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Electrical properties of sintered bodies composed of a monophase cubic spinel structure $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$ ($0 \le X \le 1$)

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The relationship between the cation distributions and electrical properties of sintered bodies composed of monophase spineltype oxides expressed by $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$ ($0.00 \le X \le 1.00$) was investigated. In particular, Nv/n (Nv is state density, n is carrier concentration) calculated from the Seebeck coefficient and c/(1-c) (c is fraction of available sites) derived from the estimated cation distribution were compared. The composition dependences of Nv/n and c/(1-c) were found to have almost the same tendency. As a result, the estimation of the cation distributions was considered to be valid.

Key words: Mn-Co-Ni spinel-type oxide, Electrical conductivity, Cation distribution, Seebeck coefficient, Thermistor

Introduction

Composite oxides composed of transition metals of Mn, Co, and Ni are used as negative temperature coefficient (NTC) thermistors because their electrical resistances decrease exponentially with increasing temperature. These thermistors are widely used in the fields of electrical products, communication equipment, motor vehicles, and many industrial instruments. Ternary system oxides with molar ratios in the vicinity of Mn:Co:Ni = 1.5:1.0:0.5 have primarily been adopted because their electrical properties are relatively stable. With the numerous uses for thermistors, research and development on thermistor materials with suitable electrical properties for the various applications are being conducted. Thus, we investigated the preparation of Mn-Co-Ni oxide thermistors, primarily the synthesis of oxides composed of the monophase cubic spinel structure important for electron conduction [1-4]. We examined the composition region of oxides that have only a cubic spinel structure as the stable phase in a ternary system at various temperatures [5]. The preparation method of sintered bodies composed of monophase cubic spinel in these oxides was also investigated because the sintering temperature (1400°C) is higher than when the cubic spinel phase is stable [1-4]. The crystal structure of these oxides is a rock salt-type at a sintering temperature of 1400°C. Phases separate irreversibly into cubic spinel, tetragonal spinel, and rock salt-type oxides during the cooling process [6]. However, we successfully fabricated sintered bodies from some systems with the ternary composition described above by oxidizing the sintered oxides with a rock salt-type structure in air or pure oxygen at temperatures at which the cubic spinel phase is stable [2-4]. The transfer from sintering temperature to oxidation temperature was conducted in nitrogen to avoid phase separation.

We reported the details of the preparation of sintered bodies with monophase cubic spinel and the electrical properties of $Mn_{(1.5\cdot0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$ ($0.00 \le X \le 1.00$) in a previous paper [4]. The present paper discusses the relationship between the cation distribution and the electrical properties of this oxide system.

Electrical Properties of the Oxides

The data, except Figs. 4, 5, and 6, has already been presented in a previous paper [4]. However, we will again explain the specimens and data on the electrical properties, since they are necessary to clarify and discuss the relationship between the cation distribution and the electrical properties of sintered bodies with a monophase cubic spinel structure. The details of the oxide preparation method are omitted here.

Table 1 lists the compositions of the sintered bodies. Figure 1 illustrates the composition dependence of the electrical conductivity (σ) of the sintered bodies. σ tends to decrease as X increases, suggesting that σ decreases with a decreasing Mn content. This indicates that specimens containing less Mn than a specimen with X=0.00, which is the most popular on the market,

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Х	$Mn_{(1.5\text{-}0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$
0.00	$Mn_{1.5}CoNi_{0.5}O_4$
0.25	Mn _{1.375} Co _{1.125} Ni _{0.5} O ₄
0.44	$Mn_{1.28}Co_{1.22}Ni_{0.5}O_4$
0.47	$Mn_{1.265}Co_{1.235}Ni_{0.5}O_4$
0.50	$Mn_{1.25}Co_{1.25}Ni_{0.5}O_4$
0.75	$Mn_{1.125}Co_{1.375}Ni_{0.5}O_4$
1.00	$MnCo_{1.5}Ni_{0.5}O_4$

Table 1. Compositions of $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$



Fig. 1. Electrical conductivities as a function of X in $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$ at various temperatures.



Fig. 2. Seebeck coefficient as a function of X in $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$ at various temperatures.

have a low σ . Thus, a change in the ratio of Mn^{3+} to Mn^{4+} must be considered. This will be discussed later.

Figure 2 demonstrates the composition dependence of the Seebeck coefficient (Qs). The values of Qs have been confirmed to decrease linearly with increasing X, and Qs is almost independent of temperature. Qs changes from positive to negative between X=0.44 and X=0.47, which implies that the semiconductor characteristics of specimens with X=0.00 to 0.44 are p-type, and specimens with X=0.47 to 1.00 are n-type.

Discussion

Estimation of cation distribution

Information regarding cation distribution is necessary to clarify the electrical properties of the oxides, and therefore we will begin with an explanation of the estimation of cation distributions in $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}$ -Ni_{0.5}O₄. The principle of cation distribution estimation is based on the following three items.

(A) The cation distribution of $Mn_{1.5}CoNi_{0.5}O_4$, the last member of the oxides dealt with in this work, has already been estimated [3].

(B) The composition dependence of the lattice constant was confirmed to be linear.

(C) The concentrations of Mn^{3+} and Mn^{4+} in a specimen with Qs=0 are identical. It is postulated in Fig. 2 that X of a specimen with Qs=0 is 0.46.

The cation distribution of $Mn_{1.5}CoNi_{0.5}O_4$ was estimated as follows in our previous paper [3].

$$(\mathrm{Co}_{0.58}^{2+}\mathrm{Mn}_{0.42}^{2+})[\mathrm{Ni}_{0.5}^{2+}\mathrm{Co}_{0.42}^{3+}\mathrm{Mn}_{0.58}^{3+}\mathrm{Mn}_{0.5}^{4+}]\mathrm{O}_4^{2-} \tag{1}$$

Here, () represents a tetrahedral site, and [] an octahedral site. Knowledge of the preferential sites of related cations is required to determine the cation distributions. Information regarding site preference was derived from the cation distributions reported by other researchers [7-15]. The detailed determination process is omitted here. As a result, the cation distribution expressed by Eq. (2) was estimated [4].

$$(\operatorname{Co}_{(0.58+0.33X)}^{2+}\operatorname{Mn}_{(0.42-0.33X)}^{2+})$$

$$[\operatorname{Ni}_{0.5}^{2+}\operatorname{Co}_{(0.42+0.17X)}^{3+}\operatorname{Mn}_{(0.58-0.17X)}^{3+}\operatorname{Mn}_{0.5}^{4+}]O_{4}^{2-}$$

$$(0.00 \le X \le 1.00)$$
(2)

Equation (2) indicates that the concentration of Mn^{2+} in the tetrahedral site decreases by 0.33X with increasing X, and also that Mn^{3+} in the octahedral site decreases by 0.17X with X. The reduction of Mn^{2+} in the tetrahedral site thus exceeds that of Mn^{3+} in the octahedral site. The concentration of Mn^{3+} and Mn^{4+} reverses in specimens with X greater than 0.46, and the semiconductor characteristics change from p-type to n-type.

Conduction mechanism of oxides

Figure 3 presents the composition dependence of carrier concentration (n) calculated from Eqs. (3) and (4).

$$Qs = (k_B/e) \{ \ln(Nv/n) + \alpha \}$$
(3)

$$Nv = b/a^3 \tag{4}$$



Fig. 3. Carrier concentration as a function of X in $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$ at various temperatures.

Here, k_B is Boltzmann's constant, e is the electronic charge, Nv is the density of states in the valence band, α is a (negligibly small) constant, b, is the number of octahedral sites occupied by Mn (16[{(0.58-0.17X)+ 0.5}/2]), and a is the lattice constant. Almost no temperature dependence is observed in any composition, reflecting the result of Qs. n increases with increasing X until X reaches 0.47, n tends to decrease above 0.47. The values of n in the specimens with $0.00 \le X \le 0.44$ were calculated from the concentration of Mn⁴⁺ as carriers, whereas those of specimens with $0.47 \le X \le 1.00$ were calculated from the concentration of Mn³⁺. The maximum point is observed at X=0.47. This is attributed to the fact that the ratio of Mn³⁺ to Mn⁴⁺ becomes a maximum at 1:1 (X=0.46).

The mobility (μ) calculated from Eq. (5) was found to increase exponentially with increasing temperature [4].

$$\sigma = n e \mu$$
 (5)

This trend agreed with the temperature dependence of σ , in which n is independent of the temperature.

The relation between μ and **T** is expressed by Eq. (6) [16].

$$\mu T = (e \ d^2 v_o / k_B) \exp(-E_{\mu} / k_B T)$$
(6)

Here, *d* is the jump distance for the charge carriers, v_o is the charge carrier jump frequency, and E_{μ} is the mobility activation energy. The plots of $ln(\mu T)$ against reciprocal T were examined to investigate the conduction mechanism of the oxides $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$ ($0.00 \le X \le 1.00$). Linear relations were consequently confirmed in all specimens. The values of E_{μ} ranged from 0.30 to 0.33 eV and no particular composition dependence of E_{μ} was observed.

Electron conduction is known to be based on a small

polaron hopping mechanism, according to generally accepted comprehensive knowledge regarding semiconductors in which μ is of the order of $10^{-8}m^2 \cdot s^{-1} \cdot V^{-1}$ and increases with increasing temperature and E_{μ} ranges from 0.1 to 0.5 eV [17-22]. Mn³⁺ and Mn⁴⁺ are thought to be the cations that contribute to electron conduction because the distance between cations occupying an octahedral site is considered to be the shortest distance possible for hopping in the spinel structure and no ion with different valence numbers exists in the octahedral site except the Mn ion.

Composition dependence of μ

The reason μ decreases with increasing X is thought to be as follows. d^2 is considered to be almost constant in Eq. (6) because d^2 of the specimens with X=0.00 and X=1.00 is calculated to be 8.7×10^{-2} nm² and 8.6×10^{-2} nm². Furthermore, μ should depend on v_o if we suppose that the values of E_µ are independent of the composition and are practically constant. Therefore, the increase of X resulting in the reduction of Mn concentration lowers v_o.

Relation between cation distributions and electrical properties

Equation (7) describes the relationship between σ and the fraction of available sites occupied by the charge carriers (c) [23].

$$\sigma = \operatorname{Nc}(1-c)(\operatorname{N}_{\operatorname{oct}} e^2 d^2 v_{o}/k_B T) \exp(-E_{\sigma}/k_B T)$$
(7)

Here, N is the concentration per formula unit of sites that are available to the charge carriers, N_{oct} is the concentration per cm³ of octahedral sites, and E_{σ} is the activation energy of electrical conduction. The plots of ln(σ **T**) versus reciprocal **T** in all specimens were found to be linear, yielding values of E_{σ} that were almost the same as those of E_{μ} .

The composition dependence of Noct and Nc(1-c) might provide useful information for investigating the composition dependence of σ . Since the concentration of Mn in octahedral sites decreases with increasing X, Noct also decreases with increasing X. The value of N $(=Mn^{3+}+Mn^{4+})$ can be calculated from the cation distribution. The content of c is expressed as Mn^{4+} $(Mn^{3+}+Mn^{4+})$ when X ranges from 0.00 to 0.44 (ptype) and as Mn³⁺/(Mn³⁺+Mn⁴⁺) when X ranges from 0.47 to 1.00 (n-type). Figure 4 plots Nc(1-c) as a function of X. Comparing Fig. 4 with Fig. 1 indicates that the composition dependence is somewhat similar in that both Nc(1-c) and σ decrease with increasing X. This tendency would indicate that N_{oct} , v_o , and the ratio of Mn^{3+} to Mn^{4+} are related to σ . The details of the incomplete accordance between Fig. 1 and Fig. 4 will be clarified in the future.

Nv/n obtained from the absolute value of Qs in Eq. (3) can be substituted into c/(1-c) [24]. The value of c/



Fig. 4. Nc(1-c) as a function of X in $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$.



Fig. 5. c/(1-c) as a function of X in $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$.



Fig. 6. Nv/n as a function of X in $Mn_{(1.5-0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$.

(1-c) is calculated from part of the octahedral site in the cation distribution. The composition dependences of c/

(1-c) and Nv/n are illustrated in Figs. 5 and 6. The composition dependence of c/(1-c) is in agreement with that of Nv/n. Furthermore, the minimum values are found to be X=0.44 or 0.47 in both figures. Therefore, we can conclude that Qs depends on the ratio of Mn³⁺ to Mn⁴⁺. This verifies that the cation distribution estimated in our previous paper [4] is pertinent.

Conclusions

This paper investigated the relationship between the cation distribution and electrical properties of sintered bodies composed of monophase spinel-type oxides, $Mn_{(1.5.0.5X)}Co_{(1+0.5X)}Ni_{0.5}O_4$ (0.00 $\leq X \leq 1.00$). The cation distributions and electrical properties reported by the authors in our previous paper [4] were quoted in this paper for discussion purposes.

The c/(1-c) and Nv/n were calculated to examine the composition dependence. The results of the composition dependences of c/(1-c) and Nv/n were found to be in good agreement.

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