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Structural studies of spinel manganite ceramics with positron annihilation lifetime spectroscopy

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Abstract. The new transition-metal manganite $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics for temperature sensors with improved functional reliability are first proposed. It is established that the amount of additional NiO phase in these ceramics extracted during sintering play a decisive role. This effect is well revealed only in ceramics having a character fine-grain microstructure, while the monolithization of ceramics caused by great amount of transferred thermal energy reveals an opposite influence. The process of monolithization from the position of evolution of grain-pore structure was studied in these ceramics using positron annihilation lifetime spectroscopy.

1. Introduction

The spinel-type $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics are widely used as one of the most perspective materials for application as negative temperature coefficient thermistors, precise temperature sensors, in-rush current limiters, etc. [1, 2]. That is why the problem of their functional stability and reliability is very important.

Previous investigations have shown that the quantity of the additional phase and its distribution in bulk and on the surface of ceramic samples are essentially influenced by temperature-time sintering regimes [3]. The reduction of NiO-phase content in ceramics unexpectedly essentially inhibited the development of thermal ageing, where the observed relative resistance changes didn't exceed 2-3 %.

As a rule, to eliminate the degradation effects in ceramics, the method of chemical modification by metallic additives at the initial technological stages of ceramics preparation is usually used [4, 5]. These metallic additives, being located in inter-granular regions closely to grain boundaries, diminish thermally-activated ageing phenomena owing by stabilizing the cationic distribution within individual ceramics grains. As a result, the chemically-modified ceramics show higher stability in comparison with non-modified ones.

Because of significant complications in the structure of these spinel-type ceramics revealed at the levels of individual grains, grain boundaries and pores [1], the further progress in this field is dependent to a great extent on the development of new characterization techniques, which can be used in addition to traditional ones. This concerns, in part, the positron annihilation lifetime (PAL) spectroscopy, the method only recently applied to fine-grained powders and ceramics [6, 7]. In general, the PAL being it sensitive to low electron density reflects a so-called void-species distribution within structural network of solids [6]. But meaningful interpretation of PAL data is well reliable only for some types of crystals. It was shown that in the case of ceramics these data were determined mainly by crystallographical features of individual grains, while structural disturbances due to intergranular contacts within ceramics were a subject for additional complications [6, 8-10].

The aim of this work is grain-pore structural studies of high-reliable transition-metal manganite $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics using PAL spectroscopy in addition to traditional methods of structural characterization.

2. Experimental

The precise amounts of high purity and previously tested carbonate salts were weighted and wet mixed. This mixture was thermally decomposed in the air at $700 \pm 5^\circ\text{C}$ for 4 h. Then the obtained powders were milled, blended with organic binder and pressed into the disks of approximately 10 mm in diameter and 1 mm in thickness. The prepared four batches of blanks were sintered in the air in respect to the time-temperature regimes (see Fig.1).

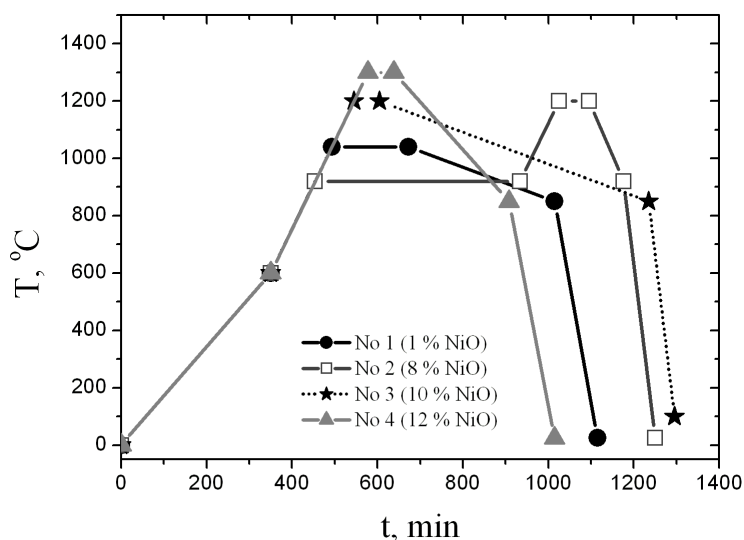


Figure 1. Time-temperature sintering regimes for $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics

It should be noted the sintering route of ceramics was performed to ensure all necessary conditions for inhibition effect in degradation [11], the content of additional NiO phase with NaCl-type structure having decisive role in the final ceramics structure. In fact, we deal with Ni-deficient ceramics in respect to stoichiometric $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ composition taken as start one in disproportionality calculations. Four batches of $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics with 1-12 % of NiO phase were prepared owing to different amounts of thermal energy transferred during the sintering (batch No 1 – 1 % NiO, batch No 2 – 8 % NiO, batch No 3 – 10 % NiO, batch No 4 – 12 % NiO). The latter was numerically determined as square value restricted by temperature-time curve above straight line corresponding to 920°C , which is the temperature of monophase $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics formation [11].

In respect to the results of microstructure characterization with X-ray diffractometry method, the lattice constant of the main spinel was slightly grown from 8.38 до 8.41 Å without significant changes in the parameter of additional NiO phase (at the level of 4.17-4.19 Å) despite increase in the content of this phase from 1 to 12 %.

The microstructure of the sintered ceramics was probed using electron microscope JSM-6700F, cross-sections morphology of the samples being tested near surface (0-70 μm depth) and chip centers.

The PAL measurements were performed with an ORTEC spectrometer using ^{22}Na source placed between two sandwiched ceramic samples [12-14]. The obtained data were treated with LT computer program [15], the best results corresponding to two-component fitting procedures. The numerical values of trapping parameters (positron lifetime in defect-free bulk τ_b , average positron lifetime τ_{av} , and positron trapping rate of defect κ_d) were calculated using short and long positron-trapping lifetimes τ_1 and τ_2 , as well as component intensities I_1 and I_2 ($I_1 + I_2 = 1$) [7, 11]:

$$\kappa_d = \frac{I_2}{I_1} \left(\frac{1}{\tau_b} - \frac{1}{\tau_2} \right), \quad (1)$$

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}, \quad (2)$$

$$\tau_{av.} = \tau_1 I_1 + \tau_2 I_2. \quad (3)$$

In addition, the difference $(\tau_2 - \tau_b)$ can be accepted as a size measure of extended defects where positrons are trapped, the τ_2/τ_b ratio represents the nature of these defects [7, 11-14].

3. Results and Discussion

To explain the above phenomena, microstructure of the prepared ceramics was studied. As it follows from Fig. 2, the prepared ceramics samples differ significantly by their grain-pore microstructure.

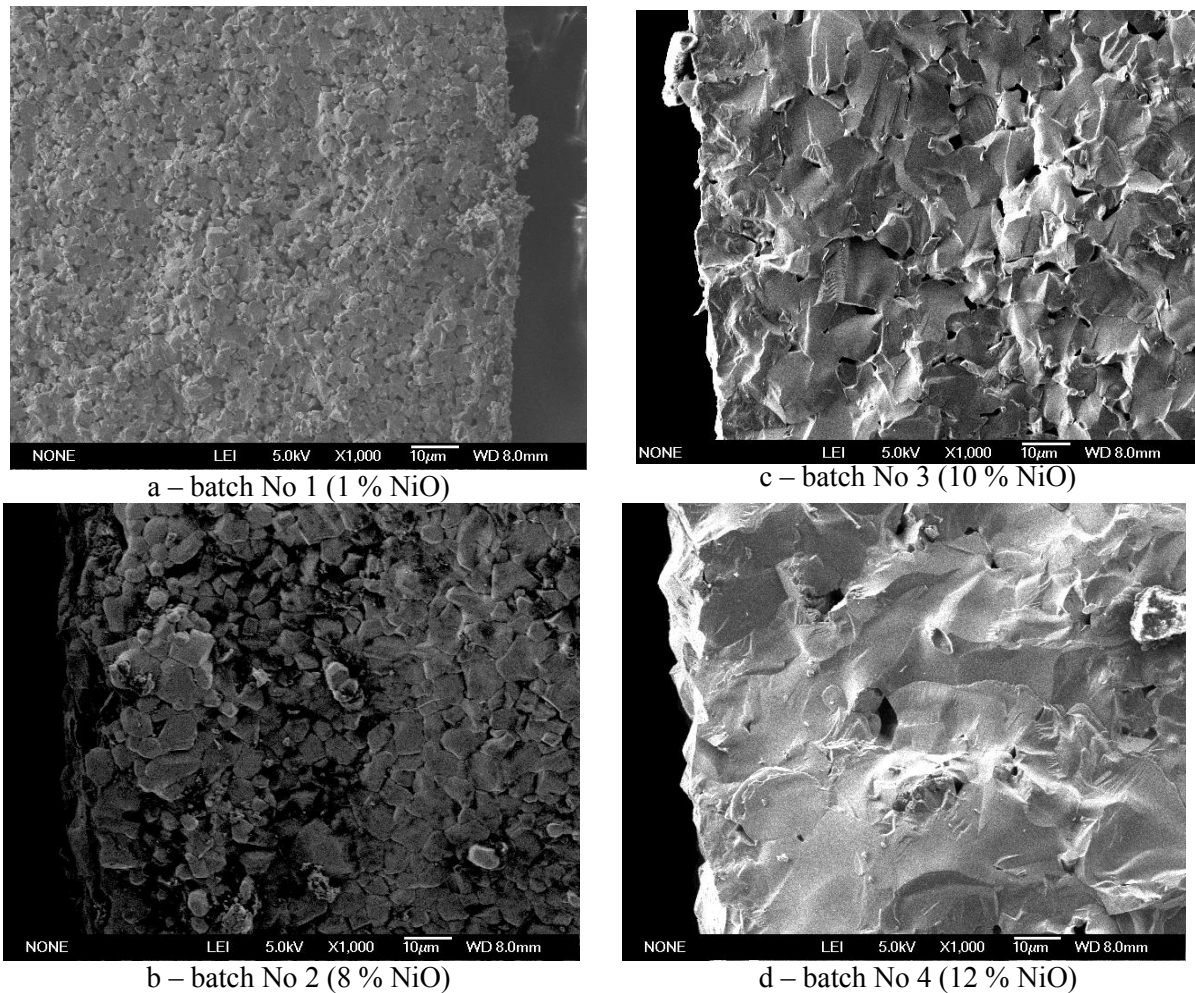


Figure 2. Microstructure of $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics

The samples of batch No 1 (Fig. 2a) are characterized by fine 1-3 μm grains. The numerous intergranular pores are small enough in these samples, their sizes not exceeding 1-2 μm . White film, which can be attributed to additional NiO phase extractions, weakly appears in these ceramics mainly near intergrain boundaries, sometimes it partially fills of pores. The samples of batch No 2 (Fig. 2a)

are characterized by larger grains with sizes near 5-7 μm , some of them achieving 10 μm . The white NiO film appears in these ceramics only in the regions of grain boundaries. The grain structure of the samples of batch No 3 (Fig. 2c) gradually changes. 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 10 μm thickness on the grain surface of these samples. In contrast, the grain structure of the samples of batch No 4 (Fig. 2d) attains fully monolithic shape. Only some individual pores of relatively large sizes (near 3-5 μm) are observed in these ceramics, the NiO appearing as uniform layer on the whole ceramics surface. The observed additional NiO phase is non-uniformly distributed within ceramics bulk, being more clearly pronounced near grain boundaries. These phase extractions serve as specific trapping centers for positrons penetrating ceramics.

By accepting two-state positron trapping model [13, 14], for spinel-type ceramic materials the first component of spectra was connected with main spinel structure and the second one – with extended defects located near grain boundaries in the vicinity of additional extracted phases. The intensity I_1 corresponds to the amounts of the main spinel phase, while the I_2 intensity – to the amount of addition NiO phase near grain boundaries.

The lifetime of the first and second components for $\text{Cu}_{0.1}\text{Ni}_{0.8}\text{Co}_{0.2}\text{Mn}_{1.9}\text{O}_4$ ceramics is typically for spinel-structured materials and equal ~ 0.37 and 0.20 ns, accordingly (see Table 1). The lower τ_1 value in the batch No 2 (0.17 ns) well correlated with Ni content in different crystallographical positions. Since the amount of grain/pores in the sample of batch No 2 was greater, the process of positron trapping in these ceramics was more intensive (the positron trapping rate of defects increased from 0.48 to 0.62 ns^{-1}).

Table 1. PAL characteristics of $\text{Cu}_{0.4}\text{Co}_{0.4}\text{Ni}_{0.4}\text{Mn}_{1.8}\text{O}_4$ ceramics mathematically treatment within two-component fitting procedure

Sample batch	Fitting parameters				Component input		Positron trapping modes				
	τ_1 , ns	I_1 , a.u.	τ_2 , ns	I_2 , a.u.	$\tau_{av.}^1$, ns	$\tau_{av.}^2$, ns	$\tau_{av.}$, ns	τ_b , ns	κ_d , ns^{-1}	$\tau_2 - \tau_b$, ns	τ_2/τ_b
No 1	0.19	0.82	0.38	0.18	0.16	0.07	0.23	0.21	0.48	0.17	1.8
No 2	0.17	0.79	0.36	0.21	0.14	0.07	0.21	0.19	0.62	0.17	1.9
No 3	0.20	0.86	0.37	0.14	0.17	0.05	0.22	0.21	0.34	0.16	1.7
No 4	0.21	0.84	0.37	0.16	0.18	0.06	0.23	0.22	0.33	0.15	1.7

The intensity of the second component for samples of batch No 1 is 18 %, although amount of additional NiO phase in this batch is small (1 %). This additional phase is localized near grain boundaries and partly fills pores. In samples of batch No 2 the intensity I_2 increase to 21 % (see Table 1) correspondingly to amount of NiO phase. In batch No 3 ceramics, the grain-pore structure was not developed because of occurred monolithization process accompanied by surface extraction of additional NiO phase. The same was character for batch No 4 ceramics samples. These transformations were in good agreement with positron trapping parameters.

Nevertheless, there were no significant changes in $\tau_{av.}$, τ_b , τ_2/τ_b and $(\tau_2 - \tau_b)$. In all cases, the same type of positron trapping centre is formed. The character size of these extended positron traps near grain boundaries estimated due to $(\tau_2 - \tau_b)$ difference is close to single-double atomic vacancies [6].

Conclusions

Thus, it should be concluded that the results of PAL measurements confirming the interphase mass-transfer processes occurred in mixed transition-metal manganite ceramics caused by monolitization processes during technological modification and owing to optimal content of additional NiO phase. Obtained results are in well agreement with microstructural X-ray diffractometry and electron microscopy data, confirming the structural changes in these ceramics caused by their technological modification.

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