9%) in stoichiometric ratio. Bi_2O_3 was added in 10% excess to compensate for the loss of bismuth oxide due to sublimation. Initially the appropriate mixture of these powders was mixed well and calcined at 1173 K for 12 h and 1373 K for 12 h in air with an intermediate grinding. Then the calcined samples were reground and pressed into dish-shaped pellets and sintered in air at 1473–1523 K for 15 h. Finally the pellets were cooled to room temperature in the furnace.

X-ray powder diffraction (XRD) analysis was carried out with Rigaku diffractometer using Cu K_{α} radiation. Cationic composition analysis was made with a Horiba EMAX-5770 energy-dispersive x-ray analysis (EDX) system. The lattice parameters were determined from the *d* values of XRD peaks using a standard least-squares refinement method. ρ was measured using a dc standard four-probe method within temperature range of

JOURNALS

1092

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300–1100 K in air. Pt paste was used for the terminal connections. *S* was obtained from the slope of the relation between thermoelectromotive forces and temperature differences with an error less than 3%. κ was determined from the thermal diffusivity and the specific heat capacity measured by a laser flash technique using Rigaku FA-8510B thermal constant measurement system with a total error less than 5%.

III. RESULTS AND DISCUSSION

XRD analysis indicates that all the samples of $Ca_{1-x}Bi_xMnO_3$ (0.02 $\leq x \leq 0.2$) are single phase with orthorhombic symmetry. EDX result shows that the cation stoichiometries are very close to the target values. Figure 1 shows the lattice parameters *a*, *b*, and *c* and the cell volume *V* as a function of *x* for $Ca_{1-x}Bi_xMnO_3$. With Bi doping, the parameters *a*, *b*, and *c* all increase monotonously, and the cell volume increases from 208 to 214 Å³ as *x* changes from 0.02 to 0.2. This result can be well understood on the basis of the fact that the ionic radius of Bi³⁺ is larger than that of Ca²⁺.

Figure 2 presents the temperature dependence of ρ within 300–1100 K. It is known that the undoped sample CaMnO₃ is an *n*-type semiconductor with rather high ρ (approximately 10 Ω cm) at room temperature. However, Bi doping, even as x = 0.02, can cause a marked



FIG. 1. Lattice parameters *a*, *b*, and *c* and the cell volume *V* of $Ca_{1-v}Bi_vMnO_3$ (0.02 $\leq x \leq$ 0.20).



FIG. 2. Electrical resistivity (ρ) as a function of temperature of Ca_{1-v}Bi_vMnO₃ (0.02 $\leq x \leq 0.20$).

decrease in ρ in 2–3 orders of magnitude at room temperature. With further increasing Bi content, the ρ decreases gradually. Obviously, substituting Bi for Ca introduces carrier into the σ^* conduction band and leads to a corresponding decrease in ρ as the carrier concentration increases.²³ On the other hand, the increase of density with Bi doping (3.73 and 4.52 g cm⁻³ for x = 0.02 and 0.20, respectively) is another reason for the decrease in ρ .

Figure 3 shows the temperature dependence of *S* for the samples of $Ca_{1-x}Bi_xMnO_3$. The *S* values are all negative, indicating *n*-type conduction. For all the samples,



FIG. 3. Temperature dependence of thermoelectric power (S) of $Ca_{1-x}Bi_xMnO_3$ (0.02 $\leq x \leq$ 0.20).

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the absolute values of *S* (|*S*|) increase with increasing temperature over the whole measured temperature range. Bi doping results in a considerable decrease in the |*S*|, which is in qualitative agreement with the decrease in ρ . Even so, the |*S*| is still moderate as 100–200 μ V K⁻¹ at 1000 K for the $x \le 0.1$ samples. For x = 0.02 and 0.04 samples, the |*S*| values are 220 and 176 μ V K⁻¹, respectively at 1000 K.

The samples with $0.02 \le x \le 0.1$ all have rather low ρ and large |S| as oxides, which is required for thermoelectric applications. Due to the ρ and |S| varying in a consistent way, optimizing the carrier concentration by modifying the compositions is needed to get the best TE performance. The calculation of PF can help us to evaluate the electrical components of the TE performance. Figure 4 shows the PF versus temperature for Ca_{1-x}Bi_xMnO₃. Clearly, the x = 0.04 sample possesses the highest PF, i.e., 3.6×10^{-4} and 2.7×10^{-4} W m⁻¹ K⁻¹ at 400 and 1000 K, respectively. An increase or a decrease in *x* results in a marked decrease in the PF, which is similar to the results observed in Ca_{1-x}La_xMnO₃ system.²²

Figure 5 shows the temperature dependence of κ . For comparison, the data for the undoped CaMnO₃ from the work of Ohtaki *et al.*¹⁸ were plotted in this figure. The κ value of the x = 0.04 sample at 300 K is 3.5 W m⁻¹ K⁻¹, slightly less than that of the undoped sample. At the same temperature the κ of the x = 0.15 sample is only 3.0 W m⁻¹ K⁻¹, markedly less than that of the x = 0.15 sample increases gradually from 3.0 to 3.6 W m⁻¹ K⁻¹ as the temperature increases from 300 to 1000 K. While for the other two samples, the κ decreases with increasing temperature



FIG. 4. Power factor as a function of temperature of $Ca_{1-x}Bi_xMnO_3$.



FIG. 5. Temperature dependence of thermal conductivity (κ) of $Ca_{1-x}Bi_xMnO_3$.

within the whole measured temperature range. With Bi doping the slope, $d\kappa/dT$, changes from negative to positive. It is known that κ can be expressed by the sun of a lattice component (κ_1) and an electronic component (κ_e) as $\kappa = \kappa_1 + \kappa_e^{24,25} \kappa_1$ is proportional to T^{-1} above Debye temperature and κ_e is proportional to δT (δ : electrical conductivity). For the $Ca_{1-x}Bi_xMnO_3$ system, on one hand, the doping of heavy element Bi can effectively decrease κ_1 ; on the other hand, the increase of carrier concentration induced by Bi doping leads to the increase in κ_{e} . At room temperature the κ_{e} is small and the κ_{1} should dominate the κ . So the markedly decrease of κ_1 leads to the κ decreases with increasing x. With increasing temperature the κ_1 decreases and κ_e increases (the σT increases with increasing temperature for all the $Ca_{1-r}Bi_rMnO_3$ samples). In consequence, the dk/dT changes to the positive value. In fact, the change of carrier concentration is one factor to cause the $d\kappa/dT$ changing from negative to positive. The true situation, however, may be more complicated. Because we have estimated the value of κ_e according to Wiedermann-Franz's law using Lorenz number for free electrons $(2.45 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2})$ and found the κ_e is too small to change the κ so much at high temperature. Some other factors, such as density, may influence κ . This study indicates that the quite large difference in density between the x = 0.04 (3.78 g/cm³) and x = 0.15 (4.41 g/ cm³) samples mainly originates from different closed pores. More closed pores could influence κ very much and lead to a different temperature dependence of κ .²⁶

Table I summarizes the results of electrical and thermal transport measurements at 300 and 1000 K. It clearly shows that the parameters S, ρ , and κ are dependent on

JOURNALS

1094

factor (<i>PF</i>), and dimensionless figure of merit (<i>ZI</i>) at 1000 K of the $Ca_{1-x}BI_xMnO_3$ (0.02 $\leq x \leq$ 0.20) system.								
x	$ ho_{300}$ (m Ω cm)	$\begin{array}{c}\rho_{1000}\\(m\Omega \text{ cm})\end{array}$	S ₃₀₀ (μV K ⁻¹)	S ₁₀₀₀ (μV K ⁻¹)	$(W m^{-1} K^{-1})$	$(W m^{-1} K^{-1})$	$\frac{PF_{1000}}{(10^{-4} \text{ W m}^{-1} \text{ K}^{-2})}$	<i>ZT</i> (1000 K)
0.02	20.6	36.5	-174	-220			1.35	
0.04	5.9	11.5	-142	-177	3.6	3.1	2.64	0.086
0.06	4.8	10.1	-115	-140			1.97	
0.08	4.6	8.9	-84	-112			1.41	• • •
0.10	4.2	8.0	-77	-99			1.24	
0.15	3.1	5.8	-37	-70	3.0	3.6	0.90	0.025
0.20	3.3	4.6	-25	-66			0.95	

TABLE I. Resistivity (ρ_{300} and ρ_{1000}), thermoelectric power (S_{300} and S_{1000}), thermal conductivity (κ_{300} and κ_{1000}) at 300 and 1000 K, power factor (*PF*), and dimensionless figure of merit (*ZT*) at 1000 K of the Ca_{1-x}Bi_xMnO₃ (0.02 $\leq x \leq 0.20$) system.



FIG. 6. Temperature dependence of figure of merit $Z(\blacksquare)$ and $ZT(\blacktriangle)$ of Ca_{0.96}Bi_{0.04}MnO₃.

each other and a compromise between them is reached at an optimal carrier concentration. The best thermoelectric performance was obtained in the x = 0.04 sample.

The relationship between figure of merit Z and temperature of $Ca_{0.96}Bi_{0.04}MnO_3$ is presented in Fig. 6. The maximum Z values obtained here are 1.0×10^{-4} and 0.86×10^{-4} K⁻¹ at 600 and 1000 K, respectively. According to the trends shown in Fig. 6, the value of ZT can reach 0.1 at 1173 K. The good TE performance and the excellent high-temperature durability in air of $Ca_{1-x}Bi_xMnO_3$ suggest the oxides are of interest as potential high-temperature TE materials.

IV. CONCLUSION

The high-temperature thermoelectric properties of $Ca_{1-x}Bi_xMnO_3$ (0.02 $\leq x \leq$ 0.20) polycrystalline samples were investigated carefully. Bi doping causes a rapid decrease in ρ . The samples with 0.22 $< x \leq$ 0.10 show rather low ρ and fairly large |*S*| (100–200 μ V K⁻¹), suggesting promising TE materials. The highest PF was reached in the x = 0.04 sample, and Z for this sample is 1.0×10^{-4} K⁻¹ at 600 K and 0.86×10^{-4} K⁻¹ at 1000 K.

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