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Thermoelectric Properties of Several Strontium Ferrites, $SrFe_{12}O_{19}$, $SrFeO_{3-x}$ and $Sr_4Fe_6O_{13+x}$

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$SrFe_{12}O_{19}$, $SrFeO_{3-x}$ and $Sr_4Fe_6O_{13+x}$ were prepared by solid state reaction and the electrical conductivity (σ) and Seebeck coefficients (α) at the temperature up to 800°C were measured, and the thermoelectricity was evaluated by the power factors ($\alpha^2\sigma$). Thermoelectric properties of the samples of $SrFeO_{3-x}$ in which Ti, Mn, Co, Cu or Zn substituted for the part of Fe were also examined. Seebeck coefficient of magnetoplumbite-type $SrFe_{12}O_{19}$ was negative at any temperature measured and was about -300 μVK^{-1} at 400°C which was large enough for the application. However, the electrical conductivity was 0.3 Sm^{-1} which was too low. On the other hand $Sr_4Fe_6O_{13+x}$ shows positive and relatively high Seebeck coefficient (188 μVK^{-1} at 800°C), but the electrical conductivity was not enough (about 60 Sm^{-1} at 800°C). Perovskite-type $SrFeO_{3-x}$ shows enough electrical conduction (1.6×10^4 Sm^{-1} at 400°C), but Seebeck coefficient was too small (-10 μVK^{-1} at 400°C and 10 μVK^{-1} at 900°C). The substitution of Co for Fe site of $SrFeO_{3-x}$ was found to make Seebeck coefficient increase positively with slight increase of electrical conductivity.
Key words: strontium ferrites, electrical conductivity, Seebeck coefficients, power factor, lattice constants

1. INTRODUCTION

Thermoelectric power generation is a system to convert thermal energy to electric energy by Seebeck effect using thermoelectric devices, and is expected to make clean energy without any environmental load, such as exhaustion gas and noise of driving part. Oxide thermoelectric materials are more advantageous for their thermal durability and chemical stability than chalcogeneide materials represented by Bi_2Te_3, which is one of the most effective materials for the energy conversion. However, oxides had been thought to have insufficient converting effect because of their low mobility of carriers. In 1997, it was found that the layer-structured oxide $NaCo_2O_4$ was a high effective thermoelectric material [1], and the dimensionless figure of merit *ZT* of single crystal of $NaCo_2O_4$ was shown to exceeds unity [2], which is the standard value for practical use. $Ca_2Co_2O_5$ and related materials are also had high performance for thermoelectricity [3,4]. Zn-In-O system homologous materials [5,6], Al-doped ZnO [7,8], $Ba_{1-x}Sr_xPbO_3$ [9] and so on, have been investigated as high effective materials.

Strontium ferrites are investigated as high performanced magnetic materials and have advantages of stability at high temperatures and low toxic nature, and moreover, low cost production process had been fabricated. However, it has not been studied as thermoelectric materials. $SrFe_{12}O_{19}$ has magnetoplumbite crystal structure, in which closed-paced layers including Ba ions are stacked up and down side of spinel-ytpe 4-layered closed-paced layers and further, 2 of closed packed layers are put both sides. $SrFeO_{3-x}$ was metallic compounds and have antiferromagnetism [10]. The crystal structure was pervskite-type in which FeO_6 octahedra connected each other in 3-dimensional manner, and Sr ions are inserted into 12-fold interstitials. And it is known that the crystal structure changes among cubic, tetragonal, orthorhombic and again cubic as the amount of oxygen nonstoichiometry and temperature change. $Sr_4Fe_6O_{13+x}$ have perovskite-related structure, in which perovskite-block (SrO-FeO_2-SrO) and $Fe_2O_{2.5}$ block is alternatively stacked [11]. And in this compound, conduction occur in the perovskite layers under high oxygen partial pressures, and defects of Fe ion are to be an electron-like carrier under low oxygen partial pressures [12]. In this study, the sintering bodies of $SrFe_{12}O_{19}$, $SrFeO_{3-x}$ and $Sr_4Fe_6O_{13+x}$ were prepared and the electrical conductivity and Seebeck coefficients of those samples were measured, and evaluated them as thermoelectric materials using power factors. And samples in which Fe-site of $SrFeO_{3-x}$ was partially substituted by other elements, Ti, Mn, Co and so on were also fabricated and evaluated with the conductivity and Seebeck coefficients.

2. EXPERIMENTAL PROCEDURE

Powders of Fe_3O_4 and $SrCO_3$ were weighed as to obtain $SrFe_{12}O_{19}$, $Sr_4Fe_6O_{13+x}$ and $SrFeO_{3-x}$, and were mixed using pastle and mortar with ethanol. After dried, the mixed powders were calcined in aluminum crucibles at 1000 or 1100°C for 12 h. The powders were then uniaxially pressed into bars whose dimensions were about 4×4×20 mm and isostatically pressed under 100 MPa at room temperature. Then, the compact bodies were sintered in a furnace at 1100 or 1200°C for 12 h. When preparing Fe-site-substituting samples, MnO, ZnO, CuO, TiO_2, Co_2O_3 or NiO were used for substituting agent. Those oxides were weighed such that the elements substituted 10 % of Fe in atomic ratio. For Cobalt substitution, the fraction, *y* in $Fe_{1-y}Co_ySrO_{3-x}$, was changed to be 0, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5. The process to prepare of those substituted samples was the same as non-substituted ones.

The phases of the calcined powders and sintered bodies were determined by X-ray diffraction analysis. The electrical conductivity was measured from room temperature to 900°C by alternate current 4-probe method. Seebeck coefficients were also measured from room temperature to 800°C by measuring thermoelectric voltage generated by the temperature gradients. The details of the measurements have been described elsewhere [13].

3. RESULTS AND DISCUSSION

3.1 Thermoelectric properties of strontium ferrites

From the XRD analysis, calcined powders containing single phase of $SrFe_{12}O_{19}$, $Sr_4Fe_6O_{13+x}$ and $SrFeO_{3-x}$ were obtained. Figure 1 shows the temperature dependence of the electrical conductivity and Seebeck coefficients of these three strontium ferrites. The electrical conductivity of $SrFe_{12}O_{19}$ was about 2×10^{-4} Sm^{-1} at room temperature and increased as temperature increased, which means that this material behaves as a semiconductor. Seebeck coefficient ranged from -310 to -70 μVK^{-1}, so the carriers were electrons. $SrFeO_{3-x}$ shows very high electrical conductivity of 2.5×10^{4} Sm^{-1} at 450°C and showed metal-semiconductor transition at 400-500°C. Seebeck coefficient of $SrFeO_{3-x}$ change its sign and the absolute value was small as was -10 μVK^{-1} at 400°C and 11 μVK^{-1} at 800°C. Electrical conductivity of $Sr_4Fe_6O_{13+x}$ ranged from 10^{-1} to 10^{2} Sm^{-1} and increased as temperature increased in the range from room temperature to 400°C and become nearly constant over that temperature. Seebeck coefficient was positive and showed 188 μVK^{-1} at 800°C. Temperature dependence of power factors ($\alpha^2\sigma$) of those compounds are shown in Figure 2. This indicates that $SrFeO_{3-x}$ is thermoelectric material below 400°C, and $Sr_4Fe_6O_{13+x}$ is suitable at higher temperatures. And it is suggested that for $SrFeO_{3-x}$, increasing the absolute value of Seebeck coefficient was more important.

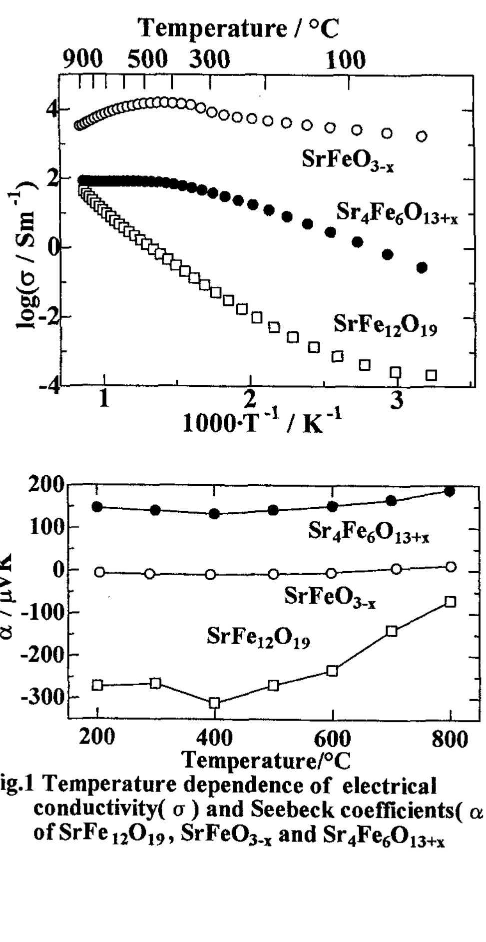

Fig.1 Temperature dependence of electrical conductivity(σ) and Seebeck coefficients(α) of $SrFe_{12}O_{19}$, $SrFeO_{3-x}$ and $Sr_4Fe_6O_{13+x}$

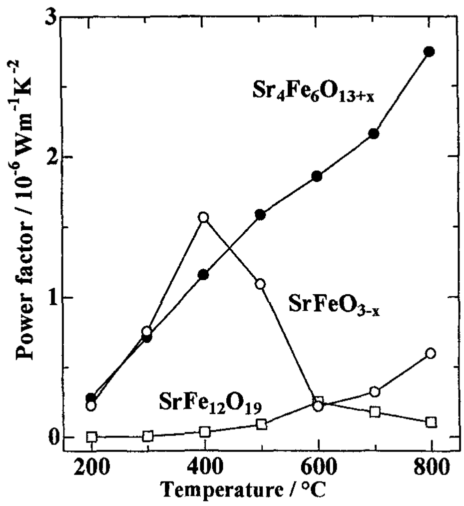

Fig. 2 Temperature dependence of power factors of $SrFe_{12}O_{19}$, $SrFeO_{3-x}$ and $Sr_4Fe_6O_{13+x}$

3.2 Substitution for Fe by other transition metals in $FeSrO_{3-x}$

Figure 3 shows temperature dependence of electrical conductivity of the sample in which 10 % of Fe in $SrFeO_{3-x}$ was substituted by Ti, Mn, Co, Cu or Zn. The whole tendency of conduction was almost the same as a non-substituted sample, but Ti, Zn and Mn-substituted samples showed a little lower conductivity. Figure 4 shows the Seebeck coefficients of these samples. Substitution let Seebeck coefficients shift to positive direction, especially with Ti, Zn, Mn and Co. And among those samples of increasing Seebeck coefficient positively, Co-substituted sample showed even higher electrical conductivity than non-substituted samples. So, Co-substitution was

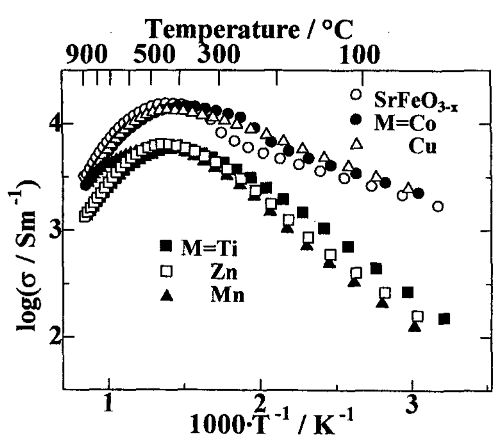

Fig. 3 Temperature dependence of electrical conductivity(σ) of $SrFe_{0.9}M_{0.1}O_3$

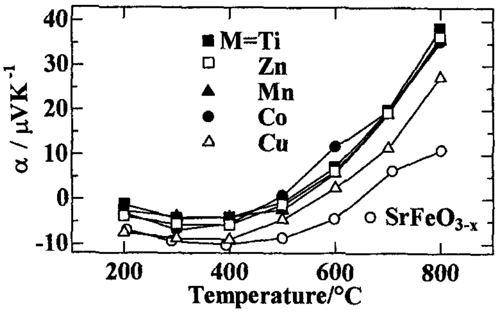

Fig. 4 Temperature dependence of Seebeck coefficients (α) of $SrFe_{0.9}M_{0.1}O_{3-x}$

selected and investigated in detail to optimize thermoelectric properties.

3.3 Substitution for Fe by Co in various ratios

Figure 5 shows the electrical conductivity of Co-substituted samples, in which the composition was described as $Fe_{1-y}Co_ySrO_{3-x}$ and y is changed from 0 to 0.5. In case of samples in which Co was substituted, it could still be said that the electrical conductivity showed highest value at about 400°C, and the metal-semiconductor transition occurred at about 400°C. Some samples showed higher conductivity than the non-substituted sample. Samples of $0 < y < 0.2$ and those of $0.3 < y < 0.5$ seemed to be different in the manner of conduction increasing with increasing temperature in the range up to 300°C. This reminds

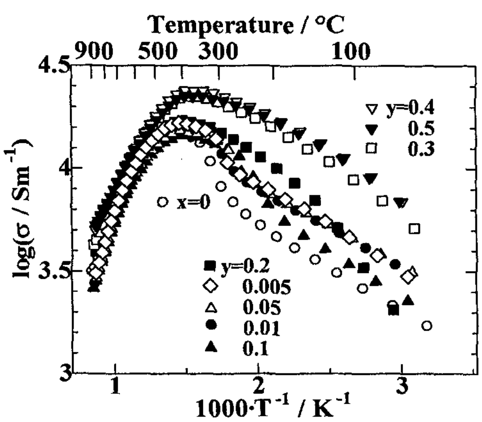

Fig.5 Temperature dependence of electrical conductivity(σ) of $SrFe_{1-y}Co_yO_{3-x}$

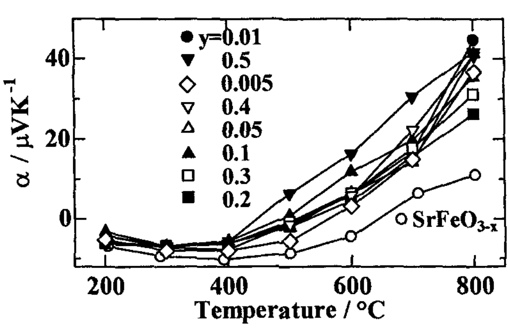

Fig. 6 Temperature dependence of Seebeck coefficients (α) of $SrFe_{1-y}Co_yO_{3-x}$

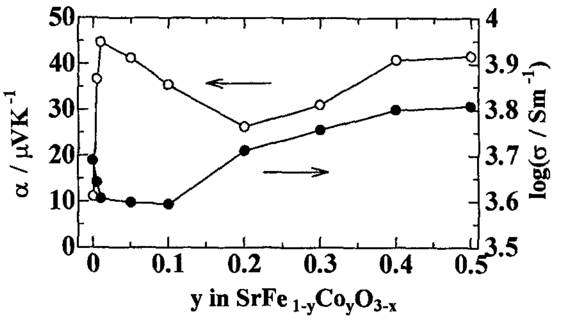

Fig. 7 Seebeck coefficients and electrical conductivity of sintered bodies of $SrFe_{1-y}Co_yO_{3-x}$ as a function of Co substitution ratio y, measured at 800°C.

that the two groups of samples have different structure of oxygen defects. Figure 6 shows temperature dependence of Seebeck coefficients of those samples. The whole tendency of temperature dependence was the same as non-substituted samples. As Co was substituted, Seebeck coefficient shifted to positive direction. However the dependence on Co content was complicated.

Figure 7 showed the dependence of electrical conductivity and Seebeck coefficients of Co-substituted samples on the amount of substitution, y, at 800°C. Slight substitution of Co up to 0.01 made Seebeck coefficient increase and electrical conductivity decrease. On the contrary, as y increased up to 0.2, Seebeck coefficient decreased and electrical conductivity increased. This tendency indicates that carrier concentration decreased rapidly up to y = 0.01, and then increased up to y = 0.2. And over y of 0.2, both electrical conductivity and Seebeck coefficient increase as y increased, showing that they were independent to the carrier concentration. Figure 8 shows the amount of Co substitution on the lattice constants of the compound calculated from XRD analysis data. This shows that the crystal structure was tetragonal up to y = 0.2 and lattice constants changed, and when $y > 0.2$ the structure was cubic and lattice constants were nearly constant as y changed. This corresponded to the electrical properties, and showing that the Co-content dependence of electrical properties was affected by the structure of samples.

Figure 9 shows the power factor of Co-substituted samples calculated from electrical conductivity and

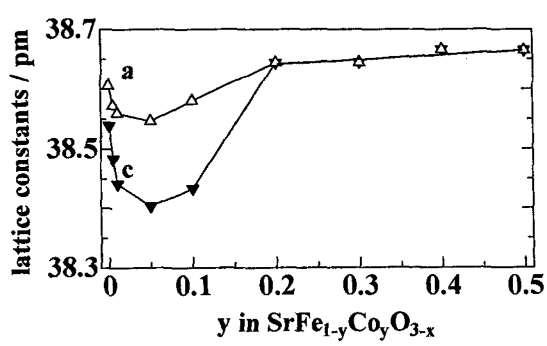

Fig. 8 Dependence of lattice constants of $SrFe_{1-y}Co_yO_{3-x}$ on Co content

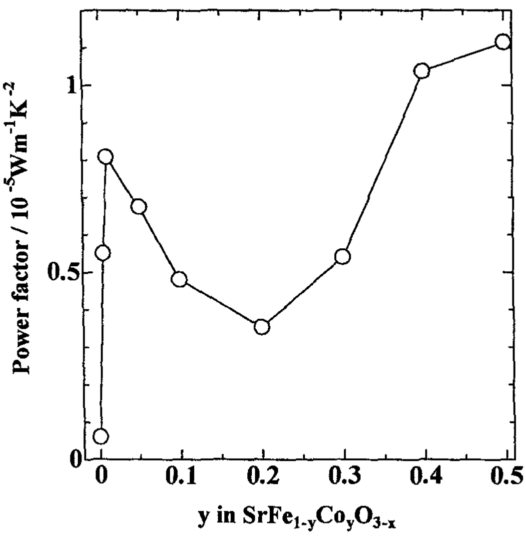

Fig. 9 Power factors at 800℃ of sintered bodies of $SrFe_{1-y}Co_yO_{3-x}$

Seebeck coefficients. It shows that the power factor increase rapidly by Co-substitution up to $y = 0.01$ and gradually decreased up to $y = 0.2$. Again it increased gradually up to $y = 0.5$. The highest power factor in this study was obtained with the $y = 0.5$ sample, and it was about 1.1×10^{-5} $Wm^{-1}K^{-2}$ at 800°C. However, this value is not enough for practical use.

4. CONCLUSION

4.1 Several strontium ferrites

$SrFeO_{3-x}$ showed highest electrical conductivity in $SrFe_{12}O_{19}$, $SrFeO_{3-x}$ and $Sr_4Fe_6O_{13+x}$. Seebeck coefficient of $SrFe_{12}O_{19}$ and $Sr_4Fe_6O_{13+x}$ were negative and positive, respectively and the absolute values of those exceeded 100 μVK^{-1}. Seebeck coefficients of $SrFeO_{3-x}$ were nearly zero and negative below 400°C and positive over 500°C. Evaluated from the power factor, $SrFeO_{3-x}$ was suitable for thermoelectric converter below 400°C.

4.2 Fe-site substitution for $SrFeO_{3-x}$

Electrical conductivity changed by Fe-site substitution, and separated into two groups by the amount of the decrease of conduction. Seebeck coefficients shifted to positive direction by the substitution by any elements.

4.3 Thermoelectric properties of $Fe_{1-y}Co_ySrO_{3-x}$

Electrical properties in $y < 0.2$ were thought to be dependent on carrier concentrations. Lattice constants decreased with Co content up to $y < 0.005$, and increased with-x in the range $0.05 < y < 0.2$ and took almost constant in the range $y > 0.2$. The highest power factor was obtained with the $y = 0.5$ sample, and it was about 1.1×10^{-5} $Wm^{-1}K^{-2}$ at 800°C.

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