Transport Properties of the Layered Transition Metal Oxypnictide \( \text{Sr}_2\text{ScCo}_{1-x}\text{Fe}_x\text{PO}_3 \) with Fe-doped \( \text{Co}_{1-x}\text{Fe}_x\text{P} \) layers

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Abstract. Polycrystalline samples of novel oxypnictides, \( \text{Sr}_2\text{ScCo}_{1-x}\text{Fe}_x\text{PO}_3 \), with Fe-doped \( \text{Co}_{1-x}\text{Fe}_x\text{P} \) layer were synthesized, and their resistivities and Seebeck coefficients were measured. These materials, \( \text{Sr}_2\text{ScCo}_{1-x}\text{Fe}_x\text{PO}_3 \), crystallize in a layered structure which represent an alternative stack of TcCrSi\(_2\) type \( \text{Co}_{1-x}\text{Fe}_x \) layers and K\(_2\)NiF\(_4\) type \( \text{Sr}_2\text{ScO}_3 \) layers. The resistivities \( \rho \) decrease with decreasing temperature like a metal. The Seebeck coefficients \( S \) show negative values at room temperature, while the \( S \) show positive values for \( x = 0.04-0.7 \) at low temperature.

1. Introduction

Since the discovery of high \( T_c \) superconductivity in F-doped La\( \text{FeP}_n\)O \( (P_n = \text{P and As}) \), many scientists focus on the transport properties of oxypnictides and oxychalcogenides\([1, 2]\). These oxypnictides have a quasi-two-dimensional structure, in which an anti-fluorite transition metal \( (M = \text{Fe, Co, Mn, Ni, \ldots}) \) pnictide layer is separated by a carrier blocking layer\([3]\). These materials are multi anion systems, containing \( P_n \) in transition metal layer and \( O \) in a carrier blocking layer. The \( \text{FeP}_n \) series, in particular, have been intensively studied because the quasi-two-dimensional structure and the \( \text{FeP}_n \) layer plays an important role in their superconductivity.

In past research, we have focused on perovskite-type oxypnictides and oxychalcogenides that have a large blocking layer\([4, 5]\), with particular interest in \( \text{Sr}_2\text{ScFePO}_3 \) with a \( \text{Sr}_2\text{ScO}_3 \) layer that was reported by Ogino et al.\([6]\). \( \text{Sr}_2\text{ScFePO}_3 \) crystallizes in an unusual intergrowth structure consisting of an anti-fluorite FeP layer and a perovskite related K\(_2\)NiF\(_4\)-type \( \text{Sr}_2\text{ScO}_3 \) layer. It was determined that \( \text{Sr}_2\text{ScFePO}_3 \) exhibited superconductivity below 17 K. In 2012, we have successfully synthesized and evaluated the transport properties of \( \text{Sr}_2\text{ScMPO}_3 (M = \text{Co}[7], \text{Mn}, \text{Ni} \) and \( \text{Co}_{0.5}\text{Fe}_{0.5}[8] \)). The resistivity \( \rho \) of \( \text{Sr}_2\text{ScCoPO}_3 \) is 4.5 m\( \Omega \)cm at room temperature and decreases with decreasing temperature \( (T) \). The Seebeck coefficient \( S \) of \( \text{Sr}_2\text{ScCoPO}_3 \) is \(-12\mu\)V/K at room temperature, decreases with decreasing temperature, and rapidly increases with decreasing temperature below 50 K\([7]\). The \( \rho \) of \( \text{Sr}_2\text{ScMnPO}_3 \) at room temperature is found to be a large value like that of an insulator\([8]\). For \( \text{Sr}_2\text{ScNiPO}_3 \) and \( \text{Sr}_2\text{ScCo}_{0.5}\text{Fe}_{0.5}\text{PO}_3 \), the values of \( \rho \) at room temperature are 1.7 m\( \Omega \)cm \( (M = \text{Ni}) \) and 6.0 m\( \Omega \)cm \( (M = \text{Co}_{0.5}\text{Fe}_{0.5}) \), and the \( \rho \) decrease with decreasing temperature like that of \( \text{Sr}_2\text{ScFePO}_3 \) although both compounds do
Figure 1. Powder XRD patterns of \( \text{Sr}_2\text{ScCo}_{1-x}\text{Fe}_x\text{PO}_3 \).

not show a superconducting phase. The \( S \) of \( \text{Sr}_2\text{ScNiPO}_3 \) is \(-1.2\mu\text{V/K}\) at room temperature, slightly decreases with decreasing temperature down to 50 K, and increases with decreasing temperature below 50 K. Although the similar \( S-T \) curve is observed for \( \text{Sr}_2\text{ScCoPO}_3 \), the absolute value of \( S \) is smaller than that of \( \text{Sr}_2\text{ScCoPO}_3 \). For \( \text{Sr}_2\text{ScCo}_{0.5}\text{Fe}_{0.5}\text{PO}_3 \), the values of \( S \) at room temperature is \(-0.6\mu\text{V/K}\), slightly increases with decreasing temperature down to 50 K, and rapidly increases with decreasing temperature below 50 K. The sign inversion of \( S \) is obtained at about 270 K, and \( S \) retains a positive value below 270 K[8]. This behavior is clearly different from that of \( \text{Sr}_2\text{ScCoPO}_3 \). In this study, we have successfully synthesized a Fe-doped oxypnictide, \( \text{Sr}_2\text{ScCo}_{1-x}\text{Fe}_x\text{PO}_3 \), and measured their \( \rho \) and \( S \) to evaluate electrical transport properties of Fe-doped samples.

2. Experiment
Polycrystalline samples of \( \text{Sr}_2\text{ScCo}_{1-x}\text{Fe}_x\text{PO}_3 \) \((x = 0.04, 0.1, 0.2, 0.7 \text{ and } 0.8) \) were synthesized by a solid state reaction in sealed quartz tubes. Precursors of the reaction are \( \text{CoP}, \text{Fe}_2\text{P}, \text{P}, \text{SrO}, \text{Sr} \) and \( \text{Sc}_2\text{O}_3 \). A mixture of starting materials with a molar ratio of \( \text{CoP}:\text{Fe}_2\text{P}:\text{P}:\text{SrO}:\text{Sr}:\text{Sc}_2\text{O}_3 = 1-x:x:x:3:1:1 \). The mixture of precursors was pressed into pellets. Weighing and pressing were done in Ar-filled glove box. \( \text{CoP} \) was prepared by a solid state reaction of \( \text{Co} \) and \( \text{P} \) with a molar ratio of 1:1 at 700 °C for 40 h. These pellets were calcined at 1200 °C for 30 h in a quartz tube filled with Ar gas under atmospheric pressure of 0.1 at room temperature.

Figure 2. Fe concentration dependence of the lattice constants on \( \text{Sr}_2\text{ScCo}_{1-x}\text{Fe}_x\text{PO}_3 \). The solid lines are a guide to the eyes.
Crystalline phases were examined by powder X-ray diffraction (XRD, Rigaku, Rint2500 with Cu Kα radiation). Lattice parameters were roughly obtained by a least-squares fitting method using the diffraction angles collected in the 2θ range from 10 to 70°.

Resistance measurements were performed by a four-probe method at temperatures from 20 to 300 K. Seebeck coefficients were measured using a steady-state technique at temperatures from 20 to 300 K. A temperature gradient of 0.3 or 0.1 K/mm was generated by a small resistive heater placed on one edge of the sample, and was monitored with a copper–constantan differential thermocouple. The thermopower of the voltage leads was carefully subtracted.

3. Result and Discussion
Figure 1 shows the powder XRD patterns of Sr$_2$ScCo$_{1-x}$Fe$_x$PO$_3$ ($x=0.04$, 0.1, 0.2, 0.7 and 0.8) with the accompanying Bragg positions calculated by the Rietveld refinement program RIETAN-FP[9]. These patterns are similar to the pattern of Sr$_2$ScFePO$_3$[6], which indicates that these compounds are isomorphic to Sr$_2$ScFePO$_3$. The powder XRD patterns were successfully indexed except for some peaks assigned to secondary phases. Figure 2 shows Fe concentration ($x$) dependense of the lattice constants on Sr$_2$ScCo$_{1-x}$Fe$_x$PO$_3$ with Sr$_2$ScCoPO$_3$ ($x=0$)[7], Sr$_2$ScCo$_{0.5}$Fe$_{0.5}$PO$_3$ ($x=0.5$)[8] and Sr$_2$ScFePO$_3$ ($x=1.0$)[6]. The lattice constants continuously increases with increasing $x$ and no structural anomaly is observed.

Figure 3 shows the temperature dependence of $\rho$ for Sr$_2$ScCo$_{1-x}$Fe$_x$PO$_3$ with that of Sr$_2$ScCoPO$_3$ ($x=0$) and Sr$_2$ScCo$_{0.5}$Fe$_{0.5}$PO$_3$ ($x=0.5$) reproduced from refs [7, 8]. In all samples, $\rho$ decreases with decreasing temperature. This metallic behavior is similar to that of Sr$_2$ScFePO$_3$[6]. For the samples of $x=0.5$, 0.7 and 0.8 below 50 K, the slopes of these $\rho - T$ curves decrease with decreasing temperature; i.e. residual resistivities increase for these samples. Such a enhancement of the residual resistivities is probably due to crystallographic and/or site specific disorder in the two dimensional metal layer. These samples do not show any superconducting phase at $T = 20$–300 K. The value of $\rho$ at room temperature continuously increases with increasing Fe concentration $x$. This behavior is observed in other 1111-type Fe-based superconductors[10, 11].

Figure 4 shows the temperature dependence of $S$ for Sr$_2$ScCo$_{1-x}$Fe$_x$PO$_3$ with that of Sr$_2$ScCoPO$_3$ ($x=0$) and Sr$_2$ScCo$_{0.5}$Fe$_{0.5}$PO$_3$ ($x=0.5$) previously reported[7, 8]. The $S$ of all...
samples at room temperature are negative. These absolute values of $S$ at room temperature is observed to decrease with increasing $x$ up to 0.5, and decrease with increasing over 0.5. $S$ of each sample rapidly increase with decreasing temperature below 50 K. Although the $S$ of $x = 0.2$ and 0.7 samples slightly increase with decreasing temperature near room temperature, like that of $x = 0.5$, the $S$ of other $x$ samples slightly decrease with decreasing temperature like that of $x = 0$. In addition, the sign inversions for $S$ appear for $x = 0.04 – 0.7$ below 50 K except for $x = 0.5$ at 270 K. This inversion of the polarity for $S$ is also observed for Sr$_2$ScFeAsO$_3$ at 100 K[12]. When it was even possible to measure the lower temperature, it is expected that the range of $x$ which is observed the sign inversion becomes wider. The observed differences of the $S – T$ curves reflect the influence of multiband electronic structures for the layered oxypnictides. According to the $ab$ initio calculations for Sr$_2$ScFePO$_3$[13, 14], the electron structure of Sr$_2$ScFePO$_3$ has hole and electron bands near Fermi Energy ($E_F$). The crystal structures of Sr$_2$ScCo$_{1-x}$Fe$_x$PO$_3$ are isomorphic to Sr$_2$ScFePO$_3$, so we presume that the electron structures of Sr$_2$ScCo$_{1-x}$Fe$_x$PO$_3$ have also hole and electron bands near $E_F$. The polarity of $S$ indicates a majority carrier-type in conductors. Majority carriers are determined by electronic band structures near $E_F$ and the Fermi-Dirac distribution function. Therefore, the $S – T$ curves are understood as results due to the multi-band electronic structure. Although the lattice constants and the $\rho$ are continuously changed with $x$ and no anomaly is observed, the $S – T$ curves for $x = 0.5$ are different from those of other samples. Therefore, this behavior suggests that there is difference among those electronic structures.

4. Conclusion

In summary, we have successfully synthesized polycrystalline samples of novel oxypnictides, Sr$_2$ScCo$_{1-x}$Fe$_x$PO$_3$ ($x = 0.04, 0.1, 0.2, 0.7$ and 0.8). The transport properties of these samples are demonstrated. The value of $\rho$ at room temperature continuously increases with $x$. The $\rho$ of all samples decrease with decreasing temperature like a metal. The $S$ of all samples at room temperature are negative. Although the $S$ of $x = 0.2$ and 0.7 samples slightly increase with decreasing temperature down to 50 K like that of $x = 0.5$, the $S$ of other $x$ samples slightly decrease with decreasing temperature like that of $x = 0$. Inversions of the polarity for $S$ appear for $x = 0.04 – 0.7$ below 50 K except for $x = 0.5$ at 270 K. In further study, local structural refinement and theoretical band structure calculations are required to quantitatively analyze the transport and magnetic properties of the materials. Higher accuracy and precisely Rietveld refinement and application of density functional theory[15, 16, 17, 18] are therefore chosen for future work.

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