

Thermoelectric properties of A-site doped perovskites ($\text{Sr}_{0.6}\text{Ba}_{0.4}$) $_{1-x}\text{M}_x\text{PbO}_3$ (M = La, K)

Masahiro Yasukawa^{a,*}, Satoru Itoh^a, Toshio Kono^b

^a Department of Materials Science and Engineering, Kochi National College of Technology, 200-1 Monobe, Nankoku 783-8508, Japan

^b Kochi Prefectural Industrial Technology Center, 3992-3 Nunoshida, Kochi 781-5101, Japan

Received 8 July 2004; accepted 23 July 2004

Abstract

La- and K-doped perovskite-type ceramics, ($\text{Sr}_{0.6}\text{Ba}_{0.4}$) $_{1-x}\text{La}_x\text{PbO}_3$ with $x = 0.0$ – 0.1 and ($\text{Sr}_{0.6}\text{Ba}_{0.4}$) $_{1-x}\text{K}_x\text{PbO}_3$ with $x = 0.00$ – 0.15 , were prepared to modify thermoelectric properties of semi-metallic $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ via the doping of electrons and holes, respectively. The electrical conductivity σ and Seebeck coefficient S for the ceramics were measured at temperatures of 373–1073 K in air. With the La doping, electron carriers were successively doped and the material changed from a semi-metal to the undoped $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ to a metal for the ($\text{Sr}_{0.6}\text{Ba}_{0.4}$) $_{0.9}\text{La}_{0.1}\text{PbO}_3$. With the K doping, the thermoelectric properties were essentially unchanged probably due to the carrier compensation effect by the generation of oxygen deficiencies. The thermoelectric power factor $S^2\sigma$ was maximized to a value of $3.1 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$ at 773 K for the undoped $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ ceramic.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Semiconductors; Chemical synthesis; Precipitation; X-ray diffraction; Electronic transport

1. Introduction

Since electroconductive oxides having high stability at high temperatures in air are applicable to thermoelectric power generators, which convert waste heat from incinerators and combustion engines to electricity, thermoelectric properties have been investigated for many electroconductive oxides [1]. Thermoelectric figure of merit Z is expressed by an equation, $Z = S^2\sigma/\kappa$, where S , σ , κ are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. The criterion for the practical use of a material is $ZT \geq 1$, where T is the absolute temperature and ZT is the dimensionless figure of merit, so that the high values of $|S|$ and σ , that is, the high power factor $S^2\sigma$, and the low κ value must be simultaneously realized for the material. In recent years, single crystals of double oxides having cobalt cations, (Ca , Sr , Bi) $_2\text{Co}_2\text{O}_5$ [2] and $\text{Na}_x\text{CoO}_{2-\delta}$ [3], were reported to be p-type thermoelectric oxides showing $ZT \geq 1$, but no

polycrystalline oxides having high ZT values applicable to the power generators have not been reported yet. Therefore, extensive investigation on the thermoelectric properties for the polycrystalline oxides has been needed.

We previously reported thermoelectric properties of perovskite-type solid solutions $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ with $x = 0$ – 1 and that the power factor $S^2\sigma$ and the figure of merit Z were maximized to $4.3 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$ at 773 K and $2.0 \times 10^{-4} \text{ K}^{-1}$ at 673 K, respectively, for a material of $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ [4,5]. This result indicated that the $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ was a promising candidate of thermoelectric oxide, but it remains some room to perform chemical modification for this material to improve the thermoelectric performance. The thermoelectric properties of the $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ revealed that the material was a semi-metal having an overlap in energy between the conduction band (CB) and the valence band (VB) [4,5]. The schematic picture of the band structure is shown in Fig. 1. The CB and VB are composed of $\text{Pb}6s$ – $\text{O}2p$ anti-bonding orbitals and $\text{O}2p$ non-bonding orbitals, respectively, and the overlap of the CB and VB is due to the large energy dispersion of the CB originated from

* Corresponding author. Tel.: +81 88 864 5563; fax: +81 88 864 5561.
E-mail address: yasukawa@ms.kochi-ct.ac.jp (M. Yasukawa).

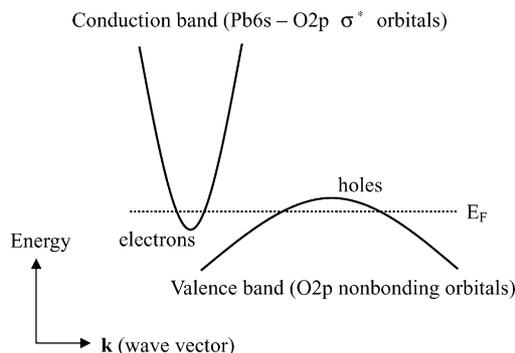


Fig. 1. Schematic picture of energy band structure for semi-metallic $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$.

the large overlap between the Pb6s and O2p orbitals. This band structure is similar to that of a semi-metallic BaPbO₃ [6,7]. The control of the Fermi level by electron doping or electron extraction is a possible way to modify the thermoelectric properties. It is worth investigating whether the doping of electrons or holes into the $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ is effective to improve the thermoelectric performance, especially the power factor $S^2\sigma$. A possible way to dope electrons or holes is substitution of A-site randomly occupied by bivalent Sr and Ba cations with trivalent La or monovalent K, respectively. In this study, La- and K-doped perovskite-type ceramics of $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{La}_x\text{PbO}_3$ and $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{K}_x\text{PbO}_3$ were prepared and the electrical conductivity and Seebeck coefficient were measured at high temperatures. The change in the thermoelectric power factor $S^2\sigma$ as well as the electronic transport properties by the A-site doping is reported.

2. Experimental

La-doped perovskite-type ceramics of $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{La}_x\text{PbO}_3$ with $x=0.000, 0.005, 0.020$, and 0.100 were prepared by oxalate co-precipitation method. Sr–Ba–La–Pb oxalate was co-precipitated from mixed solution of Sr (NO_3)₂, Ba(NO_3)₂, Pb(NO_3)₂, and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$. The reagents were weighed with molar ratios of $(\text{Sr}_{0.6}\text{Ba}_{0.4})/\text{La}/\text{Pb} = 1.000/0.000/1.000, 0.995/0.005/1.000, 0.980/0.020/1.000, 0.900/0.100/1.000$, and dissolved in deionized water. Concentration of Pb^{2+} ion in the solution was fixed to 0.1 mol l^{-1} . An excess amount of ammonium oxalate solution was added into the mixed solution, and white precipitate was formed. Then, the pH of the solution was adjusted to 8.0 with ammonium water to complete the co-precipitation. The co-precipitate was filtered, dried at 80°C in air, and heated at 700°C for 6 h in air with an intermittent grinding to form fine powder of oxides. The oxide powder was pressed into a pellet at a pressure of 200 MPa using a cold isostatic press (CIP) and sintered at 900°C for 3 h in air to form a sintered ceramic.

Preparation of K-doped ceramics of $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{K}_x\text{PbO}_3$ with $x=0.00, 0.05, 0.10, 0.15$, and 0.30 were per-

formed by the solid-state reaction among the raw materials. Reagents of $\text{SrCO}_3, \text{BaCO}_3, \text{K}_2\text{CO}_3, \text{PbO}$ were weighed stoichiometrically and mixed with ethanol in a mortar. The mixed powder was calcined at 750°C for 10 h in air. The calcined powder was ground, molded in a disk, and heated at 900°C for 10 h in air. For the samples with $x=0.10, 0.15$, and 0.30 , the ground and molded disks were additionally heated at 900°C for 20 h in air with an intermittent grinding. After the heating, there existed impurity phase in the sample with $x=0.30$, suggesting that the $x=0.30$ was beyond the solubility limit of K atoms in the perovskite. The powdered samples with $x=0.00$ – 0.15 were pressed into pellets at a pressure of 200 MPa using CIP and sintered at 900°C for 3 h in air to form sintered ceramics.

X-ray powder diffraction (XRD) patterns were measured with Cu $\text{K}\alpha$ radiation (45 kV, 40 mA). Electrical conductivity and Seebeck coefficient were measured at temperatures of 373–1073 K in air. The conductivity was measured by dc four-probe method. The Seebeck coefficient was evaluated by correcting the linear gradient of $\Delta V/\Delta T$ for thermopower of platinum [8], where ΔV and ΔT are the thermoelectromotive force and temperature difference between both ends of a sample measured with Pt leads and Pt/Pt–Rh thermocouples, respectively.

3. Results and discussion

3.1. Characterization and thermoelectric properties of $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{La}_x\text{PbO}_3$

X-ray powder diffraction (XRD) patterns of sintered samples $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{La}_x\text{PbO}_3$ with $x=0.000, 0.005, 0.020$, and 0.100 were indexed with orthorhombic cell, indicating that all the samples were single phases of perovskite-type $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{La}_x\text{PbO}_3$ after the final sintering at 900°C for 3 h. The cell lengths and cell volume were $a=5.9566(9) \text{ \AA}, b=8.425(1) \text{ \AA}, c=5.9566(9) \text{ \AA}, V=298.94(6) \text{ \AA}^3$ for the undoped $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{PbO}_3$ and $a=5.9707(9) \text{ \AA}, b=8.442(1) \text{ \AA}, c=5.9702(9) \text{ \AA}, V=300.94(6) \text{ \AA}^3$ for the $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{0.9}\text{La}_{0.1}\text{PbO}_3$, showing the increase in the cell parameters with the La doping. Since the splits of the diffraction peaks reflecting the orthorhombic cell were very small, the crystal lattice was close to pseudo-cubic cell ($\sqrt{2}a \sim b \sim \sqrt{2}c$). The substitution of A-site with La atoms will lead to the electron doping into the CB, which is composed of the Pb6s–O2p anti-bonding orbitals. This will weaken the Pb6s–O2p bonds and lead to the extension of the Pb–O distances irrespective of the ionic radius of La^{3+} (1.36 \AA) smaller than those of Sr^{2+} (1.44 \AA) and Ba^{2+} (1.61 \AA) [9]. The relative density of the sintered ceramic for the theoretical density was 88%, 89%, 76%, 79% for $x=0.000, 0.005, 0.020, 0.100$, respectively.

Temperature dependence of electrical conductivity (σ) and Seebeck coefficient (S) for the $(\text{Sr}_{0.6}\text{Ba}_{0.4})_{1-x}\text{La}_x\text{PbO}_3$ ceramics is shown in Figs. 2 and 3, respectively. The signs of the Seebeck coefficient were negative for all the samples, in-

Download English Version:

<https://daneshyari.com/en/article/9804055>

Download Persian Version:

<https://daneshyari.com/article/9804055>

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