Low-temperature sintered Ni–Zn–Co–Mn–O spinel oxide ceramics for multilayer NTC thermistors

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ABSTRACT

The phase formation, sintering behavior and electrical properties of Ni–Co–Zn–Mn spinel NTC thermistor ceramics of the series $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ with $0 \leq z \leq 1$ were studied. In contrast to NiMn_2O_4 , which exhibits limited stability in air below 730 °C and above 970 °C, the Zn–Co-substituted nickel manganite spinels are stable at $T < 730$ °C and decompose at $T_d > 900$ °C, with T_d increasing with decreasing Zn Content z . The samples were sintered at 900 °C with addition of 3 wt% Bi_2O_3 as sintering aid and densities of above 92% were achieved. The room temperature resistivity and thermistor B -constants are almost independent of composition at $0 \leq z \leq 0.6$ and start to increase at higher Zn concentrations. A multilayer NTC thermistor was fabricated using green tapes of a spinel of composition $z = 0.75$, commercial Ag paste, and cofiring at 900 °C. The firing behavior, microstructure formation and electrical properties of the multilayer thermistor are reported.

1 Introduction

Negative temperature coefficient (NTC) thermistor ceramics are widely used for temperature control in a variety of industrial and consumer electronic applications including cell phones, battery chargers, LCD displays or automotive. From the characteristic temperature dependence of the electrical resistance

$$R = R_0 \exp(E/kT) = R_0 \exp(B/T) \quad (1)$$

the activation energy of electron hopping E and the thermistor constant B is obtained, which is related to the signal output per temperature change. Typically, NTC thermistors exhibit a resistance at room

temperature of $R_{25} = 1$ kΩ to 1000 kΩ and thermistor constants of about $B = 3000$ K to 4000 K [1]. Spinel-type oxides with semiconducting charge transport behavior based on hopping-type motion of charge carriers with thermally activated mobility are typically used as material basis of NTC thermistors. A major challenge for the development of a new NTC materials is the reduction of the resistance drift, commonly associated with this type of NTC thermistors upon operation. However, fundamental understanding of the origins and mechanisms of aging phenomena is still lacking. Possible reasons include changes in the bulk chemistry of thermistors, changes in the cation distribution, or partial oxidation

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and formation of cation-deficient defect spinels upon cooling [2–4]. Therefore, search for improved NTC thermistor compositions is still ongoing.

Standard NTC thermistor compositions are based on $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ spinels, and their chemistries and properties can be altered through a variety of substituents including Co, Fe, Zn, Cu, etc. The crystal structure is of the spinel type, AB_2O_4 , with space group $Fd-3m$ (No. 227). The A and B cations occupy tetrahedral and octahedral lattice sites, respectively, in a cubic close packing of oxygen ions. If the A cations reside on tetrahedral and all B cations on octahedral sites, the spinel is of normal spinel type. If all A cations are located on octahedral and half of the B cations on tetrahedral sites, the spinel is completely inverse. The cation distribution might vary between these two limiting cases as described by the inversion parameter ν (with $0 \leq \nu \leq 1$):

The cation distribution of cubic NiMn_2O_4 was investigated by neutron diffraction and an almost inverse cation distribution with $\nu = 0.74 - 0.93$, depending on sintering temperature and cooling conditions, was reported [5]. Brabers et al. [6] proposed disproportionation of Mn^{3+} to take place simultaneously:

This cation distribution might account for the semiconducting behavior of the material through electron hopping between Mn^{3+} and Mn^{4+} on neighboring octahedral sites [1]. Macklen determined $\nu = p = 0.65$ at 900 °C based on thermogravimetry and electrical conductivity data [7]. Gillot et al. reported a $\nu = 0.88$ and $p = 0.78$ from neutron diffraction studies [8] and an inversion parameter of $\nu = 0.90$ was verified from XPS experiments [9]. Thermopower measurements showed a negative Seebeck coefficient almost independent on temperature below about 400 °C, and a stronger temperature dependence between 400 and 550 °C [10]. For samples sintered at 1000 °C and annealed at 800 °C in air, an almost temperature-independent thermopower of $S = -110 \mu\text{V/K}$ was measured between 30 and 150 °C, and a cation distribution with $\nu = p = 0.85$ was derived [11]. Studies on the thermopower of Cu-substituted nickel manganite demonstrated a decrease of the absolute Seebeck coefficient of

NiMn_2O_4 with increasing temperature, and even a change of sign to p-type thermopower at about 770 °C [12]. Recently, measurements of the thermopower vs. temperature of NiMn_2O_4 samples with different thermal history revealed a complex and temperature-dependent Mn disproportionation situation, embedded within the spinel cation distribution [13].

According to the phase diagram of the system $\text{NiO-Mn}_2\text{O}_3$ in air, NiMn_2O_4 is stable between 730 and 900 °C only [14]. At higher temperatures the spinel decomposes upon formation of NiO and a Mn-rich spinel, whereas below 700 °C decomposition into NiMnO_3 and $\alpha - \text{Mn}_2\text{O}_3$ takes place. Upon cooling with standard cooling rates, NiMn_2O_4 is conserved in a metastable state at room temperature. However, long-term annealing at operating temperatures may lead to partial decomposition, causing aging and resistance drift. Substituted nickel manganite spinels may exhibit improved stability at room temperature or operating temperatures of the thermistor. Co-substituted Ni manganites of the solid solution series $\text{Ni}_{1-x}\text{Co}_x\text{Mn}_2\text{O}_4$ were studied, and a minimum resistivity and maximum B-constant were found to exist at $x = 0.4$ [15]. A thermistor constant of about $B = 3300 \text{ K}$ was reported for the similar composition $\text{Ni}_{0.3}\text{Co}_{0.9}\text{Mn}_{1.8}\text{O}_4$ [16]. Substitution of Zn in $\text{Zn}_x\text{-NiMn}_{2-x}\text{O}_4$ has been shown to give spinels which are stable against decomposition at intermediate temperatures; the resistivities and B-constants are quite insensitive toward Zn substitution up to about $x = 0.7$ [17]. Incorporation of Zn into Ni-Co-Cu-Mn spinel thermistors was documented [18].

In this paper we report on spinel oxide ceramics of the series $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ with $0 \leq z \leq 1$. The phase formation, sintering behavior and electrical properties of bulk samples are presented. Moreover, we demonstrate the fabrication of NTC multilayer thermistors, prepared by stacking and cofiring at 900 °C of spinel green tapes. Since we are aiming at a low-temperature cofiring process of the multilayer thermistor at 900 °C allowing the use of Ag or Ag/Pd electrode pastes, the spinel layers are required to exhibit significant shrinkage and sufficient densification at 900 °C. Addition of Bi_2O_3 as sintering aid results in multilayer thermistors with excellent $R(T)$ properties.

2 Experimental

Zn-substituted spinels $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ with $0 \leq z \leq 1$ were prepared by the solid-state oxide route. ZnO (standard grade, Harzsiegel, Norzinco, Goslar, Germany), NiO (grade F, Lomberg, Mülheim a. d. Ruhr, Germany), Co_3O_4 (Alfa Aesar, Karlsruhe, Germany), and Mn_3O_4 (Erachem Comilog, Saint-Ghislain, Belgium) were used as raw materials. Bi_2O_3 (Alfa Aesar, Karlsruhe, Germany) was used as a sintering additive. After 6 h of wet homogenization with zirconia grinding media in a borosilicate glass bottle using a roller mill, the powder mixture was dried and calcined in air for 5 h at 850 °C. The calcined powders were wet milled for one hour with isopropanol in a stainless steel milling jar with zirconia grinding media (diameter 1 mm) using a planetary ball mill (Pulverisette 5, Fritsch, Idar-Oberstein, Germany). Pellets of diameter 10 mm were prepared by uniaxial pressing using a solution of poly-vinyl alcohol (PVA) as pressing aid. The samples were sintered at 900 °C, 1000 °C and 1100 °C for 2 h in air. For low-temperature sintering experiments, 3 wt% Bi_2O_3 sintering aid was added at the fine-milling step, and the pellets made from this powder were sintered at 900 °C. For preparation of NTC multilayer thermistors, the fine-milled powders were processed using a doctor blade tape casting process with PVB binder in an ethanol/MEK solvent mix; the green tape thickness was 200 μm . For multilayer fabrication, the green tapes were cut, stacked and laminated at 70 °C and 20 MPa for 10 min. Electrode layers were printed onto the thermistor green tapes using screen-printing with commercial Ag (Heraeus TC 7303) paste. The laminates were slowly heated in air to 500 °C with a rate of 0.5 K/min for binder burn-out, and then to 900 °C with 4 K/min and sintered at 900 °C for 2 h.

The particle size of the spinel powders was characterized using laser diffraction analyzer (Mastersizer 2000, Malvern Panalytical Ltd.). The specific surface area of the powders was determined by nitrogen adsorption (BET, Nova 2000, Quantachrome Instruments). The phase formation in the crushed sintered pellets was investigated using X-ray diffraction (D8 ADVANCE, Cu- K_α radiation, Bruker AXS, Karlsruhe, Germany). For characterization of the thermal

stability, powdered samples were studied in a thermogravimetric (TG) analysis system (TAG, Seteram, Caluire, France). The shrinkage behavior was characterized using dilatometry with a heating rate of 4 K/min (DIL 402E, Netzsch, Selb, Germany). The microstructure was characterized using scanning electron microscopy (EVO 15, Zeiss, Oberkochen, Germany). For electrical measurements the pellets were contacted with silver conductor. The DC resistivity was measured between 20 and 80 °C using a two-point method with the samples immersed in a heated silicon oil bath.

3 Results and discussion

Spinel powders were prepared through calcinations at 850 °C. The powders were milled down to a particle size of $d_{50} = 0.4 \mu\text{m}$ and a specific surface area of 10 m^2/g . Sintering pellets of the powders at 900 °C, 1000 °C, and 1100 °C for 2 h gave densities of 65%, 85% and 95%, respectively.

The phase composition of samples $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ with $0 \leq z \leq 1$, sintered at different temperatures, was studied using XRD. The samples sintered at 900 °C show a spinel as main phase (Fig. 1a). For small values of z ($z = 0$ and 0.25) the diffractograms show peaks of cubic and tetragonal spinel phases. Mn-rich spinels in the system $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ are known to exhibit tetragonal structures in the range $0 \leq x \leq 1.5$ (boundary between tetragonal and cubic spinel depending on temperature), which is caused by a cooperative Jahn–Teller distortion of Mn^{3+} in octahedral environment [19]. NiMn_2O_4 is of cubic spinel type [14], and $\text{Mn}_{1.5}\text{Ni}_{0.6}\text{Co}_{0.9}\text{O}_4$ was also reported to have a cubic structure [20]. $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Mn}_2\text{O}_4$, which is the starting composition of the substitution series studied here, represents a phase mixture of cubic and tetragonal spinel phases after firing at 900 °C (Fig. 1a). Substitution of Zn results in the formation of a single cubic spinel phase in the composition range $0.5 \leq z \leq 0.9$. Introduction of Zn for Mn in the spinel lattice reduces the total Mn and Mn^{3+} concentrations, and a cooperative Jahn–Teller distortion is no longer present. At large Zn concentration of $z = 1$, zinc oxide ZnO is observed as additional phase (Fig. 1a). Such behavior

Fig. 1 XRD patterns of $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ with $0 \leq z \leq 1$, sintered at 900 °C (a), 1000 °C (b), and 1100 °C (c) (ref.: PDF-numbers: NiMn_2O_4 71-0852; CoMn_2O_4 77-0471; ZnO 65-3411, $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}$ 78-0427)

has frequently been reported, for example in Zn-rich compositions of the $\text{Mn}_{2.25-x}\text{Ni}_{0.65}\text{Zn}_x\text{O}_4$ system [21]. After firing at 1000 °C (Fig. 1b) and 1100 °C (Fig. 1c) similar behavior is observed. For $0 \leq z \leq 0.5$, a cubic majority spinel is found, however, broad signals with large peak width and a large signal background indicate the existence of additional (tetragonal) spinel phases. A single cubic spinel phase is found between $0.5 \leq z \leq 0.8$ at 1000 °C, and between $0.5 \leq z \leq 0.75$ at 1100 °C. At larger z , additional peaks of ZnO and of a (Ni,Mn)O rocksalt phase are observed (Fig. 1b and c).

The phase stability of NiMn_2O_4 in air is limited to a small temperature window between about 730–900 °C according to the phase diagram $\text{NiO}-\text{Mn}_2\text{O}_3$ [14]. This stability window was determined precisely to be located between 730 and 960 °C using thermogravimetry [22]. Thermal analysis curves of NiMn_2O_4 powder show a mass gain at about 500 °C signaling oxidation and decomposition of the spinel:

The instability of NiMn_2O_4 at low temperatures in air is caused by large concentrations of Mn^{2+} (formula (3)). The reaction products of Eq. (4) contain solely Mn^{4+} or Mn^{3+} ions, respectively, which are stable in air under these conditions. The mixture of NiMnO_3 and $\alpha\text{-Mn}_2\text{O}_3$ coexists up to 730 °C and transforms upon further heating into NiMn_2O_4 in reversal of Eq. (4). In the TG-signal a mass loss appears at $T > 750$ °C that is terminated at 800 °C when re-formation of NiMn_2O_4 is complete. At $T > 950$ °C a continuous mass loss starting at the decomposition temperature T_d , suggests spinel decomposition and formation of NiO and a Mn-rich spinel according to:

as confirmed by XRD and SEM studies [22]. If NiMn_2O_4 thermistor oxides are sintered at $T > 960$ °C to achieve high density, a re-oxidation treatment at $T < 960$ °C is recommended to form a single cubic spinel phase. However, the limited stability of NiMn_2O_4 below 730 °C might pose problems during cooling/heating of sintered samples, or

during long-time operation at the upper limit of the operational temperature range.

The thermogravimetry curves of the samples of the series $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ ($0 \leq z \leq 1$) show a different picture (Fig. 2). Samples with $0 \leq z \leq 0.9$ do not show any mass gain indicating that the oxidative composition that is observed in NiMn_2O_4 (Eq. (4)) does not take place here. Moreover, at higher temperatures above the decomposition temperature T_d (indicated by arrows), decomposition of the spinels upon formation of a (Ni,Mn)O phase besides the spinel main phase sets in, as indicated by a mass loss. However, T_d changes systematically from about 1150 °C for $z = 0.50$ down to $T_d = 900$ °C for $z = 1$. This finding is consistent with the results of the X-ray diffraction study (discussed above). Samples with large Zn content z have low T_d . If sintered at 900 °C, only samples with $z = 1$ display formation of ZnO as secondary phase (Fig. 1a). Formation of a NiO-based additional phase is observed for $z \geq 0.8$ at 1000 °C (Fig. 1b), and for $z \geq 0.7$ at 1100 °C (Fig. 1c). This combined XRD/TG study confirms, that the spinels $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ exhibit wider temperature stability windows in air as compared to NiMn_2O_4 . For the starting composition ($z = 0$), based on the cation distribution of NiMn_2O_4 (formula (3)) with $v = 0.8$, we assume:

since Co^{2+} were shown to reside on tetrahedral sites in the system $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ in the compositional range $0 \leq x \leq 1$ [19]. If Mn is partially replaced by Zn ions in $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$, Zn^{2+} might completely

substitute for Mn^{2+} on tetrahedral sites in the compositional range $0 \leq x \leq 0.5$. This reduces the concentration of Mn^{2+} significantly, thus improving the stability of the spinel in the low/intermediate temperature range. An alternative scenario includes the shift of parts of the Co^{2+} ions onto octahedral sites and oxidation to Co^{3+} . This allows a residual concentration of Mn^{2+} to reside on tetrahedral sites, coupled with the reduction of the concentration of Mn^{3+} on octahedral sites. This scenario allows interpretation of the predominance of a cubic spinel structure in the Zn-substituted Ni–Co–Mn spinels due to reduced concentrations of Jahn–Teller-active Mn^{3+} ions. This mechanism seems to dominate for $0.5 \leq x \leq 1$, since predominate occupation of tetrahedral sites by Zn^{2+} forces a part of the Co ions to move to octahedral positions.

The shrinkage behavior of selected compositions of $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ ($0 \leq z \leq 1$) was monitored using dilatometry (Fig. 3). The measurements show that sintering of a sample with $z = 0.25$ requires high temperatures; the shrinkage is not finished yet at the upper measurement temperature of 1200 °C, and the temperature of the maximum shrinkage rate (T_{MSR}) is at about 1140 °C (arrow). With increasing Zn content, the shrinkage is shifted toward lower temperature. Simultaneously, the T_{MRS} are reduced as well, and a $T_{\text{MSR}} = 1095$ °C is found for $z = 0.8$ and $T_{\text{MSR}} = 1030$ °C for $z = 1$, respectively (Fig. 3). However, sintering temperatures of 1100 °C and higher are needed to sinter dense thermistor samples. In order to enable sintering to be performed at lower temperature, addition of Bi_2O_3 as sintering aid was tested. The shrinkage behavior of a sample with $z = 0.6$ and addition of 3 wt% Bi_2O_3 is shown in Fig. 3 (inset). Shrinkage starts at 700 °C and terminates at 1000 °C, the maximum shrinkage rate appears at about 800 °C. Sintering of this sample with $z = 0.6$ with sintering additive was carried out at 900 °C for 2 h. A significant increase of the relative density from 65 to 96% (theoretical density 5.25 g/cm³) from 0 wt% to 3 wt% Bi_2O_3 addition, respectively, was observed.

Electrical properties were measured for all samples of $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ ($0 \leq z \leq 1$), sintered at 900 °C with addition of 3 wt% Bi_2O_3 (Fig. 4). As an example, Fig. 4a shows the resistivity vs. $1000/T$ curves of samples with $z = 0.75$, illustrating the good reproducibility of the $\rho(T)$ behavior measured on several bulk samples. A SEM micrograph of a

Fig. 2 Thermogravimetry analysis (TG) of $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ with $0 \leq z \leq 1$

Fig. 3 Shrinkage and shrinkage rate of selected compositions of $\text{Ni}_{0.5}\text{Zn}_z\text{Co}_{0.5}\text{Mn}_{2-z}\text{O}_4$ ($0 \leq z \leq 1$) with heating rate of 4 K/min (shrinkage rate maxima marked with arrows), inset: sample with $z = 0.6$ with addition of 3 wt% Bi_2O_3 sintering aid

sample with $z = 0.75$ is shown in the inset of Fig. 4a; a dense microstructure with heterogeneous grain size distribution is observed. Some large grains with up to 5 μm size are embedded in a matrix of smaller grains with size of $< 1 \mu\text{m}$. Such microstructure is formed as result of liquid phase sintering due to the addition of 3 wt% Bi_2O_3 (melting point of 817 $^{\circ}\text{C}$). Little or no grain growth at 900 $^{\circ}\text{C}$ occurs for most grains, and few grains only experience significant grain growth, most likely due to dissolution/precipitation in the liquid phase.

The sintered bulk samples of compositions $0 \leq z \leq 0.6$ exhibit a room temperature resistivity of about $\rho_{25} = 1 \text{ k}\Omega \text{ cm}$ and a thermistor constant of $B = 3500 \text{ K}$, which do not show a significant variation with composition z (Fig. 4b). This is consistent with the substitution model described above, i.e., that in this compositional range Zn^{2+} ions are predominately substituted for tetrahedral Mn^{2+} ions. For larger Zn concentrations of $z \geq 0.7$ a moderate increase in room temperature resistivity up to $\rho_{25} = 7 \text{ k}\Omega \text{ cm}$ for $z = 1$ is observed. Simultaneously, the thermistor constant also increases to about $B = 4000 \text{ K}$. It is assumed that the low resistivity is due to electron hopping paths in the octahedral B-site sublattice, mainly between $\text{Mn}^{3+/4+}$. In the concentration range $0 \leq z \leq 0.6$, minority charge carrier

hopping might occur between $\text{Co}^{2+/3+}$ as well, which seems to be blocked at larger Zn concentration z .

NTC thermistors are typically used as bulk samples or multilayer thermistors [23]. For the fabrication of multilayer NTC thermistors, powder of composition $\text{Zn}_{0.75}\text{Ni}_{0.5}\text{Co}_{0.5}\text{Mn}_{1.25}\text{O}_4$ with addition of 3 wt% Bi_2O_3 was selected. Green tapes were prepared by tape casting. Four layers of thermistor tape were screen-printed with electrodes of Ag paste, stacked, laminated and cofired at 900 $^{\circ}\text{C}$. SEM investigations of a sintered multilayer NTC thermistor (Fig. 5a) show a homogeneous and dense microstructure of the thermistor layers (190 μm thickness). No interaction between thermistor and electrode layers was observed (Fig. 5b), and an EDX mapping of the Ag concentration does not reveal any diffusion of silver into the ceramic layers (Fig. 5c). From the electrical characterization of the multilayer thermistors a $\rho_{25} = 1.40 \text{ k}\Omega \text{ cm}$ and a thermistor constant of $B = 3320 \text{ K}$ were obtained which are in good agreement with bulk measurements. The measured $R(T)$ curves show little scattering of resistance and B-constant, revealing an excellent reproducibility of the multilayer electrical properties. This demonstrates that low-temperature sintered Zn-Co-substituted nickel manganite spinels display excellent NTC behavior and can be used as temperature sensors.

Fig. 4 Resistivity vs. inverse temperature for $\text{Ni}_{0.5}\text{Zn}_{0.75}\text{Co}_{0.5}\text{Mn}_{1.25}\text{O}_4$ (a), and room temperature resistivity and thermistor B -constant of $\text{Ni}_{0.5}\text{Zn}_x\text{Co}_{0.5}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 1$) bulk materials (b), sintered 2 h at 900 °C; SEM micrograph of a samples of $\text{Ni}_{0.5}\text{Zn}_{0.75}\text{Co}_{0.5}\text{Mn}_{1.25}\text{O}_4$ sintered for 2 h at 900 °C (inset in (a))

Fig. 5 SEM micrographs of multilayer thermistor (a), electrode area (b), and Ag EDX scan of electrode area (c)

4 Conclusions

Samples of $\text{Ni}_{0.5}\text{Zn}_x\text{Co}_{0.5}\text{Mn}_{2-x}\text{O}_4$ ($0 \leq x \leq 1$) form tetragonal/cubic spinel mixtures at small x , and a single-phase cubic spinel phase field is observed at $0.5 \leq x \leq 0.75 \dots 0.9$ (depending on temperature). At high Zn concentrations, ZnO and/or (Ni,Zn)O are found to coexist as impurity phases. Ni-Zn-Co-Mn-substituted spinels exhibits good thermal stability and, unlike NiMn_2O_4 , do not decompose at $T < 900$ °C. At higher temperature the spinels decompose at $T_d > 900$ °C, with T_d increasing with decreasing Zn content x .

Using Bi_2O_3 as sintering additive, the samples were sintered at 900 °C. The room temperature resistivity of about $\rho_{25} = 1$ kΩ cm and a thermistor B -constant of about $B = 3500$ K are almost independent of composition in the range $0 \leq x \leq 0.6$ and increase at higher Zn concentrations. A multilayer NTC thermistor was fabricated using green tapes of a spinel of composition $x = 0.75$ and commercial Ag paste. Cofiring at 900 °C leads to thermistors with high density and good NTC thermistor characteristics. The results demonstrate that the Ni-Zn-Co-Mn spinels have an excellent potential as NTC materials for multilayer thermistors.

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Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

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