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Technological modification of spinel-based $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ceramics

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Abstract

The peculiarities of electroceramics formation in $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ($0.1 \leqslant x \leqslant 0.8$; $0.1 \leqslant y \leqslant 0.9 - x$) system under different sintering conditions are studied by the methods of X-ray diffraction, optical microscopy, electron-probe microanalysis and electrical measurements. Structure-properties relations for these ceramic semiconducting materials, obtained at different sintering temperatures are discussed. The electrical conductivity and activation energy show strong dependence on sintering temperature. Two groups of investigated ceramics with a different character of electrical conductivity dependences on the temperature of sintering are distinguished. Obtained results are explained in the framework of the model of thermally induced cation rearrangement in octahedral and tetrahedral sites of electroceramics. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sintering; Spinels; Thermistors

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1. Introduction

As we reported earlier[1] a number of compositions inside of quaternary semiconducting ceramic system $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ are used for the development of NTC thermistors. With the aim to obtain the stable and reliable elements based on these complex materials the optimum technological conditions, first of all sintering temperature must be established. Formation of homogeneous solid solutions with spinel structure is the necessary condition for quality thermistor ceramics. The methods of optical microscopic characterisation, X-ray diffraction, electron-probe microanalysis and electrical measurements are used in this work with the aim to study the processes of formation of the ceramic matrix.

2. Experimental

The investigated $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ($0.1 \leqslant x \leqslant 0.8$; $0.1 \leqslant y \leqslant 0.9 - x$) system was obtained as the result of superposition of the regions of homogeneous solid solutions in quaternary Mn–Co–Ni–Cu oxide system. Fourteen compositions inside of concentration triangular, restricted by $CuMn_2O_4$, $MnCo_2O_4$ and $NiMn_2O_4$, were chosen as basic ones.

The traditional technology was used for the preparation of ceramic specimens.[1] High purity $CuCO_3 \cdot mCu(OH)_2$, $NiCO_3 \cdot mNi(OH)_2 \cdot nH_2O$, $CoCO_3 \cdot mCo(OH)_2 \cdot nH_2O$ and $MnCO_3 \cdot mMn(OH)_2 \cdot nH_2O$ salts were chosen as starting materials. Samples of various compositions were synthesized at three different sintering temperatures T_s (in 900–1300°C range) corresponding to region 1: $T_s = (0.5–0.75)T_m$ (T_m — melting point), region 2: $T_s = (0.75–0.85)T_m$ and region 3: $T_s > 0.85T_m$.

Samples were prepared in the form of disks. Microscopic investigations were carried out on the metallographic specimens polished to mirror surfaces and chemically etched. Silver paste contacts were applied on the part of the samples used for electrical measurements. Phase composition, dimension and shape of grains were studied using "Neophot" optical metallographic microscope (×200–500 magnification).

DRON-0.5 diffractometer was used for X-ray diffraction investigations. "Camebax" microanalyser was applied for electron-probe determination of chemical elements concentrations.

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3. Results and discussion

Influence of T_s on the structure of $Cu_xNi_{1-x-y}Co_{2y}$ $Mn_{2-y}O_4$ ceramics is demonstrated in Table 1. The following abbreviations are used: SS — solid solution; SPSS — single phase solid solution; TO — traces of oxides; DPSSVC — double phase solid solution of variable composition; CMC — complex multiphase composition; CMOC — complex multiphase oxide composition; DPSS — double phase solid solution; DPC — double phase composition; DPCSS — double phase composition of solid solutions; SSMIAP — solid solution with microscopic inclusions of additional phases.

Application of carbonates for ceramics synthesis permits to obtain the dispersive powder materials, which can be sintered at the temperatures near 0.5 T_m.

We established that at T_s from the range (0.5–0.75) T_m (regime 1) ceramics have low density, low mechanical

Table 1
Structural-microscopical features of $Cu_xNi_{1-x-y}Co_{2y}$ $Mn_{2-y}O_4$ semiconducting ceramics in dependence on composition and sintering temperature

Chemical composition	T_s, (°C)	Phase composition	Lattice parameter a, (Å)	Average diameter of crystallites (d μm)	Density ρ, (kg/m^3×10^3)	σ_{25}, (Ω^{-1} m^{-1})	ΔE_{17-67} (eV)	Sample no.[a]
$Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$	1100	SPSS	8.302 (3)	4.9	4.49	0.34	0.28	1_3
	1200	SPSS	8.327 (1)	13.1	4.92	0.43	0.30	1_4
	1300	DPSSVC	8.321 (3)	34.2	4.41	0.49	0.30	1_5
$Cu_{0.2}Ni_{0.1}Co_{1.4}Mn_{1.3}O_4$	1100	SPSS	8.303 (2)	6.6	4.90	0.75	0.28	2_3
	1200	SPSS	8.347 (2)	16.5	4.85	1.04	0.28	2_4
	1300	CMC	8.304 (5)	31.7	4.76	0.80	0.28	2_5
$Cu_{0.45}Ni_{0.1}Co_{0.9}Mn_{1.55}O_4$	1100	SPSS	8.330 (3)	66.7	4.73	4.61	0.25	3_3
	1200	SPSS	8.408 (4)	95.1	4.58	3.27	0.23	3_4
	1300	CMC	8.355	37.5	4.34	4.32	0.24	3_5
$Cu_{0.8}Ni_{0.1}Co_{0.2}Mn_{1.9}O_4$	900	CMOC	8.316 (1)	3.1	4.51	8.98	0.18	4_1
	1000	SPSS	8.348 (1)	6.9	4.84	15.73	0.18	4_2
	1100	DPSS	8.335 (2)	34.5	4.67	18.92	0.18	4_3
$Cu_{0.45}Ni_{0.45}Co_{0.2}Mn_{1.9}O_4$	1000	DPC	8.358 (3)	9.6	3.66	1.20	0.20	5_2
	1100	SPSS	8.366 (3)	18.7	4.75	4.32	0.18	5_3
	1200	SPSS	8.364 (2)	31.4	4.68	3.81	0.20	5_4
$Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$	1100	SS + TO	8.383 (4)	4.1	4.03	0.11	0.28	6_3
	1200	SPSS	8.382 (1)	4.4	4.54	0.30	0.29	6_4
	1300	SPSS + TO	8.389 (4)	20.8	4.72	0.39	0.30	6_5
$Cu_{0.1}Ni_{0.45}Co_{0.9}Mn_{1.55}O_4$	1100	SPSS	8.334 (3)	3.2	4.75	0.38	0.26	7_3
	1200	DPCSS	8.338 (8)	5.3	4.79	0.32	0.25	7_4
	1300	DPCSS	8.345 (4)	20.8	4.83	0.27	0.32	7_5
$Cu_{0.2}Ni_{0.2}Co_{1.2}Mn_{1.4}O_4$	1100	SPSS	8.326 (1)	5.8	4.64	0.92	0.30	8_3
	1200	DPCSS	8.343 (3)	12.8	4.58	1.43	0.29	8_4
	1300	SPSS	8.309 (2)	14.4	4.49	0.80	0.29	8_5
$Cu_{0.4}Ni_{0.2}Co_{0.8}Mn_{1.6}O_4$	1100	SPSS + TO	8.341	3.4	4.56	3.16	0.25	9_3
	1200	SPSS	8.348	22.4	4.62	4.23	0.25	9_4
	1300	SPSS	–	–	4.35	1.61	0.27	9_5
$Cu_{0.6}Ni_{0.2}Co_{0.4}Mn_{1.8}O_4$	900	SPSS	8.338 (5)	–	3.84	2.32	0.25	10_1
	1000	SPSS	8.358 (3)	38.7	4.41	7.85	0.24	10_2
$Cu_{0.4}Ni_{0.4}Co_{0.4}Mn_{1.8}O_4$	1100	SPSS	8.372 (2)	11.2	4.64	3.64	0.28	11_3
	1200	SPSS	8.328 (3)	16.7	4.74	1.83	0.23	11_4
	1300	SPSS	–	–	4.63	2.64	0.26	11_5
$Cu_{0.2}Ni_{0.6}Co_{0.4}Mn_{1.8}O_4$	1100	SPSS	8.359 (2)	5.3	4.80	1.86	0.28	12_3
	1200	SPSS	8.365 (2)	11.2	4.84	2.11	0.28	12_4
	1300	SPSS	8.368 (2)	19.2	4.83	1.34	0.28	12_5
$Cu_{0.2}Ni_{0.4}Co_{0.8}Mn_{1.6}O_4$	1100	SPSS	8.415 (16)	–	4.54	0.79	0.26	13_3
	1200	SPSS	8.347 (2)	8.3	4.62	1.53	0.26	13_4
	1300	SPSS + TO	–	–	4.71	0.86	0.26	13_5
$Cu_{0.33}Ni_{0.33}Co_{0.68}Mn_{1.66}O_4$	1100	SPSS	8.340 (2)	–	4.79	1.24	0.25	14_3
	1200	SSMIAP	8.371 (3)	13.6	4.74	1.87	0.24	14_4
	1300	SPSS	8.365 (2)	16.8	4.44	0.99	0.26	14_5

[a] Lower index in 'Sample no.' column represents the sintering temperature: 1 — 900°C, 2 — 1000°C, 3 — 1100°C, 4 — 1200°C, 5 — 1300°C.

strength and medium dimensions of grains. As we can see for $Cu_{0.2}Ni_{0.1}Co_{1.4}Mn_{1.3}O_4$ sample (Fig. 1a) the structure is characterized by a large number of pores on the crystallites boundaries. These pores look as communicating channels and closed regions while they are absent inside the crystallites. Such ceramics are very inconvenient for mechanical treatment (polishing, grinding) because of intensive movement of the crystallites out of the surface layers. It means that on this stage only sintering of separate crystallites takes place, resulting in the formation of a crystallite grid, where every component has structural individuality. This was confirmed by X-ray phase analysis that at these temperatures, along with solid solutions with spinel structure, the inclusions of Ni, Mn, Co and Cu oxides are present. These oxides are undesirable for thermistor manufacturing.

Samples obtained at (0.75–0.85) T_m (regime 2) contain large, uniformly distributed grains (Fig. 1b). Micrographs clearly reveal the rounded pores localized on the boundaries and, rarely, inside the grains. The amount of these pores is not so large as in the case of regime 1 but their effective diameter rises. It is supposed that the coalescence and the repair of smaller pores cause above-mentioned structural changes with T_s increasing. This process strongly depends on the dimensions of initial pores. If the initial pores are larger than the surrounding crystallite grains then we assume that repair takes place owing to the viscous run off under the influence of capillary pressure and the volume diffusion of substance into the pores. Contrary, if pores are smaller than crystallites, only the repair mechanism with volume diffusion takes place. Mainly, ceramics sintered at regime 2 are homogeneous solid solutions with spinel structure. Such materials have stable repetitive parameters and they are proper for the development of NTC thermistors.

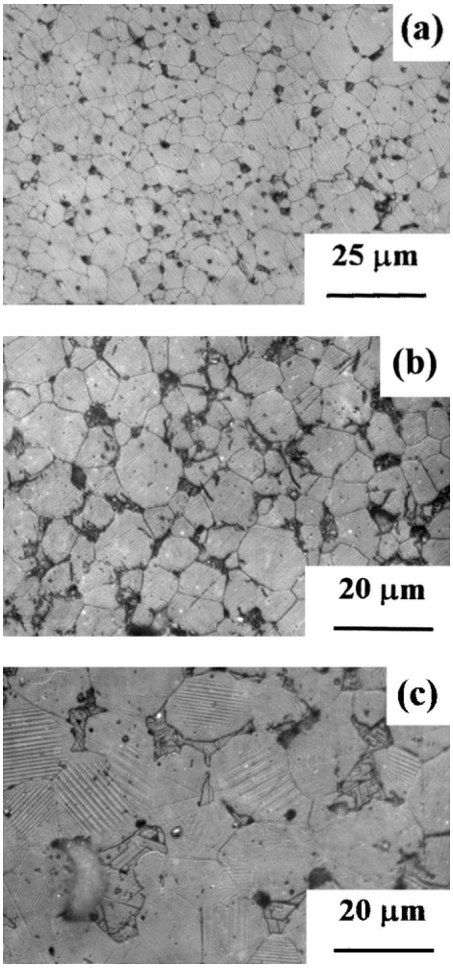

Fig. 1. Micrographs of $Cu_{0.2}Ni_{0.1}Co_{1.4}Mn_{1.3}O_4$ ceramic samples sintered at: (a) 1100°C (×500); (b) 1200°C (×400); (c) 1300°C (×400).

High-temperature sintering at $T_s > 0.85\ T_m$ (regime 3) leads to the re-crystallization of ceramics caused by thermally activated movement of grain boundaries. This conclusion is confirmed by large diameter of grains, existence of pores inside of grains as well as on the boundaries, clear orientation of separate grains, broadening and spheroidization of pores, large amount of external inclusions located on the boundaries and inside the grains (Fig. 1c). Re-crystallization leads to the decrease of density and extracting of additional phases that are confirmed by X-ray phase analysis. Thus, as a rule, ceramics sintered at regime 3 are multiphase and cannot be used for the manufacturing of thermistors. Moreover, for compositions with a large concentration of Co and Mn we can see (Fig. 1c) the high density of planar defects. These defects are similar to ones described previously,[2] where micro-twins or very thin "tweed" structure was observed in quenched NTC ceramics.

Dependences $\sigma(T)$ for four chosen ceramic compositions obtained at different sintering temperatures are shown in Fig. 2.

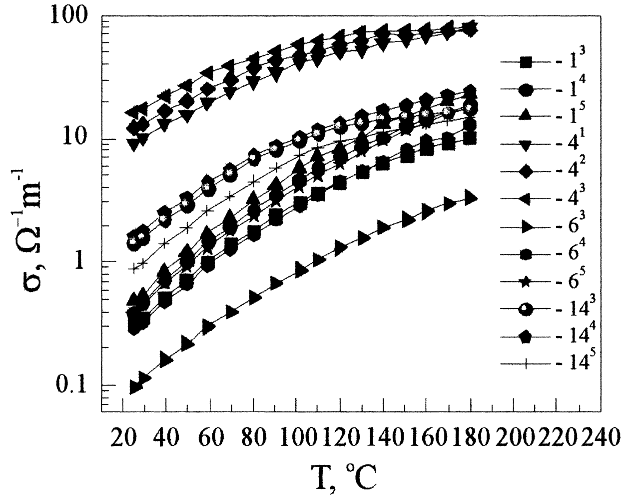

Fig. 2. Temperature dependences of electrical conductivity σ for the investigated samples of 1, 4, 6 and 14 compositions, sintered at different temperatures.

The value of σ depends strongly on T_s (see Fig. 3 and Table 1). Some compositions are characterized by the monotonous character of $\sigma(T_S)$ (curve 1), while for another set of compositions this dependence reveals the extreme points (curves 2 and 3). It must be noted that all compositions presented in Fig. 3 are characterized by a similar type of crystallite-pore inhomogeneity of polycrystalline materials at the same T_s.

The monotonous increasing of σ with T_s for $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ composition can be explained taking into account the similar character of such dependence in $NiMn_2O_4$,[3,4] which is the dominant structural unit for our system. Authors connect the above behaviour with thermally activated migration of Ni^{2+} cations between octahedral and tetrahedral sites.

Deviations from monotonicity of $\sigma(T_s)$ for Cu-enriched compositions such as $Cu_{0.4}Ni_{0.4}Co_{0.4}Mn_{1.8}O_4$ and $Cu_{0.2}Ni_{0.6}Co_{0.4}Mn_{1.8}O_4$ can be associated with the competition of two processes: the above-mentioned process of Ni^{2+} migration and the change of Cu cations valence from Cu^{1+} to Cu^{2+}.[5]

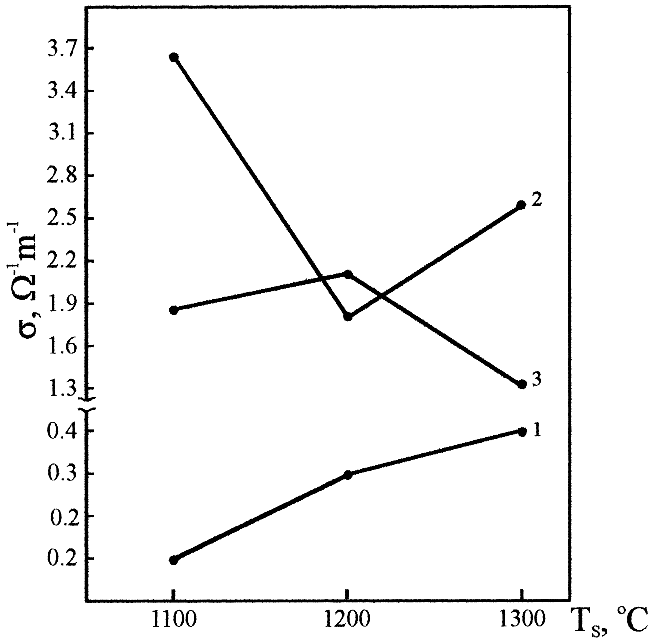

Fig. 3. Variation of the electrical conductivity σ for compositions 6, 11 and 12 (curves 1, 2 and 3) as a function of sintering temperature T_s.

4. Conclusions

Electrical conductivity and microstructure of studied $Cu_xNi_{1-x-y}Co_{2y}\ Mn_{2-y}O_4$ semiconducting ceramics are particularly dependent on sintering temperature. Technological modification, based on correct choice of T_s, gives the possibility of obtaining the materials that are optimum for NTC thermistor application. Ceramics, obtained at $T_s \sim (0.75–0.85)\ T_m$, are single phase solid solutions, possessing statistically uniform distribution of crystalline grains. It is supposed that the character of $\sigma(T_s)$ behaviour for considered ceramic compositions can be determined by the changes in cation distribution at different T_s.

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