

Fabrication and electrical properties of sintered bodies composed of $\text{Mn}_{(1.75-1.25X)}\text{Co}_{2.5X}\text{Ni}_{1.25(1-X)}\text{O}_4$ ($0 \leq X \leq 0.6$) with a cubic spinel structure

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Preparation of cubic spinel-type oxides, $\text{Mn}_{(1.75-1.25X)}\text{Co}_{2.5X}\text{Ni}_{1.25(1-X)}\text{O}_4$ ($0 \leq X \leq 0.6$), and their electrical properties were investigated. The starting oxides, containing metals with a prescribed molar ratio, were heated to 1400 °C and held for 3 h in argon. The sintered bodies were cooled to 800 °C and then oxidized for 48 h in air to convert them into a cubic spinel structure. The electrical conductivities of the sintered bodies were confirmed to increase exponentially with an increase in the temperature, indicating that they have intrinsic NTC thermistor characteristics. In the region of $0 \leq X \leq 0.4$, the electrical conductivity increased with an increase in X and decreased with an increase in X in the region of $0.4 < X \leq 0.6$. The concentration of Mn^{4+} in the octahedral sites of the spinel structure was considered to be larger than that of Mn^{3+} because the sintered bodies were n-type semiconducting. The electrical conduction of the oxides prepared in this study was concluded to be controlled by a small polaron hopping mechanism.

Key words: Mn-Co-Ni monophase cubic spinel-type oxide, Electrical conductivity, Seebeck coefficient, Cation distribution, Small polaron hopping, Thermistor.

Introduction

The authors have been studying the preparation and the electrical properties of sintered oxides with a monophase spinel structure consisting of Mn, Co, and Ni oxides with which typical thermistor materials are produced. In general, these oxides are manufactured through sintering at near 1400 °C. A simple and ordinary heating pattern, however, yields sintered bodies composed of a couple of crystal phases such as rock salt, cubic and tetragonal spinel-type oxides [1]. The electrical properties were found to depend on the ratio of existence of each crystal type [2]. We made clear that the monophase cubic spinel-type oxides can be produced by oxidizing the rock salt-type oxides formed at the sintering temperature [3-5]. In this case, it is important for the oxidation to be conducted in the temperatures range at which the cubic spinel oxides are stable. We confirmed that the electrical conductivity of the monophase cubic spinel-type oxides prepared in such way is stable for a long time [4]. The preparation of the monophase cubic spinel oxides is essential to make devices with stable electrical properties and with suitable resistances for the design of electrical circuits.

The authors have reported the region in which the

monophase cubic spinel is producible and the electrical properties of the sintered oxides [5-10]. Fig. 1(a) shows the formation region of monophase cubic spinel at 800 °C [6]. The cubic spinel oxides investigated so far are illustrated in Fig. 1(b). For analyses of the cation distributions and discussion on the electrical properties, the experiments were performed with respect to the oxides on several lines [5, 7-10]. To design thermistor materials satisfying the characteristics for practical use, detailed maps including

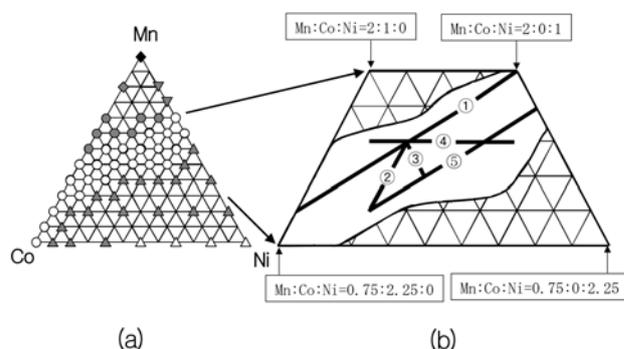


Fig. 1. Formation region of cubic spinel oxides at 800 °C (a) and the oxides investigated so far (b). ① : $\text{Mn}_{(2-3X)}\text{Co}_{2X}\text{Ni}_{(1-X)}\text{O}_4$ ($0 \leq X \leq 1$) [5], ② : $\text{Mn}_{(1.5-0.5X)}\text{Co}_{(1+0.5X)}\text{Ni}_{0.5}\text{O}_4$ ($0 \leq X \leq 1$) [7, 8], ③ : $\text{Mn}_{(1.5-0.25X)}\text{CoNi}_{(0.5+0.25X)}\text{O}_4$ ($0 \leq X \leq 1$) [9], ④ : $\text{Mn}_{1.5}\text{Co}_{(0.25+X)}\text{Ni}_{(1.25-X)}\text{O}_4$ ($0 \leq X \leq 0.75$) [10], ⑤ : $\text{Mn}_{(1.75-1.25X)}\text{Co}_{2.5X}\text{Ni}_{1.25(1-X)}\text{O}_4$ ($0 \leq X \leq 0.6$) (This study), ◆ : $\alpha\text{-Mn}_2\text{O}_3$, ○ : Cubic spinel, △ : Rock salt, ◇ : $\alpha\text{-Mn}_2\text{O}_3$ + Tetragonal spinel, ▽ : $\alpha\text{-Mn}_2\text{O}_3$ + Cubic spinel, ● : Cubic spinel + Tetragonal spinel, ▲ : Cubic spinel + Rock salt.

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the composition dependences of electrical conductivity, carrier concentration, mobility, the Seebeck coefficient, and activation energy of the conduction are considered to be helpful.

The study described here was conducted as a part of this overall research. We report the preparation and the electrical properties of the oxides composed of the monophase cubic spinel structure on the line ⑤ ($\text{Mn}_{(1.75-1.25X)}\text{Co}_{2.5X}\text{Ni}_{1.25(1-X)}\text{O}_4$ ($0 \leq X \leq 0.6$)) indicated in Fig. 1(b).

Experimental

The starting materials with the various compositions were prepared by mixing Mn, Co, and Ni nitrates followed by evaporating to dryness at around 250 °C. The starting materials were formed into disks with sizes 25 mm in diameter and 5 mm thick. These pellets were heated to 1400 °C for sintering and held at that temperature for 3 h in argon. The sintered specimens were then cooled to 800 °C and the atmosphere was switched from argon to air to oxidize the rock salt-type oxides. In these experiments, the sintered specimens with $0.7 \leq X \leq 1$ were omitted because they were found to have critical cracks unavoidable during sintering. The phases present in the specimens oxidized at 800 °C for 0–48 h were analyzed by X-ray diffraction after quenching in water. As a standard material, Si powder was added to each specimen. The precise lattice constant was calculated by the least squares method.

The electrical conductivity (σ) and the Seebeck potential (Q_e) were measured in argon using a rectangular specimen ($3 \times 3 \times 15$ mm) cut from a sintered pellet consisting of monophase cubic spinel-type oxides. σ was determined by the DC four-probe method at temperatures ranging from 100 °C to 300 °C. Q_e was measured with a difference of around 5 °C between the ends of the rectangular specimen. The measurement of Q_e was also performed at the same temperature range.

Results and Discussion

Preparation of sintered oxides with a monophase cubic spinel structure

To determine the conditions for preparation of sintered bodies consisting of a monophase cubic spinel, the oxidation time at 800 °C was examined using the specimen with $X = 0$ (Mn : Co : Ni = 1.75 : 0 : 1.25). The phase of the oxide sintered at 1400 °C was confirmed to be composed of a rock salt-type structure. Since the phase separation of the rock salt-type oxide occurred during oxidation to form cubic and tetragonal spinels, the contents of each crystal were calculated based on the XRD peak areas. The peak areas corresponding to (311) of the cubic spinel, (311) and (113) of the tetragonal spinel, and (200) of the rock salt-type were included in the denominator. The multiplicity factor [11] was taken into account in the area from the tetragonal spinel. The ratio of existence of each crystal as a function of oxidation time is shown

in Fig. 2. The rock salt-type oxide remarkably decreases with an increase in the oxidation time and perfectly disappears after 30 minutes. The phase present in the sintered body was confirmed to be cubic spinel, without tetragonal spinel, after 30 minutes. In this study, the oxidation time for perfection was fixed at 48 h. Sintered bodies for analyses of electrical properties were prepared by gradual cooling in an electric furnace after oxidation for 48 h because quenching resulted in cracks by thermal shock. However, the specimens were identified to be monophase cubic spinel irrespective of the manner of cooling.

Fig. 3 illustrates the lattice constant as a function of X in $\text{Mn}_{(1.75-1.25X)}\text{Co}_{2.5X}\text{Ni}_{1.25(1-X)}\text{O}_4$. The lattice constant decreases linearly with an increase in X, suggesting that the cation distribution changes regularly with X.

In a previous paper, we reported the cation distributions regarding the spinel oxides expressed by $\text{Mn}_{(2-X)}\text{Co}_{2X}\text{Ni}_{(1-X)}\text{O}_4$ ($0 \leq X \leq 1$) [5]. The estimation process was based on the fundamental cation distribution elucidated by other researchers. The octahedral site (B site) preference of respective cations, cation numbers occupying each site, lattice constants, composition, and electrical neutrality were taken into account to solve the supposed distributions. In the present study, the same method as in our previous paper [5] was applied to estimate the cation distribution of $\text{Mn}_{(1.75-1.25X)}\text{Co}_{2.5X}\text{Ni}_{1.25(1-X)}\text{O}_4$ ($0 \leq X \leq 0.6$). The condition that the

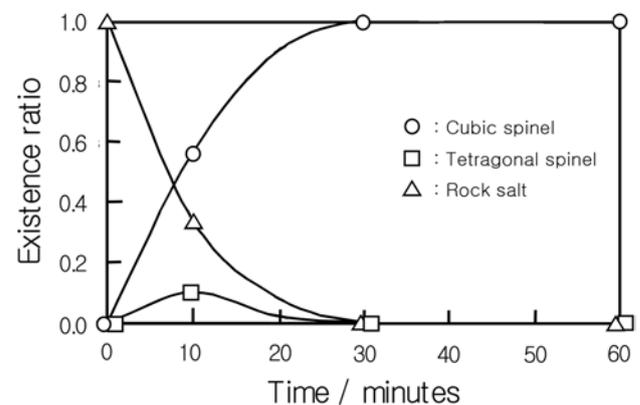


Fig. 2. Existence ratio of each crystal as a function of oxidation time for Mn-Co-Ni oxide (Mn : Co : Ni = 1.75 : 0 : 1.25).

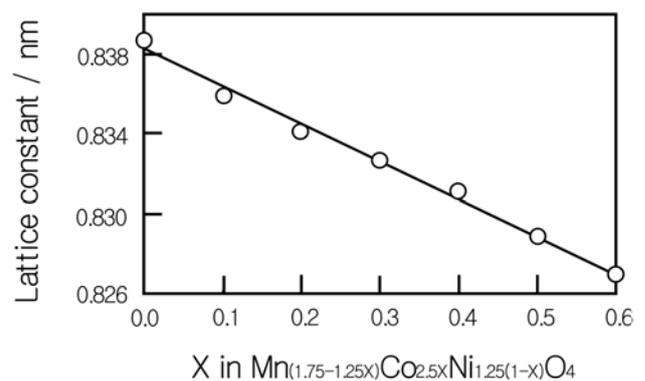
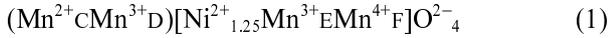
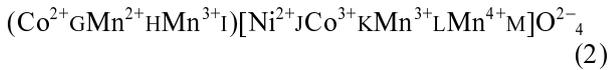


Fig. 3. Lattice constant as a function of X in $\text{Mn}_{(1.75-1.25X)}\text{Co}_{2.5X}\text{Ni}_{1.25(1-X)}\text{O}_4$.

B site preference of Ni^{2+} , Mn^{4+} , and Mn^{3+} is higher than that of Mn^{2+} was employed in addition to electrical neutrality. Thus, the basic distribution for the composition of $Mn_{1.75}Ni_{1.25}O_4$ ($X = 0$) is assumed to be Eq. (1):



Here, () represents the tetrahedral site (A site), and [] the B site. The site preference of Co must be considered in a system including Co. Since the B site preference of Co^{3+} is known to be higher than that of Co^{2+} [12], Co^{2+} and Co^{3+} are supposed to occupy both sites A and B. These conditions allow an estimate of the cation distribution as follows:



We need sufficient equations to solve the suffixes in Eq. (2) as was used in the previous paper [5]. Since one equation is lacking in this system, the distribution with an unknown, M, was discussed. The suffixes, G to M, are represented by Eqs. (3) to (9), respectively. The derivation of each equation is omitted here as the details were explained in the previous paper [5]:

$$G = (0.245M + 1.455)X \quad (3)$$

$$H = (1.422M - 0.905)X + 0.17 \quad (4)$$

$$I = -(1.667M + 0.55)X + 0.83 \quad (5)$$

$$J = 1.25(1 - X) \quad (6)$$

$$K = (1.045 - 0.245M)X \quad (7)$$

$$L = (0.905 - 1.422M)X + 0.33 \quad (8)$$

$$M = (1.667M - 0.7)X + 0.42 \quad (9)$$

According to the method described in the previous paper [5], the range of M was calculated to be $0.437 \leq M \leq 0.5$. The specimens prepared in the present study were confirmed to have negative Seebeck coefficients (Q_s) as is explained later. This fact implies that the amount of Mn^{4+} is larger than that of Mn^{3+} in the B sites. Taking this into account, the range of M can be narrowed to $0.471 < M \leq 0.5$.

Electrical properties

Electrical conductivity and the Seebeck coefficient

Fig. 4 demonstrates the composition dependence of σ in the sintered bodies. The value of σ increases exponentially with an increase in the temperature, indicating that these sintered bodies have the intrinsic characteristics of negative temperature coefficient (NTC) thermistors. In the region of $0 \leq X \leq 0.4$, σ increases with an increase in X and decreases in the region of $0.4 \leq X \leq 0.6$. The composition dependence of σ will be discussed later.

The composition dependence of the thermistor constant (B value) [13] was investigated in the temperature range from 200 °C to 300 °C using Eq. (10):

$$\sigma_2 = \sigma_1 \exp\{B(1/T_1 - 1/T_2)\} \quad (10)$$

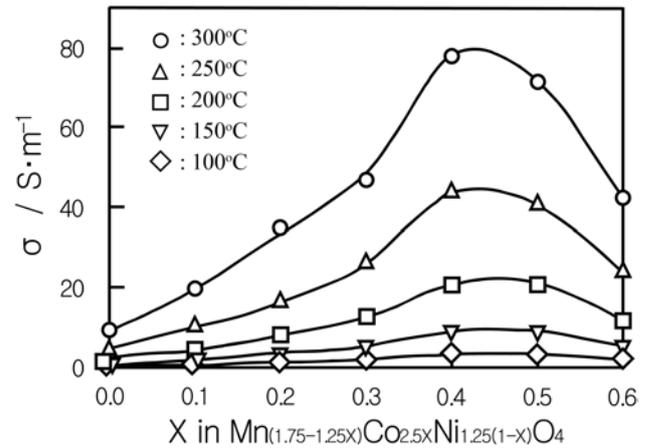


Fig. 4. Electrical conductivity as a function of X in $Mn_{(1.75-1.25X)}Co_{2.5X}Ni_{1.25(1-X)}O_4$.

Here, σ_1 and σ_2 are values at T_1 (K) and T_2 (K), respectively. The B values were evaluated to be in the range from 3400 K to 4100 K. There was a tendency for the B value to decrease with an increase in X. In general, the NTC thermistors on the market have B values ranging from 2000 K to 6000 K [14]. Therefore, these values indicate that the specimens prepared in this study are of practical use.

Fig. 5 demonstrates the composition dependence of Q_s calculated from Q_e measured at various temperatures. The sintered bodies are n-type semiconductors because all the Q_s values were negative.

Carrier concentration and mobility

The carrier concentrations (n) were calculated using Eqs. (11) and (12):

$$|Q_s| = (k/e)\{\ln(Nv/n) + \alpha\} \quad (11)$$

$$Nv = b/a^3 \quad (12)$$

k is Boltzmann's constant, e is the electric charge, Nv is the density of states in the valence band, α is a constant depending on the dominant scattering mechanism (α was

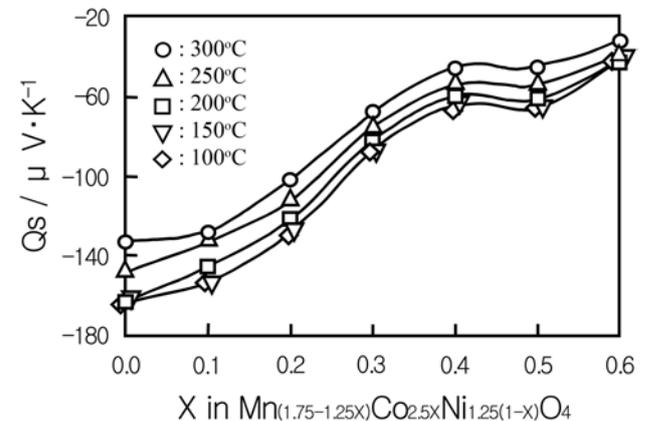


Fig. 5. Seebeck coefficient measured at various temperatures.

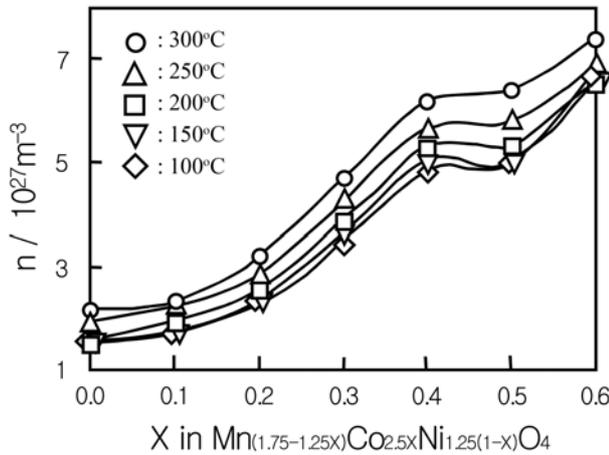


Fig. 6. Carrier concentration as a function of X.

neglected for this calculation), a is the lattice constant, and b is the number of octahedral sites occupied by Mn. The amount of Mn obtained from L+M was calculated from Eqs. (8) and (9). Since M with a narrow range gives almost no difference to the values of n , an average value was used for the following discussion. Fig. 6 shows the composition dependence of n calculated at various temperatures. The composition dependence of n is in agreement with that of Q_s . Q_s is a function of n and N_v (Eq. (11)). The composition dependence of Q_s is the same as that of n , which means that the composition dependencies of the amount of Mn in B sites and the lattice constant are also monotonic. The result shown in Fig. 3 is consistent with this argument. The amount of Mn in B sites calculated from Eqs. (8) and (9) is expressed as a linear relation $L + M = (0.245M + 0.205)X + 0.75$. This relation also supports the above discussion.

The mobility (μ) calculated by Eq. (13) is shown as a function of X in Fig. 7:

$$\sigma = ne\mu \quad (13)$$

In each composition, μ is recognized to increase exponentially with an increase in the temperature. The μ values of the order of $10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ prove that the conduction of the specimens is considered to be based on a small polaron hopping mechanism [15-17]. μ increases with an increase in X in the region of $0 \leq X \leq 0.4$ and decreases with an increase in X in the region of $0.4 < X \leq 0.6$. This tendency is in agreement with the result in Fig. 4, indicating that σ is closely related to μ .

To investigate the composition dependence of σ in Fig. 4, the relationship between n and μ at 300 °C was plotted. The result is shown in Fig. 8. The relation seems likely that the plots are dispersed. However, grouping into three categories proves that the composition dependence of σ can be explained using n and μ . In each region of I, II, and III, an arrow is drawn toward the direction for X to increase. The regions I and III imply that the change of μ is restricted within narrow limits of n . Also the region II

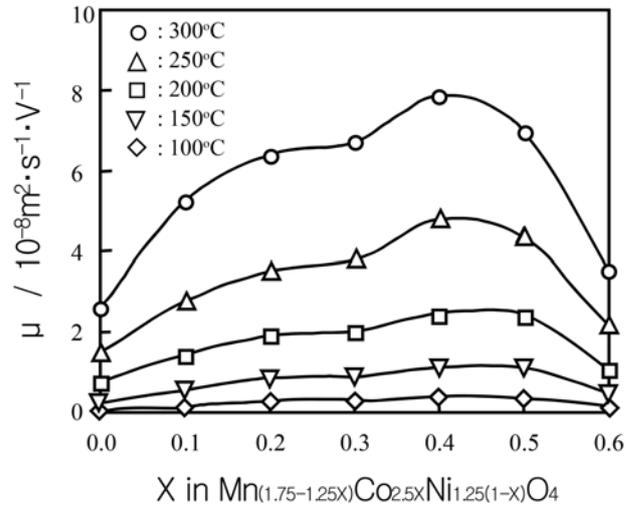


Fig. 7. Mobility measured at various temperatures.

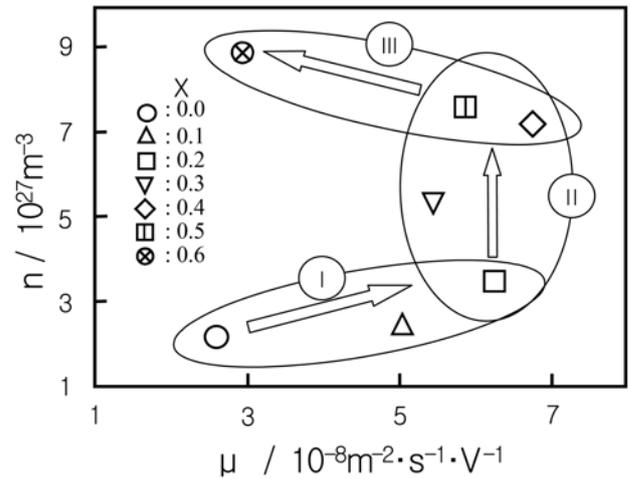


Fig. 8. Relationship between carrier concentration and mobility at 300°C.

shows that n changes within narrow limits of μ . We can understand the change of σ in $0 \leq X \leq 0.2$ shown in Fig. 4 to be dependent on the change of μ . The increase of σ in $0.2 \leq X \leq 0.5$ is considered to depend on the growth of n . The steep decrease of σ in $0.4 \leq X \leq 0.6$ can be attributed to the decline of μ .

μ is expressed by Eq. (14) [18]:

$$\mu T = (ed^2 v_0 / k) \exp(-E\mu / kT) \quad (14)$$

Here, d denotes the jump length, v_0 is the frequency, and $E\mu$ is the activation energy of the mobility. Linear plots of $\ln(\mu T)$ against $1/T$ are shown in Fig. 9. The $E\mu$ values calculated from each slope were found to be in the range from 0.31 eV to 0.38 eV, which also suggests that the conduction is due to a hopping mechanism [19].

Relation between cation distributions and electrical properties

Equation (15) describes the relationship between σ and

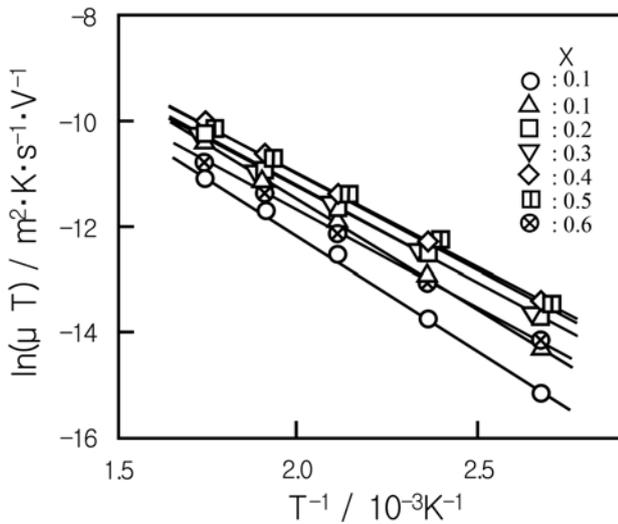


Fig. 9. Plots of $\ln(\mu T)$ as a function of reciprocal T .

c [20, 21]. c implies the fraction of the ions as carriers related to the hopping of the B site:

$$\sigma = Nc(1 - c)(N_{oct}e^2d^2v_0/kT)\exp(-E\sigma/kT) \quad (15)$$

N is the concentration per formula unit of sites available to the charge carriers. N_{oct} and $E\sigma$ are the concentration per cm^3 of B sites and activation energy of the electrical conduction, respectively. We investigated the composition dependence of σ using the items of $Nc(1 - c)$, N_{oct} , d , and v_0 . Since N and c can be replaced by $(Mn^{3+} + Mn^{4+})$ and $Mn^{3+}/(Mn^{3+} + Mn^{4+})$ respectively, $Nc(1 - c)$ yields the following equation with L and M in Eqs. (8) and (9):

$$Nc(1 - c) = (L \times M)/(L + M) \quad (16)$$

Calculations of $Nc(1 - c)$ being a function of X and M showed that $Nc(1 - c)$ linearly increases with an increase in X irrespective of M having a narrow range. N_{oct} increases linearly with an increase in X because it is a function of the Mn^{3+} concentration in B sites, L , as can be seen in Eq. (8). d is calculated from the lattice constant as the distance between B sites. The values of d^2 are in the range from $8.556 \times 10^{-2} nm^2$ to $8.791 \times 10^{-2} nm^2$, which is considered to give only a tiny effect against σ . Fig. 10 illustrates the composition dependence of v_0 calculated using Eq. (14). There is a tendency for v_0 to decrease slightly with an increase in X . The values of the v_0 in some spinel oxides have been reported by Jonkar [22], Larson *et al.* [23], Diekmann *et al.* [24], and Dorris and Mason [21]. The range of v_0 is of the order of $10^{12} - 10^{14} s^{-1}$. Larson *et al.* [23] reported that the v_0 of $Ni_{(1-X)}Mn_{(2+X)}O_4$ ($0 \leq X \leq 1$) is $6 \times 10^{13} s^{-1}$. We also described in a previous paper [10] that the v_0 of $Mn_{1.5}Co_{(0.25+X)}Ni_{(1.25-X)}O_4$ ($0 \leq X \leq 0.75$) was calculated to be $1 - 5 \times 10^{13} s^{-1}$. Although the essence of the decreasing tendency seen in Fig. 10 is unclear, it is interesting that the v_0 in this study agrees in order with those values. Therefore, the increase of σ in the range of $0 \leq X \leq 0.4$

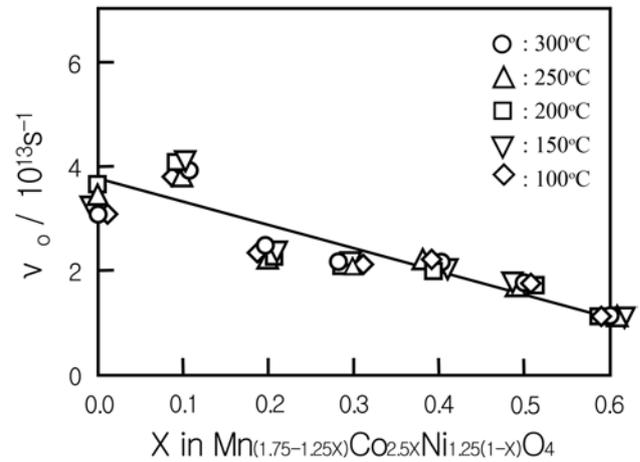


Fig. 10. v_0 as a function of X .

is considered to be due to $Nc(1 - c)$ and/or N_{oct} . However, this argument is not acceptable in the region of $0.4 < X \leq 0.6$ where σ decreases considerably with an increase in X . For discussion of this region, the concentration of Co^{3+} in B sites might be considered. Co^{3+} in B sites increases with X as known from Eq. (7). There is the possibility that Co^{3+} hinders the hopping between Mn^{3+} and Mn^{4+} . Anyway, the detail is a subject for future study.

Nv/n in Eq. (11) can be replaced by $c/(1 - c)$ [25]. $c/(1 - c)$ expressed as Mn^{3+}/Mn^{4+} in B sites is confirmed to increase with an increase in X in the range of M . The tendency for $c/(1 - c)$ to increase with X can be presumed to be roughly similar to the composition dependence of Q_s . This suggests that the ratio Mn^{3+}/Mn^{4+} in B sites is related to Q_s .

Conclusions

In this paper, the preparation and electrical properties of sintered bodies consisting of monophase cubic spinel-type oxides, $Mn_{(1.75-1.25X)}Co_{2.5X}Ni_{1.25(1-X)}O_4$ ($0 \leq X \leq 0.6$), were investigated. The conclusions of this study are summarized as follows.

1. Sintered monophase cubic spinel-type oxides, $Mn_{(1.75-1.25X)}Co_{2.5X}Ni_{1.25(1-X)}O_4$ ($0 \leq X \leq 0.6$), were confirmed to be obtained by heating mixtures of nitrates at $1400^\circ C$ in argon, followed by cooling to $800^\circ C$ and holding at this temperature for 48 h in air.

2. The electrical conductivity of the sintered bodies were recognized to increase exponentially with an increase in the temperature, which means that these sintered bodies have intrinsic NTC thermistor characteristics. The electrical conductivity increased with an increase in X in the region of $0 \leq X \leq 0.4$ and decreased with an increase in X in the region of $0.4 < X \leq 0.6$.

3. The semiconductive characteristics of the oxides were concluded to be n-type because the Seebeck coefficients were negative.

4. The cation distributions were estimated according

to the method reported in our previous paper [5].

5. The composition dependence of the Seebeck coefficient was considered to depend on the ratio of Mn^{3+}/Mn^{4+} in octahedral sites.

6. The electrical conduction of the sintered bodies was concluded to be controlled by a small polaron hopping mechanism.

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