

Structural properties and cation distribution in a $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ ($0.71 \leq x \leq 1.0$) spinel

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Cubic spinel $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ ($0.71 \leq x \leq 1$) ceramics were prepared using the mixed-oxide method. The mixed powders were investigated by TG-DSC analysis in order to study the phase formation and decomposition process. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis were employed to determine the structural properties of the nickel manganite specimens, especially the distribution of manganese ions. With an increase in nickel content, both Ni^{2+} and Mn^{3+} ions predominately occupy the octahedral sites due to their preference for large octahedral site energy. The large FWHM value of the Mn 2p signals of the NiMn_2O_4 spinel is indicative of multiplet splitting and the charging effect is due to the presence of Mn^{2+} , Mn^{3+} and Mn^{4+} ions. Manganese in all specimens exists in three oxidation states as Mn^{2+} , Mn^{3+} and Mn^{4+} ions. The lattice parameter estimated from XRD decreases with an increase in Ni content due to the replacement of larger ionic radii (Mn^{3+}) by smaller ionic radii (Ni^{2+}).

Key words: Hopping, Cubic spinel, NTCR, Cation distribution, Inversion parameter.

Introduction

Negative temperature coefficient (NTC) ceramic thermistors are being increasingly used in various industrial and domestic applications, including circuit compensation, aerospace, cryogenic, automotive, temperature measurement and control applications. Nickel manganite based compositions are the most widely used NTC materials. Nickel manganite (NiMn_2O_4) has a cubic spinel structure in contrast to many other manganite compounds (MMn_2O_4 ; M = Mn, Fe, Co, Zn, Mg), showing tetragonal distortion due to the Jahn-Teller effect of Mn^{3+} ions in the octahedral sites of the spinel lattice [1]. In a regular spinel divalent cations are located in tetrahedral lattice interstices and trivalent cations in octahedral sites. However, NiMn_2O_4 is not a regular spinel but a mixed type of spinel, which means that a fraction x of the Ni^{2+} cations are displaced from tetrahedral to octahedral interstices of the oxygen fcc sublattice, a corresponding proportion $2x$ of the Mn^{3+} cations in octahedral sites disproportionate to Mn^{2+} and Mn^{4+} , and the Mn^{2+} cations move to the tetrahedral sites to compensate for the Ni^{2+} vacancies [2, 3].

The electrical properties of NiMn_2O_4 ceramics have been found to be largely affected by the cation distribution, at the tetrahedral and octahedral sites, of the spinel structure. Therefore, it is very important to accurately know the cation distribution in these

materials. Electrical conductivity is generally believed to occur via electron jumping between Mn^{3+} and Mn^{4+} ions at the octahedral sites. In the present study, we investigated the cation distribution, the oxidation sites of the nickel and manganese cations, and the structural properties of nickel manganite $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$, where $x = 0.71$ -1.0. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were performed to provide powerful and direct analysis of the surface.

Experimental

Polycrystalline $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ ($0.71 \leq x \leq 1$) ceramics were fabricated by 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 6hrs and cooled down slowly. The nickel manganite powders were mixed with an organic binder, and then pressed into pellets with a diameter of 12 mm and thickness of 1.5 mm. Green ceramics were sintered at 1200 °C for 12 hrs and cooled slowly to 800 °C at a rate of 2 °C/min and then quenched to room temperature.

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses of the powders were carried out on a TA Instruments Q600 using a heating rate of 5 °C/min in air flow. X-ray diffraction studies were performed on a D8 Discover & GADD system using CuK_α radiation, with a wave length of 1.5418 Å and step width of 0.015 °. X-ray photoelectron spectra (XPS) were acquired with a VG Scientific ESCALAB 250 spectrometer system using AlK_α radiation. The intensity of each peak was estimated from integration after smoothing, subtracting the ‘S-shaped’ background

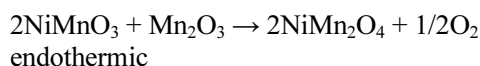
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and fitting the experimental curve to a combination of Gaussian-Lorentzian lines.

Results and Discussion

In order to investigate variations in the mass and thermal stability of oxides, TG and DSC analysis of NiMn_2O_4 powder was carried out between room temperature and 1000°C , as shown in Fig. 1. In the initial temperature range, a mass loss occurs up to approximately 200°C , corresponding to the elimination of absorbed water, accomplished with a small exothermic peak in the DSC curve. In the temperature range of 200 – 850°C , several oxidation-reduction phenomena of the mixed powders are observed. Because the powder takes up oxygen during the heating process, the oxidation of Mn^{2+} and Mn^{3+} cations on tetrahedral and octahedral sites, respectively, results in a slight weight gain [4]. With an increase in temperature, weight loss in the powders occurs due to decomposition of the spinel phase caused by the formation of Mn_2O_3 and the ilmenite NiMnO_3 , in addition to the loss of excess oxygen [5]. At temperatures above 850°C , with the appearance of a weak endothermic peak at 930°C , a stoichiometric spinel phase, NiMn_2O_4

O_4 , occurs with a mass loss due to the reduction of Mn_2O_3 and NiMnO_3 according to the following reaction:



The results of XPS investigations of the $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds are summarized in Table 1, and the Mn 2p spectra are shown in Fig. 2. The large FWHM value of the Mn 2p signals of the NiMn_2O_4 spinel is indicative of multiplet splitting and the charging effect is due to the presence of Mn^{2+} , Mn^{3+} and Mn^{4+} ions [6]. As shown in Fig. 2, the Mn 2p spectrum of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ specimens was a superimposition of Mn^{2+} , Mn^{3+} and Mn^{4+} 2p peaks which indicates that Mn occurs in three different oxidation states. The three peaks correspond with a binding energy of 641.0 – 641.6 eV, 642.1 – 642.6 eV and 643.0 – 643.8 eV, respectively. This gave rise to the formula $(\text{Ni}_{x-\delta}^{2+} \text{Mn}_{1-x-\delta}^{2+})[\text{Ni}_\delta^{2+} \text{Mn}_{2-2\delta}^{3+} \text{Mn}_\delta^{4+}]$ [7]. Peak ratios depend on the nickel content in the nickel manganite spinel compounds. It was observed that the peak area belonging to Mn^{3+} 2p decreased and Mn^{4+} 2p increased slightly with an increase in Ni

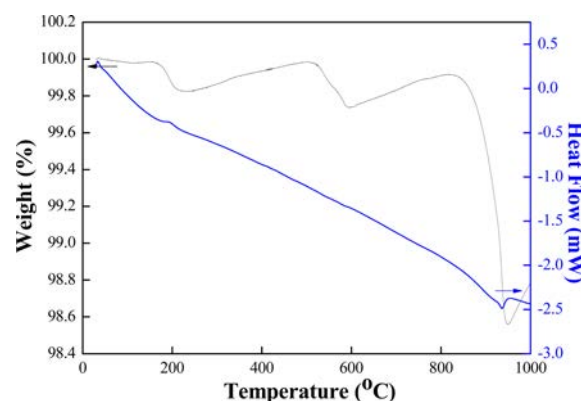


Fig. 1. Thermogravimetric (TG) and differentially scanning calorimetry (DSC) analyses of the NiMn_2O_4 powder.

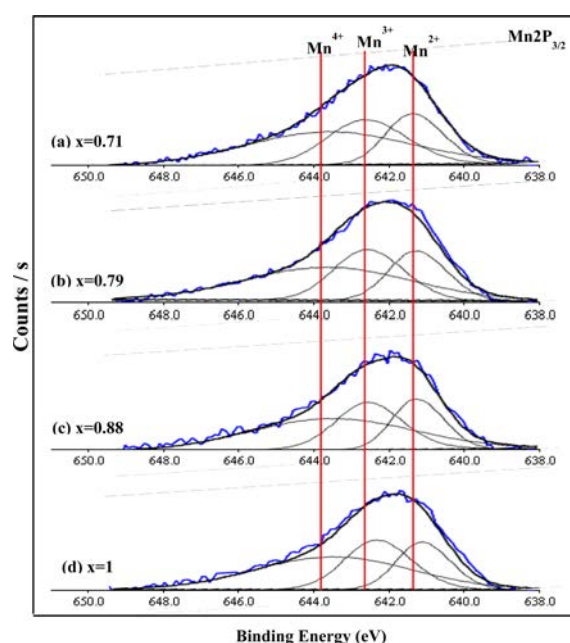


Fig. 2. XPS spectra Mn 2p signal of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds.

content x in $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ spinel ceramics.

In general, materials in bulk form with the molecular formula AB_2O_4 present a normal spinel-type structure where A atoms (divalent cations) occupy the tetrahedral sites and B atoms (trivalent cations) occupy the octahedral sites in a face-centered-cubic (fcc) close-packed oxygen sublattice. In the case of an inverse spinel structure, the A atoms occupy the octahedral sites and B atoms occupy both tetrahedral and octahedral

Table 1. Binding energy and peak area of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds.

Ni content	Binding Energy (eV)			Area (%)		
	Mn^{2+}	Mn^{3+}	Mn^{4+}	Mn^{2+}	Mn^{3+}	Mn^{4+}
0.71	641.2	642.5	643.5	24.4	31.9	43.7
0.79	641.1	642.4	643.5	24.0	31.1	44.9
0.88	641.1	642.4	643.4	23.4	29.7	46.9
1.0	641	642.2	643.4	23.8	29.1	47.1

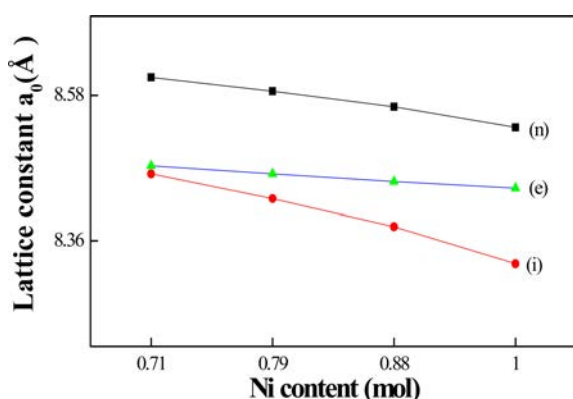


Fig. 3. Lattice parameters of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds as a function of Ni^{2+} content: curve a_E the measured lattice parameter; curves a_N and a_I the calculated lattice parameters for the theoretical normal and inverse spinel structure, respectively.

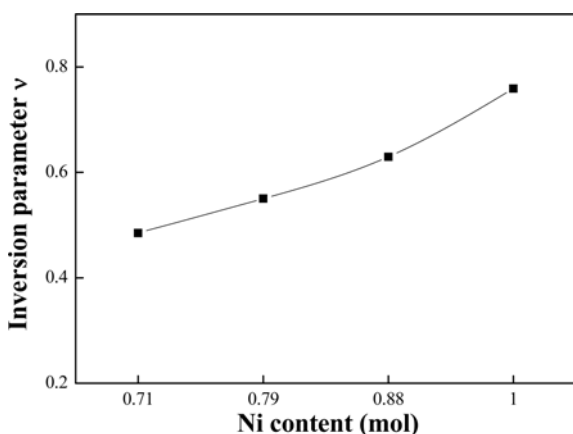


Fig. 4. Inversion parameter of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds.

sites. However, in a mixed spinel structure, A and B atoms are situated both in tetrahedral and octahedral sites in materials with the general formula of $(\text{A}_{1-x}\text{B}_x)[\text{A}_x\text{B}_{2-x}]\text{O}_4$.

In particular, nickel manganite (NiMn_2O_4) exhibits a partially inverse cubic structure, which means that some divalent Ni cations move from tetragonal to octahedral sites. Trivalent Mn cations in octahedral sites disproportionate to Mn^{2+} and Mn^{4+} and the Mn^{2+}

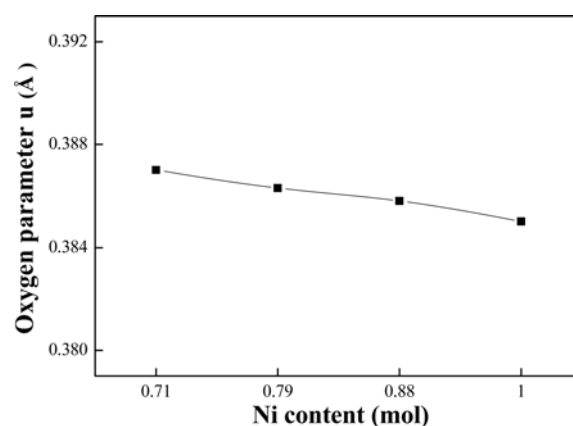


Fig. 5. Oxygen parameter of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds.

cations move to tetrahedral sites to compensate for the Ni^{2+} vacancies. The fraction of Ni^{2+} cation occupancy of the octahedral sites corresponds to the inversion parameter v of the cubic spinel structure, which has a strong effect on Mn valence states.

Fig. 3 shows the lattice parameters of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds as a function of Ni^{2+} content. a_N and a_I are the calculated lattice parameters for the theoretical normal and inverse spinel structure, respectively. a_E , the measured lattice parameter of the specimen, decreases with an increase in Ni content due to the replacement of larger ionic radii (Mn^{3+}) by smaller ionic radii (Ni^{2+}) and their distribution among the A- and B-sites in spite of its large octahedral site preference energy. The measured lattice parameter also shows an intermediate distribution between normal and inverse structure values. Thus, it is possible to calculate the inversion parameter, v , for each composition from the relation [4]: $v = (a_1 - a_E)x / (a_1 - a_I)$, where x is the content of Ni. Fig. 4 shows the inversion parameter of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds. The inversion parameter increases with an increase in the nickel ion content, while the number of Ni^{2+} ions at A-sites remains relatively unchanged. These results also agree with the XPS analysis, as shown in Fig. 2.

Generally, in a spinel structure compound, the anions

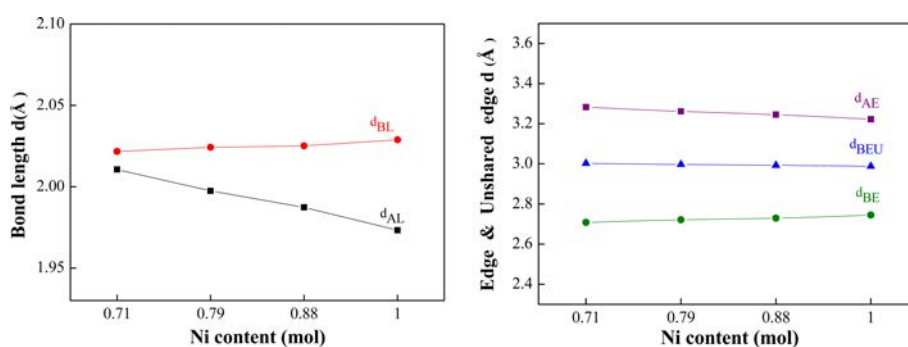


Fig. 6. Various X-ray parameters of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ compounds as a function of nickel content x : (a) tetrahedral and octahedral bond lengths (d_{AL} and d_{BL}) and (b) tetrahedral edge (d_{AE}) and the shared and unshared octahedral edges (d_{BE} and d_{BEU}).

are not located at the exact positions of the fcc sublattice, and the anion sublattice expands or contracts based on variations in the oxygen parameter until the A- and B-site volumes match the radii of the constituent cations [8, 9]. Fig. 5 shows the oxygen parameter of $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ ceramics. The oxygen parameter slowly decreases with an increase in the nickel content. This observation may be due to the smaller Ni^{2+} (0.63 Å) ion, which when substituted in the lattice, resides on an A-site and replaces the larger Mn^{3+} ion (0.785 Å) from an A-site to a B-site.

Using the experimental values of the lattice constant (a_o) and oxygen parameter (u), the values of the tetragonal (d_{AL}) and octahedral bond lengths (d_{BL}), tetrahedral edge length (d_{AE}), and shared (d_{BE}) and unshared octahedral edge lengths (d_{BEU}) were calculated from the following equation [10, 11]:

Fig. 6 shows the various calculated X-ray parameters. Variations in d_{AL} and d_{BL} as a function of nickel content x are shown in Fig. 5(a) and d_{AE} , d_{BE} and d_{BEU} are shown in Fig. 5(b). While d_{AL} , d_{AE} and d_{BEU} decrease with an increase in nickel content, d_{BL} and d_{BE} increase. This behavior may be attributed to the effect of the substitution process, that is, the replacement of larger ionic radii (Mn^{3+}) by smaller ionic radii (Ni^{2+}) and their distribution at both A- and B-sites [12].

Conclusions

Spinel $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ 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^{3+} ions decreased and Mn^{4+} ions increased slightly with an increase in Ni content. The lattice parameter estimated from XRD decreases with an increase in Ni content due to the replacement

of larger ionic radii (Mn^{3+}) by smaller ionic radii (Ni^{2+}) and their distribution among A- and B-sites in spite of its large octahedral site preference energy. For the mixed spinel structure, the measured lattice parameter shows an intermediate distribution between the calculated values of the normal and inverse structure. The oxygen parameter indicated that the expansion or contraction of the anion sublattice slowly decreases with an increase in the nickel content.

Acknowledgments

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