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# onPreparation and electrical properties of nickel manganite Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> ceramics for NTC thermistors

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Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> ceramics were prepared using the mixed-oxide method. All specimens displayed the typical XRD patterns of a single-phase cubic polycrystalline structure. The average grain size of the specimen sintered at 1200 °C was approximately 6.65  $\mu$ m. All specimens exhibited the typical NTC thermistor characteristic where the electrical resistance exponentially decreases with an increase in temperature. The conduction process can be explained well by the nearest neighbor hopping (NNH) mechanism. The NTC property, activation energy, B<sub>25/50</sub> constant and resistivity at room temperature of the Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> specimen sintered at 1150 °C were -4.2%/°C, 4024 K, 0.329 eV and 3360  $\Omega$ ·cm, respectively. These values are good enough to be applied to NTC thermistor devices.

Key words: Ni-Mn oxide, Sintering temperature, Structural properties, Electrical properties.

### Introduction

Spinel oxides with the general formula  $AB_2O_4$  are an important family of compounds that exhibit various physical and chemical properties depending on the type and amount of cations occupying the A (tetrahedral)and B (octahedral)- sites [1]. The interesting structural, electrical and magnetic properties of spinel oxides, which lead to their application in many fields, are found to depend on the distribution of cations among these sites. NiMn<sub>2</sub>O<sub>4</sub> is a mixed type of spinel, which means that a portion of the Ni<sup>2+</sup> cations are displaced from tetragonal to octahedral interstices of the oxygen face centered cubic (FCC) sublattice, a corresponding proportion of Mn<sup>3+</sup> cations in octahedral sites disproportionate to Mn<sup>2+</sup> and Mn<sup>4+</sup>, and the Mn<sup>2+</sup> cations move to the tetrahedral sites to compensate for the Ni<sup>2+</sup> vacancies [2, 3]. The electrical conduction process is believed to be due to localized electron hopping between Mn<sup>3+</sup> and Mn<sup>4+</sup> cations in octahedral sites and displays a negative temperature coefficient of resistance (NTCR) property [4, 5]. Various modes of ion transport such as nearest neighbor hopping (NNH) [6], variable range hopping (VRH) [7] and some empirical models [8, 9] have been suggested by a number of researchers to explain the conduction of spinel compounds. In the present paper, Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> ceramics were prepared using the mixed-oxide method and the structural and electrical properties were investigated according to sintering temperature for application in thermistors.

#### **Experimental**

Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> ceramics, which have demonstrated good electrical properties in our previous experiments, were fabricated by a solid-state reaction of stoichiometric amounts of NiO and Mn<sub>2</sub>O<sub>3</sub> powders. The mixed powders of NiO and Mn<sub>2</sub>O<sub>3</sub> were thermally decomposed at a temperature of 900 °C for 6hrs and cooled down slowly. The resulting oxide powders were pressed into disc form of 12-mm diameter and 1.5-mm thickness. Generally,  $Ni_x Mn_{3-x}O_{4+\delta}$  compounds crystallize in air to form a cubic spinel phase in temperatures ranging between 730 °C and 875 °C. Below 730 °C but above 300 °C the nickel manganite decomposes to NiMnO<sub>3</sub> and  $Mn_2O_3,$  and above 875  $^{\rm o}C$  NiO and  $Mn_3O_4$  tend to precipitate out and single-phase nickel manganite cannot be obtained [10]. Thus, in our experiments, these green ceramics were sintered in air at different temperatures of 1050 °C, 1100 °C, 1150°C and 1200 °C for 12 hrs, slowly cooled down to 800 °C at a rate of 2 °C/min, and then quenched to room temperature. Field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) were utilized in order to analyze the microstructure and crystalline structure, respectively, of the nickel manganite. For electrode formation, the flat surfaces of the disc-shaped specimens were coated with silver paste where Ag wires were attached to both surfaces. The electrical characteristics (electrical resistivity, sensitive index and activation energy) of the thermistor were measured

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using an electrometer (Keithley 6517A, USA).

#### **Results and Discussion**

Fig. 1 shows the surface FE-SEM micrographs of Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> specimens at various sintering temperatures. The grain size increased with an increase in sintering temperature and specimens sintered above 1100°C displayed a uniform and void-free grain structure. The average grain size of the specimen sintered at 1200°C was approximately 6.65 µm. Fig. 2 shows the XRD patterns of Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> specimens at various sintering temperatures. All specimens showed the typical XRD patterns of a single-phase cubic polycrystalline structure without a preferred orientation; no second phase was observed. Fig. 3 shows the lattice constant of Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> specimens at various sintering temperatures. The lattice constant decreased slightly with an increase in sintering temperature. The reason for this is assumed to be because the distribution of Mn ions in the B-sites becomes disordered as the sintering temperature increases [11].



Fig. 1. Surface FE-SEM micrographs of  $Ni_{0.79}Mn_{2.21}O_4$  ceramics with the variation of sintering temperature.



Fig. 2. XRD patterns of  $Ni_{0.79}Mn_{2.21}O_4$  ceramics with the variation of sintering temperature.

Fig. 4 shows the relationship between electrical resistance and temperature for  $Ni_{0.79}Mn_{2.21}O_4$  specimens at various sintering temperatures. All specimens exhibited the typical NTC thermistor characteristic where electrical resistance exponentially decreases with an increase in temperature. The  $Ni_{0.79}Mn_{2.21}O_4$  specimen sintered at 1150°C displayed an excellent NTC property of -4.2%/°C due to the dense and void-free microstructure, as shown in Fig. 1.

Fig. 5 shows the B<sub>25/50</sub> constant of Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> specimens at various sintering temperatures. The B<sub>25/50</sub> constant was calculated using the following equation:  $B_{25/50} = (ln\rho_1 - ln\rho_2)/(1/T_1 - 1/T_2)$ , where  $\rho_1$  and  $\rho_1$  are the resistances measured at temperature  $T_1$  (25°C) and  $T_2$  (50 °C), respectively. For practical applications, it is necessary to enhance the B<sub>25/50</sub> constant, i.e., high sensitivity to temperature excursions. The specimen sintered at 1150 °C showed the good value of 4024 K, and this value is large enough to be applied in NTC thermistor devices. When the sintering temperature was increased, the B<sub>25/50</sub> constant increased, which can be attributed to a change in cation distribution, modifying the number of distorting ions such as Mn<sup>3+</sup> and Mn<sup>4+</sup> in



Fig. 3. Lattice constant of  $\rm Ni_{0.79}Mn_{2.21}O_4$  ceramics with the variation of sintering temperature.



Fig. 4. Relationship between the electrical resistance and the temperature of  $Ni_{0.79}Mn_{2.21}O_4$  specimens with the variation of sintering temperature.



Fig. 5.  $B_{25/50}$  constant of  $Ni_{0.79}Mn_{2.21}O_4$  specimens with the variation of sintering temperature.



**Fig. 6.** Plot of log(R/T) vs. 1/T of  $Ni_{0.79}Mn_{2.21}O_4$  specimens with variation of the sintering temperature.

octahedral sites [11]. However, in the specimen sintered at 1200 °C, the  $B_{25/50}$  constant decreased because the decrease in the  $Mn^{3+}$  ratio is related to the re-oxidation ( $Mn^{3+} \rightarrow Mn^{4+}$ ) phenomenon during the cooling procedure of the high temperature sintering process [12].

Generally, electrical transport information can be obtained by fitting data to the hopping conductivitytemperature formula. For small polaron hopping conduction the temperature-dependent resistance can be described using a generalized expression [13]:  $R = C_0 T^a exp(T_0/T)^p$ , where R is the resistance,  $C_o$  a constant, T the temperature and  $T_o$  a characteristic temperature, determined by the slope of the log(R/T)vs.  $(1/T)^p$ . In the case of nearest neighbor hopping (NNH),  $\alpha = p = 1$  and for variable range hopping (VRH),  $\alpha = 2p$ . For Mott VRH conduction  $p = \frac{1}{4}$  [14], and for Efro-Shklovskii VRH conduction  $p = \frac{1}{2}$  [14], order to investigate the hopping model of the Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> specimens, temperature-resistance data were plotted to log(R/T) vs. 1/T curves, as shown in Fig. 6. It presented a good linear relation in terms of the measurement temperature range, i.e. fitting well to



Fig. 7. Activation energy of  $Ni_{0.79}Mn_{2.21}O_4$  specimens with the variation of sintering temperature.



Fig. 8. Resistivity of  $Ni_{0.79}Mn_{2.21}O_4$  specimens with the variation of sintering temperature.

the NNH model. Electron hopping is thought to take place between the nearest adjacent  $Mn^{3+}$  and  $Mn^{4+}$  cations via localized states in octahedral sites. However,  $Mn^{2+}/Mn^{3+}$  cations in tetrahedral sites are expected to not participate in the small polaron conduction process because the  $Mn^{3+}$  cation has a strong octahedral preference.

Fig. 7 shows the activation energy ( $E_A$ ) of  $Ni_{0.79}Mn_{2.21}O_4$  specimens at various sintering temperatures. The activation energy for small polaron conduction determined from the slope of the straight lines from Fig. 6 was calculated to be 0.329 ~ 0.35 eV, and these values agreed well with those reported by other researchers [16].

Fig. 8 shows the resistivity of  $Ni_{0.79}Mn_{2.21}O_4$  specimens at various sintering temperatures. The specimen sintered at 1150 °C showed a good value of 3360  $\Omega$ -cm. The resistivity decreased with an increase in sintering temperature. This is due to the fact that the grain size with a low resistivity increased and pores decreased with an increase in sintering temperature. However, the resistivity of the specimen sintered at 1200 °C increased because of a decrease in  $Mn^{3+}$  ions due to the re-oxidation phenomenon during the cooling procedure, as discussed in Fig. 5.

## Conclusions

Ni<sub>0.79</sub>Mn<sub>2.21</sub>O<sub>4</sub> ceramics were prepared using the mixed-oxide method and their structural and electrical properties according to sintering temperature were investigated. All specimens displayed the typical XRD patterns of a single-phase cubic polycrystalline structure without any ambiguous reflections. The lattice constant decreased slightly with an increase in sintering temperature because the distribution of Mn ions in Bsites becomes disordered as sintering temperature increases. When the sintering temperature is increased, a change in cation distribution occurs, modifying the number of distorting ions such as  $Mn^{3+}$  and  $Mn^{4+}$  in octahedral sites. However, if the sintering temperature is too high, the concentration of Mn<sup>3+</sup> cations decreases due to the re-oxidation  $(Mn^{3+} \rightarrow Mn^{4+})$  phenomenon during the cooling procedure. Electron hopping is thought to occur between the nearest adjacent Mn<sup>3+</sup> and Mn<sup>4+</sup> cations (NNH mechanism).

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