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PECULIARITIES OF PROCESSES OCCURRING AT PREPARATION OF $Ca_3Co_4O_{9+\delta}$ CERAMICS AND ITS PROPERTIES

Using colorimetry, turbidimetry, thermogravimetry, differential thermal analysis and X-ray analysis the processes taking place at preparation of $Ca_3Co_4O_{9+\delta}$ ceramics by means of different methods were studied. The crystal structure and microstructure, thermal expansion, electrical conductivity and thermo-EMF of the samples were investigated and values of their power factor were calculated. It is shown that presence of solution stage let us obtain more dense and fine-grained ceramics, which characterizes more higher values of electrical conductivity and power factor.

Introduction. Layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$ characterizes high thermoelectric parameters, it is stable in air at elevated temperatures and has relatively low cost (in comparison with traditional thermoelectrics), so, it can be considered as prospective material for high-temperature thermoelectroconversion [1]. It is known, that functional properties of ceramic samples of $Ca_3Co_4O_{9+\delta}$ synthesized by means of solid-state reactions method is worse than for monocrystals, but can be improved by preparation of $Ca_3Co_4O_{9+\delta}$ by means of «soft», solution methods of synthesis [2, 3]. Taking it into account, investigation of processes occurring at preparation of $Ca_3Co_4O_{9+\delta}$ ceramics by means of different methods as well as effect of preparation method on the microstructure and properties obtained hereby ceramics is actual problem which have scientific and practical importance.

In this work using complex of independent methods the processes occurring at synthesis of $Ca_3Co_4O_{9+\delta}$ ceramics by means of different methods was investigated, as well as influence of preparation method on the crystal structure, microstructure and physic-chemical properties of $Ca_3Co_4O_{9+\delta}$ was studied.

Experimental technique. At preparation of $Ca_3Co_4O_{9+\delta}$ ceramics by means of solid-state reactions method (A method) the $CaCO_3$ (pure grade) and Co_3O_4 (pure grade) were used, which were mixed in the 9 : 4 molar ratio in Pulverizette 6 (Fritsch,Germany) the planetary mill with addition of ethanol, pressed at pressure of 0,13 MPa into disks having 25 mm diameter and 3–5 mm thickness мм and annealed during 12 h at 1173 K, regrinded in Pulverizette 6 planetary mill (with addition of ethanol), re-pressed at pressure of 0,26 MPa into bars having 5x5x30 mm dimensions, which were sintered during 4–20 h at 1193 K.

To synthesize the samples using B method (CM) we used the water solutions of $Ca(NO_3)_2 \cdot 4H_2O$ (pure for analysis) ($C = 0,6$ M), $Co(NO_3)_2 \cdot 6H_2O$ (pure for analysis) ($C = 0,8$ M) and $C_6H_8O_7$ (pure grade) ($C = 0,5$ M), which were mixed in the 1 : 1 : 5 volume ratio. At using of polymeric (PM) and sol-gel methods (SGM) to the solution obtained the ethylene glycol solution was added ($n(C_2H_6O_2) : n(C_6H_8O_7) = 1 : 1$). At synthesis of the samples by means of sol-gel method the pH of prepared solution was adjusted to about 2,5 by adding of concentrated solution of NH_4OH (super pure grade). pH monitoring was performed using pH-150M pH-meter. Obtained solutions were evaporated at 343 K on the magnetic stirrer with heating IKA RH basic 2 at 343–363 K to form of viscous pink gel. Over the course of processes occurring in solutions during the mixing and evaporation followed using CFK-3-01 photometer by means of colorimetry and tyrbidimetry methods.

Obtained gels were dried at 383–403 K on the electroheating plate to form pink but for polymeric and sol-gel methods dark-grey xerogels. Xerogels were milled and then dried on the electroheating plate at 433–453 K to form black powders, which were annealed in the muffle furnace during 4 h at 873 K. The calcined black powders were thoroughly grinded and pressed into disks and bars, which were annealed during 10–12 h within 1123–1173 K with following sintering during 8 h at 1183 K.

Identification of the samples and determination of their lattice constants using X-ray diffraction analysis (XRD) (diffractometer D8 Advance Bruker AXS (Germany), CuK_α – radiation) were performed. The values of coherent scattering areas (CSA, t) of ceramics were calculated using Debye – Sherrer equation $t = 0,9\lambda/\beta\cos\Theta$, where λ – X-ray wavelength, β – reflex broadening, Θ – diffraction angle [4]. The oxygen nonstoichiometry index (δ) of the samples by means of iodometric titration was determined.

Thermal analysis of the $CaCO_3$ and Co_3O_4 powders mixture as well as the powder of xerogels which are semiproducts at synthesis of $Ca_3Co_4O_{9+\delta}$ by means of B–D methods after drying at 403 K was conducted by means of the Mettler Toledo (Swiss) thermal analysis system in

air within 298–1173 K temperature region at $10 \text{ K} \cdot \text{min}^{-1}$ heating rate.

Microstructure of the sintered ceramics was studied using JSM-5610 LV (Japan). Apparent density of the samples (ρ_{exp}) was determined using their mass and geometric dimensions.

Thermal expansion, electrical conductivity (σ) and thermo-EMF(S) of ceramics was measured in air within 300–1100 K temperature region using methods described in details in [5, 6]. Power factor values of ceramics were calculated using equation of $P = S^2\sigma$. Linear thermal expansion coefficient (LTEC, α) and apparent activation energy of electrical conductivity (E_a) values of the samples were calculated from the linear parts of $\Delta l / l_0 = f(T)$ and $\ln(\sigma T) = f(1/T)$ dependences respectively.

Results and their discussion. Absorption spectra of solutions used at synthesis of ceramics by means of B and C methods during their evaporation did not changed practically. So, we can conclude that "solution stage" of these methods is not accompanied by chemical transformations but results only in homogenization of the samples on the molecular level.

One of the most important parameters at synthesis of oxide ceramics by means of sol-gel method is pH of solution, which must be thoroughly monitored, because at too small pH values (highly acid solution) hydroxide sol is not formed, but at too high pH (neutral or alkaline solution) in solution is formed not sol but suspension which disperse phase particles rapidly precipitate to the bottom of the vessel. In our experiments, the precipitate formed at pH > 4,5[1] and increase of pH of solutions was accompanied by a change of their color (fig. 1). Analysis of the literature data [7] allows you to explain the change of solutions colors by changing in coordination environment of the cobalt cations from $[Co(H_2O)_6]^{2+}$ (pink, $1 < \text{pH} < 4$) to $[Co(NH_3)_{6-n}(H_2O)_n]^{2+}$ (blue, $5 < \text{pH} < 8$).

In contrast to the true solution sol can scatter light so its formation process can be monitored by tyrbidimetry. As can be seen from the fig. 2, increase of the optical density of solution connected with the beginning of colloid particles formation in it begins at pH = 3,7. Trying to get sol from solution with pH = 3,7 we observed that during evaporation of the solution from it began to precipitate the $Ca(OH)_2$ particles. To avoid the formation of precipitate, the solution was acidified, bringing its pH to 2.5.

The results of the thermal analysis of the mixture of $CaCO_3$ and Co_3O_4 powders as well as the powders of xerogels which are semiproducts at synthesis of

$Ca_3Co_4O_{9+\delta}$ using B–D methods are given in the fig. 3 and in the table 1. As can be seen, thermogravimetric curve (TG) of the mixture of $CaCO_3$ and Co_3O_4 powders (fig. 3, *a*) may be divided in three parts and on the 1st–2nd parts mass of the sample decreased but on the 3rd part mass increased.
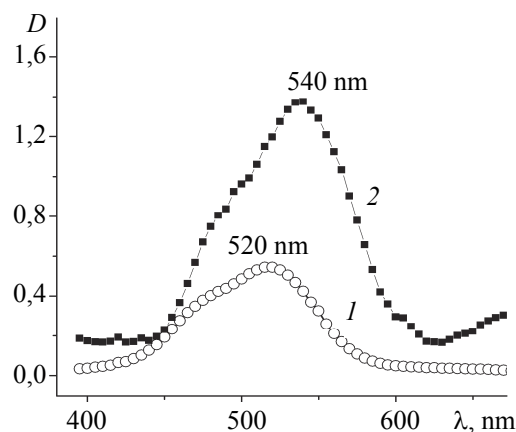

Fig. 1. Absorption spectra of working solutions having different pH values:
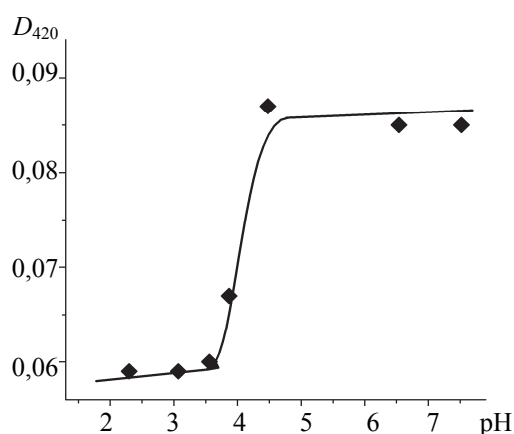*1* – pH = 1,3 (pink color); *2* – pH = 8,2 (violet color)

Fig. 2. Dependence of optical density of working solution versus pH value

The mass loss of the sample on the 1st stage is small ($\approx 0,37$ и $\approx 0,21\%$ within $298 < T < 473$ K and $473 < T < 893$ K temperature regions respectively) and take place, probably, due to the evolution from the sample adsorbed and weakly-bonded water as well as, perhaps, decomposition of $CaCO_3$ particles having submicron size [8]. The intensive ($\approx 20,06\%$ or $\approx 10,12$ mg, which is close to the calculated mass loss – $\approx 10,72$ mg) mass loss begins at 893 K. It follows by the large endothermic effect with extremum at 1083 K (fig. 3, *a*, DSC curve) and corresponds to the $CaCO_3$ decomposition (according to [9], calcium carbonate decomposition in air begins near 900 K). On this stage forms the product of reaction – layered calcium cobaltite:

$$3CaCO_3 + 4/3Co_3O_4 + (1 - 3/2\gamma)/3O_2 \rightarrow$$
$$\rightarrow Ca_3Co_4O_{9-\gamma} + 3CO_2\uparrow.$$

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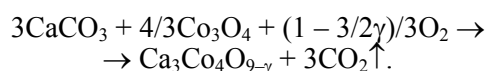
[1] Solutions with precipitates also were used in preparation of ceramics according to the method applied in the B–D methods. This ceramic preparation method in paper was named as E method.
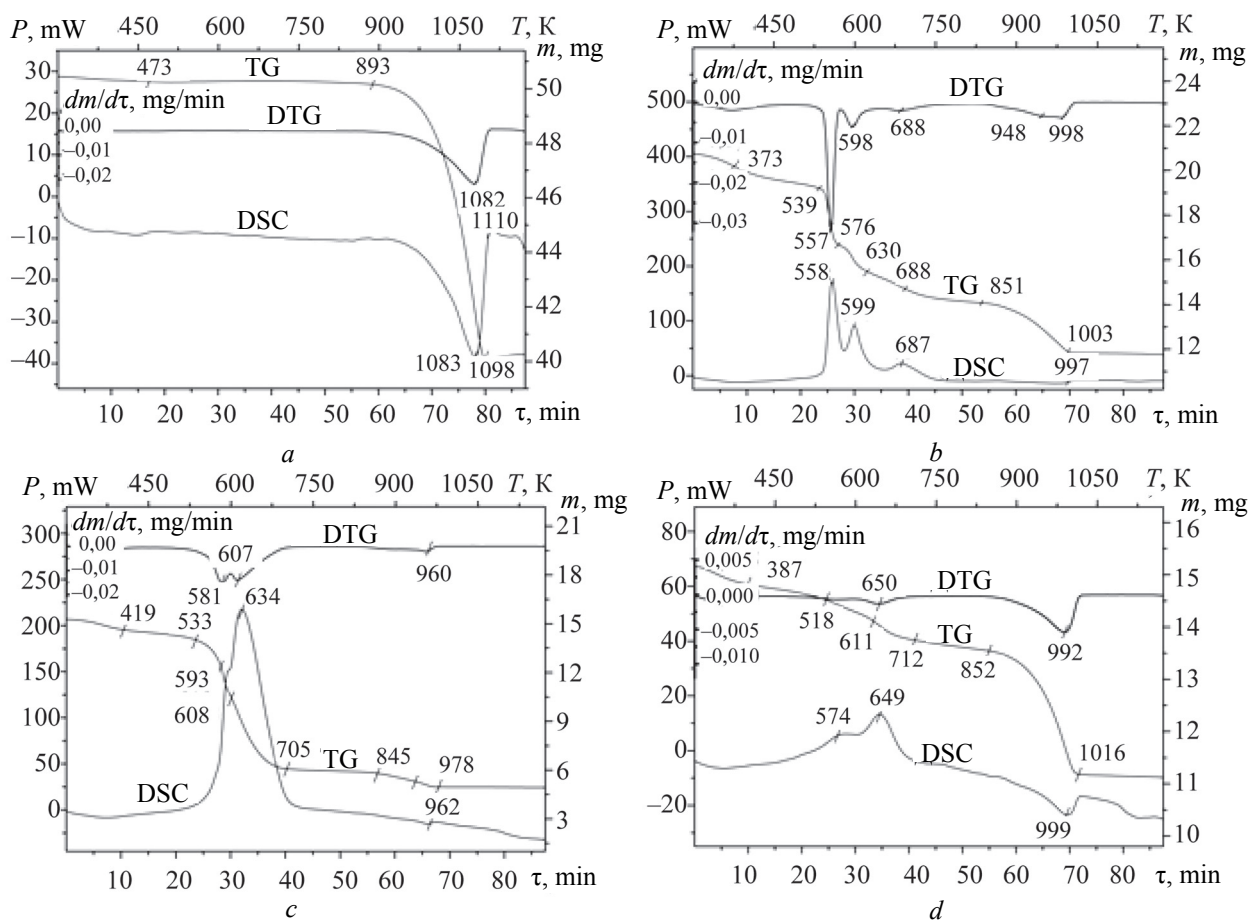
Fig. 3. Results of the thermal analysis of the calcium carbonate $CaCO_3$ and cobalt oxide Co_3O_4 mixture (*a*)
and xerogels used at preparation of $Ca_3Co_4O_{9+\delta}$ by means of B (*b*), C (*c*) and D methods (*d*)

Mass gain at the 3rd stage of the TG curve
($1098 < T < 1197$ K) ($\approx 0,41\%$), which follows by
the small and diffuse exothermic effect with ex-
tremum at 1110 K, took place due to the saturation
of the calcium cobaltite with oxygen:

$$Ca_3Co_4O_{9-\gamma} + (\gamma + \delta)/2O_2 \rightarrow Ca_3Co_4O_{9+\delta}.$$
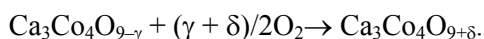
Decomposition of the xerogels formed at syn-
thesis of $Ca_3Co_4O_{9+\delta}$ by means of B–D methods
also occur in three stages (fig. 3, *b–d*, table 1),
which, however, had somewhat different nature.
On the first stage (298–≈530 K) the free and bond-
ed water goes out of the samples, which contents in
the xerogels varies within 3,67–7,89%.

Mass loss of the xerogels on the second stage
(≈530–≈850 K) is 7,51–53,54%, follows by the
large exothermic effects at 558–687 K (B method),
634 K (C method), 574–649 K (D method) and took
place due to the oxidation of organic components of
xerogels into $CaCO_3$ and Co_3O_4 by the atmospheric
oxygen as well as by oxygen, which evolves at cal-
cium and cobalt nitrates decomposes [5, 6]. Interest-
ingly, that mass loss of xerogel formed at prepara-
tion of $Ca_3Co_4O_{9+\delta}$ using C method is much higher
than mass loss of other samples and this mass loss is
accompanied by a very large heat evolution

($P_{max} \approx 225$ mW). This is caused, probably, due to
organic components (citric acid, ethylene glycol) of
solutions used in B and D methods during the evap-
oration partially evolves into gas phase (leaving the
solution), but at heating of solution used in C meth-
od between these components the polycondensation
reaction occurs, which results in formation of rather
hard polymeric matrix.

Mass loss of xerogels at third (≈850–1173 K) is
accompanied by the weak and diffuse endothermic
effect at 997 (B method), 962 (C metod) and
999 K (D method) is 6,29–16,01% and corresponds
to the calcium carbonate decomposition with for-
mation of the reaction product – $Ca_3Co_4O_{9+\delta}$ [5, 6, 8].
Mass loss of all the xerogels on the 3rd stage is about
20% from the final product mass, which means that
after 2nd stage of decomposition of xerogels the calci-
um in the samples is indeed in the form of carbonate
($CaCO_3$) and not in the other form, such as oxalate
(CaC_2O_4) or hydroxide ($Ca(OH)_2$).

As can be seen from the Fig. 4, the xerogel ob-
tained by B method has a large-cell structure, in
which the cells having dimension ≈40 μm separated
by larger cavities; the structure of xerogels prepared
by B and E methods is also cellular and consists of
cells (bubbles) having dimensions of the order of 10–

20 μm ^{2}, and in the nodes of E xerogel the particles of $Ca(OH)_2$ with dimensions about 1–2 μm (Fig. 4, *d*) are observer, which are more or less evenly distributed throughout the volume of xerogel. The cellular structure of xerogel obtained by C method on the microfotograph is not seen (Fig. 4, *b*), which is obviously due to the such reasons: the polymeric matrix formed by polycondensation of citric acid and ethylene glycol in the solution, which is precursor of xerogel, is rather hard and decomposes at temperatures which are higher than those at which it was obtained (383–403 K). In the other words, due to the high strength of the framework of xerogel obtained by C method in its structure are mostly closed pores, whereas in xerogels obtained by other solution methods the individual pores are opened and connected to form a 3D network of open pores.

Prepared using A method samples after finishing of synthesis was, within XRD accuracy, monophase and was a calcium cobaltite $Ca_3Co_4O_{9+\delta}$ (Fig. 5, curve *5*), and its lattice constants (Table. 2) were in a good accordance with the literature data: $a = 0,48376(7)$; $b_1 = 0,45565(6)$; $b_2 = 0,28189(4)$; $c = 1,0833(1)$ nm; $\beta = 98,06(1)°$ [9].

As can be seen from the Fig. 5, formation of $Ca_3Co_4O_{9+\delta}$ in the samples obtained by means of B–D methods begins at 873 K[3] (curve *2*) and practically finishes after sample annealing during 4 h at 1123 K (Curve *3*). So, using of the these methods of synthesis allows us to essentially decrease of temperature (for 50 K) and time of the synthesis (up to 3 times) of calcium cobaltite.

Table 1

Processes, which is occurred during heating of $Ca_3Co_4O_{9+\delta}$ precursors obtained by the solution methods

| Stage	Preparation method						Occuring processes
	B		C		D		
	Temperature interval, K	Mass loss, %	Temperature interval, K	Mass loss, %	Temperature interval, K	Mass loss, %	
1	298−539	7,55	298−533	7,89	298−518	3,67	Evolution of free and bonded water
2	539−851	24,69	533−845	53,54	518−852	7,51	Oxidation of organic components
3	851−1173	11,09	845−1173	6,29	852−1173	16,01	Decomposition of $CaCO_3$, formation of $Ca_3Co_4O_{9+\delta}$

a   *b*   *c*   *d*

e   *f*   *g*   *h*
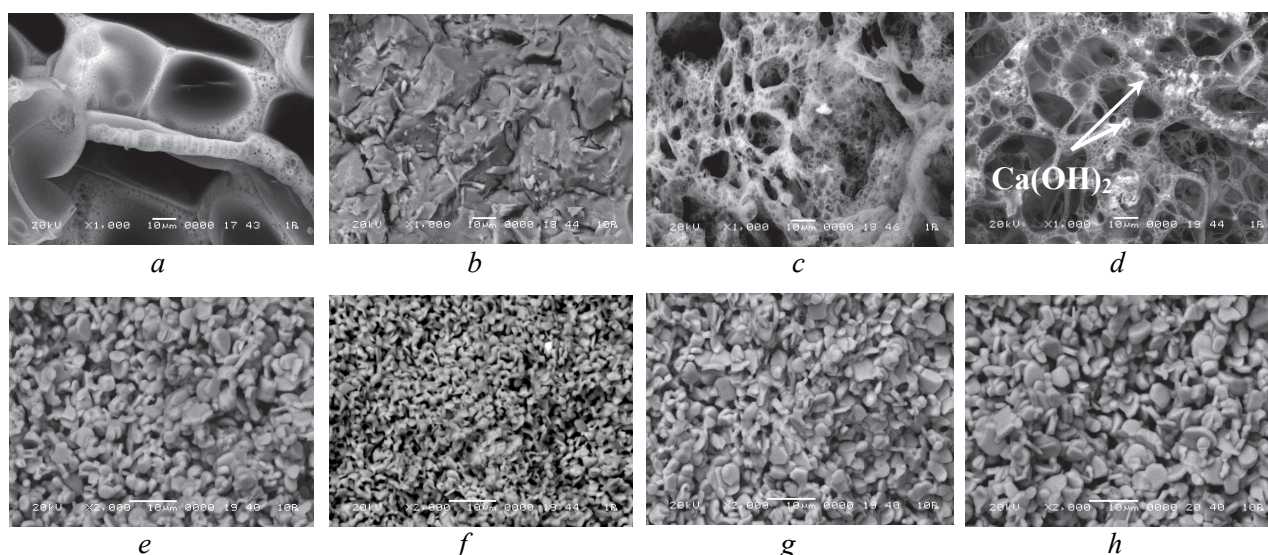
Fig. 4. Microstructure of xerogels (*a – d*) and surfaces of cleaved ceramics (*e – h*) of $Ca_3Co_4O_{9+\delta}$ prepared by means of B (*a, e*), C (*b, f*), D (*c, g*) and E methods (*d, h*)

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[2] In the solidified Plateau channels and nodes forming spatial framework of xeroges (solid foams) a great number of bubbles (cells) having micron and submicron dimensions are seen (Fig. 4); so, xerogels are polydisperse solid foams and polydispersity more pronounced for the xerogels obtained by means of sol-gel method and precipitation method.

[3] When C method of synthesis is used the most intensive reflexes of $Ca_3Co_4O_{9+\delta}$ phase are seen after heat treatment of the sample at 423 K yet (fig. 5, *c*, curve *1*). On the diffractograms of the powders obtained by means of D method with the same thermal prehistory are seen pronounced reflexes of synthesis semiproducts ($CaCO_3$ and Co_3O_4 phases), which are absent in the powder obtained by B method (fig. 5, *b*, curve *1*).
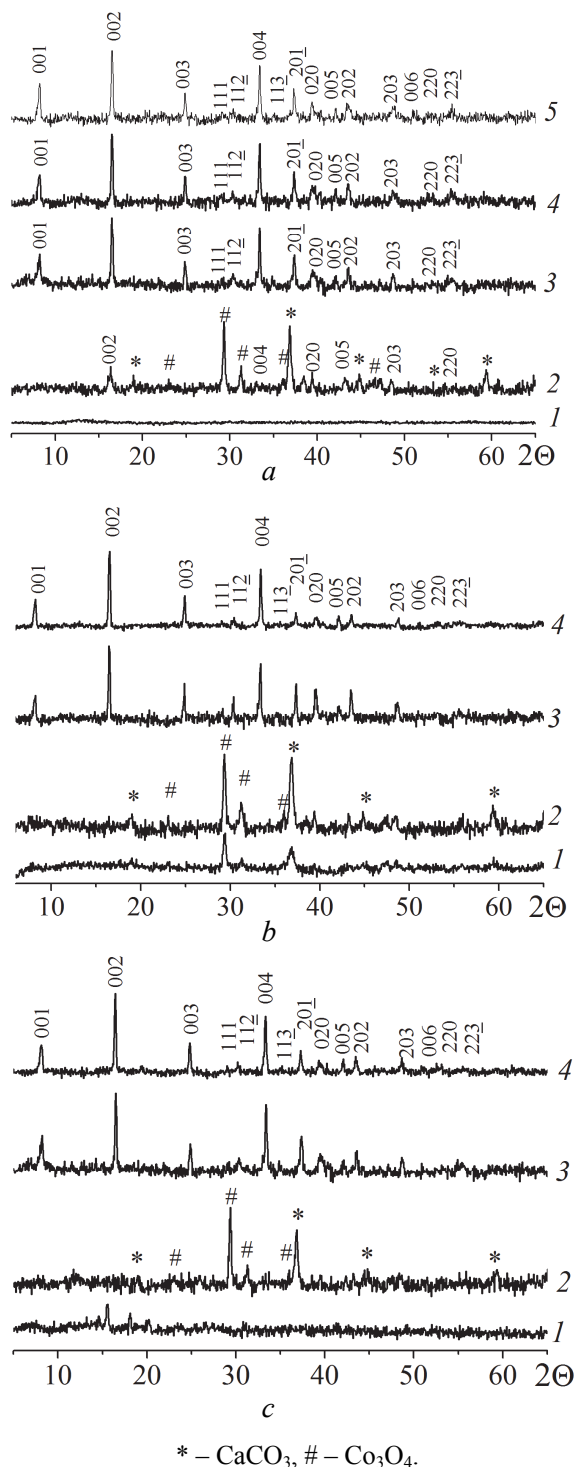
* – $CaCO_3$, # – Co_3O_4.

Fig. 5. X-ray diffractograms of $Ca_3Co_4O_{9+\delta}$
powders obtained by means of A (*a*, curve *5*),
B (*a*, curves *1 – 4*),
D (*b*) and C methods (*c*):
1 – sample dried at 423 K;
2 – sample annealed during 4 h at 873 K;
3 – sample annealed during 4 h at 1123 K;
4 – sample annealed 10 h at 1123 K and 8 h at 1183 K;
5 – sample prepared using A method
and annealed during 12 h at 1173 K
and during 12 h at 1193 K

After heat treatment at 1183 K the ceramic samples of the layered calcium cobaltite prepared using solution method were, within XRD accuracy, monophase and had structure of $Ca_3Co_4O_{9+\delta}$ [10] with lattice constants of $a = 0{,}4820{-}0{,}4835$; $b_1 = 0{,}4554{-}0{,}4571$; $b_2 = 0{,}2802{-}0{,}2885$; $c = 1{,}085{-}1{,}088$ nm; $\beta = 97{,}82{-}98{,}37°$ (Table 2). The value of oxygen nonstoichiometry index (δ) of the sample obtained by means of A method was 0,29, but for samples prepared using B–E methods was slightly higher ($\delta = 0{,}35{-}0{,}58$ (table 2)) due to their heat treatment temperature was lower. As can be seen from the data given in Table 2, lattice constants of the $Ca_3Co_4O_{9+\delta}$ samples prepared using different methods taking into account the differences of their oxygen stoichiometry are in a good agreement with each other.

The CSA values of ceramics prepared using different methods which corresponded to sizes of their individual grains were similar and equal about 40 nm (except sample obtained using D method, which CSA values were slightly higher – $\approx$50 nm) (Table2). Considering the results obtained by means of XRD method we can conclude that preparation method of $Ca_3Co_4O_{9+\delta}$ ceramics do not influence practically their structural characteristics.

The crystallites of $Ca_3Co_4O_{9+\delta}$ ceramics were anisometric and had form of plates (flakes), which thickness, as a rule, was less than one micron and other dimensions varied within one–ten microns (Fig. 4, *e–h*) and was smallest for ceramics prepared using C method.

The ceramics porosity was 30% for the sample prepared using A method and 14–17% for samples obtained using B–E methods (Table 2).

Comparing the results of X-ray analysis, measurements of apparent density and electronic microscopy, we can conclude, that presence of solution stage of synthesis (B–E methods) let us obtain more dense and fine-grained ceramics with reduced energy consumption in comparison with solid-state reactions method (method A).

The $\Delta l/l_0 = f(T)$ dependences for the ceramics studied were practically linear, which means, that in the temperature range 300–1100 K calcium cobaltite did not undergo the phase transitions. As can be seen from the data given in Table 2, LTEC of ceramics prepared using solution methods (except sample obtained by means of sol-gel method) is lower than for than ceramic obtained using solid-state reactions method due to, probably, the lower porosity of the samples prepared by means of solution methods.

The results of the study of electrophysical and thermoelectric properties of the $Ca_3Co_4O_{9+\delta}$ ceramics prepared using different methods are given in the fig. 6. As can be seen, the materials synthesized are the *p*-type semiconductors ($\partial\sigma / \partial T > 0$, $S > 0$, Fig. 6, *a*, *b*), hereby their conductivity character

above 800–900 K changes from semiconducting to the metallic ($\partial\sigma / \partial T < 0$) due to evolution of the weakly-bonded oxygen (δ) from the volume of ceramics to the environment.

Conductivity value of ceramics prepared using B–D methods was larger (for ceramics synthesized using E method was smaller) than for samples synthesized by means of A method (Fig. 6, *a*) and highest conductivity values was characterized the ceramics prepared using C and B methods ($\sigma_C/\sigma_A \approx \approx \sigma_D/\sigma_A \approx 1,25$), obviously, due to their lower porosity. The values of apparent activation energy of electrical conductivity (E_A) of the samples prepared using different methods varied within 0,060–0,069 eV (Table 2) and for ceramics obtained using solution methods was slightly lower. So, results of electrical conductivity measurements let us conclude that use of solution stage at synthesis of layered calcium cobaltite provides more electrical conductive ceramics in which the charge transfer occurs with lower energy

difficulties.

As can be seen from the data given in Fig. 6, *b*, thermo-EMF values of $Ca_3Co_4O_{9+\delta}$ ceramics increased at temperature increasing and at high temperatures for ceramics synthesized using solution methods (except sample prepared using C method) were slightly higher than for ceramic prepared by means of solid-state reactions method (method A).

The power factor values for the ceramics studied also increased at temperature gain and at elevated temperatures for all samples prepared using B–E methods was higher than for ceramics synthesized by means of A method (Fig. 6, *c*) due to the larger values both electrical conductivity and thermo-EMF of these materials. The maximal value of power factor demonstrates the prepared using D method $Ca_3Co_4O_{9+\delta}$ ceramics – ≈ 190 μW/(m·K^2) at 1100 K which more than two times higher than for ceramics synthesized by means of A method (≈ 90 μW/(m·K^2) at the same temperature).

Table 2

Values of lattice constants (a, b_1, b_2, c, β, V, b_1/b_2), LTEC (α), apparent activation energy of electrical conductivity (E_A), oxygen nonstoichiometry index (δ), porosity (Π) and coherent scattering areas (t) of ceramics based on layered calcium cobaltite

Preparation method	SSRM	CM	PM	SGM	PrM
a, nm	0,4836(5)	0,4830(7)	0,4835(8)	0,4835(8)	0,4826(5)
b_1, nm	0,4561(5)	0,4562(8)	0,4554(9)	0,4554(9)	0,4567(7)
b_2, nm	0,2821(5)	0,2812(6)	0,2802(7)	0,2802(7)	0,2843(9)
c, nm	1,083(1)	1,085(1)	1,088(1)	1,088(1)	1,084(8)
β,°	98,19(5)	98,28(8)	98,37(9)	98,37(9)	97,88(6)
V, nm^3	0,2365(2)	0,2365(9)	0,2390(9)	0,2370(9)	0,2367(8)
b_1/b_2	1,617	1,622	1,617	1,625	1,606
δ	0,29	0,35	0,56	0,58	0,57
$\alpha\cdot10^5$, K^{-1}	1,29	1,28	1,22	1,31	1,20
E_A, eV	0,069	0,065	0,066	0,068	0,060
Π, %	30	14	16	14	17
t, nm	40,8	36,7	36,8	51,9	37,7

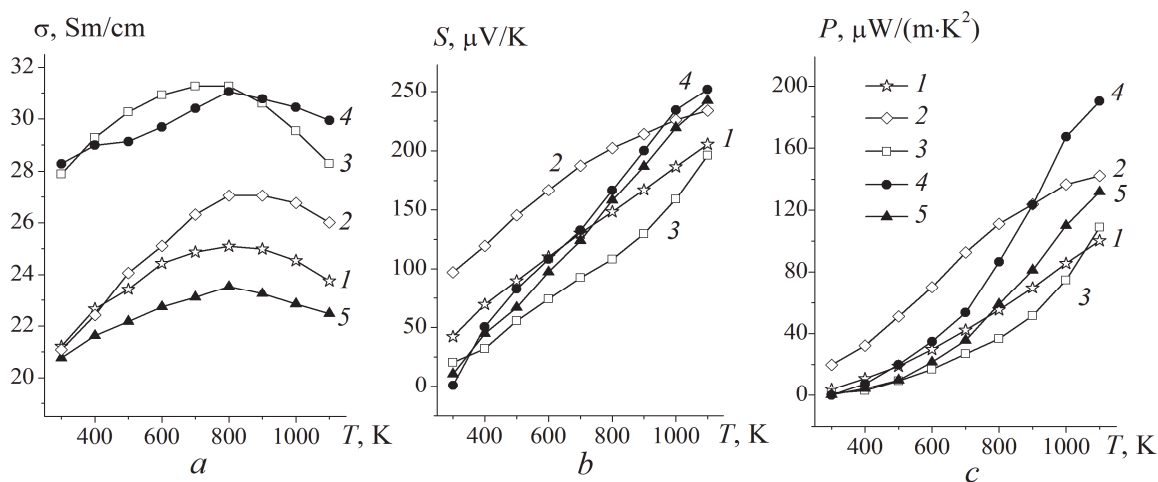Fig. 6. Temperature dependences of electrical conductivity (σ) (*a*), thermo-EMF (S) (*b*) and power factor (P) (*c*) of $Ca_3Co_4O_{9+\delta}$ ceramics prepared using A (*1*), B (*2*), C (*3*), B (*4*) and E methods (*5*)

Conclusion. So, in this work using complex of independent methods the processes occurring at preparation of $Ca_3Co_4O_{9+\delta}$ ceramics using solid-state reactions method and different solution methods (citrate, polymeric and sol-gel methods) were studied as well as influence of preparation method on the crystal structure, microstructure, thermal expansion, electrophysical and thermoelectric properties of $Ca_3Co_4O_{9+\delta}$ ceramics was investigated.

By means of optical investigation methods (colorimetry and tyrbidimetry) selected pH interval in which formarion of $Ca_3Co_4O_{9+\delta}$ precursors flows through the stage of sol formation. Influence of preparation on the microstructure of xerogels which are precursors at synthesis of $Ca_3Co_4O_{9+\delta}$ ceramics by means of solution methods is studied.

It was found that decomposition of these xerogels obey the general laws (particularly, occurs in three stages), but formation of polymeric matrix in the sample prepared by C method lead to the intensification of the 2nd stage of xerogel decomposition and to the formation of more fine-grained ceramics than at using of B and D methods.

It is shown, that precipitation of $Ca(OH)_2$ at synthesis of $Ca_3Co_4O_{9+\delta}$ ceramics using sol-gel method did not prevent to obtain the monophase sample (within XRD accuracy), which crystal structure, microstructure and thermo-EMF are practically the same as for sample prepared by means of sol-gel method. It is established, that presence of solution stage let us obtain more dense and fine-grained ceramics of layered calcium cobaltite which characterizes higher values of electrical conductivity and power factor.

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