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Transport Properties of the Layered Transition Metal Oxypnictide Sr_2ScMPO_3 with MP layers (M =Mn, Ni and $Co_{0.5}Fe_{0.5}$)

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Abstract. Polycrystalline samples of novel oxypnictides, Sr_2ScMPO_3, with MP layer (M = Mn, Ni and $Co_{0.5}Fe_{0.5}$) were synthesized, and their resistivities and Seebeck coefficients were measured. Sr_2ScMPO_3 crystallizes in a stacked, layered structure comprised of a $ThCr_2Si_2$–type MP layer alternating with a K_2NiF_4–type Sr_2ScO_3 layer. $Sr_2ScMnPO_3$ is an insulator at room temperature. The resistivities (ρ) of $Sr_2ScNiPO_3$ and $Sr_2ScCo_{0.5}Fe_{0.5}PO_3$ decrease with decreasing temperature like a metal. The Seebeck coefficients (S) of these materials are negative at room temperature. For $Sr_2ScNiPO_3$, S initially decreases slightly with decreasing temperature, and increases with decreasing temperature below 50 K. However, for $Sr_2ScCo_{0.5}Fe_{0.5}PO_3$, S increases with decreasing temperature, and attains to a positive value below 270 K.

1. Introduction

Since the discovery of high T_c superconductivity in F-doped LaFePnO (Pn = P and As), numerous scientists have been interested in the transport properties of oxypnictides and oxychalcogenides [1, 2]. These oxypnictides are multi anion systems, containing O and Pn, and have a quasi-two-dimensional structure, in which an anti-fluorite transition metal (M = Fe, Co, Mn, Ni, $\cdots$) pnictide layer is separated by a carrier blocking layer [3]. The FePn series, in particular, have been intensively studied because the quasi-two-dimensional structure and the FePn layer plays an important role in their superconductivity. However, various phenomena are observed in the materials with an MP layer. For example, LaMnPO with an MnP layer is an antiferromagnetic semiconductor [4–6], LaCoPO with a CoP layer is a ferromagnetic metal having a Curie temperature of ∼60 K [7], and LaNiPO with an NiP layer is a Pauli para metal with a superconducting critical temperature (T_c) of 3 K [8].

In past research, we have focused on perovskite-type oxypnictides and oxychalcogenides that have a large blocking layer [10, 11], with particular interest in $Sr_2ScFePO_3$ with a Sr_2ScO_3 layer that was reported by Ogino *et al.* [9]. $Sr_2ScFePO_3$ crystallizes in an unusual intergrowth structure consisting of an anti-fluorite FeP layer and a perovskite related K_2NiF_4-type Sr_2ScO_3 layer, as shown in Fig. 1. It was determined that $Sr_2ScFePO_3$ exhibited superconductivity below 17 K. In addition, we have successfully synthesized and evaluated the transport properties

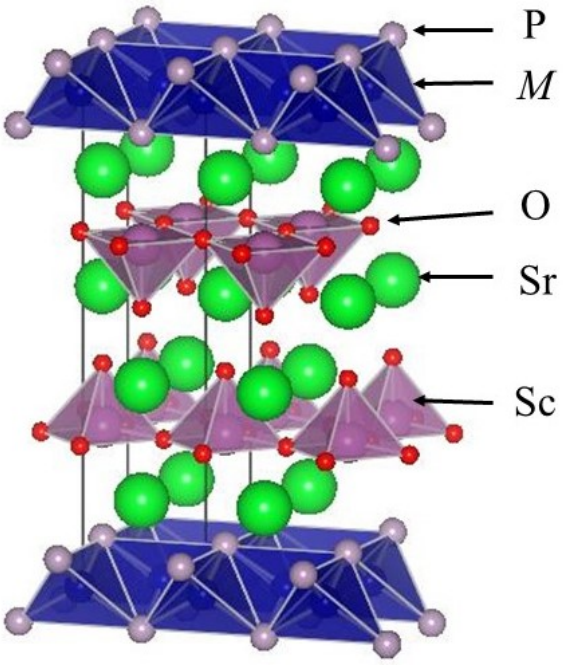

Figure 1. Crystal structure of Sr_2ScMPO_3 (M=Fe, Co, Mn, Ni and $Co_{0.5}Fe_{0.5}$). This figure was created by VESTA [13].

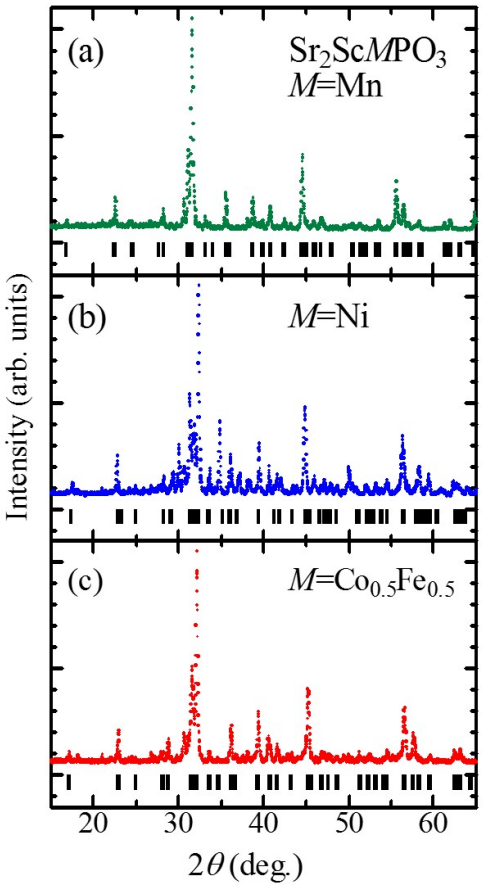

Figure 2. Powder XRD patterns of (a) $Sr_2ScMnPO_3$, (b) $Sr_2ScNiPO_3$, and (c) $Sr_2ScCo_{0.5}Fe_{0.5}PO_3$. Vertical bars denote Bragg positions.

of $Sr_2ScCoPO_3$ [12]. The resistivity (ρ) of $Sr_2ScCoPO_3$ is 4.5 mΩcm at room temperature and decreases with decreasing temperature. The Seebeck coefficient (S) of $Sr_2ScCoPO_3$ is -12 μV/K at room temperature, decreases with decreasing temperature, and rapidly increases with decreasing temperature below 50 K . To evaluate the role of the Sr_2ScO_3 layer in $Sr_2ScCoPO_3$, it is necessary to compare the transport properties of other compounds that have a Sr_2ScO_3 layer. To this end, we have, in the present study, successfully synthesized the novel oxypnictides Sr_2ScMPO_3 with MP layers (M = Mn, Ni and $Co_{0.5}Fe_{0.5}$) and evaluated their transport properties.

2. Experiment

Polycrystalline samples of Sr_2ScMPO_3 (M =Mn and Ni) were synthesized by a solid state reaction method in a quartz tube from M_2P, P, SrO, Sr and Sc_2O_3. A mixture of starting materials with a molar ratio of M_2P:P:SrO:Sr:Sc_2O_3 = 1:1:3:1:1 was pressed into pellets in a glovebox filled with Ar gas. In the case of $Sr_2ScCo_{0.5}Fe_{0.5}PO_3$ (M = $Co_{0.5}Fe_{0.5}$), the starting materials were $Co_{0.5}Fe_{0.5}P$, SrO, Sr and Sc_2O_3. The precursor $Co_{0.5}Fe_{0.5}P$ was prepared by a solid state reaction of Co, Fe_2P and P with a molar ratio of 2:1:1 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

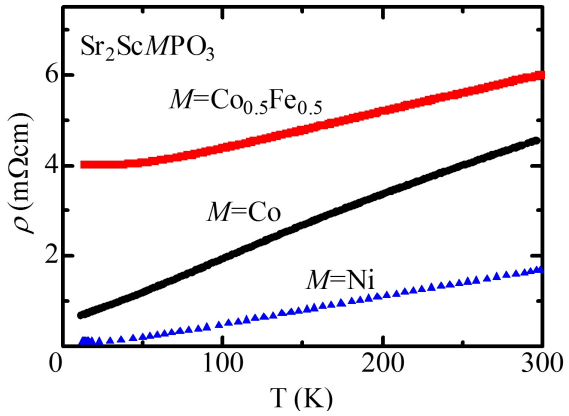

Figure 3. Temperature (T) dependence of th resistivity (ρ) for Sr_2ScMPO_3 (M = Co, Ni and $Co_{0.5}Fe_{0.5}$).

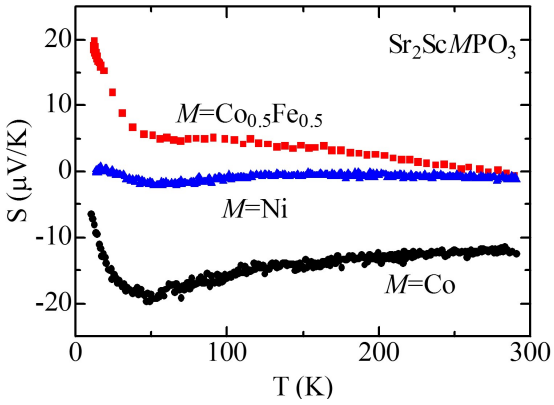

Figure 4. Temperature (T) dependence of the Seebeck coefficient (S) for Sr_2ScMPO_3 (M = Co, Ni and $Co_{0.5}Fe_{0.5}$).

of 0.1 at room temperature. Crystallographic phases were examined by powder X–ray diffraction (XRD, Rigaku, Rint2500). Lattice parameters were roughly obtained by a least–squares fitting method using the diffraction angles collected in the 2θ range from 10 to 70°.

Resistivity 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. Results and Discussion

Figure 2 shows the powder XRD patterns of Sr_2ScMPO_3 (M = Mn, Ni and $Co_{0.5}Fe_{0.5}$) with the accompanying Bragg positions calculated by the analysis program RIETAN-FP [14]. These patterns are similar to the pattern of $Sr_2ScFePO_3$ [9], which indicates that these compounds are isomorphic to $Sr_2ScFePO_3$. The powder XRD patterns were successfully indexed except for some peaks assigned to secondary phases. The space group of Sr_2ScMPO_3 is $P4/nmm$. The lattice constants are a = 0.4065(1) nm and c = 1.5803(6) nm for M = Mn, a = 0.4027(2) nm and c = 1.5310(11) nm for M = Ni, and a = 0.4009(1) nm and c = 1.5506(9) nm for M = $Co_{0.5}Fe_{0.5}$.

Figure 3 shows the temperature dependence of ρ for Sr_2ScMPO_3 (M = Ni and $Co_{0.5}Fe_{0.5}$) with that of $Sr_2ScCoPO_3$ previously reported [12]. In $Sr_2ScMnPO_3$, ρ at room temperature was found to be a large value like that of an insulator. In all samples except M = Mn, ρ decreases with decreasing temperature. This metallic behavior is similar to that of $Sr_2ScFePO_3$ [9]. The superconducting transition is not observed in Figure 3 for any of the materials measured in the temperature interval 20–300 K. The value of ρ for M = Ni at room temperature is 1.7 mΩ cm, smaller than that for M = Co over the entire range 20–300 K. The value of ρ for M=$Co_{0.5}Fe_{0.5}$ at room temperature is 6.0 mΩ cm, larger than that for M = Co over the entire temperature range considered.

Figure 4 shows the temperature dependence of S for Sr_2ScMPO_3 (M = Ni and $Co_{0.5}Fe_{0.5}$) with that of $Sr_2ScCoPO_3$ previously reported [12]. In $Sr_2ScNiPO_3$, S is observed to slightly decrease with decreasing temperature down to 50 K, and increase with decreasing temperature below 50 K. Although this behavior is similar to that of $Sr_2ScCoPO_3$, the absolute value of S is smaller than that of $Sr_2ScCoPO_3$ over the entire temperature range considered. In

$Sr_2ScCo_{0.5}Fe_{0.5}PO_3$, S slightly increases with decreasing temperature down to 50 K, and rapidly increase with decreasing temperature below 50 K. Figure 4 indicateds that S is negative for M = Ni over the entire temperature range 20–300 K, and that S is negative for $M = Co_{0.5}Fe_{0.5}$ only over the range 270–300 K. As such, the sign inversion of S is obtained at about 270 K for $M = Co_{0.5}Fe_{0.5}$, and S retains a positive value below 270 K. This sign inversion of S is also observed for $Sr_2ScFeAsO_3$ at 100 K [15]. The $S - T$ curves for each of the materials considered are clearly different from each other. The observed differences of the $S - T$ curves reflect the influence of multiband electronic structures.

4. Conclusion

In summary, we have successfully synthesized polycrystalline samples of novel oxypnictides, Sr_2Sc*M*PO_3 with *M*P layers (M = Mn, Ni and $Co_{0.5}Fe_{0.5}$). The transport properties of these samples are demonstrated. $Sr_2ScMnPO_3$ is found to be an insulator at room temperature. In Sr_2Sc*M*PO_3 (M = Ni and $Co_{0.5}Fe_{0.5}$), *rho* decreases with decreasing temperature like in a metal. In Sr_2Sc*M*PO_3 (M = Ni and $Co_{0.5}Fe_{0.5}$), S exhibits negative values at room temperature. In $Sr_2ScNiPO_3$, S slightly decreases with decreasing temperature, and increases with decreasing temperature below 50 K. However, S for $Sr_2ScCo_{0.5}Fe_{0.5}PO_3$ increases with decreasing temperature, and attains a positive value around 270 K. Local structural refinement and theoretical band structure calculations are required to quantitatively analyze the transport and magnetic properties of the materials considered in the present study. Higher accuracy and precisely Rietveld refinement and application of density functional theory [16–19] are therefore chosen for future work.

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