

Thin Layer NTC Semiconductor Ceramics Based on NiMn_2O_4 and $\text{Zn}_z\text{NiMn}_{2-z}\text{O}_4$ ($z = 1/3, 2/3$)

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(Received 18 May 1992; revised version received 30 June 1992; accepted 10 July 1992)

Abstract

The formation of $\text{Zn}_z\text{NiMn}_{2-z}\text{O}_4$ films, where $z = 0, 1/3$ or $2/3$, on Al_2O_3 substrates precoated with a semiconductive intermediate layer of SnO_{2-x} was studied. The method employed was one of electrophoretic deposition. Deposition takes place in a suspension of defect spinel powder, dispersed in isoamyl alcohol. After sintering at 1000°C and annealing at 800°C , conductivity of the ceramic layers in the temperature range between 20 and 300°C was measured. The morphology of the surface and of the cross-section of these layers was observed with the help of scanning electron microscopy.

Es wird über die elektrophoretische Abscheidung von Pulvern zur Bildung von $\text{Zn}_z\text{NiMn}_{2-z}\text{O}_4$ -Schichten ($z = 0, 1/3$ oder $2/3$) auf Al_2O_3 -Substraten mit halbleitender SnO_{2-x} -Zwischenschicht berichtet. Die Abscheidung erfolgt aus einer Suspension eines Defektspinnelpulvers in Isoamylalkohol. Nach Sinterung der Schichten bei 1000°C und Reoxidation bei 800°C werden Leitfähigkeitsmessungen im Temperaturbereich zwischen 20 und 300°C durchgeführt. Mit Hilfe der Rasterelektronenmikroskopie werden die Morphologie der Oberfläche und des Querschnittes der erhaltenen Keramiksichten untersucht.

Les auteurs ont étudié la formation de films de $\text{Zn}_z\text{NiMn}_{2-z}\text{O}_4$ où $z = 0, 1/3$ ou $2/3$ sur des substrats en Al_2O_3 prétraités par une couche semi-conductrice intermédiaire en SnO_{2-x} . La méthode utilisée relève de la déposition électrophorétique. La déposition a lieu à partir d'une suspension de la spinelle dans l'alcool isoamylique. Après frittage à 1000°C et cuisson à 800°C , on a mesuré la conductivité des couches céramiques dans la gamme de température comprise entre 20 et 300°C . La morphologie de la surface et la tranche de ces couches ont été observées par microscopie électronique à balayage.

1 Introduction

The production and properties of thin, semiconductive layers of Ni-Mn-O and Co-Ni-Mn-O have been recently described in the literature.^{1,2} By means of the rf magnetron sputtering process, well-developed layer structures of cubic crystallites with thicknesses of 10 – $12\ \mu\text{m}$ may be obtained. Such structures are suitable for use as precise thermistor devices, because their conductivity varies dramatically with changes in temperature. The literature gives no specifications, however, either of the composition of the layers or of the reproducibility of their conductivity values.

The process of rf magnetron sputtering has also been applied successfully to produce thin, superconducting ceramic layers.³ A major drawback of this method, however, is the difficulty of producing $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and related compounds of the correct stoichiometry. It is for this reason that research has recently begun on the older established process of electrophoretic deposition of powders.^{4–8} With an understanding of the chemical synthesis of the materials, their composition and structure may be controlled before their deposition. The particles may be deposited on a substrate previously overlaid with conducting tracks which act as electrodes. If well-dispersed colloidal suspensions are used, a high geometric resolution may be obtained.

The thickness of the layer may be controlled by varying certain process parameters, e.g. deposition time, applied voltage and current density.⁹ Within a few minutes layers of $10\ \mu\text{m}$ in thickness or more may be produced.

Highly stable and precise oxide thermistors based on Mn-spinels have been the object of much research.^{10,11} The aim of the authors' work was to produce, and to characterize electrically, these materials in thin layer structures. The application of an electrophoretic deposition method is especially suitable as it guarantees for the ceramic a definite

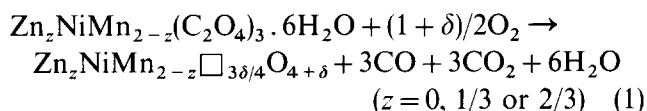
stoichiometric composition. The subject of this paper is the investigation of NiMn_2O_4 ceramic layers which decompose in the temperature region below 730°C in air, and that of $\text{Zn}_z\text{NiMn}_{2-z}$ ceramic layers with $z = 1/3$ and $2/3$, where decomposition does not occur.¹² The properties of these respective layer structures were compared.

2 Experimental

2.1 Powder preparation

To produce NiMn_2O_4 and related systems it is convenient to decompose mixed oxalate crystals.¹³⁻¹⁵ For the authors' studies mixed oxalate crystals of compositions $\text{NiMn}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}_z\text{NiMn}_{2-z}(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, where $z = 1/3$ or $2/3$, were decomposed for 5 h at 450°C in air. This produced powders with a narrow grain size distribution. The decomposition provided a homogeneous defect spinel (eqn (1)) which was well suited as a precursor for the preparation of ceramic layers.

The powders produced in this way had BET surfaces of $40\text{--}44 \text{ m}^2 \text{ g}^{-1}$. Through the application of sedimentation analysis, the d_{50} values were found to be $3.5\text{--}4.5 \mu\text{m}$, which indicated that agglomeration had taken place:



2.2 SnO_{2-x} -coated alumina

Alumina substrates coated with SnO_{2-x} were used for the electrophoretic deposition of ceramic layers. For the authors' purposes it was not possible to use conducting metals as substrates for the deposition, as described in the literature, since it was the electrical behaviour of the ceramic layer which was to be measured. The powders had to be deposited on to a substrate which had only negligible influence on the conductivity of the ceramic layer. The use of layers of SnO_{2-x} was therefore suitable here, for this material loses its conductivity during the sintering process when in contact with the substrate and the ceramic layer.

Electrodes used for the Al_2O_3 substrates were either of painted silver or of sputtered platinum layers, $0.5 \mu\text{m}$ in thickness. Once these were in place, layers of SnO_{2-x} were built up. Vapour deposition was achieved according to the method of Yamazaki *et al.*¹⁶

SnO was prepared from tin dichloride via tin dioxhydrate, and then analysed by oxidimetric titration.¹⁷ The deposition of SnO took place under a vacuum of $6 \times 10^{-3} \text{ Pa}$. The deposition thickness was monitored by measuring the frequency change

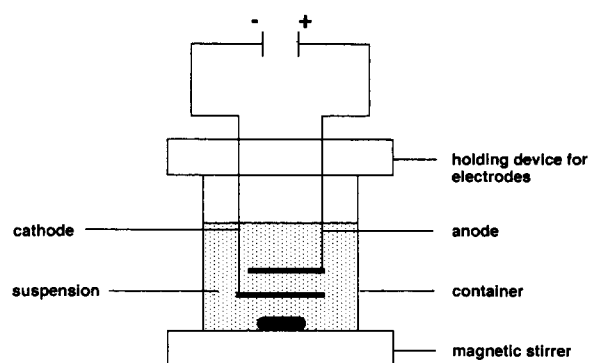


Fig. 1. Experimental set-up for electrophoretic deposition.

(due to the mass change) of an oscillating quartz crystal suspended close to the substrate and simultaneously subjected to the deposition of SnO . Following this, it was necessary to heat the samples slowly (2 K min^{-1}) to 400°C under oxygen. The temperature having been maintained for 10 min at 400°C , the samples were then quenched by removal from the furnace.

Before deposition, the contacts were painted with a lacquer to ensure that they did not become coated with the powder.

2.3 Electrophoretic deposition

Electrophoretic deposition took place in a suspension produced by the dispersal of 2 g of powder in 100 ml distilled isoamyl alcohol. In order to increase the deposition rate, the powder was precoated with 0.2 g trichloroacetic acid, which acted also as a stabilizer. A suspension produced by this method is stable over a period of a few days. Figure 1 shows the experimental set-up of the authors' electrophoresis equipment.

By changing the conditions for deposition it was possible to produce ceramic layers of thicknesses varying between 10 and $100 \mu\text{m}$. Equation (2) relates the mass of deposited material to the parameters of deposition:⁹

$$m \propto E \cdot A \cdot c \cdot t \cdot \mu \quad (2)$$

where m is deposited mass, E is field strength, A is area, c is concentration of the suspension, t is deposition time, and μ is electrophoretic velocity.

Figure 2 shows the results of the experiments. Two conclusions may be drawn from these. First, the relationship between the thickness of the ceramic layer and the applied voltage is approximately linear. Secondly, the deposition rate increases and decreases relative to the surface area of the powder used. This was predicted from the equations relating to electrophoretic velocity (eqns (3) and (4)):¹⁸

$$\mu = \zeta \cdot \epsilon \cdot E / 4\pi \cdot \eta \quad (3)$$

where ζ is zeta potential, ϵ is dielectric constant of the solvent used, and η is viscosity of the solvent used;

$$\mu = Q / 4\pi \cdot r \cdot \eta \quad (4)$$

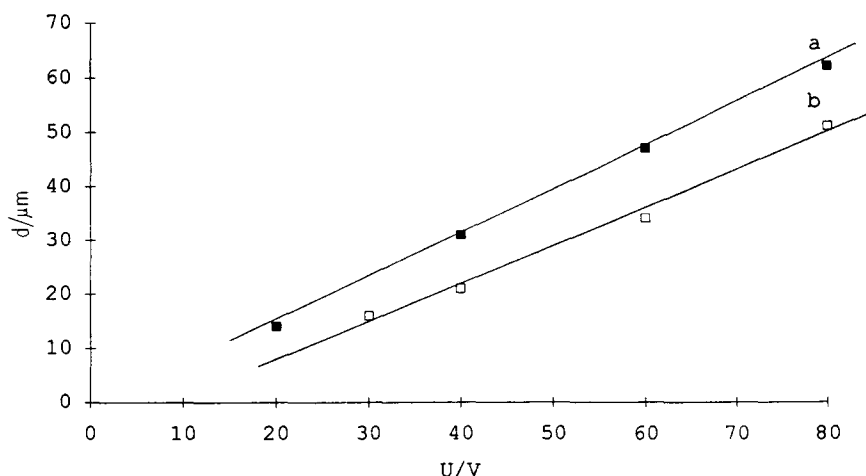


Fig. 2. Relationship between the layer thickness and the applied voltage, using different NiMn₂O₄ powders: (a) 450 °C, 5 h, 40 m² g⁻¹; (b) 800 °C, 5 h, 1.2 m² g⁻¹; and a suspension of 2 g of the powder in 100 ml isoamyl alcohol.

where *Q* is surface charge of the particles and *r* is radius of the particles.

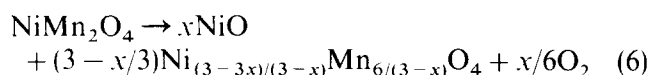
Therefore

$$\zeta \propto 1/r \tag{5}$$

Powders with a larger surface area have a higher zeta potential and hence a higher velocity.

2.4 Formation of the ceramic layer

Previous research has shown that sintering temperatures of 1000–1050 °C have proved effective for the production of NiMn₂O₄ and Zn_zNiMn_{2-z}O₄ ceramics. In such compositions a NiO separation takes place within this temperature region (eqn (6)).^{12,13,19}



This partial decomposition proved necessary for achieving a sintering effect. For a homogeneous single phase composition to be effected, re-oxidation of the material below the decomposition temperature and under pure oxygen is necessary. The authors used the following sintering regime: the material was heated (40 K min⁻¹) to 1000 °C, maintained at this temperature for a period of 2 h, then for a further 5 h at 800 °C. In the case of NiMn₂O₄ layers the samples must be quenched, since this substance is not stable below 730 °C. NiMn₂O₄ decomposes under absorption of O₂, forming NiMnO₃ and α-Mn₂O₃ (eqn (7)):



3 Results and Discussion

3.1 Characterization of the SnO_{2-x} layers

The conductivity of the SnO_{2-x} layers is influenced by many parameters, e.g. the method of production, dopants and temperature.¹⁹ The results of 20

experiments using Pt as contact material and SnO_{2-x}-coated Al₂O₃ substrates showed a mean resistance of (3.5 ± 0.5) kΩ at room temperature. These resistances were converted into conductivity values using eqn (8):

$$\sigma = 1/R \cdot L/F \tag{8}$$

where *R* is resistance at ambient temperature, *L* is distance between the electrodes, and *F* is cross-sectional area of the layer.

It is feasible to produce SnO_{2-x} layers with conductivity at room temperature high enough to enable electrophoretic deposition to take place. Values of σ = (400 ± 100) S m⁻¹ may be achieved with layer thicknesses of (0.3 ± 0.05) μm.

The arrangement of the electrodes and the SnO_{2-x} intermediate layer on the substrate is shown in Fig. 3.

3.2 Characterization of the morphology of the ceramic layer

SEM photographs of NiMn₂O₄ layers have shown that, under the conditions imposed, a very loose structure with a high internal surface area was achieved. Figures 4(a) and (b) show the surface of a 43-μm-thick layer at different magnifications. It may be seen that only partial sintering has occurred within the ceramic layer. This is evident from the small number of sintering necks that have developed

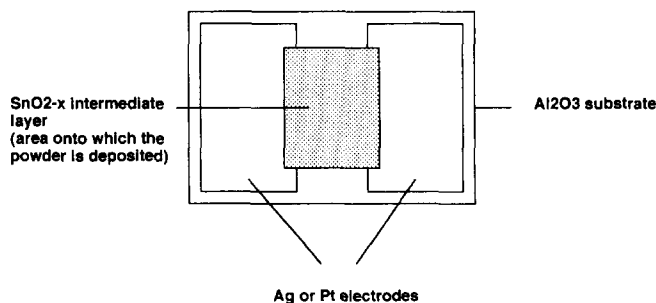
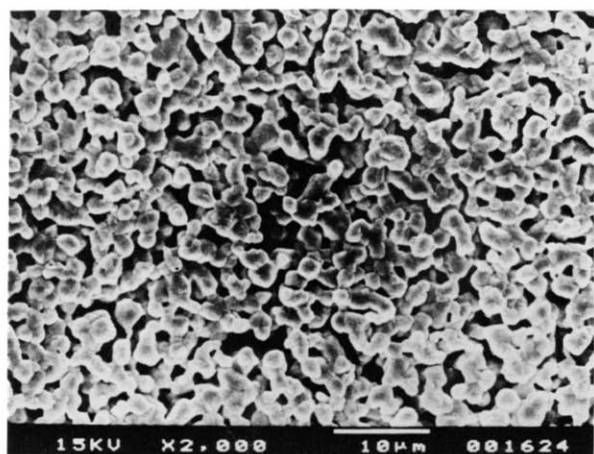
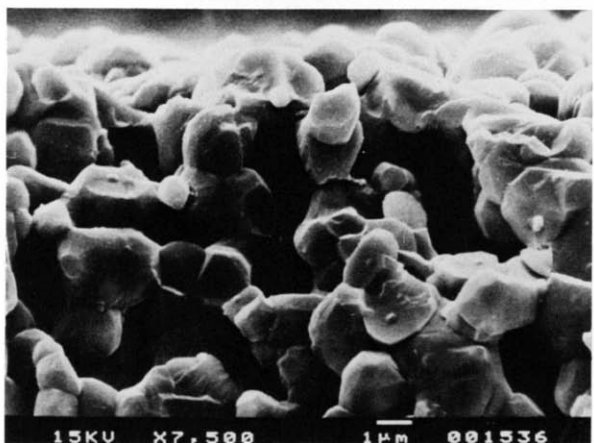


Fig. 3. Plan view of the substrate.



(a)



(b)

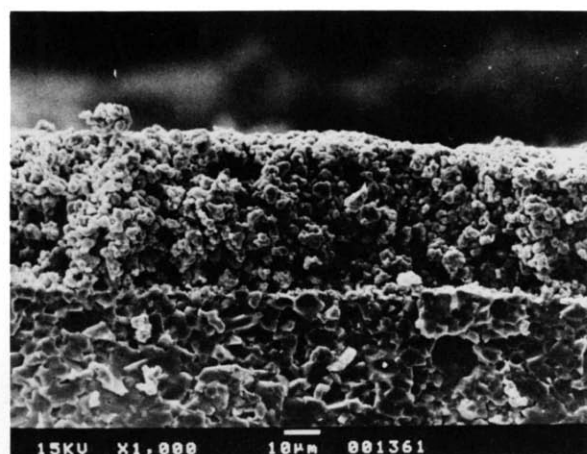
Fig. 4. SEM photographs of the surface of a 43- μm -thick NiMn_2O_4 layer at different magnifications.

between the particles; these expanded until grain boundary equilibrium was reached. Many particles show a grain boundary angle of 120° , indicating that sintering has halted. The grain sizes are approximately $1\text{--}3\ \mu\text{m}$. The process of grain growth is not observed to have taken place. It may further be seen that some of the particles show the cubic structure of the spinel.

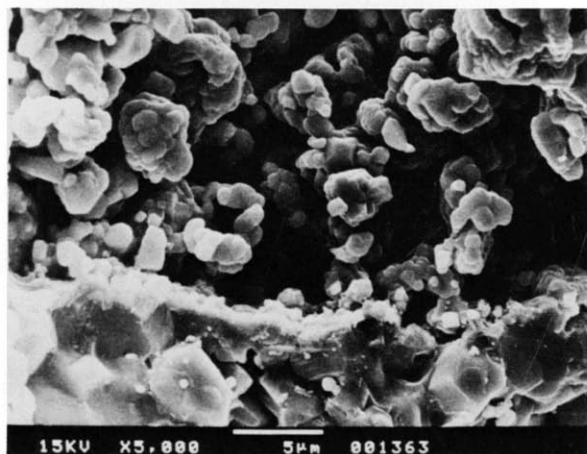
Figures 5(a) and (b) show the cross-section of Fig. 4. The loose packing structure is readily visible. The boundary between the Al_2O_3 and the ceramic layer is also well defined, indicating that the intermediate SnO_{2-x} layer has good contact with both the substrate and the ceramic.

Figure 6 shows a layer sintered at 1050°C , but incompletely re-oxidized. Cube-shaped second phase crystals may be observed at the surface of the spinel crystals. Similar crystals were also observed on bulk ceramic samples and were identified as NiO with the help of electron beam analysis.²⁰

Even though a very loose structure was achieved through electrophoretic deposition and subsequent sintering, long re-oxidation times were necessary after sintering at temperatures of $1000\text{--}1050^\circ\text{C}$. To



(a)



(b)

Fig. 5. SEM photographs of the cross-section of the NiMn_2O_4 layer of Fig. 4.

guarantee phase homogeneity the reaction illustrated in eqn (6) must be completely reversed.

3.3 Conductivity measurements

The d.c. conductivity of samples with different thicknesses of the semiconducting ceramic layer deposited on both Ag and Pt contacts was measured over a temperature range between 20 and 300°C in air. Layer thicknesses varied between 20 and $100\ \mu\text{m}$.

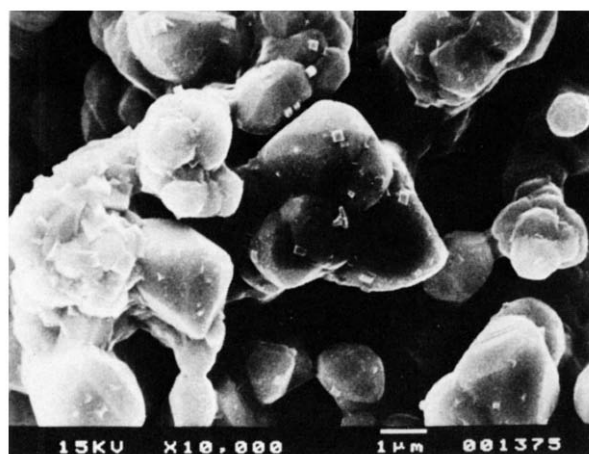


Fig. 6. SEM photograph of an incompletely re-oxidized NiMn_2O_4 layer.

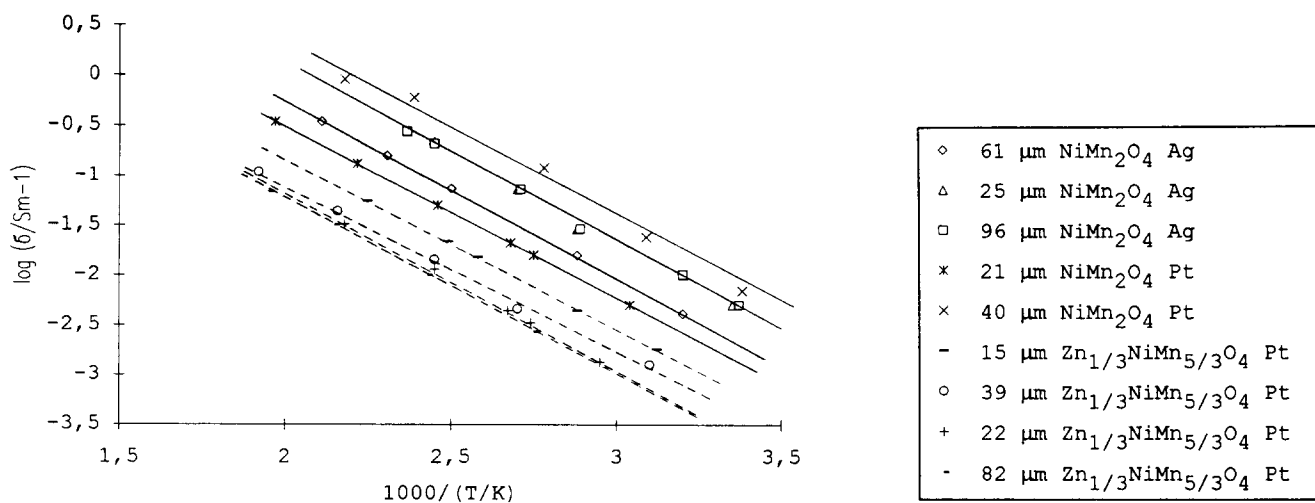


Fig. 7. Relationship between conductivity and temperature for NiMn₂O₄ and Zn_zNiMn_{2-z}O₄ layers of different thicknesses: —, NiMn₂O₄; ---, Zn_{1/3}NiMn_{5/3}O₄.

Scatter plots showing the specific conductivity versus the test temperature (Fig. 7) demonstrate that the conductivity varies with thickness. It is important to note, however, that such variation is not progressive. It must be remembered that conductivity is dependent upon the effective cross-section, which, owing to the loose packing structure, is not equal to the measured thickness. Therefore, the scatter in the specific conductivity may be attributed to fluctuation in the structure. Further investigations are necessary in this respect.

A good agreement between the activation energies or the *B*-constants of samples of varying thickness is noticeable. The results of the conductivity values at

20°C (calculated using eqn (8)) and *B*-constants are combined in Table 1. The corresponding values of compact ceramic samples (density 85–90%) are displayed for comparison in the table. It may be seen that the specific conductivity of the NiMn₂O₄ layer is approximately 10 times, and in the case of the composition containing Zn about 10–100 times, lower than that of the compact ceramic. In comparison, the *B*-constant is only negligibly increased. Alternative investigations using bulk ceramic samples showed similar variations with respect to conductivity in relation to density, where the density varied between 50% and 100%. In these compacts there is a negligible increase in the *B*-

Table 1. Electrical properties of NiMn₂O₄ and Zn_zNiMn_{2-z}O₄ layers of varying thickness

Sample	Thickness (μm)	$\sigma_{20^\circ\text{C}}$ ($S\text{m}^{-1}$)	<i>B</i> (K)
<i>Sintering 1000°C, 3 h; O₂ atmosphere annealing 800°C, 5 h</i>			
NiMn ₂ O ₄	61	2.8×10^{-3}	3887
	25	4.1×10^{-3}	3922
	96	3.5×10^{-3}	3925
	21	1.6×10^{-3}	3978
	40	6.3×10^{-3}	3961
		$(3.6 \pm 2) \times 10^{-3}$	3934 ± 36
Zn _{1/3} NiMn _{5/3} O ₄	39	3.3×10^{-4}	3948
	15	1.3×10^{-4}	4018
	22	1.7×10^{-4}	3970
	82	2.2×10^{-4}	3956
		$(2.1 \pm 1) \times 10^{-4}$	3973 ± 31
Zn _{2/3} NiMn _{4/3} O ₄	22	8.5×10^{-4}	3914
	50	3.9×10^{-4}	3968
	21	3.5×10^{-4}	3962
	36	7.7×10^{-4}	3926
		$(5.9 \pm 3) \times 10^{-4}$	3942 ± 26
<i>Sintering 1000°C, 40 h; O₂ atmosphere annealing 800°C, 40 h</i>			
NiMn ₂ O ₄ ceramic compacts ^a		$(3.2 \pm 0.4) \times 10^{-2}$	3800 ± 15
Zn _{1/3} NiMn _{5/3} O ₄ ceramic compacts ^b		$(2.9 \pm 0.4) \times 10^{-2}$	3778 ± 9
Zn _{2/3} NiMn _{4/3} O ₄ ceramic compacts ^b		$(2.1 \pm 0.2) \times 10^{-2}$	3801 ± 18

^a Ref. 21.

^b Ref. 12.

constants, similar to that observed in the ceramic layer structures.

During repeated heating and cooling between 20 and 300°C, NiMn₂O₄ layers have shown a good reproducibility of the dependence illustrated in eqn (9):

$$\log \sigma = \log \sigma_0 + B/T \quad B = E_A/k \quad (9)$$

where E_A is activation energy and k is the Boltzmann constant.

The variation in σ values in three cycles of heating and cooling amounted to only $\pm 0.07\%$.

4 Conclusion

Electrophoretic deposition is a suitable method for depositing Ni-Mn-oxide and Zn-Ni-Mn-oxide powders to produce thin ceramic layers. Through variation of the deposition parameters, ceramic layers with thicknesses of between 10 and 100 μm are obtainable. Investigations of the conductivity dependence upon temperature have shown a similar behaviour to that observed in respect of pressed compacts. SnO_{2-x} intermediate layers proved to be a good conducting intermediate substrate for electrophoretic deposition of powders on to non-conductive materials, since their influence on the conductivity behaviour of the ceramic layer loses significance after sintering.

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