Multifunctional thick-film structures based on spinel ceramics for environment sensors

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Abstract. Temperature sensitive thick films based on spinel-type NiMn₂O₄-CuMn₂O₄-MnCo₂O₄ manganites with p- and p'-types of electrical conductivity and their multilayer p'-p structures were studied. These thick-film elements possess good electrophysical characteristics before and after long-term ageing test at 170 °C. It is shown that degradation processes connected with diffusion of metallic Ag into film grain boundaries occur in one-layer p- and p'-conductive films. Some part of the p'-p structures were of high stability, the relative electrical drift being no more than 1 %.

1. Introduction

Spinel ceramics based on mixed transition-metal manganites and/or magnesium aluminates are known to be widely used for temperature measurement, in-rush current limiting, liquid and gas sensing, flow rate monitoring and indication, etc. [1-5]. But their sensing functionality is sufficiently restricted because of bulk performance allowing, as a rule, no more than one kind of application.

At the present time, a number of important problems connected with hybrid microelectronic circuits, multilayer ceramic circuits, temperature sensors, thermal stabilizers, etc. requires such resolution, when not bulk (e.g. sintered as typical bulk ceramics), but only thick-film performance of electrical components (possessing the possibility to group-technology route) is needed [5]. The well-known advantages of screen printing technology revealed in high reproducibility, flexibility, attainment of high reliability by glass coating as well as excellent accuracy, yield and interchangeability by functional trimming are expected to be very attractive now, for new-generation sensing electronics [6]. No less important is the factor of miniaturization for developed thick-film elements and systems, realized in a variety of their possible geometrical configurations. Thus, the development of high-reliable nanostructured thick films and their multilayers based on spinel-type compounds for multifunctional environment sensors operating as simultaneous negative temperature coefficient thermistors and integrated temperature-humidity sensors are very important task [6-8].

To fabricate the integrated temperature-humidity thick-film sensors, only two principal approaches have been utilized, they being grounded on temperature dependence of electrical resistance for humidity-sensitive thick films and/or on humidity dependence of electrical resistance for temperature-sensitive thick films.
The first approach was typically applied to perovsite-type thick films like to BaTiO$_3$ [9]. Within second approach grounded on spinel-type ceramics of mixed Mn-Co-Ni system with RuO$_2$ additives, it was shown that temperature-sensitive elements in thick-film performance attain additionally good humidity sensitivity [10]. Despite improved long-term stability and temperature-sensitive properties with character material B constant value at the level of 3000 K, such thick-film elements possess only small humidity sensitivity. This disadvantage occurred because of relatively poor intrinsic pore topology proper to semiconducting mixed transition-metal manganite in contrast to dielectric aluminates with the same spinel-type structure.

Thick-film performance of mixed spinel-type manganites restricted by NiMn$_2$O$_4$-CuMn$_2$O$_4$-MnCo$_2$O$_4$ concentration triangle has a number of essential advantages, non-available for other ceramic composites. Within the above system, can be prepare the fine-grained semiconductor materials possessing p$^+$-conductive Cu$_{0.1}$Ni$_{0.9}$Mn$_{1.2}$Co$_1$O$_4$ and p-conductive Cu$_{0.1}$Ni$_{0.9}$Mn$_{1.6}$Co$_{0.4}$O$_4$. So, a real possibility to prepare multilayer thick-film spinel-type structures for principally new device application, such as thermoelectric transformers in a power supply, high-accurate temperature sensors and compensators exploring current-voltage dependence, temperature difference detecting elements utilizing thermoderomotive force, etc. seems to be a quite realistic one. In addition, the prepared multilayer thick-film structures involving semiconductor NiMn$_2$O$_4$-CuMn$_2$O$_4$-MnCo$_2$O$_4$ and dielectric MgAl$_2$O$_4$ spinels can be potentially used as simultaneous thermistors and integrated temperature-humidity sensors with extremely rich range of exploitation properties.

The aim of this work is development of high-reliable temperature and humidity sensitive thick films and multilayered structures based on spinel-type ceramics for multifunctional application in integrated temperature/humidity sensors.

2. Experimental

Bulk temperature sensitive ceramics were prepared by a conventional ceramics processing route using reagent grade cooper carbonate hydroxide and nickel (cobalt) carbonate hydroxide hydrates [11]. Chemical composition of these ceramics and the main points in their sintering schedules are presented in Table 1.

| Chemical composition | Sintering temperature/duration | Phase composition | B K |
|----------------------|-------------------------------|------------------|-----|
| Cu$_{0.1}$Ni$_{0.1}$Co$_{0.8}$Mn$_{1.2}$O$_4$ | 1040 °C/4 h | spinel | 3540 |
| Cu$_{0.1}$Ni$_{0.9}$Co$_{0.2}$Mn$_{1.9}$O$_4$ | 920 °C/8 h + 1200 °C/1 h +920 °C/24 h | spinel + NiO (11.5 %) | 3378 |

The bulk MgAl$_2$O$_4$ ceramics were prepared via conventional sintering route as was described in more details elsewhere [12]. The pellets were sintered in a special regime with maximal temperature 1300 °C during 5 h.

Temperature sensitive Cu$_{0.1}$Ni$_{0.1}$Co$_{1.6}$Mn$_{1.2}$O$_4$/Cu$_{0.1}$Ni$_{0.8}$Co$_{0.2}$Mn$_{1.9}$O$_4$-based and humidity sensitive MgAl$_2$O$_4$-based pastes were prepared by mixing powders of basic ceramics (sintered bulk ceramics were preliminary destroyed, wet-milled and dried) with ecological glass powders (without PbO), inorganic binder Bi$_2$O$_3$ and organic vehicle (Table 2).

| Constituents | Content, % mass | MgAl$_2$O$_4$-based paste |
|-------------|-----------------|---------------------------|
| Basic ceramics | 72.8 | 58 |
| Bi$_2$O$_3$ | 2.9 | 4 |
| Ecological glass | 2.9 | 8 |
| Organic vehicle | 21.4 | 30 |

Table 1. Characteristics of temperature sensitive bulk ceramics

Table 2. Composition of temperature/humidity sensitive pastes
The prepared pastes were printed on alumina substrates (Rubalit 708 S) with Ag-Pt electrodes using a manual screen-printing device equipped with a steel screen. Then thick films were fired in furnace PEO-601-084.

To prepare multifunctional temperature/humidity sensitive elements we used typical design performance in respect to the scheme shown in Fig. 1. In the case under consideration, the main advantages proper to bulk transition-metal manganite ceramics (wide range of electrical resistance with high temperature sensitivity) and humidity-sensitive MgAl$_2$O$_4$ ceramics were transformed into thick-film multilayers resulting in a principally new and more stretched functionality. The spinel-type Cu$_{0.1}$Ni$_{0.1}$Mn$_{1.2}$Co$_{1.6}$O$_4$ compound with p$^+$-type of electrical conductivity, Cu$_{0.1}$Ni$_{0.8}$Co$_{0.2}$Mn$_{1.9}$O$_4$ compound with p-type of electrical conductivity and dielectric magnesium aluminate d-MgAl$_2$O$_4$ were designed as overall integrated p$^+$-p and p-d structures shown in the topological scheme (Fig. 1).

The topology of the obtained thick films was investigated using 3D-profilograph Rodenstock RM600. The electrical resistance of temperature-sensitive thick films was measured using temperature chambers HPS 222. The temperature constant $B$ for these thick films was calculated according to the equation:

$$B = 2.3026 \cdot \log \left( \frac{R_1}{R_2} \right) \cdot \frac{T_1 - T_2}{T_2 - T_1}.$$  

where $R_1$ and $R_2$ were corresponding resistance at $T_1 = 25 \, ^\circ C$ and $T_2 = 85 \, ^\circ C$, accordingly. The current-voltage I-V characteristics were measured at 50, 25 and 5 $^\circ C$ ($\pm 0.1 \, ^\circ C$) using a precise digital multimeter. The humidity-sensitivity of thick-film elements based on MgAl$_2$O$_4$ ceramics was evaluated on dependence of electrical resistance from relative humidity (RH). The measurements were performed at 20 $^\circ C$ and 1000 Hz frequency in direction of RH increase and in reverse one. The long-term ageing test at 170 $^\circ C$ for p-, p$^+$-conductive thick films and p$^+$-p structures was carried for study of their reliability. The relative change of electrical resistance ($\Delta R/R_0$) was used as a controlled parameter ($R_0$ - initial value of electric resistance, $\Delta R$ – absolute change of electric resistance caused by a ageing test).

3. Results and Discussion

In respect to the obtained 3D-profilograph data, the thickness of temperature sensitive p$^+$-conductive thick films based on Cu$_{0.1}$Ni$_{0.1}$Co$_{1.2}$Mn$_{1.9}$O$_4$ ceramics and p-conductive thick films based on Cu$_{0.1}$Ni$_{0.6}$Co$_{0.2}$Mn$_{1.9}$O$_4$ ceramics were near 47-49 $\mu$m and 54-63 $\mu$m, accordingly. The thickness of thick films based on humidity sensitive dielectric MgAl$_2$O$_4$ ceramics was ~ 90 $\mu$m. The topology of multilayered p$^+$-d and p$^+$-p thick-film structures are shown in Fig. 2.

The temperature sensitive p$^+$-p-conductive thick films and their p$^+$-p structures based on spinel-type NiMn$_2$O$_4$-CuMn$_2$O$_4$-MnCo$_2$O$_4$ ceramics posses good linear electrophysical characteristics in the region from 298 to 358 K in semi-logarithmic scale (Fig. 3). The values of $B$ constants were 3589, 3630 and 3615 K for p-, p$^+$-conductive thick films and p$^+$-p structure, respectively.
As was shown early [12], the bulk humidity-sensitive ceramics characterizes of hystereses in desorption cycles. It’s connected with peculiarities of pore-grain structure and quantity of addition phases localized near grain boundaries. These failings were succeeded in thick films based on MgAl$_2$O$_4$ ceramics using the optimum amount of Bi$_2$O$_3$, organic solvent, organic copula and pine oil. So, the studied d-type MgAl$_2$O$_4$ thick films possess linear dependence of electrical resistance from relative humidity without hysteresis in the range of RH $\sim$ 40-99 % (see Fig. 4).

It is shown that electrical resistance of p- and p'-conductive thick films incidentally decreases in the process of degradation test (see Fig. 5). This effect is supposed to be connected with thermally-induced compression of thick films and diffusion of metallic Ag into the grain boundaries. The value of $\Delta R/R_o$ reaches -(2-5) %. However, the p+-p thick-film structures shows high reliability after long-term ageing test at 170$^\circ$C. The relative electrical drift is no more than 1 %.

The values of temperature constant $B$ are decreases on 20-50 K after degradation test both p/p'-conductive thick films and p'-p structures, while the activation energy of electrical conductivity was not changed significantly, being at the level of 0.31 eV. Typical current-voltage characteristics for p-conductive thick films are presented in Fig. 6.
4. Conclusions

The separate temperature and humidity sensitive thick-film elements based on spinel-type NiMn$_2$O$_4$-CuMn$_2$O$_4$-MnCo$_2$O$_4$ manganites with p$^+/p$-type of electrical conductivity, p$^+$-p structures and dielectric magnesium aluminate MgAl$_2$O$_4$ were prepared using ecological glass constituents. These thick films can be used to produce multifunctional high-reliable integrated temperature/humidity sensors for effective environment monitoring and control.

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References
[1] Sheftel I T 1973 Thermoresistors (Nauka. Moscow) p 415
[2] Zaharov V I and Olesk A O 1989 Materials and technology for NTC thick-film thermistors manufacturing. Elektronnaja Teknika: Ser. Radiodetali i Komponenty 63 30-34
[3] Zaharov V I and Olesk A O 1983 Film thermistors. Zarubeznaja Elektroennaja Teknika 5 43-74
[4] Zhong J and Bau H H 2001 Thick-film thermistors printed on LTCC tapes. Am. Ceram. Soc. Bull. 80 39-42
[5] Feingold A H, Wahlers R L, Amstutz P, Huang C, Stein S J and Mazochette J 2000 New microwave applications for thick-film thermistors. Microwave Journal 1 90-98
[6] Qu W 2000 Development of multi-functional sensors in thick-film and thin-film technology. Meas. Sci. Technol. 11 1111-1115
[7] White N W and Turner J D 1997 Thick-film sensors: past, present and future. Meas. Sci. Technol. 8 1-4
[8] Dziedzic A 1997 Thick-film resistive temperature sensors. Meas. Sci. Technol. 8 78-81
[9] Holc J 1995 Temperature characteristics of electrical properties of (Ba,Sr)TiO$_3$ thick-film humidity sensors. Sensors and Actuators B 26/27 99-102
[10] Huang J 2003 Preparation and characteristic of the thermistor materials in the thick-film integrated temperature-humidity sensor. Mat. Sci. Eng. B 99 523-526
[11] Vynnyk I, Hadzaman I, Klym H, Mrooz O and Shpotyuk O 2006 Peculiarities of thermodegradational effects in thick film of mixed transition-metal oximanganites. Technology and Design in Electronics 2 60-62
[12] Shpotyuk O, Ingram A, Klym H, Vakiv M, Hadzaman I and Filipecki J 2005 PAL spectroscopy in application to humidity-sensitive MgAl$_2$O$_4$ ceramics J. Europ. Ceram. Soc. 25, 2981-2984