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Preparation and electrical properties of monophase cubic spinel, $Mn_{1.5}Co_{0.95}Ni_{0.55}O_4$, derived from rock salt type oxide

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The purpose of this study was to prepare a sintered body consisting of monophase cubic spinel type oxide, $Mn_{1.5}Co_{0.95}Ni_{0.55}O_4$, and to evaluate its electrical properties. It was found that cooling from 1400 to 1000 °C in nitrogen did not affect the preservation of the sintered rock salt type oxide formed at 1400 °C. A crack free sintered body of monophase cubic spinel may be obtained by heat treatment at 1000 °C in air, using a specimen cooled from 1400 °C at a rate of 500 °C min^{-1}. A heat treatment time in air at 1000 °C of more than 48 h was required to convert the rock salt type structure into a perfect cubic spinel structure. The electrical conductivity, σ, of the sintered cubic spinel oxide synthesized in this work was found to be stable at 100 and 200 °C in air and at 100, 200 and 300 °C in nitrogen. The sintered spinel oxide was a *p*-type semiconductor, based on small polaron hopping conduction. The intrinsic hole concentration, n, was estimated to be constant, with a value of $1.6–1.8 \times 10^{28}\ \text{m}^{-3}$. The mobility, μ, increased exponentially with increasing annealing temperature in both atmospheres, suggesting that the change in σ is dependent on μ.

1. Introduction

Composite oxides composed of transition metals, such as manganese, iron, cobalt and nickel, are widely used for negative temperature coefficient (NTC) thermistor because the electrical resistance decreases greatly with increasing temperature. Such thermistors are generally manufactured by calcining materials at about 1000 °C, then fired at around 1400 °C, and finally glass coated and annealed. Investigations of manufacturing processes and research and development of new material compositions are being made, aiming at lower cost and higher quality.

An NTC thermistor material, with a molar ratio of Mn:Co:Ni = 3.0:1.9:1.1 ($Mn_{1.5}Co_{0.95}Ni_{0.55}O_4$), has been studied, and the changes in crystal structure and electrical properties during the processes of sintering, cooling down, and annealing [1–6] have been reported. Phase separation into cubic spinel, tetragonal spinel, and rock salt type oxide has been found to occur during the cooling down process from 1400 °C to room temperature [2, 3]. The change in electrical properties was confirmed to depend on the existence ratio of each type of crystal [5]. It was considered that phase separation might cause a change in the electrical properties following long term use. Consequently, research for preparation of a monophase spinel oxide was required in order to manufacture electrically stable thermistor elements with high yield. It has been reported [6] previously, that an Mn–Co–Ni monophase cubic spinel oxide could be synthesized through 1000 °C oxidation of the related rock salt type oxide fired at 1400 °C. Though the monophase powder was prepared in this way, a crack free sintered body could not be obtained because water quenching from 1400 °C was applied.

In order to search for an alternative method, without water-quenching processes, quenching conditions and atmospheric adjustment have been investigated. As a result 1000 °C heat treatment of a rock salt type oxide, with a composition of $Mn_{1.5}Co_{0.95}Ni_{0.55}O_4$, which was sintered at 1400 °C in nitrogen, for oxidation to spinel was found to be effective. This paper deals with the preparation of sintered monophase spinel type oxide and its electrical properties.

2. Experimental

Mn, Co and Ni nitrates were weighed in a molar ratio of 3.0:1.9:1.1 and well mixed. The composition was close to that of a thermistor currently on the market. To produce a starting specimen, the mixture was preheated at 1000 °C for 3 h in air, and was then pelletized to a size of 25 mm in diameter and 5 mm in thickness. The pellet was heated from room temperature to 1000 °C for 1 h, and then was further heated to 1400 °C for 1 h, followed by holding for 3 h, in nitrogen to produce a monophase rock salt type oxide.

As will be described later, X-ray diffraction (XRD) confirmed that the phase consisted of monorock salt type oxide, using a specimen quenched in water from 1400 °C. In this study, oxidation of the rock salt type oxide, at 1000 °C (where spinel type oxide is stable) was investigated. The atmosphere was switched from nitrogen to air after the temperature reached 1000 °C. Various cooling rates from 1400 to 1000 °C were examined in nitrogen at 500, 40, 6.7, 2.2 and 0.6 °C min^{-1}. The effect of oxidative heat treatment time on the conversion to spinel at 1000 °C was checked with the specimen which was cooled at 500 °C min^{-1}. The phase present in the specimen heat treated at 1000 °C for various times was determined by XRD after quenching into water.

Electrical measurements of electrical conductivity, σ, and Seebeck potential, E_S, were conducted at 100–300 °C in air and nitrogen, using a rectangular bar (3 × 3 × 16 mm) which was cut off from a pellet prepared by cooling down to room temperature after oxidizing at 1000 °C for 144 h in air. The Seebeck coefficient, Q_S, was calculated from E_S by Equation 1

$$Q_S = -E_S/\Delta T \qquad (1)$$

where ΔT is the difference between high and low temperatures (the difference was less than 5 °C).

3. Results and discussion

3.1. Preparation of a sintered body consisting of monophase cubic spinel oxide

In the authors' studies, the phase relations of the ternary system Mn–Co–Ni oxide, with a molar ratio of 3.0 : 1.9 : 1.1, have been understood as follows. In air, cubic spinel is stable below 1040 °C, and at 1400 °C the rock salt type structure is stable [4]. After sintering, phase separation occurs during cooling from 1400 to 1000 °C. Recovery to the monophase from the separated phase is difficult, even though the separated phase is heat treated at 1000 °C for a fairly long time [6]. On the other hand, in nitrogen, the rock salt type structure is stable in the range 1200–1400 °C [4]. On the basis of such a phase relation, the temperature of 1000 °C was selected for oxidation of rock salt type oxide sintered at 1400 °C in nitrogen.

Fig. 1 shows the phases present in the specimen cooled down from 1400 to 1000 °C. The phase of rock salt type oxide, *R*, in all specimens is confirmed on the heating profiles. This fact implies that the rock salt structure can be preserved in nitrogen irrespective of the cooling rate.

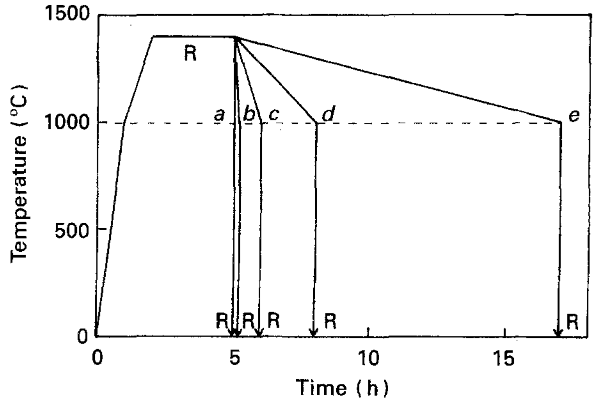

Figure 1 Phase present in specimens heat treated at 1000 °C for 0 h after firing at 1400 °C in nitrogen. Cooling rate to 1000 °C: (a) 500 °C min^{-1}, (b) 40 °C min^{-1}, (c) 6.7 °C min^{-1}, (d) 2.2 °C min^{-1}, (e) 0.6 °C min^{-1}. (R) rock salt.

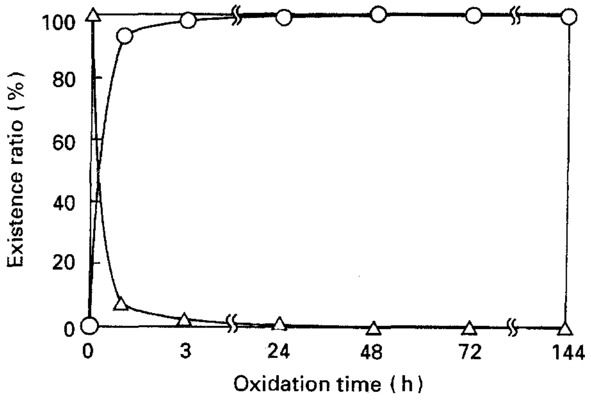

Figure 2 Existence ratio of each crystal as a function of heat-treatment time: (○) cubic spinel, (△) rock salt.

Fig. 2 illustrates the crystal existence ratio calculated from the integrated peak intensity of specimens which were heat treated at 1000 °C in air, after sintering at 1400 °C for 3 h in nitrogen. As shown in the figure, the rock salt type oxide is almost converted into cubic spinel within 24 h. This suggests that the crystal change to the stable phase is relatively rapid. After 48 h, the crystal phase is perfectly transformed to the cubic spinel structure.

3.2. Electrical properties of monophase cubic spinel oxide

For the electrical measurements, the specimen heat treated for 144 h at 1000 °C was used. Fig. 3 demonstrates the electrical conductivity, σ, measured at 100, 200 and 300 °C in air and nitrogen as a function of annealing time. No appreciable change of σ is observed during annealing, except for the specimen heat treated at 300 °C in air, which begins to decrease after about 100 h. This fact shows that the electrical resistance is affected by oxygen at relatively high temperatures in air.

Table I shows the electrical properties derived from the values of σ and Q_S measured at 100, 200 and 300 °C after 24 h. Deducing that the electrical conduction of the specimen synthesized in this study is due to a hopping mechanism, which is confirmed by oxides, (Mn–Co–Ni–Cu oxide [7], Mn–Fe–Co–Ni oxide [1], Mn_3O_4 [8] and $Mn_{1.93}Ni_{0.66}Cu_{0.41}O_4$ [9]), composed of similar components, hole

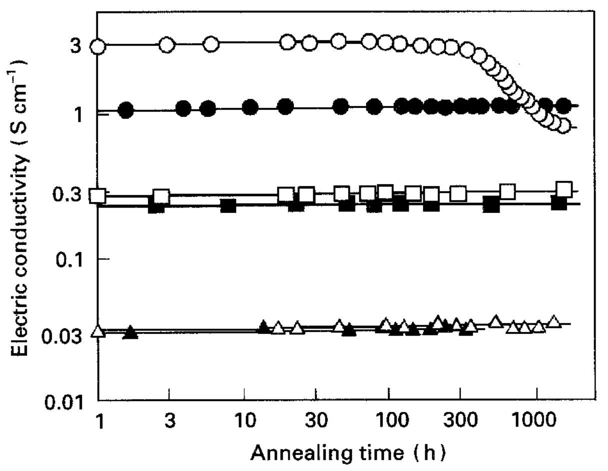

Figure 3 Electrical conductivity changes of $Mn_{1.5}Co_{0.95}Ni_{0.55}O_4$ during annealing at various temperatures. In air: (△) 100 °C, (□) 200 °C, (○) 300 °C. In nitrogen: (▲) 100 °C, (■) 200 °C, (●) 300 °C.

TABLE I Electrical properties of $Mn_{1.5}Co_{0.95}Ni_{0.55}O_4$ monophase cubic spinel

Temperature (°C)		Q_S (μV K^{-1})	σ (S cm^{-1})	n (10^{28} m^{-3})	μ (10^{-9} m^2 s$^-$V$^-$)
Air	100	39.5	0.03	1.74	1.1
	200	47.1	0.27	1.59	10.4
	300	36.8	3.04	1.80	105.0
N_2	100	39.0	0.03	1.75	1.1
	200	41.0	0.23	1.71	8.4
	300	41.7	1.08	1.70	39.8

concentration, n, and mobility, μ, were calculated using Equations 2–4

$$Q_S = (k/e)\,[\ln(N_V/n) + A] \qquad (2)$$

$$N_V = 16/a^3 \qquad (3)$$

$$\sigma = en\mu \qquad (4)$$

where k is the Boltzmann constant, e is the electronic charge, N_V is the density of states in the valence, A is a constant which depends on the dominant scattering mechanism (A was neglected for calculation), and a is the lattice constant.

All the Seebeck potentials measured in various conditions were positive, indicating a p-type semiconductor. It is clear that the Seebeck coefficients were almost constant with about 40 μ V K^{-1} and independent of atmosphere, annealing temperature and annealing time as shown in Table I. Dependency of the hole concentration on the annealing conditions is not recognized. The intrinsic hole concentration is considered to be 1.6–1.8 × 10^{28} m^{-3}. On the other hand, the values of σ and μ increase exponentially with increasing annealing temperature in air and nitrogen, respectively. Consequently, it is concluded that the change in σ depends on μ.

The temperature dependence of μ is given by the following Equation [10]

$$\mu T = (ed^2\upsilon_0/k)\exp(-E_\mu/kT) \qquad (5)$$

where d is the jump distance for the charge carrier, υ_0 is the charge carrier jump frequency and E_μ is the activation energy of mobility. Fig. 4 illustrates the relationship between the ln(μT) and 1/T. ln(μT) increases linearly with decreasing 1/T in both atmospheres. The activation energies of μ were calculated from the slopes. The difference between μ in air (0.45 eV) and in nitrogen (0.37 eV) is not so large, but detailed measurements are thought to be needed to clarify the effect of oxygen on electrical conduction.

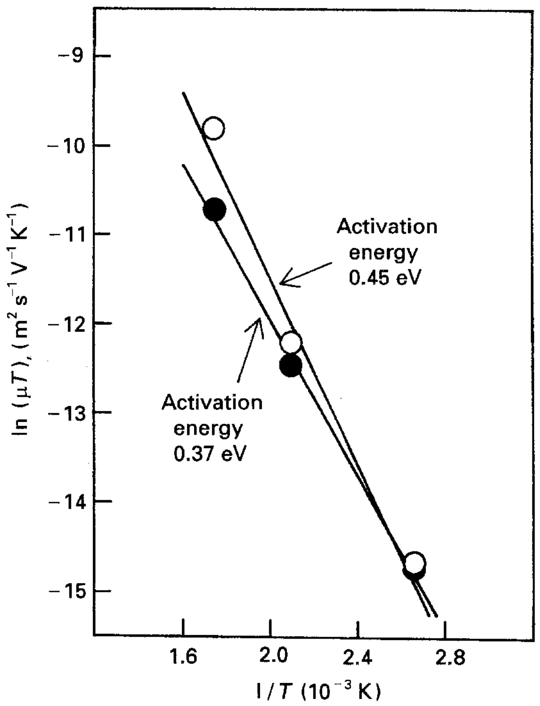

Figure 4 Plots of ln(μT) as a function of reciprocal T: (○) in air, (●) in nitrogen.

In this sample, n is considered to be constant, as mentioned above. Therefore, E_σ and E_μ, derived from the plots of ln(σT) or ln(μT) versus 1/T, are expected to be equal, as is clear in Equation 4. Activation energies of electrical conduction based on hopping by small polaron have been reported by some oxides related to this study. The values of E_σ in compounds Mn_3O_4 [8] and $Mn_{1.93}Ni_{0.66}Cu_{0.41}O_4$ [9], and of E_μ in compound $Mn_{1.40}Fe_{0.98}Co_{0.37}Ni_{0.25}O_4$ [1], were evaluated as 0.77–0.79, 0.55 and 0.26 eV, respectively. It is recognized that E_μ in this work is situated in the region of those in the references.

The small hopping mechanism is also supported by the fact that the temperature dependence of μ is positive, and that the values of μ are much smaller than 10^{-4} m^2 s^{-1} V^{-1} [11–13].

4. Conclusions

In this study, a preparation method for a sintered body consisting of monophase cubic spinel type oxide, with a molar ratio of Mn:Co:Ni = 3.0:1.9:1.1 ($Mn_{1.5}Co_{0.95}Ni_{0.55}O_4$), was investigated, and its electrical properties were measured and discussed. The results are summarized as follows:

1. It was found that cooling from 1400 to 1000 °C in nitrogen did not affect the preservation of the sintered rock salt type oxide formed at 1400 °C.

2. A crack free sintered body of monophase cubic spinel could be obtained by heat treatment at 1000 °C for oxidation in air, using a specimen which was cooled from 1400 °C at a rate of 500 °C min^{-1}.

3. A heat treatment time in air at 1000 °C of > 48 h was required to convert the rock salt type oxide phase into a perfect cubic spinel phase.

4. The electrical conductivity, σ, of the sintered cubic spinel oxide synthesized in this work was found to be stable at 100 and 200 °C in air and 100, 200 and 300 °C in nitrogen.

5. The sintered spinel oxide was a p-type semiconductor based on small polaron hopping conduction. The intrinsic hole concentration, n, was estimated to be constant, with a value of $1.6\text{–}1.8 \times 10^{28}\ \text{m}^{-3}$. The mobility, μ, increased exponentially with increasing annealing temperature in both atmospheres, suggesting that the change in σ is dependent on μ.

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