Thermoelectric Properties of Mn and Ni doped Magnetite

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Abstract

Effects of co-substitution of Mn and Ni were investigated on the thermoelectric properties of sintered magnetite (Fe_3O_4). Based on the previous study, investigations were focused on (1): $0 \leq x \leq 0.4$ with $y=2/3$ and (2): $0 \leq y \leq 1$ with $x=0.2$, in $(Mn_yNi_{1-y})_xFe_{3-x}O_4$. From these experiments thermoelectric power factor manifested a maximum near $y=2/3$, where the number of 3d electrons in magnetite was preserved by substitution. The highest power factor obtained was 1.2 $\mu W/K^2cm$ at 973K, exceeding that of pure magnetite.

Introduction

Magnetite (Fe_3O_4) is one of the most studied transition metal oxides on magnetic and electrical properties. With respect to the electrical properties, the Verwey transition at 127K has been in a central part of the studies of electronic structure and transport mechanism. In recent decade, the transport properties of electron correlation systems, including the transition metal oxides and chalcogenides, have attracted great attention for their novel electronic structures and transport mechanism and numerous studies have been made. As for the thermoelectric properties, layered Cobalt oxide ($NaCoO_3$) [1] and titanium dichalcogenide (TiS_2) [2,3] have shown a large Seebeck coefficient with relatively low eletrical resistivity. In the recent years, the demand for thermoelectric generation has been increasing to restore effectively the huge amount of waste heat from industrial and private activities. For this purpose, the oxide materials have an advantage as they are in general resistant against oxidation at higher temperature. Magnetite is a heat resistant transition metal oxide composed of nontoxic and high Clark-number elements, and thus, it has a potential for a mass-productive thermoelectric material operating at medium to high temperature. There have been studies on substitution effects of Mn [4], Ti [5] and Ni[6,7] on the thermoelectric properties of Fe_3O_4 single crystal. However, the report on the thermoelectric properties of polycrystalline magnetite is very few.

In the previous study, [8,9] we investigated the thermoelectric properties of sintered magnetite and its substitution effects of Mn and/or Ni. It was found that the grain boundary in magnetite didn't affect the electrical transport remarkably. With respect to the Mn and/or Ni substitutions, $(Mn_yNi_{1-y})_xFe_{3-x}O_4$, experiments were carried out for substitution content x=0, 0.4, 0.8 and 1.2, and with relative Mn content y=0, 1/2, 2/3 and 1. The substitution with y=2/3 preserves the total number of 3d electrons in magnetite. It was found that the substitution with x=0.4 and y=2/3 yielded a thermoelectric power factor exceeding that of magnetite.

In the present study, after the results of our previous study, investigations are focused on the thermoelectric properties of magnetite with lower substitution concentration of Mn and Ni $0 \leq x \leq 0.4$, for various y.

Experimental

The sample preparation condition and the measurement system in this study were the same as those in the previous study [8]. That is, the polycrystalline magnetite samples were prepared by sintering the Fe_3O_4 pellets at 1373K for 10 hours in Ar atmosphere. The pellets were prepared by pressing the 99.9% purity Fe_3O_4 powder with 100MPa for 10 minutes. The dimensions of pellet were 13mm diameter and 1mm thickness. For the substitutions of Mn and/or Ni, 99.9% purity Mn_3O_4 and NiO powders were weighed and mixed well with Fe_3O_4 powder and then pellets were prepared. The substitution content x in $(Mn_yNi_{1-y})_xFe_{3-x}O_4$ was chosen as 0, 0.1, 0.2, 0.3, and 0.4, with $y=0.67(=2/3)$. The relative Mn content y, in the substitution content x, was changed as 0, 0.2, 0.4, 0.5, 0.6, 0.67, 0.7, 0.8 and 1, with $x=0.2$. Samples for electrical measurements were obtained by cutting the center part of pellets in 3.5mm width. Pt was evaporated on both ends for current electrodes.

The electrical resistivirity ρ and the Seebeck coefficient S were measured simultaneously at each step in the temperature run between 473K and 973K. The ρ was obtained by a conventional 4-probe method. In this method the potential difference (ΔV) was measured by using the Pt wires of the two Pt-PtRh13% thermocouples, used to measure the temperature difference (ΔT), placed on the sample surface between the Pt evaporated current electrodes.

The S was derived from the slope of the plot array in the ΔV vs. ΔT graph with $-2K \leq \Delta T \leq 2K$

Results and Discussion

In this study, we concentrated on the x in the region $0 \leq x \leq 0.4$ and $y=2/3$ in $(Mn_yNi_{1-y})_xFe_{3-x}O_4$, because it was found in the previous study [8] that the sample with x=0.4, among 0.4, 0.8 and 1.2, and y=2/3, among 0, 1/2, 2/3 and 1, yielded a higher power factor (PF) than that of magnetite (x=0).

Figure 1 shows the scanning electron microscope (SEM) images of pellet surface (top frame) and cleaved cross section (bottom frame) for samples (a):x=0 and (b):x=0.2, both for y=2/3. It is shown that in (a) (x=0) the average grain size is several μm and in (b) (x=0.2) about 10μm.

Figure 2 (a) shows the X-ray diffraction (XRD) patterns for $(Mn_{0.67}Ni_{0.33})_xFe_{3-x}O_4$ with x=0, 0.1, 0.2, 0.3, and 0.4. As is shown in Fig.2 (a), all signals observed in the substituted samples were assigned to the cubic spinel structure as well as those in magnetite. The lattice constant derived from the XRD signals are shown in Fig.2 (b). Reflecting the ionic radii of Mn^{2+}: 0.91nm, Ni^{2+}: 0.78nm and Fe^{2+}: 0.82nm, and that the composition ratio Mn/Ni=2, the lattice constant increases linearly with the total substitution content x.

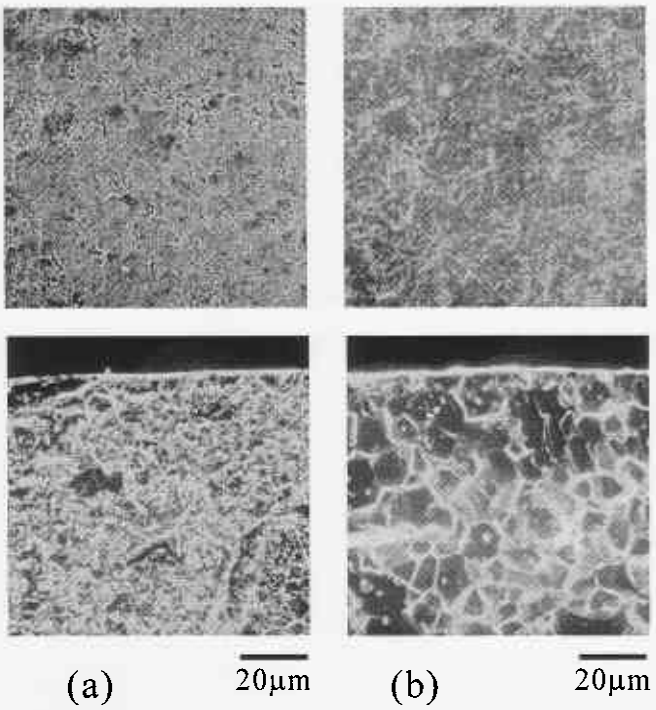


Figure 1: SEM images of pellet surface (top frame) and cleaved cross section (bottom frame) for samples (a): x=0 and (b): x=0.2.

Figure 3 shows the temperature dependences of (a) Seebeck coefficient *S*, (b) electrical resistivity ρ and (c) thermoelectric power factor PF derived from (a) and (b). It is to be noted that, while *S* increases with x over the measured temperature range, ρ for x=0.2 is comparable to that for x=0 over the measured temperature range. This behavior was ascertained for several samples with x=0.2. The origin of this is not yet understood, but one possibility might be that, as shown in Fig.1, the size of the grain in the sample with x=0.2 is large.

Figure 4 shows the substitution content x dependences of (a) *S*, (b) ρ and (c) PF for three temperatures. Reflecting the low value of ρ for x=0.2, the PF for x=0.2 gives the highest value at higher temperature among the measured x. Based on this result, similar experiments were carried out by changing y for x=0.2.

Figure 5 (a) shows the XRD patterns of samples with x=0.2 for various y. As shown in this figure, all signals observed were assigned to the cubic spinel structure. Figure 5 (b) shows the lattice constant as a function of y. Reflecting the difference in the ionic radii of Mn^{2+} and Ni^{2+}, the lattice constant increases with Mn content y.

Figure 6 shows the Mn content y dependences of (a) *S*, (b) ρ and (c) PF with x=0.2 for three temperatures. While *S* is less sensitive to y, ρ shows a remarkable y dependence. As a whole, ρ increases with y, but there appears a depression around y=2/3. Reflecting this behavior, the PF shows a maximum around y=2/3. The highest value of PF in this study was 1.2 $\mu W/K^2cm$ for x=0.2 and y=0.6.

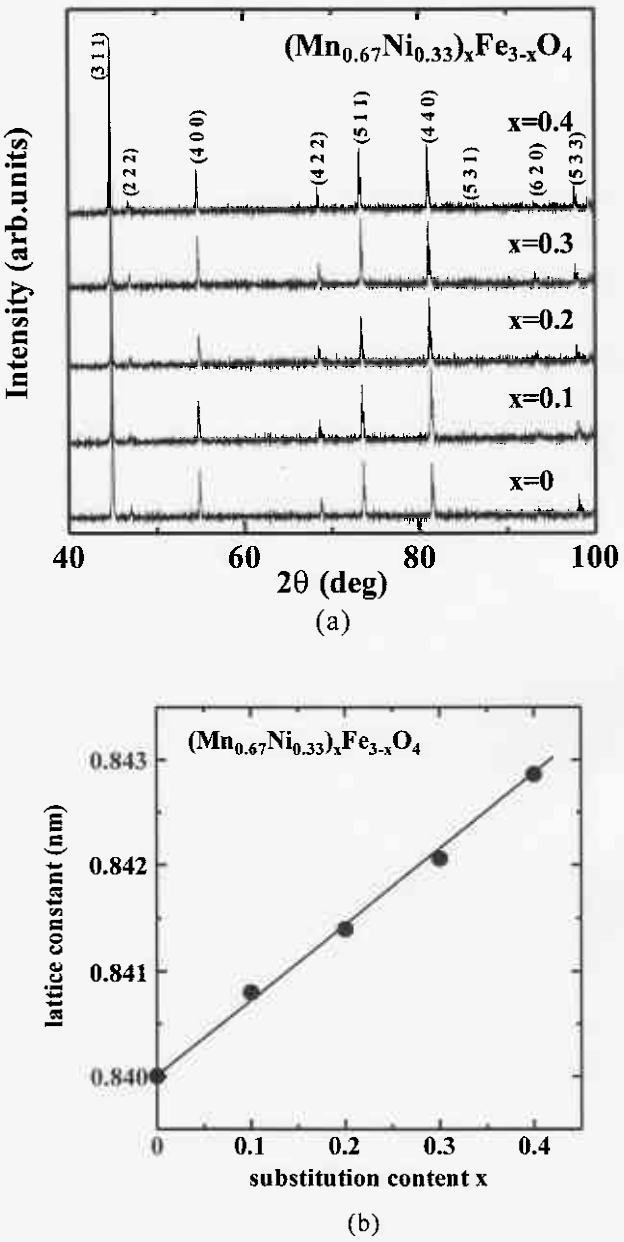


Figure 2: (a) XRD patterns, with cubic spinel lattice indices, for $(Mn_{0.67}Ni_{0.33})_xFe_{3-x}O_4$ with x=0, 0.1, 0.2, 0.3 and 0.4.
(b) Lattice constant as a function of x derived from XRD results.

There are the reports on the thermoelectric properties of Mn substituted $Mn_xFe_{3-x}O_4$ (x=0, 0.5, 0.8 and 0.4) [4] and Ni substituted $Ni_xFe_{3-x}O_4$ (x=0, 0.1, 0.2, 0.4, 0.6, 0.8 and 0.9) [6,7], both for single crystal. In both studies, the power factor of substituted materials didn't exceed that of pure magnetite. Similar results were obtained in our previous study for Mn or Ni substitutions in sintered magnetite, but it was found that the co-substitution of Mn and Ni can yield a PF exceeding that of pure magnetite [8]. In the present study, the x and y dependences of PF in sintered magnetite has been elucidated, though the value of PF is still not sufficient for practical uses.

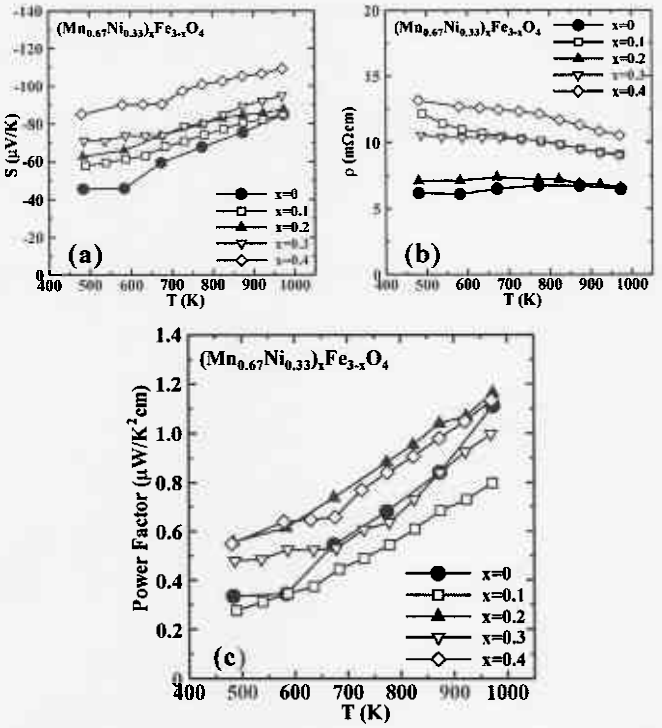


Figure 3: Temperature dependences of (a) Seebeck coefficient (*S*), (b) electrical resistivity (ρ) and (c) thermoelectric power factor (PF), for Mn composition ratio Mn/Ni=2.

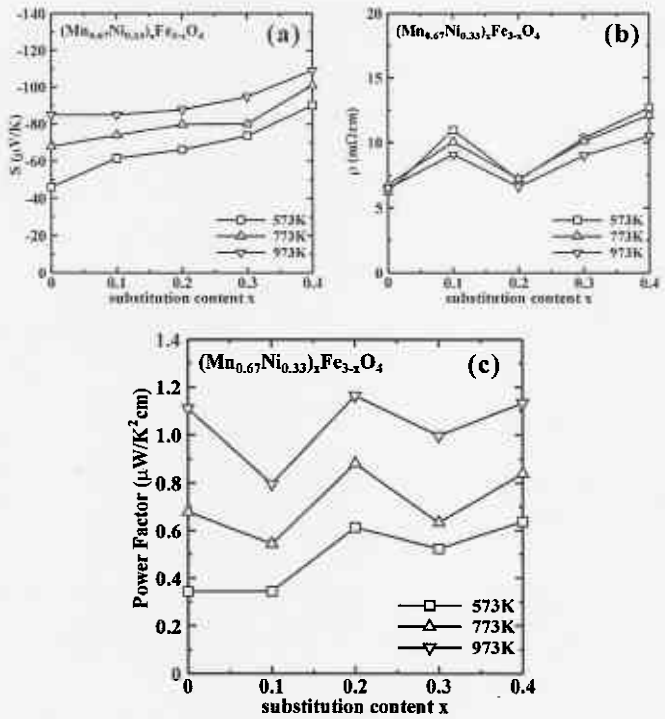
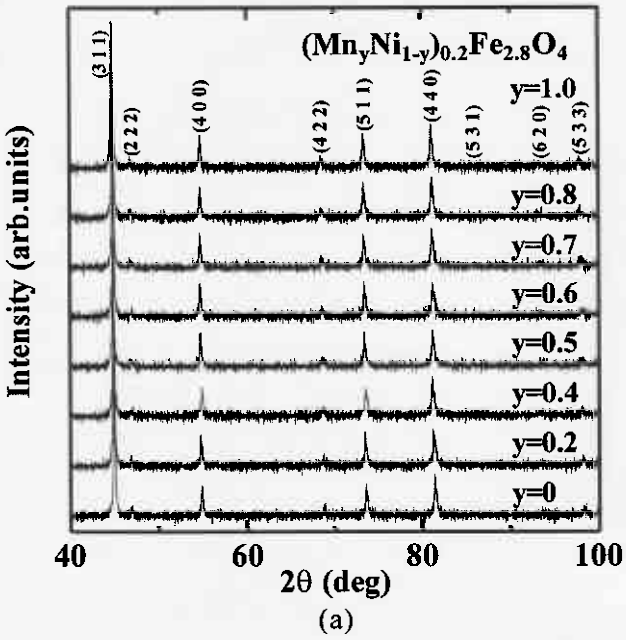


Figure 4: Substitution content x dependences of (a) *S*, (b) ρ and (c) PF, for Mn/Ni=2, at three temperatures.



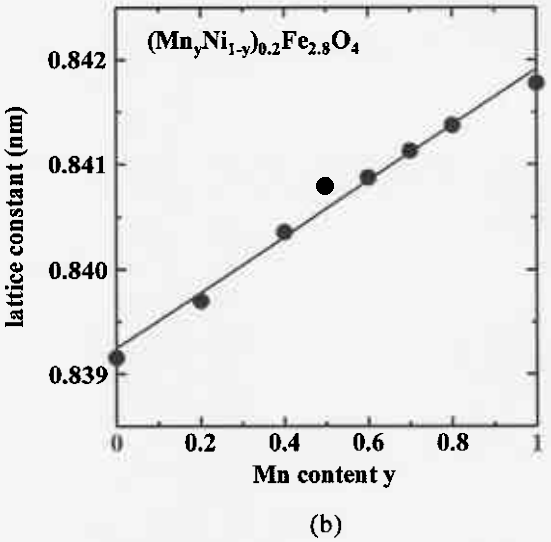


Figure 5: (a) XRD patterns, with cubic spinel lattice indices, for $(Mn_yNi_{1-y})_xFe_{3-x}O_4$ with x=0.2 for various y.
(b) Lattice constant as a function of y derived from XRD results.

We chose Mn and Ni for the substitution elements for the sake of comparison with the studies on single crystal. Mn^{2+} has less 3d electrons than Fe^{2+} by one. On the other hand, Ni^{2+} has two more 3d electrons than Fe^{2+}. Therefore, the co-substitution of Mn and Ni with the composition ratio Mn/Ni=2 preserves the total number of 3d electrons in the materials. The cause of the reduction in the electrical resistivity by such a co-substitution is to be elucidated for further improvement of thermoelectric properties. In addition to this effect, co-substitution will introduce an alloying disorder in the lattice, which will lower the thermal conductivity κ, and hence, increases the thermoelectric figure of merit $Z=S^2/\rho\kappa$. Many factors should be considered for further improvement of the thermoelectric properties of magnetite based materials. It is known that

80-90% of Mn^{2+} occupies the A site in Mn ferrite ($MnFe_2O_4$), while Ni^{2+} occupies the B site in Ni ferrite ($NiFe_2O_4$). It is also considered that, in the discrete ionic model, the electron conduction occurs in the B site in magnetite. The recent band calculation [10] showed that the Fermi level of magnetite lies in the minority-spin B-site band, which supports the B site electron conduction. If Mn^{2+} and Ni^{2+} occupy, in the substituted magnetite, the same sites as in those respective ferrites, Ni^{2+} affect directly the electron conduction, which occurs in B-site, while Mn^{2+} acts indirect because it occupies the A site.

Cobalt substitution, in place of Ni, has a possibility of improving the thermoelectric properties as it needs a half amount of Ni for preserving the number of 3d electrons in the co-substitution with Mn. Moreover, the ionic radius of Co^{2+} is nearer to that of Fe^{2+} compared with Ni^{2+}, and thus, Co^{2+} might less disturb the electrical conduction than Ni^{2+}.

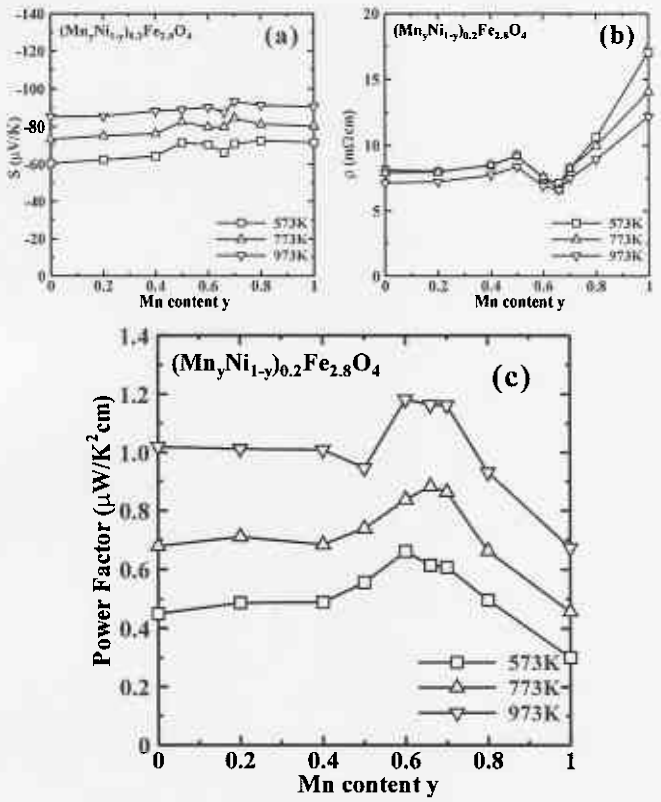


Figure 6: Mn content y dependences of (a) *S*, (b) ρ and (c) PF, for x=0.2 at three temperatures.

Summary

Effects of co-substitution of Mn and Ni were investigated on the thermoelectric properties of sintered magnetite (Fe_3O_4).

Based on the previous study, investigations were focused on (1): $0 \leq x \leq 0.4$ with y=2/3 and (2): $0 \leq y \leq 1$ with x=0.2, in $(Mn_yNi_{1-y})_xFe_{3-x}O_4$.

From these experiments it was found that the thermoelectric power factor manifests a maximum near y=2/3, where the number of 3d electrons in magnetite is preserved by substitution.

In the present study, the highest power factor obtained was 1.2 $\mu W/K^2cm$ at 973K, exceeding that of pure magnetite.

Several factors were discussed to improve further the thermoelectric figure of merit.

Acknowledgments

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