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## EFFECT OF COBALT SUBSTITUTION ON THE MICROSTRUCTURE AND PROPERTIES OF $Na_{0.9}CoO_2$ BASED CERAMICS

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- Ceramics of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  ( $M = Sc, Ti, Cr-Zn, Mo, W, Pb, Bi$ ) composition has been synthesized. Its structure and microstructure, thermoEMF, electric conductivity, thermal conductivity and thermal expansion have been studied. The resulting materials are *p*-type conductors with a metal conductivity. The effect of the nature of cobalt-substituting metal on the physics-chemical and functional properties of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  oxides has been analyzed. The highest values of power factor among the investigated compositions are typical of  $Na_{0.9}Co_{0.9}Cu_{0.1}O_2$ ,  $Na_{0.9}Co_{0.9}Bi_{0.1}O_2$  and  $Na_{0.9}Co_{0.9}Ni_{0.1}O_2$  solid solutions, namely 643, 660 and 918  $\mu W/(m \cdot K^2)$ , respectively, at 1100 K, which is a factor of 1.4 – 2.0 higher than for the basic phase  $Na_{0.9}CoO_2$ .

### Introduction

Layered sodium cobaltite  $Na_xCoO_2$  is characterized by high thermoEMF and electric conductivity values and a low thermal conductivity [1, 2], owing to which it can be considered as a promising basis for the development of new efficient oxide thermoelectrics. One of the methods for improvement of  $Na_xCoO_2$  thermoelectric properties is partial substitution of cobalt cations entered into its composition by cations of other metals, transient or nontransient. Thus, substitution of cobalt by copper or zinc in  $Na_{0.5}CoO_2$  leads to increase of electric conductivity  $\sigma$  and thermoEMF  $S$  of ceramics, due to which the values of power factor  $P$  of  $Na_{0.5}(Co, M)O_2$  ( $M = Cu, Zn$ ) solid solutions grow as compared to the unsubstituted phase  $Na_{0.5}CoO_2$  [3, 4]. Partial substitution of cobalt by nickel reduces the electric conductivity of  $Na_{0.5}(Co, Ni)O_2$  ceramics, but increases its thermoEMF and, as a consequence, power factor [5]. In the works [6-8], attempts were made to improve the thermoelectric properties of  $Na_xCoO_2$  cobaltites ( $x = 0.75, 0.85$ ) due to partial substitution of silver for cobalt. It was found that solubility of  $Ag_2O$  in  $Na_xCoO_2$  is low, owing to which samples of  $Na_xCo_{2-y}Ag_yO_2$  composition are microcomposites the matrix of which is  $Na_x(Co, Ag)O_2$  solid solution, and silver is precipitated on the grain boundaries as  $Ag$  or  $Ag_2O$  [6, 7]; the functional characteristics of  $Na_xCo_{2-y}Ag_yO_2$  composites are substantially improved as compared to the unsubstituted sodium cobaltite [7, 8].

Analysis of literary data shows that most frequently the objects of research have been cobaltites with a low sodium content ( $x \approx 0.5$ ); at the same time, according to the results of [9, 10], the thermoelectric properties of ceramics  $Na_xCoO_2$  are improved with the increase of sodium content in it, so production of solid solutions based on sodium-rich  $Na_xCoO_2$  phases and study of their physics-chemical and functional properties is of considerable scientific and practical interest.

In this paper, we have investigated the influence of the nature of cations of different metals substituting cobalt cations in sodium-rich layered cobaltite  $Na_{0.9}CoO_2$  on the crystal structure, microstructure, thermal and electrophysical and thermoelectric properties of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  ( $M = Sc, Ti, Cr-Zn, Mo, W, Pb$  and  $Bi$ ) solid solutions.

## Experimental

Samples of composition  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  were obtained by solid-phase method from analytical grade  $Na_2CO_3$ , mainly pure  $Sc_2O_3$ , analytical grade  $TiO_2$ , analytical grade  $Cr_2O_3$ , mainly pure  $Mn_2O_3$ , mainly pure  $Fe_2O_3$  mainly pure  $Co_3O_4$ ,  $NiO$ , analytical grade  $CuO$ , pure  $ZnO$ , pure  $MoO_3$ , pure  $WO_3$ , analytical grade  $PbO$ , pure  $Bi_2O_3$ , taken in the ratio  $Na : Co : M = 1.2 : 0.9 : 0.1$  (the design-integrated surplus of  $Na_2CO_3$  in the initial charge compensates the loss of  $Na_2O$  by samples in the course of their thermal treatment and yields ceramics of assigned composition [11]) in the air in the temperature range of 1133 to 1203 K.

Identification of samples and determination of their crystal structure parameters was done using x-ray phase analysis (X-ray diffractometer Bruker D8 XRD Advance). The apparent density  $\rho$  of the samples was found according to their mass and geometrical dimensions. The thermal expansion, electric conductivity  $\sigma$  and thermoEMF  $S$  of sintered ceramics was studied in the air in the temperature range of 300 to 1100 K according to procedures described in [10 – 12]. The linear thermal expansion coefficient  $\alpha$  of samples was calculated from the linear portions of dependences  $\Delta l/l_0 = f(T)$ . The thermal conductivity  $\lambda$  of ceramics was studied in the air in the temperature range of 298 to 423 K using thermal conductivity meter IT- $\lambda$ -400. The lattice  $\lambda_{lat}$  and electron  $\lambda_{el}$  contributions to thermal conductivity were determined with the aid of relationships

$$\lambda = \lambda_{lat} + \lambda_{el}, \quad (1)$$

$$\lambda_{el} = \sigma \cdot L \cdot T, \quad (2)$$

where  $L$  is the Lorentz number ( $L = 2.45 \cdot 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ ).

The values of power factor ( $P$ ) and dimensionless thermoelectric figure of merit of ceramics ( $ZT$ ) was calculated by the formulae:

$$P = S^2 \cdot \sigma, \quad (3)$$

$$ZT = (P \cdot T) / \lambda. \quad (4)$$

## Discussion of results

On completion of synthesis,  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid solutions were, within the error of X-ray phase analysis, single-phase (Fig. 1) and had a hexagonal structure corresponding to  $\gamma$ - $Na_xCoO_2$  structure [13],

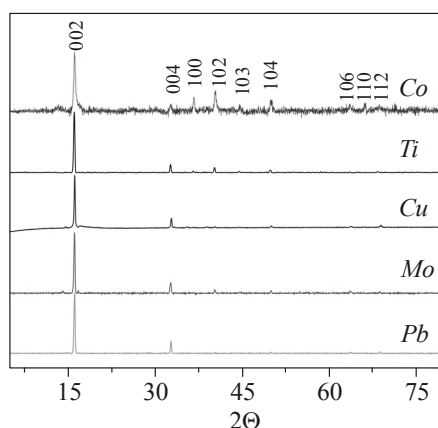


Fig. 1. Powder patterns ( $Cu_{K\alpha}$ -radiation) of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid solutions.

and parameters of their unit cells varied within  $a = 0.2813 - 0.2836 \text{ nm}$ ,  $c = 1.091 - 1.097 \text{ nm}$ , which is close to parameters of the unsubstituted phase  $Na_{0.9}CoO_2$  ( $a = 0.2826 \text{ nm}$ ,  $c = 1.093 \text{ nm}$ ) (Table). The apparent density of ceramics varied within  $2.82 - 3.47 \text{ g/cm}^3$ , decreasing with a partial substitution of cobalt by scandium, manganese or iron and increasing in all other cases, this increase being most considerable with a partial substitution of cobalt by nickel or bismuth (Table). Crystallites of phases  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  had the shape of plates, mainly oriented with their broad side in a direction perpendicular to compaction axis (Fig. 2), which points to partial texturing of ceramics that we obtained. As can be seen from Fig. 2, the microstructure of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid solutions

depends on the nature of cobalt-substituting  $3d$ -metal: the dimensions of crystallites increase with a partial substitution of cobalt by copper, titanium or chromium and decrease in the other cases, this decrease being most considerable with a substitution of cobalt by scandium, manganese or iron.

*Table*

The values of parameters  $a$ ,  $c$ , axial ratio  $c/a$  and volume  $V$  of the unit cell, apparent density  $\rho$  and the average linear thermal expansion coefficient  $\alpha$  of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid solutions

$M$	$a$ , nm	$c$ , nm	$c/a$	$10^3 \cdot V$ , nm <sup>3</sup>	$\rho$ , g/cm <sup>3</sup>	$\alpha \cdot 10^6$ , K <sup>-1</sup>
<i>Sc</i>	0.2828	1.091	3.860	75.61	2.82	14.8
<i>Ti</i>	0.2836	1.096	3.866	76.32	3.05	17.5
<i>Cr</i>	0.2828	1.093	3.867	75.69	3.18	13.7
<i>Mn</i>	0.2813	1.096	3.872	76.12	2.87	16.8
<i>Fe</i>	0.2827	1.096	3.877	75.84	2.94	20.5
<i>Co</i>	0.2826	1.093	3.868	75.60	3.04	13.4
<i>Ni</i>	0.2834	1.091	3.849	75.87	3.46	14.2
<i>Cu</i>	0.2821	1.093	3.876	75.36	3.23	12.5
<i>Zn</i>	0.2826	1.094	3.872	75.71	3.26	13.6
<i>Mo</i>	0.2823	1.096	3.881	75.62	3.22	14.7
<i>W</i>	0.2825	1.097	3.883	75.83	3.20	13.5
<i>Bi</i>	0.2822	1.095	3.880	75.49	3.47	12.5
<i>Pb</i>	0.2824	1.092	3.868	75.47	3.34	12.6

The values of linear thermal expansion coefficient of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid solutions varied within  $(12.5 - 20.5) \cdot 10^{-6} K^{-1}$ , decreasing with a partial substitution of cobalt by copper, bismuth or lead and increasing in all other cases (Table).

Comparing the results of dilatometry, densitometry and electron microscopy, it can be concluded that the linear thermal expansion coefficient of ceramics increases with a decrease in the apparent density of samples and with a decrease in the dimensions of crystallites that form them.

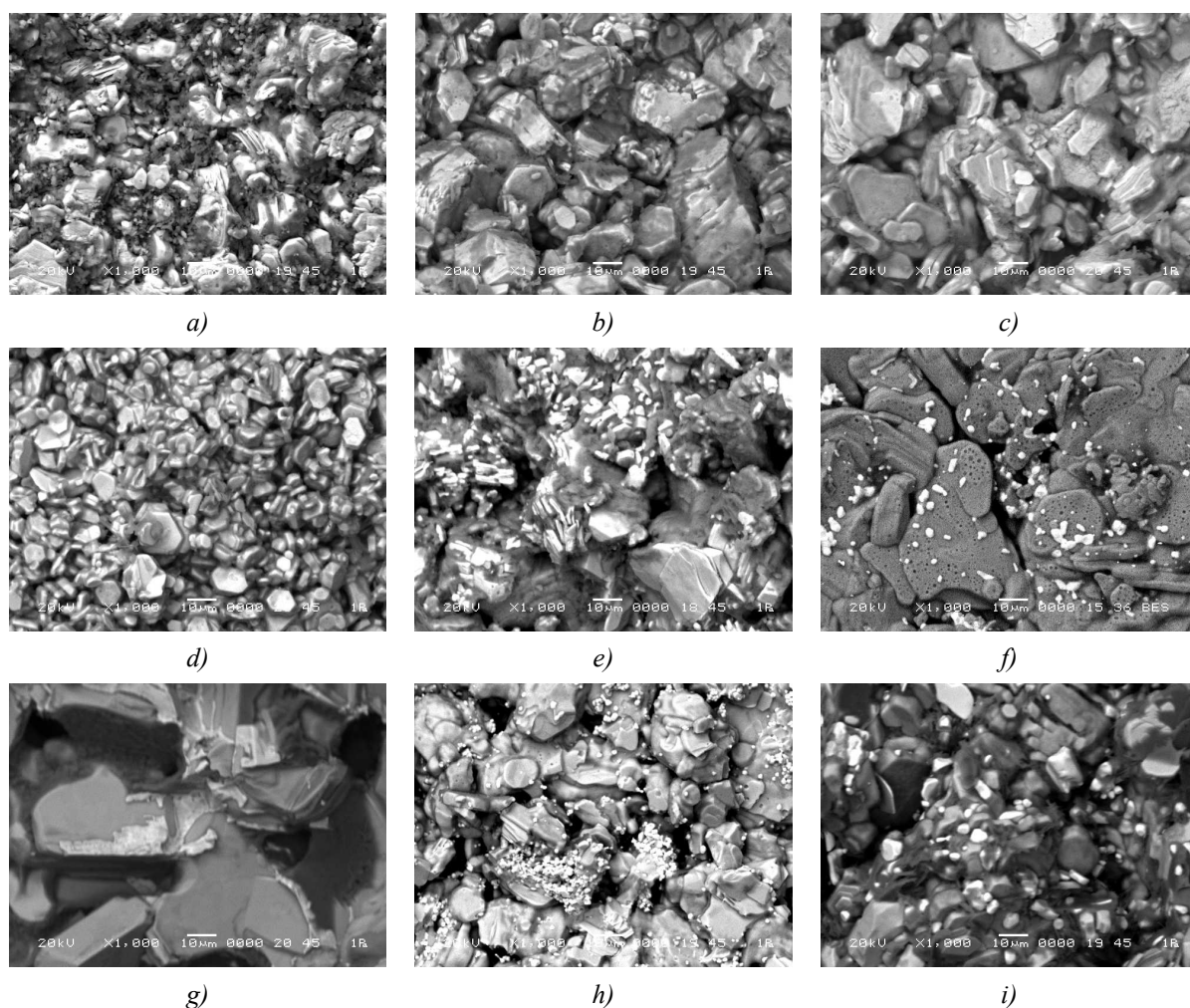
As can be seen from Fig. 3a, the conductivity of  $Na_{0.9}CoO_2$  cobaltite and solid solutions on its basis is of metal nature ( $\partial\sigma/\partial T < 0$ ), the value of ceramics electric conductivity decreasing with increase in oxidation degree of cobalt-substituting metal  $M$  ( $\sigma(Na_{0.9}Co_{0.9}Ni_{0.1}O_2) > \sigma(Na_{0.9}CoO_2) > \sigma(Na_{0.9}Co_{0.9}Pb_{0.1}O_2)$ ) (Table), which is in good agreement with the results [3, 4] and attributable to a decrease in concentration of the major carriers (“holes”) with increase in the average oxidation degree of cations in conducting –  $(Co, M)O_2$  – layers of crystalline structure of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  phases.

The thermoEMF of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid solutions grew with a rise in temperature and was mainly increased with a growth of oxidation degree of cobalt-substituting metal  $M$  (Fig. 3b), which is typical of conventional conductors for which the increase in concentration of major carriers leads to thermoEMF reduction. At the same time, the thermoEMF of  $Na_{0.9}Co_{0.9}Ni_{0.1}CoO_2$ ,  $Na_{0.9}Co_{0.9}Cu_{0.1}O_2$ ,  $Na_{0.9}Co_{0.9}W_{0.1}O_2$  and some other solid solutions was much higher than for the unsubstituted phase  $Na_{0.9}CoO_2$ , which cannot be explained within a quasi-chemical approach.

The electron subsystem of layered cobaltites is strongly correlated, and their thermoEMF is generally described by means of the Heykes equation:

$$S = \frac{k}{e} \ln \left[ \frac{g_3 \cdot [Co^{3+}]}{g_4 \cdot [Co^{4+}]} \right], \quad (5)$$

where  $k$  is the Boltzmann constant;  $e$  is electron charge;  $g_4$  and  $g_3$  is the number of configurations whereby the state of  $Co^{4+}$  and  $Co^{3+}$  cations, respectively, can be realized;  $[Co^{3+}]$  and  $[Co^{4+}]$  are concentrations of  $Co^{3+}$  and  $Co^{4+}$  cations in conducting –  $CoO_2$  – layers of  $Na_xCoO_2$  crystal structure [14].



*Fig. 2. Electron microphotographs of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  ceramic cleavages:  
 $M = Sc$  (a),  $Ti$  (b),  $Cr$  (c),  $Mn$  (d),  $Fe$  (e),  $Co$  (f),  $Ni$  (g),  $Cu$  (h),  $Zn$  (i).*

Thus, the thermoEMF of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid solutions is determined both by the concentration ratio  $[Co^{3+}] / [Co^{4+}]$  which depends on the oxidation degree of cobalt cations-substituting metal cation  $M^{+}$  and on the ratio  $g_4/g_3$  which depends on the spin states of cobalt cations  $Co^{3+}$ ,  $Co^{4+}$  and cations of substituent metal  $M^{+}$ .

As can be seen from Fig. 3 *d, e*, the electric conductivity of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  oxides increases, and the thermoEMF decreases with a growth of the number of electrons on the outer shell of metal cation  $M^{+}$  substituted for cobalt cations. The results that we obtained allow concluding that the electric transport properties of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid solutions are determined both by the charge and spin states of cations in conducting –  $(Co, M)O_2$  – layers of their structure, which is in conformity with conclusions made by the authors of [14] in the analysis of thermoEMF of  $Na_xCoO_2$  cobaltites.

The values of power factor of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  ceramics increased with a rise in temperature and, on the whole, with increasing the number of electrons on the outer shell of metal cation  $M^{+}$  substituted for cobalt cations (Fig. 3 *c, f*), reaching the highest values for  $Na_{0.9}Co_{0.9}Ni_{0.1}O_2$ ,  $Na_{0.9}Co_{0.9}Bi_{0.1}O_2$  and  $Na_{0.9}Co_{0.9}Cu_{0.1}O_2$  solid solutions, namely 918, 660 and 643  $\mu W/(m \cdot K^2)$ , respectively, at 1100 K, which is a factor of 1.4 – 2.0 higher than for the basic sodium cobaltite and due to the high thermoEMF values of these samples.

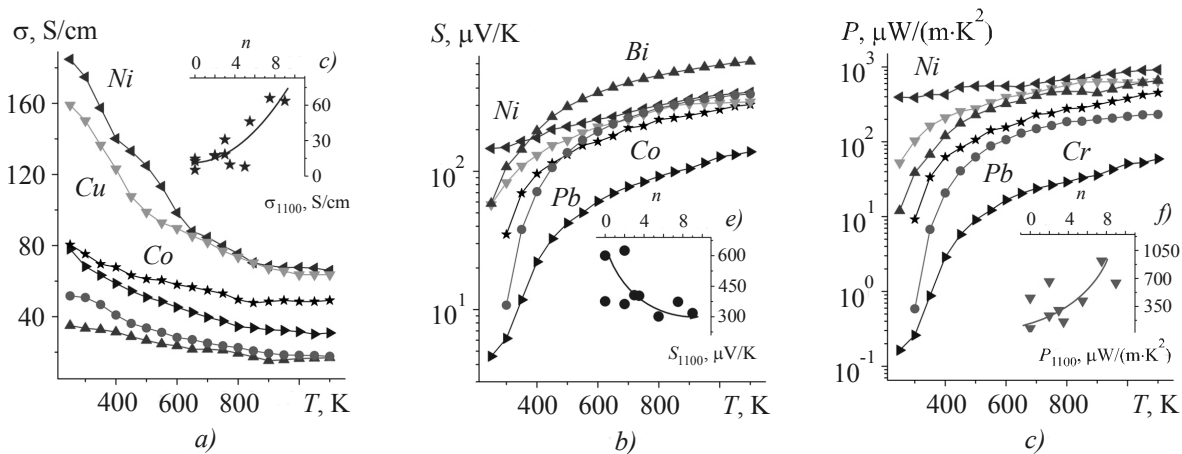


Fig. 3. Temperature dependences of electric conductivity  $\sigma$  (a), thermoEMF  $S$  (b) and power factor  $P$  (c) of sintered ceramics  $Na_{0.9}Co_{0.9}M_{0.1}O_2$ . On the insets are given dependences of electric conductivity  $\sigma_{1100}$  (d), thermoEMF  $S_{1100}$  (e) and power factor  $P_{1100}$  (f) of  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  solid on the number of electrons  $n$  on the external electron shell of metal cation substituting cobalt cations in  $Na_{0.9}CoO_2$  phase.

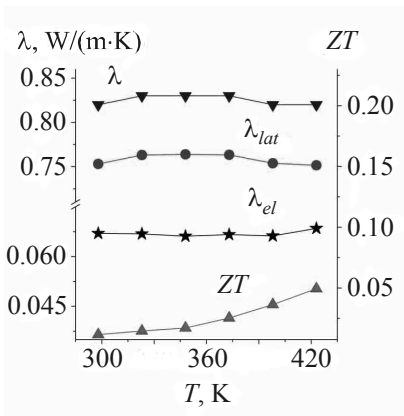


Fig. 4. Temperature dependences of total thermal conductivity  $\lambda$ , its lattice  $\lambda_{lat}$  and electron contributions  $\lambda_{el}$ , as well as the dimensionless parameter of thermoelectric figure of merit  $ZT$  for cobaltite  $Na_{0.9}CoO_2$ .

1.01, 0.726 and 0.707, respectively, owing to which these oxides can be considered as possible materials for  $p$ -legs of thermoelectric modules operated at high temperatures.

## Conclusions

Using a three-phase method, an oxide ceramics of composition  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  ( $M = Sc, Ti, Cr-Zn, Mo, W, Pb$  and  $Bi$ ) has been obtained, its crystal structure and microstructure, thermal and electrophysical and thermoelectric properties have been studied. The  $Na_{0.9}Co_{0.9}M_{0.1}O_2$  samples are  $p$ -type conductors with a metal conductivity. The effect of the nature of metal cation substituted for cobalt cations in  $Na_{0.9}Co_{0.9}O_2$  phase on the physics-chemical and functional characteristics of the resulting solid solutions has been discussed. The greatest values of power factor are in  $Na_{0.9}Co_{0.9}Ni_{0.1}O_2$ ,  $Na_{0.9}Co_{0.9}Bi_{0.1}O_2$  and  $Na_{0.9}Co_{0.9}Cu_{0.1}O_2$  oxides, namely 918, 660 and 643  $\mu W/(m \cdot K^2)$ , respectively, at 1100 K, owing to which these materials can be considered as a

basis for the development of new high-temperature thermoelectrics.

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