



Enhanced thermoelectric figure of merit through electrical and thermal transport modulation by dual-doping and texture modulating for $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxide materials



C.S. Huang^a, F.P. Zhang^{b, c, *}, X. Zhang^c, Q.M. Lu^c, J.X. Zhang^c, Z.Y. Liu^d

^a Department of Physics and Electronic Engineering, Guangxi Normal University for Nationalities, 532200, Chongzuo, Guangxi, People's Republic of China

^b Henan Provincial Center of Physical Properties Simulation, Institute of Applied Physics, Henan University of Urban Construction, 467036, Henan, People's Republic of China

^c National Key Laboratory of Advanced Functional Materials, Chinese Ministry of Education, The College of Materials Science and Engineering, Beijing University of Technology, 100124, Beijing, People's Republic of China

^d College of Physics and Electrics Engineering, Henan Normal University, 453007, Xinxiang, People's Republic of China

ARTICLE INFO

Article history:

Received 29 April 2016

Received in revised form

1 June 2016

Accepted 7 June 2016

Available online 11 June 2016

Keywords:

$\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$

Dual-doping

Microstructure modulating

Thermoelectric performance

ABSTRACT

The realization of high figure of merit for thermoelectric materials relies on modulating the electrical and thermal transport at the same time. In this work, the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxide based material specimens with regulated carrier transport, phonon transport as well as enhanced figure of merit are prepared through barium and praseodymium dual doping and spark plasma sintering. The microstructures, textures as well as the thermoelectric performances are successfully tuned by dual doping and preparation procedure adjustment. The bulk specimen shows the largest figure of merit 0.31 at 973 K for $\text{Ca}_{2.8}\text{Ba}_{0.1}\text{Pr}_{0.1}\text{Co}_4\text{O}_{9+\delta}$ bulk specimen due to improved power factor and suppressed thermal conductivity. The figure of merit value is very much higher than that of the comparing specimen, and the combining effect of dual doping is indeed positive for optimizing the thermoelectric performance for the titled oxide materials.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The transitional metal oxide materials have attracted renewed research interest for their structural topology, carrier transportation, electric, magnetic and superconductive properties [1–8]. As one of these types of materials, the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxide material has misfit crystal structure and tuning sensitivity of physical properties, it has interesting physical phenomena and potential applications. It has driven much research mobility during the past two decades [7]. The meaningful physical properties have been associated with spin fluctuation, spin entropy, orbital splitting and so on. The mechanism needs investigation yet. It is noteworthy that Shikano et al. had reported the highest TE figure of merit ZT ($ZT_{973} = 0.87$) of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ single crystal in 2003, and this type of materials had attracted wide attention within TE fields thereafter for its high TE performances and potentials [9–11]. Among the p

type oxide TE materials, the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxides based TE materials have many advantages such as environmental amity, temperature stability, materials cheapness and easy preparation over those greatly developed alloy-based TE materials such as the tellurides, antimonides and half-Heusler alloys [12–15]. The $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxide material is thought as one of the best p type TE materials for its high performance. Unfortunately, although efforts have been made in the past years, the mission to improve TE properties of the polycrystalline materials for the sake of widely application is still arduous.

The above mentioned ZT is the measuring ruler for the performance of a TE material, which is called the dimensionless figure of merit expressed as:

$$ZT = \alpha^2 T / \rho \kappa \quad (1)$$

where α is the Seebeck coefficient (thermopower), ρ is the electrical resistivity, T is the temperature and κ is the total thermal conductivity, respectively [15–17]. TE materials should be materials with electron crystal like carrier conduction and phonon glass like

* Corresponding author. Institute of Applied Physics, Henan University of Urban Construction, 467036, Henan, People's Republic of China.

E-mail addresses: zhfp@emails.bjut.edu.cn, zhfp163@163.com (F.P. Zhang).

phonon conduction, namely the type of materials called electron crystal and phonon glass (ECPS) [16,17]. In fact, high Seebeck coefficient, low resistivity and thermal conductivity are inevitably needed for good TE materials. However, these parameters are interdependent, this make the single modulation of these parameters to obtain high figure of merit ZT value difficult. For the titled oxide materials, these parameters are also related with the microstructure and texture. Relatively high thermoelectric figure of merit can be reached by tuning the carrier transport and phonon transport through microscopic crystal structure modulation, at the same time, by tuning the material microstructure and texture in macrostructural scale. The titled material is suitable for doping aiming to adjust the crystal structure and thus to tune the TE transport parameters, and rare earth elements doping had been verified to be a successful way optimizing TE transport properties [18–20], as a result of modulated atomic recombination, lattice vibration, local strain, defects scattering, carrier density, effective mass, mobility as well the interaction mechanism between these. The $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxide is also suitable for spark plasma sintering preparation in order to fabricate highly particle-aligned bulk materials [21–23]. The doping for Ca site is beneficial for the bulk materials' particle-alignment modulation, too [22,23]. It is found that the same valent elements doping for Ca site is positive for texture formation, while the doping for Ca site with different valent elements shows reverse behavior [18–20]. The Ba doping for Ca site is favorable for bulk texture formation and the electrical resistance reduction [22], while the Pr doping for Ca site shows reverse behavior for the texture formation, nevertheless the Pr doping would redound to heightening the Seebeck coefficient [24]. In this paper, the transports of carriers and phonons, microstructure and texture of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ bulk material are successfully tuned by barium and praseodymium dual doping. The doped oxide bulk specimens are analyzed as to their phase components, microstructures, electrical transport and thermal transport properties by X-ray diffraction (XRD), scanning electron microscope (SEM) and the measuring apparatus for the first time to our knowledge. The thermoelectric figure of merit ZT value is elevated very much higher than that of the comparing specimen.

2. Experimental details

The barium and praseodymium dual doped $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxide polycrystalline powders were synthesized by the sol-gel method with citrate acid and ethylene glycol as chelating agents according to the nominal composition $\text{Ca}_{2.8}\text{Ba}_x\text{Pr}_y\text{Co}_4\text{O}_{9+\delta}$ ($x, y = 0, 0.05, 0.1, 0.15$ and 0.2). Nitrates of Ca, Ba, Pr and Co with stoichiometric ratios were dissolved in an aqueous solution of citric acid, a small amount of ethylene glycol was added in to the solution. The solution was slowly heated to 353 K and it was maintained at 353 K with continuous stirring to form the precursor gel. Afterward, the obtained gel was firstly dried at 353 K for 5 h and then dried at 393 K for 12 h. Then the dry gel was thoroughly ground and heated at 1073 K for 5 h to obtain the $\text{Ca}_{2.8}\text{Ba}_x\text{Pr}_y\text{Co}_4\text{O}_{9+\delta}$ ($x, y = 0, 0.05, 0.1, 0.15$ and 0.2) polycrystalline powders. The resulting powders were preheated at 773 K with flowing oxygen in the tube furnace for 5 h. The bulk material specimens were prepared by the SPS method with quick process. The powder was firstly pressed into pellets within a graphite die. Then the pellets were sintered by SPS procedure (SPS-3.20 MK-V). The holding time was 3 min, the temperature was 1073 K, the pressure was 40 MPa and the heating rate was 100–120 K/min, respectively.

The phase constitutions of the bulk material specimens were analyzed by X-ray diffraction (XRD) at room temperature on a Rigaku diffractometer with $\text{CuK}\alpha$ radiation in a 2 theta range of 5° – 75° , with steps of $0.02^\circ(2\theta)$ and a time per step of 1s. The

microscopic images of the bulk material specimens were obtained with the scanning electron microscope (SEM) using secondary electron mode by Carl Zeiss SUPRA 40 operated at 10 KV. The energy dispersive X-ray (EDX) spectrometer was used to determine the stoichiometric deviation of the specimens. The density d was measured by Archimedes method. The electrical resistivity and Seebeck coefficient were measured in He atmosphere from room temperature up to 1000 K using a conventional dc standard four-probe method on ULVAC ZEM-2 system. The thermal diffusivity λ and specific heat C_p were measured by the laser flash method (ULVAC TC-7000) in vacuum. The thermal conductivity κ was then calculated from the measured λ , C_p and density d using the formula $\kappa = \lambda C_p d$. The overall measurement errors for the electrical resistivity, Seebeck coefficient and thermal conductivity were estimated to be $\pm 5\%$, $\pm 2\%$ and $\pm 5\%$, respectively.

3. Results and discussion

3.1. Phase component

Fig. 1(a) shows the XRD patterns of the barium and praseodymium dual doped $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ polycrystalline bulk specimens. The XRD patterns of the barium and praseodymium dual doped $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ bulk specimens are in good agreement with the

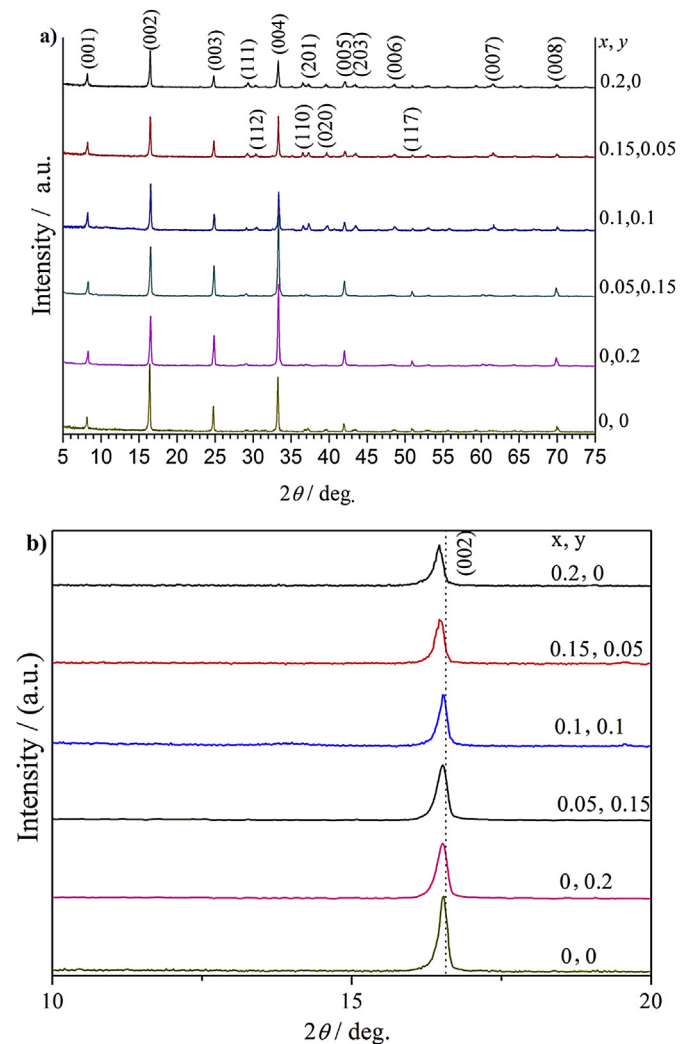


Fig. 1. XRD patterns of the Ba and Pr dual doped $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ bulk specimens.

Download English Version:

<https://daneshyari.com/en/article/7995635>

Download Persian Version:

<https://daneshyari.com/article/7995635>

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