Structural and electrical properties of new filled skutterudite compound BaRu$_4$As$_{12}$ prepared at high pressure

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Abstract. X-ray powder diffraction patterns of BaRu$_4$As$_{12}$ with synchrotron radiation have been studied at ambient pressure and at high pressures. A crystal structure of BaRu$_4$As$_{12}$ was refined by the Rietveld analysis of the x-ray powder diffraction data at ambient pressure. The electrical property of BaRu$_4$As$_{12}$ have been studied at low temperature. This arsenide shows the metallic behavior. The volume vs. pressure curve for this arsenide has in detail been investigated at room temperature. The cell volume of BaRu$_4$As$_{12}$ decreased smoothly with increasing pressure up to 10 GPa. A bulk modulus was estimated from the volume vs. pressure curve fitted by a Birch equation of state. The bulk modulus ($B_0$) and its pressure derivative ($B'_0$) of BaRu$_4$As$_{12}$ are 127.0(2) GPa and 5.2(4), respectively. The value of $B_0$ for this arsenide is the same as that of CeRu$_4$As$_{12}$, smaller than that of LaRu$_4$As$_{12}$.

1. Introduction

Ternary metal arsenides with composition, LnT$_4$As$_{12}$ (Ln = lanthanide; T = Fe, Ru and Sb) were synthesized by reaction of the elemental components in silica ampoules [1]. These compounds crystallize in the skutterudite (CoAs$_3$-type) structure filled by lanthanide atoms [1]. The structure is cubic, space group $Im\bar{3}$, $Z = 2$. Ln atoms locate at (000) and (1/2 1/2 1/2) of a cubic structure like bcc packing. Transition metal atoms (T) are in the center of a distorted octahedral environment of six As atoms. We have prepared LnT$_4$As$_{12}$ at high temperatures and high pressures [2, 3]. The electrical and magnetic properties of these arsenides have been studied at low temperatures. LaRu$_4$As$_{12}$ and LaOs$_4$As$_{12}$ show the superconducting transition at 10.3 K and 3.2 K, respectively [2, 3]. The superconducting transition temperature (T$_c$) of LaRu$_4$As$_{12}$ is highest among filled skutterudite compounds. A metal to insulator transition for PrRu$_4$P$_{12}$ was found at 62 K under ambient pressure [4]. In contrast, PrRu$_4$As$_{12}$ behaves as an interesting superconductor with $f$ electrons below 2.4 K [2]. CeRu$_4$As$_{12}$ exhibits a semiconducting behavior with a small activation energy of 50 K [5].

We have prepared new filled skutterudite with alkaline earth metal BaRu$_4$As$_{12}$ at high temperature and high pressure and have studied the electrical property of this compound at low temperature. By use of synchrotron radiation, we have studied x-ray powder diffraction of BaRu$_4$As$_{12}$ at ambient pressure and high pressures. The crystal structure of BaRu$_4$As$_{12}$ is
refined by the Rietveld analysis of the x-ray powder diffraction data at ambient pressure. The volume vs. pressure curve for this arsenide has in detail been studied at room temperature.

2. Experimental details
Using a wedge-type cubic-anvil high-pressure apparatus, filled skutterudite compounds have been prepared at high temperatures and high pressures [2-5,8]. BaRu$_4$As$_{12}$ was prepared by reaction of stoichiometric amounts of each metal and arsenic powders at around 4 GPa. The reaction temperature was 850 °C. The product was characterized by x-ray powder diffraction using CuKα radiation and silicon as a standard at ambient pressure.

Copper lead was attached polycrystalline sample with silver paste, and four-lead electrical resistance measurement was performed at low temperature.

Using synchrotron radiation, x-ray powder diffraction patterns of BaRu$_4$As$_{12}$ were systematically measured with a diamond-anvil cell (DAC) and an imaging plate at room temperature and high pressures [7]. High-pressure diffraction experiments were performed at the beam line (18C) of the KEK Photon Factory in Tsukuba. We employed the DAC with diamond culet diameters of 500 μm. The sample was finely ground and loaded in the 100 μm diameter hole drilled in a stainless steel (T301) gasket. The pressure in the diamond-cell was measured before and after each exposure based on the shifts of the ruby R1 and R2 fluorescence lines. A 4:1 methanol-ethanol solution was used as the pressure medium.

The x-ray powder diffraction pattern of BaRu$_4$As$_{12}$ is measured with synchrotron radiation at ambient pressure. The synchrotron radiation experiments with $\lambda = 0.4126$ Å were performed at the BL10XU in the SPring-8 with the approval of Japan Synchrotron Radiation Institute (JASRI). The Rietveld refinement was carried out with the program (RIETAN-2000) developed by Izumi [9].

![Figure 1. Observed x-ray diffraction pattern, calculated profile and respective differences for BaRu$_4$As$_{12}$.](image)

**Table 1.** Positional parameters in BaRu$_4$As$_{12}$ obtained by the Rietveld analysis.

|      | Ba    | Ru    | As     |
|------|-------|-------|--------|
| Im3  | 2(a)  | 8(c)  | 24(g)  |
| $a$  | 8.55548(1) Å |       |        |
| $R_{wp}$ | 3.0% |       |        |
| $R_I$ | 3.8% |       |        |
| $S$  | 1.3   |       |        |
| $x$  | 0     | 1/4   | 0      |
| $y$  | 0     | 1/4   | 0.3536(1) |
| $z$  | 0     | 1/4   | 0.1509(1) |
| $B_{eq}$ | 0.53(3) | 0.39(2) | 0.58(2) |
3. Results and Discussion

The crystal structure of BaRu₄As₁₂ is refined with the Rietveld method for the x-ray powder diffraction data. The entire profile of x-ray diffraction in this compound is fitted to the calculated pattern. Figure 1 shows the observed x-ray diffraction pattern, the calculated profile and the respective differences for BaRu₄As₁₂. The agreement between both profiles is good. The structure is refined to \( R_{wp} = 3.0 \% \). The positional parameters in BaRu₄As₁₂ obtained by the Rietveld analysis are given in Table 1. We have already determined the crystal structure of CeRu₄As₁₂ by Rietveld analysis [6]. Bond distances and bond angles of BaRu₄As₁₂ and CeRu₄As₁₂ are summarized in Table 2. The skutterudite structure is characterized by formation of rectangular \( X_4^4^- \) clusters (\( X = P, As \) and \( Sb \)). The shape of the As₄ clusters in CeRu₄As₁₂ is close to square compared with that of BaRu₄As₁₂. The distance between Ru and As atoms is 2.4659 Å, shorter than the sum (2.53 Å) of the atomic radius (1.34 Å) of Ru and the covalent radius of As (1.19 Å). Thus, the Ru-As bond has a covalent character. The thermal equivalent isotropic parameter (\( B_{eq} \)) of BaRu₄As₁₂ is 0.53 Å². This value is smaller than that (1.3 Å²) of CeRu₄As₁₂.

| Table 2. Bond distances and bond angles for BaRu₄As₁₂ and CeRu₄As₁₂. |
|-------------------------------------------------|
| \( \text{BaRu}_4\text{As}_{12} \)               | \( \text{CeRu}_4\text{As}_{12} \) |
| \( a \) (Å)                                   | 8.5555                                | 8.4963                                |
| Ln-As (Å)                                    | 3.2893(4)                             | 3.2342(9)                             |
| Ln-Ru (Å)                                    | 3.7046                                | 3.6790                                |
| Ru-As (Å)                                    | 2.4659(9)                             | 2.4414(2)                             |
| As-As' (Å)                                   | 2.504(1)                              | 2.549(1)                              |
| As-As" (Å)                                   | 2.581(1)                              | 2.543(2)                              |
| Ln-As-Ru (°)                                 | 78.71(2)                              | 79.47(2)                              |
| Ln-As-As' (°)                                | 156.90(8)                             | 156.85(1)                             |
| Ln-As-As" (°)                                | 66.90(3)                              | 66.85(1)                              |
| Ru-As-As' (°)                                 | 111.07(7)                             | 110.37(2)                             |
| Ru-As-As" (°)                                 | 110.12(7)                             | 110.44(2)                             |
| Ru-As-Ru' (°)                                 | 120.31(5)                             | 120.92(1)                             |

Figure 2 shows the temperature dependence of the resistivity ratio \( \rho/\rho_{300K} \) of BaRu₄As₁₂. The resistivity of this compound decreases monotonically with decreasing temperature. BaRu₄As₁₂ shows the metallic behavior down to 2 K.

We have studied the x-ray powder diffraction of BaRu₄As₁₂ with the diamond anvil cell up to 10 GPa at room temperature. The \( d \)-values of the diffraction lines decrease with increasing pressure up to 10 GPa. The lattice constant (\( a \)) of BaRu₄As₁₂ decreases from 8.5361 Å at 0.3 GPa to 8.3578 Å at 10 GPa. New diffraction lines do not appear up to 10 GPa. When pressure is reduced from 10 GPa to the ambient pressure, the \( d \)-values of the diffraction lines return to those at ambient pressure. This behavior is completely reversible.

Figure 3 shows the relative cell volume \( (V/V_0) \) vs. pressure curve for BaRu₄As₁₂. The cell volume of BaRu₄As₁₂ monotonically decreases with increasing pressure up to about 10 GPa. This experimental data can be fitted by a Birch equation of state [10]:

\[
P = \frac{3}{2}B_0 \left\{ \left( \frac{V}{V_0} \right)^{-\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{-\frac{5}{3}} \right\} \cdot \left[ 1 - \frac{3}{4} \left( 4 - B'_0 \right) \left\{ \left( \frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right\} \right],
\]

(1)
where $B_0$ is the bulk modulus, $B_0'$ its first pressure derivative, $V$ the volume, and $P$ the pressure. A least-squares fit to the data of BaRu$_4$As$_{12}$ gives the following values: $B_0 = 127.0(3)$ GPa and $B_0' = 5.2(4)$. The bulk moduli of LaRu$_4$As$_{12}$ and CeRu$_4$As$_{12}$[6] have already been estimated from the x-ray diffraction data at high pressure. Lattice constant, $B_0$ and $B_0'$ of LnRu$_4$As$_{12}$ ($Ln =$ Ba, La and Ce) are summarized in Table 3. The largest bulk modulus is obtained for LaRu$_4$As$_{12}$. The value of $B_0$ for BaRu$_4$As$_{12}$ is the same as that of CeRu$_4$As$_{12}$, smaller than that of LaRu$_4$As$_{12}$.

| Compound     | Lattice constant (Å) | $B_0$ (GPa) | $B_0'$ |
|--------------|----------------------|------------|--------|
| BaRu$_4$As$_{12}$ | 8.5555               | 127.0(2)   | 5.2(4) |
| LaRu$_4$As$_{12}$ | 8.5081               | 136(3)     | 4.3(6) |
| CeRu$_4$As$_{12}$ | 8.4963               | 127(3)     | 5.5(9) |

4. Summary
We have synthesized new filled skutterudite with alkaline earth metal BaRu$_4$As$_{12}$ at high temperature and high pressure and the electrical property of BaRu$_4$As$_{12}$ have been measured at low temperature. This skutterudite shows the metallic behavior. A crystal structure of BaRu$_4$As$_{12}$ was refined by the Rietveld analysis of the x-ray powder diffraction data at ambient pressure. The bulk modulus of BaRu$_4$As$_{12}$ has been estimated from the x-ray diffraction data under high pressure. The value of $B_0$ for this arsenide is 127.0(2) GPa.

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