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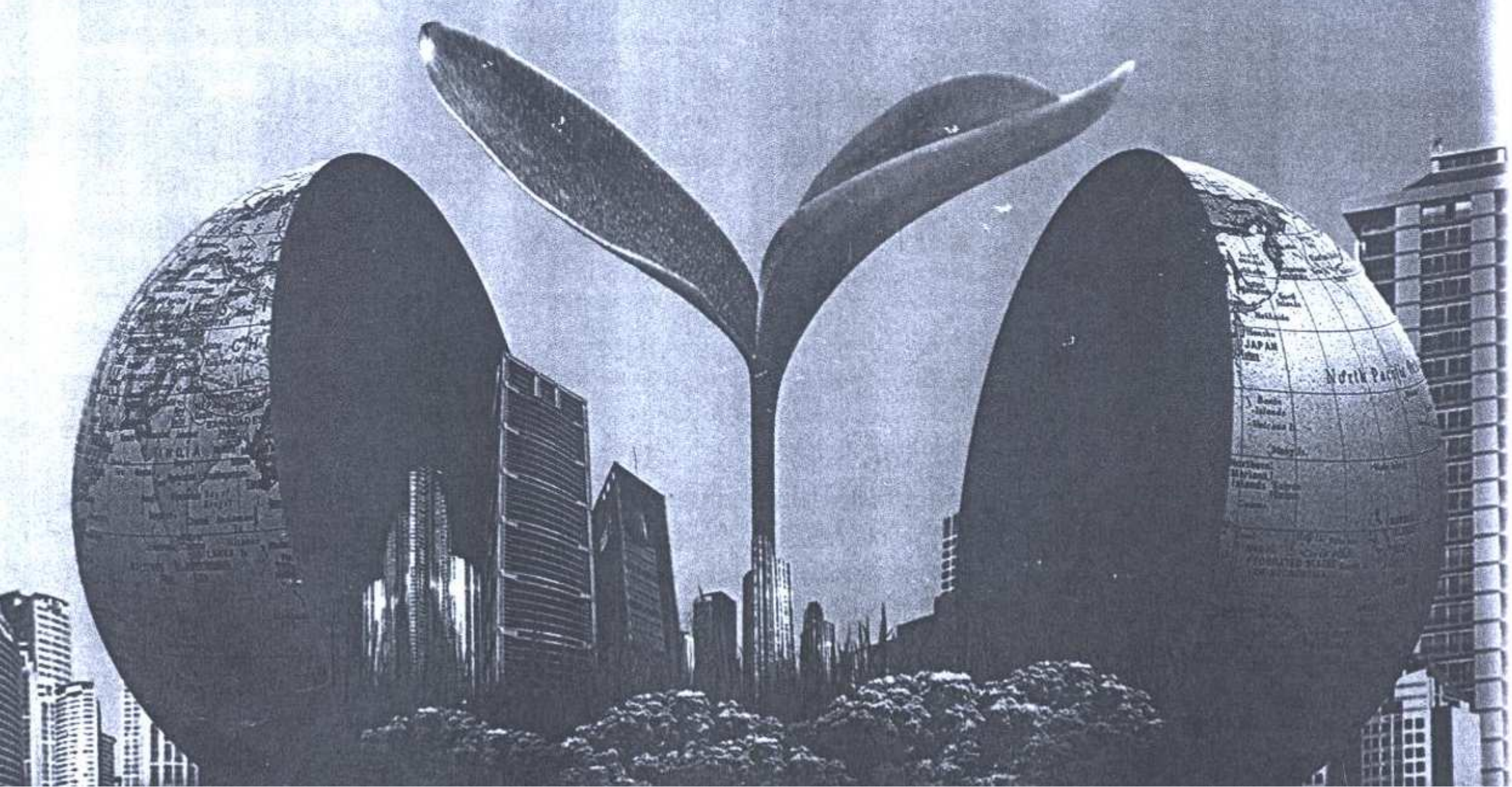

ENVIRONMENTAL FORENSICS

This book was prepared by
the Organizing Committee of the "Experts Workshop"
on Environmental Forensics (Tbilisi, Georgia)
12th-16th September 2011

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This book provides information on a broad range of scientific topics related to environmental forensics. The contributing authors are from leading academic institutions, universities and government departments throughout the former Soviet Union and draw on their current research advances as well as emerging technologies to prevent, identify and treat all forms of environmental pollution. We also acknowledge the important contributions of international experts.

HIGH-RELIABLE NANOSTRUCTURED MULTILAYERS FOR PERMANENT CLIMATE-CHANGE MONITORING AND ENVIRONMENTAL ECOLOGICAL CONTROL

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INTRODUCTION

The basic principle of simultaneous temperature (T) measuring systems is grounded on some changes in physical properties, such as electrical conductivity, resistance, capacity, optical absorption, magnetic susceptibility etc. stimulated by ambient temperature variations [1]. Despite time delay in system response on these variations caused by relative durability of T-influenced effects, the controlled parameter can be determined finally with a high accuracy. In contrast, the relative humidity (RH) measurements are based on changes in physical properties of solid bulk or surface produced by absorbed water. The greater amount of absorbed water, the better exploitation sensitivity of RH-measuring system can be achieved.

To combine both T- and RH-measuring working cycles, the combined resolution built on independent T determination for conventional RH-sensitive functional element and, vice versa (RH determination for conventional T-sensitive element) was proposed. Results in the field of integrated T- and RH- sensors are described in [2 and 3]. The use of spinel-based $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ manganites with negative temperature coefficient (NTC) of electrical resistance for fabrication of disc-type thermistors and RH-sensitive $MgAl_2O_4$ aluminate by means of conventional ceramics technology was described earlier [4-6]. However, modern microelectronics application (T and RH sensors, fire detectors, power-sensing terminations, T-compensating attenuators, etc. [7-10]) require these materials to be in thick-film performance. The advantages of screen-printing technology include; high reproducibility, flexibility, attainment of high reliability by glass coating, accuracy, yield and inter-changeability by functional trimming. These characteristics are of major importance for the development of the new generation of sensing electronics [10]. No less important is the factor of miniaturization for thick-film elements and systems in a variety of geometrical configurations. Thus, the development of high-reliable nanostructured thick films and their multi-layers based on spinel-type compounds for environmental sensors operating as integrated T-RH sensors are very important task [11-13].

Thick-film performance of mixed spinel-type manganites restricted by $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ concentration triangle has a number of essential advantages, which are not possible with other ceramic composites. Within the above system, the fine-grained semiconductor materials possessing p+-type $Cu_{0.1}Ni_{0.1}Mn_{1.2}Co_{1.6}O_4$ and p-type $Cu_{0.1}Ni_{0.8}Mn_{1.9}Co_{0.2}O_4$ electrical conductivity can be easily prepared. Thus, the possibility to prepare integrated multilayer thick-film spinel-type structures for principally new device application is opened with mixed oxymanganospinel ceramics. In addition, the prepared multilayer thick-film structures involving semiconductor $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ and dielectric (d-type) $MgAl_2O_4$ spinels can be used as integrated T and RH environmental sensors with a broad range of exploitation parameters. The aim of this work is the development of integrated T and RH-sensitive thick films and multilayered structures

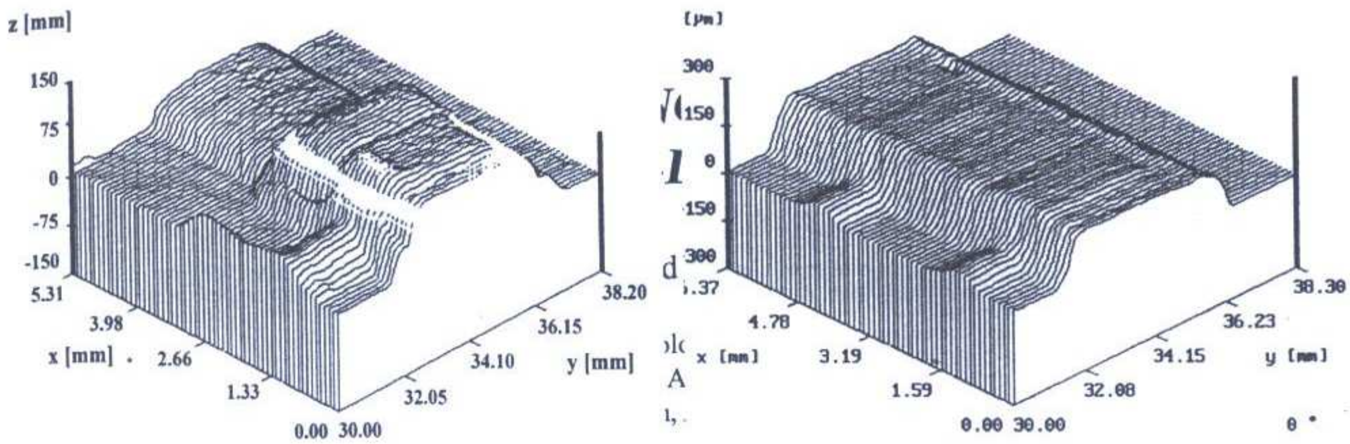

Fig. 2 Topology of p+-p (left) and p+-d (right) thick-film structures obtained with 3D-profilogramph Rodenstock RM600

XRD measurements for film based on p+-conductive $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ ceramics show, that this film contains one cubic spinel crystalline phase (MgAl2O4 structural type, space group Fd m, a=8.30130(9) nm, V=0.572057(11) nm3, Fig. 3,a). The residuals are as follows: RBragg=0.0450, RF=0.0375, X^2=7.60, Rp=0.0452, Rwp=0.0566. Thick film based on p-conductive $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics contains two crystalline phases: cubic spinel with a=8.3794(1) nm, V=0.58835(1) nm3, RBragg=0.0498, RF=0.0396, $X^2$2=3.61, Rp=0.0360, Rwp=0.0456) and traces of NiO-based phase of NaCl type and Fm m space group (Fig. 3,b).

Previously, formation of such NiO-based secondary phase traces was observed in $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics sintered for 1 hour at 1200 °C due to decomposition reactions [19,20]. We expected that reverse reactions in ceramics will proceed during following long-term sintering for 24 hours at 920 °C and a single-phase cubic spinel will be obtained. It can be seen that traces of secondary phase are present after the sintering procedure. This suggested that the duration of this additional thermal treatment was insufficient, i.e. sintering of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ceramics was not perfect for a single-phase material. However, XRD studies for p+-conductive thick film based on $Cu_{0.1}Ni_{0.1}Mn_{1.2}Co_{1.6}O_4$ ceramics show only spinel phase, pattern of alumina substrate and did not reveal any traces of NiO-phase. It can be concluded that the reverse reactions came to end during thermal treatment of films.

XRD patterns of d-type $MgAl_2O_4$ thick film testify in a favor of main spinel-type $MgAl_2O_4$ phase of 99.8 % (space group Fd m) with lattice param-

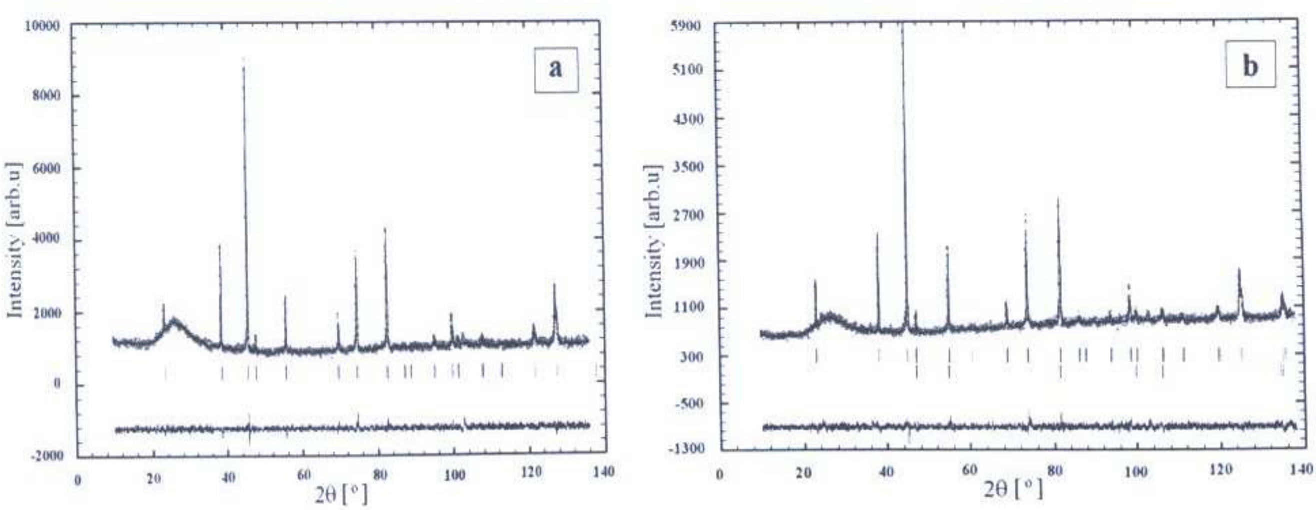

Fig. 3 Observed and calculated XRD profiles for p+- $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ (a) and p-conductive $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ (b) thick films (the overhead row of reflexes is spinel phase, the lower row of reflexes is NiO phase)

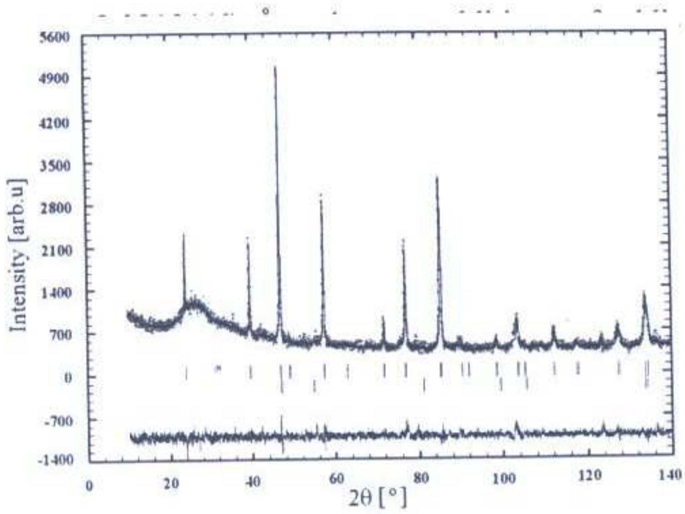

Fig. 4. Observed and calculated XRD profiles for d-type $MgAl_2O_4$ thick film (the overhead row of reflexes is spinel phase, the lower row of reflexes is MgO phase)

T-sensitive p+ and p-conductive thick films based on spinel-type NiMn2O4-$CuMn_2O_4$-$MnCo_2O_4$ ceramics possess good linear electrophysical characteristics in the region from 298 to 358 K in semilogarithmic scale (Fig. 5). The values of B constants were 3589 and 3630 K for p-, p+-conductive thick films, respectively.

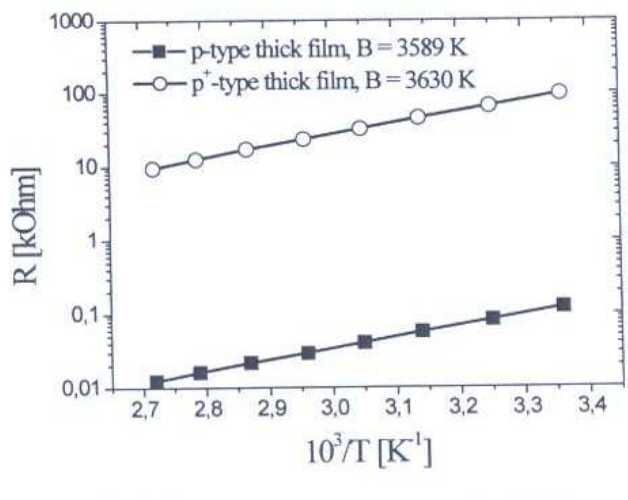

Fig. 5 Exploitation resistance-temperature characteristics of p- and p+-conductive thick films

Dielectric d-type RH-sensitive thick film based on $MgAl_2O_4$ ceramics possesses good linear dependence of electrical resistance without hysteresis in the range of RH=40-99 % (Fig. 6). Since all components (p-, p+- 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 T-RH-sensitive elements, we used typical design performance in respect to the scheme shown in Fig. 1, where the RH-sensitive d-type layer is placed between p+ and p-type layers (p+-d-p-structure). Within proposed configuration, a several simultaneous functions will be available via resistance measurements between different points of this multifunctional element.

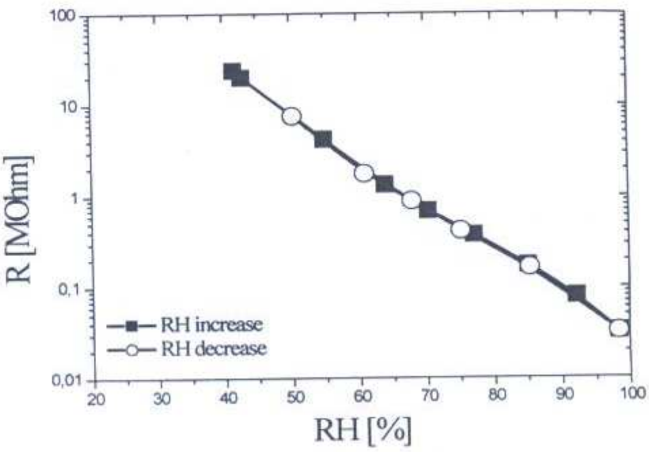

Fig. 6 Resistance-RH characteristics of RH-sensitive spinel-type thick films

CONCLUSIONS

T-sensitive thick-film elements based on spinel-type $NiMn_2O_4$-$CuMn_2O_4$-MnCo2O4 manganites with p+ and p-type of electrical conductivity and dielectric $MgAl_2O_4$ thick films were prepared using ecological glass constituents. These thick films can be used to produce multifunctional integrated p+-d-p T and RH sensors for effective environmental sensing, ecological monitoring and control.

ACKNOWLEDGEMENTS

The authors acknowledge support from Science and Technology Center in Ukraine and helpfull assistance of Dr. P. Demchenko from Ivan Franko National University of Lviv for XRD measurements.

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