

# Thermoelectric Properties of Misfit Layered Bismuth-Based Rhodium Oxides, (Bi,Pb)<sub>2</sub>Sr<sub>2</sub>Rh<sub>2</sub>O<sub>y</sub>

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# Abstract

Rhodium oxides, including a misfit-layered structure with alternate stacking of a rock salt-type layer and a hexagonal RhO<sub>2</sub> layer, are expected to have good thermoelectric properties. Among them, the thermoelectric properties (electrical conductivity ( $\sigma$ ), Seebeck coefficient (*S*), Figure of merit (*ZT*) and calculated thermal conductivity ( $\kappa$ ) by *S*,  $\sigma$ , *ZT*, and absolute temperature (*T*)) of bismuth-based rhodium oxides ((Bi<sub>1- $x\rho$ </sub>Pb<sub>x</sub>)<sub>2</sub>Sr<sub>2</sub>Rh<sub>2</sub>O<sub><math>y</sub>, x = 0 and 0.02, hereafter BSR and BPSR, respectively) were investigated. In comparison with Bi<sub>2</sub>Sr<sub>2</sub>Co<sub>2</sub>O<sub>y</sub> (BSC) at 700°C, *S* and  $\kappa$  enhanced (increased *S*, 110 (BSR) and 105  $\mu$ V K<sup>-1</sup> (BPSR) from 85  $\mu$ V K<sup>-1</sup> (BSC) and decreased  $\kappa$ , 0.32 (BSR) and 0.50 W m<sup>-1</sup> K<sup>-1</sup> (BPSR) from 1.75 W m<sup>-1</sup> K<sup>-1</sup> (BSC)), whereas  $\sigma$  decreased (15 (BSR) and 31 S cm<sup>-1</sup> (BPSR) from 70 S cm<sup>-1</sup> (BSC)). BPSR reached the highest *ZT* value of 0.067 at 700°C, compared to those of 0.056 (BSR) and 0.027 (BSC).</sub></sub>

## **Keywords**

Electroceramics, Layered Rhodium Oxide, Misfit Layer Structure, Thermoelectric Material, Harman Method

# **1. Introduction**

Thermoelectricity through the Seebeck effect is a technology for converting heat energy to electric power, thus it has a potential for recycling energy in the form of exhausted heat and is therefore expected to generate environmentally clean energy. Thermal-electric (TE) conversion efficiency is represented by a dimensionless figure of merit,  $ZT = S^2 \sigma T/\kappa$ , where *S*,  $\sigma$ ,  $\kappa$ , and *T* are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively [1] [2]. From these equations, large *S* and  $\sigma$  values and a low  $\kappa$  are necessary for high thermoelectric performance. After the discovery of NaCo<sub>2</sub>O<sub>4</sub> in 1997 [3], the two-dimensional structure with alternate stacking of Na (not fully-occupied) and CoO<sub>2</sub> layers attributes to the high *ZT* and thus, materials having CoO<sub>2</sub> as a common building block have been extensively investigated. Then, misfit layered oxides, such as Ca<sub>3</sub>Co<sub>4</sub>O<sub>9+ $\delta$ </sub> Bi<sub>2</sub>Ca<sub>2</sub>Co<sub>2</sub>O<sub>y</sub>, and Bi<sub>2</sub>Sr<sub>2</sub>Co<sub>2</sub>O<sub>y</sub> have been recognized as potential thermoelectric materials [4] [5] [6].

Regarding  $Bi_2Sr_2Co_2O_y$  (hereafter BSC), it is regarded as a candidate as a high-performance oxide thermoelectric material which can be used in high-temperature environments, ~1000 K [6]. BSC consists of an alternative stack of a rock salt-type  $Bi_2Sr_2O_4$  layer and a hexagonal CoO<sub>2</sub> layer along *c*-axis with a misfit along *b*-axis. To improve the TE performance, extensive studies have been performed mainly by doping such as Pb and Na at a Bi-site, Ca at a Sr-site, and Ir at a Co-site [7] [8] [9] and by introducing a second phase [10] and a textured microstructure [11] [12]. In addition, different forms of BSC, a poly-crystal, single crystal, and thin film, were obtained by using various synthetic methods such as techniques of partial melting, pulsed laser deposition, floating-zone, and magnetic-field sputtering [13] [14] [15].

Rh oxides with a RhO<sub>2</sub> layer are expected to have similar electronic states as Co oxides with a CoO<sub>2</sub> layer, and may be promising candidates for high-*ZT* materials as Co oxides. In fact, several Rh oxides with the RhO<sub>2</sub> layer, including  $Sr_{1-x}Rh_2O_4$ , CuRh<sub>1-x</sub>Mg<sub>x</sub>O<sub>2</sub> and so forth, exhibit high *S* by analogy to Co oxides [16] [17] [18].

Bi<sub>2</sub>Sr<sub>2</sub>Rh<sub>2</sub>O<sub>y</sub> (BSR), total substitution of Rh for Co, was firstly prepared, and its  $\sigma$  and *S* values were reported [19]. Afterwards, magnetic properties of Bi-Ba-Rh-O system as well as  $\sigma$  and *S* were investigated [20]. However, as far as we know,  $\kappa$  and *ZT* of BSR have not been reported so far. By analogy with BSC, BSR is also expected to be a high-temperature, high-performance thermoelectric oxide. Then, herein we report thermoelectric properties (electrical conductivity ( $\sigma$ ), Seebeck coefficient (*S*), thermal conductivity ( $\kappa$ ), Figure of merit (*ZT*)) of BSR at 700°C. In addition, the effect of Pb substitution for Bi in BSR, (Bi<sub>1-x</sub>, Pb<sub>x</sub>)<sub>2</sub>Sr<sub>2</sub>Rh<sub>2</sub>O<sub>y</sub> (x = 0.02, BPSR), on the thermoelectric properties was investigated.

#### 2. Experimental

BSR and BPSR powders were synthesized using a conventional solid-state reaction with  $Bi_2O_3$  (Kanto Kagaku, purity 99.9%), PbO (Kanto Kagaku, purity 99.5%), SrCO<sub>3</sub> (Kanto Kagaku, purity 96.0%),  $Co_3O_4$  (Kanto Kagaku, purity 99.95%) and  $Rh_2O_3$  (Kanto Kagaku, purity 99.9%) powders as starting materials. Stoichiometric amounts of the starting materials for BSR and BPSR were wet-ball milled in polyethylene bottles for 20 h using  $ZrO_2$  balls as the milling medium. The mixture was dried and calcined in air at 700°C for 12 h, followed

by calcination in air at 800°C for 24 h twice, to obtain calcined BSR or BPSR powders. The calcined powder was uniaxially pressed into a rectangular pellet (60 kN cm<sup>-2</sup>) with the dimensions ~  $5 \times 1.3 \times 20$  mm, followed by sintering in air at 930°C for 24 h. The crystal structures of the prepared samples were characterized by X-ray diffraction (XRD, PW-1700, Panalytical) after pulverizing the pellets. Quantitative analyses were performed by X-ray fluorescence (XRF) using a ZSXP PrimusII system (Rigaku). The valency of Rh ions was measured by X-ray photoelectron spectroscopy (XPS; Axis-Ultra, Shimadzu).

To measure  $\sigma$  and *S*, two or four Pt wires, respectively, were attached to the rectangular pellets using a Ag conductive paste. The temperature dependences of *S* (Digital Multi-meter, Model 7563, Yokogawa) with a temperature gradient of 5-15°C and that of  $\sigma$  (Source/Monitor Unit, E5273A, Agilent Technologies) for the rectangular pellets were measured at 100 and 700°C by conventional two-probe steady-state and four-probe methods, respectively. A modified Harman method was used to measure *ZT* at 700°C, and then  $\kappa$  was calculated using the measured  $\sigma$ , *S*, and *ZT* values and the absolute temperature.

## 3. Results and Discussion

The XRD patterns of BSR and BPSR indicated that they included single phase of BSR indexed after previous report (**Figure 1(a)**) [19]. The degree of (00*I*) orientation of BSR was determined using the Lotgering's factor (*f*) [21]. The *f* value was calculated to be 54%, indicating the moderate orientation (complete orientation when f = 100%, and complete random, non-orientation when f = 0%). In **Figure 1(b**), the XRD peak of BPSR shifted to a lower 2 $\theta$  angle compared to BSR. This result is reasonable when one considers that the effective ionic radii of Bi<sup>3+</sup> and Pb<sup>2+</sup> (six-coordination) are 0.102 and 0.118 nm, respectively. The radius of Sr<sup>2+</sup> (six-coordination) is 0.116 nm, being quite similar to that of Pb<sup>2+</sup>, and the previous reports on Pb substitution in Bi<sub>2</sub>Sr<sub>2</sub>Co<sub>2</sub>O<sub>v</sub> (BSC), concluding the Pb



Figure 1. (a) XRD patterns of BSR and BPSR. XRD patterns were indexed after [19]; (b) Precisely obtained XRD patterns of BSR and BPSR.

substitution for a Bi site, not a Sr site [7], so it is unlikely that Sr was replaced by Pb. Elemental analysis by XRF indicated that the molar ratio of Bi: Sr: Rh in BSR was 1.5:1.6:2.0, and that of Bi: Pb: Sr: Rh in BPSR was 1.6:0.017:1.6:2.0. This molar ratio was not consistent with the starting ratios used in the preparation of BSR and BPSR. The reason might be owing to the evaporation during repeated calcination and sintering processes.

XPS spectra were recorded to quantitatively determine the  $Rh^{4+}/Rh^{3+}$  atomic ratios. **Figure 2** shows the measured spectra for the Rh 3d orbital (Rh  $3d_{5/2}$  and Rh  $3d_{3/2}$ ; open circles) of BSR and BPSR. The component peaks determined by deconvolution using a Gaussian lineshape (broken line), and the baseline (gray solid line) and fitted peaks (black solid line) are also shown in the figure. The atomic ratios of  $Rh^{4+}/Rh^{3+}$ , which were determined by summing the areas of  $3d_{5/2}$ and  $3d_{3/2}$  for  $Rh^{4+}$  divided by those for  $Rh^{3+}$ , were 1.0 and 1.1 for BSR and BPSR, respectively.

**Figures 3(a)-(d)** show  $\sigma$ , S,  $\kappa$ , and ZT for BSR and BPSR at 700°C.  $\sigma$  and  $\kappa$  increased upon Pb substitution for Bi. This is reasonable to consider that the substitution of Pb<sup>2+</sup> for Bi<sup>3+</sup> causes the hole doping (*i.e.*, carrier doping) as was observed in the BSC. In fact, the Rh<sup>4+</sup>/Rh<sup>3+</sup> ratio was raised. S slightly decreased from BSR to BPSR. This behavior is not consistent with the previous report, demonstrating that S once increased up to x = 0.1 in (Bi<sub>1-x</sub>Pb<sub>x</sub>)<sub>2</sub>Sr<sub>2</sub>Rh<sub>2</sub>O<sub>y</sub> and then decreased with further increasing x [19]. This discrepancy is still unknown, however, would be attributable to the increase in the Rh<sup>4+</sup>/Rh<sup>3+</sup> ratio (increase in



**Figure 2.** XPS spectra for Rh 3d (Rh  $3d_{3/2}$ , Rh  $3d_{5/2}$ ) of BSR and BPSR. The plotted experimental data and the fitted curves closely coincided. The deconvolution curves of Rh<sup>3+</sup> and Rh<sup>4+</sup> are included. The Rh 3d peak was calibrated using the C 1s peak derived from the hydrocarbon surface contaminant with a binding energy of 284.4 eV. After performing the peak deconvolution of the spectra, the binding energies of the component peak tops were shown. Note that the reported Rh  $3d_{5/2}$  binding energies are 308.1 eV for hexagonal Rh<sub>2</sub>O<sub>3</sub> (Rh<sup>3+</sup>), 308.3 eV for orthorhombic Rh<sub>2</sub>O<sub>3</sub> (Rh<sup>3+</sup>), and 309.4 eV for tetragonal RhO<sub>4</sub> (Rh<sup>4+</sup>) [22].



**Figure 3.** Thermoelectric properties of BSR, BPSR, and BSC at 700°C, (a)  $\sigma$ , (b) *S*, (c)  $\kappa$ , and (d) *ZT*.

the Rh<sup>4+</sup> concentration) by Pb substitution. The increase in the Rh<sup>4+</sup> concentration gives the smaller *S* value by Heike's formula [14] [20]. The Pb substitution led to the enhancement of the *ZT* value up to 0.067.

Now, BSR is compared with BSC. In Figures 3(a)-(d),  $\sigma$ , S,  $\kappa$ , and ZT at 700°C for BSC are also shown. Not shown here, but BSC was synthesized exactly the same way as BSR except for using Co<sub>3</sub>O<sub>4</sub> in place of Rh<sub>2</sub>O<sub>3</sub>. The thermoelectric values of BSC were quite consistent with those reported previously [6].  $\sigma$  of BSC was higher than that of BSR. This tendency is explained by the different sizes of the hexagonal block, CoO<sub>2</sub> and RhO<sub>2</sub>, the RhO<sub>2</sub> block is larger than the CoO<sub>2</sub> block.  $\sigma$  of the Bi-based misfit oxides are predominantly determined by the relative size of the rock-salt block (Bi<sub>2</sub>Sr<sub>2</sub>O<sub>4</sub> in both BSC and BSR) to the conducting hexagonal block, and the smaller relative size gives the smaller  $\sigma$  [19]. Accordingly the Ioffe's theory, higher  $\sigma$  of BSC leads to the lower *S* and higher  $\kappa$ . The *ZT* value of BSC at 700°C was 0.027, which was lower than that of BSR, 0.056.

## 4. Conclusions

The thermoelectric performance of hole doped BPSR increased up to ZT =

0.067, compared to ZT = 0.056 of BSR at 700°C, due to the fact that the increase in  $\sigma$  dominated the moderate decrease in *S* and increase in  $\kappa$ . The *ZT* values of BPSR and BSR were higher than that of BSC (*ZT* = 0.027). The *ZT* value for BPSR, which needs to be enhanced more than one order of magnitude to reach the minimum value considered to be required for practical use, which is greater than 1. We are currently seeking to achieve a higher *ZT* value by applying previously proposed methods to improve *ZT* of BSC.

This study has added one example, demonstrating that the  $RhO_2$  can be a superior building block to  $CoO_2$ , responsible for the enhanced thermoelectricity. Using the  $RhO_2$  block, we could design new Rh oxides, such as Sm-Sr-Rh-O, Bi-Ca-Rh-O and so on.

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