Journal of the European Ceramic Society 21 (2001) 1783–1785

www.elsevier.com/locate/jeurceramsoc

Controlled thermistor effect in the system $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$

M. Vakiv [a], O. Shpotyuk [a,b,*], O. Mrooz [a], I. Hadzaman [a,c]

[a] *Scientific Research Company "Carat", 202, Stryjska Str., Lviv, 79031, Ukraine*
[b] *Physics Institute of Pedagogical University, 13/15, al. Armii Krajowej, Czestochowa, 42201, Poland*
[c] *Drohobych State Pedagogical University, 24, I.Franko Str., 82100, Drohobych, Ukraine*

Received 4 September 2000; received in revised form 2 November 2000; accepted 15 November 2000

Abstract

The problem of selection guidelines for oxide semiconducting ceramics with controlled thermistor effect, prepared on the basis of complex $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ($0.1 \leqslant x \leqslant 0.8$; $0.1 \leqslant y \leqslant 0.9-x$) chemical system and restricted by $CuMn_2O_4$, $MnCo_2O_4$ and $NiMn_2O_4$ spinel-structured compounds, is discussed. It is shown that the developed ceramic thermistors with a wide range of predetermined exploitation parameters (rated resistance from 2 to 21,500 Ω, material-specific constant B of NTC thermistor from 2435 to 3365 K), as well as a high level of reliability can be obtained using the proper methods of technological, compositional and design modifications. The attempt to establish a general relationships between chemical composition, technological features of sintering and electrical properties for single-phase ceramics is made, using the method of simplex matrices of the 4-fold D-optimum plan.

Keywords: Electrical conductivity; Electrical properties; Spinels; Thermistors

1. Introduction

Spinel-structured semiconducting ceramics (SSSC) with high value of negative temperature coefficient (NTC) of resistance are the most known materials for NTC thermistors manufacturing.[1–3] Traditionally a solid solutions based on transition metal oxides are used. In particular, the sets of NTC thermistors with a wide range of exploitation parameters, a low dependence of electrical properties on cation content and, as a result, a high level of technological reproducibility can be obtained in the limits of ternary Mn–Cu–Co, Mn–Co–Ni and Mn–Cu–Ni oxide systems.[4] But sometimes it is impossible to obtain by this way the suitable materials for industrial manufacturing of NTC thermistors, possessed a predetermined range of rated resistances, a high temperature sensitivity (determined by a material-specific constant B) and a high level of reliability and reproducibility. Thus, it is important to work out a correct approach to the problem on the selection of SSSC for practical applications.

With the above aim, we consider in this paper the selection possibilities in quaternary Cu–Ni–Co–Mn oxide system, restricted by cubic spinels $CuMn_2O_4$, $MnCo_2O_4$ and $NiMn_2O_4$. Being within the limits of $CuMn_2O_4$–$MnCo_2O_4$–$NiMn_2O_4$ concentration triangle (which can be presented as $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ chemical system at $0.1 \leqslant x \leqslant 0.8$ and $0.1 \leqslant y \leqslant 0.9-x$) and having precisely determined technological conditions, we can select the continuous solid solutions, which are the most suitable for thermistors manufacturing. The attempts to resolve partially this problem have been carried out previously for some chosen SSSC compositions from this chemical system.[5]

The final essence of this work is to establish for the $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ system the general relationships between SSSC chemical composition, from the first side, technological features of sintering for single-phase ceramics preparation, from the second side, and electrical properties of the prepared thermistors, from the third side, using the method of simplex matrices of the 4-fold D-optimum plan.[6]

2. Experimental

Fig. 1 shows the whole variety of the investigated SSSC compositions, being uniformly distributed in the limits of $CuMn_2O_4$–$MnCo_2O_4$–$NiMn_2O_4$ concentration triangle.

* Corresponding author. Tel.: +380-322-63-83-03; fax: +380-322-63-22-28.

E-mail address: shpotyuk@novas.lviv.ua (O. Shpotyuk).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00115-7

The traditional ceramic technology was used in order to obtain the investigated samples.[4,5] The high purity and tested raw materials ($CuCO_3{\cdot}mCu(OH)_2$, $NiCO_3{\cdot}mNi(OH)_2{\cdot}nH_2O$, $CoCO_3mCo(OH)_2{\cdot}nH_2O$ and $MnCO_3{\cdot}mMn(OH)_2{\cdot}nH_2O$) were chosen as initial components. By changing the relative content of these components in a wide range, determined by x and y parameters, we achieve the possibility for compositional modification of the prepared SSSC.

Ceramic pellets were sintered in air at different temperatures in the region of $T_s = 900–1300°C$ depending on their chemical compositions. Three different samples of each chemical composition were obtained changing the sintering temperature T_s. Only the single-phase SSSC samples possess a high level of technological repeatability and, consequently, can be selected for applications. In order to control the phase composition and microstructure of the prepared samples, we used the DRON-0.5 diffractometer (Fe K_α-radiation) and "NEOPHOT" metallographic microscope.

The resistance R of NTC thermistors were measured in the temperature range of 20–180°C using a well-known compensation method and a four-wire line.[1] The activation energy values ΔE_{20-70} were calculated for a linear section of $\sigma(1/T)$ dependences at 20–70°C, in order to calculate the material-specific constant B.

The exploitation parameters of the prepared thermistors could be also corrected, changing the configuration and geometrical sizes.

3. Results and discussion

The experimentally obtained temperature dependences of electrical conductivity show that all NTC samples of $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ($0.1 \leqslant x \leqslant 0.8$; $0.1 \leqslant y \leqslant 0.9-x$) chemical system are characterized by strong thermistor effect. The main electrical parameters, such as electrical conductivity σ_{25} at 25°C and activation energy ΔE_{20-70} for ceramic NTC thermistors are determined, in the first hand, by sintering temperature T_s. This tight correlation is connected with the structural peculiarities of investigated ceramics as it is for similar Mn-based spinels, where semiconducting processes are determined mainly by the hopping of electrons between Mn^{3+} and Mn^{4+} cations located in the octahedral sites of spinel matrix.[4,7,8] So, samples with different values of electrical conductivity can be obtained, changing the cation rearrangements owing to different sintering temperatures T_s. This conclusion can be typically illustrated by the next examples.

All samples of $Cu_{0.4}Ni_{0.4}Co_{0.4}Mn_{1.8}O_4$ ceramics obtained at three different sintering temperatures 1100, 1200 and 1300°C are single-phase ones, their σ_{25} values being 3.64, 1.83 and 2.64 Ω^{-1} m^{-1}, respectively. That is why a wide range of electrical exploitation parameters can be relatively easy achieved by technological modification of this SSSC composition.

On the other hand, the thermistor $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics can be prepared in the single-phase form only at the sintering temperature T_s = 1200°C. Any temperature deviations from this optimum value lead to the multiphase structure formation and, as a result, to the possible phase separation at the conditions of high temperature and electrical fields.

Using the statistical-mathematical estimations (the method of simplex matrices of 4-fold D-optimum plan), we plotted the diagrams of electrical conductivity at

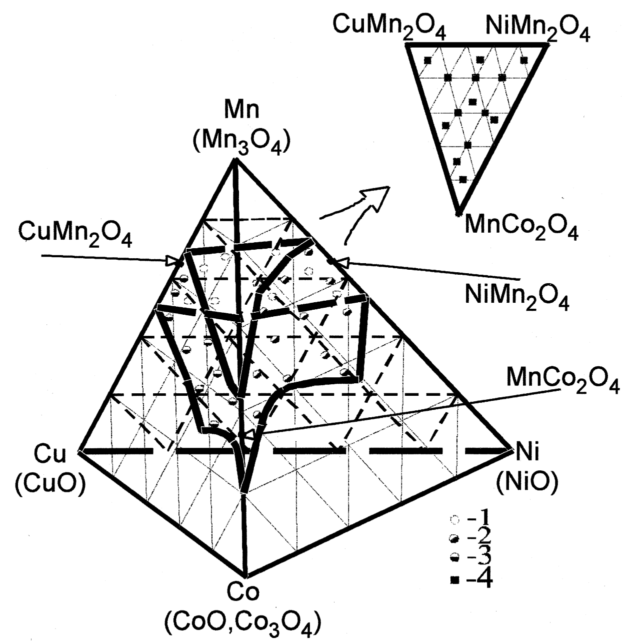

Fig. 1. Selected section of the Cu–Ni–Co–Mn oxide system, restricted by $CuMn_2O_4$, $MnCo_2O_4$ and $NiMn_2O_4$ spinels.

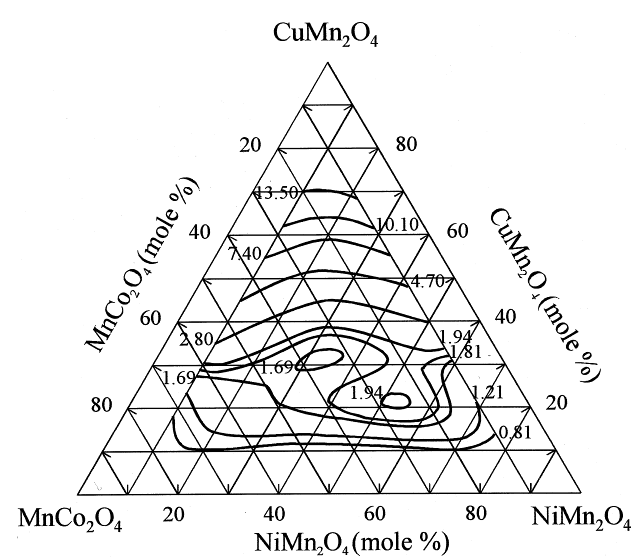

Fig. 2. Isolines of the electrical conductivity σ_{25} (Ω^{-1} m^{-1}) for the SSSC of the $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ system.

25°C (σ_{25}), the activation energy ($\Delta E_{20\text{-}70}$) and the lattice parameter (a) of spinel phase as a function of SSSC chemical compositions. They are presented in Fig. 2–4 in the form of corresponded isolines of these parameters.

The obtained results mean that by changing the composition of SSSC, the real possibilities to obtain ceramic semiconductors with the electrical conductivity values in the range of 0.81–13.50 Ω^{-1} m^{-1} and activation energy 0.21–0.29 eV (these values ensure the material-specific constant B at the level of 2435–3365 K) are achieved.

When the disk configuration of NTC thermistors is chosen, the components with different exploitation characteristics can be obtained by changing the geometrical sizes (diameter and thickness) of ceramic disk. By this way the $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$-based NTC thermistors with rated resistances from 2 to 21500 Ω can be manufactured at the disc size changing from 2 to 30 mm in diameter and from 1 to 5 mm in thickness.

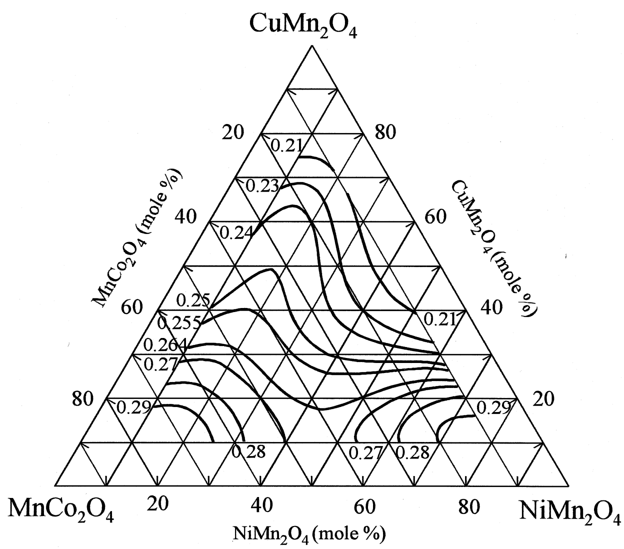

Fig. 3. Isolines of the activation energy $\Delta E_{20\text{-}70}$ (eV) for the SSSC of the $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ system.

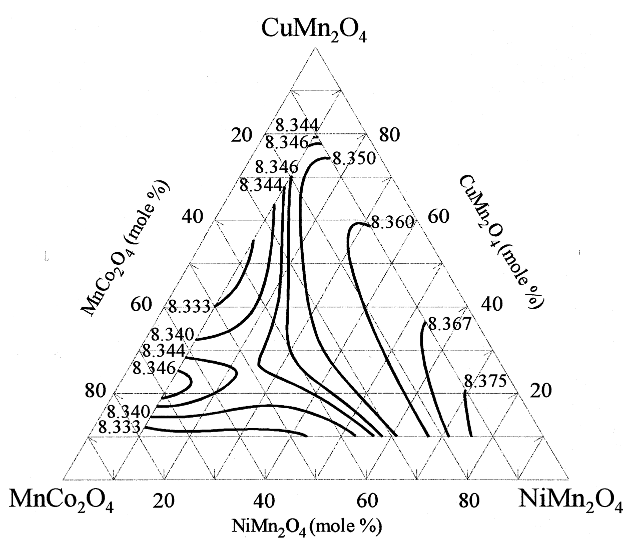

Fig. 4. Isolines of the lattice parameter a (Å) of spinel phase for the SSSC of the $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ system.

4. Conclusions

Thus, we conclude at the basis of the obtained experimental results, that promising electroceramics with beforehand-determined parameters of controlled thermistor effect can be obtained, using the quaternary Cu–Ni–Co–Mn oxide system with smooth content deviations of the main cubic spinels ($CuMn_2O_4$, $MnCo_2O_4$ and $NiMn_2O_4$). It means that the continuous solid solutions of cation-variable compositions in Cu_x-$Ni_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ($0.1 \leqslant x \leqslant 0.8$; $0.1 \leqslant y \leqslant 0.9–x$) system, obtained at the optimally determined technological conditions, can be considered as advanced semiconducting materials for NTC thermistors applications.

Acknowledgements

This work was carried out in the framework of STCU Project No. 2080.

References

1. Lavenuta, G., Negative temperature coefficient thermistors. *Sensors (Peterborough, Nh)*, 1997, **14**, 46–55.
2. Edwards, L. and Murthy, R., Versatile thermistors for wide-ranging applications. *Electrotechnology*, 1987, **15**, 89–91.
3. Hata, T., Kuroda, T. and Matsuo, Y., New thermistor materials. *National Technical Report (Matsushita Electric Industry Company)*, 1982, **28**, 1123–1134.
4. Sheftel, I. T., *Thermistors*. Nauka, Moscow, 1973. , 1973.
5. Hadzaman, I. V., Kovalsky, A. P., Mrooz, O. Ya. and Shpotyuk, O. I., Thermal modification of ceramic composites based on manganese-containing cube spinels. *Materials Letters*, 1996, **29**, 195–198.
6. Drejper, N. and Smit, G., *Processes Analysis by Statistical Methods*. Mir, Moscow, 1973.
7. Fritsch, S., Sarrias, J., Brieu, M., Couderc, J. J., Baudour, J. L., Snoeck, E. and Rousset, A., Correlation between the structure, the microstructure and the electrical properties of nickel manganite negative temperature coefficient (NTC) thermistors. *Solid State Ionics*, 1998, **109**, 229–237.
8. Elbadraoui, E., Baudour, J. L., Leroux, C., Fritsch, S., Bouree, F., Gillot, B. and Rousset, A., Cation distribution, short-range order and small polaron hopping conduction in nickel manganites, from a neutron diffraction study. *Phys. Stat. Sol. (b)*, 1999, **212**, 129–139.