Thermoelectric properties of the layered Pd oxide $R_2\text{PdO}_4$ ($R = \text{La, Nd, Sm and Gd}$)

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We prepared polycrystalline samples of $R_2\text{PdO}_4$ ($R = \text{La, Nd, Sm and Gd}$) using a NaCl-flux technique. The measured resistivity is of the order of $10^{-10} \Omega \text{cm}$ at room temperature, which is two orders of magnitude smaller than the values reported so far. We further studied the substitution effects of Ce for Nd in Nd$_{1.9}$Ce$_{0.1}$PdO$_4$, where the substituted Ce decreases the resistivity and the magnitude of the thermopower. The activation energy gap of 70-80 meV and the effective mass of 15 evaluated from the measured data are suitable for thermoelectric materials, but the mobility of $10^{-6} \text{cm}^2/\text{Vs}$ is much lower than a typical value of 1-10 cm$^2$/Vs for other thermoelectric oxides.

PACS numbers:

I. INTRODUCTION

The thermoelectric properties of transition-metal oxides have attracted increasing attention year by year, since the good thermoelectric properties of the layered Co oxide Na$_2\text{CoO}_2$ were discovered. Although the layered Co oxides are promising candidates for p-type thermoelectric materials, various n-type oxides, e.g., (Zn$_{1-x}$Al$_x$)$_2$O, (ZnO)$_x$In$_2$O$_3$, Sr$_{0.9}$Dy$_{0.1}$TiO$_3$, and Sr$_{1.9}$Y$_{0.1}$TiO$_3$ are not yet better than them. Thus, a new n-type thermoelectric oxide is desired for all-oxide thermoelectric devices.

Recently, Ca$_{1-x}$Li$_2$Pd$_3$O$_4$ turned out to be a good p-type thermoelectric material, and Ca$_{1-x}$Bi$_2$Pd$_3$O$_4$ was found to be an n-type material. Ca$_{1-x}$Bi$_2$Pd$_3$O$_4$ is the first example of the n-type Pd oxide, and is interesting in the sense that electrons are doped in the $d_{x^2-y^2}$ band separated from the $d_{3z^2-r^2}$ band by a small energy gap of 0-10 meV. One serious drawback against good thermoelectrics was a small effective mass with a low mobility. In addition, substitution of Bi for Ca cannot change the doping level so widely, because the solubility limit of Bi is at most 15 % that corresponds to only 5 % of electrons per Pd. Thus, we had to find another Pd oxide for n-type thermoelectric materials in which carrier concentration can be changed more widely.

Among various Pd oxides, we focused on R$_2$PdO$_4$ ($R = \text{La, Nd, Sm and Gd}$) which is isomorphic to Nd$_{2-x}$Ce$_x$CuO$_4$, a famous n-type high-temperature superconductor. The Pd$^{2+}$ ion of 4$d^8$ is surrounded with four planar oxygen atoms, in which the $d_{x^2-y^2}$ orbital is expected to be the lowest unoccupied state. Through substitution of Ce for R, we expect that electrons can be doped in the $d_{x^2-y^2}$ band, and let the sample be an n-type conductor. As is similar to the CuO$_2$ plane in Nd$_{2-x}$Ce$_x$CuO$_4$, we expect that the PdO$_2$ plane would be metallic with a wide pd$\sigma^*$ band.

II. EXPERIMENT

Polycrystalline samples of R$_2$PdO$_4$ ($R = \text{La, Nd, Sm and Gd}$) and Nd$_{1.9}$Ce$_{0.1}$PdO$_4$ were prepared by a solid-state reaction using a NaCl-flux technique. Stoichiometric amounts of La$_2$O$_3$, Nd$_2$O$_3$, Sm$_2$O$_3$, Gd$_2$O$_3$, CeO$_2$ and PdO of 99.9 % purity were thoroughly mixed. NaCl was then added in a mass ratio of 2:1, thoroughly mixed again, and were fired at 1073 K for 24 h in air. The product was finely ground, and NaCl was rinsed out in hot distilled water. The powder was dried, palletized and sintered at 1073 K for 12 h in air. The low sintering temperature of 1073 K prevented cations from evaporating from the pellets, which was verified through the composition analyses of Ca$_{1-x}$Li$_2$Pd$_3$O$_4$ previously. We did not check the oxygen content, but as shown below, the magnitude of the thermopower of R$_2$PdO$_4$ is 200-600 $\mu\text{V/K}$ at 300 K, clearly indicating that they are almost undoped. This implies that the formal valence of Pd is close to 2+, and that the oxygen content is almost 4. Thus we refer the samples by nominal compositions in the present paper.

The black-colored samples were characterized by powder x-ray diffraction (XRD) using Cu $K\alpha$ radiation from 2$\theta = 10$ to 100 deg. The resistivity was measured by a four-probe method, and the thermopower was measured by a steady method. The magnetization measurement was done with an SQUID susceptometer (Quantum Design MPMS) from 6 to 300 K in a field $B_{ex}$ of 0.1 T.

III. RESULTS AND DISCUSSION

Figure 1(a) shows typical XRD patterns of the prepared samples, which are indexed as R$_2$PdO$_4$ with a small amount of unreacted PdO and CeO$_2$. In previous
works, polycrystalline samples of La$_2$PdO$_4$ included impurity phases like La$_2$Pd$_2$O$_5$ or La$_4$PdO$_7$. Figure 1(a) shows no trace of such phases, which indicates that the NaCl-flux technique is very effective to stabilize La$_2$PdO$_4$. Lattice constants evaluated from Fig. 1(a) are plotted as a function of ionic radius of R in Fig. 1(b), indicating that the a- and c-axis lengths systematically decrease with decreasing ion radius of R.

In order to check the magnetic state of the Pd ion, we measured the susceptibility of La$_2$PdO$_4$. Note that Nd, Sm and Gd are magnetic ions with localized f electrons, which will obscure the susceptibility of the Pd ions. As shown in Fig. 2, the susceptibility of La$_2$PdO$_4$ is as small as that of a diamagnetic substance like water. This means that the susceptibility is determined by the diamagnetism of core electrons, and that Pd$^{2+}$ is nonmagnetic. Thus we can safely assume that the Pd ions are in the low-spin state with the configuration of $(t_{2g})^6(d_{x^2-y^2})^2(d_{z^2})^0$, and that the $d_{x^2-y^2}$ band is unoccupied, as expected in the introduction. Toward 0 K, the susceptibility slightly increases, possibly caused by a small amount of impurity phases. Fitting the data with the Curie-Weiss law, we evaluated a maximum volume fraction of the magnetic impurity to be 0.1%.

Figure 2(b) shows the thermopower of the prepared samples. All the samples show a negative sign, indicating that R$_2$PdO$_4$ is an n-type conductor. A similar negative thermopower is seen in the n-type copper oxide Nd$_2$CuO$_4$ that is isomorphic to the title compound. The magnitude is as large as 200-600 $\mu$V/K at 300 K, which indicates that the carriers are almost undoped. Considering that conventional thermolectric materials show a thermopower of 200 $\mu$V/K at 300 K, we conclude that the carrier density is somewhat lower than that of them. Comparing with a typical carrier density ($10^{19}$-$10^{20}$ cm$^{-3}$) of conventional thermolectric materials, we estimate the carrier density of R$_2$PdO$_4$ to be of the order of 0.01 electrons per Pd ion.

One may notice that the magnitude of the thermopower systematically increases in going from R = La to Gd, which suggests that the carrier density systematically decreases from La to Gd. Similarly, the resistivity is highest for Gd$_2$PdO$_4$, and is lowest for Nd$_2$PdO$_4$. (La$_2$PdO$_4$ shows higher resistivity than Sm$_2$PdO$_4$. This does not follow the trend, possibly owing to poorer sintering. In fact, a larger amount of PdO is detected in the parent insulator of high-temperature superconductor Bi$_2$Sr$_2$Er$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$, in which the carrier density systematically decreases with increasing $x$.

Let us analyze the resistivity and thermopower more quantitatively. As mentioned above, R$_2$PdO$_4$ is a nearly undoped semiconductor with an energy gap between the $d_{x^2-y^2}$ and $d_{x^2-z^2}$ bands. Thus we expect a conventional semiconductor physics that the transport properties at high temperatures are of activation type characterized by the band gap, and those at low temperatures are of variable-range-hopping (VRH) type. The crossover will occur when the thermally activated carriers are comparable to the doped carriers in number. That is, the more carriers are doped, the higher the crossover temperature is. Accordingly, we expect that the activation-type conduction is realized below 300 K for the least doped sample Gd$_2$PdO$_4$.

The activation-type resistivity and thermopower are
In this context, the relation $E_g \sim E_s$ in Gd$_2$PdO$_4$ is rather unusual in the transition-metal oxides, which implies that a band picture works well to some extent in the 4$d$ transition-metal oxides, possibly owing to the broader 4$d$ bands than the 3$d$ bands.[19] The other three samples (La$_2$PdO$_4$, Nd$_2$PdO$_4$ and Sm$_2$PdO$_4$) are more doped than Gd$_2$PdO$_4$, and show the VRH-type transport expressed by

$$\rho \propto \exp \left( \frac{T_0}{T} \right)^{\frac{d}{d+1}} ,$$  \hspace{1cm} (3)

where $d$ is the dimension of the system [20]. The data are fitted well with $d = 2$ or $d = 3$, as shown in Fig. 4. The characteristic temperature $T_0$ is a measure of the localization length $\xi$ through $T_0 \propto 1/k_B D \xi^d$, where $D$ is the density of states at the Fermi energy. Figure 4 shows that $T_0$ is roughly the same among $R = \text{La, Nd and Sm}$. Since $D$ does not change very much with $R$, the localization length $\xi$ is roughly the same in R$_2$PdO$_4$.

The thermopower of the three samples shows a broad maximum around 100-200 K in Fig. 3(b), which is consistent with the VRH picture of a slightly doped semiconductor. The VRH-type thermopower is given by

$$S \propto T^{-\frac{2}{3}} .$$ \hspace{1cm} (4)

Accordingly, the sublinear thermopower ($S \propto T^{1/3}$ for $d = 2$ or $S \propto T^{1/2}$ for $d = 3$) is expected at low temperatures, and the activation-type thermopower of Eq. (2) is expected at high temperatures. The broad maximum observed around 100-200 K is a sign for the crossover between the two regimes. The sublinear thermopower should have been observed below 100 K, but the sample resistance was too high to measure reliable thermoelectric voltage below 100 K in our experimental setup.

The thermoelectric performance is characterized by the power factor ($S^2/\rho$), which is a measure of the maximum electric power generated from thermal energy.[10] Figure 4 shows that $S^2/\rho$ at 300 K takes the maximum for $R = \text{Nd}$. Thus we partially substituted Ce for Nd in Nd$_2$PdO$_4$ to see the doping effects. Although a tiny peak of CeO$_2$ is present in $x = 0.1$ in Fig. 4(a), the resistivity and thermopower decrease from those for Nd$_2$PdO$_4$, as shown in Fig. 3. This suggests that a substantial portion of Ce is substituted for Nd to supply holes, and further suggests that Nd$_{1.9}$Ce$_{0.1}$PdO$_4$ is a metal (or a degenerate semiconductor) with a finite Fermi energy $E_F$ in the low temperature limit ($T \to 0$). Then the thermopower at low temperatures is given by

$$S = -\frac{\pi^2 k_B^2 T}{2e} \frac{1}{E_F} .$$ \hspace{1cm} (5)

On the other hand, in the high temperature limit of $E_F \ll k_B T$, the thermopower becomes temperature-independent, and obeys the Heikes formula given by

$$S \propto T^{-\frac{2}{3}} .$$ \hspace{1cm} (6)
FIG. 4: Resistivity for $R_2\text{PdO}_4$ ($R =$ La, Nd and Sm) plotted as a function of (a) $T^{-1/4}$ and (b) $T^{-1/3}$.

FIG. 5: Thermopower of Nd$_{1.9}$Ce$_{0.1}$PdO$_4$. The solid and dotted lines represent Eqs. 3 and 4, respectively. The crossover temperature $T^*$ is indicated by an arrow.

\[ S = -\frac{k_B}{e} \ln \left| \frac{2(1-N)}{N} \right|, \tag{6} \]

where $N$ is the number of carriers per Pd.

As shown by the solid and dotted lines in Fig. 5, the fitting with Eqs. 3 and 4 are satisfactory. $E_F$ is evaluated to be 16.5 meV from Eq. 4, corresponding to a thermal energy of 200 K that is close to the crossover temperature $T^* \sim 100$ K. Substituting the saturated value of $S = -200 \mu V/K$ into Eq. 4, we get the carrier density $n = 1.6 \times 10^{21} \text{ cm}^{-3}$, which is of the same order of the ideal value that each Ce ion supplies one electron. Combining with $n$ and $E_F$, we evaluate the effective mass $m^*$ to be 15 through the following equation

\[ E_F = \hbar^2 \pi d_c \frac{n}{m^*}, \tag{7} \]

where $d_c$ is the interlayer distance \[23\]. The heavy $m^*$ and the small $E_g$ are favorable to good thermoelectrics \[10\], but the mobility $\mu$ evaluated from $\mu = 1/ne\rho$ is of the order of $10^{-6} \text{ cm}^2/\text{Vs}$ at 300 K which is much smaller than a typical mobility of thermoelectric oxides (1-10 cm$^2$/Vs at 300 K).

IV. SUMMARY

We prepared polycrystalline samples of $R_2\text{PdO}_4$ ($R =$ La, Nd, Sm and Gd) and Nd$_{1.9}$Ce$_{0.1}$PdO$_4$ using NaCl flux. They are n-type materials with the thermopower of $-600 \sim -200 \mu V/K$ at room temperature. The resistivity of $R_2\text{PdO}_4$ is semiconductive, characterized by an activation energy of 70-80 meV. By the Ce substitution, electrons are doped to reduce the resistivity and thermopower in magnitude. From the thermopower, the carrier concentration and the effective mass are evaluated to be $1.6 \times 10^{21} \text{ cm}^{-3}$ and 15, respectively. The mobility is poor, which might be improved through different synthetic routes.

Acknowledgments

We thank W. Kobayashi, S. Okada and S. Ishiwata for useful comments.

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