

Preparation and electrical properties of sintered bodies composed of $\text{Mn}_{(1+0.5X)}\text{FeNi}_{(1-0.5X)}\text{O}_4$ ($0 \leq X \leq 1.00$) with cubic spinel structure

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The preparation and electrical properties of sintered bodies consisting of monophase cubic spinel oxides, $\text{Mn}_{(1+0.5X)}\text{FeNi}_{(1-0.5X)}\text{O}_4$ ($0 \leq X \leq 1.00$), were investigated. Sintered bodies composed of monophase cubic spinel structure were prepared through heat treatment at 1000 °C for oxidation after sintering at 1400 °C in Ar. The required time for oxidization exceeded 48 h for specimens with $X = 0$ to 0.375 and more than 96 h for those with $X = 0.50$ to 1.00. Electrical conduction (σ) and Seebeck potential (Q_e) were measured using rectangular bars cut from sintered pellets. The electrical characteristics were determined based on the change of cation distribution related to the disproportionation of Mn ions. We concluded that the electrical conduction of sintered bodies is controlled by a small polaron hopping mechanism.

Key words: Mn-Fe-Ni monophase cubic spinel oxide, Electrical conductivity, Seebeck coefficient, Small polaron hopping, NTC thermistor.

Introduction

Sintered oxides composed of several elements (e.g., Mn-Fe-Ni and Mn-Co-Ni systems) are widely used as negative temperature coefficient (NTC) thermistor materials because their electrical resistance decreases exponentially with increasing temperature. Mn-Fe-Ni and Mn-Co-Ni oxides are employed as thermistor elements for temperature measurement or temperature control in the field of electrical products, communication equipment, motor vehicles, and many industrial instruments in the range from room temperature to 300 °C, and from –30 °C to 150 °C.

We reported the preparation method [1,2] for sintered bodies of Mn-Co-Ni oxide systems with monophase cubic spinel structure and the composition region [3] of the cubic spinel structure. Furthermore, we summarized the results on some maps demonstrating the composition dependences of electrical properties and semiconductor characteristics of the oxides with cubic spinel structure [4]. These maps enable us to select suitable compositions corresponding to the application region of temperature.

This paper reports on Mn-Fe-Ni oxides in which specific compositions are actually employed as thermistors for high temperatures. The preparation method and the

evaluation of related characteristics of sintered oxides with cubic spinel structure were examined in order to map composition dependences on electrical properties and semiconductor characteristics. The basis of this study is to heat-treat sintered bodies in the temperature range at which the stable phase of the oxides is the cubic spinel structure. Therefore, we must determine the composition region in which the oxides have cubic spinel structure at a prescribed temperature. Since temperatures for sintering of the oxide are somewhat higher than those of the stable phase with cubic spinel structure, phase separation in the ordinary sintering process occurs. Not all oxides with compositions yielding monophase cubic spinel below sintering temperature recover from phase separation through heat treatment at the prescribed temperature after sintering. Accordingly, the composition region of sintered bodies with monophase cubic spinel structure at a prescribed temperature must be investigated. For the Mn-Co-Ni oxide system, we could prepare sintering bodies with monophase cubic spinel structure by heat-treating the oxides in air after sintering at 1400°C in an inert gas (PMSR method) [2]. Since fabrication of sintered oxides composed of Mn, Fe, and Ni with monophase cubic spinel structure applying a simple firing process in air was assumed to be difficult as well for the Mn-Co-Ni system, this study adopted this PMSR method. We could confirm that a sintered body of Mn-Fe-Ni oxide (Mn : Fe : Ni = 1 : 1 : 1 in molar ratio) with monophase cubic spinel structure could be fabricated using the PMSR method [5]. The

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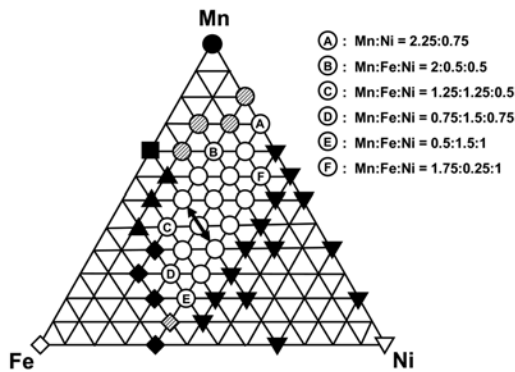


Fig. 1. Phase diagram of Mn-Fe-Ni oxides fired at 1000 °C for 3 h in air. ○: cubic spinel, ⊙: cubic spinel and tetragonal spinel, ●: tetragonal spinel, ▲: cubic spinel and bixbyite, ▼: cubic spinel and NaCl-type, ◆: cubic spinel and hematite, ◇: cubic spinel, hematite, and NaCl-type, ■: bixbyite and hematite, ◇: hematite, ▽: NaCl-type, double pointed arrow is the region of this study.

heat treatment for oxidation was conducted at 1000 °C for 48 h.

The phase of the Mn-Fe-Ni oxide system present at 1000 °C was reported in our previous paper [6]. Formation of cubic spinel phase can be found in the region enclosed with (A)-(F), as depicted in Fig. 1.

In this work, the oxides located between Mn : Fe : Ni = 1 : 1 : 1 and 1.5 : 1 : 0.5 in the ternary system were targeted for preparation and evaluation of sintered bodies with monophase spinel structure. This composition line is denoted with a double pointed arrow in Fig. 1. Seven compositions, expressed as $\text{Mn}_{(1+0.5X)}\text{FeNi}_{(1-0.5X)}\text{O}_4$ ($0 \leq X \leq 1.00$), were examined.

Experimental

Starting materials with various compositions were prepared by mixing Mn, Fe, and Ni nitrates followed by evaporating to dryness at around 250 °C in air. They were formed into disks 25 mm in diameter and 5 mm thick by uniaxial pressing. These pellets were heated to 1400 °C and held for 3 h in Ar for sintering. The sintered specimens were then cooled to 1000 °C where cubic spinel oxide has a stable phase [6], and the atmosphere was switched from Ar to air in order to oxidize them for the prescribed time. Finally, the specimens were quenched by dropping into water. The phases of the specimens present were analyzed by X-ray diffraction (XRD) (Rigaku, RINT-2500, Cu K α radiation).

The σ value of a rectangular specimen ($3 \times 3 \times 15 \text{ mm}^3$) cut from a sintered pellet consisting of monophase cubic spinel oxide was measured using the DC four-probe method in the range of 100 °C to 700 °C in N₂. Those measurements employed gradually cooled specimens rather than quenched specimens because sintered pellets without cracks through the cooling process from 1000 °C to room temperature

were needed. Q_e was measured in the same temperature range using a rectangular bar. A temperature gradient of 5 °C between the ends of the bar was applied. The Seebeck coefficient (Q_s) was calculated using Eq. 1 [7].

$$Q_e = Q_s(T_A - T_B) \quad (1)$$

Here, T_A and T_B are the absolute temperatures of the ends of the rectangular specimen ($T_A > T_B$). For XRD analysis of the rectangular bars, Si powder was added to each pulverized specimen to calculate the precise lattice constant by applying the least-squares method.

Results and Discussion

In all compositions, sintered bodies composed of monophase cubic spinel oxide were prepared according to the PMSR method. The required time of heat treatment for oxidization exceeded 48 h for specimens with $X = 0$ to 0.375 and more than 96 h for those with $X = 0.50$ to 1.00. The measured σ values were discussed in the relationship between $\ln(\sigma)$ and T^{-1} (Fig. 2). The relationship between them consisted of two straight lines with slightly different slopes in all specimens. Turning points are observed in the temperature range of 300 °C to 400 °C. A linear relationship with a negative slope is confirmed as a characteristic of NTC thermistors. The B values [8] necessary to evaluate the characteristics of thermistors were calculated using Eq. 2 for two lines (low-temperature range (100 °C to 300 °C) and high-temperature range (400 °C to 700 °C)).

$$\sigma_1 = \sigma_2 \exp B \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2)$$

Here, σ_1 corresponds to T_1 , σ_2 corresponds to T_2 , and B is the “ B value” (apparent activation energy of σ). Figure 3 demonstrates the composition dependence of B value. The relationship between B and X consists of two straight lines having a turning point at $X = 0.50$.

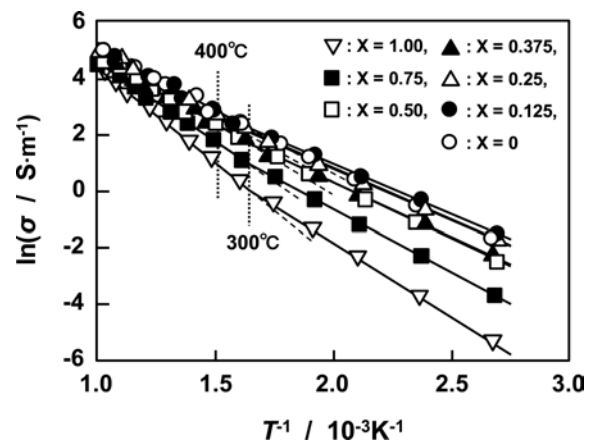


Fig. 2. Plots of $\ln(\sigma)$ as a function of T^{-1} of various composition.

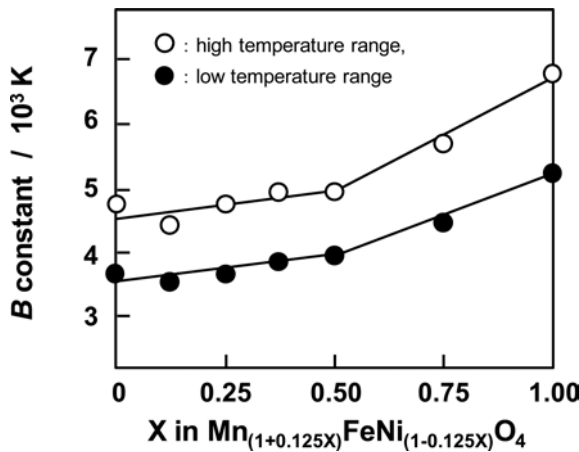


Fig. 3. Changes in thermistor constant, B constant, as a function of X in $Mn_{(1+0.5X)}FeNi_{(1-0.5X)}O_4$.

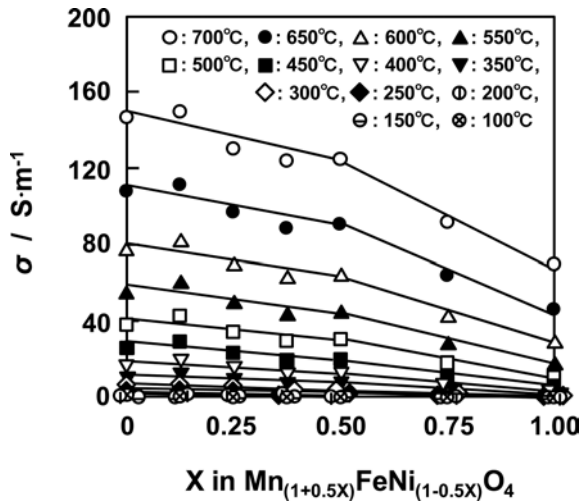


Fig. 4. Electrical conductivity as a function of X in $Mn_{(1+0.5X)}FeNi_{(1-0.5X)}O_4$ at various temperatures.

The values measured here are within the values of practical thermistors [9]. The B values differ between the low-temperature range and the high-temperature range, and the presence of the turning points of the straight lines in Fig. 2 suggests a change of cation distribution in the spinel structure. This will be discussed later.

Figure 4 demonstrates the composition dependence of σ at various temperatures. In the region $0 \leq X \leq 0.50$, σ values are relatively scattered. However, we determined that regarding them as approximately straight lines was reasonable. The negative slope changes at $X = 0.50$, corresponding to the results in Fig. 3.

Figure 5 depicts the change of the precise lattice constant as a function of X in $Mn_{(1+0.5X)}FeNi_{(1-0.5X)}O_4$. The lattice constant increases linearly with increasing X , suggesting that the cation distribution changes regularly with X . The cation distribution related to the spinel oxides, $Mn_{(1+0.5X)}FeNi_{(1-0.5X)}O_4$, remains unclear. However, Töpfer *et al.* [10] estimated the cation

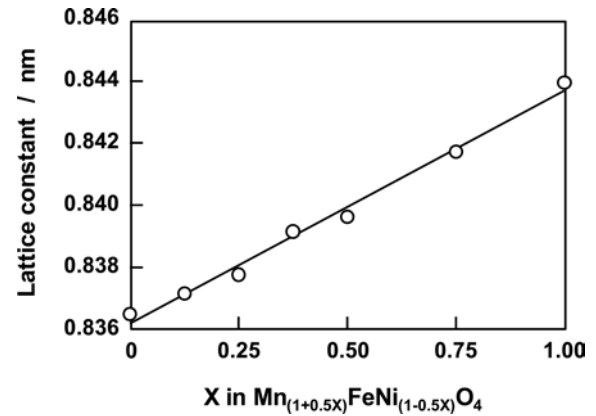


Fig. 5. Lattice constant as a function of X in $Mn_{(1+0.5X)}FeNi_{(1-0.5X)}O_4$.

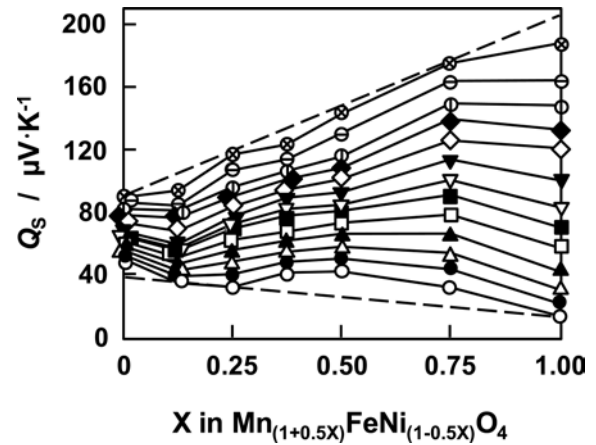
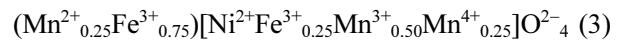


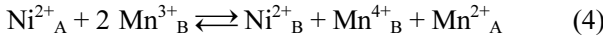
Fig. 6. Seebeck coefficient as a function of X in $Mn_{(1+0.5X)}FeNi_{(1-0.5X)}O_4$ at various temperatures. Symbol is the same as Fig. 4.

distribution of the spinel, $MnFeNiO_4$. This oxide advantageously corresponds to our oxide with $X = 0$. This distribution can be described as follows.



Here, () represents the tetrahedral site (A site), and [] represents the octahedral site (B site). We cannot adopt Eq. 3 for our oxide with $X = 0$ because the preparation method by Töpfer *et al.* is different from that of our study. However, it seems that the cations occupying the B site in the spinel in this study are limited to Ni^{2+} , Fe^{3+} , Mn^{3+} , and Mn^{4+} . If this assumption holds, the relationship in amount between Mn^{3+} and Mn^{4+} in hopping conduction must be in a condition $Mn^{3+} > Mn^{4+}$ since the semiconductor characteristic shows p -type as explained below. The results of X-ray and Q_s may provide a clue to clarify this condition. Figure 6 illustrates the composition dependence of Q_s . The semiconductive characteristics indicate p -type because the values of Q_s are all positive throughout the entire temperature range. In Fig. 5, the lattice constant tends to increase linearly with X , suggesting that the concentration of Mn^{3+} with the larger size of 0.0771 nm [11] in the B

site increases with increasing X . Simultaneously, this tendency implies that the concentration of Ni^{2+} with the smaller size of 0.0711 nm [11] decreases with increasing X , and that of Mn^{4+} with the size of 0.0734 nm [11] also decreases because of compensation for the valence of Ni^{2+} . Although this is a rough explanation, the data with a positive gradient in the wide range of X (upper dotted straight line in Fig. 6) might mean that the decrement of carrier concentration (n) is caused by the increment of Mn^{3+} concentration and the decrement of Mn^{4+} concentration. To analyze the changes in Q_s , the disproportionation of Mn ions as indicated in Eq. 4 [12] must be considered.



Here, the subscript A corresponds to the A site, and B corresponds to the B site. In Fig. 2, each line is composed of two straight lines. The data in the higher-temperature region are located on somewhat higher $\ln(\sigma)$ than the lines extrapolated from the lower-temperature region, which indicates that the equilibrium relationship shifts to the right-hand side at higher temperatures. Regarding the tendency in higher temperatures, the dotted line in the lower part of Fig. 6 is based on the equilibrium that shifted to the right side, whereas that in the upper part is based on the equilibrium at lower temperatures. The effect of temperature on the change of electrical characteristics becomes clear with analysis of the relationship between n and mobility (μ).

The value of n was calculated from Eqs. 5 and 6 using the values of Q_s , and μ was calculated by Eq. 7

$$Q_s = \frac{k}{e} \left\{ \ln\left(\frac{N_v}{n}\right) + \alpha \right\} \quad (5)$$

$$N_v = \frac{16}{\alpha^3} \quad (6)$$

$$\sigma = ne\mu \quad (7)$$

Here, e is the electric charge, k is Boltzmann's constant, N_v is the density of states in the valence band, α is the transport coefficient (α was neglected for this calculation, because α is extremely small between 0 and 1 [13]), and 16 is the number of B sites in a unit cell. The relationships between n and μ of specimens with $X=0$, 0.50, and 1.00 are plotted in Fig. 7 to examine the comprehensive composition and temperature dependences of σ . The relationship between n and μ can be divided into three regions. The region from 100 °C to 300 °C (region (I)) indicates that the temperature dependence of μ exceeds that of n . Therefore, the increase of σ in this region strongly depends on μ . In region (III) (from 500 °C to 700 °C), σ strongly depends on n because the temperature dependence of n

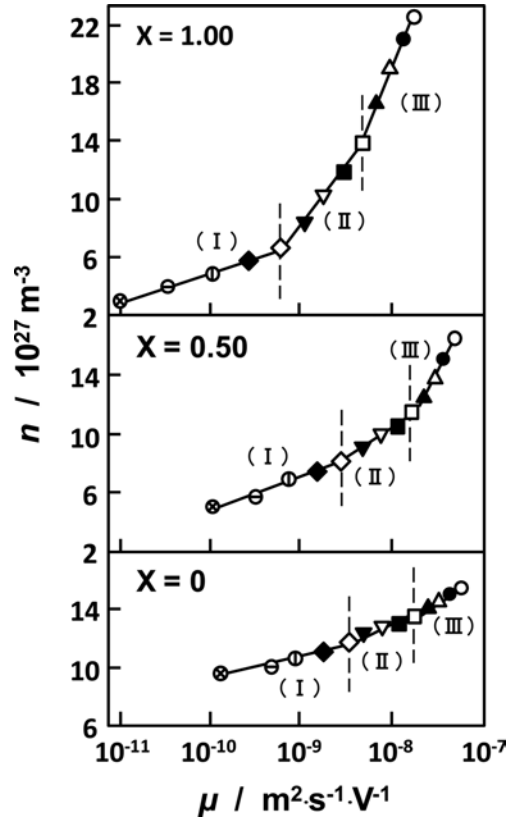


Fig. 7. Relationship between carrier concentration and mobility of specimens with $X=0$, 0.50, and 1.00. (I): 100 °C ~ 300 °C, (II): 300 °C ~ 500 °C, (III): 500 °C ~ 700 °C, symbol is the same as Fig. 4.

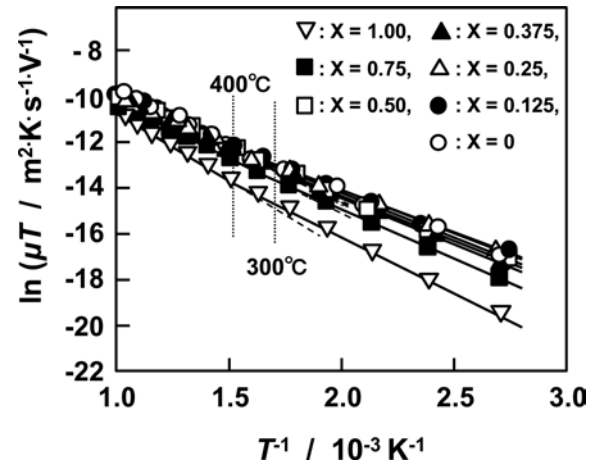


Fig. 8. Plots of $\ln(\mu T)$ as a function of T^{-1} of various composition.

is significantly greater than that of μ . Region (II) (from 300 °C to 500 °C) is thought to be in the area where the contribution to σ transfers from μ to n . The tendency for n to increase in each composition is remarkable above 300 °C, especially above 500 °C, except for the specimen with $X=0$. The increment of n in higher temperatures is assumed to be due to the concentration of Mn^{4+} increasing with temperature based on the equilibrium (Eq. 4). The specimen with $X=1.00$ had the greatest temperature dependence, suggesting that

the concentration of Mn^{4+} derived from Mn^{3+} according to the disproportion reaction (Eq. 4) in higher temperatures is the highest among the specimens.

In general, it is known that the conduction is due to a small polaron hopping mechanism in case where μ , being less than $10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, tends to increase with increasing temperature [14-17]. An illustration of the temperature dependence of μ is omitted in this report. However, the result satisfied the above conditions. Therefore, it was concluded that the electrical conduction of the sintered bodies with cubic spinel structure is controlled by a small polaron hopping mechanism.

Generally, the relationship between μ and T is expressed by Eq. 8 [13].

$$\mu T = \frac{ed^2 v_0}{k} \exp\left(-\frac{E_\mu}{kT}\right) \quad (8)$$

Here, d is the jump distance for the charge carriers, v_0 is the jump frequency, and E_μ is the activation energy of μ . Figure 8 illustrates the relationship between $\ln(\mu T)$ and T^{-1} . This relationship is denoted by two straight lines having a turning point at 300 °C to 400 °C, even though the differences between the slopes are extremely small in all specimens. Equation 8 indicates that the plot of $\ln(\mu T)$ against T^{-1} yields a linear relationship with a slope from which E_μ can be calculated. The resultant values of E_μ were 0.32 eV to 0.42 eV in the temperature range below 300 °C, and 0.38 eV to 0.51 eV above 400 °C. The E_μ values of some oxides with conduction by the hopping mechanism in the range of 0.1 eV to 0.5 eV have been reported [18, 19]. Therefore, we can conclude that the conduction of the monophase sintered bodies is also due to the hopping mechanism.

Conclusions

This study investigated the preparation and the electrical properties of sintered bodies consisting of monophase cubic spinel oxides, $\text{Mn}_{(1+0.5X)}\text{FeNi}_{(1-0.5X)}\text{O}_4$ ($0 \leq X \leq 1.00$). The conclusions of this study are as follows.

1. The sintered bodies composed of the monophase cubic spinel structure were prepared through heat treatment at 1000 °C for oxidizing specimens sintered at 1400 °C in Ar. The required time of oxidation exceeded 48 h for the specimens with $X = 0$ to 0.375 and 96 h for those with $X = 0.50$ to 1.00.
2. The relationship between $\ln(\sigma)$ and T^{-1} consists of two straight lines with slightly different slopes for all specimens. The presence of turning points was determined based on the disproportionation of Mn

ions.

3. Semiconductive characteristics of the oxides were determined to be p -type because the Seebeck coefficients were positive.
4. The relationship between n and μ was divided into three regions based on the temperature dependence. In region (I) (100 °C to 300 °C), σ strongly depends on μ . In region (III) (500 °C to 700 °C), σ strongly depends on n . Region (II) (300 °C to 500 °C) was thought to be in the transition region of (I) and (III).
5. We concluded that the electrical conduction of the sintered bodies was controlled by a small polaron hopping mechanism.

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