High-pressure Synthesis and Physical Properties of New Filled Skutterudite Compound BaOs4P12

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Abstract. We have succeeded in synthesizing samples of new filled skutterudite compound $BaOs_4P_{12}$ using the high-pressure synthesis technique. The physical properties of the compound are reported for the first time. The electrical resistivity decreases with decreasing temperature, and drop sharply around 1.8K. This indicates that $BaOs_4P_{12}$ is a new superconductor. Before the high-pressure synthesis, using synchrotron radiation x-ray, we tried to observe synthesizing processes of $BaOs_4P_{12}$ in-situ at high temperature and high pressure to obtain the optimum condition for synthesis.

1. Introduction

Filled skutterudite compounds AT_4X_{12} (A = alkali metal, alkaline earth metal, lanthanide (Ln), and actinide; T = Fe, Ru, Os, and Pt; X = P, As, Sb, and Ge) crystallize in a body-centered cubic structure with a space group $Im\bar{3}$ (T^5_h, No. 204) [1]. Filled skutterudite compounds, especially compounds including Ln, have attracted much attention owing to their wide variety of strongly correlated electron behaviors, such as anomalous metal-insulator transition [2], multipole ordering [3] and unconventional superconductivity [4]. The various attractive features in these systems are believed to be mainly due to the large hybridization between f electrons of Ln and p electrons of X. The d electrons of Fe, Ru and Os atoms should also play important roles in the physical properties. However, the roles have not been well understood yet. Matsuoka *et al*. reported that filled skutterudite compounds including alkaline earth metal AFe_4Sb_{12} (A = Ca, Sr, and Ba) have revealed strong ferromagnetic spin fluctuations of the Fe 3d electrons and the properties of nearly ferromagnetic metals [5]. Furthermore, AOs_4Sb_{12} (A=Sr, Ba) show the character of enhanced Pauli paramagnets where Os 5d electrons play important roles [6]. The filled skutterudite compounds including alkaline earth metal could be a favorable system to systematically investigate the effect of d electrons in skutterudite systems because alkaline earth ions carry no magnetic moments. However, only preliminary studies have been conducted on the properties of P and As-based compounds including alkaline earth metal because the compounds are quite difficult to prepare. In this study, we focused on P-based filled skutterudite compounds including alkaline earth metal as part of our search for new materials using a high-pressure synthesis technique.

2. Experimental

In-situ x-ray diffraction patterns were taken by an energy-dispersive method using synchrotron radiation and a solid-state detector. High pressure was applied using a multi-anvil assembly 6-6 with a cubic-anvil high-pressure apparatus, the MAX80 system, installed at the beam line AR-NE5C, at Photon

Factory (PF) in High Energy Accelerator Research Organization (KEK) (Tsukuba, Japan). The sample container made of pyrophyllite is formed a cube. The starting materials, which are mixture of Ba, Os and P, are put into a BN crucible. The crucible with a graphite heater is inserted in a cube-shaped pyrophyllite solid pressure medium. Pressure was determined by the lattice constant of NaCl internal pressure marker. The details of the in-situ observation method were described in previous reports [7, 8].

$BaOs_4P_{12}$ samples for measurements were prepared at high temperatures and high pressures using a double-stage multi-anvil high-pressure apparatus. The sample cell assembly is similar to that used for the high-pressure synthesis of $CeRu_4As_{12}$ [9]. The prepared samples were characterized by powder x-ray diffraction using Co$K_{\alpha 1}$ radiation and silicon as a standard. Resistivity was measured by a standard dc four-probe method in the temperature region from 0.4K to 300K.

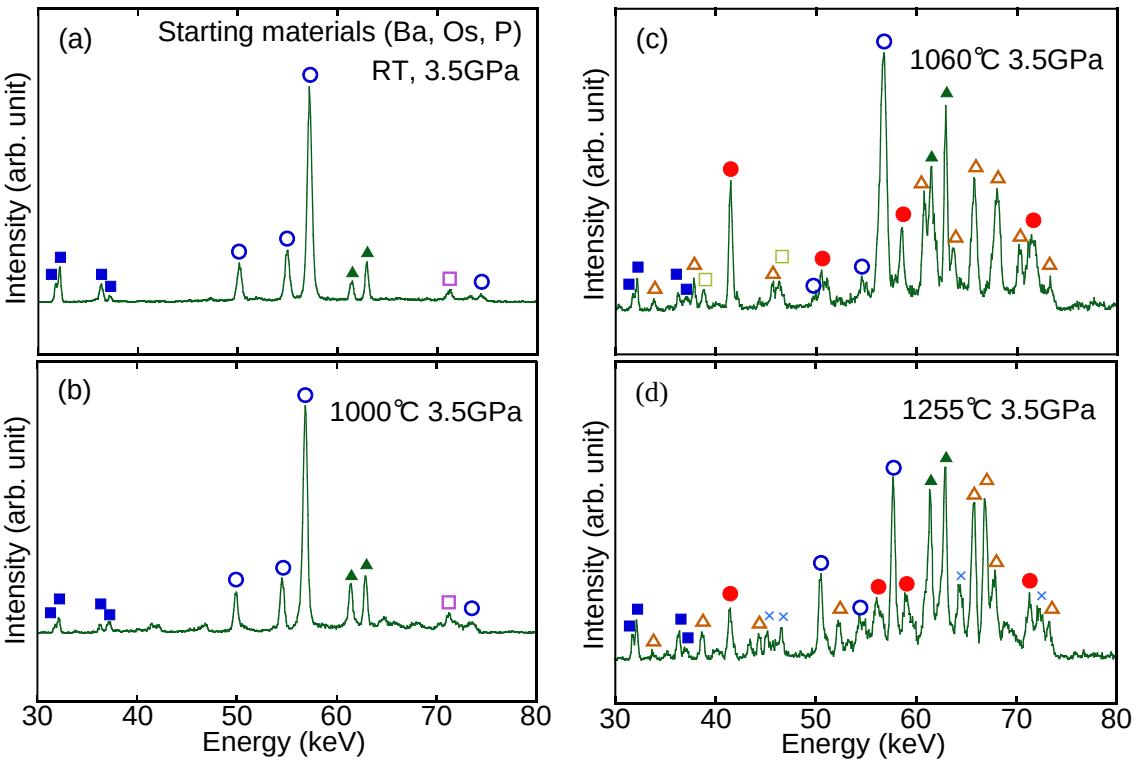

Figure 1. X-ray diffraction patterns of synthesizing process of $BaOs_4P_{12}$ at 3.5 GPa. Open blue circles designate the Bragg peaks of Os. Solid blue squares and solid green triangles indicate the characteristic x-ray of Ba and Os. Open purple squares indicate the peaks of BN used for crucible. Solid red circles designate the Bragg peaks of the skutterudite structure. Open brown triangles, open green squares and blue crosses indicate the peaks of an impurity phase of OsP_4, P_4O_8 and OsP_2, respectively. (a) The starting materials at room temperature, (b)1000℃, (c) 1060℃ and (d) 1255℃.

3. Results and discussion

The results of in-situ x-ray diffraction experiments are shown in figure 1. Figure 1(a) shows x-ray diffraction pattern of the starting materials, which are mixture of each metal and phosphorus powder in the atomic ratio of Ba : Os : P = 1 : 4 : 12, at room temperature and 3.5 GPa. Open blue circles designate the Bragg peaks of Os. Solid blue squares and solid green triangles indicate the characteristic x-ray for Ba and Os, respectively. Open purple squares indicate the Bragg peaks of BN used for crucible. The

diffraction peaks show no change up to 1000˚C (figure 1(b)). With increasing temperature above 1000˚C, the peaks of the skutterudite structure were observed above 1060˚C (closed red circles in figure 1(c)). The peaks for impurity phases of OsP_4 and P_4O_8, which are indicated by open brown triangles and open green squares, respectively, also appeared at this temperature. Elevating temperature up to 1255˚C, the peaks of the skutterudite structure weakened and another impurity phase of OsP_2 was observed (blue crosses in figure 1(d)). In series of the experiments, we found an appropriate temperature range of 1050-1200˚C for synthesizing $BaOs_4P_{12}$ at 3.5 GPa.

Based on the synthesis condition determined by the in-situ experiments, we have actually synthesized $BaOs_4P_{12}$ at 4GPa and 1050˚C using a Kawai-type two-stage anvil apparatus. Figure 2 shows a powder x-ray diffraction pattern of $BaOs_4P_{12}$ prepared under high pressure. Most of the observed diffraction peaks were indexable using the skutterudite structure. The lattice constant determined by a least-squares fit to the data was 8.124Å. Figure 3 plots the lattice constant of $BaOs_4P_{12}$ along with values reported earlier for filled skutterudite phosphides $LnOs_4P_{12}$ [10]. Starting with La, one observes the typical reduction of the lattice constant due to the contraction of the trivalent ionic radii of the lanthanides with increasing atomic number except for Ce and Eu compounds. The small lattice constant of Ce compound is due to the strong hybridization between 4*f* electrons and conduction electrons, while the large lattice constants of Eu compound is caused by the Eu ions being in the divalent or mixed-valence state. The large lattice constant of $BaOs_4P_{12}$ is considered to be due to the divalent Ba ions.

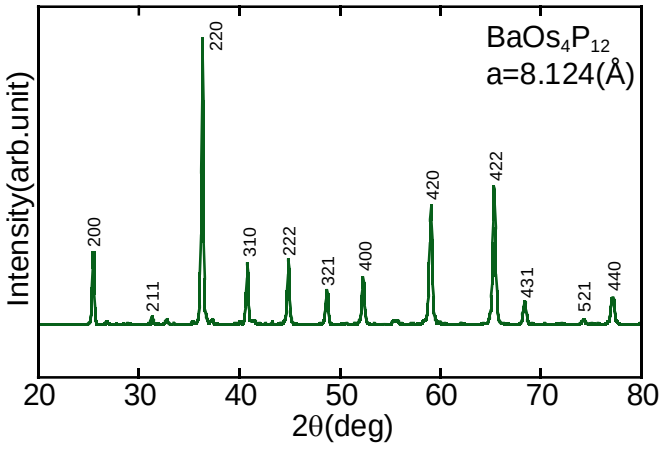

Figure 2. Powder x-ray diffraction pattern of $BaOs_4P_{12}$ prepared under high pressure.

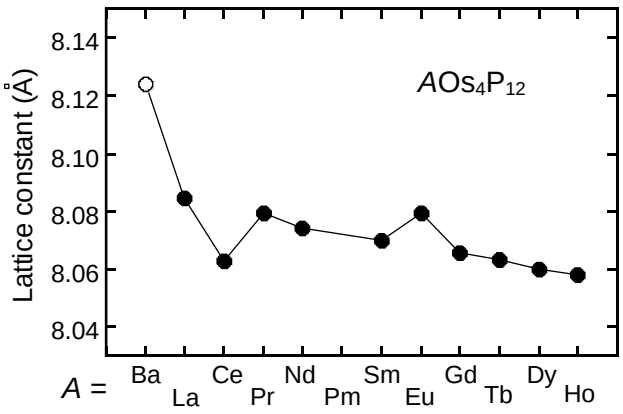

Figure 3. Lattice constants of filled skutterudite phosphides AOs_4P_{12}.

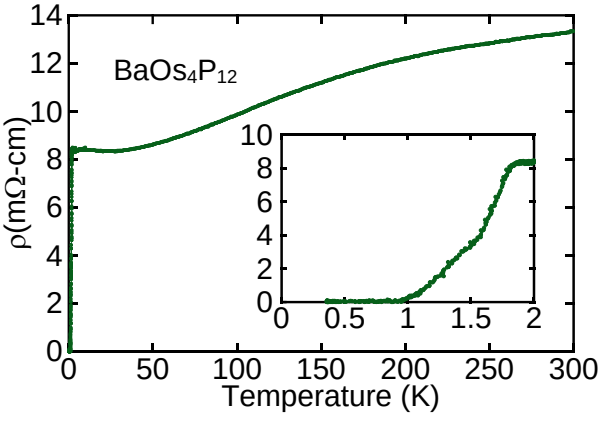

Figure 4. Temperature dependence of electrical resistivity of $BaOs_4P_{12}$. The inset shows the low temperature data on an expanded scale.

Figure 4 shows the temperature dependence of electrical resistivity ρ(T) for $BaOs_4P_{12}$. The inset shows the low temperature data on an expanded scale. The ρ(T) exhibits a positive temperature dependence like typical metals below room temperature and shows a sharp drop below 1.8K. This compound is a new superconductor. The application of a magnetic field suppresses superconductivity at fields above 1T. Furthermore, a broad shoulder around 170K in ρ(T) was observed. The strong curvature of the compound may be due to strong electron-phonon interactions, which was discussed for $A Os_4Sb_{12}$ (A = Sr, Ba). Matsuoka *et al*. proposed that the strong electron-phonon interaction in the presence of tunneling states of A^{2+} ions in the Os_4Sb_{12} cage is the origin of a similar shoulder observed in the resistivity of $A Os_4Sb_{12}$ (A = Sr, Ba) [6]. The electron-phonon interaction seems to be responsible for the formation of Cooper pairs in this system.

4. Summary

Using the high-pressure synthesis technique, we have succeeded in synthesizing a new skutterudite compound $BaOs_4P_{12}$ with lattice constant of 8.124Å. $BaOs_4P_{12}$ was found to be a new superconductors around 1.8K. We could obtained the optimum condition for synthesizing $BaOs_4P_{12}$ under high pressure by the in-situ x-ray experiments. This is an excellent method for determining the condition for obtaining only target material without impurity phases for solid-phase reaction synthesis under high pressure.

Acknowledgments

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