



# Electrical properties of Dy<sup>3+</sup>/Na<sup>+</sup> Co-doped oxide thermoelectric [Ca<sub>1-x</sub>(Na<sub>1/2</sub>Dy<sub>1/2</sub>)<sub>x</sub>]MnO<sub>3</sub> ceramics



Y.C. Zhou<sup>a,\*</sup>, C.L. Wang<sup>a,b</sup>, W.B. Su<sup>a</sup>, J. Liu<sup>a</sup>, H.C. Wang<sup>a</sup>, J.C. Li<sup>a</sup>, Y. Li<sup>a</sup>, J.Z. Zhai<sup>a</sup>,  
Y.C. Zhang<sup>a</sup>, L.M. Mei<sup>a</sup>

<sup>a</sup> School of Physics, Shandong University, Jinan, 250100, China

<sup>b</sup> State Key Laboratory of Crystal Material, Shandong University, Jinan, 250100, China

## ARTICLE INFO

### Article history:

Received 19 January 2016

Received in revised form

31 March 2016

Accepted 16 April 2016

Available online 19 April 2016

### Keywords:

Dy<sup>3+</sup>/Na<sup>+</sup> co-doping

Ceramics

Thermoelectric

Geometric distortion

Carrier concentration

## ABSTRACT

A new Dy<sup>3+</sup>/Na<sup>+</sup> co-doping system was attempted for improving the thermoelectric properties of CaMnO<sub>3</sub> system in this paper. [Ca<sub>1-x</sub>(Na<sub>1/2</sub>Dy<sub>1/2</sub>)<sub>x</sub>]MnO<sub>3</sub> samples were produced by the solid state reaction method, and the electrical properties and the microstructure were investigated. The X-ray diffraction data and tolerant factor were obtained, indicating the second phase and the geometric distortion in this system. Besides, compared with the resistivity and the Seebeck coefficient of single Dy-doped system, Dy<sup>3+</sup>/Na<sup>+</sup> co-doping method could partially decrease the variation of carrier concentration as our expectation. More specifically, the holes introduced by doping Na<sup>+</sup> could compensate electrons introduced by doping Dy<sup>3+</sup>, leading to a low variation of carrier concentration. As the result, a relatively high Seebeck coefficient (−251.6 μV/K) and a relatively low resistivity (8.7 mΩ cm) were gained in this system, and the highest power factor value of 298.0 μW/K<sup>2</sup>m was obtained at 323 K in [Ca<sub>0.95</sub>(Dy<sub>1/2</sub>Na<sub>1/2</sub>)<sub>0.05</sub>]MnO<sub>3</sub>.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Thermoelectric material is a kind of material which is able to convert thermo power directly into electric power through Seebeck effect, a clean process with little damage to the environment. However, the relatively low efficiency of thermoelectric materials makes it hard to replace traditional ways of generating electricity. Therefore, new thermoelectric materials with better efficiency are needed to be investigated. The factor to determine the quality of thermoelectric materials is the dimensionless figure of merit  $ZT = S^2T/\rho\kappa$ , where  $S$  is the Seebeck coefficient,  $\rho$  is the electrical resistivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature, respectively [1,2]. For focusing only on the electrical properties, power factor (PF) has been defined as  $S^2/\rho$  [3].

For the last decades, investigations of alloy thermoelectric materials such as SiGe and Bi<sub>2</sub>Te<sub>3</sub> have grown very fast due to their significant properties in thermoelectric field [4,5]. However, for finding a thermoelectric material with low cost and high chemical stability at high temperature, oxide materials earned more and

more attention. Two types of oxide materials flourish in the field: p-type thermoelectric materials which have been achieved high properties such as Ca–Co–O and Na–Co–O systems, and n-type materials such as SrTiO<sub>3</sub> and CaMnO<sub>3</sub> system [3,6–8]. However, n-type thermoelectric materials cannot provide a good enough property to match p-type materials. Thus, n-type materials are necessary to be further explored.

CaMnO<sub>3</sub>-based materials are claimed as one of the most hopeful n-type materials because of a relatively high Seebeck coefficient (350 μV/K) [3,9]. Unfortunately, pure CaMnO<sub>3</sub> has a high resistivity (2 Ω cm), leading to a low PF [9]. Many papers published in the past claimed that single-type doping methods such as doping M<sup>3+</sup> (Y, La, Bi, Ce, Sm, Sb, Pb, In and Sn) could increase the thermoelectric properties of CaMnO<sub>3</sub> [10,11]. In those published papers, single or dual high valence dopants performed as single-type carrier doping in order to modify both the carrier concentration and the microstructure. For CaMnO<sub>3</sub> system, high carrier concentration always leads to a low resistivity. However, according to these published results, the Seebeck coefficient was also related to the carrier concentration, and high carrier concentration would result in low Seebeck coefficient, causing a limit improvement of the thermoelectric properties [10].

In order to achieve a low resistivity with a relatively high

\* Corresponding author.

E-mail address: [allenzye@163.com](mailto:allenzye@163.com) (Y.C. Zhou).

Seebeck coefficient, in this paper, dual dopants  $\text{Dy}^{3+}$  and  $\text{Na}^+$  were introduced into the Ca-site of  $\text{CaMnO}_3$  system with the ratio of 1:1.  $\text{Dy}^{3+}$  performed as the n-type doping leading to a high electron concentration while  $\text{Na}^+$  acted as the p-type doping for increasing the hole concentration. These holes introduced by doping  $\text{Na}^+$  could compensate the electrons introduced by doping  $\text{Dy}^{3+}$  [12,13]. In other words, doping  $\text{Dy}^{3+}$  and  $\text{Na}^+$  simultaneously would not introduce as many electrons as the single Dy-doped system do, which means a relatively low resistivity could be obtained and the Seebeck coefficient could be maintained at a relatively high level, leading to a high  $PF$ .

## 2. Experimental

$[\text{Ca}_{1-x}(\text{Na}_{1/2}\text{Dy}_{1/2})_x]\text{MnO}_3$  samples were produced with four different  $x$  which were equal to 0.05, 0.10, 0.15 and 0.20, using the solid state reaction method. Original matters we used were appropriate quantities of  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Dy}_2\text{O}_3$  and  $\text{MnO}_2$  powders, mixed via ball-milling method for 16 h. The mixed powders were then pressed by a cylindrical mould into several cylindrical pieces in order to make the powders react more perfectly. Heat them up to 1273 K, maintaining it for 4 h for reaction. The sintering process was kept in a closed condition to minimize the volatilization of Na. After the method, sintered pieces were smashed into powders, mixed by the ball-milling method for 16 h. Then press them into smaller cylindrical pieces by a smaller mould with agglutinants for sintering into porcelains. For the pieces being porcelains, we maintain the temperature of 1473 K for 4 h. Finally, we cut the ceramic pieces by a diamond wire saw into bars and silver the bars at the areas which would be touched by probes of LSR-3 for measuring. Smash the rest of the ceramic samples into powders for the X-ray diffraction (XRD) experiment.

We measured electrical properties of the samples: resistivity and absolute Seebeck coefficient. For being more overall, we also did the XRD about the samples. The crystal structure of all samples was measured by the powder X-ray diffraction method (XRD) with  $\text{Cu K}\alpha$  radiation from a Bruker AXS D8 ADVANCE diffractometer at room temperature. For measuring resistivity and absolute Seebeck coefficient, we use a professional machine named LSR-3. The resistivity was measured via four-point probe method in LSR-3 automatically and at the same time, the relative Seebeck coefficient was measured in LSR-3 as well because LSR-3 would create the temperature difference between probes which is the requirement of measuring the Seebeck coefficient. Both of them were under a helium condition and the temperature was ranging from 323 K to 1073 K, measured at the step of 50 K. The absolute Seebeck coefficient would then be calculated by software linking with LSR-3 with the relative Seebeck coefficient.

## 3. Results and discussion

The XRD patterns for different doping amount  $x$  of  $[\text{Ca}_{1-x}(\text{Dy}_{1/2}\text{Na}_{1/2})_x]\text{MnO}_3$  are shown in Fig. 1. According to Fig. 1, XRD patterns of all samples did not indicate a perfectly single phase with orthorhombic symmetry of  $Pnma$ , and the second phase patterns showed was  $\text{CaMn}_2\text{O}_4$  with orthorhombic symmetry of  $Pmab$ . Besides, the second phase preformed more clearly with the increasing amount of dopants. The same phenomenon that an appearance of  $\text{Mn}^{3+}$  often happens in some high valence single doping at A-site such as doping  $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$  or  $\text{Yb}^{3+}$  [14,15]. The emergence of  $\text{Mn}^{3+}$  which is the essence of the second phase induces numerous electronic carriers and promotes the electron transit between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ , resulting in a decrease of resistivity [16]. In this case, it probably resulted from not only the effect of  $\text{Dy}^{3+}$  but also the difficulty of sustaining  $\text{Na}^+$  ions inside

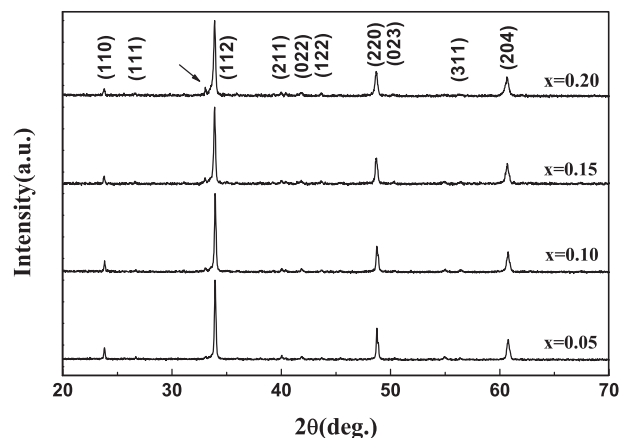


Fig. 1. X-ray powder diffraction patterns of  $[\text{Ca}_{1-x}(\text{Dy}_{1/2}\text{Na}_{1/2})_x]\text{MnO}_3$  ceramics, with  $x = 0.05, 0.10, 0.15$  and  $0.20$  at room temperature.

because  $\text{Na}^+$  is so unstable that it will volatilize during the sintering process [17]. The more amount of Na prepared to be doped, the easier the volatilization happens. And thus, Na will be insufficient compared to the amount of Dy, Ca, and Mn, causing the second phase.

The lattice parameters, and lattice volumes of  $[\text{Ca}_{1-x}(\text{Dy}_{1/2}\text{Na}_{1/2})_x]\text{MnO}_3$  ceramics, with  $x = 0.05, 0.10, 0.15$  and  $0.20$  are shown in Table 1. According to Table 1, when  $x = 0.05$ , the lattice parameters and the lattice volumes are very similar to the pure  $\text{CaMnO}_3$ . That is because of the little amount of dopants and the similar ionic radii of  $\text{Dy}^{3+}$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$ . However, when  $x = 0.10, 0.15$  and  $0.20$ , both the lattice parameters and the lattice volumes are clearly distinctive to the pure  $\text{CaMnO}_3$ .

The tolerant factor “ $t$ ” defined as  $t = (r_A + r_O) / 2(r_B + r_O)$  is considered and calculated to describe the geometric distortion of all the samples [18]. Since the coordination number in orthorhombic distorted perovskites is usually nine, the ionic radius for nine-coordinated  $\text{Ca}^{2+}$  (1.18 Å, 9-coordinated),  $\text{Na}^+$  (1.24 Å, 9-coordinated) and  $\text{Dy}^{3+}$  (1.083 Å, 9-coordinated) is used [9,19]. Shannon’s ionic radii are used in this study, and  $\text{Mn}^{4+}$  (0.53 Å, 6-coordinated) and  $\text{O}^{2-}$  (1.4 Å, 6-coordinated) for six-coordinated are used to calculate the tolerant factors [20]. As a result, the tolerant factors of samples in this study are shown in Fig. 2, theoretically ignoring the effect of  $\text{Mn}^{3+}$  ions and the oxygen vacancy. Considering the increasing amount of  $\text{Mn}^{3+}$  (0.645 Å, 6-coordinated) which has a bigger ionic radii than  $\text{Mn}^{4+}$  and the volatilization of  $\text{Na}^+$  (1.24 Å, 9-coordinated) which has a bigger ionic radii than both the  $\text{Dy}^{3+}$  and  $\text{Ca}^{2+}$ , the “ $t$ ” will decrease more sharply from 1 practically. The decrease from 1 of “ $t$ ” indicates that the geometric distortion gradually increases, which is consistent with the above results of lattice parameters. Besides, the more “ $t$ ” decreases from 1, the more difficult to build a perfectly single phase [18]. The lattice parameter data is showed in Table 1.

The temperature dependence of electrical resistivity of  $[\text{Ca}_{1-x}$

Table 1

The lattice parameters, and lattice volumes of  $[\text{Ca}_{1-x}(\text{Dy}_{1/2}\text{Na}_{1/2})_x]\text{MnO}_3$  ceramics, with  $x = 0.05, 0.10, 0.15$  and  $0.20$ .

$x$	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$v(\text{Å}^3)$
0	5.282	7.455	5.266	207.36
0.05	5.2864	7.4661	5.2775	208.30
0.10	5.4186	7.4650	5.2778	213.49
0.15	5.4163	7.5312	5.1779	211.21
0.20	5.4175	7.6349	5.1632	213.56

Download English Version:

<https://daneshyari.com/en/article/1605335>

Download Persian Version:

<https://daneshyari.com/article/1605335>

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