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Decomposition of $NiMn_2O_4$ spinel: an NTC thermistor material

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Abstract

Nickel manganate based NTC thermistors are widely used in industrial and domestic applications where cost efficient but reliable temperature sensing, fluid flow rate or pressure sensing devices are required. Single phase, ceramic samples of $NiMn_2O_4$ (2:1 Mn:Ni) were synthesised using a conventional mixed oxide route. Thermal analysis confirmed the 2:1 spinel structured material decomposes upon heating above 907°C. After heating at temperatures between 1050 and 1200°C and subsequently quenching to room temperature, regions containing florets of spinel structured material were found using TEM. The surrounding matrix was a NiO rich rock-salt structured material and the florets were manganese rich. A decomposition mechanism based on degree of inversion is proposed to explain the appearance of the florets. Slowly cooling samples from 1250°C led to a microstructure principally composed of cubic spinel but also with regions of much smaller spinel florets in a rock-salt structured phase. The slow-cooled samples showed a larger drift in resistance over time than single phase samples when held at 400°C. XRD measurements carried out before and after electrical characterisation showed a reduction in the amount of rock-salt structured material present in the slow-cooled samples. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Decomposition mechanism; Electrical conductivity; Electron microscopy; Spinels; Thermistors

1. Introduction

Nickel manganate based NTC thermistors are widely used in industrial and domestic applications where cost efficient but reliable temperature sensing, fluid flow rate or pressure sensing devices are required. The devices are also widely used as surge protection devices that exploit the material's self heating characteristics.

Nickel manganate ($NiMn_2O_4$) is a cubic, spinel-structured material. The nickel cations almost exclusively occupy the octahedral B-sites in preference to the tetrahedral A-sites of the cubic close packed oxygen sublattice (an inverse spinel). Conduction in this material is generally believed to propagate by an electron hopping mechanism along chains of Mn^{3+} Mn^{4+} cations on the octahedral B-sites.[1,2]

It is the intention of this paper to present a new model of decomposition in $NiMn_2O_4$ using data obtained by transmission electron microscopy and X-ray diffraction. The new model will be used to interpret electrical properties.

2. Experimental

Methods of ceramic processing and characterization will be dealt with in detail in a forthcoming publication. Briefly however, single phase, 96% dense (from the theoretical maximum) ceramic samples of $NiMn_2O_4$ were synthesised from a mixed oxide route then subjected to several different heat treatments including slow cooling and quenching from various temperatures. Decomposition temperatures were obtained using differential thermal and thermogravimetric analysis (DTA and TGA, respectively). Samples were routinely characterised by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

3. Thermal analysis

DTA and TGA showed that upon heating $NiMn_2O_4$ powder samples in air an endothermic reaction occurs at around 907°C accompanied by a 1.25% weight loss Heating a similar sample in oxygen however, increased the reaction temperature to around 946°C. These results confirmed reports in the literature which showed that the spinel structured material decomposes around 900°C, evolving O_2.

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4. X-ray diffraction

Single phase ceramic samples were decomposed at temperatures between 1050 and 1200°C for a period of 30 min and subsequently quenched in air to room temperature. Fig. 1 shows the XRD patterns collected from these samples. The patterns reveal reflections associated with a rock-salt structured phase as well as those from spinel. Spinel {311} reflections show broadening which could indicate the onset of a tetragonal distortion, typical of more manganese rich spinels.[3] The peak broadening is stronger in samples heated at higher temperatures. Mn^{3+} shows a strong Jahn–Teller distortion when in octahedral co-ordination[4] which, if present in sufficiently high concentrations, will bring about a tetragonal distortion of the unit cell.

Boucher showed that the degree of inversion in $NiMn_2O_4$ is reduced from $\lambda = 0.47$ at room temperature to $\lambda = 0.37$ after quenching from 940°C (where $\lambda = 1/2$ denotes a fully inverse spinel and $\lambda = 0$ denotes a normal spinel).[5] This reduction in the degree of inversion inevitably leads to a higher concentration of manganese cations in octahedral co-ordination which could be responsible for the tetragonal distortion. However, XRD data reveals the presence of a rock-salt structured phase (following decomposition) that may influence the composition of the spinel. If the second phase is NiO rich, as suggested by Wickham,[6] then the spinel will be Mn-rich compared to the bulk, also favouring a tetragonal distortion.

5. Microstructure

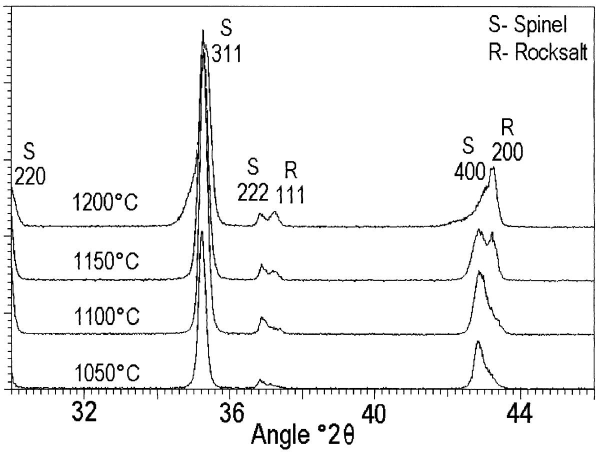

Fig. 1. XRD patterns from $NiMn_2O_4$ ceramic samples following quenching from various temperatures.

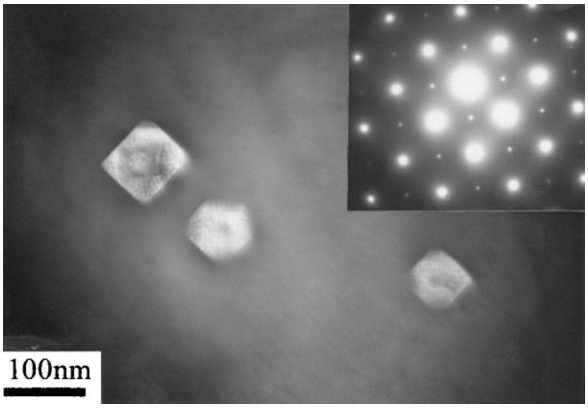

Fig. 2. DF TEM image of a spinel structured "island" in a rock-salt structured matrix.

Fig. 2 is a dark field (DF) TEM image of a sample quenched from 1050°C with the associated electron diffraction pattern inset. It shows a region of the material containing "islands" which, when analysed with EDS (see Fig. 3), proved to be manganese rich surrounded by a nickel rich matrix. The matrix also contained some Mn, suggesting that it is composed of a NiO–MnO solid solution. The number of NiO rich regions are fewer and the islands generally smaller in samples quenched from 1050°C than from 1150°C (Fig. 4). The electron diffraction patterns from the NiO rich regions, typified by the inset in Fig. 2, revealed fundamental spots attributable to a rock-salt matrix and '*superlattice*' arising from the florets at all half integer positions except the 1/2{200} reflection (when viewed along <100> zone axes). The above data is consistent with presence of islands of spinel in a rock-salt matrix for which the 1/2{200} reflection along <100> zone axis is absent due to the diamond glide of the spinel space group ($Fd\bar{3}m$). The 1/2{200} reflections appear in other zone axes such as <110> due to double diffraction. The cube//cube relationship between the rock-salt and spinel lattice is well known and occurs because spinel and rock-salt are structures based on a cubic close packed oxygen sublattice.[7]

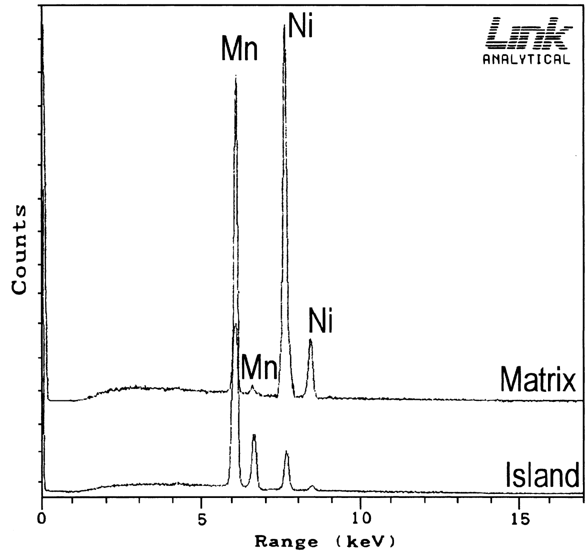

Fig. 3. EDS of island in comparison to the matrix shown in Fig. 2.

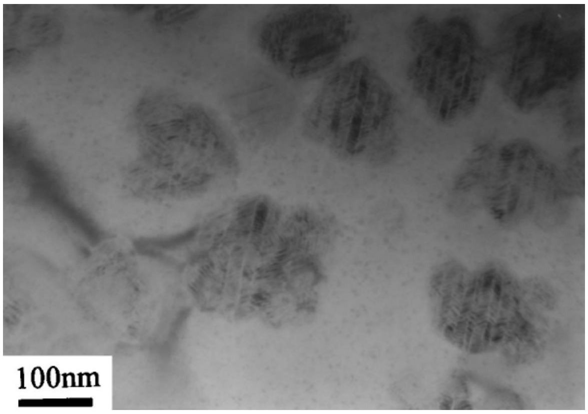

Fig. 4. BF TEM image of more complex florets in a $NiMn_2O_4$ sample after quenching from 1150°C.

Visible within some of the more complex "floret" shaped islands present in samples quenched from 1150°C are planar defects that resemble ferroelastic domain walls (Fig. 4), commonly observed in tetragonal spinels.[3] This observation is consistent with peak broadening in the XRD data. Samples quenched from 1200°C showed not only larger florets but also a more complex domain structure within their boundaries. Samples slow cooled from 1250°C exhibited a similar microstructure to that quenched from 1050°C, except the spinel grains were cubic and the florets in the NiO rich regions were smaller (Fig. 5).

6. Decomposition mechanism

From the information presented, a decomposition mechanism is proposed whereby localized regions of higher Mn^{3+} cation concentration, referred to as clusters, form upon heating. The driving force for the Mn^{3+} clustering can be attributed to the Jahn-Teller distortion of the octahedra[3] and the decrease in the degree of inversion on heating. As discussed previously, a reduction in the degree of inversion (after Boucher[5]) results in Mn^{3+} being forced onto the B-site. In order to reduce the overall energy of the system, Mn^{3+} clusters to form either small tetragonal regions or ones that will distort to tetragonal on cooling. Initially, no phase boundary will form during this reaction since cubic Mn^{3+} rich regions are present in the bulk cubic spinel phase. Ni^{2+} also has a strong octahedral site preference but, as the Mn^{3+} clustering proceeds, the surrounding matrix becomes increasingly Ni rich on the energetically unfavoured tetrahedral A-sites. This process can only be sustained for a short period until the driving force is sufficient to displace Ni^{2+} into octahedral coordination, resulting in a transformation to a rock-salt structure in which all cation species are CN6. In the TEM micrographs this appears as a macroscopic change but the transformation from spinel to rock-salt involves only a short cation displacement from a tetrahedral to an octahedral site of 1/8, 1/8, 1/8, of a unit cell ($\approx$ 1.8 Å). In addition, the 'floret-like' decomposition microstructure ensures that diffusion distances between rock-salt and spinel are also short (10 nm). Mn^{3+} clusters are rich enough in Mn not to transform to rock-salt and retain their spinel structure. They will, however, continue to act as "sinks" for manganese cations and grow as temperature and time increases (until equilibrium is achieved). Slowly cooling samples from 1250°C results in partial reversal of the decomposition process, giving rise to smaller florets, fewer NiO-rich regions and cubic spinel grains.

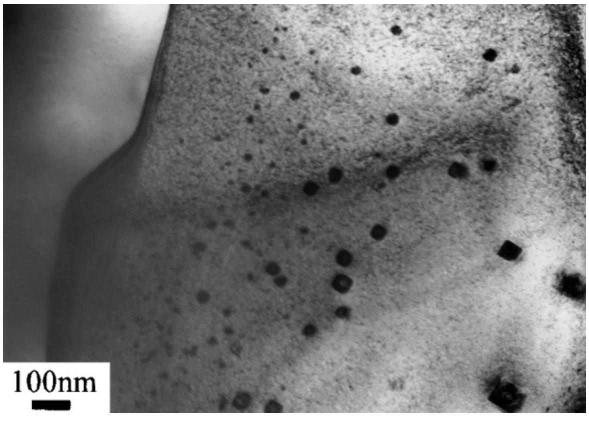

Fig. 5. BF TEM image from a $NiMn_2O_4$ sample after cooling slowly from 1250C°.

Thermal analysis strongly supports the premise that decomposition is accompanied by the loss of oxygen above 907°C. Therefore, it is reasonable to assume that recomposition requires the uptake of O_2. The oxygen stoichiometry of the system will not be at equilibrium under the conditions described here, leading to a complex series of charge compensation mechanisms in the spinel phase probably related to the variable valence state of the Mn cation.

7. Electrical properties

The change in electrical resistance as a function of time in slow cooled samples (cooled from 1250°C at 2°/min — which can be regarded as a partially reversed decomposition) were compared with that of single phase samples. Specimens were held at 400°C and the temperature and resistance were recorded each minute for up to 32 h. The slow cooled samples showed a larger drift in resistance over time than the single phase samples (Fig. 6). XRD carried out before and after the measurements (Fig. 7) revealed a significant reduction in the amount of rock-salt structured material present in the slow cooled samples. This result suggests that some of the floret containing, rock-salt structured phase may be transformed back to bulk spinel at temperatures as

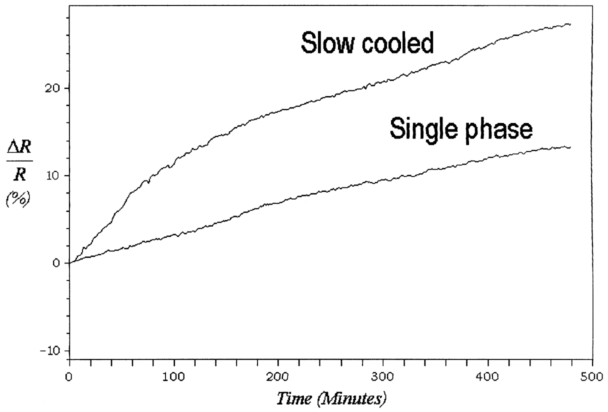

Fig. 6. Comparison of drift in resistance at 400°C in slowly cooled and single phase samples.

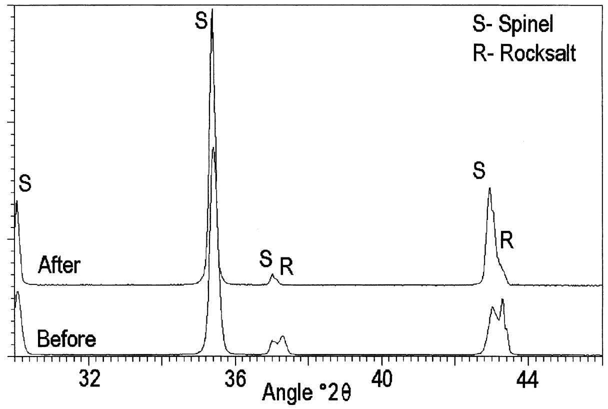

Fig. 7. XRD of slow cooled sample before and after electrical measurement.

low as 400°C. Therefore, the differences in the $\Delta R/R$ as a function of time can be attributed to a change in composition of the charge carrying phase due to Ni^{2+} being re-introduced into a spinel lattice. Re-composition at such low temperatures is feasible because of the intrinsically short diffusion distances that are necessary to transform rock-salt to spinel as well as the unique floret decomposition microstructure.

8. Conclusions

The decomposition mechanism in $NiMn_2O_4$ is believed to proceed as a consequence of the reduction of inversion in the spinel structured phase which at a critical temperature (907°C according to DTA) places sufficient nickel on the A-sites to bring about a phase transformation from spinel structure to rock-salt structure. The formation of a rock-salt structured phase is driven by the strong octahedral site preference shown by Ni^{2+} cations.

Regions of the material remain rich enough in manganese to maintain a spinel structure, forming islands in the rock-salt structured matrix that, if given sufficient time and temperature, will grow and merge together to form complete grains.

High temperature electrical measurements of slow cooled compared with single phase samples show that after several hours at 400°C reversal of the decomposition is accompanied by a change in the resistance of the material, due to a change in Ni^{2+} concentration in the spinel phase.

References

1. Macklen, E. D., Thermistors. *J. Phys. Chem. Sol.*, 1986, **47**, 1073–1079.
2. Jung, J., Topfer, J., Murbe, J. and Feltz, A., Microstructure and phase development in $NiMn_2O_4$ spinel ceramics during isothermal sintering. *J. Eur. Ceram. Soc.*, 351–359.
3. Couderc, J. J., Fritsch, S., Brieu, M., Vanderschaeve, G., Fagot, M. and Rousset, A., A transmission electron-microscopy study of lattice-defects in Mn_3O_4 hausmannite. *Philosophical Magazine B*, 1994, **70**, 1077–1094.
4. Fishman, Y. A., Ivanov, M. A., Mitrofanov, V. Ya and Shemyakov, A. A., Hyperfine interactions of Jahn-Teller ion Mn^{3+} in cubic magnets with spinel and garnet structures. *Physica Status Solidi B*, 1990, **160**, 153–157.
5. Boucher, B., Buhl, R. and Perrin, M., Etude cristallographique du manganite spinelle cubique $NiMn_2O_4$ par diffraction de neutrons. *Acta Crystallogr B*, 1969, **25**, 2326–2333.
6. Wickham, D. G., Solid phase equilibria in the system NiO-Mn_2O_3–O_2. *J. Inorg. Nucl. Chem.*, 1963, **26**, 1369–1377.
7. Csete de Györgyfalva, G. D. C., Nolte, A. N. and Reaney, I. M., Correlation between Microstructure and Conductance in NTC Thermistors Produced from Oxide Powders. *J. Eur. Ceram. Soc.*, 1999, **19**, 857–860.