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Systematic high-pressure synthesis of new filled skutterudites with heavy lanthanide, $LnFe_4P_{12}$ (Ln = heavy lanthanide, including Y)

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Abstract

New filled skutterudites with heavy lanthanide, $LnFe_4P_{12}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) have systematically been prepared for the first time by the high-pressure technique. The relationship between lattice constants and atomic numbers of lanthanide (including Y) is established for $LnFe_4P_{12}$. Electrical and magnetic properties of several new filled skutterudites with heavy lanthanide have been studied at low temperatures; YFe_4P_{12} shows a superconducting transition at around 7 K, and $DyFe_4P_{12}$ behaves as a ferromagnet below 10 K. Electrical and magnetic anomalies in $DyFe_4P_{12}$ and YFe_4P_{12} are mainly discussed.

Keywords: High pressure; New filled skutterudite with heavy lanthanide; New superconductor; Magnetic property

1. Introduction

Filled skutterudites LnT_4X_{12} (Ln = lighter lanthanide, T = Fe, Ru and Os, X = P, As and Sb) show interesting physical properties at low temperatures. Superconducting [1–3], semiconducting [4], metal–insulator transition [5,6] and magnetic [7], heavy fermion [8], intermediate valence [9] and non-Fermi liquid behavior [10] have been observed in these materials. Further, skutterudite compounds exhibit remarkable thermoelectric properties [11]. These materials crystallize in a filled skutterudite-type structure (cubic, space group: *Im*-3) [6,12]. Filled skutterudites with lighter lanthanide were frequently prepared by fluxed methods [1,12]. However, we have prepared many filled skutterudites with lighter lanthanide at high temperatures and high pressures [2,4,5]. On the other hand, filled skutterudites with heavier lanthanide, $GdRu_4P_{12}$ and $TbRu_4P_{12}$ were prepared only at high pressure [13,14]. We have succeeded to prepare for the first time new filled skutterudites with heavy lanthanide, $LnFe_4P_{12}$ (Ln = heavy lanthanide, including Y) by the high-pressure technique. Electrical and magnetic properties in new interesting skutterudites $DyFe_4P_{12}$ and YFe_4P_{12} are discussed.

2. Experimental

By use of a wedge-type cubic-anvil high-pressure apparatus, many filled skutterudites with lighter lanthanide have been prepared at high temperatures and high pressures [2,4,5]. The upper and lower stages of the high-pressure apparatus consist of three anvils that slide on the wedge formed in shallow V-shaved grooves. The anvil's movement is completely synchronized by means of a wedge system. The sample assembly for the preparation of filled skutterudites is similar to that used for the high-pressure synthesis of black phosphorus [15]. New filled skutterudites with heavy lanthanide, $LnFe_4P_{12}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) were systematically prepared by the reaction of stoichiometric amounts of each metal and red phosphorus powders at pressures between 4 and 5 GPa. The reaction temperatures were between 1000°C and 1100°C. These products were characterized by powder X-ray diffraction using Cu$K\alpha$ radiation and silicon as a standard at ambient pressure.

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3. Results and discussion

Fig. 1 shows an X-ray diffraction pattern of $DyFe_4P_{12}$ at room temperature and at ambient pressure. This profile is indexed in the filled skutterudite-type structure. X-ray diffraction patterns of $Ln\mathrm{Fe_4P_{12}}$ (Ln = Tb, Ho, Er, Tm, Yb, Lu and Y) are very similar to those of $DyFe_4P_{12}$. Lattice constants and densities of new compounds prepared at high pressure are summarized in Table 1. Fig. 2 shows the relationship between lattice constants and atomic numbers of lanthanide (including Y). The lattice constants of $Ln\mathrm{Fe_4P_{12}}$ (Ln = lanthanide) basically decrease with increasing atomic number. However, some anomalies in this curve are observed for Ce, Eu and Yb compounds. These may closely be related to the valence states in the materials.

Fig. 3 shows dc magnetic susceptibility and inverse susceptibility of $DyFe_4P_{12}$ measured in a magnetic field of 1 Tesla (T) at low temperatures. The susceptibility of $DyFe_4P_{12}$ follows a Curie–Weiss behavior at high temperatures. The linear slope of χ^{-1} vs. T curve from 20 to 300 K yields an effective magnetic moment of 10.70 μ_B. This value is in good agreement with the magnetic moment of Dy^{3+} ion calculated from Hund's rule, 10.63 μ_B. The magnetic feature at around 10 K in $DyFe_4P_{12}$ suggests the occurrence of ferromagnetic ordering below this temperature. The electrical anomaly based on the magnetic ordering in this compound is observed at around 10 K.

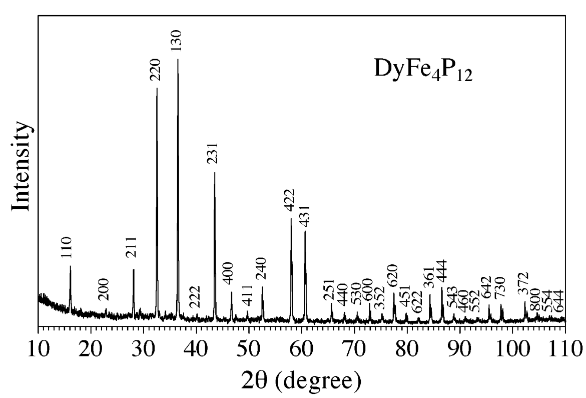

Fig. 1. X-ray diffraction pattern of $DyFe_4P_{12}$ at ambient pressure.

Table 1
Lattice constant, cell volume and density for new filled skutterudites with heavy lanthanide, $Ln\mathrm{Fe_4P_{12}}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) prepared at high pressure

—	a (Å)	Volume (Å^3)	Density (g/cm^3)
$TbFe_4P_{12}$	7.7926(2)	473.20(5)	5.292
$DyFe_4P_{12}$	7.7891(2)	472.56(3)	5.324
$HoFe_4P_{12}$	7.7854(1)	471.89(2)	5.349
$ErFe_4P_{12}$	7.7832(2)	471.49(4)	5.370
$TmFe_4P_{12}$	7.7802(1)	470.96(2)	5.388
$YbFe_4P_{12}$	7.7832(1)	471.50(2)	5.410
$LuFe_4P_{12}$	7.7771(3)	470.38(5)	5.437
YFe_4P_{12}	7.7896(1)	472.65(1)	4.806

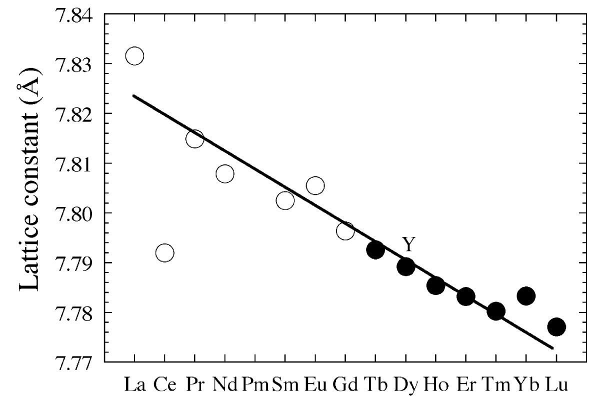

Fig. 2. Relationship between lattice constants and atomic numbers of lanthanide (including Y) for $Ln\mathrm{Fe_4P_{12}}$ (Ln = lanthanide). Black circle shows new filled skutterudites with heavier lanthanide, $Ln\mathrm{Fe_4P_{12}}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) prepared by us. The lattice constant of YFe_4P_{12} almost agrees with that of $DyFe_4P_{12}$. This is shown by the symbol Y in the figure.

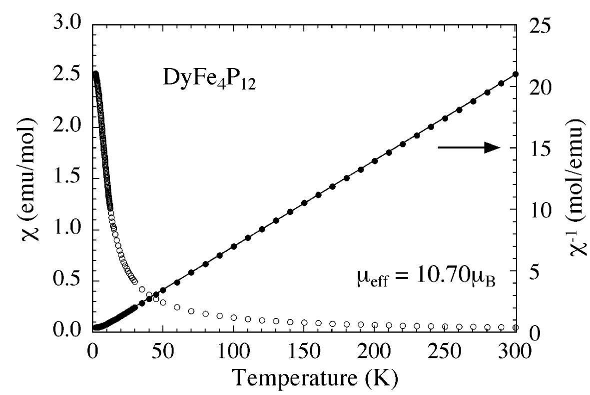

Fig. 3. Magnetic susceptibility and inverse susceptibility of $DyFe_4P_{12}$ measured in a magnetic field of 1 T at low temperatures.

Fig. 4 shows the resistivity vs. temperature curve for YFe_4P_{12} at low temperatures. The resistivity decreases with decreasing temperature, and drops sharply at around 7 K. Magnetic susceptibility measurements of this compound are carried out at low temperatures. The sample cooled in zero field shows a magnetic shielding equal to approximately 100% of that expected for perfect diamagnetism. This compound is a new superconductor. One of the most striking features of filled skutterudites is the occurrence of the superconductivity in $LaFe_4P_{12}$ and YFe_4P_{12} with the ferromagnetic element Fe. The T_c (on set) of YFe_4P_{12} is about 3 K higher than that (4.1 K) of $LaFe_4P_{12}$ [1]. Recently, Shimizu et al. have reported that iron behaves as a superconductor below 2 K at pressures between 15 and 30 GPa [16]. The superconducting transitions in $M_2\mathrm{Fe_3Si_5}$ (M = Sc, Y and Lu) were observed at around 2–6 K [17]. A new superconductor YFe_4P_{12} has the

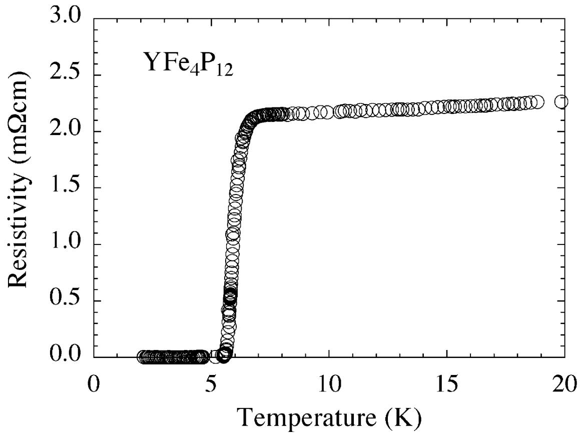

Fig. 4. Resistivity vs. temperature curve for YFe_4P_{12} at low temperatures.

highest T_c among the materials containing ferromagnetic element Fe.

Acknowledgments

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