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Sm系及びCe系充填スクッテルダイト化合物の熱電特性

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Thermoelectric Properties of Sm and Ce Based Filled Skutterudite Compounds

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Filled skutterudites have been actively studied as potentially useful thermoelectric materials. $\text{SmT}_4\text{P}_{12}$ ($T=\text{Fe, Ru, Os}$) and $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ ($T=\text{Ru, Os}$) ($0 \leq x \leq 0.2$) with the filled skutterudite-type structure have been prepared at high temperature and high pressure. The structure of samples was characterized by powder X-ray diffraction. The thermoelectric properties of these compounds have been investigated by means of electrical resistivity, Seebeck coefficient and thermal conductivity measurements. $\text{SmFe}_4\text{P}_{12}$ and $\text{SmOs}_4\text{P}_{12}$ behaved metallic down to 5K, while $\text{SmRu}_4\text{P}_{12}$ shows metal-insulation transition around 16K. $\text{SmFe}_4\text{P}_{12}$ showed significantly high values of Seebeck coefficient ($46\mu\text{V/K}$), comparing to other metallic compounds at the temperature 600K. $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ ($T=\text{Ru, Os}$) ($0 \leq x \leq 0.2$) showed semiconducting behavior, and the power factor was optimized by doping 10% La in $\text{CeRu}_4\text{P}_{12}$

Keywords: Skutterudite compounds, Seebeck coefficient, Power factor, Thermal conductivity.

1. INTRODUCTION

Thermoelectric effect in materials was discovered by Thomas Seebeck in 1823, when he noticed that a voltage drop occurs across a material with a temperature gradient ⁽¹⁾. In 1950s doped semiconductors like bismuth telluride, lead telluride and bismuth-antimony alloys showed a much larger thermoelectric (TE) effect than other materials. Binary semiconductor Bi_2Te_3 showed the greatest thermoelectric effect at room temperature ⁽²⁾. TE devices are not popular due to low efficiency and high cost. However, TE devices are used in specialized applications in which reliability is more important than economy ⁽¹⁾. Such as high-density IC cooler of computer, portable TE cooler, which can be powered from car battery. NASA's deep space probes use TE

generators as power sources ⁽³⁾. Semiconductor thermoelectric coolers offer several advantages over conventional systems. They are entirely solid-state devices, with no moving parts; this makes them rugged, reliable, and quiet. They use no ozone-depleting chlorofluorocarbons, potentially offering a more environmentally responsible alternative to conventional refrigeration. They can be extremely compact, compare to compressor-based systems. However, their efficiency is lower than conventional refrigerators. TE materials are of interest for the power generation from exhaust and engine heat of cars and waste heat from industries. The main drawback of TE devices is their low efficiency. The efficiency of TE device depends on TE material properties. The TE performance of a material is given by a dimension-less figure of merit $ZT=S^2T/\kappa\rho$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is electrical

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resistivity and κ is the thermal conductivity. Thermoelectric home refrigerators would make economically competitive with traditional compressor-based refrigerators, if the value of $ZT=3$ of TE material could be found⁽²⁾. At present the highest value of ZT in the bulk material is 1.8, at the temperature of 650K⁽⁴⁾.

Filled skutterudite compounds are derived from the skutterudite crystal structure (space group $Im\bar{3}$) and can be represented by the general formula MT_4X_{12} where "M" denotes one of the alkaline earth or rare earth; "T" denotes Fe, Ru or Os; and "X" pnicogen elements P, As, or Sb⁽⁵⁾⁽⁶⁾⁽⁷⁾. In the crystal structure of filled skutterudite (Fig. 1)⁽⁸⁾, the M atoms are located at (0, 0, 0) and (1/2, 1/2, 1/2) in the cubic structure. The transition metals T which are located at (1/4, 1/4, 1/4), are bounded by six "X" atoms as their nearest neighbors in a form of slightly distorted octahedrons. Filled skutterudite structure can be obtained by filling M atoms into the case like voids in binary skutterudite like $CoAs_3$. Binary skutterudite compounds AX_3 (A=Co, Rh, Pd) possess high hole mobility and large Seebeck coefficient, but also have high thermal conductivity (κ), which can be expressed as the sum of lattice and electronic thermal conductivities ($\kappa = \kappa_L + \kappa_e$). High κ is unfavorable for obtaining high ZT values. Filled skutterudite compounds have much lower thermal conductivity due to additional phonon scattering by M atoms which rattle inside the large cages, cause reduce the κ_L parts⁽⁹⁾. In fact, filled skutterudites $CeFe_4Sb_{12}$ and $La(Fe,Co)_4Sb_{12}$ showed high ZT values ($ZT > 1$) in the high temperatures⁽¹⁰⁾. Thermoelectric properties of some phosphide including $CeFe_4P_{12}$ have also been reported⁽¹¹⁾. CeT_4P_{12} (T=Ru,Os) have showed high power factor in wide range of temperatures⁽¹²⁾. These previous results of

filled skutterudite compounds motivated us to further investigate CeT_4P_{12} (T=Ru, Os) by La doping, in order to optimize TE properties, because it is believed that La dopant effect causes change in carrier concentration and hybridization between conduction electron and localized f electron. On the other hand, $SmRu_4P_{12}$ shows semiconductor-like behavior at low temperatures⁽⁸⁾⁽¹³⁾. It also motivated us to investigate Sm based filled skutterudite phosphide as a thermoelectric materials. In this paper we investigated doping effect of La on CeT_4P_{12} (T=Ru, Os). We also studied thermoelectric properties of metallic filled skutterudite compounds SmT_4P_{12} (T=Fe, Ru Os).

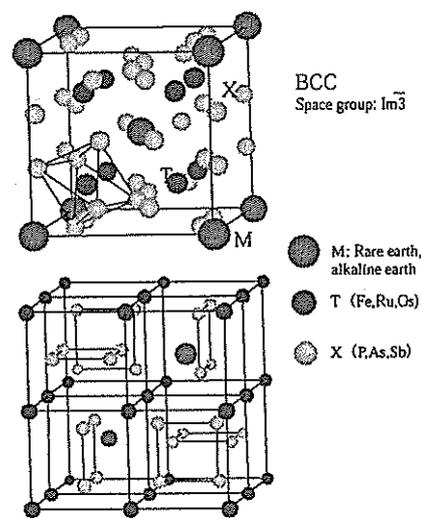


Fig. 1. Crystal structure of filled skutterudite MT_4X_{12}

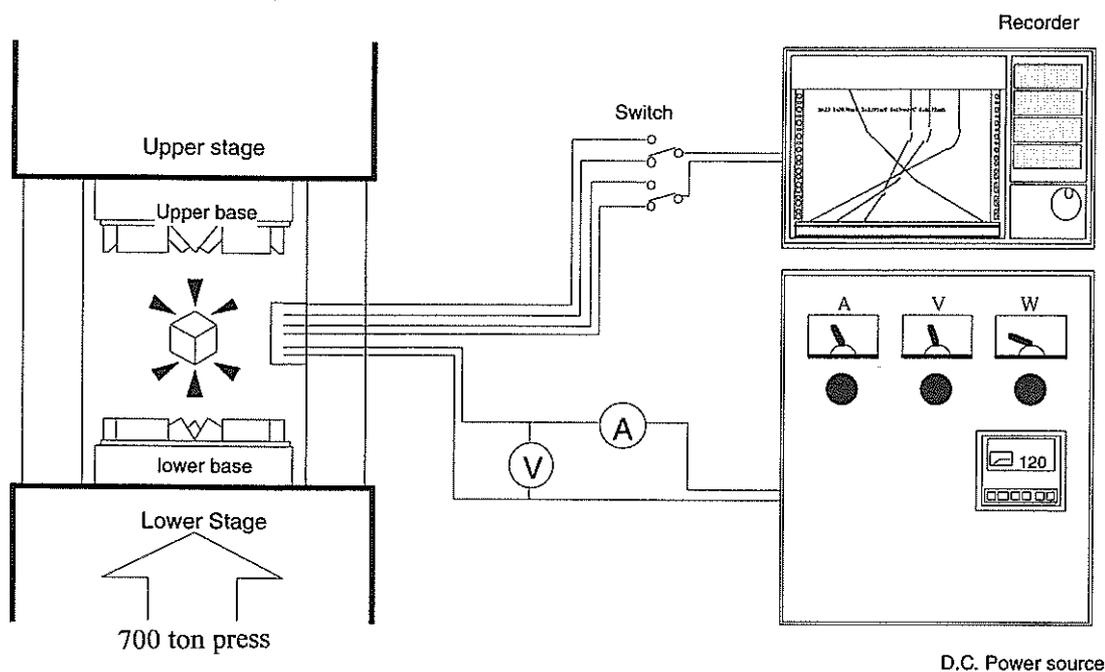


Fig. 2. High temperature high pressure apparatus for sample preparation

2. EXPERIMENT

2.1 Synthesis

Filled Skutterudite compounds $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ ($\text{T}=\text{Ru}, \text{Os}$) ($0 \leq x \leq 0.2$) and $\text{SmT}_4\text{P}_{12}$ ($\text{T}=\text{Fe}, \text{Ru}, \text{Os}$) have synthesized by high pressure, high temperature method, using a wedge-type cubic anvil high-pressure apparatus⁽¹⁴⁾. This apparatus has upper and lower stages consisting of three cubic anvil in each stage, slide on the wedges formed in the shallow V-shaped grooves (Fig. 2). The movements of anvils are completely synchronized by the wedge system. The anvils are fabricated from tungsten carbide, having a $16 \times 16 \text{ mm}^2$ top-square face. Cubic pyrophyllite ($21 \times 21 \times 21 \text{ mm}^3$) was used as a sample container. The sample assembling technique to prepare skutterudite phosphides is similar to that used for the synthesis of black phosphorus⁽¹⁵⁾. Powders of high purity, Ce, Sm, Fe, Ru, Os (99.9% respectively) and P (99.999%) were used as starting materials. The starting materials were mixed as stoichiometric amounts and sealed in a crucible, made of Boron-nitride (BN). The BN crucible, which is fitted inside a graphite heater is placed into the cubic pyrophyllite container. This pyrophyllite is kept in the center of the anvils, and the pressure is applied gradually. After the pressure reached about 4GPa, the temperature is increased to the desired value (1000~1200°C) in about 30min. Temperature is held for about 30 to 60 min. and then quenched to room temperature.

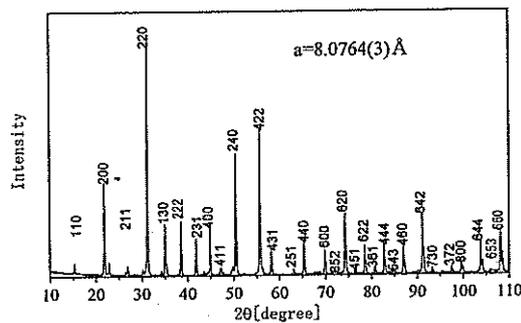


Fig. 3. X-ray diffraction pattern of $\text{SmOs}_4\text{P}_{12}$

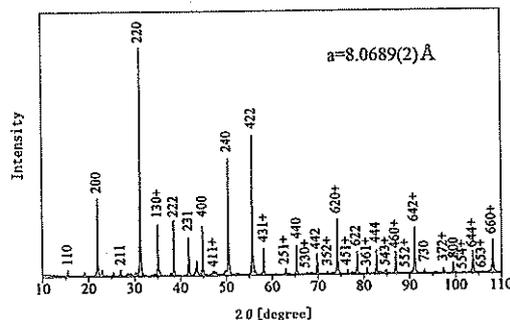


Fig. 4. X-ray diffraction pattern of $\text{La}_{0.1}\text{Ce}_{0.9}\text{Os}_4\text{P}_{12}$

2.2 Characterization

The samples were characterized by powder X-ray diffraction using $\text{CuK}\alpha_1$ radiation and silicon as a standard. X-ray diffraction patterns of $\text{SmOs}_4\text{P}_{12}$ and $\text{La}_{0.1}\text{Ce}_{0.9}\text{Os}_4\text{P}_{12}$ are shown in Fig. 3 and Fig. 4 respectively. Both samples are predominantly in the filled skutterudite phase with a negligible amount of OsP_4 as a impurity phase. Lattice constants of some skutterudite compounds are listed in table I.

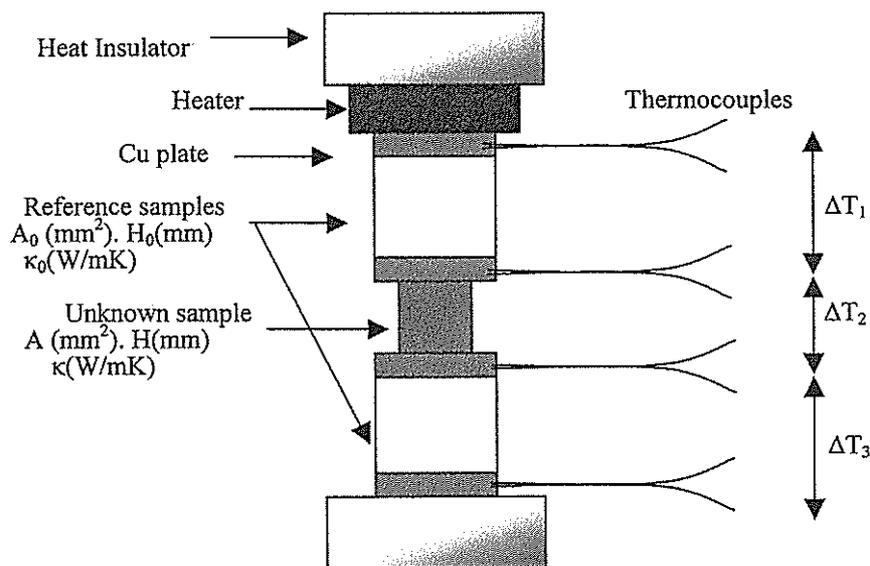


Fig. 5. Schematic diagram of Thermal conductivity measurement

ΔT (Temperature difference)

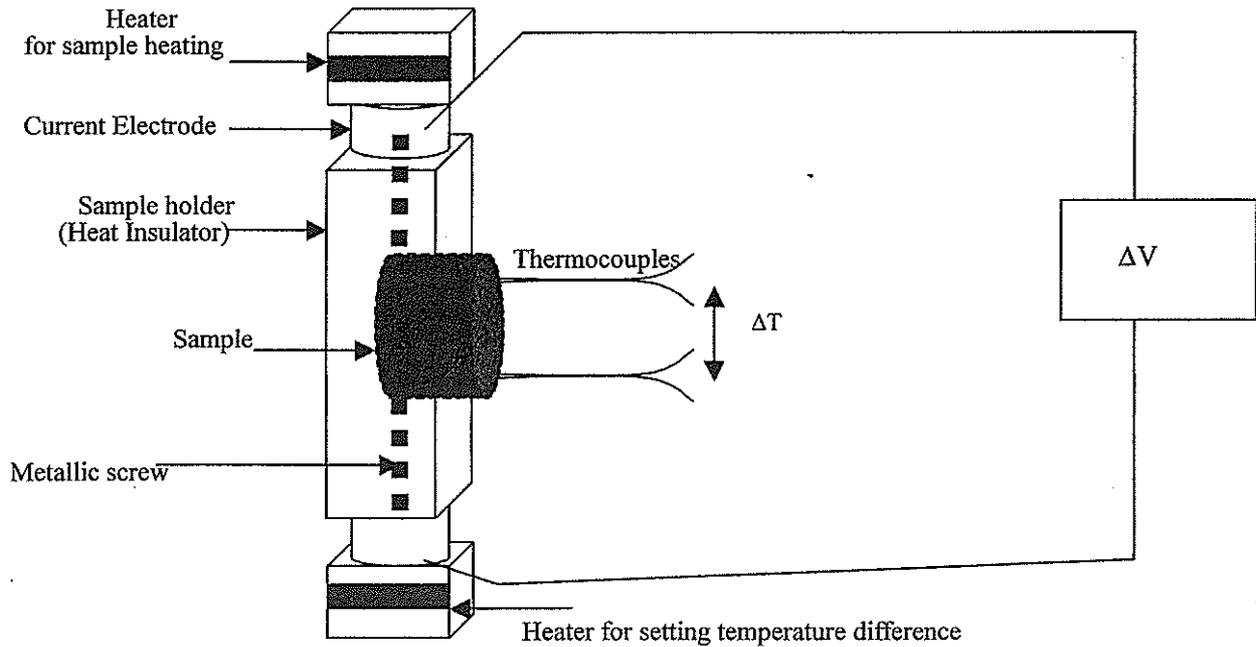


Fig. 6. Schematic diagram of Seebeck coefficient measurement

2.3 Resistivity Measurement

Resistivity was measured by using standard four-probe direct current method over a temperature range from 2 to 300K.

2.4 Thermal conductivity measurement

Thermal conductivity is measured using a steady state comparative method in room temperature. The schematic diagram is shown in Fig. 5. In this method, the unknown sample, whose thermal conductivity is to be measured, is sandwiched between two reference materials of known thermal conductivity. The temperature gradients in the standards and unknown samples are measured with applying constant heat flux. The samples sizes are measured to calculate the thermal conductivity, is given by equation (1)

$$\kappa = \frac{H \cdot A_0 \cdot \Delta T_1 + \Delta T_3}{H_0 \cdot A \cdot 2\Delta T_2} \kappa_0 \quad (1)$$

Where κ W/mK is thermal conductivity, H mm is the height and A mm² is the area of the unknown sample, while κ_0 , H_0 and A_0 are of reference samples. ΔT_1 , ΔT_2 and ΔT_3 are temperature gradient between the samples. 100 Ω metal film resistor was used as a heater. Heater currents were set at 0, 20, 40 and 60mA. The temperature gradients were measured at a stable temperature state of all the thermocouples. K type thermocouples are connected with 2mm thick Cu block

(5×5mm²) to measure the temperature. Heat conductive grease ($\kappa=9.6$ mW/cmK) was used to connect the Cu plates and samples. Quartz glass ($\kappa=13.6$ mW/cmK) of dimension 5×5mm², was used as a standard samples. Chamber was vacuumed by turbo molecular pump at 1.4×10^{-6} Torr during the measurement. Thermal resistivity of heat conductive grease, heat leak from thermocouples and radiative losses are likely to cause error. Error was found $\pm 5\%$, while measuring quartz glass as an unknown sample. Re-measurement showed less than 1% error. When the size of unknown sample is very smaller than standard samples, values of thermal resistivity appears less than actual values. These errors and losses were estimated and corrected for the data.

2.5 Seebeck coefficient measurement

Seebeck coefficient was measured by DC method. When a temperature difference is applied between two ends of the material, a voltage V_0 is produce. The temperature difference ΔT can be measured by means of thermocouples. The average thermoelectric power, which is also called Seebeck coefficient S as a function of average temperature difference ΔT is given by

$$S = V_0 / \Delta T$$

Schematic diagram of Seebeck coefficient

measurement is shown in Fig. 6. The sample was fixed between the two stages with the support of heat insulated sample holder. Temperature difference is applied to the sample by the heater from the lower block at the temperature gradient of 2 K. Two thermocouple probes, which also push the two different points of the sample, are used to measure the temperature difference and thermoelectric power. Measuring unit is surrounded by low pressure He gas.

3. RESULTS

The variation of electrical resistivity with temperature of the $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ ($\text{T}=\text{Ru}, \text{Os}$) ($0 \leq x \leq 0.2$) is plotted in Fig. 7 and Fig. 8. All these compounds show semiconducting behavior. We reported that $\text{CeOs}_4\text{P}_{12}$ shows low resistivity values, because of large carrier mobility compare to $\text{CeRu}_4\text{P}_{12}$ ⁽¹²⁾. La dopant causes decrease in resistivity with increase of La percentage in $\text{CeRu}_4\text{P}_{12}$. Resistivity of $\text{La}_{0.1}\text{Ce}_{0.9}\text{Ru}_4\text{P}_{12}$ observed 10 times lower than $\text{CeRu}_4\text{P}_{12}$ at room temperature and 16 times at 125 K. The shoulder has found in the resistivity as a function of temperature in $\text{CeRu}_4\text{P}_{12}$ at around 100 to 150 K and disappeared after La doping. However in case of $\text{CeOs}_4\text{P}_{12}$, La doping effect in electrical resistivity is negligible above 100 K.

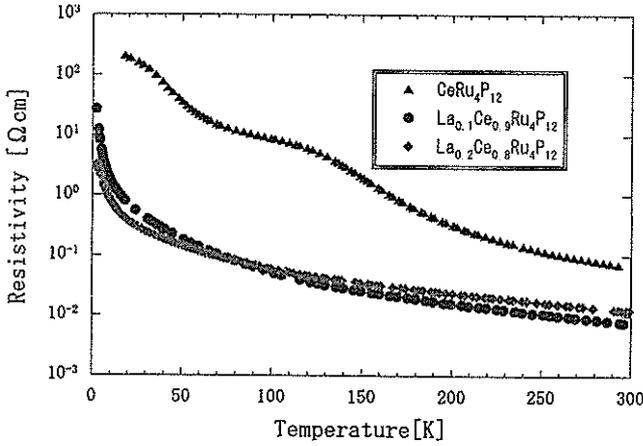


Fig. 7. Resistivity versus temperature for $\text{La}_x\text{Ce}_{1-x}\text{Ru}_4\text{P}_{12}$ ($x=0, 0.1, 0.2$)

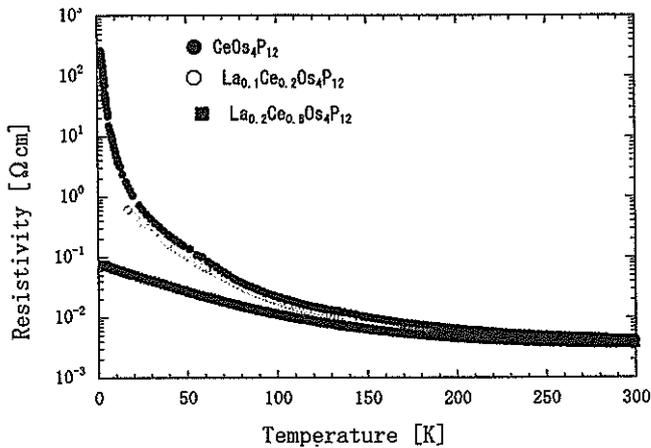


Fig. 8. Resistivity as a function of temperature for $\text{La}_x\text{Ce}_{1-x}\text{Os}_4\text{P}_{12}$ ($x=0, 0.1, 0.2$)

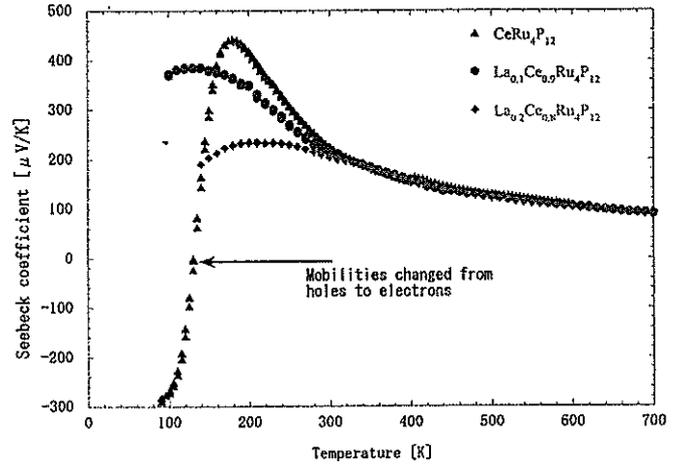


Fig. 9. Seebeck coefficient versus temperature for $\text{La}_x\text{Ce}_{1-x}\text{Ru}_4\text{P}_{12}$ ($x=0, 0.1, 0.2$)

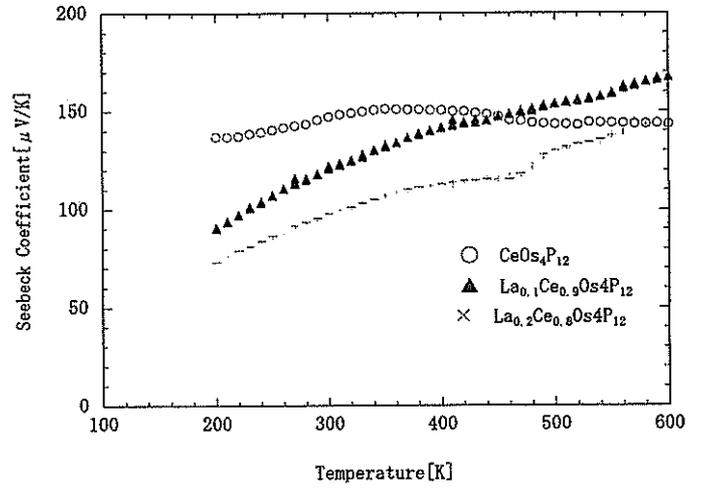


Fig. 10. Seebeck coefficient versus temperature for $\text{La}_x\text{Ce}_{1-x}\text{Os}_4\text{P}_{12}$ ($x=0, 0.1, 0.2$)

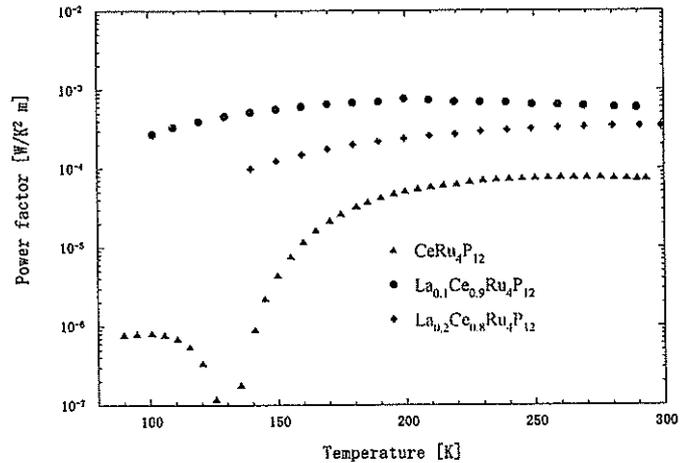


Fig. 11. Power factor (S^2/ρ) versus temperature for $\text{La}_x\text{Ce}_{1-x}\text{Ru}_4\text{P}_{12}$ ($x=0, 0.1, 0.2$)

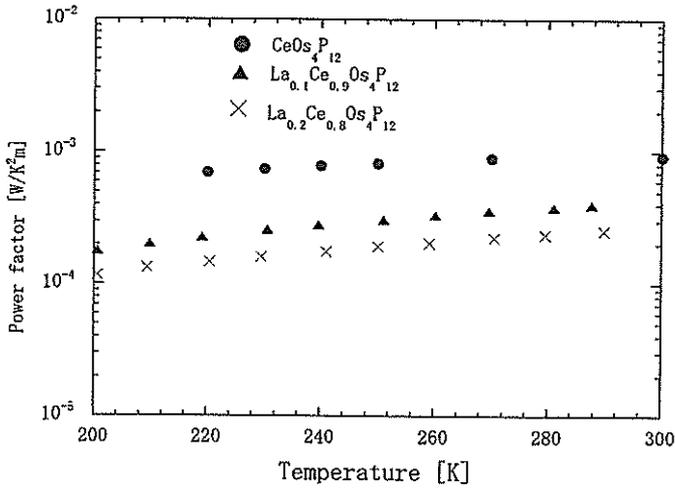


Fig. 12. Power factor (s^2/ρ) versus temperature for $\text{La}_x\text{Ce}_{1-x}\text{Os}_4\text{P}_{12}$

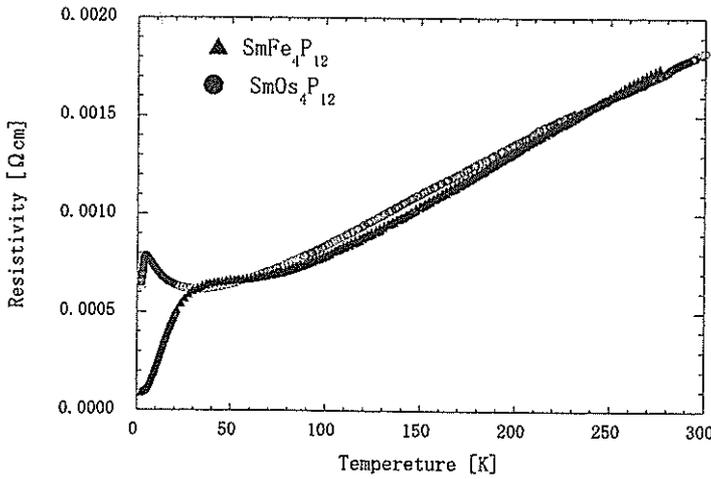


Fig. 13. Resistivity versus temperature for $\text{SmFe}_4\text{P}_{12}$ and $\text{SmOs}_4\text{P}_{12}$

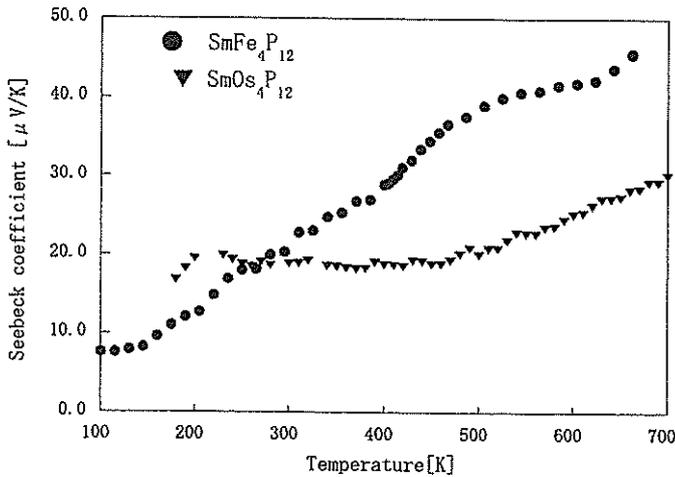


Fig. 14. Seebeck coefficient versus temperature for $\text{SmFe}_4\text{P}_{12}$ and $\text{SmOs}_4\text{P}_{12}$

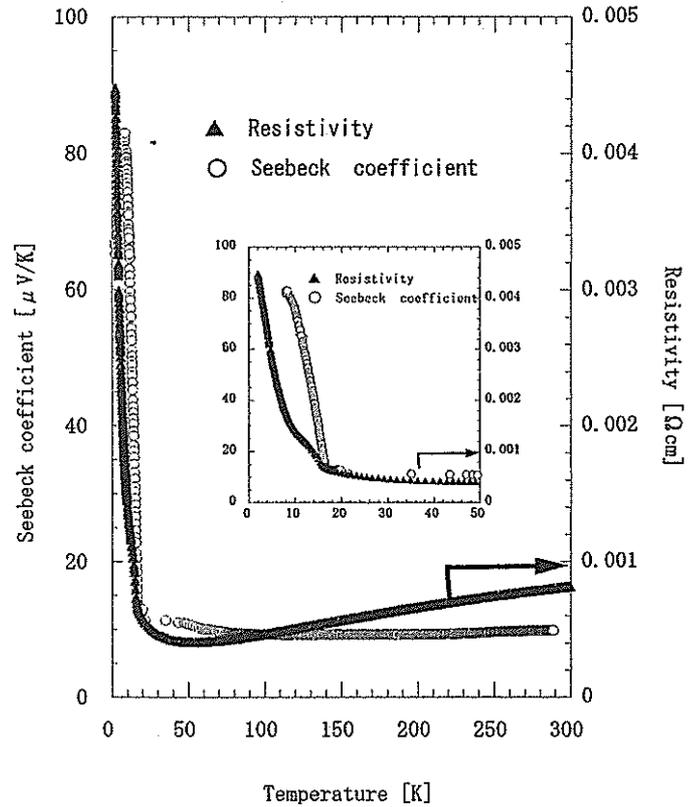


Fig. 15. Resistivity and Seebeck coefficient as a function of temperature of $\text{SmRu}_4\text{P}_{12}$

The Seebeck coefficient of $\text{La}_x\text{Ce}_{1-x}\text{Ru}_4\text{P}_{12}$ ($0 \leq x \leq 0.2$) as a function of temperature is shown in Fig. 9. High Seebeck coefficient ($500 \mu\text{V/K}$) of $\text{CeRu}_4\text{P}_{12}$ has been reported down to 200 K⁽¹²⁾. In this study, Seebeck coefficient was measured down to 100 K. It is invented that, Seebeck coefficient of $\text{CeRu}_4\text{P}_{12}$ is positive down to 140 K, which indicate hole conductor. However below 140 K it changes to negative, which indicate electron conductor. The maximum peak ($437 \mu\text{V/K}$) was found at 180K. The variation of Seebeck coefficient of $\text{La}_x\text{Ce}_{1-x}\text{Os}_4\text{P}_{12}$ ($0 \leq x \leq 0.2$) is plotted in Fig. 10. $\text{CeOs}_4\text{P}_{12}$ also shows high Seebeck coefficient ($140 \mu\text{V/K}$) over a wide temperature range with the weak temperature dependence⁽¹²⁾. High Seebeck coefficient was found above 450 K with 10% La dopant. The power factors of $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ ($\text{T}=\text{Ru}, \text{Os}$) ($0 \leq x \leq 0.2$) are shown in Fig.11 and Fig. 12. Power factor values in $\text{CeRu}_4\text{P}_{12}$ increased with La dopant. $\text{La}_{0.1}\text{Ce}_{0.9}\text{Ru}_4\text{P}_{12}$ shows high power factor value in the order of 10^{-3} mW/K over a wide temperature range. Variation of electrical resistivity and Seebeck coefficient of $\text{SmT}_4\text{P}_{12}$ ($\text{T}=\text{Fe}, \text{Ru}, \text{Os}$) are plotted in Fig. 13, Fig. 14 and Fig. 15. All Sm based compounds show metallic behavior in contrast with the semiconducting behavior of Ce based phosphide

compounds. However, $\text{SmRu}_4\text{P}_{12}$ shows metal-insulator transition at 16K, which is in agreement with the previous report⁽¹²⁾. High seebeck coefficient value ($82 \mu\text{V/K}$) was observed at around 10 K in $\text{SmRu}_4\text{P}_{12}$. Seebeck coefficient of $\text{SmFe}_4\text{P}_{12}$ and $\text{SmOs}_4\text{P}_{12}$ increase with temperature. Maximum seebeck coefficient value ($46 \mu\text{V/K}$) was found at around 700 K in $\text{SmFe}_4\text{P}_{12}$, which is comparatively high in the metallic compounds.

Thermal conductivity of Sm and Ce based compounds at room temperature are listed in Table 1. The thermal conductivities of some Ce based compounds at room temperature are in agreement with the previous study^{10,11)}. The thermal conductivity of $\text{SmFe}_4\text{P}_{12}$, $\text{SmRu}_4\text{P}_{12}$ and $\text{SmOs}_4\text{P}_{12}$ is 75.5 mW/cmK , 63.7 mW/cmK and 58.54 mW/cmK respectively. The calculated dimensionless thermoelectric figure of merit ZT values for the $\text{CeRu}_4\text{P}_{12}$, $\text{CeOs}_4\text{P}_{12}$, $\text{SmFe}_4\text{P}_{12}$, $\text{SmRu}_4\text{P}_{12}$ and $\text{SmOs}_4\text{P}_{12}$ are relatively low at room temperature of 0.003, 0.02, 0.0006, 0.0001 and 0.001 respectively. These low values can be attributed to their high thermal conductivity. In order to increase their ZTs, reduction in both electrical resistivity and thermal conductivity should be carried out. In metals, like Sm based filled skutterudite compounds, the ratio of $\kappa/\sigma \approx$

constant ($\sigma=1/\rho$) and it is not possible to simultaneously reduce one value and increase the other. In case of semiconductors, however doping process increase in conductivity and reduce thermal conductivity due to phonon scattering in disordered compounds, which can achieve high ZTs materials. We succeeded to improve power factor by La doping into the $\text{CeRu}_4\text{P}_{12}$, which showed the possibilities of increasing the values of ZT of these filled skutterudite semiconductors. Measurements of thermal conductivity for the $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ (T=Ru, Os) ($x= 0.1$ and 0.2) are planned in the very near future.

4. SUMMARY

$\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ (T=Ru, Os) ($0 \leq x \leq 0.2$) and $\text{SmT}_4\text{P}_{12}$ (T=Fe, Ru, Os) have been synthesized under high pressure and their thermoelectric properties have been measured. The room temperature properties of $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ (T=Ru, Os) ($0 \leq x \leq 0.2$) and $\text{SmT}_4\text{P}_{12}$ (T=Fe, Ru, Os) are listed in Table 1. $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ (T=Ru, Os) ($0 \leq x \leq 0.2$) are p-type semiconductors and have good thermoelectric properties. Power factor was optimized by 10% La doping in $\text{CeRu}_4\text{P}_{12}$. Thermal

Table 1

Room temperature properties of some Sm and Ce based filled skutterudite compounds.

| | Units | $\text{CeRu}_4\text{P}_{12}$ | $\text{La}_{0.1}\text{Ce}_{0.9}\text{Ru}_4\text{P}_{12}$ | $\text{La}_{0.2}\text{Ce}_{0.8}\text{Ru}_4\text{P}_{12}$ |
|------------------------|---------------------------|---------------------------------|--|--|
| Lattice constant | Å | 8.0446 | 8.0478 | 8.0478 |
| Electrical resistivity | $\text{m}\Omega\text{cm}$ | 71.9 | 7.7 | 12.2 |
| Seebeck coefficient | $\mu\text{V/K}$ | 256 | 214 | 204 |
| Thermal conductivity | mW/cmK | 107 | | |
| ZT | | 0.003 | | |
| | Units | $\text{CeOs}_4\text{P}_{12}$ ** | $\text{La}_{0.1}\text{Ce}_{0.9}\text{Os}_4\text{P}_{12}$ | $\text{La}_{0.2}\text{Ce}_{0.8}\text{Os}_4\text{P}_{12}$ |
| Lattice constant | Å | 8.0700 | 8.0689 | 8.0708 |
| Electrical resistivity | $\text{m}\Omega\text{cm}$ | 2.26 | 3.52 | 3.60 |
| Seebeck coefficient | $\mu\text{V/K}$ | 147 | 120 | 97 |
| Thermal conductivity | mW/cmK | 105 | | |
| ZT | | 0.02 | | |
| | Units | $\text{SmFe}_4\text{P}_{12}$ | $\text{SmRu}_4\text{P}_{12}$ | $\text{SmOs}_4\text{P}_{12}$ |
| Lattice constant | Å | 7.7986 | 8.0395 | 8.0764 |
| Electrical resistivity | $\text{m}\Omega\text{cm}$ | 1.9 | 5.2 | 1.8 |
| Seebeck coefficient | $\mu\text{V/K}$ | 18 | 11 | 19 |
| Thermal conductivity | mW/cmK | 75.5 | 63.7 | 58.54 |
| ZT | | 0.0006 | 0.0001 | 0.001 |
| | Units | $\text{CeFe}_4\text{P}_{12}$ * | $\text{CeFe}_4\text{Sb}_{12}$ * | $\text{CeRu}_4\text{Sb}_{12}$ * |
| Lattice constant | Å | 7.7917 | 9.1350 | 9.2657 |
| Electrical resistivity | $\text{m}\Omega\text{cm}$ | 20.5 | 0.75 | 0.31 |
| Seebeck coefficient | $\mu\text{V/K}$ | 58 | 59 | 31 |
| Thermal conductivity | mW/cmK | 140 | 14 | 42 |
| ZT | | 0.0003 | 0.1 | 0.022 |

*Ref.¹⁰⁾ **Ref.¹¹⁾

conductivity decrease in the order of transition metal Fe, Ru, Os in Ce based phosphides and vice versa in Ce based antimonides. $\text{SmT}_4\text{P}_{12}$ (T=Fe, Ru, Os) show metallic behavior and posses high Seebeck coefficient at high temperatures. Thermal conductivity decreases in the order of transition metals Fe, Ru, Os. It can be believed that, thermal conductivity of filled skutterudite compounds can be reduced by not only selecting a good rattler but also selecting a proper transition metal, which makes optimum size of atomic cage for rattler. We found that, Os makes optimum size for phosphides and Fe for antimonides filled skutterudite compounds.

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Sm系及びCe系充填スキテルダイト化合物の熱電特性

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概要

充填スキテルダイト化合物は新熱電材料の候補として精力的に研究されている。この結晶構造を持つ化合物 $\text{SmT}_4\text{P}_{12}$ (T=Fe, Ru, Os) 及び $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ (T=Ru, Os) ($0 \leq x \leq 0.2$) を高温高压合成法により作製した。粉末 X 線回折により結晶構造の同定を行ない、電気抵抗率、ゼーベック係数 及び熱伝導率を測定し、熱電特性を調べた。 $\text{SmRu}_4\text{P}_{12}$ は 16K で金属-絶縁体転移を示すのに対し $\text{SmFe}_4\text{P}_{12}$ 及び $\text{SmOs}_4\text{P}_{12}$ は 5K まで金属的な振舞を示した。 $\text{SmFe}_4\text{P}_{12}$ は通常金属に比べて大きなゼーベック係数の値 (600K で $46 \mu\text{V/K}$) を示した。 $\text{La}_x\text{Ce}_{1-x}\text{T}_4\text{P}_{12}$ (T=Ru, Os) ($0 \leq x \leq 0.2$) はすべての組成が半導体的な性質を示した。 $\text{CeRu}_4\text{P}_{12}$ は 10% La 置換により出力因子を最適化できた。

キーワード: スキテルダイト化合物、ゼーベック係数、出力因子、熱伝導率

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