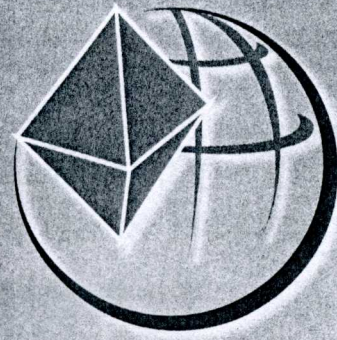




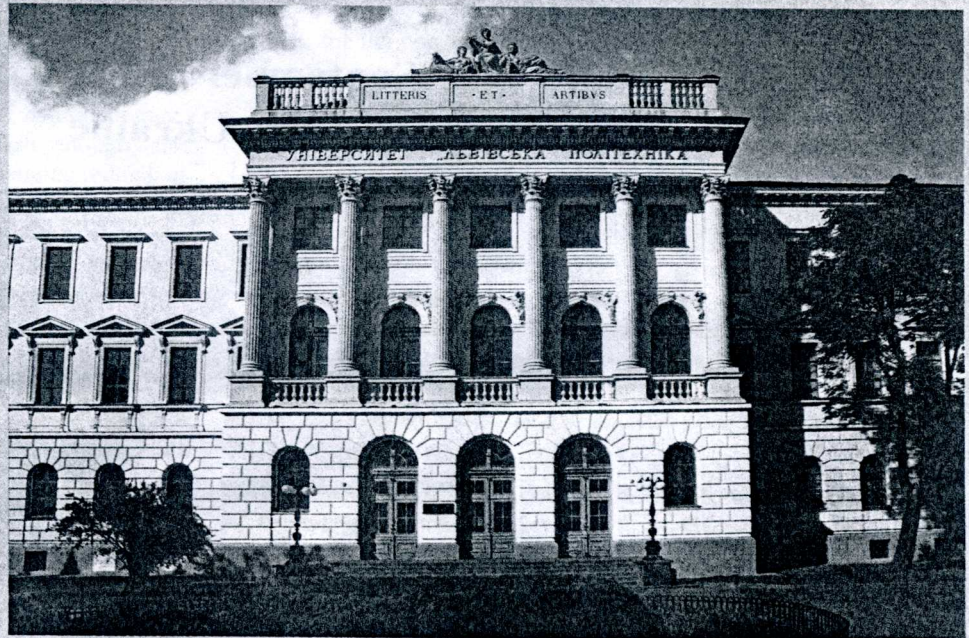
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Sintering-Modified Oxymanganospinel Ceramics for NTC Thermistor Application

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Abstract. Mixed Ni-Co-Cu oxymanganospinels of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ chemical composition are first developed for possible application as high-precise NTC thermistors using nanophase segregation effects controlled by sintering technological route. It is shown that rock-salt NiO phase in these ceramics occurs a decisive role on parasitic degradation caused by thermal storage of the ceramics at the elevated temperatures.

Key words: nanostructure, oxide spinel, ceramics, degradation.

I. INTRODUCTION

Oxymanganospinel ceramics of mixed $(Ni,Cu,Mn,Co)_3O_4$ system are one of the most perspective materials for device application as negative temperature coefficient (NTC) thermistors, precise temperature measuring and sensors, in-rush current limiters, etc. [1]. That is why the problem of their functional stability and reliability is of high importance.

As a rule, to eliminate parasitic influence of uncontrolled degradation in NTC electroceramics, the methods of their chemical modification by metallic additives at the initial stages of technological preparation has been usually used [2]. These metallic additives, being located near intergranular regions in the vicinity of grain boundaries, diminish thermally-activated ageing phenomena by stabilizing intrinsic cationic distribution within individual ceramics grains. As a result, chemically-modified ceramics show a higher stability in comparison with non-modified ones.

An alternative approach to the above is developed in this work. In part, an additional rock-salt phase, which was not externally introduced at the initial stages of ceramics processing, but only segregated in the form of nanostructured extractions near inter-grain boundaries owing to purposefully modified high-temperature sintering route serves as an effective barrier to inhibit further degradation in spinel-type ceramics.

II. EXPERIMENTAL

Precise amounts of high-purity and previously tested carbonate salts corresponding to the final composition of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ were weighted and wet mixed. The mixture was thermally decomposed in the air at 700 ± 5 °C for 4 h. The prepared blanks were sintered in the air at different temperatures of T_s being 1040, 1200 and 1300 °C.

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The sintering route was arranged in such a way to ensure the necessary conditions for inhibition effect in degradation, the content of additionally extracted NiO phase with rock-salt NaCl-type structure having a decisive role. In fact, we deal with Ni-deficient ceramics in respect to stoichiometric $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ composition taken as a starting one in disproportionality calculations.

Four batches of ceramics with 1-12 % of NiO extractions were prepared according to the special regimes [3]. These regimes correspond to different portions of thermal energy transferred into ceramics during sintering. The latter was numerically determined as a square restricted by temperature-time curve above horizontal line corresponding to 920 °C (Fig. 1), the temperature of monophasic $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics formation.

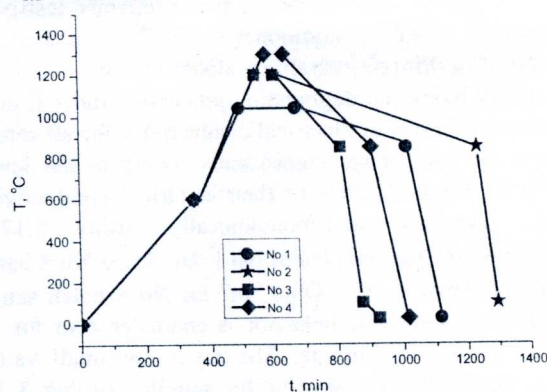


Fig. 1. Temperature-time curves corresponding to different technological regimes of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics preparation.

The values of thermally-transferred energy and amount of NiO phase in the studied ceramics estimated with XRD are presented in Table 1.

Table 1. Thermal energies transferred during sintering in $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics

Ceramics batch No	Thermally-transferred energy		Maximal T_s °C	NiO content %
	°C · min.	a.u.		
1	175	1.0	1040	1
2	465	2.7	1200	10
3	190	1.1	1200	12
4	465	2.7	1300	12

Electrical resistance measurements were performed with digital multimeter. The results of ageing tests were controlled by relative resistance drift (RRD) $\Delta R/R_0$ caused by ceramics storage at the temperature of 170 °C. These measurements were carried out in the normal conditions at 25 °C after certain hours of thermal exposure (24, 72, 144, 288, 500 hours). With a purpose of adequate mathematical description of the observed degradation kinetics, the

numerical values of different fitting parameters in the typical relaxation functions were calculated in such a way to minimize the mean-square deviation *err* of experimentally measured points from chosen relaxation function [4].

III. RESULTS AND DISCUSSION

The degradation of $(\text{Cu,Ni,Co,Mn})_3\text{O}_4$ mixed transition-metal manganite ceramics is known to be mainly governed by thermally-stimulated exchange in the occupation of tetra- and octahedral sites within spinel-structured grains by transition-metal cations preferentially such as Mn^{3+} and Mn^{4+} [4]. These cation redistribution processes can be effectively blocked by additional rock-salt phase extracted at the intergranular boundaries between ceramics grains. So it is expected the more content of this extracted phase, the high stability of the prepared ceramics will be achieved. Being within above assumption, we tried to choose the spinel-type $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics with optimal amount of additional NiO rock-salt phase served as a barrier to inhibit cation-redistribution degradation. The sintering route was arranged in such a way to prepare ceramics of principally different microstructural morphology. This allows to clear conditions necessary to inhibit degradation processes in the $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics.

The results of our electrical measurements testify that extractions of additional NiO phase in $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics alone are not necessary to effectively block the degradation processes. Indeed, despite activation energies of electrical conductivity for all ceramics batches do not change significantly, being at the level of 0.29-0.30 eV, the values of their electrical conductivity at 25 °C increases non-monotonically from 0.17 to 0.36 $\text{Ohm}^{-1}\cdot\text{m}^{-1}$ for samples of No 1, No 3 and No 2 batches, but drops down to 0.21 $\text{Ohm}^{-1}\cdot\text{m}^{-1}$ for No 4 batch samples. The above anomalous behavior is character also for RRD caused by 170 °C storage. The extremely small value of RRD near 2.5% is character for samples of No 3 batch (sintered at 1200 °C) having 12% of additional NiO phase, while ceramics samples of batch No 4 having the same amount of NiO phase but sintered at higher temperature (1300 °C) demonstrate sharp increase in RRD up to 18%.

As it follows in [3], the prepared ceramics differ significantly by evolution of their grain-pore microstructure. The batch No 1 samples are characterized by fine 1-3 μm grains [3]. The numerous intergranular pores are small enough, their sizes not exceeding 1-2 μm . White film, which can be attributed to additional rock-salt NiO phase extractions, weakly appears in these ceramics mainly near intergranular boundaries, sometimes it partially fills of pores. The samples of batch No 2 are characterized by larger grains with character sizes near 5-7 μm , some of them achieving 10 μm . White NiO film appears in these ceramics only in the regions of intergranular boundaries. The grain structure of the samples of batch No 3 is gradually different. The corresponding chip structure of these ceramics is more monolithic, it being characterized only by separate pores with 1-3 μm in sizes. White NiO film appears as bright layer of approximately 10 μm in thickness on the grain surface of

these samples. In contrast, the grain structure of the samples of batch No 4 attains a fully monolithic shape. Only some separate pores of relatively large sizes (near 3-5 μm) are observed in these ceramics, the NiO phase extractions appearing as uniform layer on ceramics surface.

Thus, the results of morphological study show that ceramics microstructure changes from fine-grained to monolithic one with corresponding increase in thermal energy transferred into ceramics bulk during sintering. This monolithization process reveals an inhibition influence on the degradation owing to additional NiO phase extractions. The samples of No 4 batch having as high as 12% of NiO phase reveal a relatively sharp increase in the RRD value achieving 18%.

The results of degradation kinetics modeling for $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics give an additional confirmation for the above conclusion. The fitting of experimentally observed degradation kinetics by stretched-exponential function is shown to be most optimal in terms of mean-square deviations. It should be noted that fitting route with partially-generalized relaxation function gives also a quite good correspondence, but this function is not optimal one in view of large number of fitting parameters.

It is quite understandable that extraction of additional NiO phase from spinel-structured $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics enlarges the dispersivity of the system, while the monolithization of ceramics structure causes an opposite effect. As a result, the ceramics samples of batch No 3 demonstrate the best suitability for stretched-exponential relaxation kinetics. That is why the non-exponentiality index L grows from 0.10 (batch No 1) to 0.66 for batch No 2 ceramics having a large amount of NiO, the similar increase being character for time constant τ too. However, the further increase in NiO content from 10 (batch No 2) to 12% (batches No 3 and 4) is associated with principally different processes of microstructural evolution. The batch No 3 ceramics has a more fine-grained structure, while those, the batch No 4, is more monolithized one.

IV. CONCLUSIONS

The spinel-type mixed transition-metal manganite ceramics of $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ composition with improved functional stability and reliability are prepared within modified sintering route owing to optimal combination in the amount of extracted rock-salt NiO phase and inner monolithization of bulk ceramics nanostructure.

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