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Conductivity Data and Preparation Routes for $NiMn_2O_4$ Thermistor Ceramics

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Abstract

Requirements for the formation of $NiMn_2O_4$ *thermistor ceramics with highly reproducible electrical parameters are reported. The application of the defect spinel powder* $NiMn_2\square_{3\delta/4}O_{4+\delta}$ *prepared by low temperature decomposition of (Ni, Mn)-oxalate mixed crystals together with a small addition of* $Pb_5Ge_3O_{11}$ *as sintering aid is shown to be most advantageous. Thus single-phase* $NiMn_2O_4$ *ceramics of sufficient density are obtained on sintering at 1000°C (40 h,* O_2 *atmosphere) and annealing at 800°C (40 h) for reoxidation. The electrical conductivity of* $NiMn_2O_4$ *is found to be* $\sigma_{20°C} = 5{\cdot}0 \pm 0{\cdot}2 \times 10^{-4}\,\Omega^{-1}\,cm^{-1}$. *The activation term,* $B = 3775 \pm 7\,K$ *is deduced from simple Arrhenius analysis in the range* $273 < T < 343\,K$ *allowing possible exchange of thermistors with an accuracy* $\Delta T \leq \pm 0{\cdot}1\,K$. *A more accurate linearization of the experimental data succeeds from the equation*

$$\sigma(T) = \sigma(T_1)(T_1/T)^k \exp[-B_k(1/T - 1/T_1)]$$

with $k = 2{\cdot}91 \pm 0{\cdot}05$, *yielding* $B_k = 2853 \pm 15\,K = 0{\cdot}246 \pm 0{\cdot}001\,eV$ *as the activation energy representative for* $NiMn_2O_4$. *Ageing behaviour and the influence of decomposition in air with rising temperature on the electrical properties are studied.*

Es wird über Anforderungen zur Bildung von $NiMn_2O_4$ *Thermistorkeramik mit hochreproduzierbaren elektrischen Parametern berichtet. Besonders vorteilhaft ist die Anwendung eines Defektspinellpulvers* $NiMn_2\square_{3\delta/4}O_{4+\delta}$ *in Kombination mit einem geringen Zusatz von* $Pb_5Ge_3O_{11}$ *als Sinterhilfsmittel. Der Precursor wird durch thermische Zersetzung der Oxalatmischkristalle bei relativ niedriger Temperatur erhalten. Einphasige* $NiMn_2O_4$*-Keramik hinreichender Dichte entsteht, indem man bei 1000°C (40 h,* O_2 *Atmosphäre) sintert und zum Zweck der Rückoxidation bei 800°C (40 h) tempert. Als spezifische Leitfähigkeit von* $NiMn_2O_4$ *wird* $\sigma_{20°C} = 5{\cdot}0 \pm 0{\cdot}2 \times 10^{-4}\,\Omega^{-1}\,cm^{-1}$ *gemessen.* $B = 3775 \pm 7\,K$ *ergibt sich nach einem einfachen Arrhenius-Ansatz im Temperaturbereich* $273 < T < 343\,K$. *Dadurch wird eine Austauschbarkeit von Thermistorproben mit einer Genauigkeit* $\Delta T \leq \pm 0{\cdot}1\,K$ *möglich. Eine bessere Linearisierung der experimentellen Daten gelingt mittels der Gleichung*

$$\sigma(T) = \sigma(T_1)(T_1/T)^k \exp[-B_k(1/T - 1/T_1)]$$

mit $k = 2{\cdot}91 \pm 0{\cdot}05$. *Daraus folgt für* $B_k = 2853 \pm 15\,K = 0{\cdot}246 \pm 0{\cdot}001\,eV$ *als die für* $NiMn_2O_4$ *gültige Aktivierungsenergie. Das Alterungsverhalten und der Einfluß der Zersetzung an Luft bei steigender Temperatur auf die elektrischen Eigenschaften werden untersucht.*

On traite des exigences liées à la réalisation de thermistors céramiques $NiMn_2O_4$ *à caractéristiques électriques hautement reproductibles. On montre que l'emploi de la poudre spinelle déficitaire* $NiMn_2\square_{(3\delta/4)}O_{4+\delta}$, *préparée par décomposition thermique lente de cristaux d'oxalate de Ni et Mn mélangés, auxquels on ajoute une petite quantité de* $Pb_5Ge_3O_{11}$ *comme additif de frittage, est la technique la plus favorable. Des céramiques monophasées* $NiMn_2O_4$, *suffisamment denses, sont obtenues par frittage à 1000°C (40 h, atmosphère* O_2*) et recuit à 800°C (40 h) pour assurer la réoxydation. La conductivité électrique à 20°C s'élève à* $5{\cdot}0 \pm 0{\cdot}2 \times 10^{-4}\,\Omega^{-1}\,cm^{-1}$. *Le terme d'activation,* $B = 3775 \pm 7\,K$, *est déduit d'une simple analyse d'Arrhenius dans*

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le domaine $273 < T < 343$ K, permettant l'échange de thermistors avec une précision de $\Delta T \leq \pm 0{\cdot}1$ K. Une linéarisation plus fine des résultats expérimentaux est possible à partir de l'équation:

$$\sigma(T) = \sigma(T_1)(T_1/T)^k \exp[-B_k(1/T - 1/T_1)]$$

avec $k = 2{\cdot}91 \pm 0{\cdot}05$, conduisant à $B_k = 2853 \pm 15$ K $= 0{\cdot}246 \pm 0{\cdot}001$ eV comme l'énergie d'activation représentative pour $NiMn_2O_4$. Le comportement au vieillissement et l'influence sur les propriétés électriques de la décomposition dans l'air à température croissante sont étudiés.

1 Introduction

Preceding studies on the behaviour of manganese oxide containing oxide systems demonstrated the important role of oxygen liberation and/or absorption during sintering.[1] Semiconductor ceramics $Ni_xMn_{3-x}O_4$ ($x < 1$) are known to have applications as highly precise thermistors,[2,3] despite the fact that spinels based on this system decompose below 730°C in air, forming $NiMnO_3$ and α-Mn_2O_3. This reaction is in accordance with the phase diagram:[4]

$$NiMn_2O_4 + \tfrac{1}{4}O_2 \rightarrow NiMnO_3 + \tfrac{1}{2}\alpha\text{-}Mn_2O_3 \quad (1)$$

At room temperature $NiMn_2O_4$ is in a metastable state. However, with rising temperature, and already at 150°C, the homogeneous spinel phase starts to decompose by oxidation.

The upper limit of stability is given by the reaction

$$NiMn_2O_4 \xrightarrow[\text{air}]{>950^\circ C} xNiO + \frac{3-x}{3} Ni_{(3-3x)/(3-x)}Mn_{2x/(3-x)}Mn_2^{III}O_4 + \frac{x}{6}O_2 \quad (2)$$

It has been found that a small degree of intermediate NiO separation is an accompaniment to densification by sintering above 975°C in an oxygen atmosphere.[5] Ceramics having sufficient density and a homogeneous structure require the use of precursors with an improved sintering activity. Cubic metastable defect spinel powders prepared by the thermal decomposition of $NiMn_2(C_2O_4)_3 \cdot 6H_2O$ mixed crystals at 350°C have been shown to be appropriate.[6] Decomposition of $[Ni(OH_2)_6](MnO_4)_2$ leading to amorphous manganate(IV) as an intermediate compound in the result of thermal decomposition is also effective.[7]

It is the aim of this paper to study the conductivity data of $NiMn_2O_4$ ceramics prepared by different preparation routes. Conventional synthesis starting from a mixture of the carbonates is also involved.

2 Experimental

2.1 Sample preparation

High purity Ni and Mn carbonate (p.a.) as well as raw materials at technical grade were used. The main impurities of the latter were found to be 0·1% Ca, 0·03 Co, 0·02% Fe, 0·03% Ca for $MnCO_3$ and 0·1% Ca, 0·01% Co, 0·5% Mg, 0·01% Fe and 0·03% Na for NiO.

Following the carbonate route (A) Ni and Mn carbonate in the molar ratio 1:2 are transformed into a mixture of NiO and α-Mn_2O_3 by decomposition at 600°C (6 h), yielding a powder with a specific surface area of about $12\,m^2\,g^{-1}$. The oxalate route (B) provides homogeneous defect spinels as a precursor:

$$Ni_xMn_{3-x}\square_{3\delta/4}O_{4+\delta} = (4+\delta)/4Ni_{4x/(4+\delta)} \times Mn_{4(3-x)/(4+\delta)}\square_{3\delta/(4+\delta)}O_{4\cdot 00}$$

by thermal decomposition of the mixed crystals $NiMn_2(C_2O_4)_3 \cdot 6H_2O$ at about 350°C. The specific surface area may be adjusted to a comparable value by careful annealing up to 450°C. The comparison of routes (A) and (B) concerning microstructure and phase development during isothermal sintering has already been reported.[5,8] The permanganate route (C) starts from $[Ni(OH_2)_6](MnO_4)_2$ yielding, at 300°C, an amorphous product of the composition $Ni(HMnO_{2\cdot 945}) \cdot 0{\cdot}6H_2O$ containing predominantly Mn^{IV}, which is transformed at 750°C into $NiMn_2O_4$ powder with a specific surface area of about $4\,m^2\,g^{-1}$.[7] Granulometric pretreatment and an addition of 5% of a 5% aqueous solution of polyvinyl alcohol allow compaction by pressure (150 MPa) up to about 50% of the theoretical density. After burning out of the pressing aid, the samples were sintered in an oxygen flow or in air at temperatures between 950°C and 1100°C (25 to 40 h). Annealing was carried out at 800°C (up to 50 h) for reoxidation by reversal of eqn (2).

One problem is to determine the conditions for homogeneous $NiMn_2O_4$ formation. Ceramic samples of high density often require high sintering temperatures, which then result in phase separation according to eqn (2). On the other hand, oxygen contamination for reoxidation and NiO resorption in the bulk needs a sufficient residual porosity. Consequently, in order to avoid a higher degree of phase separation the sintering activity of the powders should be high and the distribution of the cations as uniform as possible.

For improvement of densification, a sintering aid was applied. Samples $(A_0)(B_0)$ without and $(A_1)(B_1)(C_1)$ with 1 mol% $(Pb_5Ge_3O_{11})_{3/8}$ were prepared, i.e. where 1 mol% of the cations of $NiMn_2O_4$ are formally substituted by Pb and Ge in the molar ratio 5:3.

2.2 Electrical conductivity measurements and error estimation

The direct current conductivity of the samples contacted by Ag paste (fired at 800°C, for 1/2 h) was measured between 0 and 70°C utilizing a high-resolution digital voltmeter equipped with a constant current source. Temperature calibration of the equipment by means of standardized Pt 100 resistivity devices (100·00Ω at 0°C) ascertained an error ΔT_F not more than $\pm 0{\cdot}015$ K. The error of the resistivity measurement was found to be $\Delta R/R = \leq \pm 1 \times 10^{-4}$. Details of the apparatus have already been published.[9]

Assuming Arrhenius behaviour

$$R(T) = R(T_1)\exp\left[B\left(\frac{1}{T} - \frac{1}{T_1}\right)\right] \qquad (3)$$

the total error of a specimen taken from a set of samples of one and the same charge and of different charges is given by the relation

$$\left|\frac{\Delta R(T_2)}{R(T_2)}\right|_{\text{tot.}} = \left|\frac{\Delta R}{R}\right|_{\text{m}} + \left|\frac{B}{T^2}\Delta T_F\right|_m + \left|\frac{\Delta R(T_1)}{R(T_1)}\right|_{\text{s}} + \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\Delta B_{\text{s}} \qquad (4)$$

with

$$\Delta B_{\text{s}} = 2\frac{T_1 T_2}{T_2 - T_1}\left(\frac{\Delta R}{R}\right)_{\text{m}} + B\frac{T_1^2 + T_2^2}{(T_2 - T_1)T_1 T_2}\Delta T \qquad (5)$$

deduced from partial differentiation of eqn (3). $(\Delta R/R)_{\text{m}} = \pm 10^{-4}$ and $\Delta T_F = \pm 0{\cdot}015$ K as the measuring errors labelled by m may be certainly kept smaller than the error resulting from individual sample variation labelled by s. The sample error $\Delta R(T_1)/R(T_1)$ containing the effects of small variations of geometry has to be reduced by sample finishing to smaller than 10^{-2} or 1%. In order to evaluate the reproducibility, ΔB_{s} appears as the most important contribution. Interchangeability of thermistor samples guaranteeing the accuracy $\Delta T = \pm 0{\cdot}1$ K in the range $T_1(273\,\text{K}) < T < T_2(343\,\text{K})$ with $B_{\text{s}} = 4000$ K sets a limit of acceptable alteration of $\Delta B_{\text{s}} = \pm 13$ K.

Accurate measurements have shown that the equation

$$R(T) = R(T_1)\left(\frac{T_1}{T}\right)^k \exp\left[B_k\frac{1}{T} - \frac{1}{T_1}\right] \qquad (6)$$

is a better approximation for modelling the experimental data.[10,11] The resistivity was measured at 15 different temperatures in the range $273 < T < 343$ K. B calculated for the intervals using eqn (3) clearly indicates a temperature dependence of the activation energy. Numerous different analytical expressions were tested.[11] The best description of the resistivity/temperature characteristic for $NiMn_2O_4$ was found to be fulfilled when eqn (6) is applied with $k = 2{\cdot}91 \pm 0{\cdot}05$.[11] Thus eqn (6) has to be taken for determination of the activation energy as a characteristic property of the compound.

3 Results and Discussion

The conductivity data measured are collected in Table 1. Densification at 1100°C seems to be inhibited by the impurity content of the technical grade raw materials (batches A_0). However, this effect may be compensated either by the help of a sintering aid (labelled with index 1) or by application of the defect spinel precursor formed by low-temperature decomposition of the oxalate mixed crystals. The combination of both appears to be most effective (batches B_1).

At 800°C reoxidation by reversal of eqn (2) remains incomplete after 0·5 h. Residual NiO has been detected by microprobe.[5] The average oxidation number of manganese is found to be slightly less than 3·0, or, in other words, a spinel phase with a small Mn^{II} content is formed, leading to a somewhat higher activation energy. The data in Table 1 indicate that homogeneity of the spinel phase is achieved if the sintering temperature is lowered to 1000°C. Moreover, holding of the specimens at 800°C for a longer time (50 h) has been found to be favourable.

In regard to the variation of the B values, sample sets resulting from A_0 and A_1 batches of the conventional route are not so bad. The residual porosity seems to be influenced by the impurity content of the raw materials. The final density is improved by adding of the sintering aid. Application of the precursor powder provided by oxalate decomposition allows easier to obtain homogeneous ceramic specimens in the result of sintering at 1000°C and annealing at 800°C, which leads to $\sigma_{20\,^\circ\text{C}} = 5{\cdot}0 \times 10^{-4}\,\Omega^{-1}\,\text{cm}^{-1}$ and $B = 3774 \pm 3$ K as the representative data for $NiMn_2O_4$. It is significantly more complicated to prepare homogeneous $NiMn_2O_4$ ceramics following the conventional method. Batches B_1 were found to provide sets of samples with the lowest standard deviation of their conductivity data. The preparation of $NiMn_2O_4$ by thermal decomposition of $Ni(MnO_4)_2 \cdot 6H_2O$ (route C) was found to be less appropriate.

Table 1. Preparation routes A, B and C and electrical properties of ceramic specimens $NiMn_2O_4$ showing the reproducibility observed

Kind of preparation	*Temperature of calcination of the initial mixture*	s $(m^2\,g^{-1})$	$\rho_{rel.}$ (%)	B (K)	$\sigma_{20°C} \times 10^4$ $(\Omega^{-1}\,cm^{-1})$	*Number of specimens*	B_k (K)	E_σ (eV)
Sintering 1100°C, 40 h, O_2-atmosphere–annealing 800°C, 0·5 h, $k = 2{\cdot}91 \pm 0{\cdot}05$								
A_0 (p.a.)	600	12	95	3 817 ± 2	3·1 ± 0·2	10	2 895 ± 15	0·249
A_0 (technical grade)	600	5	74	3 818 ± 4	1·8 ± 0·06	30	2 896 ± 15	0·250
A_1 (p.a.)	600	12	98	3 826 ± 6	4·2 ± 0·2	10	2 904 ± 15	0·250
A_1 (technical grade)	600	5	77	3 842 ± 6	2·0 ± 0·05	10	2 920 ± 15	0·252
B_0 (p.a.)	350	36	97	3 755 ± 4	5·5 ± 0·2	8	2 833 ± 15	0·244
B_0 (technical grade)	450	10	90	3 778 ± 12	4·4 ± 0·4	30	2 856 ± 15	0·246
B_0 (technical grade)	450	10	96	3 759 ± 10	5·1 ± 0·3	10	2 837 ± 15	0·244
B_1 (p.a.)	350	36	98	3 776 ± 9	4·5 ± 0·1	10	2 854 ± 15	0·250
B_1 (technical grade)	450	10	98	3 800 ± 8	4·7 ± 0·2	29	2 878 ± 15	0·248
B_1 (technical grade)	800	2	96	3 802 ± 4	4·7 ± 0·6	15	2 880 ± 15	0·248
Sintering 1000°C, 40 h, O_2-atmosphere–annealing 800°C, 0·5 h								
B_1 (technical grade)	450	18	96	3 774 ± 3	5·0 ± 0·1	10	2 852 ± 15	0·246
B_1 (technical grade)	450	11	94	3 778 ± 5	4·8 ± 0·1	30	2 856 ± 15	0·246
C_1 (p.a.)	750	4	88	3 803 ± 6	3·2 ± 0·7	20	2 881 ± 15	0·248
Sintering 1000°C, 40 h, O_2-atmosphere–annealing 800°C, 40 h								
A_0 (p.a.)	600	5	77	3 806 ± 6	2·0 ± 0·3	20	2 884 ± 15	0·249
A_1 (p.a.)	600	5	41	3 804 ± 8	3·6 ± 0·4	20	2 882 ± 15	0·248
B_0 (p.a.)	600	8	88	3 800 ± 6	3·2 ± 0·4	20	2 878 ± 15	0·248
B_1 (p.a.)	600	8	97	3 775 ± 7	5·0 ± 0·2	20	2 853 ± 15	0·246

The data show that $NiMn_2O_4$ thermistor ceramics with highly reproducible electrical parameters are prepared advantageously following the oxalate route. Less expensive technical raw materials may be used in combination with a sintering aid.

4 Ageing

Ageing has been studied keeping the samples at 150°C for up to 1000 h. The B parameter increases by about 0·1% and at the same time the electrical conductivity decreases. Already after 600 h the data remain approximately unchanged. The ageing behaviour of the B parameter follows the equation

$$B(t) = B_{\text{final}} - (B_{\text{final}} - B_{\text{initial}})\,e^{-t/\tau_B}$$

The data are collected in Table 2.

Table 2. Ageing of the samples at 150°C in air

Sample	B_{initial} (K)	$B(800\,h)$ (K)	B_{final} (K)	τ_B (h)
A_0 (technical grade)	3 818	3 840	3 840	79
A_1 (technical grade)	3 842	3 865	3 865	120
B_0 (technical grade)	3 751	3802	3 802	89
B_1 (technical grade)	3 782	3 825	3 826	195

Annealing at 250°C in air also provides a drift of the electrical parameters. Within 100 h, decomposition still appears to be inhibited. On the other hand, at 350°C decomposition starts, according to eqn (1). After 100 h annealing, a broad dispersion of the B parameter and of the electrical conductivity values, and formation of α-Mn_2O_3 and $NiMnO_3$ were observed.

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