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## MULTIFUNCTIONAL SPINEL-TYPE CERAMICS FOR ENVIRONMENT SENSORS

**H. Klym<sup>1,2</sup>, I. Hadzaman<sup>1</sup>, O. Shpotyuk<sup>1</sup>, M. Brunner<sup>3</sup>, V. Balitska<sup>1,4</sup>**

<sup>1</sup>*Lviv Institute of Materials of SRC “Carat”  
202, Stryjska str., 79031 Lviv, Ukraine  
e-mail: [shpotyuk@novas.lviv.ua](mailto:shpotyuk@novas.lviv.ua)*

<sup>2</sup>*Lviv Polytechnic National University  
12, Bandera str., 79013 Lviv, Ukraine*

<sup>3</sup>*Fachhochschule Köln / University of Applied Sciences  
2, Betzdorfer Strasse, 50679 Köln, Germany*

<sup>4</sup>*Lviv State University of Vital Activity Safety  
35, Kleparivska str., 79007 Lviv, Ukraine*

Temperature and humidity sensitive thick-film elements based on spinel-type  $\text{NiMn}_2\text{O}_4\text{-CuMn}_2\text{O}_4\text{-MnCo}_2\text{O}_4$  manganites with *p*- and *n*-types of electrical conductivity and dielectric magnesium aluminate  $\text{MgAl}_2\text{O}_4$  were prepared. These elements are shown to be successfully applied for integrated temperature/humidity sensors of environment monitoring and control.

*Key words:* spinel, thick-film, sensor, multilayer structure.

Spinel-type 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. The aim of this work is to develop the high-reliable multifunctional sensors based on the above spinel-type compounds, allowing integrated temperature-humidity sensitivity for effective environment monitoring and control.

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 perovskite-type thick films like to BaTiO<sub>3</sub> [9]. Within second approach grounded on spinel-type ceramics of mixed Mn-Co-Ni system with RuO<sub>2</sub> 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 manganites in contrast to dielectric aluminates with the same spinel-type structure.

Thick-film performance of mixed spinel-type manganites restricted by NiMn<sub>2</sub>O<sub>4</sub>-CuMn<sub>2</sub>O<sub>4</sub>-MnCo<sub>2</sub>O<sub>4</sub> 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*- (Cu<sub>0,1</sub>Ni<sub>0,1</sub>Mn<sub>1,2</sub>Co<sub>1,6</sub>O<sub>4</sub>) and *n*-type of electrical conductivity (Cu<sub>0,1</sub>Ni<sub>0,8</sub>Mn<sub>1,9</sub>Co<sub>0,2</sub>O<sub>4</sub>). So, a real possibility to prepare multilayer thick-film spinel-type structures for principally new device application, such as temperature-sensitive *p*-*n*-type diode junctions (thermoelectric transformers in a power supply, high-accurate temperature sensors and compensators exploring current-voltage dependence, thick-film diode structures, temperature difference detecting elements utilizing thermoelectromotive force, etc.) seems to be a quite realistic one. In addition, the prepared multilayer thick-film structures involving semiconductor NiMn<sub>2</sub>O<sub>4</sub>-CuMn<sub>2</sub>O<sub>4</sub>-MnCo<sub>2</sub>O<sub>4</sub> and dielectric MgAl<sub>2</sub>O<sub>4</sub> 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 and selection the high-reliable separate temperature and humidity sensitive thick-film elements based on spinel-type ceramics for multifunctional application in integrated temperature/humidity sensors.

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.

Table 1

Characteristics of temperature sensitive bulk ceramics

Chemical composition	Sintering temperature/duration	Phase composition	B <sub>25/85</sub> , K
Cu <sub>0,1</sub> Ni <sub>0,1</sub> Co <sub>1,6</sub> Mn <sub>1,2</sub> O <sub>4</sub>	1040 °C/ 4 h	spinel	3540
Cu <sub>0,1</sub> Ni <sub>0,8</sub> Co <sub>0,2</sub> Mn <sub>1,9</sub> O <sub>4</sub>	920 °C/8 h + 1200 °C/1 h +920 °C/24 h	spinel + NiO (11,5 %)	3378

The bulk MgAl<sub>2</sub>O<sub>4</sub> ceramics were prepared via conventional sintering route as was described in more details elsewhere [12, 13]. The pellets were sintered in a special

regime with maximal temperature  $T_s$  1 300 °C during 5 h. In a result, the humidity-sensitive ceramics with a so-called trimodal pore size distribution and character values of pore radiuses centered near ~2,5, 85 and 450 nm and surface area near 6,93 m<sup>3</sup>/g were obtained.

Temperature sensitive Cu<sub>0,1</sub>Ni<sub>0,1</sub>Co<sub>1,6</sub>Mn<sub>1,2</sub>O<sub>4</sub>/Cu<sub>0,1</sub>Ni<sub>0,8</sub>Co<sub>0,2</sub>Mn<sub>1,9</sub>O<sub>4</sub>-based and humidity sensitive MgAl<sub>2</sub>O<sub>4</sub>-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<sub>2</sub>O<sub>3</sub> and organic vehicle (see table 2).

Table 2

Composition of temperature/humidity sensitive pastes

Constituents	Content, % mass	
	Cu <sub>0,1</sub> Ni <sub>0,1</sub> Co <sub>1,6</sub> Mn <sub>1,2</sub> O <sub>4</sub> / Cu <sub>0,1</sub> Ni <sub>0,8</sub> Co <sub>0,2</sub> Mn <sub>1,9</sub> O <sub>4</sub> -based paste	MgAl <sub>2</sub> O <sub>4</sub> -based paste
Basic ceramics	72,8	58
Bi <sub>2</sub> O <sub>3</sub>	2,9	4
Ecological glass	2,9	8
Organic vehicle	21,4	30

The prepared paste were printed on alumina substrates (Rubalit 708 S) with Ag-Pt electrodes using a using a manual screen-printing device equipped with a steel screen. Then, thick films were fired in furnace PEO-601-084. The typical planar type of design of the prepared films was shown elsewhere [14].

The topology of the obtained thick films was investigated using 3D-profilograph Rodenstock RM600. The electrical resistance of thermistor thick films was measured using temperature chambers MINI SABZERO, model MC-71 and HPS 222. The temperature constant B<sub>25/85</sub> for these thick films was calculated according to the Eq.[1]:

$$B_{25/85} = 2,3026 \cdot \log\left(\frac{R_1}{R_2}\right) \cdot \frac{T_1 \cdot T_2}{T_2 - T_1}, \quad (1)$$

where  $R_1$  and  $R_2$  were corresponding resistance at  $T_1 = 25$  °C and  $T_2 = 85$  °C, accordingly.

The humidity-sensitivity of thick-film elements based on MgAl<sub>2</sub>O<sub>4</sub> ceramics was evaluated on dependence of electrical resistance from relative humidity (RH). The measurements were performed at 20 °C and 1 000 Hz frequency in direction of RH increase and in reverse one.

In respect to the obtained 3D-profilogram data, the thickness of thick films based on temperature sensitive Cu<sub>0,1</sub>Ni<sub>0,1</sub>Co<sub>1,6</sub>Mn<sub>1,2</sub>O<sub>4</sub> ceramics with p-type of electrical conductivity, Cu<sub>0,1</sub>Ni<sub>0,8</sub>Co<sub>0,2</sub>Mn<sub>1,9</sub>O<sub>4</sub> ceramics with n-type of electrical conductivity were 56,16 and 66,67 μm, accordingly. The thickness of thick films based on humidity sensitive dielectric MgAl<sub>2</sub>O<sub>4</sub> ceramics was 52,08 μm.

All obtained separate temperature sensitive thick-film elements based on spinel-type NiMn<sub>2</sub>O<sub>4</sub>-CuMn<sub>2</sub>O<sub>4</sub>-MnCo<sub>2</sub>O<sub>4</sub> ceramics have good electrophysical characteristics. These thick-film elements show exponential temperature dependences of resistances (fig. 1). The values of B<sub>25/85</sub> constant were 4 095 and 3 671 K for Cu<sub>0,1</sub>Ni<sub>0,1</sub>Co<sub>1,6</sub>Mn<sub>1,2</sub>O<sub>4</sub> and Cu<sub>0,1</sub>Ni<sub>0,8</sub>Co<sub>0,2</sub>Mn<sub>1,9</sub>O<sub>4</sub> ceramics, respectively. The both thick films possess good temperature sensitivity in the region from 298 to 358 K. They are distinguished by well-defined profile, but their flatness can be partially lost provided aged pastes were used for

screen-printing. This effect is connected with increasing in the viscosity of the prepared pastes. Therefore, only as-prepared pastes (aged no more a few weeks) should be used to produce high-reliable thick-films elements.

The studied thick-film elements based on *d*-type  $\text{MgAl}_2\text{O}_4$  ceramics possess linear dependence of electrical resistance from relative humidity (RH) in semilogarithmic scale with minimal hysteresis in desorption cycle in the range of RH ~60–99 % (see fig. 2). Thus, these thick-film elements are suitable for humidity sensors working in the most important range of RH. These thick films are insensitive to low RH, which can be attributed to bad Ag-Pt contacts between wires and defectiveness of thick film connecting with their viscosity. However, these technological obstacles can be easily removed by modifying screen-print process.

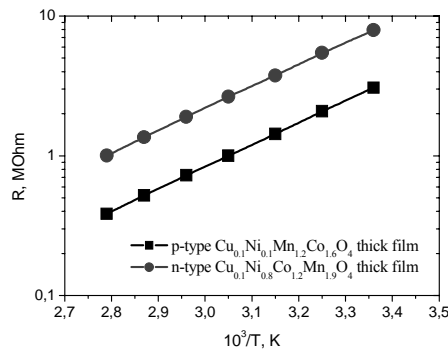


Fig. 1. Typical work characteristics for temperature sensitive thick films based on *p*-type  $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Mn}_{1.2}\text{Co}_{1.6}\text{O}_4$  and *n*-type  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$  ceramics

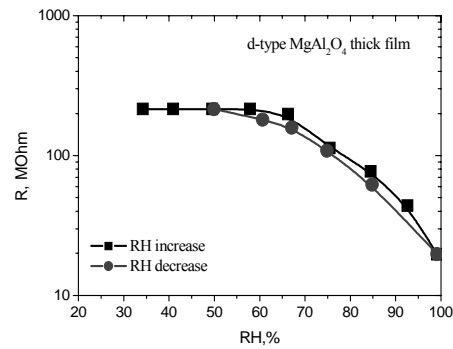


Fig. 2. Typical work characteristics for thick film based on  $\text{MgAl}_2\text{O}_4$  ceramics

Since all investigated separate components (*p*-, *n*- and *d*-type thick films) are of the same chemical type (spinel-like) and possess high temperature/humidity sensitivities, they will be positively distinguished not only by wider functionality (simultaneous temperature-humidity sensing), but also unique functional reliability and stability. To prepare such multifunctional temperature/humidity sensitive elements, we can use typical design performance in respect to the scheme shown in fig. 3. 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  $\text{MgAl}_2\text{O}_4$  ceramics will be transformed into thick-film multilayers, resulting in a principally new and more stretched functionality. The spinel-type  $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Mn}_{1.2}\text{Co}_{1.6}\text{O}_4$  compound with *p*-type of electrical conductivity (yellow-distinguished),  $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Mn}_{1.9}\text{Co}_{0.2}\text{O}_4$  compound with *n*-type of electrical conductivity and dielectric magnesium aluminate *d*- $\text{MgAl}_2\text{O}_4$  will be designed as overall integrated structure shown in the topological scheme at right. It should be noted that only three levels of basic spinels (*p*-, *n*- and *d*-type) should be interconnected by four commutation levels to achieve the final temperature-humidity sensing functionality.

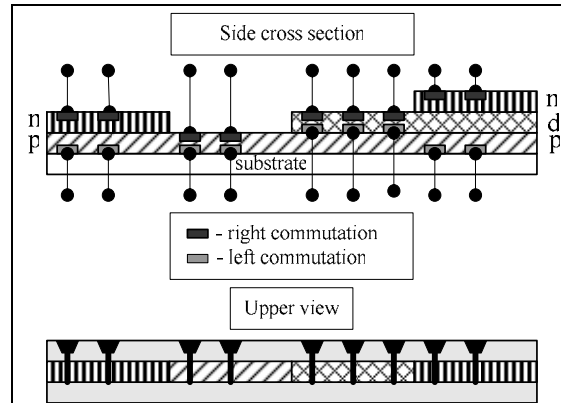


Fig. 3. Topological scheme illustrating integrated humidity/temperature sensing in spinel-type multilayer structures

Within proposed configuration (see fig. 3), a several simultaneous functions will be available via resistance measurements between different points of this multifunctional element: *p*-type thick-film element will be used as in-rush current limiter and temperature sensors utilizing current-voltage dependence of thick-film *p-n* junction, *n*-type thick film element will be used as temperature sensor and humidity sensor utilizing thick-film capacitor *p-d-n* with water-sensitive dielectric layer *d*.

The separate temperature and humidity sensitive thick-film elements based on spinel-type  $\text{NiMn}_2\text{O}_4\text{-CuMn}_2\text{O}_4\text{-MnCo}_2\text{O}_4$  manganites with *p*- and *n*-types of electrical conductivity and dielectric magnesium aluminate  $\text{MgAl}_2\text{O}_4$  were prepared using ecological glass constituents. These thick-film elements can be used as starting components to produce multifunctional integrated temperature/humidity sensors for effective environment monitoring and control.

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#### БАГАТОФУНКЦІОНАЛЬНА ШПІНЕЛЬНА КЕРАМІКА ДЛЯ СЕНСОРІВ НАВКОЛИШНЬОГО СЕРЕДОВИЩА

Г. Клим<sup>1,2</sup>, І. Гадзаман<sup>1</sup>, О. Шпотюк<sup>1</sup>, М. Бруннер<sup>3</sup>, В. Балицька<sup>1,4</sup>

<sup>1</sup>Науково-виробниче підприємство “Карат”  
вул. Стрийська 202, 79031 Львів, Україна

<sup>2</sup>Національний університет “Львівська політехніка”  
вул. Бандери 12, 79013 Львів, Україна

<sup>3</sup>Вища Фахова Школа Кьольну /Університет Прикладних Наук  
вул. Бецдорфе 2, 50679 Кьольн, Німеччина

<sup>4</sup>Державний університет безпеки життєдіяльності  
вул. Клепарівська 35, 79007 Львів, Україна

Отримано температурно та вологочутливі товстоплівкові елементи на основі шпінельної кераміки NiMn<sub>2</sub>O<sub>4</sub>-CuMn<sub>2</sub>O<sub>4</sub>-MnCo<sub>2</sub>O<sub>4</sub> з *p*- та *n*-типами електричної провідності і діелектричної кераміки MgAl<sub>2</sub>O<sub>4</sub>. Показано, що такі елементи можуть успішно використовуватися як інтегровані температурно/вологочутливі сенсори навколишнього середовища.

*Ключові слова:* шпінель, товста плівка, сенсор, багат шарова структура.

**МНОГОФУНКЦИОНАЛЬНАЯ ШПИНЕЛЬНАЯ КЕРАМИКА  
ДЛЯ СЕНСОРОВ ОКРУЖАЮЩЕЙ СРЕДЫ****Г. Клим<sup>1,2</sup>, И. Гадзаман<sup>1</sup>, О. Шпотюк<sup>1</sup>, М. Бруннер<sup>3</sup>, В. Балицкая<sup>1,4</sup>**

<sup>1</sup>Научно-производственное предприятие “Карат”  
ул. Стрыйская 202, 79031 Львов, Украина

<sup>2</sup>Национальный университет “Львовская политехника”  
ул. Бандеры 12, 79013 Львов, Украина

<sup>3</sup>Вицая профессиональная школа Кельна. Университет прикладных наук  
ул. Бецдорфе 2, 50679 Кельн, Германия

<sup>4</sup>Государственный университет безопасности жизнедеятельности  
ул. Клепаривска 35, 79007 Львов, Украина

Получены температурно и влагочувствительные толсто пленочные элементы на основе шпинельной керамики  $\text{NiMn}_2\text{O}_4\text{-CuMn}_2\text{O}_4\text{-MnCo}_2\text{O}_4$  из *p*- и *n*-типов электрической проводимости и диэлектрической керамики  $\text{MgAl}_2\text{O}_4$ . Показано, что такие элементы могут успешно использоваться как интегрированные температурно/влагочувствительные сенсоры окружающей среды.

*Ключевые слова:* шпинель, толстая пленка, сенсор, многослойная структура.

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