

Low-temperature sintered NTC ceramics for thick film temperature sensors

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Abstract:

Printed thick film NTC thermistors and multilayer devices are frequently used for temperature control in hybrid circuits. NiMn₂O₄ and substituted spinels are the most established materials for this application. For low-temperature sintering at 900 °C the shrinkage behavior of the thermistor material has to be adjusted by the addition of proper sinter additives.

We investigated the chemical stability of NiMn₂O₄ and substituted spinels in air between 25 °C and 1200 °C. The compound NiMn₂O₄ is stable from 700 °C to 970 °C only and interacts with the sinter additives. Stable cubic spinels were found in the system Zn_xNi_{0.5}Co_{0.5}Mn_{2-z}O₄. Addition of liquid phase sintering additives to the spinel powders results in complete densification at 900 °C. No chemical interaction between spinel and additive was observed. The effect of Cu-substitution into the spinel was also investigated.

Functional NTC pastes were printed on alumina substrates and post-fired at 900 °C. The NTC thermistor films have a sheet resistivity of about 300 kOhm/sq and B = 3300 K. The firing behavior, microstructure formation and electric properties of NTC thick films will be reported.

Key words: NTC thick films, NiMn₂O₄ and substituted spinels, low temperature ceramic post-firing.

Introduction

NTC (Negative Temperature Coefficient) thermistor ceramics are widely used for temperature control in a variety of industrial and electronic applications including cell phones, battery chargers, LCD displays or hard disc drives or as liquid level sensor. The applicability of these materials is based on a defined temperature dependence of the electrical resistance:

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

with E as the activation energy of electron hopping and B as the so-called thermistor constant that is related to the signal output per temperature change. For most NTC thermistors the resistance at room temperature is in the order of $R_{25} = 1 \dots 1000$ k Ω and typical values of the thermistor constant are around $B = 3000 \dots 4000$ K [1].

The materials used for standard NTC thermistors are based on NiMn₂O₄ which can be altered by a variety of different substituting elements including

Co, Fe, Zn, Cu, etc. The crystal structure is of the spinel-type AB₂O₄, i.e. the A and B cations occupy tetrahedral and octahedral lattice sites 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 also be between these two limiting cases and the cation distribution may be described by the inversion parameter ν :



The cation distribution defines most of the material's physical properties including phase stability, thermal stability, resistivity, magnetic properties, etc. In NiMn₂O₄ the cubic spinel has an almost inverse character with $\nu = 0.74 - 0.93$ depending on temperature [2]. Additionally, disproportionation of Mn³⁺ has to be taken into

consideration. This results in a complex cation distribution



that accounts for the semiconducting behavior of the material through electron hopping between Mn^{3+} and Mn^{4+} on neighboring octahedral sites [3]. Typically NTC thermistors are fabricated as ceramic discs via a standard oxide process or as multilayer resistors [4] through tape casting and ceramic multilayer technology. Another option is to use NTC thermistor thick films prepared by printing a NTC paste on a ceramic substrate (alumina or LTCC) and subsequent firing. However, reports on printed thick film NTC thermistors are scarce [5-7] and only few commercial sources of NTC pastes exist, e.g. [8].

In this paper we report on the development of a screen printable NTC thermistor paste that is fired at 900°C and shows excellent R(T) properties. We will discuss the shrinkage and sintering behavior of the spinels, problems of materials incompatibility between thermistor and sintering additives, and the electrical properties of the thick films. The materials covered include NiMn_2O_4 , Zn-Co- and Cu-Zn-Co-substituted spinels,

Experimental

NiMn_2O_4 , a Zn-Co-substituted spinel of composition $\text{Zn}_{0.75}\text{Ni}_{0.5}\text{Co}_{0.5}\text{Mn}_{1.25}\text{O}_4$ and a Cu-Zn-Co-substituted $\text{Zn}_{0.52}\text{Cu}_{0.37}\text{Ni}_{0.44}\text{Co}_{0.44}\text{Mn}_{1.23}\text{O}_4$ compound were prepared by the traditional solid-state oxide route. ZnO (Harzsigel, Germany), NiO (Lomberg, Germany), Co_3O_4 (AlfaAesar, Germany) and Mn_3O_4 (Erachem, Belgium) were used as raw materials. The oxides were mixed by the appropriate molar ratio. After 6 hours of wet homogenization with zirconia grinding media the mixed powders were dried and calcined in an open platinum crucible for 5 hours at 850 °C. The calcined powders were wet milled using a planetary ball mill Pulverisette (Fritsch, Germany) for one hour using zirconia grinding media (diameter 1 mm). Sintering additives were added at the fine-milling step. Pellets were prepared by uniaxial pressing.

The shrinking behavior was characterized (NETZSCH DIL 402E). The phase formation of the calcined powders and sintered pellets was investigated with X-ray diffraction (Bruker D8, Cu-K_α radiation). For electrical measurements the pellets were painted with silver conductor. The DC resistivity was measured between 20 and 80 °C using a two-point method in a heated silicon oil bath. For the characterization of the thermal stability powdered samples were studied in a TG analysis system (Setaram TAG, France).

For the preparation of NTC-thermistor pastes the fine-milled powders were mixed with an organic vehicle and binders. The pastes were screen printed on alumina thin and thick film substrates (Al_2O_3 99.9 and 96 %). The NTC-films were post-fired for two hours at 900 °C. The thickness of the sintered films is approximately 15 μm . The thick films were characterized by scanning electron microscopy (Zeiss, DSM 900, Germany) and electrical resistivity measurements were performed between 20 and 80 °C.

Results and Discussion

NiMn_2O_4 thick films

Single-phase NiMn_2O_4 powders were prepared through calcinations at 850 °C. The powders were fine-milled down to a particle size of $d_{50} = 0.8 \mu\text{m}$. In order to enhance the shrinkage behavior different sintering additives in the concentration range 0 to 3 wt% were tested using dilatometry and sintering tests. Bi_2O_3 turned out to be an effective additive. The shrinkage rates of NiMn_2O_4 powders with different Bi_2O_3 additions signal a shrinkage rate maximum decreasing to lower temperatures with increasing Bi_2O_3 concentrations down to 860 °C for 3 wt% Bi_2O_3 (Fig. 1).

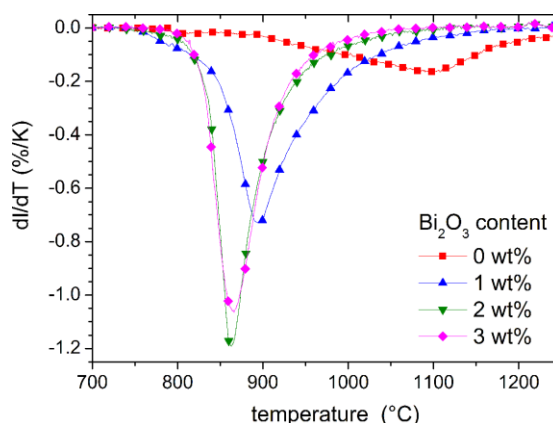


Fig.1: Shrinkage rate of NiMn_2O_4 with different Bi_2O_3 additive concentrations

The densification behavior of NiMn_2O_4 samples with different additive concentrations was evaluated after sintering at 900 °C for 2 hours. A significant increase of the relative density from 60 to 96 % (theoretical density 5.25 g/cm^3) from 0 to 3 wt% Bi_2O_3 additions, respectively, was observed (Fig. 2).

The sintered samples were studied with XRD (Fig. 3). The sample without additive consists of a pure spinel phase only. This is in agreement with the phase stability of NiMn_2O_4 . The phase diagram $\text{NiO} - \text{Mn}_2\text{O}_3$ [9] shows that a composition with the Ni/Mn-ratio of $\frac{1}{2}$ consists of a mixture of NiMnO_3 and $\alpha\text{-Mn}_2\text{O}_3$ below 730 °C that transforms into the NiMn_2O_4 spinel upon further

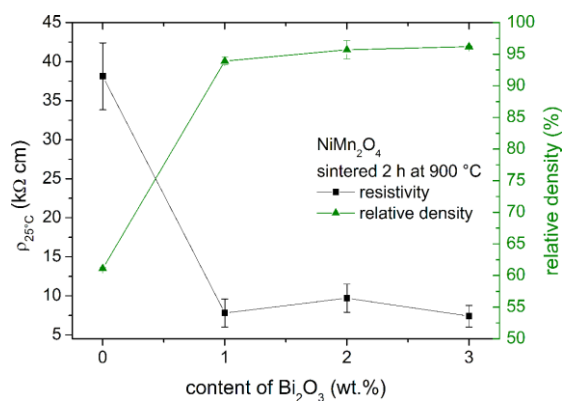


Fig. 2: Relative density and room-temperature resistivity of NiMn₂O₄ vs. Bi₂O₃ additive concentration

heating. At $T > 1000$ °C the spinel decomposes with formation of NiO. The stability range of NiMn₂O₄ in air was determined more precisely to be between 730 and 960 °C [10]. Addition of Bi₂O₃ leads to the formation of Bi₂Mn₄O₁₀ as a second phase with the intensity of the corresponding reflections increasing with Bi₂O₃ additive concentration (Fig. 3). The same result is observed in a SEM study: the sample with 3 wt% Bi₂O₃ exhibits white spots of the Bi-Mn-O second phase in a grey spinel matrix (Fig. 4).

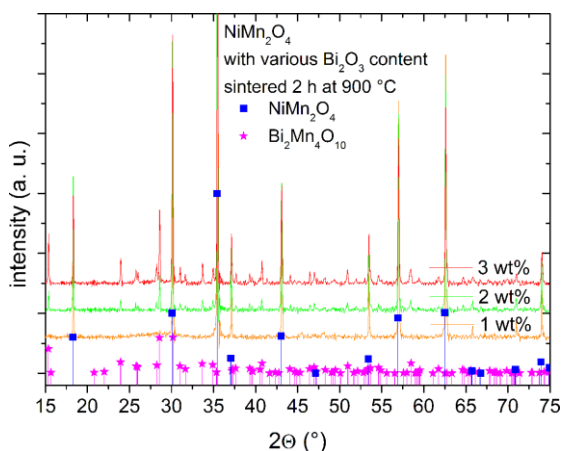


Fig. 3: XRD patterns of NiMn₂O₄ sintered at 900 °C for 2 hours with different concentrations of Bi₂O₃

The variation of the room-temperature resistivity with additive concentration is shown in Fig. 2; the sintered additive-containing samples exhibit a resistivity in the order of 9 kΩ cm without significant variations. However, thick films of NiMn₂O₄ with 3 wt% Bi₂O₃ addition did not show sufficient densification. It was revealed by SEM investigations that the additive reacts with the alumina substrate and hence does not properly act as liquid phase sintering aid. The films exhibit resistances in the MΩ range. Therefore all further studies were performed with substituted spinel compositions.

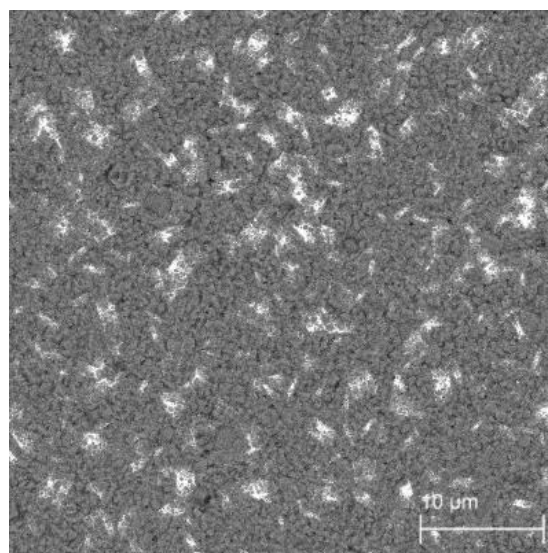


Fig. 4: SEM micrograph of NiMn₂O₄ sintered at 900 °C for 2 hours with addition of 3 wt% Bi₂O₃

Zn-Co-substituted spinel thick films

A modified spinel powder of composition Zn_{0.75}Ni_{0.5}Co_{0.5}Mn_{1.25}O₄ was prepared. Thermal analysis shows that this material is stable between room temperature and 1070 °C. In order to enhance the shrinkage at $T < 900$ °C different amounts of Bi₂O₃ were added. The sample with addition of 3 wt% Bi₂O₃ has a broad shrinkage maximum with the temperature of maximum shrinkage at about $T_{MSR} = 850$ °C (Fig. 5).

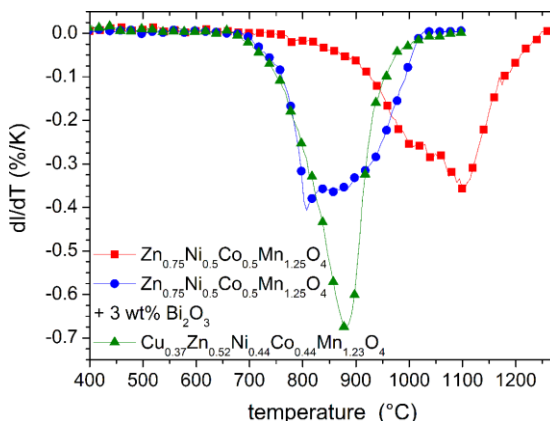


Fig. 5: Shrinkage rate of Zn-Co-substituted spinels with and without Bi₂O₃ additive and a Cu-Zn-Co-substituted spinel

Sintering of powder compacts with 3 wt% additive at 900 °C results in a density of 5.4 g/cm³. XRD investigations confirm that the spinel is stable upon sintering at 900 °C (Fig. 6). The material is single-phase: only the reflections of a cubic spinel phase appear and no reaction with the additive takes place. SEM micrographs confirm a spinel matrix

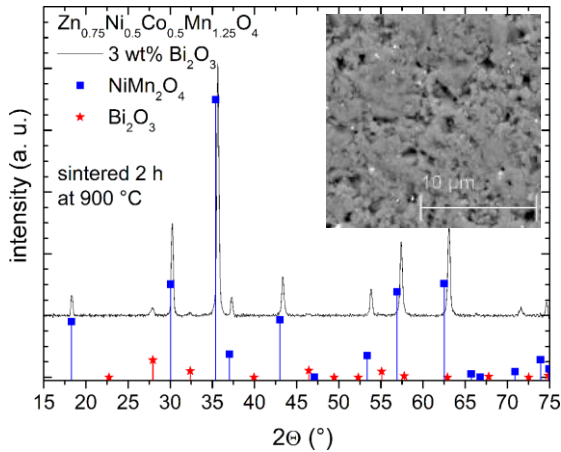


Fig. 6: XRD patterns of $\text{Zn}_{0.75}\text{Ni}_{0.5}\text{Co}_{0.5}\text{Mn}_{1.25}\text{O}_4$ with 3 wt% Bi_2O_3 sintered at $900\text{ }^\circ\text{C}$ for 2 hours (inset: SEM image)

phase with additive inclusions as white spots (inset of Fig. 6). Films of the Zn-Co-substituted spinel were printed on alumina substrates and sintered at $900\text{ }^\circ\text{C}$. The measured $\log R$ vs. $1000/T$ curves are shown in Fig. 7. It appears that the sheet resistances of both types of thick films are quite large in the $\text{M}\Omega$ range. In the case of films on thick film alumina substrates (96 % Al_2O_3) the room-temperature sheet resistance is somewhat larger ($R_{S,25^\circ\text{C}} = 10\text{ M}\Omega/\text{sq}$) compared to the films printed on high-purity (99.9 % Al_2O_3) alumina substrates ($R_{S,25^\circ\text{C}} = 4.7\text{ M}\Omega/\text{sq}$). The thermistor constant is around $B = 4000\text{ K}$ in both cases.

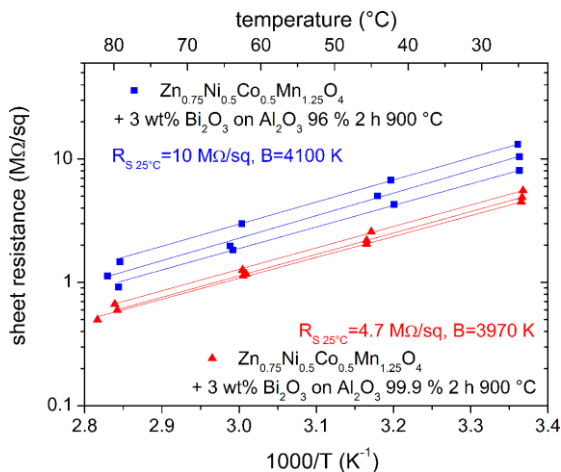


Fig. 7: Sheet resistance vs. $1000/T$ of NTC-films of Zn-Co-substituted spinel on Al_2O_3 substrates (96 and 99.9 %) sintered at $900\text{ }^\circ\text{C}$ for 2 hours

The sintered films were investigated with SEM (Fig. 8). One striking difference is that the film on the high-purity substrate (Fig. 8b) exhibits a smaller sintered thickness implying an improved densification compared to the film on a thick film substrate (Fig. 8a). Closer inspection reveals that in the case of 96 % alumina substrates portions of the

Bi_2O_3 additive can be found within the pores of the substrate indicating that the additive migrates within the glass phase of the substrate. The insufficient densification of the films results in the observed large film resistances.

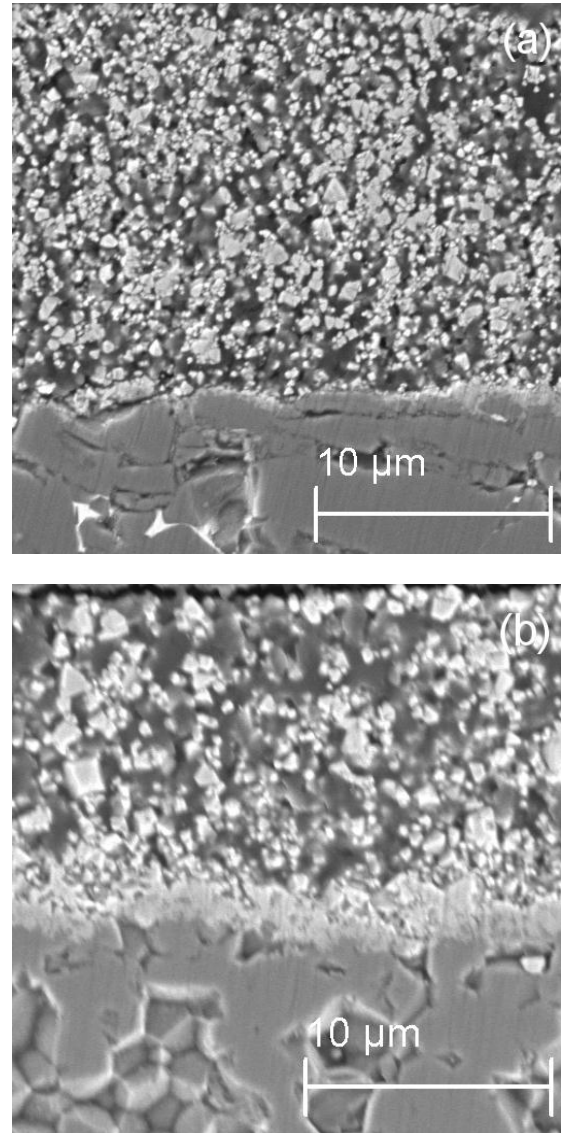


Fig. 8: SEM micrographs of NTC-films of Zn-Co-substituted spinels sintered at $900\text{ }^\circ\text{C}$ for 2 hours on thick film alumina substrates (96 % Al_2O_3), top (a) and on high-purity alumina substrates (99.9 % Al_2O_3), bottom (b)

Cu-Zn-Co-substituted spinel thick films

Another modified spinel with composition $\text{Cu}_{0.37}\text{Zn}_{0.52}\text{Ni}_{0.44}\text{Co}_{0.44}\text{Mn}_{1.23}\text{O}_4$ was prepared. Thermal analysis also confirms that this spinel oxide is stable between room temperature and $950\text{ }^\circ\text{C}$. The shrinkage behavior of the material (Fig. 5) is characterized by a peak in the shrinkage rate at $T_{\text{MSR}} = 880\text{ }^\circ\text{C}$. This indicates that the Cu-containing composition can be sintered without

additives. Sintering tests with compacts at 900 °C for 2 hours demonstrated an excellent densification to 5.3 g/cm³.

Films of this composition were printed on thick film alumina substrates (96 % Al₂O₃) and sintered at 900 °C for 2 hours; the films exhibit a good adhesion to the substrates. XRD studies confirm that the films consist of a single cubic spinel phase (Fig. 9). SEM micrographs confirm a sufficient densification of the films (Fig. 10).

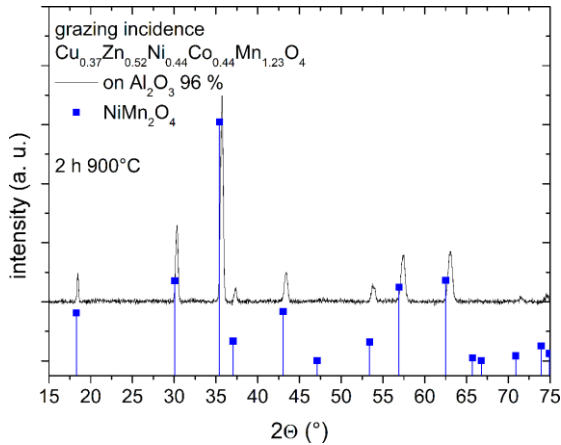


Fig. 9: XRD pattern of a Cu-Zn-Co substituted spinel film sintered at 900 °C for 2 hours

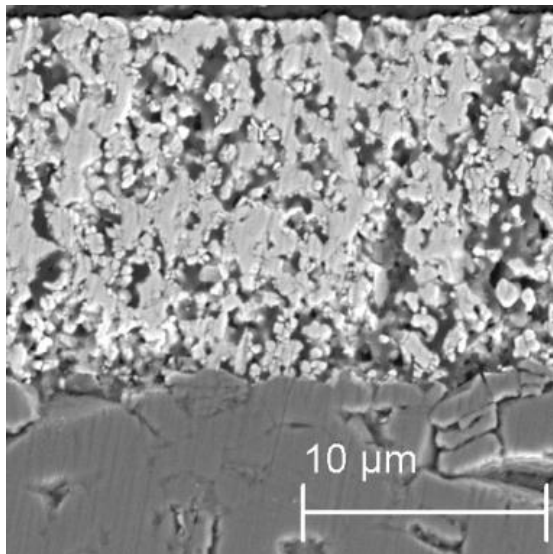


Fig. 10: SEM micrograph of NTC-films of Cu-Zn-Co-substituted spinels sintered at 900 °C for 2 hours on thick film alumina substrates (96 % Al₂O₃)

The electrical properties of the sintered films are shown in Fig. 11. The samples have a room-temperature sheet resistance of around 300 kΩ/sq and a thermistor constant of B = 3300 K.

This demonstrates that films of Cu-Zn-Co-substituted films sintered at 900 °C display an

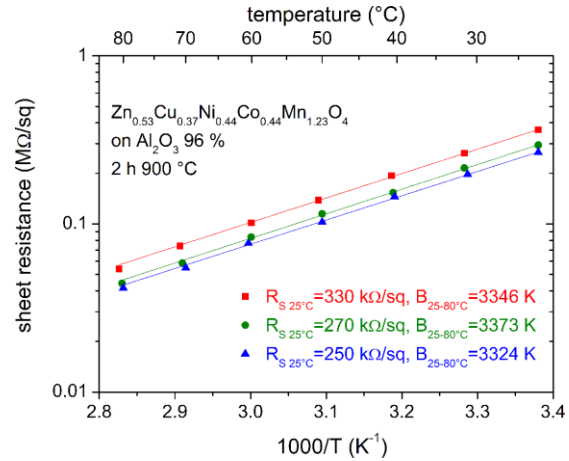


Fig. 11: Sheet resistance vs. 1000/T of NTC-films of Cu-Zn-Co-substituted spinel on 96 %-alumina substrates sintered at 900 °C for 2 hours

excellent NTC behaviour and can be used for implementing temperature sensor functions into hybrid circuitry on ceramic substrates.

Conclusions

It has been shown that the parent NTC thermistor material NiMn₂O₄ might be sintered to high density at temperatures as low as 900 °C using sintering additives, e.g. Bi₂O₃, but thick films of that material are highly resistive due to insufficient densification of the films.

Zn-Co-substituted spinels have better thermal stability since (unlike NiMn₂O₄) they do not decompose at T < 900 °C. Using sintering additives this material might be sintered at 900 °C. Sintering of printed thick films on alumina substrates, however, gives films of low density and high sheet resistance.

The new Cu-Zn-Co-substituted spinel exhibits good thermal stability and shrinkage behaviour. The spinel might be sintered at 900 °C additive-free to give high density. Firing of printed films of this substituted spinel at 900 °C leads to thick films of good adherence and density with good NTC thermistor characteristics. The results demonstrate that the Cu-Zn-Co-substituted spinels have an excellent potential as NTC-materials for screen-printed thick films. This allows integration of temperature sensor elements into thick films and hybrid circuitry printed on ceramic substrates.

Acknowledgements

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