High-Pressure Synthesis and Structure of New Filled Skutterudite Compounds with Ge-substituted Host Network; *Ln*$Rh_4Sb_9Ge_3$, *Ln* = La, Ce, Pr, and Nd

Hiroshi Fukuoka* and Shoji Yamanaka

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527, Japan

Abstract

New filled skutterudite compounds $LnRh_4Sb_9Ge_3$ (Ln = La, Ce, Pr, and Nd) were prepared by high-pressure and high-temperature reactions at 800 ºC under a pressure of 7 GPa. The cubic lattice constants were 9.112(1), 9.118(2), 9.113(2) and 9.107(1) Å for La, Ce, Pr, and Nd compounds, respectively. Rietveld analysis of $LaRh_4Sb_9Ge_3$ confirmed that network Sb atoms were exclusively substituted with Ge atoms. The magnetic susceptibility measurement showed that the oxidation state of La, Ce, and Pr ions was 3+.

Keywords

A. rare earth alloys and compounds, B. solid state reactions, C. crystal structure D. high-pressure

*Corresponding Author
Dr. Hiroshi Fukuoka
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1
Kagamiyama, Higashi-Hiroshima, 739-8527, Japan
Phone: +81-82-424-7742.
Fax: +81-82-424-5494.
E-mail: hfukuoka@hiroshima-u.ac.jp

Introduction

From the finding of the anomalous superconductivity of $PrOs_4Sb_{12}$ [1], skutterudite compounds have attracted much attention of the researchers of solid state science. The filled skutterudite structure is illustrated in Fig. 1. It is composed of corner sharing MX_6 octahedra, where M represents transition metals of Group 8 and 9 and X shows elements of Group 15. Although the linkage of the octahedra is topologically the same with that in the ReO_3 structure, the bond angles of M – X – M are not linear in skutterudite compounds, and X – X bonds are formed as shown in Fig. 1. The X atoms form the host network having a cage-like structure which encloses guest atoms, usually rare earth elements, represented by Ln in Fig. 1.

So many filled skutterudite compounds having interesting physical properties such as superconductivity, heavy fermion, and non-Fermi liquid behavior, promising thermoelectric and non-linear optical properties, etc., have been reported [2-7]. Recently, new filled skutterudite compounds with heavy lanthanide elements have been synthesized by high-pressure and high-temperature reactions [8-11]. These findings have remarkably expanded the skutterudite chemistry, but the combination of Ln, M and X of filled skutterudite compounds is still limited. Most skutterudite compounds are categorized in the 9-15 type (M = Group 9, X = Group 15) or the 3-8(9)-15 type (Ln = Group 3, M = Group 8 or 9, and X = Group 15). Furthermore, the X site of filled skutterudite compounds is almost exclusively occupied by elements of Group 15. To our knowledge, only a series of iridium skutterudites were reported to contain Ge atoms in the Group 15 site [12-14]. We have, therefore, tried to prepare compounds containing elements other than Group 15 in the host network of the rhodium skutterudite structure.

In the present work, a series of new skutterudite compounds containing Ge in the host network have been prepared by high-pressure and high-temperature reactions. The structure and magnetic properties of them are discussed.

Experimental

We used a high pressure synthesis technique for the preparation of Ge-substituted skutterudite compounds. It is a very useful technique for the preparation of host-guest compounds of Group 14 elements [15], and the filled skutterudites can be considered as host-guest compounds. We used a Kawai-type (6-8 type) high-pressure system. In this system a sample is put in a pressure medium having an octahedral shape. Eight truncated cubic anvils made of WC surround and enclose the octahedron. The WC cubes are pressed in a high-pressure press having six anvils surrounding the cubes in order to apply a high-pressure to the sample.

Each starting mixture with an molar ratio of Ln (99.9%) : Rh (99.9%) : Sb (99.999%) : Ge (99.999%) = 1 : 4 : 9 : 3, where Ln = La, Ce, Pr or Nd, was placed in a small h-BN container with 2 mm in inner diameter and 4 mm in depth. The container was covered with Ta foil having a role of heater during reaction, and was put in a pyrophyllite tube with 6mm in diameter and 1 mm thick. A thermo couple was put around the BN container to control the reaction temperature. This sample unit was placed in an octahedral MgO pressure medium, and was put at the center of the eight WC anvils, and pressed in the way described above.

The samples for La, Ce and Pr were heated at 800 ºC under a pressure of 7 GPa for 1 hour and after decrease the temperature, the pressure was released slowly to ambient pressure. Only the Nd compound was prepared at 740 ºC. The products were examined using a Bruker D8 powder X-ray diffractmeter with CuKα radiation.

Rietveld structure analysis was performed on a powder sample of the La compound. The intensity data were collected stepwise on every 0.00738 º from $2\theta = 29$ to 109 º with Bulker D8 diffractometer using Cu Kα radiation. The structure refinement was performed using RIETAN-2000: Multi-Purpose Pattern-Fitting System [16]. The diffraction peaks were described by a Split Pearson VII function. In the refinement, occupational parameters of the Ge and Sb sites were refined using the next restriction: Ocp(Ge) + Ocp(Sb) = 1. Ocp(La) and Ocp(Rh) were also refined alternately. In the final least square cycle, Ocp(Rh) was fixed and other occupational parameters were refined.

Chemical compositions of the samples were determined with an electron probe microanalyzer (EPMA) (JEOL 733II). The standards used were Ge, Sb, LaB_6, CeB_6, PrB_6, and NdB_6. The magnetic susceptibility measurements were performed with a SQUID magnetometer applying a magnetic field of 3000 or 5000 Oe.

Results and Discussion

$RhSb_3$ with the skutterudite structure has a lattice constant of 9.232 Å [17]. As far as the authors know, no filled skutterudite compounds have been reported in the Rh-Sb system. Only a partially filled skutterudite $La_{0.05}Rh_4Sb_{12}$ with a lattice constant of 9.221 Å was reported [18]. However, the high-pressure reactions in the present work have successfully yielded filled skutterudite compounds. Observed XRD pattern of the La compound is shown in Fig.2(a). The pattern could be indexed in the filled skutterudite type structure having a cubic cell with a lattice constant of 9.112(1) Å. The smaller lattice constant of this compound than those of $RhSb_3$ and $La_{0.05}Rh_4Sb_{12}$ is due to the substitution of Ge for Sb. The chemical composition determined by EPMA was $La_{0.98}Rh_{3.86}Sb_{9.13}Ge_{2.87}$ and it is well corresponding to the composition of the starting mixture.

In order to confirm the substitution of Ge atoms for Sb atoms, Rietveld analysis was performed. It was found that the sample contained a small amount of $RhSb_2$ and RhGe. In the structure refinement, profile and atomic parameters of those minor products were also refined. The final refinement converged with Rwp = 4.66%, Rp = 3.59%, Re = 3.10%, R_I = 3.14%, R_F = 2.23%, and S = 1.5012. The result is shown in Fig. 3. The atomic parameters of $LaRh_4Sb_9Ge_3$ are listed in Table 1. The analysis clearly showed that the Ge atoms are substituted exclusively for the Sb atoms. The composition was calculated to be $La_{0.90(1)}Rh_{3.97}Sb_{8.3(2)}Ge_{3.7(2)}$. It is in good agreement with the composition determined by EPMA considering standard deviations. This is the first filled rhodium skutterudite compound containing a Group 14 element in the host cage.

$LnRh_4Sb_9Ge_3$ with Ln = Ce, Pr, and Nd were also prepared by the same reaction condition. The XRD patterns of them are shown in Figs. 2(b) to (d). The powder pattern of the Ce compound was indexed with a unit cell with a = 9.118(2) Å. The lattice constants for Pr and Nd compounds were 9.113(2) and 9.107(1) Å, respectively. The chemical compositions of Ce, Pr, and Nd compounds determined by EPMA were $Ce_{0.98}Rh_{3.87}Sb_{9.22}Ge_{2.78}$, $Pr_{0.92}Rh_{3.90}Sb_{9.25}Ge_{2.75}$, and $Nd_{0.91}Rh_{3.92}Sb_{9.50}Ge_{2.50}$, respectively. The result of chemical analysis as well as the similarity of the unit cell parameters with La compound shows that those are the filled skutterudite compounds including Ge atoms in the host network. In the Gd – Rh – Sb – Ge system, however, no skutterudite compounds were obtained as shown in Fig. 2(e). The product was a mixture of $RhSb_2$ and Gd_5Ge_4. The size of guest atoms is provably too small to fit inside the skutterudite cage in this system.

The lattice constants of the Ge-substituted skutterudite compounds are summarized in Fig. 4 with those of $RhSb_3$ and $La_{0.05}Rh_4Sb_{12}$ for comparison. The lattice constants for new compounds are much smaller than those of the compared compounds, but among the new compounds the lattice constants are almost the same even though the gust atoms are different. This would be due to the difference of the Ln and Ge contents among them. The size of the host cage becomes larger if the compound contains a smaller amount of Ge atoms. On the other hand, if the compound contains the guest atoms having small ionic radii and/or vacancies on the Ln site, the unit cell size becomes small. The observed lattice constants are determined by these two conflicting effects. The Nd compound contains the smallest amount of Ge among the new compounds. This is probably the reason why the lattice constant of the new skutterudite compounds becomes almost the same.

The reason why Ge atoms were successfully substituted in the present work can be explained using the total number of valence electrons as described by Tritt et al [14]. Skutterudite $CoAs_3$ has 96 valence electrons per 4 formula units (Co_4As_{12}). This condition fulfills the octet and 18 electron rules for As and Co atoms, respectively [2], and it is, therefore, considered as the electron precise condition. Meanwhile, most of the stable filled skutterudite compounds such as $LaRu_4P_{12}$ have 95 valence electrons per the formula unit. From these observations, it seems that the skutterudite compounds are easy to prepare if they have 95 to 96 valence electrons. In the present study we have designed the composition of new Ge-substituted compounds to have 96 electrons. According to this strategy, we have selected the 3-9-(15, 14) system having the composition of $LnM_4X_9Ge_3$, and have successfully substituted Ge atoms for a Group 15 element. The numbers of valence electrons for the obtained compounds are calculated to be 94.8, 95.1, 95.1, and 95.5e for La, Ce, Pr, and Nd compounds, respectively. Tritt et. al. applied a similar electron counting rule to the preparation of iridium skutterudite compounds containing Ge atoms [14]. The Ge substitution was succeeded in Rh and Ir systems by using this rule indicating it would be generally applicable to other filled skutterudite systems.

It is noteworthy that the chemical analysis suggested the transition metal site was not fully occupied. In the filled skutterudite compounds, the defect is often observed in the guest atom site but the defect of transition metal is quite rare. The detailed composition and structure of the Ge-substituted skutterudite compounds are now under investigation using single crystal X-ray analysis.

The temperature dependence of the magnetic susceptibility of Ce and Pr compounds showed the Curie-Weiss behavior. Figure 5 shows the results for the Pr compound. The calculated effective magnetic moments for Ce, and Pr compounds are 2.38 and 3.81 μ_B, respectively, which are well corresponding to the theoretical values of 2.54 (Ce^{3+}), and 3.58 (Pr^{3+}). Only the La compound did not show paramagnetic behavior. The susceptibility of it was very weak and temperature-independent. This can be explained by the non magnetic property of La^{3+}.

Conclusions

A series of filled skutterudite compounds $LnRh_4Sb_9Ge_3$ (Ln = Ln, Ce, Pr, and Nd) were prepared by high-pressure and high-temperature reactions. These compounds proved to have Ge atoms in the site for Group 15 elements from the results of EPMA and Rietveld structure refinement. The oxidation state of the guest atoms was

3+.

Acknowledgement

We are grateful to Mr. Yasuhiro Shibata of Hiroshima University for his help with the EPMA measurements. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan, Grant No. 16037212, 16750174, 18750182, and 18027010.

References

[1] E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, M. B. Maple, Phys. Rev. B 65 (2002) 1005061-1005064.

[2] A. F. Wells: *Structural Inorganic Chemistry* 5th Ed. (Oxford University Press, Oxford 1984), Chap. 6, p.267.

[3] G. P. Meisner, Physica B 108 (1980) 763-764.

[4] I. Shirotani, T. Uchiumi, K. Ohno, C. Sekine, Y. Nakazawa, K. Kanoda, S. Todo, T. Yagi, Phys. Rev. B 56 (1997) 7866-7869.

[5] N. Takeda, M. Ishihara, Physica B, 259-261 (1999) 92.

[6] H. Sugawara, T.D.Matuda, K. Abe, H. Sato, S. Nojiri, Y. Inada, R. Setti, Y. Onuki, Phys. Rev. B 66 (2002) 1344111-1344115.

[7] K. Nouneh, R. Viennois, I.V.Kityk, F.Terki, S.Charar, S.Benet, S.Paschen. Physica Status Solidi B 241 (2004) 3069.

[8] I. Shirotani, Y. Shimaya, K. Kihou, C. Sekine, T. Yagi, J. Solid State Chem., 174 (2003) 32-34.

[9] C. Sekine, T. Uchiumi, I. Shirotani, K. Matsuhira, T. Sakakibara, T. Goto, T. Yagi, Phys. Rev. B 62 (2000) 11581-11584.

[10] K. Kihou, I. Shirotani, Y. Shimaya, C. Sekine, T. Yagi, Mater. Res. Bull., 39 (2004) 317-325.

[11] I. Shirotani, N. Areseki, Y. Shimaya, R. Nakata, K. Kihou, C. Sekine, T. Yagi, J. Phys.: Condens. Matter., 17 (2005) 4383-4391.

[12] G.S.Nolas, G.A.Slack, T.Caillat, and G.P.Meisner, J. Appl. Phys., 79 (1996) 2622.

[13] G.S.Nolas, G.A.Slack, D.T.Morelli, T.M.Tritt and A.C.Ehrlich, J.Appl. Phys., 79 (1996) 4002.

[14] T.M.Tritt, G.S.Nolas, G.A.Slack, a.C.Ehrlich, D.J.Gillespie, J.L. Cohn, J. Appl. Phys., 79 (1996) 8412.

[15] A. San Miguel and P. Toulemonde, High pressure Research, 25 (2005) 159-185.

[16] F. Izumi and T. Ikeda, Mater. Sci. Forum, 321-324 (2000) 198-203.

[17] A. Kjekshus, T. Rakke: Acta Chim. Scand., A28 (1974) 99.

[18] L. Zeng, H. F. Franzen: J. Alloys Comp., 311 (2000) 224-225.

Table 1

Refined atomic parameters and isotropic thermal vibrational parameters of $LaRh_4Sb_9Ge_3$.

Space Group *Im*-3, *a* = 9.10125(13) Å, *V* = 753.88(2) Å

	Wyckoff notaion	Ocp	x	y	z	B
La	2a	0.947(11)	0	0	0	3.4(2)
Rh	8c	0.9856	1/4	1/4	1/4	1.21(8)
Sb	24g	0.690(13)	0	0.34402(11)	0.15575(11)	1.23(7)
Ge	24g	0.310	0	0.34402	0.15575	1.23

Figure Captions

[Fig.1] A unit cell of the filled skutterudite structure. Large and small black balls represent guest rare earth (Ln) and transition metal (M = Fe, Co, Ru, Os, etc.) elements, respectively. White balls show elements of Group 15 (P, As, and Sb). It is found in the manuscript that the Ge substitutes Sb atoms in $Ln\mathrm{Rh_4Sb_9Ge_3}$.

[Fig. 2] Powder XRD pattern of $\mathrm{LnRh_4Sb_9Ge_3}$; (a) La, (b) Ce, (c) Pr, (d) Nd, and (e) product of Gd – Rh – Sb – Ge system. The x mark indicates an unknown impurity phase.

[Fig.3] The result of Rietveld analysis of $\mathrm{LaRh_4Sb_9Ge_3}$. The observed data are shown as small crosses, the calculated fits and difference curves as solid lines. Tick marks of upper, middle, and lower rows indicate the calculated positions of peaks of $\mathrm{LaRh_4Sb_9Ge_3}$, $\mathrm{RhSb_2}$, and RhGe, respectively.

[Fig. 4] Comparison of the lattice constant of Ge-substituted skutterudite compounds $\mathrm{LnRh_4Sb_9Ge_3}$, Ln = La, C, Pr, and Nd. Lattice constants of $\mathrm{RhSb_3}$ and $\mathrm{La_{0.05}Rh_4Sb_{12}}$ are also shown for comparison. The double circle shows the lattice constant obtained by Rietveld analysis.

[Fig. 5] The temperature dependence of the magnetic susceptibility of $\mathrm{PrRh_4Sb_9Ge_3}$.

Figure 1

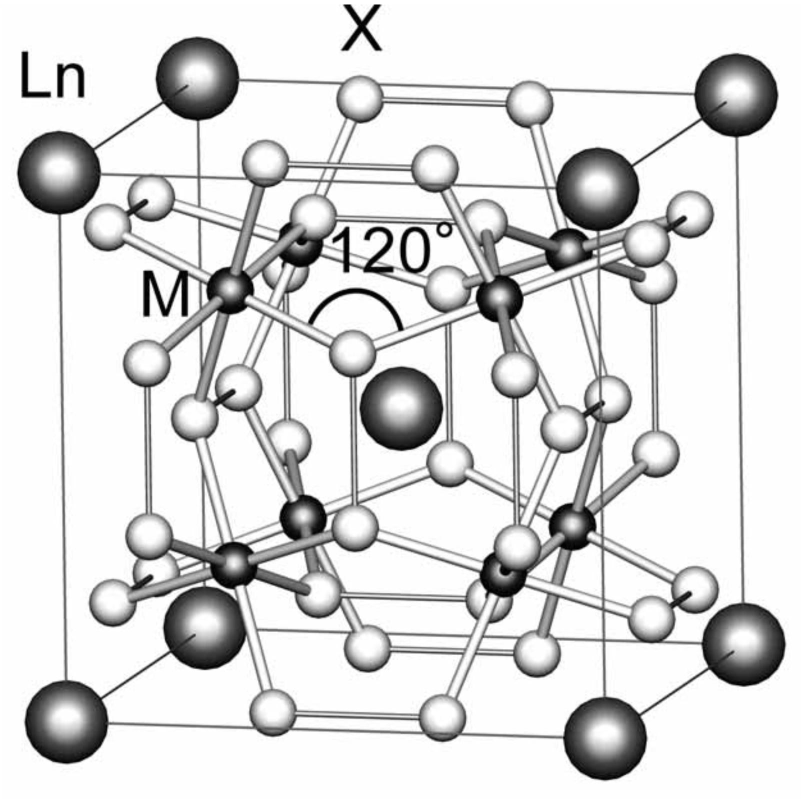


Figure 2

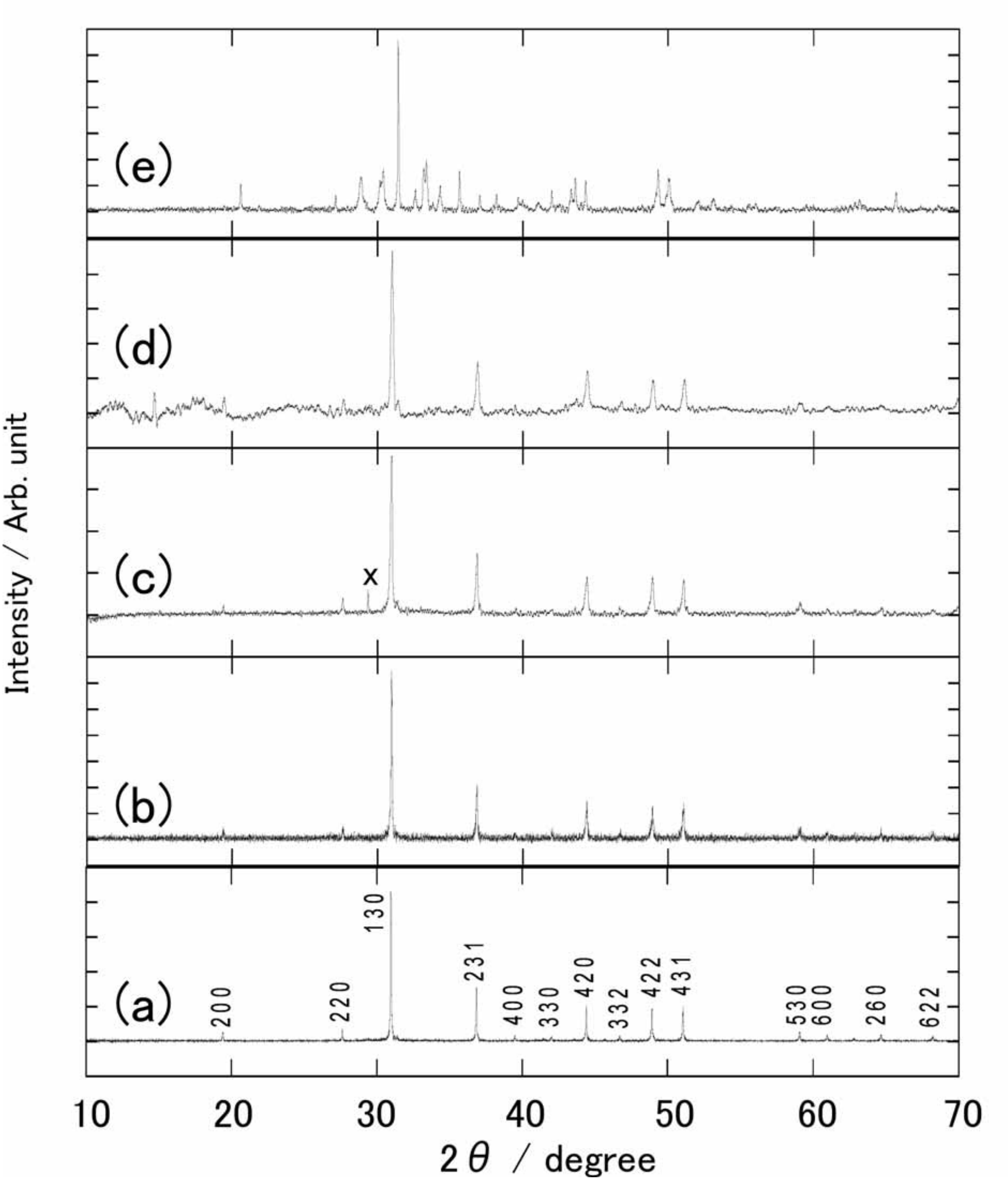

(e)
(d)
(c)
x
(b)
(a)
200
220
130
231
400
330
420
332
422
431
530
600
260
622
Intensity / Arb. unit
10
20
30
40
50
60
70
2θ / degree

Figure 3

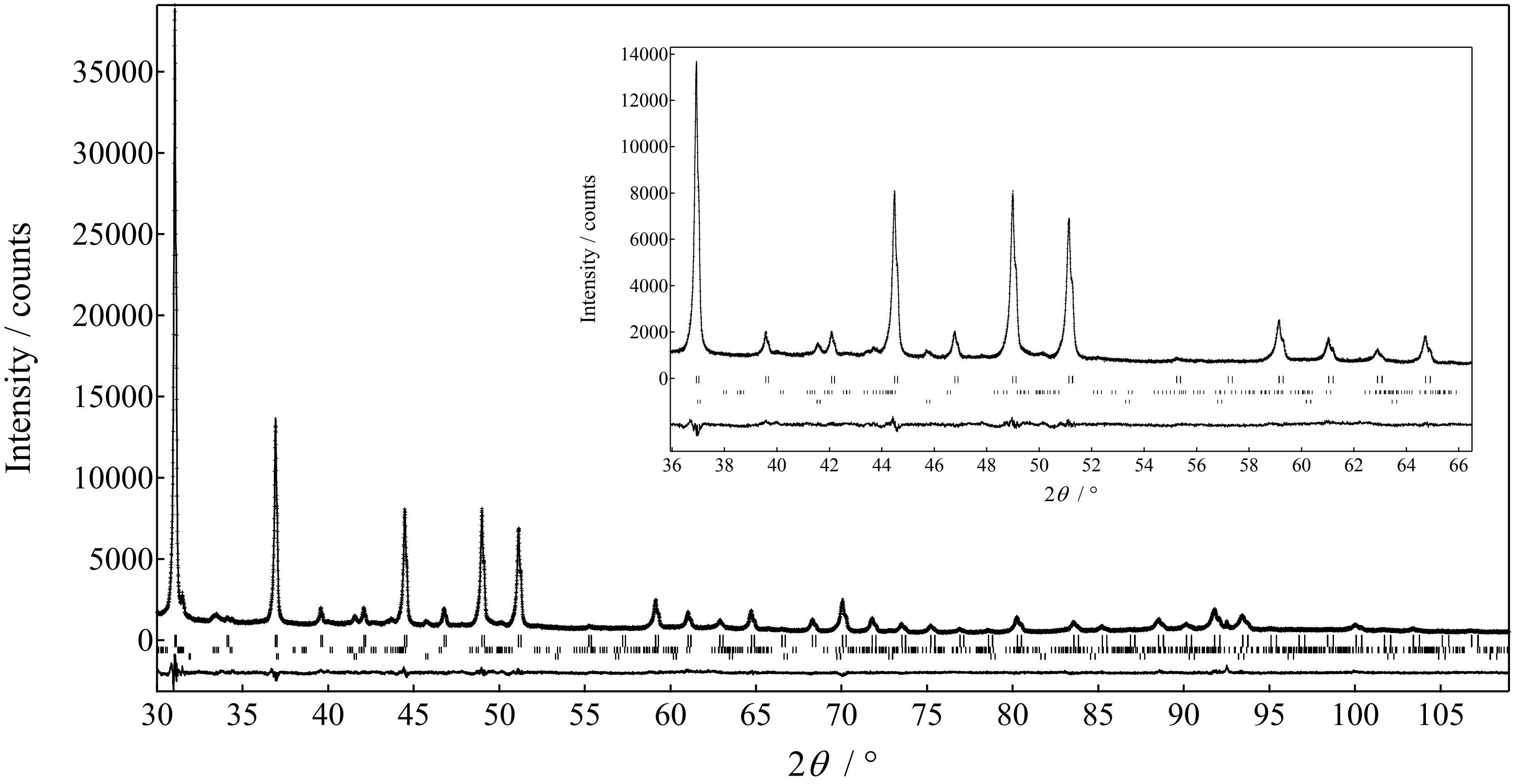

Intensity / counts
35000
30000
25000
20000
15000
10000
5000
0
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
2θ / °
Intensity / counts
14000
12000
10000
8000
6000
4000
2000
0
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
2θ / °

Figure 4

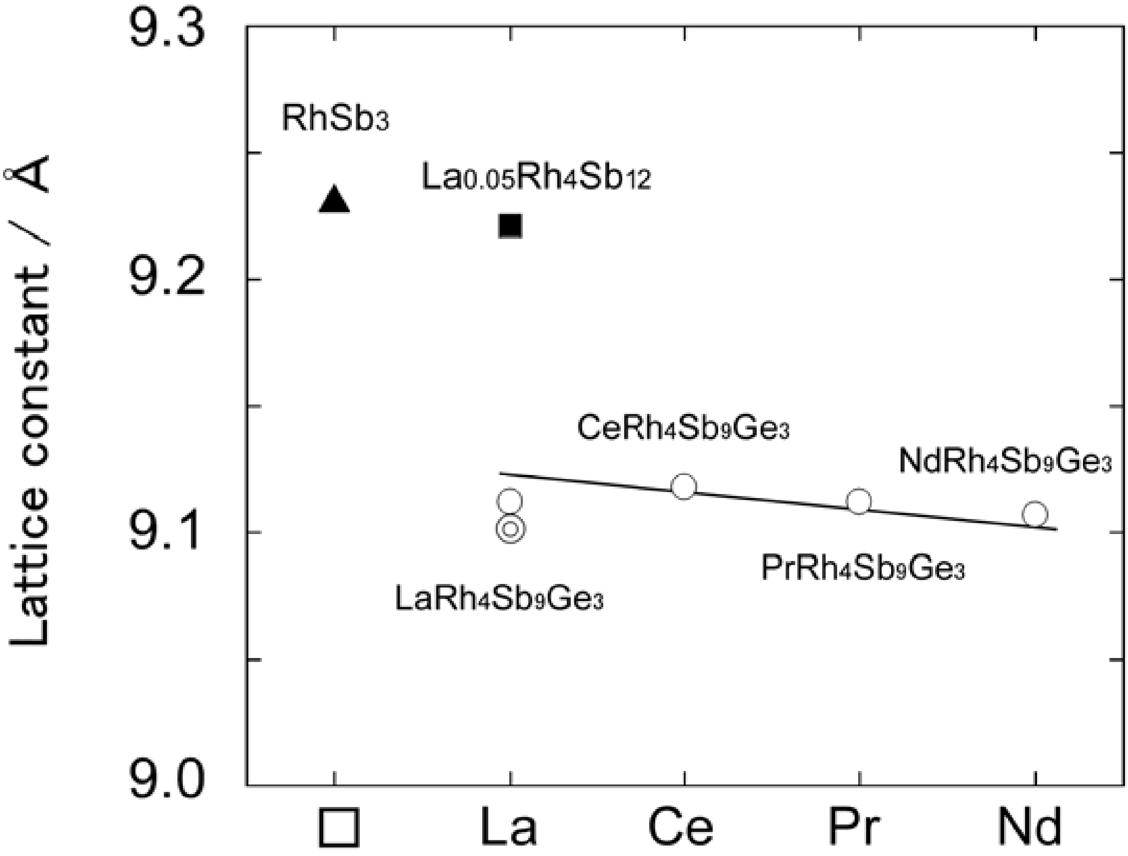
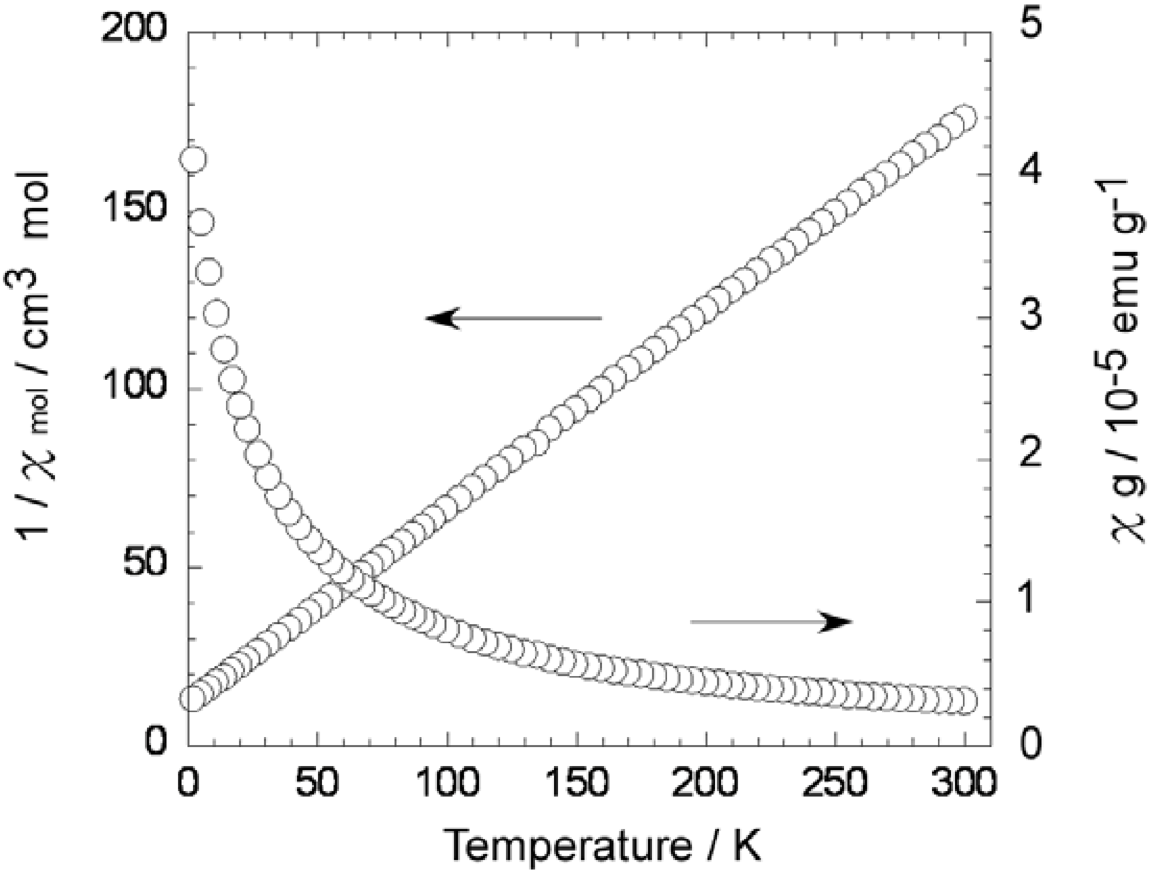

Lattice constant / Å
9.3
9.2
9.1
9.0
RhSb3
La0.05Rh4Sb12
CeRh4Sb9Ge3
NdRh4Sb9Ge3
PrRh4Sb9Ge3
LaRh4Sb9Ge3
□
La
Ce
Pr
Nd

Figure 5


200
150
100
50
0
1 / χ mol / cm3 mol
5
4
3
2
1
0
χ g / 10-5 emu g-1
0
50
100
150
200
250
300
Temperature / K