Electrical and magnetic properties of La$_{0.5}$Rh$_4$Sb$_{12}$ filled skutterudite synthesized at high pressure

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Abstract

A filled skutterudite, La$_{0.5}$Rh$_4$Sb$_{12}$, with a lattice constant of 9.284(2) Å was synthesized using a high-pressure technique. The electrical resistivity of La$_{0.5}$Rh$_4$Sb$_{12}$ showed semiconducting behavior and the energy gap was estimated to be more than 0.08 eV. Magnetic susceptibility measurements indicated temperature-independent diamagnetism, which originates from Larmor diamagnetism. The electrical properties of this compound are more similar to the La$_{0.5}$Rh$_4$As$_{12}$ semiconductor with an energy gap of 0.03 eV than to the La$_{0.6}$Rh$_4$P$_{12}$ superconductor.

Keywords: Semiconductors, Solid state reactions, Electronic properties, X-ray diffraction

1. Introduction

Filled skutterudites $R_xM_4X_{12}$ ($R$ = rare-earth; $M$ = Fe, Ru, Os, etc.; $X$ = P, As, and Sb), which crystallize with the LaFe$_4$P$_{12}$-type structure (Space group: $Im\bar{3}$, $Z$ = 2) [1], exhibit a variety of physical properties, including superconductivity, semiconductivity, ferromagnetism and antiferromagnetism, depending on the combination of $R$, $M$ and $X$ [2, 3].

The highest superconducting transition temperature $T_c$ among $R_xM_4X_{12}$ was 10.3 K for LaRu$_4$As$_{12}$ [4] before the discovery of superconductivity with $T_c = 17$ K for La$_{0.6}$Rh$_4$P$_{12}$, which was synthesized using the high-pressure technique.

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technique reported by Shirotani and colleagues in 2005 [5–8]. The relatively high $T_c$ in the latter filled skutterudite has encouraged materials scientists to search for new superconductors with the similar composition. One feature of La$_{0.6}$Rh$_4$P$_{12}$ is that it includes a cobalt group element, $M = \text{Rh}$; most of the existing filled skutterudites involve iron group elements. If filled skutterudites with cobalt group elements are synthesized under ambient pressure, then the site occupancy of $R$ atom becomes rather low, as reported for La$_{0.2}$Co$_4$P$_{12}$ [9] and La$_{0.05}$Rh$_4$Sb$_{12}$ [10]. Thus, the high site-occupancy of La$_{0.6}$Rh$_4$P$_{12}$ will be attributed to high-pressure synthesis, and is supposed to be essential to the superconductivity. A candidate for the new superconductor is La$_x$Rh$_4$Sb$_{12}$, because La$_{0.5}$Rh$_4$As$_{12}$ synthesized at high pressure was reported not to be a superconductor but rather a semiconductor with a narrow energy-gap $E_g$ of 0.03 eV [11, 12]. Therefore, with the aim of finding a new superconductor, a filled skutterudites La$_x$Rh$_4$Sb$_{12}$ was synthesized utilizing high-pressure techniques. The synthesis conditions were optimized to reduce the impurity phases and to obtain a sample with a high La-site-occupancy. Then, the electrical resistivity and magnetic susceptibility measurements were performed to verify whether La$_x$Rh$_4$Sb$_{12}$ is a superconductor.

2. Materials and methods

To determine the optimal conditions for the solid-state synthesis of polycrystalline La$_x$Rh$_4$Sb$_{12}$, samples were synthesized using starting materials with various atomic ratios at different temperatures and pressures. The purity of the starting materials was 99.9% for La, 99.9% for Rh and 99.999% for Sb. Rh$_{3.7}$Sb$_{12}$, which consists of RhSb$_3$ and Sb, was prepared in advance by solid state reaction at ambient pressure. These materials were weighed with molar ratios of La:Rh:Sb = 1:4:12 and 0.5:3.7:12, La:Rh$_{3.7}$Sb$_{12}$ = 0.5:1, and La:Sb = 1:3 in an argon-gas-filled glove box, and ground for 3 min using a vibrating mill. The following procedures are different between the high pressure and ambient pressure syntheses. For high pressure synthesis, the resulting powder was pressed into a pellet, placed in a hexagonal boron nitride capsule, sealed in a gold capsule under an argon gas atmosphere, and heat-treated at 1073 or 1173 K under pressures of 5.5 or 7.7 GPa for 2 h using a belt-type high-pressure apparatus [13]. For ambient pressure synthesis, a pellet of the milled materials was placed in an alumina crucible, sealed in a quartz tube under an argon gas atmosphere, and heat-treated at 1073 K for 100 h in an electric furnace. The samples were characterized using pow-
der X-ray diffraction (XRD; RINT TTR-III, Rigaku) with Cu Kα radiation (40 kV/150 mA). A one-dimensional position-sensitive Si detector was used. The chemical composition was determined from wavelength-dispersive X-ray spectroscopy (WDS) measurements using an electron probe microanalyzer (JXA-8500F, JEOL) and by energy-dispersive X-ray spectroscopy (EDS) with a scanning electron microscope (SU70, Hitachi High-Technologies). For physical property measurements, the sample with the least impurity phases was selected. Dc magnetization measurements were conducted using a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) under an applied field of $H = 10000$ Oe from room temperature down to 2.0 K. Four-probe electrical resistivity measurements were performed using an in-house-built apparatus with dc current density of 0.1 mA/mm$^2$. A $^3$He closed-cycle cryostat, of which the lowest temperature was 2.8 K, was used to cool the sample.

3. Results

3.1. Optimizing synthesis conditions

The synthesis pressure was initially optimized for a synthesis temperature of 1073 K with a stoichiometric 1:4:12 molar mixture of La, Rh and P as starting materials. Fig. 1(a), (b) and (c) show XRD patterns of three samples synthesized at ambient pressure, and at 5.5 and 7.7 GPa, respectively. All the strong peaks are indexed to RhSb$_3$ [14], which indicates that RhSb$_3$ or La$_x$Rh$_4$Sb$_{12}$ were formed. It is noted that filled skutterudites have similar diffraction patterns to unfilled skutterudites because they both have the same space group of $Im\bar{3}$ [6]. The $a$ lattice constants were estimated to be 9.231(1), 9.285(1) and 9.285(1) Å for the samples synthesized at ambient pressure, 5.5 and 7.7 GPa, respectively. The $a$ lattice constant for the sample synthesized at ambient pressure is the same as that for RhSb$_3$(9.232 Å) [14], while those for the samples synthesized at 5.5 and 7.7 GPa are significantly larger than that of RhSb$_3$. The weak extra XRD peaks of the samples produced at ambient pressure and at 5.5 and 7.7 GPa are attributed to LaSb$_2$ and RhSb$_2$, respectively. There was little difference between the samples synthesized at 5.5 and 7.7 GPa; therefore, 7.7 GPa was selected as the synthesis pressure for further experiments. A backscattered electron composition (BEC) image of the sample prepared at 7.7 GPa is shown in Fig. 2(a). The composition of the gray area was determined by WDS to be La$_{0.50}$Rh$_{3.72}$Sb$_{12.0}$. Here, we note that the compositional formula for the filled skutterudite is described with
Figure 1: XRD patterns for the prepared samples. For samples (a)-(c), the starting materials and synthesis temperature were fixed at La:Rh:Sb = 1:4:12 and 1073 K, while the synthesis pressures were ambient, 5.5 GPa, and 7.7 GPa, respectively. For sample (d), the synthesis conditions were La:Sb = 1:3, 1073 K and 7.7 GPa. The solid bars represent the Bragg peak positions for RhSb\textsubscript{3}, RhSb\textsubscript{2} and LaSb\textsubscript{2}. For RhSb\textsubscript{3}, the index numbers are noted beside the bars.
Figure 2: BEC images of samples prepared at 7.7 GPa with a starting material ratio of \(\text{La:Rh:Sb} = 1:4:12\) at (a) 1073 K and (b) 1173 K, and at 7.7 GPa and 1073 K with (c) \(\text{La:Rh:Sb} = 0.5:3.7:12\) and (d) \(\text{La:Rh}_{3.7}\text{Sb}_{12} = 0.5:1\).
Figure 3: XRD patterns of samples prepared with the starting material ratio and synthesis pressure fixed at La:Rh:Sb = 1:4:12 and 7.7 GPa for synthesis temperatures of (a) 1173 K and (b) 1073 K. The Bragg peak positions are marked for RhSb$_3$ and RhSb$_2$ with solid bars; the index numbers for RhSb$_3$ are noted beside the bars.
Figure 4: XRD patterns for samples prepared with synthesis conditions fixed at 1073 K and 7.7 GPa, and with starting material ratios of (a) La:Rh:Sb = 0.5:3.7:12, (b) La:Rh\textsubscript{3.7}Sb\textsubscript{12} = 0.5:1, and (c) La:Rh:Sb = 1:4:12. The peak positions are marked for RhSb\textsubscript{3} and RhSb\textsubscript{2} with solid bars; the index numbers for RhSb\textsubscript{3} are noted beside the bars.
the molar ratio of Sb being 12 in this article. Both the composition and XRD spectrum indicate that the filled skutterudite was successfully synthesized. The La site occupancy $x = 0.50$ was higher than La$_x$Rh$_4$Sb$_{12}$ ($x = 0.05$) synthesized at ambient pressure [10], which indicates that high pressure is effective for La insertion into unfilled skutterudites. In addition, these results suggest that the $a$ lattice constant increases with $x$. A large amount of impurity phases was also observed in Fig. 2(a). The white, dark gray and black areas were assigned to LaSb$_3$, RhSb and a mixture of Rh and Rh$_3$Sb, respectively. The XRD pattern of the largest impurity phase, LaSb$_3$, has not been reported; therefore LaSb$_3$ was synthesized at 7.7 GPa and 1073 K with the starting material ratio La:Sb = 1:3, and was confirmed by BEC imaging to consist of single phase LaSb$_3$ (not shown). The XRD pattern for LaSb$_3$ is presented in Fig. 1(d). The peaks are broad, which indicates the structural correlation length is short. The character makes it difficult to detect LaSb$_3$ impurity with XRD in La$_x$Rh$_4$Sb$_{12}$ sample (Fig. 1(c)), although a large amount of LaSb$_3$ exists.

The synthesis temperature was subsequently optimized for a synthesis pressure of 7.7 GPa. Figs. 3(a) and (b) present XRD patterns for the samples synthesized at 1173 K and 1073 K, respectively, using a starting material ratio of La:Rh:Sb = 1:4:12. The latter pattern is the same as that in Fig. 1(c), but is shown again for ease of comparison. Fig. 2(b) shows BEC image of the sample prepared at 1173 K. Besides peaks for La$_x$Rh$_4$Sb$_{12}$, strong RhSb$_2$ peaks are observed in Fig. 3(a). La$_{0.47-0.58}$Rh$_{3.77}$Sb$_{12.0}$, of which the composition was determined by WDS, occupies the small area in Fig. 2(b), and impurities of LaSb$_3$, Rh, and Rh-Sb phases such as RhSb$_2$, RhSb, Rh$_2$Sb, Rh$_3$Sb occupy a large area. The volume fraction of impurities is the larger for the sample prepared at the higher temperature of 1173 K than that at 1073 K, which indicates incongruent melting of La$_x$Rh$_4$Sb$_{12}$. For these reasons, 1073 K was selected as the optimal synthesis temperature. The appearance of a large amount of LaSb$_3$ impurity phase in both samples was attributed to an excess supply of La. Rh and the surrounding Rh-Sb phase were deduced to be non-equilibrium phases that appear due to the high melting temperature of Rh and the finite reaction time.

Finally, the starting material ratio was optimized by fixing the synthesis pressure and temperature at 7.7 GPa and 1073 K. Two starting material mixtures were attempted: a 0.5:3.7:12 molar mixture of La, Rh, and Sb and a 0.5:1 molar mixture of La and Rh$_3$Sb$_{12}$. Fig. 4 shows XRD patterns for the samples synthesized from these mixtures at 7.7 GPa and 1073 K,
together with the XRD pattern for the sample synthesized using a 1:4:12 molar ratio of La, Rh, and Sb. The peak intensity for the impurity phases is much smaller in the XRD pattern for the 0.5:3.7:12 molar ratio sample than that of the 1:4:12 molar ratio. BEC images of the sample synthesized using \( \text{La:Rh:Sb} = 0.5:3.7:12 \) and that using \( \text{La:Rh}_{3.7}\text{Sb}_{12} = 0.5:1 \) are presented in Figs. 2(c) and (d), respectively. The chemical compositions were determined from EDS measurements. The sample synthesized from the 0.5:3.7:12 molar ratio of La, Rh, and Sb consists of an almost single phase of \( \text{La}_{0.55(5)}\text{Rh}_{3.99(4)}\text{Sb}_{12.0(2)} \), although a small amount of \( \text{Au}_{0.14}\text{Sb}_{0.86} \) impurity phase was evident \cite{15, 16}, which could be due to contamination from the gold cell. In the sample synthesized using the mixture of La and \( \text{Rh}_{3.7}\text{Sb}_{12} \), a large amount of \( \text{RhSb}_2 \) impurity phase was confirmed from the results in Fig. 2(b) and Fig. 2(d), although a Rh impurity was absent. The La composition \( x \) in \( \text{La}_x\text{Rh}_4\text{Sb}_{12} \) fluctuates between 0.1 and 0.6 which indicates that the phase has not reached the equilibrium state within the heating time of 2 h. This may be because the reaction between La and \( \text{Rh}_{3.7}\text{Sb}_{12} \) is slow, because \( \text{RhSb}_3 \) is more stable than Rh and Sb. As a result, an appropriate condition for the synthesis of \( \text{La}_x\text{Rh}_4\text{Sb}_{12} \) was determined to be 1073 K and 7.7 GPa with a starting material ratio of \( \text{La:Rh:Sb} = 0.5:3.7:12 \).

The sample synthesized under the optimized conditions had a lattice constant of 9.284(2) Å and the chemical composition was 3.9(3) wt% La, 21.1(2) wt% Rh, and 74.9(2) wt% Sb, which corresponds to the chemical formula \( \text{La}_{0.55(5)}\text{Rh}_{3.99(4)}\text{Sb}_{12.0(2)} \).

### 3.2. Physical property measurements

The sample prepared with the optimized condition was used for physical property measurements. The temperature \( T \) dependence of the magnetic susceptibility \( \chi \) for \( \text{La}_{0.5}\text{Rh}_4\text{Sb}_{12} \) from 2 K to room temperature is shown in Fig. 5 which indicates weak diamagnetism that is independent of \( T \). The absence of perfect diamagnetism indicates that \( \text{La}_{0.5}\text{Rh}_4\text{Sb}_{12} \) is not a superconductor. In addition, the lack of paramagnetism derived from free electrons implies that this is not a metal, but a semiconductor or insulator. The diamagnetism was approximately \(-3.1\times10^{-7} \text{emu/(gOe)} \), which corresponds to \(-6\times10^2 \text{ cm}^3/\text{mol} \) for \( \text{La}_{0.5}\text{Rh}_4\text{Sb}_{12} \). This value is comparable to Larmor diamagnetism. The weak increase at low temperatures may be due to magnetic impurities.

Fig. 6 shows \( T \) dependence of the electrical resistivity \( R \) for \( \text{La}_{0.5}\text{Rh}_4\text{Sb}_{12} \). At \( T > 80 \text{ K} \), \( R \) decreases with increasing temperature, showing semicon-
Figure 5: Temperature $T$ dependence of the magnetic susceptibility $\chi$ of La$_{0.5}$Rh$_4$Sb$_{12}$ from 2 K to room temperature.
Figure 6: Temperature $T$ dependence of the electrical resistivity $R$ for La$_{0.5}$Rh$_4$Sb$_{12}$ from 2.8 K to room temperature. The inset shows the inverse temperature dependence of the conductivity, $1/R$, where the solid line represents the fit with the exponential function above 270 K.
ducting behavior. This is consistent with the diamagnetic susceptibility. In addition, the $R(T)$ curve has a plateau below 80 K, which may originate from extrinsic semiconductivity, in which temperature region, the carriers are supplied by impurities as dopants. This type of $R - T$ dependence has been observed in narrow gap semiconductors such as SrSi$_2$ [17] and FeSi [18]. The conductivity $1/R$ could not be fitted above 100 K with either the exponential function $\exp(-E_g/k_BT)$ or the variable range hopping model function $\exp(-(T_0/T)^{1/(1+d)})$ [19], where $k_B$ is the Boltzmann constant, $T_0$ is a characteristic temperature, and $d$ is the dimension ($d = 1, 2$ and $3$). Fitting with the exponential function above 270 K, as shown in the inset of Fig. 6, gives an energy gap of $E_g = 0.08$ eV, which indicates that $E_g$ is greater than 0.08 eV.

4. Discussion

The La site occupancy $x$ is roughly the same between La$_x$Rh$_4$X$_{12}$ synthesized at high pressures: La$_{0.6}$Rh$_4$P$_{12}$ [3], La$_{0.5}$Rh$_4$As$_{12}$ [11], and La$_{0.5}$Rh$_4$Sb$_{12}$. They are classed into two groups according to the electronic properties; La$_{0.6}$Rh$_4$P$_{12}$ is a superconductor, while La$_{0.5}$Rh$_4$As$_{12}$ and La$_{0.5}$Rh$_4$Sb$_{12}$ are semiconductors with $E_g = 0.03$ eV [12] and $E_g > 0.08$ eV, respectively. Corresponding unfilled skutterudites are similarly classified; an unfilled skutterudite RhP$_3$, which corresponds to La$_{0.6}$Rh$_4$P$_{12}$, is reported experimentally to be a metal [20, 21]. RhAs$_3$ and RhSb$_3$, which correspond to La$_{0.5}$Rh$_4$As$_{12}$ and La$_{0.5}$Rh$_4$Sb$_{12}$, respectively, are semiconductors with $E_g > 0.85$ eV [22] and $E_g = 0.8$ eV [23, 24], respectively. Thus, La$_{0.5}$Rh$_4$As$_{12}$ and La$_{0.5}$Rh$_4$Sb$_{12}$ have the similarities not only in the electrical properties but also in the changes in the electrical properties by La filling. This suggests that La insertion into metallic unfilled skutterudites will be a future strategy to find new superconductors.

The three compounds LaRu$_4$X$_{12}$ ($X = P$, As, Sb) are all superconductors [4, 25, 26], which implies that the superconductivity is insensitive to the difference of the species of pnictogens with the high La-site-occupancy. Thus, if higher occupancy is realized by higher pressures, superconductivity may be induced in La$_x$Rh$_4$Sb$_{12}$ and La$_x$Rh$_4$As$_{12}$, as in La$_{0.6}$Rh$_4$P$_{12}$. On the assumption that $x$ increases in proportion to the pressure, the full occupancy ($x = 1$) is realized at approximately 15 GPa for La$_x$Rh$_4$Sb$_{12}$. 
5. Summary

We have successfully synthesized the La$_{0.5}$Rh$_4$Sb$_{12}$ filled skutterudite with a high La concentration by utilizing a high-pressure technique. This adds a new example to filled skutterudites which involve cobalt group elements. In addition, the existence of the binary phase LaSb$_3$ at high pressure was confirmed. Electrical resistivity and magnetic susceptibility measurements revealed that La$_{0.5}$Rh$_4$Sb$_{12}$ is not a superconductor, but a semiconductor with an energy gap greater than 0.08 eV. The electrical properties are more similar to those of La$_{0.5}$Rh$_4$As$_{12}$ than those of La$_{0.6}$Rh$_4$P$_{12}$.

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