

Characterization and site distributions of cation in nickel manganite thermistors

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Cubic spinel $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ ceramics with varying sintering temperatures were prepared using the mixed-oxide method. Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis were used to determine the structural properties of the nickel manganite specimens, especially the distribution of manganese ions. The specimens sintered at 1200 °C showed a uniform and pore-free grain structure and the average grain size was approximately 5.08 μm . All specimens exhibited the typical XRD patterns of a single-phase cubic spinel structure. Based on the results of XPS investigations, in all specimens, manganese existed in three oxidation states as Mn^{2+} , Mn^{3+} and Mn^{4+} ions. The inversion parameter estimated from XRD increased with an increase in sintering temperature due to some of the Mn ions in octahedral sites moving to tetrahedral sites. The $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimen sintered at 1150 °C showed the lowest activation energy value of 0.329 eV.

Key words: Ceramics, Oxides, X-ray diffraction, X-ray photoelectron spectroscopy.

Introduction

Negative temperature coefficient (NTC) thermistors have been extensively used in various applications, such as temperature sensing, device protection, automotive, control applications and infrared detectors [1-3]. Nickel manganite ($\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$) is the most widely studied NTC material due to its excellent temperature-sensitive characteristics. It can be prepared through a commonly used solid-state reaction, milling with mixed oxalates or chemically from different precursors [4-6].

The NiMn_2O_4 spinel structure has a cubic close packing of oxygen atoms with cations distributed in tetrahedral A-sites and octahedral B-sites. The interesting physical and electrical properties of NiMn_2O_4 spinels arise from their ability to distribute the cations among the available tetrahedral and octahedral sites. The NiMn_2O_4 system possesses a mixed spinel structure and the degree of inversion depends upon the heat treatment [7]. The structural and electrical properties of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ spinel materials are very sensitive to the chemical composition, method of preparation and cation distribution. During the past decades, many researchers have reported the cation distribution in $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ systems [8-9]. Some of the Ni^{2+} cations have a strong preference for octahedral interstices and their occupation induces the appearance of Mn^{4+} ions. Mn^{3+} ions in octahedral sites disproportionate to Mn^{2+} and Mn^{4+} , with Mn^{2+} ions moving to tetrahedral sites to compensate for Ni^{2+} vacancies. Electrical conductivity is caused by the thermally activated

hopping mechanism between Mn^{3+} and Mn^{4+} ions placed in octahedral sites of the spinel [10].

In the present work, we present that the structural properties of NiMn_2O_4 specimens fabricated by the mixed-oxide method are significantly influenced by sintering temperature. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were used to determine the valence and site occupancy of cations, and the structural and electrical properties of specimens were investigated in relation to the cation distribution.

Experimental

Polycrystalline $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens were synthesized through a solid-state reaction of stoichiometric amounts of high-purity NiO and Mn_2O_3 powders. The mixed powders were calcined at 900 °C for 6 hrs and cooled down slowly (heating rate: 5 °C/min, cooling rate: 2 °C/min). The calcined powders were milled in ethanol, dried, blended with an organic binder, and then pressed into pellets with a 12-mm diameter and 1.5-mm thickness. The green disks were sintered at 1200 °C for 12 hrs, cooled down slowly to 800 °C at a rate of 2 °C/min, and then quenched to room temperature. Thermogravimetric (TG) and differentially scanning calorimetry (DSC) analyses of the powders were carried out on TA Instruments Q600 using a heating rate of 5 °C/min in air flow. X-ray powder diffraction patterns were collected on a D8 Discover & GADD diffractometer system using CuK_α radiation ($\lambda = 0.15418 \text{ nm}$). XPS spectra were obtained with a VG Scientific ESCALAB 250 spectrometer using AlK_α radiation. The intensity of each peak was estimated from integration after having smoothed, subtracted an

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‘S-shaped’ background and fitted the experimental curve to a combination of Gaussian-Lorentzian lines.

Results and Discussion

Fig. 1 shows surface FE-SEM micrographs of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens with varying sintering temperatures. The grain size increased and pores reduced with an increase in sintering temperature. The specimens sintered at 1200 °C displayed a uniform and pore-free grain structure, and the average grain size was approximately 5.08 μm . Fig. 2 shows the X-ray diffraction patterns of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of sintering temperature. All specimens exhibited the typical XRD patterns of a single-phase cubic spinel structure and dependence on sintering temperature was not observed. Fig. 3 shows the oxygen parameter of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$

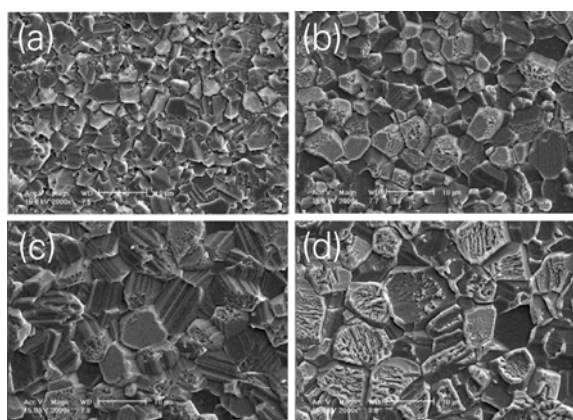


Fig. 1. Surface FE-SEM micrographs of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens sintered at (a) 1050 °C and (b) 1100 °C, (c) 1150 °C and (d) 1200 °C

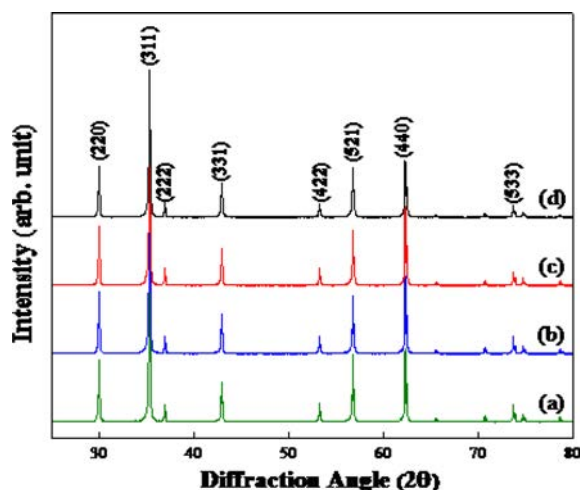


Fig. 2. X-ray diffraction patterns of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of the sintering temperature: (a) 1050 °C, (b) 1100 °C, (c) 1150 °C and (d) 1200 °C.

specimens as a function of sintering temperature. The oxygen ions in the spinel structure are not generally located at the exact positions of the FCC sublattice.

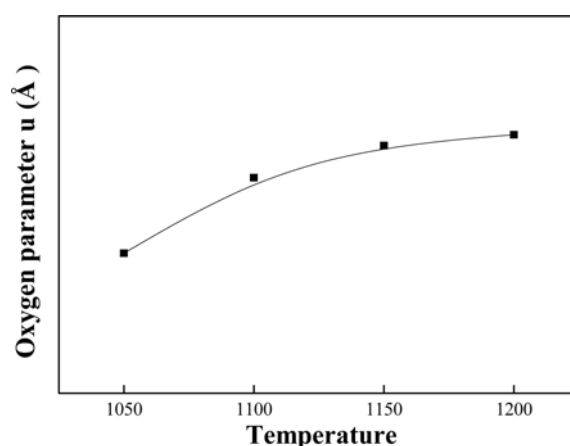


Fig. 3. Oxygen parameter of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of the sintering temperature.

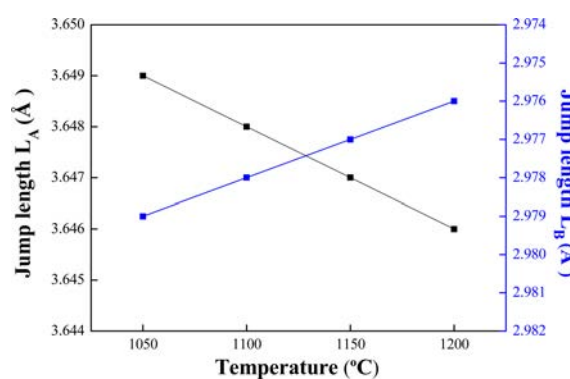


Fig. 4. Jumping length of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of the sintering temperature.

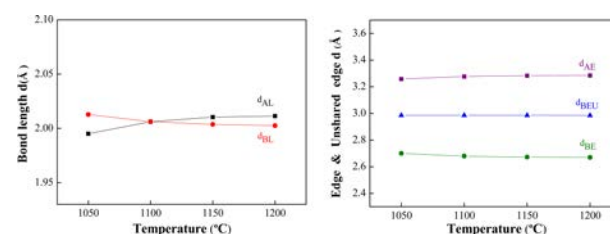


Fig. 5. Various X-ray parameters of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of the sintering temperature: (a) tetrahedral and octahedral bond lengths (d_{AL} and d_{BL}) and (b) tetrahedral edge (d_{AE}) and the shared and unshared octahedral edges (d_{BE} and d_{BEU}).

Their detailed positions are determined by the oxygen parameter, which reflects adjustments of the structure to accommodate differences in the radius ratio of the cations in the tetrahedral and octahedral sites [11]. The oxygen parameter slowly increased with an increase in sintering temperature. This phenomenon can be explained by the fact that the oxygen ions in tetrahedral sites were moving in place as some of the Mn ions in octahedral sites moved to tetrahedral sites.

Fig. 4 shows the jumping length of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of sintering temperature. It has been reported that the jumping length of electrons influences the electrical properties of the spinel system [12].

The values of the tetragonal (d_{AL}) and octahedral

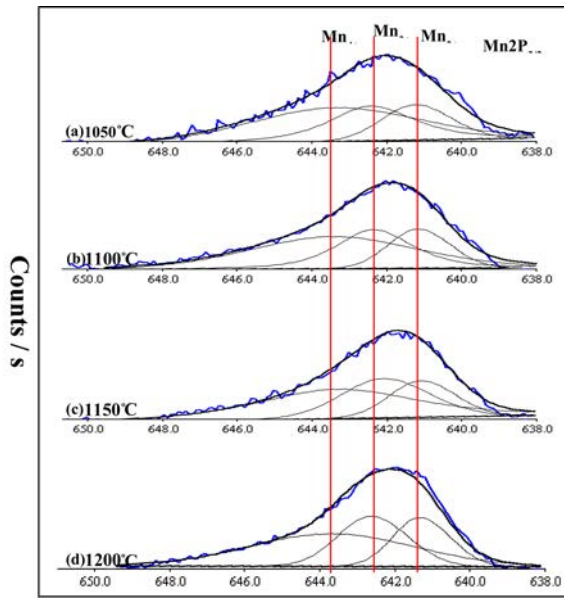


Fig. 6. X-ray photoelectron spectra (XPS) Mn 2p signal of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of the sintering temperature.

Table 1. Binding energy and peak area of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ compounds.

Sintering Temp.	Binding Energy (eV)			Area (%)		
	Mn^{2+}	Mn^{3+}	Mn^{4+}	Mn^{2+}	Mn^{3+}	Mn^{4+}
1050 °C	641.1	642.3	643.3	21.3	33.4	45.3
1100 °C	641.1	642.3	643.4	21.7	33.8	44.5
1150 °C	641	642	643.3	22.9	34.0	43.1
1200 °C	641.1	642	643.2	24.0	33.7	42.3

bond length (d_{BL}), tetrahedral edge length (d_{AE}), and shared (d_{BE}) and unshared octahedral edge lengths (d_{BEU}) were calculated using the experimental values of the lattice constant (a_o) and oxygen parameter (u) from the following equation[13-14]:

$$d_{AL} = a\sqrt{3}(u-0.25) \quad (1)$$

$$d_{BL} = a\left(3u^2 - \frac{4}{11}u + \frac{43}{63}\right)^{1/2} \quad (2)$$

$$d_{AE} = a\sqrt{2}(2u-0.5) \quad (3)$$

$$d_{BE} = a\sqrt{2}(1-2u) \quad (4)$$

$$d_{BEU} = a\left(4u^2 - 3u + \frac{11}{16}\right)^{1/2} \quad (5)$$

Fig. 5 shows the various calculated X-ray parameters. The variation of d_{AL} and d_{BL} as a function of sintering temperature are shown in Fig. 5(a), and d_{AE} , d_{BE} and d_{BEU} in Fig. 5(b). While d_{AL} and d_{AE} increase slightly with an increase in sintering temperature, d_{BL} and d_{BE} decrease. This is because some of the Mn ions in octahedral sites moved to tetrahedral sites, as discussed in Fig. 3. The results of XPS investigations of the $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens are summarized in Table 1,

and Mn2p_{3/2} spectra are shown in Fig. 6. The large FWHM value of the Mn2p signals of the NiMn_2O_4 spinel seems to be strong evidence for the simultaneous presence of the three oxidation states Mn^{2+} , Mn^{3+} and Mn^{4+} in this compound [15]. The three peaks were assigned to the binding energy of 641-641.1 eV for Mn^{2+} (tetrahedral), 642-642.3 eV for Mn^{3+} (octahedral) and 643.2-643.4 eV for Mn^{4+} (octahedral). The peak ratio depends on the manganese content in the spinel nickel manganite compounds; when the sintering temperature increases, the peak area belonging to Mn^{2+} increases and Mn^{4+} decreases. These results also agree with the oxygen parameter and jumping length measurements of the $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimen.

In general, the nickel manganite $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ system exhibits a partially inverse spinel structure due to the strong octahedral site preference of the Ni^{2+} ion. Therefore, the measured lattice parameter shows an intermediate distribution between the normal and inverse structure values. Thus, it is possible to calculate the inversion parameter v from the relation: $v = (a_i - a_m)x / (a_i - a_E)$, where x is the content of Ni, a_m is the measured lattice parameter, a_i and a_n and represent

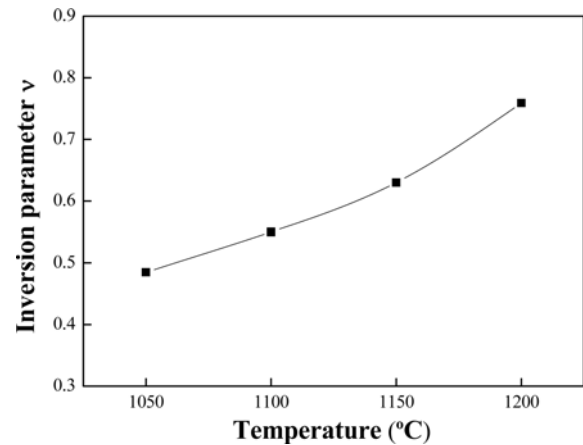


Fig. 7. Inversion parameters of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of the sintering temperature.

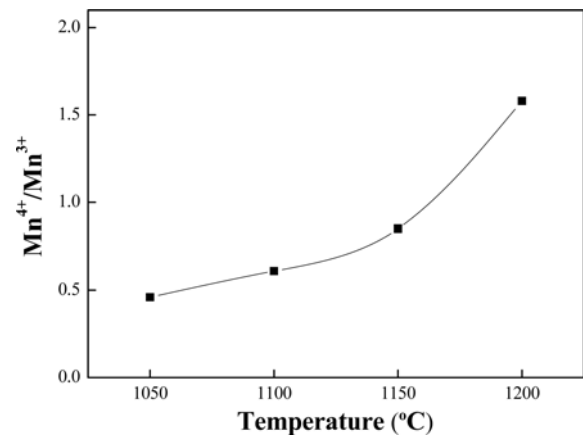


Fig. 8. $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of the sintering temperature.

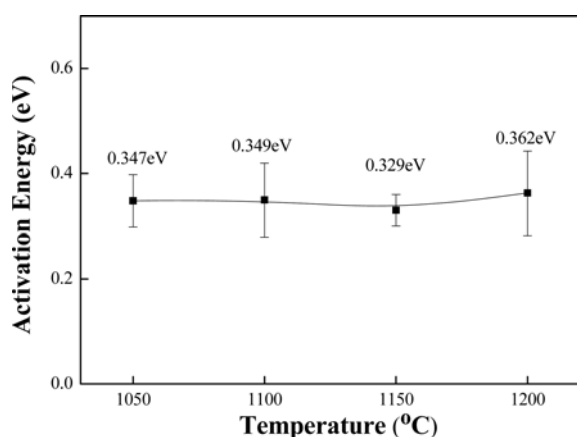


Fig. 9. Activation energy of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of the sintering temperature.

the theoretical lattice parameters of the inverse and normal structure, respectively [16]. Fig. 7 shows the inversion parameters of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of sintering temperature. The inversion parameter increases with an increase in sintering temperature because some of the Mn ions in octahedral sites move to tetrahedral sites.

From the variation of the inversion parameter, the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio can be calculated as a function of sintering temperature. Fig. 8 shows the $\text{Mn}^{4+}/\text{Mn}^{3+}$ cation ratio as a function of sintering temperature. Sintering conditions drastically influence the cation distribution and electrical conductivity of the nickel manganite system. The specimen sintered at 1150 °C exhibited the closest value to the ideal 1 : 1 ratio, which is the most favorable for supporting $\text{Mn}^{4+}/\text{Mn}^{3+}$ localized electron hopping. In the specimen sintered at 1200 °C, the inversion parameter increased rapidly due to the decrease in Mn^{3+} cations related to the oxidation phenomena ($\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$) [17].

Fig. 9 shows the activation energy of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimens as a function of sintering temperature. It is generally accepted that electrical conduction on a nickel manganite spinel compound is via hopping of electrons between the Mn^{3+} and Mn^{4+} ions at the octahedral sites. According to this mechanism, the activation energy for electrical conduction is inversely proportional to the concentration product of Mn^{3+} and Mn^{4+} ions [18]. However, in our study, the $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ specimen sintered at 1150 °C, which had a relatively small value of $[\text{Mn}^{3+}][\text{Mn}^{4+}]$, as shown in Table 1, showed the lowest activation energy value of 0.329 eV. This can be explained by considering the microstructure factors that influence electrical conductivity. The increasing of the sintering temperature in our study leads to an increase in the grain size and a decrease in pores, as shown in Fig. 1. This is responsible for the reduction of the lattice scattering of charge carriers due to the homogeneous single phase formation, which thereby increases conductivity. Based on the above consideration, it is believed that the

concentration of Mn^{3+} and Mn^{4+} ions and structural properties such as pore and grain size have a significant effect on activation energy and resistivity properties.

Conclusions

Spinel $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ ceramics were fabricated by a solid-state reaction and their structural properties were investigated using X-ray diffraction and X-ray photoelectron spectroscopy. XPS investigations show that manganese in all the specimens exists in three oxidation states as Mn^{2+} , Mn^{3+} and Mn^{4+} ions, and the peak area belonging to the Mn^{4+} ions decreased and that of the Mn^{2+} ions increased with an increase in sintering temperature. Jumping length is dependent on sintering temperature due to rearrangement of the cations in the tetrahedral and octahedral sites of the unit cell. The oxygen parameter indicated that the expansion or contraction of the anion sublattice slowly increases with an increase in sintering temperature. This phenomenon can probably be explained by the fact that the oxygen ions in tetrahedral sites were moving in place as some of the Mn ions in octahedral sites moved to tetrahedral sites. The concentration of Mn^{3+} and Mn^{4+} ions and structural properties such as pore and grain size have a significant effect on activation energy and resistivity properties.

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