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THERMOELECTRIC PROPERTIES OF $(\text{Na},M)_x\text{CoO}_2$ ($M = \text{Li, K, Cs}$) CERAMICS

The $(\text{Na},M)_x\text{CoO}_2$ ($M = \text{Li, K, Cs}$; $x = 0.55; 0.89$) ceramics was synthesized, and its phase composition, thermal expansion, electrical conductivity and thermo-EMF were investigated. The materials obtained were polyphase ones and they consisted of sodium cobaltite ($\gamma\text{-Na}_x\text{CoO}_2$), Co_3O_4 and of other alkaline metals cobaltites (LiCoO_2 , KCoO_2 , Cs_2CoO_3). The temperature dependences of electrical conductivity of the $(\text{Na},M)_{0.55}\text{CoO}_2$ ($M = \text{K, Cs}$) and $(\text{Na},M)_{0.89}\text{CoO}_2$ samples had semiconducting character, but $(\text{Na},\text{Li})_{0.55}\text{CoO}_2$ ones had metallic character. The materials studied were p -type conductors, which thermo-EMF and power factor (P) values rose at temperature increasing, and values of linear thermal expansion coefficient varied within $(11.1\text{--}14.9) \cdot 10^{-6} \text{ K}^{-1}$. Inserting into $\text{Na}_{0.55}\text{CoO}_2$ ceramics the lithium or potassium oxides increased its power factor; thus, for $\text{Na}_{0.28}\text{K}_{0.27}\text{CoO}_2$ compound $P_{1100} = 361 \mu\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$, which was 85% higher than for $\text{Na}_{0.55}\text{CoO}_2$.

Introduction. Layered sodium cobaltite Na_xCoO_2 demonstrates high values of electrical conductivity and thermo-EMF, which let us consider it as prospective thermoelectric material [1]. Thermoelectric properties of Na_xCoO_2 improve at increasing of sodium content in it [2, 3] and at partial substitution of cobalt by other transition metals [4, 5]. Authors of [6] obtained the $\text{Li}_{0.48}\text{Na}_{0.35}\text{CoO}_2$ solid solution and showed that its thermo-EMF was essentially higher than for lithium (Li_xCoO_2) and sodium cobaltites (Na_xCoO_2). Taking into account the results of [6], substitution of sodium by other alkaline metals in Na_xCoO_2 can be considered as prospective way to improve thermoelectric properties of ceramics based on it, so, synthesis of $(\text{Na},M)_x\text{CoO}_2$ (M – alkaline metal, $M = \text{Li, K, Cs}$) materials and studying of their properties is in great interest for thermoelectric materials science.

The aim of this work was the study of influence of substitution of sodium by other alkaline metals (lithium, potassium, cesium) in the layered sodium cobaltite Na_xCoO_2 on the crystal structure and physicochemical properties of obtained hereby materials.

Experimental technique. The samples of compositions $\text{Na}_{0.6-x}M_x\text{CoO}_2$ and $\text{Na}_{0.6}M_{0.6}\text{CoO}_2$ ($M = \text{Li, K, Cs}$; $x = 0.2; 0.3; 0.4; 0.5$) were obtained from Na_2CO_3 (pure for analysis), Li_2CO_3 (pure), K_2CO_3 (pure), CsNO_3 (chemically pure) and Co_3O_4 (pure for analysis) using solid-state reactions method in air within 1,133–1,203 K by means of method described in [7].

Phase composition of the samples was determined using X-ray diffraction analysis (XRD) (diffractometer D8 Advance Bruker AXS (Germany), CuK_α – radiation). The apparent density of the samples (ρ) was found using their mass and geometrical dimensions. Thermal expansion, electrical conductivity (σ) and thermo-EMF (S) of ceramics were studied in air within 300–1,100 K using methods

described in [8, 9]. Values of the linear thermal expansion coefficient (LTEC, α) were obtained from linear parts of $\Delta l/l_0 = f(T)$ dependences. The power factor values (P) were calculated as $P = S^2\sigma$.

Results and their discussion. During heat treatment of sodium cobaltite the part of Na_2O sublimates into environment [10]. The compositions of ceramics after synthesis finishing calculated on the base of data obtained by us earlier [3, 8] are given in the table.

According to the XRD results, all the obtained materials were polyphase: on the diffractograms of $(\text{Na},M)_x\text{CoO}_2$ powders along with reflexes of sodium cobaltite ($\gamma\text{-Na}_x\text{CoO}_2$) (Fig. 1, 2, *a*) the reflexes of other phases were observed, which were identified by us as LiCoO_2 , KCoO_2 , Cs_2CoO_3 for $M = \text{Li, K, Cs}$ respectively [11]; along with alkaline metals cobaltites ceramics contained a small amounts of Na_2CO_3 and Co_3O_4 phases [11], which, according to the results of [3], formed due to the partial degradation of the samples surface owing to their interaction with atmospheric CO_2 . The reflexes positions on the diffractograms of $(\text{Na},M)_{0.55}\text{CoO}_2$ powders and lattice constants of sodium cobaltite which is part of the samples (Table, Fig. 1, *b*), within the accuracy of experiment, did not changed at changing of $\text{Na} : M$ ratio. On the base of the data obtained one can conclude that alkaline metals cobaltites which are parts of heterogeneous ceramics of $(\text{Na},M)_{0.55}\text{CoO}_2$ are not solid solutions but individual compounds ($\gamma\text{-Na}_x\text{CoO}_2$, LiCoO_2 etc.).

The unit cell parameters of sodium cobaltite which was part of $\text{Na}_{0.445}M_{0.445}\text{CoO}_2$ ($M = \text{K, Cs}$) powders were practically equal to the same of $\text{Na}_{0.89}\text{CoO}_2$ phase and did not changed at increasing of heat treatment time. Lattice constants of sodium cobaltite which was part of $\text{Na}_{0.445}\text{Li}_{0.445}\text{CoO}_2$ obtained after annealing during 25 h at 1,203 K were essentially smaller than for basic sodium cobaltite ($\text{Na}_{0.89}\text{CoO}_2$) and did not changed at increasing

of heat treatment time at 1,203 K (Table, Fig. 2, *b*). So, $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ ($M = \text{K}, \text{Cs}$) ceramics in addition to impurity phases of Na_2CO_3 and Co_3O_4 contains individual alkaline metals cobaltites ($\gamma\text{-Na}_x\text{CoO}_2$, K_xCoO_2 , Cs_2CoO_3), but $\text{Na}_{0.445}\text{Li}_{0.445}\text{CoO}_2$ ceramics contains $(\text{Na},\text{Li})_{0.89}\text{CoO}_2$ solid solution and lithium cobaltite LiCoO_2 .

The result of our experiment let us conclude that monophasic samples of $(\text{Na},\text{M})_x\text{CoO}_2$ ($M = \text{Li}, \text{K}, \text{Cs}$; $x = 0.55, 0.89$) solid solutions cannot obtain using solid-state reactions method; the obtained ceramics is heterogeneous and consists of cobaltites of individual alkaline metals. In the $\text{Na}_{0.89}\text{CoO}_2\text{-Li}_{0.89}\text{CoO}_2$ system the limited solubility of lithium cobaltite in the sodium cobaltite is found which results in formation of $(\text{Na},\text{Li})_{0.89}\text{CoO}_2$ solid solution.

Apparent density of $(\text{Na},\text{M})_{0.55}\text{CoO}_2$ and $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ ceramics varied within $2.80\text{--}3.78\text{ g/cm}^3$ and $2.76\text{--}3.17\text{ g/cm}^3$ respectively (Table) and, except $(\text{Na},\text{Li})_{0.55}\text{CoO}_2$ compounds, was smaller than for unsubstituted sodium cobaltites $\text{Na}_{0.55}\text{CoO}_2$ (3.64 g/cm^3) and $\text{Na}_{0.89}\text{CoO}_2$ (3.38 g/cm^3), and the lowest values of density possessed $(\text{Na},\text{K})_x\text{CoO}_2$ ceramics. Comparing results of apparent density of the samples measurements and XRD one can conclude that porosity of heterogeneous ce-

ramics $(\text{Na},\text{M})_x\text{CoO}_2$ ($M = \text{Li}, \text{K}, \text{Cs}$) is higher than for single-phase sodium cobaltites and the highest values of porosity have the $(\text{Na},\text{K})_{0.55}\text{CoO}_2$ samples.

The $\Delta l/l_0 = f(T)$ dependences for ceramics studied were practically linear and their LTEC values varied within $(11.1\text{--}14.9)\cdot 10^{-6}\text{ K}^{-1}$ and $(13.2\text{--}14.6)\cdot 10^{-6}\text{ K}^{-1}$ for $(\text{Na},\text{M})_{0.55}\text{CoO}_2$ and $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ ceramics respectively (Table) and, except $(\text{Na},\text{Li})_{0.55}\text{CoO}_2$ compounds, were higher than for unsubstituted sodium cobaltites $\text{Na}_{0.55}\text{CoO}_2$ ($12.2\cdot 10^{-6}\text{ K}^{-1}$) and $\text{Na}_{0.89}\text{CoO}_2$ ($12.4\cdot 10^{-6}\text{ K}^{-1}$) and the highest LTEC values were found for $(\text{Na},\text{K})_{0.55}\text{CoO}_2$ ceramics obviously due to its high porosity.

Electrical conductivity of $\text{Na}_{0.55}\text{CoO}_2$, $(\text{Na},\text{Li})_{0.55}\text{CoO}_2$ and $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ ceramics had semiconducting ($\partial\sigma/\partial T > 0$), but $\text{Na}_{0.89}\text{CoO}_2$ and $(\text{Na},\text{M})_{0.55}\text{CoO}_2$ ($M = \text{K}, \text{Cs}$) samples had metallic character ($\partial\sigma/\partial T < 0$) (Fig. 3, *a, d*), and, as a whole, electrical conductivity values of $(\text{Na},\text{M})_{0.55}\text{CoO}_2$ ($M = \text{Li}, \text{Cs}$) ceramics was larger, but $(\text{Na},\text{K})_{0.55}\text{CoO}_2$ and $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ samples was smaller than for unsubstituted sodium cobaltites Na_xCoO_2 (Fig. 3, *g, j*, Table). In addition, within the $(\text{Na},\text{M})_{0.55}\text{CoO}_2$ series decreasing of $\text{Na} : \text{M}$ ration resulted in lowering of electrical conductivity of ceramics (Fig. 3, *g*, Table).

Composition. time of annealing (τ). apparent density (ρ). average linear thermal expansion coefficient (α). electrical conductivity (σ_{1100}). thermo-EMF (S_{1100}) and power factor (P_{1100}) of ceramics based on the layered sodium cobaltites $\text{Na}_{0.55}\text{CoO}_2$ and $\text{Na}_{0.89}\text{CoO}_2$, as well as values of unit cell parameters (*a, c*) and volume (*V*) sodium cobaltite which is part of these compounds

Composition	τ , h	<i>a</i> , nm	<i>c</i> , nm	$V\cdot 10^3$, nm ³	ρ , g/cm ³	$\alpha\cdot 10^6$, K ⁻¹	σ_{1100} , S/cm	S_{1100} , $\mu\text{V/K}$	P_{1100} , $\mu\text{W}/(\text{m}\cdot\text{K}^2)$
$\text{Na}_{0.55}\text{CoO}_2$	12	0.285	1.116	78.5	3.64	12.2	23.3	289	195
$\text{Na}_{0.37}\text{Li}_{0.18}\text{CoO}_2$		0.283	1.108	77.1	3.52	12.5	21.6	260	146
$\text{Na}_{0.27}\text{Li}_{0.28}\text{CoO}_2$		0.285	1.101	77.6	3.58	12.1	22.6	315	224
$\text{Na}_{0.18}\text{Li}_{0.37}\text{CoO}_2$		0.284	1.123	78.2	3.37	11.1	10.6	296	93.2
$\text{Na}_{0.09}\text{Li}_{0.46}\text{CoO}_2$		0.284	1.126	78.4	3.64	12.6	14.7	427	268
$\text{Na}_{0.37}\text{K}_{0.18}\text{CoO}_2$		0.286	1.145	80.9	2.86	14.3	20.3	199	80.7
$\text{Na}_{0.27}\text{K}_{0.28}\text{CoO}_2$		–	–	–	2.74	14.2	17.6	453	361
$\text{Na}_{0.18}\text{K}_{0.37}\text{CoO}_2$		0.290	1.043	75.9	2.80	14.9	10.0	481	232
$\text{Na}_{0.09}\text{K}_{0.46}\text{CoO}_2$		0.289	1.143	82.9	2.85	13.5	9.64	467	145
$\text{Na}_{0.37}\text{Cs}_{0.18}\text{CoO}_2$		0.285	1.088	76.5	3.21	11.6	27.2	205	115
$\text{Na}_{0.27}\text{Cs}_{0.28}\text{CoO}_2$		–	–	–	3.34	11.7	28.9	279	224
$\text{Na}_{0.18}\text{Cs}_{0.37}\text{CoO}_2$		0.286	1.070	75.6	3.54	13.6	23.3	318	235
$\text{Na}_{0.09}\text{Cs}_{0.46}\text{CoO}_2$		0.283	1.114	77.4	3.78	12.0	14.6	378	209
$\text{Na}_{0.89}\text{CoO}_2$		0.283	1.093	75.6	3.38	12.4	41.1	449	829
$\text{Na}_{0.445}\text{Li}_{0.445}\text{CoO}_2$	25	0.277	1.069	71.3	3.07	–	–	–	–
	50	0.277	1.070	71.1	2.98	–	–	–	–
	75	0.288	1.015	72.7	2.81	–	–	–	–
	100	0.277	1.105	73.2	2.76	14.2	1.72	330	18.8
$\text{Na}_{0.445}\text{K}_{0.445}\text{CoO}_2$	25	0.281	1.093	74.8	3.12	–	–	–	–
	50	0.283	1.091	75.7	3.07	–	–	–	–
	75	0.283	1.094	76.3	2.94	–	–	–	–
	100	0.283	1.074	74.7	2.89	14.6	14.3	300	129
$\text{Na}_{0.445}\text{Cs}_{0.445}\text{CoO}_2$	25	0.283	1.094	75.6	3.17	–	–	–	–
	50	0.283	1.094	75.8	3.10	–	–	–	–
	75	0.283	1.095	75.7	2.98	–	–	–	–
	100	0.282	1.096	75.7	2.94	13.2	4.89	319	50.0

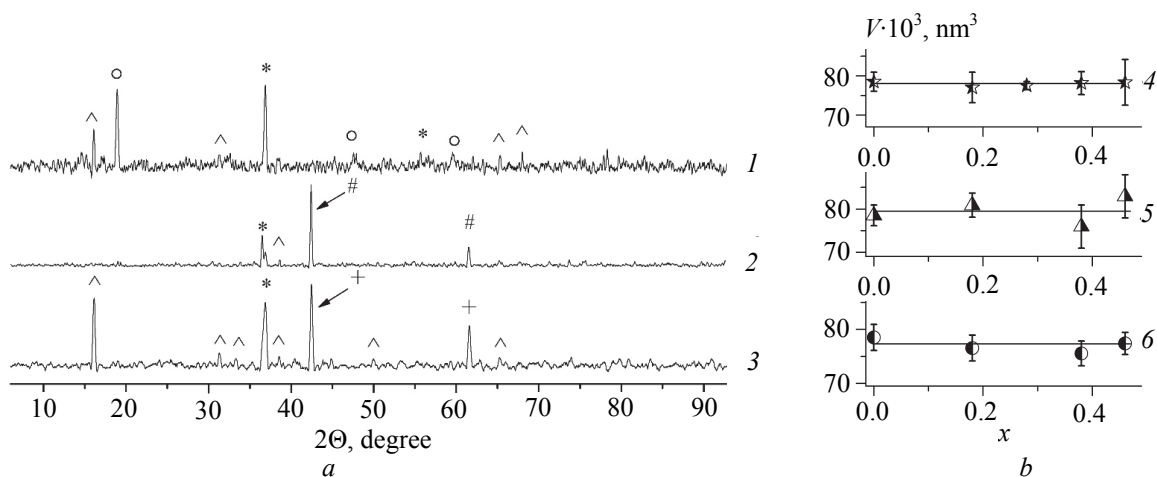


Fig. 1. X-ray diffractograms of $\text{Na}_{0.18}\text{M}_{0.37}\text{CoO}_2$ ($M = \text{Li}$ (1), K (2), Cs (3)) powders (a) and dependences of unit cell volume of sodium cobaltite, which is part of these powders on the substitution degree of sodium by lithium (4), potassium (5), cesium (6) (b). \wedge – $\gamma\text{-Na}_x\text{CoO}_2$; \circ – LiCoO_2 ; $\#$ – KCoO_2 ; $+$ – Cs_2CoO_3 ; $*$ – Co_3O_4

The samples thermo-EMF value at all temperatures studied was positive from which one can conclude that $(\text{Na},M)_x\text{CoO}_2$ samples as well as $\text{Na}_{0.55}\text{CoO}_2$ phase were p -type semiconductors. Thermo-EMF of the ceramics studied increase at temperature increasing (Fig. 3, *b*, *e*) and for $(\text{Na},M)_{0.55}\text{CoO}_2$ samples was, generally, higher, than for $\text{Na}_{0.55}\text{CoO}_2$ phase (except ceramics of $\text{Na}_{0.37}\text{K}_{0.18}\text{CoO}_2$ composition and $(\text{Na},\text{Cs})_{0.55}\text{CoO}_2$ samples at $T < 580$ K) (Fig. 3, *b*, *h*), which was probably due to the heterogeneity of the samples. The thermo-EMF values for $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ samples were smaller than for unsubstituted cobaltite $\text{Na}_{0.89}\text{CoO}_2$ (Fig. 3, *e*, *k*, Table). Comparing the results of the study of thermo-EMF of samples of different series one can conclude that producing of phase nonhomogeneity in the Na_xCoO_2 ceramics at low sodium content ($x = 0.55$) increases and at high ($x = 0.89$) decreases its thermo-EMF.

The power factor values of the ceramics studied increased at temperature increasing and for $(\text{Na},M)_{0.55}\text{CoO}_2$ samples were, in a whole, higher, but for $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ ones – smaller, than for basic sodium cobaltites Na_xCoO_2 (Fig. 3, *c*, *f*, *i*, *l*,

Table). Herewith maximal values of power factor at elevated temperatures possess ceramics with composition $\text{Na}_{0.09}\text{Li}_{0.46}\text{CoO}_2$ and $\text{Na}_{0.27}\text{K}_{0.28}\text{CoO}_2$ – 268 and $361 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ respectively at 1,100 K, which is mainly due to high values of thermo-EMF of the samples. Thus, addition of alkaline metals oxides (Li_2O , K_2O) to the ceramics on the base of sodium cobaltite can increase the values of its power factor that can be used in practice at development of new oxide thermoelectrics with improved functional characteristics.

Conclusion. In this work by means of solid-state reactions method the $(\text{Na},M)_x\text{CoO}_2$ ($M = \text{Li}$, K , Cs ; $x = 0.55$, 0.89) ceramics was prepared, its phase composition was determined, its thermal expansion, electrical conductivity and thermo-EMF were studied. It was shown, that obtained ceramics was nonmonophase and consist of alkaline metal cobaltites ($\gamma\text{-Na}_x\text{CoO}_2$, LiCoO_2 , KCoO_2 , Cs_2CoO_3). In the $\text{Na}_{0.89}\text{CoO}_2\text{-Li}_{0.89}\text{CoO}_2$ system the limited solubility of lithium cobaltite in sodium cobaltite was found which resulted in formation of $(\text{Na},\text{Li})_{0.89}\text{CoO}_2$ solid solution.

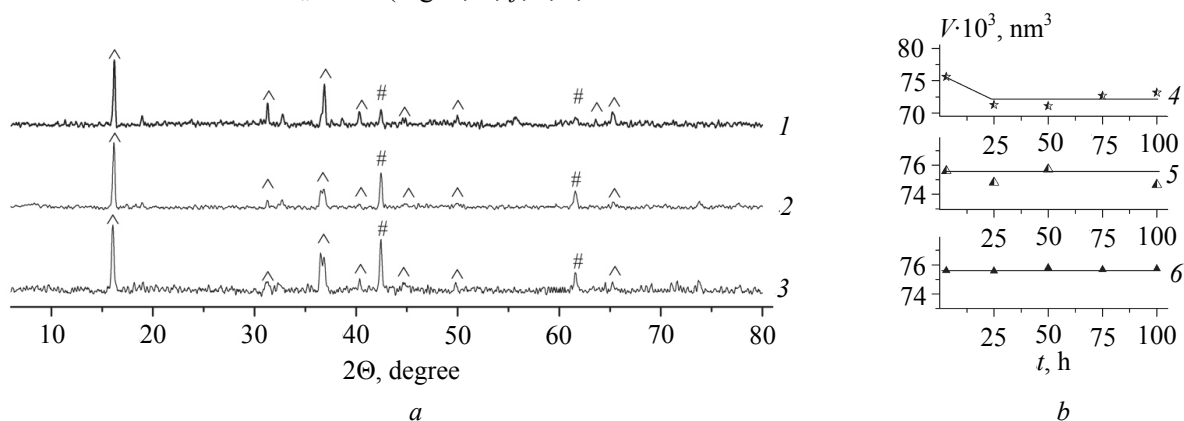


Fig. 2. X-ray diffractograms of the $\text{Na}_{0.445}\text{K}_{0.445}\text{CoO}_2$ powders (a) after annealing at 1203 K during 25 (1), 75 (2), 100 (3) hours and dependences of the unit cell volume of sodium cobaltite (b), which is part of $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ ($M = \text{Li}$ (4), K (5), Cs (6)) powders. \wedge – $\gamma\text{-Na}_x\text{CoO}_2$; $\#$ – KCoO_2

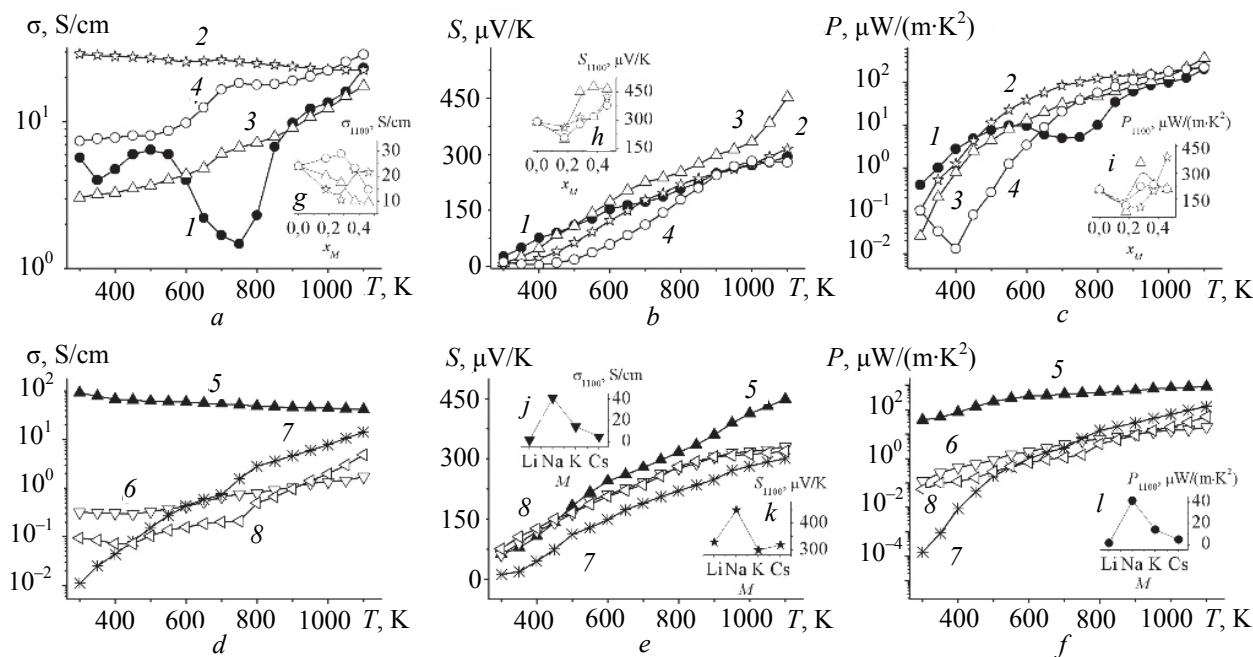


Fig. 3. Temperature dependences of electrical conductivity (σ) (a, d), thermo-EMF (S) (b, e) and power factor (P) (c, f) of ceramics with composition of $\text{Na}_{0.28}\text{M}_{0.27}\text{CoO}_2$ (a–c) and $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ (d–f), where M – Na (1, 5), Li (2, 6), K (3, 7), Cs (4, 8). On the insets the dependences of electrical conductivity (σ_{1100}), thermo-EMF (S_{1100}) and power factor (P_{1100}) of $(\text{Na},\text{M})_x\text{CoO}_2$ ceramics on the substitution degree of sodium cations (g–i) and nature of substituting cations (j–l) are given

On the base of results of apparent density and thermal expansion of the samples measurements the conclusion is made that LTEC of $(\text{Na},\text{M})_x\text{CoO}_2$ ceramics increases at increasing of its porosity.

It was found, that electrical conductivity of $(\text{Na},\text{Li})_{0.55}\text{CoO}_2$ and $\text{Na}_{0.445}\text{M}_{0.445}\text{CoO}_2$ samples had semiconducting, but $(\text{Na},\text{M})_{0.55}\text{CoO}_2$ ($M = \text{K}, \text{Cs}$) ones had metallic character, and all the materials studied are p -type conductors, which thermo-EMF and power factor (P) values increased at temperature and for $(\text{Na},\text{M})_{0.55}\text{CoO}_2$ were, in the whole, higher, but for $(\text{Na},\text{M})_{0.89}\text{CoO}_2$ were smaller, than for basic sodium cobaltites Na_xCoO_2 ($x = 0.55, 0.89$) due to the heterogeneity of the materials studied. It was established, that maximal value of power factor possess $\text{Na}_{0.28}\text{K}_{0.27}\text{CoO}_2$ ceramics – $361 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ at 1,100 K, which is 85 % higher, than for $\text{Na}_{0.55}\text{CoO}_2$ cobaltite. On the base of obtained results we conclude that addition of alkaline metal oxides ($\text{Li}_2\text{O}, \text{K}_2\text{O}$) into ceramics on the base of layered sodium cobaltite with low sodium content let us improve its power factor values, which can be used in practice at development of new oxide thermoelectric with ameliorated functional characteristics.

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