Inner-structured analysis of Ni-enriched ceramics by PALS method

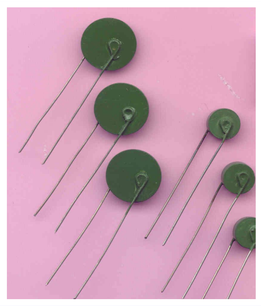
H. Klym[1], A. Ingram[2], Yuriy Kostiv[1], O. Shpotyuk[3]

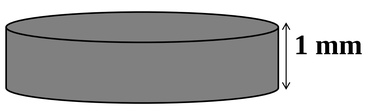
[1]Lviv Polytechnic National University, Lviv, Ukraine
yura.kostiv@gmail.com, klymha@yahoo.com
[2]Opole University of Technology, Opole, Poland
[3]Vlokh Institute of Physical Optics, Lviv, Ukraine

Introduction

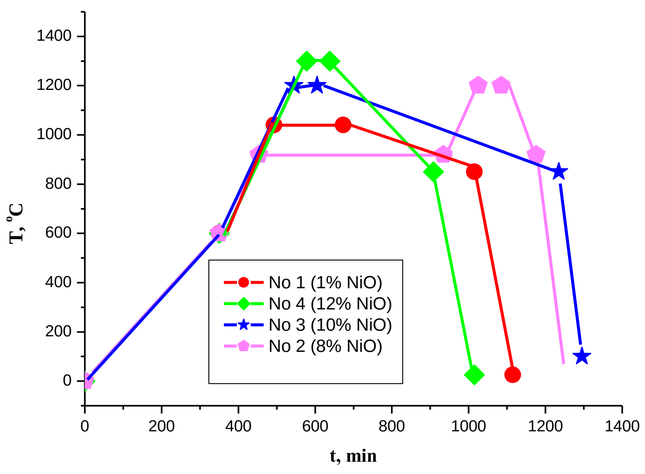
The spinel-type ceramics based on mixed transition-metal manganites have been widely used as one of the most perspective materials for sensor application. The aim of this work is structural studies of these ceramics exemplified by $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ with positron annihilation lifetime spectroscopy, the method successfully applied previously to nanoscaled fine-grained materials.

OBJECT:
temperature-sensitive spinel-type $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics





Technological time-temperature regimes:

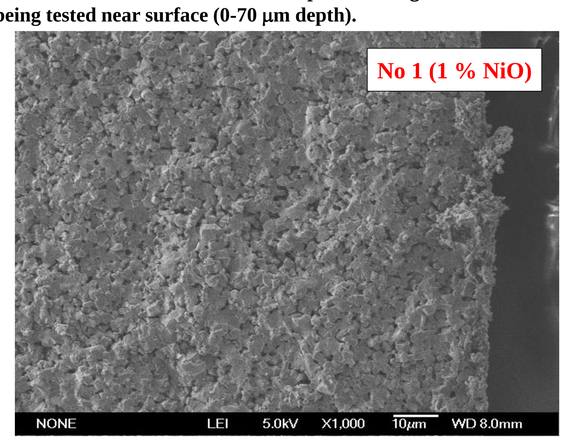


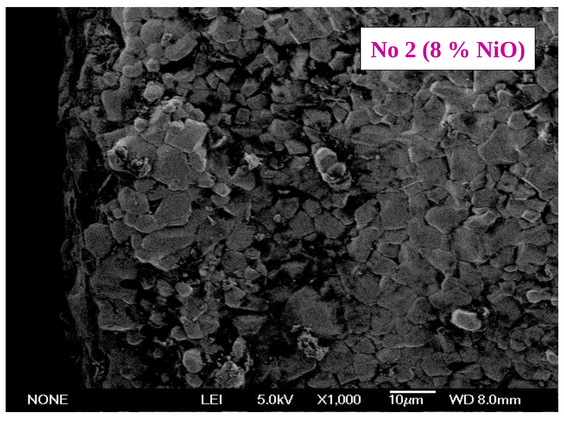
The prepared blanks were sintered in the air at the sintering temperature.
The content of additional NiO phase with NaCl-type structure having decisive role in the final ceramics structure. In fact, we deal with Ni-deficient ceramics in respect to stoichiometric $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ composition taken as start one in disproportional calculations.
Four batches of ceramics with 1-12 % of NiO phase were prepared owing to different amounts of thermal energy transferred during the sintering:
No 1– 1 % NiO,
No 2 – 8 % NiO,
No 3 – 10 % NiO,
No 4 – 12 % NiO.

No 1		No 2		No 3		No 4	
t, min	T, ^{0}C	t, min	T, ^{0}C	t, min	T, ^{0}C	t, min	T, ^{0}C
350	600	350	600	350	600	350	600
493	1040	454	920	545	1200	578	1300
673	1040	934	920	605	1200	638	1300
1015	850	1025	1200	1235	850	908	850
1115	25	1095	1200	1295	100	1015	25
		1176	920	1350	100		

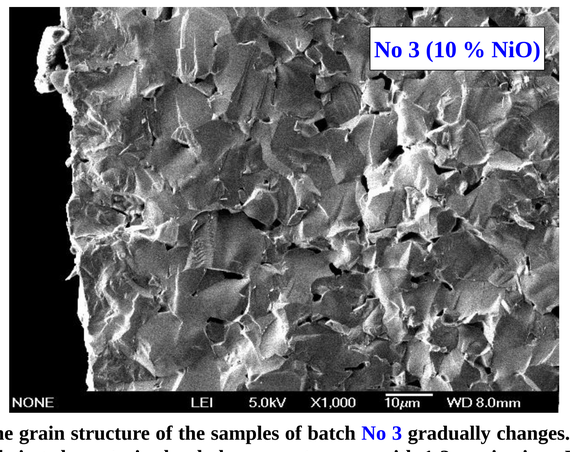
Microstructure of ceramics

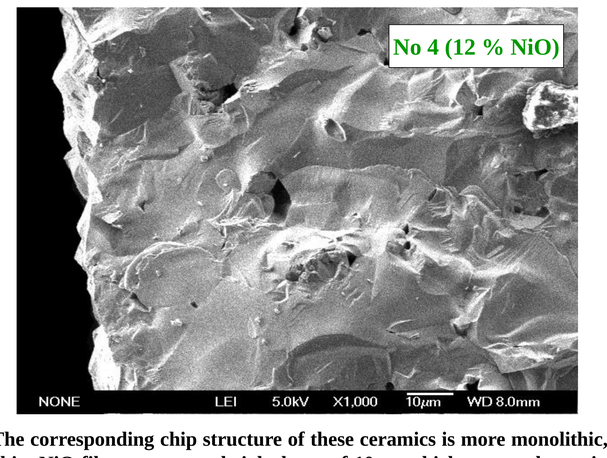
The microstructure of ceramics was probed using electron microscope JSM-6700F (Japan) cross-sections morphology of the samples being tested near surface (0-70 μm depth).





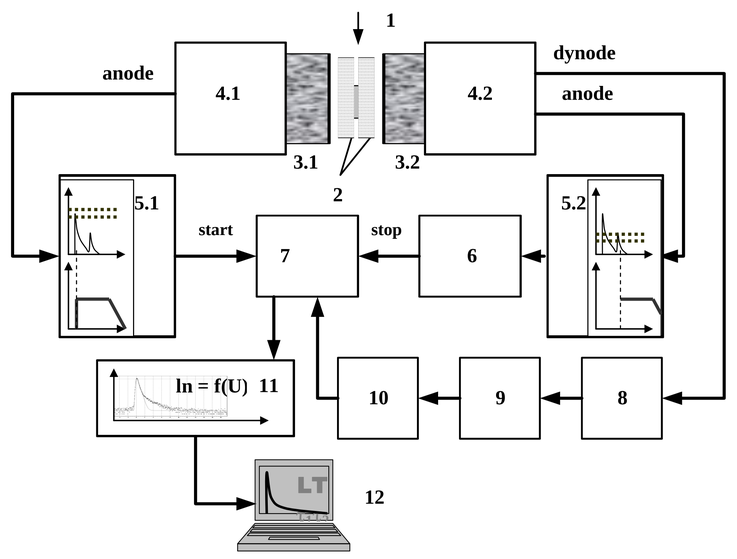
The samples of batch No 1 are characterized by fine 1-3 μm grains. The numerous intergranual pores are small enough in these samples, their sizes not exceeding 1-2 μm.White film, which can be attributed to additional NiO phase extractions, weakly appears in these ceramics mainly near grain boundaries, sometimes it partially fills of pores.
The samples of batch No 2 are characterized by larger grains with sizes near 5-7 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 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 attains fully monolithic shape.

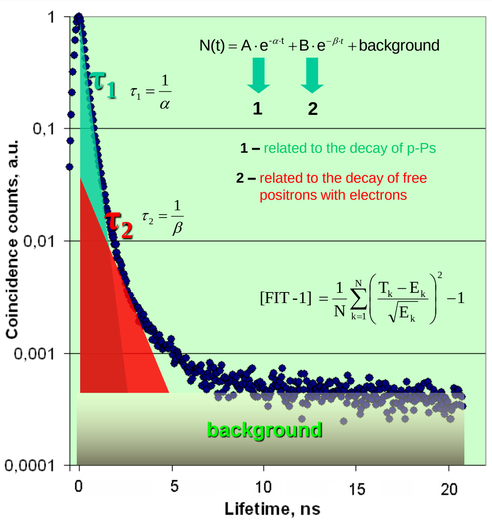
EXPERIMENTAL:
Positron Annihilation Lifetime (PAL) Spectroscopy



Block-scheme of conventional sample-source "sandwich" arrangement for PAL measurements using the ORTEC apparatus:

1 – foil-covered ^{22}Na source,
2 – two identical samples,
3.1 and 3.2 – scintillators of γ-quanta,
4.1 and 4.2 – photomultipliers,
5.1 and 5.2 – constant fraction discriminators,
6 – delay line,
7 – time-pulse height converter,
8 – preamplifier,
9 – amplifier,
10 – single channel analyzer,
11 – multichannel analyzer,
12 – personal computer.

MATHEMATICAL TREATMENT of PAL DATA:
LT computer program, 2-component fitting procedure



$\tau_{av.} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}$	**Mean positron lifetime:** reflects cumulative defect environment prevailing in sample
Lifetime τ_b: associated with the positron trapping in defect-free bulk	$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}$
$\kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right)$	**Positron trapping rate in defects**
$\tau_2 - \tau_b$	Size measure of extended defects where positrons are trapped
Represents the nature of defects	τ_2 / τ_b

RESULTS:
PAL characteristics

Sample	Fitting parameters				Components input	
	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	$\tau_{av.}^{1}$, ns	$\tau_{av.}^{2}$, ns
No 1 (1 % NiO)	0.19	0.82	0.38	0.18	0.16	0.07
No 2(8 % NiO)	0.17	0.79	0.36	0.21	0.14	0.07
No 3 (10 % NiO)	0.20	0.86	0.37	0.14	0.17	0.05
No 4 (12 % NiO)	0.21	0.84	0.37	0.16	0.18	0.06

The intensity I_1 corresponds to the amounts of the main spinel phase, the I_2 intensity – to the amount of addition NiO phase near grain boundaries.

Sample	Positron trapping modes				
	$\tau_{av.}$, ns	τ_b, ns	κ_d, ns^{-1}	$\tau_2 - \tau_b$, ns	τ_2/τ_b
No 1 (1 % NiO)	0.23	0.21	0.48	0.17	1.8
No 2 (8 % NiO)	0.21	0.19	0.62	0.17	1.9
No 3 (10 % NiO)	0.22	0.21	0.34	0.16	1.7
No 4 (12 % NiO)	0.23	0.22	0.33	0.15	1.7

The τ_2 lifetime is typically for spinel ceramics (~0.37 ns, and $\tau 1 \approx 0.20$ ns).
The lower τ_1 value in the batch No 2 (0.17 ns) well correlated with Ni content in different crystalographical 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}).
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.
There were no significant changes in $\tau_{av.}$, τ_b, τ_2/τ_b and $(\tau_2-\tau_b)$ testifying in a favor of the same nature of trapping sites.

Conclusions

The results of positron annihilation lifetime measurements are in well agreement with microstructural X-ray dfiffractometry and scanning electron microscopy data, confirming the structural changes in manganite ceramics caused by their technological modification.