



High-temperature thermoelectric performance of $\text{Ca}_{0.96}\text{Dy}_{0.02}\text{RE}_{0.02}\text{MnO}_3$ ceramics (RE=Ho, Er, Tm)

Yuanhu Zhu*, Chunlei Wang, Wenbin Su, Jichao Li, Jian Liu, Yanling Du, Liangmo Mei

School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

Received 8 June 2014; received in revised form 26 June 2014; accepted 3 July 2014

Available online 11 July 2014

Abstract

Perovskite-type $\text{Ca}_{0.98}\text{Dy}_{0.02}\text{MnO}_3$ (CDM) and $\text{Ca}_{0.96}\text{Dy}_{0.02}\text{RE}_{0.02}\text{MnO}_3$ (RE=Ho, Er, Tm) (marked as CDM-Ho, CDM-Er, CDM-Tm) ceramics were prepared by solid state reaction. Their thermoelectric properties were evaluated between 300 K and 1000 K. All the samples are single phase with an orthorhombic structure. The introduction of second doping elements for RE=Ho, Er, Tm lead to a larger carrier concentration. As a result, the resistivity decreases from 36.1 m Ω cm for CDM to 12.4 m Ω cm for CDM-Ho at 973 K, while absolute Seebeck coefficient decreases from -300 $\mu\text{V}/\text{K}$ for CDM to -196 $\mu\text{V}/\text{K}$ for CDM-Tm. The highest power factor is obtained 350 $\mu\text{W}/(\text{K}^2\text{m})$ at 923 K for $\text{Ca}_{0.96}\text{Dy}_{0.02}\text{Er}_{0.02}\text{MnO}_3$ sample. And also the introduction of second element contributes to lower thermal conductivity. The highest figure of merit 0.23 is obtained for RE=Ho, Er samples at 973 K, representing an improvement of about 109% compared with $\text{Ca}_{0.98}\text{Dy}_{0.02}\text{MnO}_3$ sample. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Sintering; C. Electrical properties; C. Thermal conductivity; Ceramics; Oxides

1. Introduction

Renewed attention has been paid on thermoelectric materials for their potential applications in converting heat to electricity and vice versa. The efficiency of thermoelectric materials is evaluated by the dimensionless thermoelectric figure of merit, $ZT = S^2\sigma T/\kappa$, where S , σ , T , and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively [1,2].

On account of the low cost of raw materials and chemical stability, thermoelectric bulk oxides have been considered as promising candidate for power generation, especially at high temperature [3–5]. Since the discovery of Na_xCoO_2 by Terasaki et al. [6], modified cobaltates, such as $\text{Ca}_3\text{Co}_4\text{O}_9$ [7–9], LaCoO_3 [10,11], have been extensively studied as p-type legs for thermoelectric devices. However, as a counterpart, there are relatively few n-type oxide materials to be studied. Recently, CaMnO_3 has attracted attention as a prospective candidate of n-type thermoelectric oxides

[12–14]. Thermoelectric performance of CaMnO_3 doped with rare-earth metals was first reported by Takizawa et al. [15] and Ohtaki et al. [16]. And following experiments, doping with some other trivalent elements, were carried out by Funahashi et al. [17] and Koumoto et al. [18]. They found that lanthanide elements doping at Ca site is an effective way to increase electrical conductivity and keep a moderate absolute Seebeck coefficient. And then Wang et al. [19–21] studied lanthanide elements substitution with a higher doping level of 10% and reported a large thermoelectric response of CaMnO_3 by doping Dy at Ca site. Whereafter, Liu et al. [22,23] found that a lower Dy doping level of 2% would also lead to a significant modification in CaMnO_3 . On the basis of their study, we reported the thermoelectric performance of Dy/Bi dual doped CaMnO_3 and obtained a remarkable $ZT=0.21$ in $\text{Ca}_{0.96}\text{Dy}_{0.02}\text{Bi}_{0.02}\text{MnO}_3$ [24]. This result indicates that 2% dual doping at Ca site is effective in further improving thermoelectric performance of CaMnO_3 . It was also reported the thermoelectric performance of CaMnO_3 improved by substituting Ho, Er etc. [15,19,25], indicating heavy lanthanide elements might be helpful in improving thermoelectric performance of CaMnO_3 . Herein, in

*Corresponding author.

this paper we prepared $\text{Ca}_{0.96}\text{Dy}_{0.02}\text{RE}_{0.02}\text{MnO}_3$ with $\text{RE}=\text{Ho}$, Er , Tm (marked as CDM-Ho, CDM-Er, CDM-Tm), and also $\text{Ca}_{0.98}\text{Dy}_{0.02}\text{MnO}_3$ (CDM) as a comparison. Their thermoelectric properties were evaluated in temperature range between 300 K and 1000 K.

2. Experimental procedure

Solid state reaction method was used to synthesize samples of $\text{Ca}_{0.98}\text{Dy}_{0.02}\text{MnO}_3$ and $\text{Ca}_{0.96}\text{Dy}_{0.02}\text{RE}_{0.02}\text{MnO}_3$ ceramics, with $\text{RE}=\text{Ho}$, Er , Tm . The starting materials were CaCO_3 (99.8%), MnO_2 (99.9%), Dy_2O_3 (99.9%), Ho_2O_3 (99.99%), Er_2O_3 (99.99%) and Tm_2O_3 (99.99%) with the same provider of Sinopharm Group Co., Ltd. These raw materials were weighed in stoichiometric proportions and mixed by ball-milling in ethanol with zirconia balls for 12 h. After the wet mixtures dried, the powder was calcinated for 12 h at 1423 K and 12 h at 1523 K in ambient atmospheric condition with an intermediate grinding. The calcined powder was ball-milled for 12 h to obtain a fine powder. The products were pressed into pellets at 300 MPa, and sintered in air at 1573 K for 12 h. The sintered pellets were cut into rectangular columns with dimensions of 18 mm \times 2.0 mm \times 2.0 mm for measurement of thermoelectric properties.

X-ray powder diffraction (XRD) analysis was carried out using a Bruker AXS D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation and scanning (a step width of 0.020°) over the angular range $20\text{--}70^\circ$. The density of the samples was measured by the Archimedes method. The electrical resistivity

measurements were carried out with a standard four-probe in a helium atmosphere, and the Seebeck coefficient was measured simultaneously in the temperature range between 300 and 1100 K using LINSEIS LSR-3 equipment. Thermal conductivity values (κ) were calculated from the thermal diffusivity (λ), the specific heat capacity (C_p), and the density (d) by applying the following relationship:

$$\kappa = \lambda C_p d \quad (1)$$

The thermal diffusivity and specific heat capacity were measured with a laser flash apparatus (Netzsch LFA 457) and different thermal analyzers (Netzsch STA 449C), respectively. Then power factor, ZT and compatibility factor were calculated.

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns at room temperature of CDM, CDM-Ho, CDM-Er, and CDM-Tm. All the diffraction peaks for the series of samples can be indexed based on an orthorhombic CaMnO_3 structure [24]. No second phase occurs, suggesting that the ions of Dy^{3+} and RE^{3+} have entered into the CaMnO_3 lattice. Lattice parameters are obtained from the X-ray data, theoretical density are calculated from the data and all listed in Table 1. As seen in Table 1, lattice parameters of dual doped samples are a little larger than that of CDM. However, we can get that the ionic radius of Ho^{3+} (1.015 Å), Er^{3+} (1.004 Å), and Tm^{3+} (0.994 Å) are all smaller than that of Ca^{2+} (1.12 Å) ions [26]. So the variation in lattice parameters may be mainly due to the increasing value of $\text{Mn}^{3+}/\text{Mn}^{4+}$, because of the different size in the ionic radii between Mn^{3+} (0.645 Å) and Mn^{4+} (0.530 Å) [26]. This phenomenon has also been reported by us in Dy/Yb dual-doping CaMnO_3 [5]. Experimental densities are 4.561 g/cm^3 , 4.590 g/cm^3 , 4.568 g/cm^3 and 4.629 g/cm^3 for samples of CDM, CDM-Ho, CDM-Er, and CDM-Tm, respectively. For dual doping samples, the measured density increases with the increase of atomic number, mainly due to the contribution from the heavier mass of Ho, Er, and Tm elements. The relative densities, defined as the experimental density over the theoretical density, are all 96.0–97.2%, which means the samples are of good compactness.

The temperature dependence of resistivity for CDM, CDM-Ho, CDM-Er, and CDM-Tm is shown in Fig. 2. All samples exhibit metal-like behavior, i.e., the resistivity decreases with increasing temperature ($d\rho/dT > 0$) which is observed in the entire temperature range. Similar tendency was also reported in other doped CaMnO_3 samples [20–24]. At high temperature

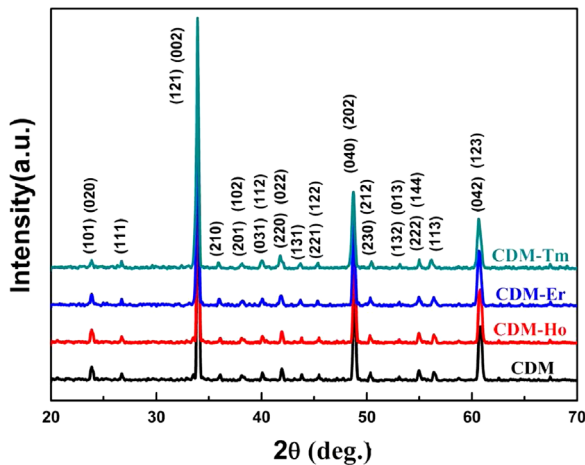


Fig. 1. Room temperature X-ray diffraction patterns for $\text{Ca}_{0.98}\text{Dy}_{0.02}\text{MnO}_3$ and $\text{Ca}_{0.96}\text{Dy}_{0.02}\text{RE}_{0.02}\text{MnO}_3$ ($\text{RE}=\text{Ho}$, Er , Tm).

Table 1
Lattice parameters, densities of $\text{Ca}_{0.98}\text{Dy}_{0.02}\text{MnO}_3$ and $\text{Ca}_{0.96}\text{Dy}_{0.02}\text{RE}_{0.02}\text{MnO}_3$ ($\text{RE}=\text{Ho}$, Er , Tm).

Samples	a (Å)	b (Å)	c (Å)	Theoretical density (g/cm^3)	Experimental density (g/cm^3)	Relative density (%)
CDM	5.272(6)	7.466(2)	5.270(4)	4.701	4.561	97.0
CDM-Ho	5.285(3)	7.481(2)	5.280(1)	4.752	4.590	96.6
CDM-Er	5.289(6)	7.490(3)	5.281(5)	4.758	4.568	96.0
CDM-Tm	5.291(5)	7.494(2)	5.286(9)	4.763	4.629	97.2

Download English Version:

<https://daneshyari.com/en/article/10624843>

Download Persian Version:

<https://daneshyari.com/article/10624843>

[Daneshyari.com](https://daneshyari.com)