Thermoelectric properties of LaRh$_{1-x}$Ni$_x$O$_3$

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Abstract
We report measurements and analyses of resistivity, thermopower and thermal conductivity of polycrystalline samples of perovskite $LaRh_{1-x}Ni_xO_3$. The thermopower is found to be large at 800 K (185 μV K^{-1} for $x = 0.3$), which is ascribed to the high-temperature stability of the low-spin state of Rh^{3+}/Rh^{4+} ions. This clearly contrasts with the thermopower of the isostructural oxide $LaCoO_3$, which rapidly decreases above 500 K owing to the spin-state transition. The spin state of the transition-metal ions is one of the most important parameters in oxide thermoelectrics.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the best advantages of oxides as thermoelectric materials is their stability at high temperatures. Thermoelectric materials are characterized by the dimensionless figure-of-merit, $ZT = S^2T/\rho\kappa$, where S, ρ, κ and T represent thermopower, resistivity, thermal conductivity and absolute temperature, respectively. Na_xCoO_2 [1] was found to be useful for high-temperature power generation and a large number of researchers now study thermoelectric oxides [2–8]. In particular, the layered Co oxides with the CdI$_2$-type CoO$_2$ block show large thermopower up to 1000 K with low resistivity [2–4]. Koshibae *et al* successfully revealed that the spin and orbital degeneracy of the d orbitals is important to the thermopower [9]. According to their theoretical prediction, conduction between $(t_{2g})^5$ and $(t_{2g})^6$ causes large thermopower at high temperatures in Co oxides. Rh oxides have been investigated for oxide thermoelectrics. Because Rh is just below Co in the periodic table, chemical properties of Rh are expected to be similar to those of Co. We should note that Rh ions favour the low-spin state more than Co ions. In fact, the layered Rh oxides with the CdI$_2$-type RhO$_2$ block are found to show similar thermoelectric properties to those of the layered Co oxides [10–14].

Although Rh is promising for oxide thermoelectrics, almost all the layered Rh oxides show similar but poorer thermoelectric properties than the Co oxides. Here we focus on the perovskite-type Rh oxide LaRhO$_3$, because $LaCo_{1-x}Ni_xO_3$ and $La_{1-x}Sr_xCoO_3$ show good thermoelectric properties around room temperature [5–8]. However, the thermopower of $LaCoO_3$ suddenly decreases with the spin-state transition around 500 K [7, 15], which means that $LaCoO_3$-based materials cannot be used above 500 K. In contrast, Rh ions favour the low-spin state up to high temperature, and we expect that LaRhO$_3$-based materials can show better thermoelectric properties than the Co analogues at high temperature. We found that Rh-site substitution improves the thermoelectric properties in CuRhO$_2$ [14] and ZnRh$_2$O$_4$ [16]. Especially in the case of CuRhO$_2$, Mg substitution for Rh makes the system metallic, whereas Cu-site substitution does not increase conductivity. Thus, we substituted Ni for Rh in LaRhO$_3$ as a reference material to $LaCo_{1-x}Ni_xO_3$.

In this paper, we present the high-temperature thermoelectric properties of perovskite $LaRh_{1-x}Ni_xO_3$ and compare them with those of $LaCo_{1-x}Ni_xO_3$. We find that the thermopower of LaRhO$_3$ remains large above 500 K and that the spin state of the Co^{3+}/Rh^{3+} ions determines the high-temperature thermoelectrics.

2. Experimental details

Polycrystalline samples of $LaRh_{1-x}Ni_xO_3$ were prepared by a solid-state reaction. Stoichiometric amounts of La$_2$O$_3$, Rh$_2$O$_3$ and NiO were mixed and calcined at 1273 K for 24 h in air. The calcined products were thoroughly ground, pelletized and sintered at 1373 K for 48 h in air. The x-ray diffraction (XRD) of the samples was measured using Cu Kα
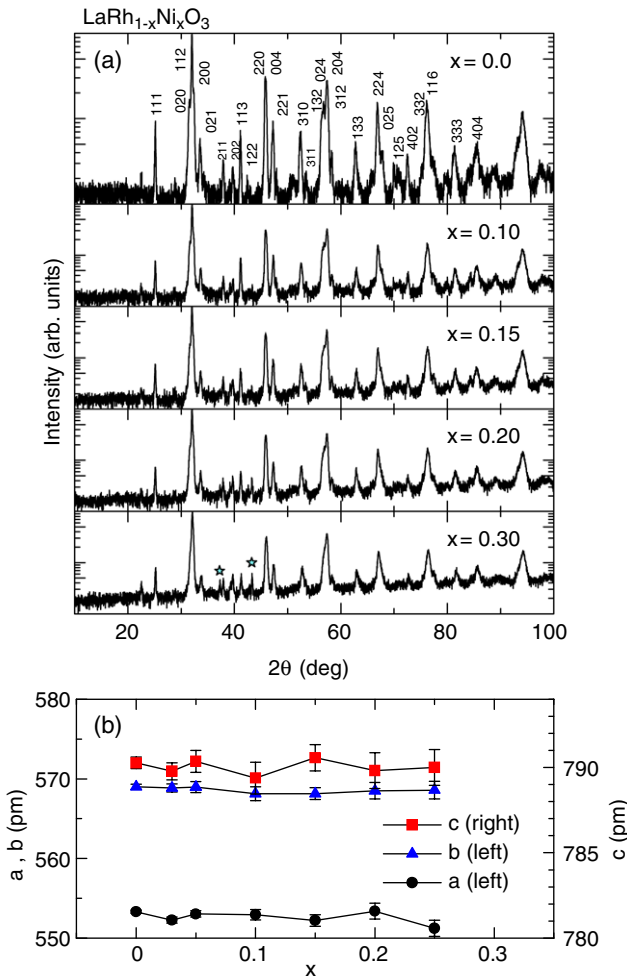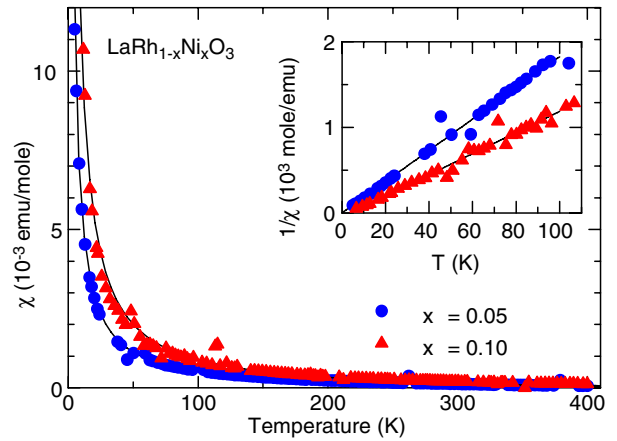
Figure 1. (a) XRD patterns and (b) lattice constants of LaRh$_{1-x}$Ni$_x$O$_3$. The impurity peaks of NiO are marked with stars.

Figure 2. Susceptibility of LaRh$_{1-x}$Ni$_x$O$_3$. An external field of 0.1 T is applied. The solid lines are guides to the eye.

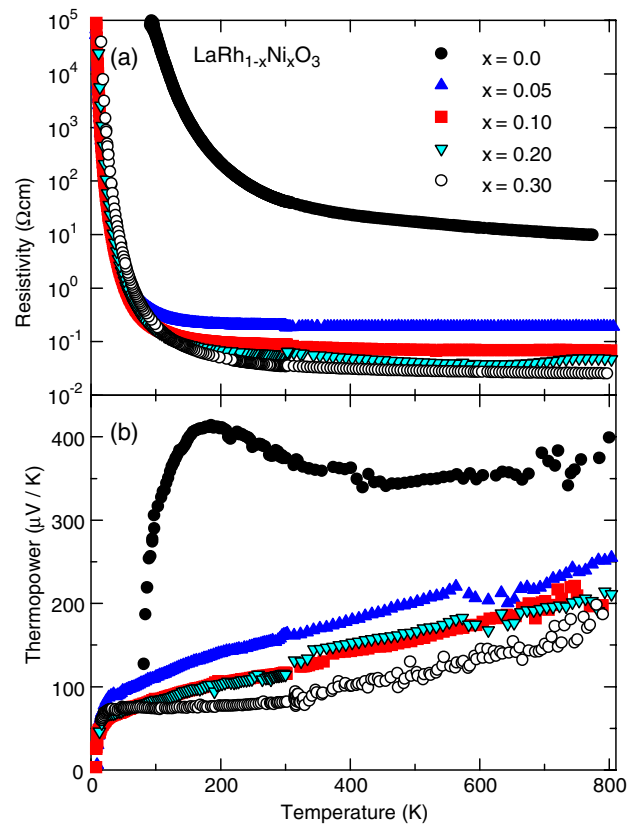**Figure 3.** (a) Resistivity and (b) thermopower of LaRh$_{1-x}$Ni$_x$O$_3$ from 4.2 to 800 K.

radiation by a θ–2θ method from 10 to 100°. The magnetic susceptibility measurements were performed using a magnetic property measurement system (MPMS, Quantum Design) with an external field of 0.1 T from 5 to 400 K. The low-temperature resistivity and the thermopower measurements were performed in a liquid He cryostat from 4.2 to 300 K. The high-temperature resistivity and thermopower measurements were performed in vacuum from 300 to 800 K. The resistivity was measured using a conventional four-probe technique and the thermopower was measured using a steady-state technique with a typical temperature gradient of 0.5–1 K. The thermal conductivity measurements were performed in a closed refrigerator using a steady-state technique from 8 to 300 K.

3. Results and discussion

Figure 1(a) shows the XRD patterns of LaRh$_{1-x}$Ni$_x$O$_3$ from $x = 0$ to 0.3. The lattice constants of these materials are shown in figure 1(b). The samples are in single phase for $x \leqslant 0.15$ and a small amount of NiO is detected above $x = 0.2$. We evaluate the volume fraction of the NiO impurity from the Rietveld simulation [17] to be less than 4% for $x = 0.3$. This suggests that more than 85% of the doped Ni ions are substituted for
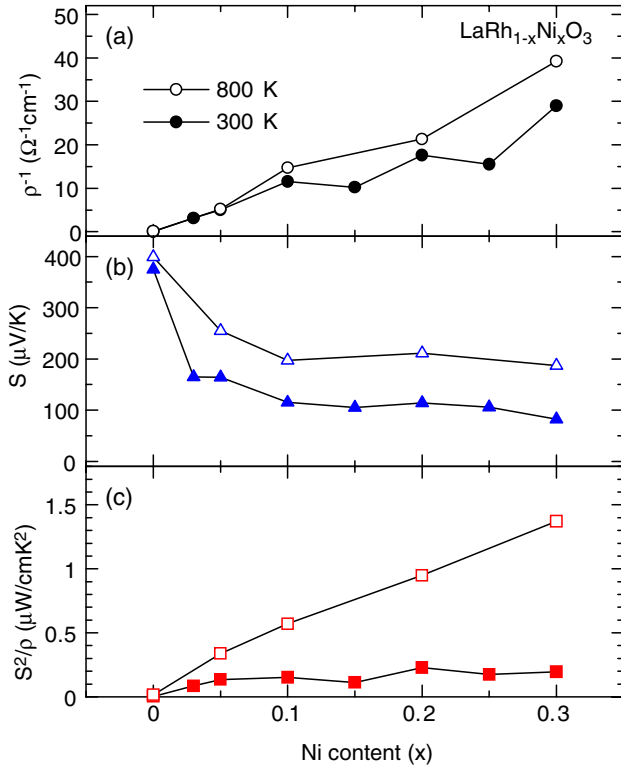
Rh ions in the $x = 0.3$ sample and we can safely neglect the effect of the NiO phase. We further note that the resistivity and the thermopower systematically change up to $x = 0.3$ (see figures 3 and 4), suggesting that the NiO impurity little affects the thermoelectric properties.

In our sintering condition, we expect that Ni ions are stable as divalent. On the other hand, a possible existence of Ni^{3+} was reported in La$_2$NiRhO$_6$ [18], and hence we measured the susceptibility of LaRh$_{1-x}$Ni$_x$O$_3$ in order to determine the valence state of Ni. Figure 2 shows the susceptibility of

Figure 4. Ni content (x) dependence of electric conductivity (ρ^{-1}), thermopower (S) and power factor (S^2/ρ) of $LaRh_{1-x}Ni_xO_3$ at 300 K (filled) and 800 K (unfilled).

Table 1. Comparison between $LaRh_{0.7}Ni_{0.3}O_3$ and $LaCo_{0.8}Ni_{0.2}O_3$. The subscripts represent measured temperatures.

	$LaRh_{0.7}Ni_{0.3}O_3$	$LaCo_{0.8}Ni_{0.2}O_3$
$\rho_{300 K}$ (mΩ cm)	36	10[a]
$\rho_{800 K}$ (mΩ cm)	25	1[b]
$S_{300 K}$ (μV K^{-1})	85	100[a]
$S_{800 K}$ (μV K^{-1})	185	15[b]
$S^2/\rho_{800 K}$ (μW cm K^{-2})	1.37	0.23[b]
$\kappa_{300 K}$ (mW cm K^{-1})	20	14[a]

[a] Reference [5].
[b] Reference [7].

decreases with x and reaches as low as 25 mΩ cm at 800 K for $x = 0.3$. The insulating behaviour of the resistivity at low temperature suggests that the substituted Ni ions work as scattering centres. This further assures us to regard the Ni ions as divalent. If the Ni ions were trivalent, the system could be regarded as a solid solution of $LaRhO_3$ and $LaNiO_3$, in which the resistivity would be dominated by the volume fraction of metallic $LaNiO_3$. Figure 3(b) shows the thermopower of $LaRh_{1-x}Ni_xO_3$ from 4.2 to 800 K. After the thermopower drastically decreases from $x = 0$ to 0.05, it gradually decreases with x above $x = 0.1$. We should note that the sign is always positive for all the samples, which further excludes the possible existence of Ni^{3+} ions giving negative thermopower [21]. We observe large thermopower up to 800 K, which suggests that Rh ions are in the low-spin state up to high temperature.

Figure 4 shows the electrical conductivity (ρ^{-1}), the thermopower (S) and the power factor (S^2/ρ) at 300 and 800 K as a function of Ni content x. We clearly see that the conductivity increases with x, which suggests that Ni is a suitable dopant. The thermopower is weakly dependent on x at high concentration. Thanks to these behaviours, we obtain a fairly large power factor which increases up to $x = 0.3$ in $LaRh_{1-x}Ni_xO_3$. Recently, Usui *et al* theoretically calculated the thermopower of doped $LaRhO_3$ as a function of carrier concentration [22], which agrees well with our experiment. This is quantitatively different from the power factor of conventional semiconductors, where it takes a maximum at an optimum carrier density of 10^{19}–10^{20} cm^{-3}. The thermoelectric parameters are listed for $LaRh_{0.7}Ni_{0.3}O_3$ and $LaCo_{0.8}Ni_{0.2}O_3$ in table 1. While the resistivity of $LaRh_{0.7}Ni_{0.3}O_3$ is 25 times higher than that of $LaCo_{0.8}Ni_{0.2}O_3$, its thermopower is 12 times larger at 800 K. This indicates that $LaRh_{0.7}Ni_{0.3}O_3$ shows a larger power factor at 800 K.

The thermal conductivity is essential to evaluating ZT. Figure 5(a) shows the thermal conductivity of $LaRh_{1-x}Ni_xO_3$ below 300 K. The magnitude of the thermal conductivity of $LaRhO_3$ and $LaRh_{0.7}Ni_{0.3}O_3$ is almost the same as that of $LaCo_{1-x}Ni_xO_3$ [5]. The electronic contribution is evaluated to be less than 1 mW cm K^{-1} at 300 K for $LaRh_{0.7}Ni_{0.3}O_3$ from the Wiedemann–Franz law, which means that the lattice contribution is dominant. ZT is calculated to be 3×10^{-3} for $x = 0.3$ and 6×10^{-5} for $x = 0$ at 300 K. The lattice thermal conductivity is dominant in both materials and the magnitude is almost the same. We assume the thermal conductivity of $LaCoO_3$ (25 mW cm K^{-1} at 800 K) [8] and evaluate ZT to be 0.044 for $x = 0.3$. We notice that this value itself is

$LaRh_{1-x}Ni_xO_3$ from 5 to 400 K. The inset of figure 2 shows the inverse susceptibility of $LaRh_{1-x}Ni_xO_3$. We obtain Curie constants of 6.10×10^{-2} and 1.11×10^{-1} emu mol^{-1} K^{-1} for $x = 0.05$ and 0.1 using the Curie law, respectively. Adopting a g factor of 2, we calculate Curie constants assuming Ni^{2+} in the high-spin state to be 5.0×10^{-2} and 1.0×10^{-1} emu mol^{-1} K^{-1} for $x = 0.05$ and 0.1, respectively. From these values, we conclude that substituted Ni ions are divalent (high spin) in our system. Conduction occurs in the Rh–O network and it is hard to see the magnetic susceptibility of Rh ions. Nakamura *et al* showed that both Rh^{3+} and Rh^{4+} ions are in the low-spin state [19]. Assuming that the oxygen content does not change greatly, we expect that the substitution of Ni^{2+} (the ion radius [20] $r = 0.70$ Å) for Rh^{3+} ($r = 0.67$ Å) creates Rh^{4+} ($r = 0.62$ Å) owing to the charge neutrality condition. In other words, two Rh^{3+} ions are replaced by Ni^{2+} and Rh^{4+} ions through this substitution. Then the 'average' ion radius of the dopant is $(0.70 + 0.62)/2 = 0.66$ Å, which is nearly equal to the ion radius of Rh^{3+}. Accordingly the lattice parameters are expected to depend weakly on x, which is consistent with the data in figure 1(b). A similar tendency is observed in $CuRh_{1-y}Mg_yO_2$, where Mg^{2+} (0.72 Å) ions are substituted for Rh^{3+} to create Rh^{4+} [14].

Now let us discuss the thermoelectric properties of $LaRh_{1-x}Ni_xO_3$. Figure 3(a) shows the resistivity of $LaRh_{1-x}Ni_xO_3$ from 4.2 to 800 K. Nakamura *et al* previously reported that the resistivity of $LaRhO_3$ was 45 Ω cm at room temperature with semiconducting behaviour [19], which is reproduced in our measurement. The resistivity systematically
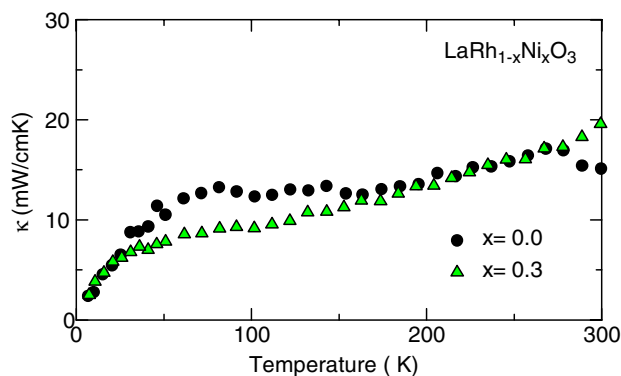
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Figure 5. Thermal conductivity of $LaRh_{1-x}Ni_xO_3$ from 8 to 300 K.

not yet satisfactory but should emphasize that it is three times larger than $ZT = 0.015$ for $LaCo_{0.95}Ni_{0.05}O_3$ at 800 K [8]. As far as we know, this is the first report for a Rh oxide to show better thermoelectric properties than the isostructural Co oxide. Assuming that the lattice thermal conductivity is zero, we find $ZT = S^2T/\kappa_{el}\rho = S^2/L_0$ by using the Wiedemann–Franz law, where L_0 is the Lorentz number [23]. Then $ZT > 1$ requires $S > 160\ \mu V\ K^{-1}$, which is satisfied in the present compound at 800 K. The thermopowers of the layered Co/Rh oxides and $LaRh_{1-x}Ni_xO_3$ exceed this value at high temperature. This comes from the stability of the low-spin state of the Co/Rh ions [9]. On the other hand, $LaCoO_3$-based materials show a thermopower less than 30 $\mu V\ K^{-1}$ at high temperature, which means that these compounds do not show $ZT > 1$ at high temperature. Thus we conclude that the spin state of Co/Rh ions in Co/Rh oxides plays a crucial role in oxide thermoelectrics. Unfortunately, the resistivity of $LaRh_{0.7}Ni_{0.3}O_3$ is still high, and hence ZT is low. This is perhaps because we substituted the Rh site, not the La site. We expect better thermoelectric properties in La-site-substituted $LaRhO_3$.

4. Summary

In summary, we have presented the transport data of $LaRh_{1-x}Ni_xO_3$ and have compared them with those of $LaCo_{1-x}Ni_xO_3$. Unlike $LaCo_{1-x}Ni_xO_3$, the thermopower remains large up to 800 K, which is ascribed to the conduction between the low-spin states of Rh^{3+} and Rh^{4+} ions. The dimensionless figure-of-merit is evaluated to be 0.044 for $x = 0.3$ at 800 K, which is almost three times larger than that for Ni-doped $LaCoO_3$. We propose that the spin-state control is a unique strategy for thermoelectric-materials design in transition-metal oxides.

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