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Correlation between Microstructure and Conductance in NTC Thermistors Produced from Oxide Powders

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Abstract

A detailed study of spinel-structured $Ni_{1-x}Mn_{2+x}O_4$ formed by a mixed oxide route has shown that when x≈0 a high proportion of NiO is residual in the sintered ceramic. Wickham (Wickham, D. G., Solid phase equilibria in the system $NiO–Mn_2O_3–O_2$. J. Inorg. Chem., *1964,* ***26****, 1369–1377) demonstrated that the spinel phase decomposes in air above 900°C. Sintering in this system is usually performed around 1200°C. Decomposition of the spinel phase is therefore inevitable. The effect of decomposition on the microstructure and electrical properties of Ni_{1-x} $Mn_{2+x}O_4$ based ceramics is discussed.* © *1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

Negative temperature coefficient (NTC) thermistors are found in an ever increasing number of electrical and electronic products. $Ni_{1-x}Mn_{2+x}O_4$, where x denotes the deviation from the stoichiometric 1:1 $NiO:Mn_2O_3$ ratio, offers a range of properties that are suitable for most temperature sensing applications. When $x=0$, (nickel manganite, $NiMn_2O_4$), the solid solution has an inverse cubic spinel structure, based on a 2×2×2 array of face centred cubic (fcc) oxygen subunits. When $x=1$, Mn_3O_4 is present which is a tetragonally distorted spinel.

The properties routinely used to characterise NTC thermistors are resistance, R_1 and R_2, at 25°C (T_1) and 85°(T_2) and a B value (with units of temperature in Kelvin) which is a measure of the sensitivity of the device over a given temperature range:

$$B = \frac{T_1 T_2}{T_2 - T_1} \ln\left(\frac{R_1}{R_2}\right) \quad (1)$$

The exact mode of conduction in nickel manganite is poorly understood, but several models invoke the small polaron theory.[1,2] Small polaron conduction is sometimes referred to as a 'hopping' mechanism, as it involves the transfer of polarisation from one cation to another. In the nickel manganite system, it has been postulated that the mixed valence, Mn^{4+}, Mn^{3+} cations present on the octahedral sites give rise to these small polaron pathways.[1] The octahedral cations in the spinel structure lie in chains along some <110> directions. These vectors represent the smallest intercationic distances within the unit cell.

Another important parameter when considering applications for $Ni_{1-x}Mn_{2+x}O_4$ ceramics is their thermal stability or aging characteristics (changes in conductance over long periods, i.e. lifetime of the component). Reports indicate that better thermal stability is found in tetragonal ceramics rather than cubic materials though the conductivity of the latter is 10 to 100 times higher.[2,3] This could be explained by a reduction in the concentration of Mn^{4+} compared to Mn^{2+} and Mn^{3+} or possibly by the presence of planar defects such as ferroelastic domain walls.[4]

$Ni_{1-x}Mn_{2+x}O_4$ ceramics have been prepared by the carbonate and oxalate methods, in addition to the more conventional mixed oxide route.[5] Irrespective of the preparation route, sintering (typically around 1200°C) is always carried out above the decomposition temperature in air for the system (~900°C) as discussed by Wickham.[5] Consequently, ceramics fired using conventional processing will contain multiple phases, e.g. NiO from

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the decomposed spinel and Mn-rich regions,[3,6,7] in accordance with the equation:

$$\mathrm{NiMn_2^{III}O_4} \rightarrow x\mathrm{NiO} + \frac{3-x}{3}\mathrm{Ni^{II}_{(3-3x)/(3-x)}} \\ \mathrm{Mn^{II}_{(2x)/(3-x)}Mn_2^{III}}O_4 + \frac{x}{6}O_2 \quad (2)$$

It is the intention of this paper to demonstrate how the degree of decomposition from single phase influences conductivity and, in particular, aging. X-ray diffraction and transmission electron microscopy will be used to monitor the degree of decomposition and accelerated aging tests (470°C) will be performed.

2 Experimental Procedure

The NiO and Mn_2O_3 powders in a 1:1 Mn_2O_3:NiO molar ratio were weighed out using an electronic balance ($\pm 0{\cdot}01$ g) and transferred to a polypropylene vessel with a charge of ZrO_2 milling media (the weight of ZrO_2 varied with the weight of the batch being processed). The batch was milled for 6 h to reduce particle size distribution to a mean of 6 μm and a maximum of 12 μm then drawn through a suction filter. The resulting slurry was dried in a 70°C oven overnight. The dried powder was calcined in a mullite crucible at 900°C for 16 h and subjected to a further 6 h milling under the above conditions. One one cm diameter pellets were pressed from the powders and sintered at 1250°C, achieving densities better than 95%.

Microstructural and structural characterisation were carried out using transmission electron microscopy (TEM) and X-ray diffraction (XRD), respectively. XRD was performed on solid ceramics and loose powders using a Phillips PW1050 diffractometer with a CuK_α source. A 0·02° step size was used at a scan rate of $0{\cdot}5°\,\mathrm{min}^{-1}$. TEM samples were prepared by grinding the ceramic to a thickness of 20 μm and ion beam milling to perforation. Images were obtained using JEOL 200CX and 3010 TEMs: the latter was equipped with a LINK energy dispersive X-ray detector.

Accelerated aging tests were carried out using a non-induction wound furnace held at 470°C. Temperature flux was monitored in the furnace using a thermocouple mounted immediately adjacent to the test piece. Platinum wires leading to a high precision HP 4284A LCR meter were used to make contact to the electroded surface of the ceramic. Changes in the resistance of the leads and contacts as a function of temperature were taken into account by performing a closed circuit run. Typically, temperature varied within a $\pm 0{\cdot}2$°C range over 10 h.

3 Results and Discussion

Wickham,[5] in his study of the $Ni_{1-x}Mn_{2+x}O_4$ solid solution, demonstrated that above 900°C decomposition occurs resulting in the formation of NiO and a Mn-rich spinel phase. The higher the temperature above the onset of the decomposition reaction, the more rapid the rate. In order to study the decomposition reaction in more detail and its potential effect on electrical properties, single phase ceramics (within the sensitivity of conventional XRD) were fabricated, as demonstrated in Fig. 1. Figure 2 shows a series of XRD traces from single phase samples heat treated at 1000, 1100 and 1200°C for 1 h. The evolution of peaks corresponding to NiO can be observed in accordance with the predictions of Wickham.[6] The relative intensities of the NiO peaks (marked) increase with increasing temperature.

Figure 3 is a bright field (BF) TEM image showing a typical region of spinel grains in single phase material. The grain boundaries and interiors are free from second phase. Inset in Fig. 3 is a $<110>$ zone axis diffraction pattern (ZADP) from one of the spinel grains in the image. Figure 4 is a

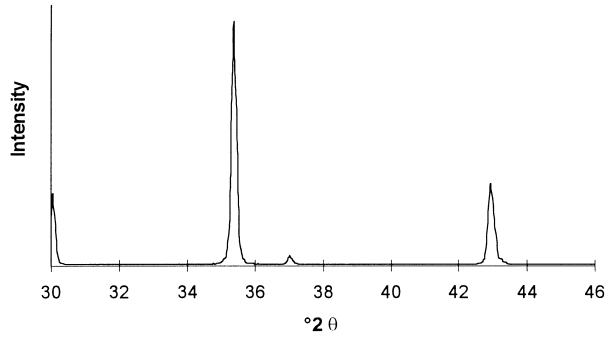

Fig. 1. XRD trace of single phase ceramic. Note absence of NiO peaks.

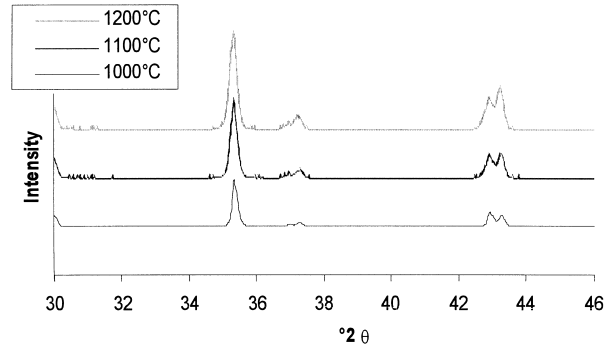

Fig. 2. XRD spectra of samples held at 1000, 1100, 1200°c for 1 h. NiO peaks are marked.

BFTEM image obtained from a sample decomposed for 9 h at 1250°C. Inset is a <110> ZADP pattern from the imaged region. The fundamental reflections can be indexed according to a <110> zone axis from rock salt structured NiO. The weak reflections at half integer positions arise from regions of spinel phase, observed as dark contrast. Rock salt (NiO) and spinel structured compounds invariably exhibit a cube//cube orientation relationship. Oxides with the rock salt structure are based around single fcc oxygen subunits whereas spinel structured compounds have a 2×2×2 fcc oxygen sublattice.

In order to study the aging characteristics of the ceramics as a function of decomposition, conductance measurements were performed over 10 h at 470°C ± 0.2°C. Figure 5 shows the change in conductance normalised to the initial value, against time at 470°C for (A) single phase spinel and (B) 'partially' decomposed spinel (heat treated for 9 h at 1250°C). The single phase sample showed a negligible drift in resistivity over the test period, whereas the 'partially' decomposed sample exhibited a steady decline in conductance. Differences in the absolute starting values can be attributed to small variations in the dimensions of the samples. Figures 6 and 7 are XRD traces showing the samples before and after the accelerated aging experiments. Figure 6, which corresponds to Fig. 5(A) (decomposed), shows a reduction in the

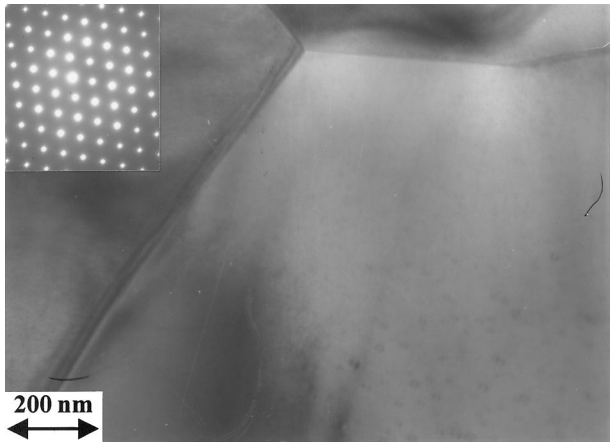

Fig. 3. BFTEM image of spinel grains in single phase material. Inset is a <110> zone axis diffraction pattern (ZADP) from a spinel grain.

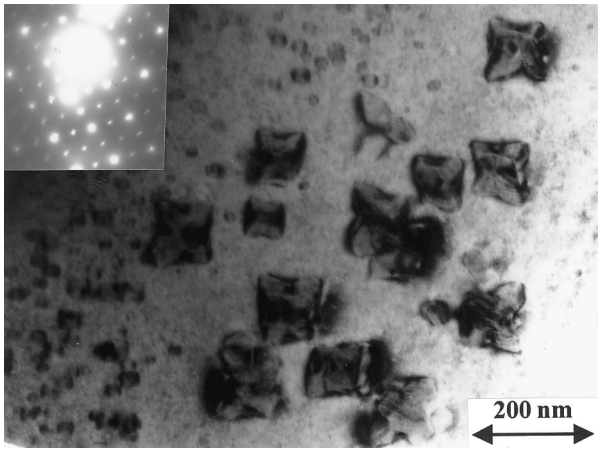

Fig. 4. BFTEM image of spinel regions in a NiO matrix. Inset is a <110> ZADP from the NiO. Faint reflections are present at half integer positions arising from the dark regions of spinel.

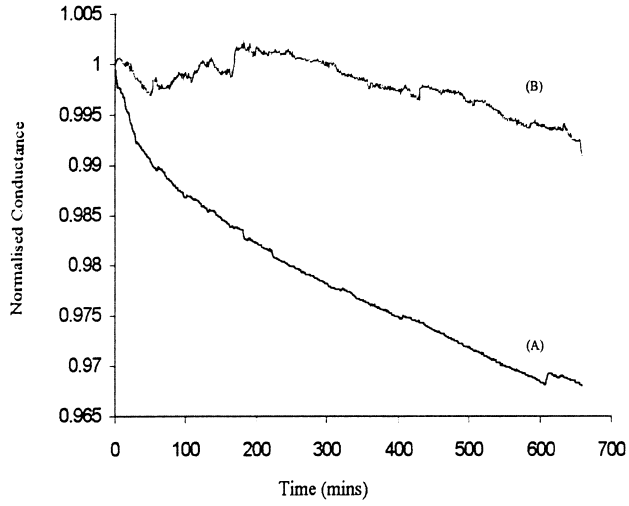

Fig. 5. Graph showing normalised conductance versus time at 470°C for (A) single phase and (B) decomposed (9 h at 1250°C) material.

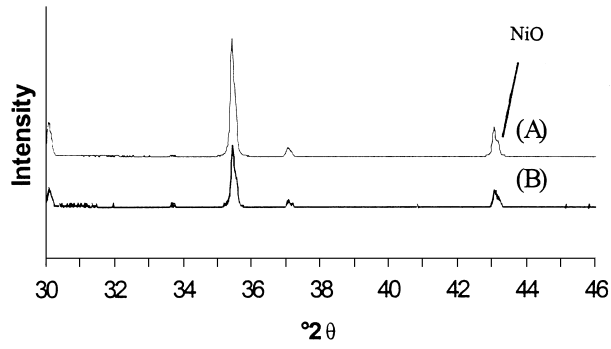

Fig. 6. XRD spectra of single phase sample (A) before and (B) after accelerated aging.

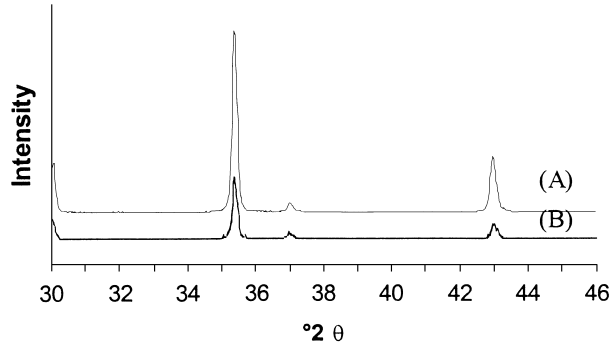

Fig. 7. XRD spectra of decomposed sample (A) before and (B) after accelerated aging.

intensity of the NiO peaks (A) before and (B) after the experiment. However, Fig. 7, which corresponds to Fig. 5(B) (single phase), shows traces that are identical (A) before and (B) after. It is thought that the accelerated aging at 470°C leads to NiO being re-absorbed into the ceramic during the lifetime of the experiment. It is proposed that the decomposition reaction occurs homogeneously throughout the ceramic, and the NiO is intimately mixed with the spinel phase, as evidenced by Fig. 4. The reverse process may therefore occur relatively quickly because of the short diffusion distances involved (of the order of nm according to Fig. 4). However, it should be noted that aging at room temperature may be related to different phenomena than suggested by these accelerated tests.

4 Conclusions

- The reaction between NiO and Mn_2O_3 proceeds forwards slowly at temperatures less than 900°C, but will reverse as temperature increases above this value.
- The rate of decomposition increases with increasing temperature resulting in a microstructure of intimately mixed NiO and Mn-rich spinel.
- Initial investigations indicate that a single phase ceramic gives rise to substantial improvements in thermal stability under accelerated aging.

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