Anomalous Temperature Dependence of the Thermoelectric Power for

$Ln_{0.9}Sr_{0.1}FeO_{3-\delta}$ (Ln=La and Nd)

Kiyoshi Kobayashi, Masateru Nishioka, Koichi Sato, Tomoya Inoue, Satoshi Hamakawa, Tatsuo Tsunoda, Toru Higuchi*, and Shu Yamaguchi**

National Institute of Advanced Industrial Science and Technology, 4-2-1, Nigatake, Miyagino-ku, Sendai 983-8551, Japan
Fax: 022-366-5708, e-mail: kiyoshi-kobayashi@aist.go.jp
*Department of Applied Physics, Science University of Tokyo, 1-3, Kagurasaka, Shinjuku-ku, Tokyo162-0825, Japan
**Department of Materials Science, University Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656

Anomalous temperature dependence of thermoelectric power was observed below the critical temperature of 620 K for $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and 550 K for $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$. The accurate Heikes model including the heat of transport of holes was able to explain the temperature dependence of thermoelectric power in air between 1273 K and the critical temperature. On the other hand, the thermoelectric power increased with decreasing temperature below the critical temperature. We were unable to explain the temperature dependence using the Heikes model. The critical temperature showed good agreement with the temperature of magnetic phase transition (Néel Temperature). A qualitative explanation is shown based on solid-state electrochemistry.

Key words: thermoelectric power, orthoferrite, Néel temperature, Heikes model, solid-state electrochemistry

1. INTRODUCTION

Strontium-doped lanthanum ferrite, $La_{1-x}Sr_xFeO_{3-\delta}$, is a typical oxide semiconductor; the relationships between the electrical transport properties and defect structure in the high temperature region have been investigated using electrical conductivity, thermoelectric power, and oxygen nonstoichiometry measurements [1–6]. This study revealed that thermoelectric powers of $Ln_{0.9}Sr_{0.1}FeO_{3-\delta}$ (Ln=La and Nd) in air do not conform to the theoretical thermoelectric power values calculated using electrical transport and defect chemical parameters estimated from data between 1273 K and 1073 K. Moreover, the critical temperature showed good agreement with the magnetic phase transition temperature (Néel temperature) of the $Ln_{0.9}Sr_{0.1}FeO_{3-\delta}$. To elucidate this phenomenon, we examined a qualitative explanation based on solid-state electrochemistry.

2. EXPERIMENTAL

Samples with compositions of $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$ were prepared using conventional solid-state reaction method. Starting materials were La_2O_3, Nd_2O_3, $SrCO_3$, and Fe_2O_3 (4N purity; Rare Metallic Co. Ltd., Tokyo, Japan). These raw powder materials were weighed to stoichiometric composition of $La_{0.9}Sr_{0.1}FeO_{2.95}$ and $Nd_{0.9}Sr_{0.1}FeO_{2.95}$ and mixed in an alumina mortar with

ethanol. The mixture was air-dried at 373 K, then pressed into disks by mechanical pressing. The disks were fired at 1573 K under O_2 atmosphere. Then the disks were crushed into powder after addition of a small amount of polyvinyl alcohol; the powder was pressed into disks again by mechanical pressing at 179 MPa. Disks with dimensions of 2.0-cm diameter and 2 mm thickness were then sintered at 1673 K for 10 h in O_2. X-ray diffraction analyses confirmed the sample to be a single-phase perovskite structure.

Block shape samples with dimensions of 2 mm × 2 mm × 5 mm were cut from the sintered disks and used for thermoelectric power measurements. Thermoelectric power was measured in a cell constructed from alumina tubes and alumina blocks. A platinum sub-heater fixed at one end of the sample was used to generate the temperature gradient along the sample block. For thermo-electromotive force readings, R-type thermocouples attached to both ends of the sample rod with platinum paste were used as the temperature probes' lead wires. Detailed procedures have already been reported elsewhere [6–7].

Differential scanning calorimetry (DSC) measurements were carried out between 373 K and 723 K at a heating rate of 20 K / min.

3. RESULTS

Relationships between absolute temperature and thermoelectric power (Q_p) of $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$ are shown respectively in Figs. 1(a) and 1(b). Theoretical Q_p values were calculated from the accurate Heikes formula [7, 8]:

$$Q_p \approx \frac{R}{F}\ln\frac{1}{[Fe_{Fe}^{\cdot}]} + \frac{q_p^*}{RT}, \qquad (1)$$

where R, F, and T respectively denote the gas constant, Faraday constant, and absolute temperature. The $[Fe_{Fe}^{\cdot}]$ is the mole fraction of relatively single positive-charged Fe ions on Fe ion site; q_p^* is the heat of transport of holes. The $Fe_{Fe}^{\cdot}$ indicates the hole-localized Fe ions. The $[Fe_{Fe}^{\cdot}]$ and q_p^* values are calculable using the following equations and parameters listed in Table I [7]:

$$K_{ox} = \frac{(3-[V_O^{\cdot\cdot}])[Fe_{Fe}^{\cdot}]}{[V_O^{\cdot\cdot}](1-[Fe_{Fe}^{\cdot}])^2 p_{O_2}^{1/2}}, \qquad (2)$$

$$2[V_O^{\cdot\cdot}] = [Sr_{Ln}'] - [Fe_{Fe}^{\cdot}], \qquad (3)$$

$$K_{ox} = K_{ox}^o \exp\left(-\frac{\Delta H_{ox}}{RT}\right), \qquad (4)$$

$$p_{O_2} = 0.21 \text{ and } [Sr_{Ln}'] = 0.1, \qquad (5)$$

where $[V_O^{\cdot\cdot}]$ and $[Sr_{Ln}']$ respectively represent the mole fractions of the relatively double negative-charged oxide ion vacancy on the oxide ion site and relatively single negative-charged Sr ions on the Ln ion site. Also, K_{ox} is the equilibrium constant of reaction for annihilation of the oxide ion vacancy, p_{O_2} is the oxygen fugacity equilibrated with the sample, and ΔH_{ox} and K_{ox}^o are the enthalpy change of K_{ox} and the constant including the entropy term.

The Q_p values for $Ln_{0.9}Sr_{0.1}FeO_{3-\delta}$ (Ln=La and Nd) show no discontinuous jump, but their temperature dependence exhibited drastic changes at critical temperatures of 620 ± 50 K for $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and 550 ± 50 K for $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$. Based on DSC measurements, the second-order phase transition suggested to exist at the

critical temperature of the thermoelectric power measurements because the slopes of the base-lines of the DSC chart were changed near the critical temperature, as shown in Fig. 2.
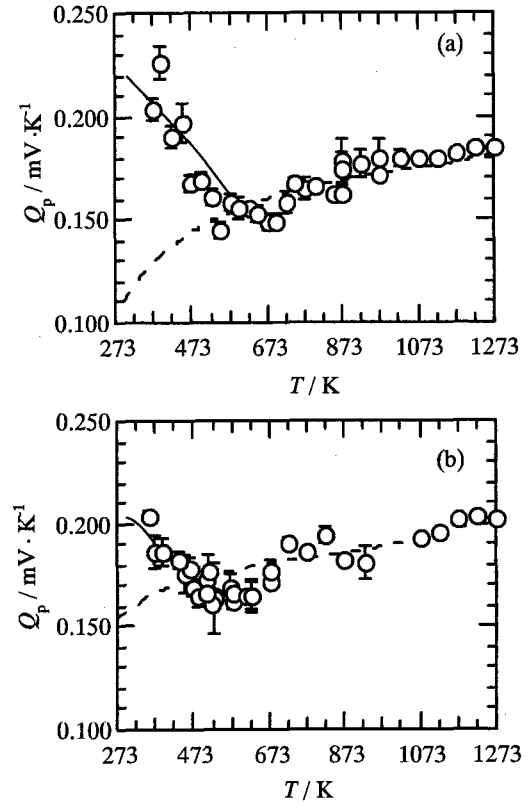

Fig. 1. Relationships between the thermoelectric power (Q_p) and temperature (T) under air of (a) $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and (b) $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$. Broken curves are calculated values using Eqs. (1)-(5).

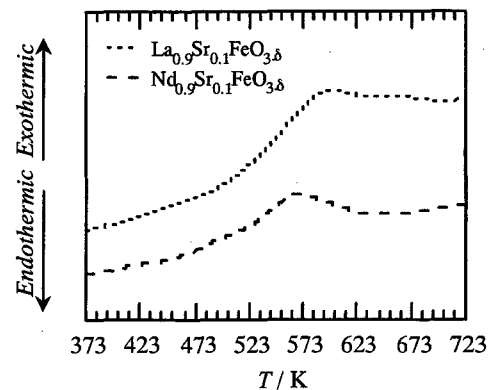Fig. 2. Differential scanning calorimetry chart of $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ (dotted curve) and $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$ (broken curve) measured in an air atmosphere.

Table I. Values of the defect chemical parameters and the heat of transport of holes for $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$.

	K_{ox}^o	ΔH_{ox} / eV	q_p^* / eV
$La_{0.9}Sr_{0.1}FeO_{3-\delta}$	9.68×10^{-4}	-1.05	-0.04
$Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$	1.23×10^{-2}	-0.68	-0.02

Figure 3 shows that the relationship between the Néel temperature (T_N) of $La_{1-x}Sr_xFeO_{3-\delta}$ and $\left[Fe^{\cdot}_{Fe}\right]$, as already reported by Wattiaux *et al.* [9], and the critical temperature of the Q_p for $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ located on the line. Hence, the cause of the anomalous temperature dependence of the Q_p for $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ is the magnetic phase transition between the paramagnetic phase and antiferromagnetic phase.
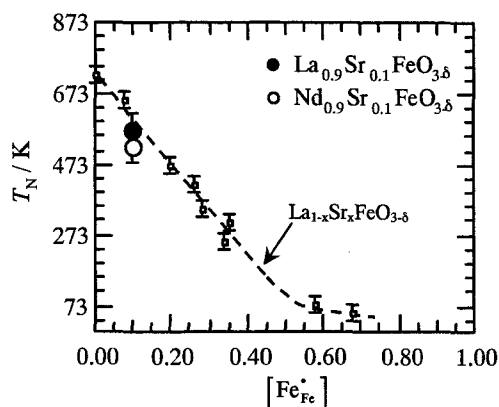

Fig. 3.   Comparison of the Néel temperature of $La_{1-x}Sr_xFeO_{3-\delta}$ by Wattiaux *et al.* [9] (small square mark and broken curve) to the critical temperature of $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$ measured by the thermoelectric power as a function of $\left[Fe^{\cdot}_{Fe}\right]$.

The difference between the critical temperature of $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$ was about 70 K; this temperature difference was close to the T_N difference (53 K) between $LaFeO_3$ $(T_N = 740$ K) and $NdFeO_3$ $(T_N = 687$ K) [10]. Experimental results of the critical temperature difference between $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ and $Nd_{0.9}Sr_{0.1}FeO_{3-\delta}$ also support that the anomalous temperature dependence of the thermoelectric power appeared because of the magnetic phase transition. Similar to our results, the influences of the magnetic phase transition on thermoelectric power have been reported for $MnFe_2O_4$ [11], Nd_2CuO_4 [12], and $NiFe_2O_4$-Fe_3O_4 [13] solid solutions, but the phenomena's theoretical aspects have not been clarified.

4. DISCUSSION

Based on solid-state electrochemistry, eq. (1) is derived from the quasi-binary system of $Fe^{\cdot}_{Fe}$ - Fe^x_{Fe} in perovskite oxides, where Fe^x_{Fe} are relatively neutral Fe ions in the Fe ion site [7, 8, 15]. In addition, eq. (1) is applicable when the $Fe^{\cdot}_{Fe}$ - Fe^x_{Fe} quasi-binary system is treated as a $Fe^{\cdot}_{Fe}$ dilute solution in Fe^x_{Fe} solvent [8]

because the first term of eq. (1) includes the mixing entropy of the dilute $Fe^{\cdot}_{Fe}$ ions in the solvent of the Fe^x_{Fe} ion site.

Below the Néel temperature of $LaFeO_3$ and $NdFeO_3$, the Fe ion site is distinguishable as an $Fe^\uparrow$ site and an $Fe^\downarrow$ site by the spin direction [10]. Below the Néel temperature, we must treat a quasi-ternary system of $Fe^{\cdot}$ - $Fe^\uparrow$ - $Fe^\downarrow$ when we calculate the distribution of $Fe^{\cdot}$ ion on the $Fe^\uparrow$ site and $Fe^\downarrow$ site, where $Fe^{\cdot}$ is a single positive-charged Fe ions on $Fe^\uparrow$ site and $Fe^\downarrow$ site.

The $Fe^\uparrow$ ion on $Fe^\downarrow$ site ($Fe^\uparrow_{Fe^\downarrow}$) and $Fe^\downarrow$ ion on $Fe^\uparrow$ site ($Fe^\downarrow_{Fe^\uparrow}$) also exist below T_N because of the strong interaction between the iron ions as similar to the order − disorder phase transition of metallic alloy [15, 16]. The $Fe^{\cdot}$ ion solution in $Fe^\uparrow$ - $Fe^\downarrow$ solvent must be treated as the $Fe^{\cdot}$ ion solution in strong interacted solvent. We cannot employ models of a dilute solution and an ideal solution used for derivation of the conventional Heikes model.

We must determine the interaction energy as a function of short-range ordered coordination of Fe ions for analyses by numerical calculation. Moreover, the influence of the magnetic phase transition on the heat of transport of holes has not been clarified yet. Hence, further experiments are necessary for statistical modeling such as the applied quasi-chemical method for ionic crystals [17].

5. CONCLUSION

Anomalous temperature dependencies of the thermoelectric power for $Ln_{0.9}Sr_{0.1}FeO_{3-\delta}$ (Ln=La and Nd) were found below the Néel temperatures. Below the Néel temperature, $Fe^{\cdot}_{Fe}$ coordination on the two kinds of iron ion sites distinguished by the stable spin direction might be influenced strongly by coordination of the relative single-charged iron ions with spin direction, i.e. the degree of order. We must calculate the distribution of $Fe^{\cdot}$ ions in the strong-interacted quasi-ternary system if the Heikes model is applied to Sr-doped $LnFeO_3$.

6. References

[1] J. Mizusaki, T. Sasamoto, W. R. Cannon, and H. K. Bowen, J. Am. Ceram. Soc., 65 (1982) 363.

[2] J. Mizusaki, T. Sasamoto, W. R. Cannon, and H. K. Bowen, J. Am. Ceram. Soc., 66 (1983) 247.

[3] J. Mizusaki, M. Yoshihiro, S. Yamauchi, and K. Fueki, J. Solid State Chem., 58 (1985) 257.

[4] J. Mizusaki, M. Yoshihiro, S. Yamauchi, and K. Fueki,

J. Solid State Chem., 67 (1987) 1.

[5] M. C. Kim, S. J. Park, H. Haneda, J. Tanaka, and S. Shirasaki, Solid State Ionics, 40-41 (1990) 239.

[6] K. Kobayashi, S. Yamaguchi, T. Higuchi, S. Shin, T. Tsukamoto, and T. Tsunoda, *Electrochem.* **72** (2004) 870.

[7] K. Kobayashi, S. Yamaguchi, T. Tsunoda, and Y. Imai, *Solid State Ionics*, **144** (2001) 123.

[8] K. Kobayashi, T. Tsunoda, T. Higuchi, and S. Yamaguchi, in "Solid State Ionics: The Science and Technology of Ions' Motion" (Eds. B.V.R. Chowdari et al., World Scientific Pub. Co., NJ 2004) pp. 979.

[9] A. Wattiaux, J. Grenier, M. Pouchard, and P. Hagenmuller, *J. Electrochem. Soc.*, **134** (1987) 1718.

[10] M. Eibschütz, S. Shtrukman, and D. Treves, Phys. Rev., 156 (1967) 562.

[11] T. E. Whall, N. Salerno, and Y. G. Proykova, Phil. Mag. B., 56 (1987) 99.

[12] A. A. Sattar, K. M. El-Shokroft, and A. M. Samy, Phys. Stat. Sol. (a)., 174 (1999) 449.

[13] B. A. Griffiths, D. Elwell, and R. Parker, Phil. Mag., 22(1970) 163.

[14] K. Kobayashi, S. Yamaguchi, M. Mukaida, and T. Tsunoda, *Solid State Ionics*, **144** (2001) 315.

[15] R. A. Swalin, in "Thermodynamics of Solids" (John Wiley & Sons. Inc., New York, 1962) pp. 109-131.

[16] E. A. Guggenheim, in "Mixtures: The theory of the equilibrium properties of some simple classes of mixtures solutions and alloys" (Oxford Univ. Press, London, 1952) pp. 101-143.

[17] S. Yamaguchi, H. Kajino, and Y. Iguchi, Abstract of 64th Annual Meeting of Electrochemical Society of Japan (Yokohama, 1997) p. 169.