Electrical resistivity in filled skutterudite La$_{x}$Rh$_{4}$As$_{12}$ at high pressures

K Arii$^{1}$, H Takahashi$^{1}$, H Okada$^{2}$, H Takahashi$^{2}$, M Imai$^{3}$, T Aoyagi$^{3}$, T Kimura$^{3}$, C Sekine$^{4}$, J Hayashi$^{4}$, N Hoshi$^{4}$, I Shirotani$^{4}$

$^{1}$Graduate School of Integrated Basic Science, Nihon University, Setagaya, Tokyo 156-8550, Japan
$^{2}$College of Humanities and Sciences, Nihon University, Setagaya, Tokyo 156-8550, Japan
$^{3}$National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan
$^{4}$Department of Electrical and Electronic Engineering, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

hiroki@chs.nihon-u.ac.jp

Abstract. A filled skutterudite La$_{0.48}$Rh$_{4}$As$_{12}$ was synthesized at 4 GPa and 1220 K. La$_{0.48}$Rh$_{4}$As$_{12}$ is a semiconductor with an energy gap of 0.03 eV at ambient pressure. Electrical resistance measurements at low temperatures and high pressures have indicated that La$_{0.48}$Rh$_{4}$As$_{12}$ is a semiconductor even at 20.0 GPa although a temperature change in the resistivity becomes small with pressure.

1. Introduction

Skutterudite TX$_{3}$ (T = transition metal elements, and X=P, As, and Sb) has the CoAs$_{3}$-type structure, in which T and X atoms form vertices-shared TX$_{6}$ octahedra [1]. Between the octahedral, there are large voids. Filling of large voids by A atoms (A = rare earth elements and so on) results in filled skutterudites AT$_{4}$X$_{12}$. AT$_{4}$X$_{12}$ have attracted attention because of their A-dependent physical properties including various interesting phenomena such as superconductivity, ferromagnetism and so on. Thus far, fourteen filled skutterudites have been reported to be superconducting at ambient pressure. La$_{4}$Rh$_{4}$P$_{12}$ exhibits the highest critical temperature for superconducting transition $T_{C}$ (17 K) among superconducting filled skutterudites [2]. When the value of $T_{C}$ is compared among the filled skutterudites that consist of the same A and T and different X elements, the value of $T_{C}$ in arsenides is
higher than that of phosphides or antimonides. For example, $T_C$ of LaRu$_4$As$_{12}$ (10.3 K) [3] is higher than those of LaRu$_4$P$_{12}$ (7.2 K) [4] and LaRu$_4$Sb$_{12}$ (3.58 K) [5]. Thus, La$_x$Rh$_4$As$_{12}$ is expected to have a higher $T_C$ than La$_x$Rh$_4$P$_{12}$. Namiki et al. reported the synthesis of La$_x$Rh$_4$As$_{12}$ at high pressures and high temperatures [6]. Although the electrical resistivity of La$_x$Rh$_4$As$_{12}$ shows the metallic behavior, an increase in resistivity with temperature, La$_x$Rh$_4$As$_{12}$ showed no superconducting transition down to 2K. Since a filled skutterudite PrRu$_4$P$_{12}$ shows pressure-induced superconductivity with a $T_C$ of 2.0 K at 14.7 GPa [7], it is interesting to measure the electrical resistivity of La$_x$Rh$_4$As$_{12}$ at high pressures.

In this study, we synthesized the filled skutterudite La$_x$Rh$_4$As$_{12}$ at high pressures and high temperatures, and characterized the chemical compositions. We also measured the pressure dependence of electrical resistivity at pressures up to 20.0 GPa and temperatures from 4 to 300 K. The results are partly described in Ref. 8.

2. Experimental

A starting material, a 1:4:12 molar mixture of La, Rh, and As, loaded in a h-BN capsule were pressurized and heated at 4.0 GPa and 1220 K for using a multi-anvil-type apparatus. Details of sample assembly were published elsewhere [9]. Chemical compositions were determined using electron-probe microanalysis (EPMA). Crystal structure of the synthesized sample was evaluated using powder X-ray diffractometry (Cu Kα).

A piston-cylinder-type clamp cell was used in electrical resistance measurements up to 1.5 GPa. A mixture of Fluorinert (FC70 : FC77 = 1 : 1) was used as a pressure-transmitting media. Electrical resistivity was measured by the dc four-probe method. Gold wires were attached to the sample using silver epoxy. The generated pressure in the cell was calibrated against the load using the pressure-fixed point of the Bi I-II transition.

A diamond anvil cell (DAC) was used in measurements at pressures ranging from 3 to 20 GPa. 0.2 mm thickness Re plate was used as gasket. Powdered NaCl was used as a pressure-transmitting media. Electrical resistivity was measured by the dc four-probe method using Pt thin films as lead wires.

**Figure 1.** X-ray diffraction pattern of sample together with simulated diffraction pattern of La$_{0.5}$Rh$_4$As$_{12}$. 
Sample and wires were electrically insulated from Re gasket by Al₂O₃ powder. The pressure in DAC was measured using ruby fluorescence method.

3. Results and discussion

Observations using a scanning electron microscope show that the synthesized sample consists of a single filled skutterudite phase. Chemical compositions were determined to be 2.8(1), 23.8(2), and 73.4(2) at. % for La, Rh, and As, respectively, which results in a chemical formula La₀.₄₈Rh₄As₁₂. Figure 1 shows the X-ray diffraction pattern of the sample together with a simulated pattern assuming that La₀.₃₅Rh₄As₁₂ has a lattice parameter of 8.5157 Å and internal parameter are the same as those of La₉Rh₄P₁₂ [10]. The main peaks in the observed pattern were reproduced in the simulated pattern, which indicates that La₀.₄₈Rh₄As₁₂ is the main phase in the sample. This result is consistent with EPMA results. The lattice parameter was evaluated to be 8.5157 Å, which is 0.77 % larger than that of RhAs₃ (8.4507(3) Å) [11].

Figure 2 shows an electrical resistance $R$ at various pressures up to 1.5 GPa as a function of temperature. An electrical resistivity at 292 K and ambient pressure is 6.71 mΩcm. The electrical resistance shows the semiconducting behavior, a decrease of $R$ with temperature, at ambient pressure. The inset shows electrical conductance, $1/R$, as a function of inverse temperature $1/T$. We obtained an energy gap to be 0.03 eV by fitting the data to the equation: $1/R = 1/R_0 \exp(-E_g/kB T)$, where $E_g$, $k_B$, and $R_0$ are an energy gap, the Boltzmann’s constant, and a constant, respectively. The semiconducting behavior was observed at high pressures up to 1.5 GPa.

![Figure 2](image1.png)

**Figure 2.** Electrical resistance at pressures ranging from 0 to 1.5 GPa as a function of temperature. The inset shows an electrical conductance as a function of inverse temperature $1/T$.

![Figure 3](image2.png)

**Figure 3.** Electrical resistance at pressures ranging from 3.1 to 20.0 GPa as a function of temperature.
Figure 3 shows electrical resistance at various pressures ranging from 3.1 to 20.0 GPa as a function of temperature. The temperature change in the resistivity becomes small with increasing pressure, which suggests a decrease of energy gap with pressure. The semiconducting behavior, however, was observed at highest pressures in this study, 20.0 GPa.

We observed a semiconducting behavior in the electrical resistivity of La$_{0.48}$Rh$_4$As$_{12}$, which is inconsistent with the results of previous report on LaRh$_4$As$_{12}$ [6], metallic behavior in the resistivity. In Ref. 6, LaRh$_4$As$_{12}$ was synthesized under the same pressure-temperature conditions as that used in this study; there is no description on La content. In order to discuss the discrepancy, we need systematic study on La content effect on physical properties in La$_x$Rh$_4$As$_{12}$.

4. Conclusion

We synthesized a filled skutterudite La$_{0.48}$Rh$_4$As$_{12}$ at 4 GPa and 1220 K. La$_{0.48}$Rh$_4$As$_{12}$ is a semiconductor with an energy gap of 0.03 eV at ambient pressure. Electrical resistance measurements at low temperature and high pressure indicate that La$_{0.48}$Rh$_4$As$_{12}$ is a semiconductor even at 20.0 GPa although the temperature change in the resistivity becomes small with pressure. Synthesis of La$_x$Rh$_4$As$_{12}$ at higher pressures is important for a further understanding of physical properties in La$_x$Rh$_4$As$_{12}$.

References

[1] Uher C 2001 Recent Trends in Thermoelectric Material Search I (Semicond. Semimetals 69), ed. T.M. Tritt (San Diego: Academic Press) chapter 5
[2] Shirotani I, Sato S, Sekine C, Takeda K, Inagawa I, Yagi T 2005 J. Phys.: Condens. Matter 17 7353
[3] DeLong L E, Meisner G P 1985 Solid State Commun. 53 119
[4] Shirotani I, Uchiumi T, Ohno K, Sekine C, Nakazawa Y, Kanoda K, Todo S, Yagi T 1997 Phys. Rev. B 56 7866
[5] Uchimi T, Shirotani I, Sekine C, Todo S, Yagi T, Kinoshita M 1999 J. Phys. Chem. Solids 60 689
[6] Namiki T, Hoshi N, Sekine C, Shirotani I 2005 Rev. High Press. Sci. Tech. 15, Special Issue, 1D03 (in Japanese).
[7] Miyake A, Shimizu K, Sekine C, Kihou K, Shirotani I 2004 J. Phys. Soc. Jpn. 73 2370
[8] Arii K, Igawa K, Okada H, Takahashi H, Imai M, Akaishi M, Sekine C, Hayashi J, Hoshi N, Shirotani I 2009 J. Phys.: J.Phys.: Conf. Ser. 052009
[9] Shirotani I 2003 Bull. Chem. Soc. Jpn. 76 1291
[10] Takeda K, Sato S, Hayashi J, Sekine C, Shirotani I 2007 J. Mag. Mag. Mater. 310, e1
[11] Kjekshus A, Rakke T 1974 Acta Chem. Scand. A 28 99