Single Crystal Growth of Skutterudite CoP$_3$
under High Pressure

C. H. Lee$^a$, H. Kito$^a$, H. Ihara$^a$, K. Akita$^b$, N. Yanase$^b$, C. Sekine$^b$ and I. Shirotani$^b$

$^a$AIST, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
$^b$Muroran Institute of Technology, 27-1 Mizumoto, Muroran 050-8585, Japan

Abstract

A new method to grow single crystals of skutterudite compounds is examined. Using a wedge-type, cubic-anvil, high-pressure apparatus, single crystals of CoP$_3$ were grown from stoichiometric melts under a pressure of 3.5 GPa. Powder x-ray diffraction and electron probe microanalysis measurements indicate that the as-grown boules are a single phase of CoP$_3$. The results suggest that CoP$_3$ is a congruent melting compound under high pressure.

Key words: High pressure, Phosphides, Skutterudite, Thermoelectric materials

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1 Introduction

Filled skutterudite compounds, RM$_4$X$_{12}$ (R = rare earth, M = Fe, Ru or Os; X = P, As or Sb), are of interest to the scientific community because of their potential as thermoelectric materials and the instability of their $f$ electrons. It is believed that the $f$ electron instability contributes to a wide variety of phenomena in the skutterudites, such as superconductivity, a metal-insulator transition [1,2,3] and magnetic ordering.

To clarify the nature of the $f$ electron instability, as well as to develop the thermoelectric performance of skutterudites, studies based on single crystals are essential. In particular, to improve the thermoelectric properties, it is important to clarify the origin of their superior thermoelectric performance. Filled skutterudites exhibit a remarkably low thermal conductivity, which enhances their performance. Great efforts, thus, have been made to clarify the origin of this low thermal conductivity. One proposed model that could explain the phenomenon is the so-called rattling effect. It is conjectured that phonons are scattered effectively by the free vibration of rare earth atoms in large lattice cages [4,5]. To examine the rattling
effect, phonon behavior should be studied by neutron scattering, which requires large single crystals.

To date, a number of groups have grown single crystals of various skutterudites. According to their reports, skutterudites are incongruent melting compounds. In the growth process, Sb or Sn were typically used as flux, and samples were sealed in evacuated silica tubes. The volume of grown binary skutterudites, such as CoSb$_3$ was typically 0.6 cm$^3$ [6]. For ternary filled skutterudites, on the other hand, a typical sample size was about 1 \times 1 \times 1 \text{ mm}^3 [7,8], considerably smaller than that of binary skutterudites.

In the growth of skutterudite single crystals by the flux method, however, several limitations have been identified. First, only a few skutterudite compounds have been able to be crystallized. This is a disadvantage in a comprehensive study of physical properties, where single crystals of a number of different skutterudites are necessary. Second, the size of the grown crystals of ternary filled skutterudites is limited. Larger single crystals are necessary in order to study fundamental properties by some methods, for example, by neutron scattering measurements. To solve these problems, the development of an original approach to the growth of skutterudite crystals may be beneficial.

In this study, we analyze the growth of single crystals of skutterudites performed under high pressure using a wedge-type, cubic-anvil, high-pressure apparatus. This technique was previously applied to enhance the growth of black phosphorus single crystals [9]. Using this method, single crystals of black phosphorus of dimension $4 \times 2 \times 0.2$ mm$^3$ were successfully grown under a pressure of 2.3 GPa. In this paper, we report that this technique is also useful for growing single crystals of skutterudites.

2 Experimental Details

CoP$_3$ single crystals were grown using a wedge-type, cubic-anvil, high-pressure apparatus (CAP-07, RIKEN). Fig. 1 shows a schematic representation of the sample cell assembly used in the experiment. The sample container is a cube composed of pyrophyllite with sides of length 15.3 mm. A carbon heater tube and a BN (boron nitride) crucible were inserted into the container. The size of the BN crucible was 6 mm in length and 4.5 mm in diameter. To estimate the temperature in the crucible during crystal growth, the relationship
between the applied electrical power and the temperature was predetermined without encasing the samples. Temperatures were measured up to \( \sim 1100^\circ \text{C} \) at the center of the carbon tube using Chromel-Alumel thermocouples at ambient pressure without employing any emf correction for the pressure effect. Temperatures above \( 1100^\circ \text{C} \) were estimated by extrapolating the obtained temperature calibration curve.

The raw materials of Co and P of 99.9\% crucibles after mixing them in a stoichiometric ratio. The filled crucibles were then immediately placed in the container and compressed to 3.5 GPa at room temperature. The samples were then heated to \( \sim 1100^\circ \text{C} \) and sintered for 1 hour to pre-synthesize CoP\(_3\) polycrystals. Subsequently, the samples were heated to \( \sim 1500^\circ \text{C} \) and maintained at that temperature for 1 hour. Finally, the samples were cooled to 1000°C over a period of 5 hours, followed by quenching to room temperature before pressure release.

The grown crystals were characterized by the following methods. Phase identification of the grown crystals was performed by powder x-ray diffraction (RINT-1000, RIGAKU) at room temperature using Cu Ka radiation. The composition of the grown crystals, as well as the distribution of the Co and P atoms, was examined by a JEOL JSM-6301F scanning electron microscope-x-ray energy dispersion spectrometer (SEM-EDS) with an accelerating voltage of 20 kV. A Li doped Si crystal was used as the SEM-EDS detector with an ultra-thin polymer window (CDU-Super-UTW, EDAX), that could detect elements ranging from Be to U. To estimate the concentration of Co and P atoms, characteristic x-rays of Co Ka and P Ka were used. A mapping analysis of the Co and P atoms was conducted with a scanning time of 10 ms/point and a measurement point density of 2500 points/mm\(^2\) over the entire boule cross-section. For the SEM-EDS measurements, the as-grown crystals were mechanically polished to mirror-like-surfaces. Back-reflection Laue x-ray measurements were performed with a collimator 1 mm in diameter to confirm that the grown crystals were single crystals.

### Results

Fig. 2(a) shows a cross section of the as-grown boule of CoP\(_3\). The shape of the boule is cylindrical, about 3.4 mm in diameter, with a number of cracks. The as-grown boule split quite easily along the radial direction to generate specimens \( \sim 1 \) mm in diameter and \( \sim 0.3 \) mm in length (Fig. 2(b)). Fig. 3 shows a back-reflection Laue x-ray photograph of the spec-
immen displayed in Fig. 2(b). In the photograph, 2mm symmetry is observed, indicating a (100) crystallographic plane. This result suggests that the specimen is a single crystal.

Powder x-ray diffraction measurements were carried out using powder ground from the as-grown boule (Fig. 4). The observed diffraction lines are all indexable using the skutterudite structure (space group Im3). No impurity phases are observed, suggesting that the entire as-grown boule is a single phase of CoP$_3$. The lattice constant determined by a least squares fit to the data was $a = 7.7067\,\text{Å}$, which is close to the literature value [10]. This agreement suggests that the grown crystals are of high purity.

Fig. 5 shows the distribution of Co and P atoms within the as-grown boule measured by SEM-EDS. The presence of the darker regions in the map is due to cracks, presumably formed during the cooling process. In the other regions, a homogeneous distribution of Co and P atoms is observed. We checked carefully that there were no additional elements present, especially around the cracks.

4 Discussion

In this study, single crystals of CoP$_3$ were grown from a stoichiometric melt under high pressure using a wedge-type, cubic-anvil, high-pressure apparatus. The entire as-grown boule was characterized as a single phase of CoP$_3$ by powder x-ray diffraction and SEM-EDS measurements. These results suggest that CoP$_3$ is a congruent melting compound under high pressure. Around ambient pressures, however, it is still unclear whether CoP$_3$ is a congruent melting compound or not, since the phase diagram of Co-P is incomplete [11]. Note that other skutterudites whose phase diagrams are well known, for example CoAs$_3$ and CoSb$_3$, are all incongruent melting
compounds around ambient pressures [12,13]. It is, thus, natural to assume that CoP$_3$ is also an incongruent melting compound around ambient pressures in contrast to the results under high pressure. Most likely, CoP$_3$ transforms from an incongruent to a congruent melting compound by the application of high pressures. If this presumption is true, other skutterudites may also melt congruently under high pressure, which would be a great advantage for growing single crystals.

The size of the CoP$_3$ single crystals produced in this study is typically \(\sim 1\) mm in diameter and \(\sim 0.3\) mm in length. To enlarge the size of single crystals, the cracks in the as-grown boules need to be eliminated. One possible solution to prevent cracking is to use a slower cooling rate. Another solution could be to apply a more homogeneous pressure by using a smaller crucible. Crystal growth from a single seed is also important for obtaining large single crystals. For this to take place, the temperature distribution in the furnace must be further optimized.

5 Conclusion

Single crystals of CoP$_3$ were grown from a stoichiometric melt under a pressure of 3.5 GPa using a wedge-type, cubic-anvil, high-pressure apparatus. The size of the grown single crystals is typically \(\sim 1\) mm in diameter and \(\sim 0.3\) mm in length. The as-grown boules were characterized by powder x-ray diffraction and SEM-EDS measurements and were determined to be a single phase of CoP$_3$. These results suggest that CoP$_3$ melts congruently under high pressure.

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