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## **Effect of the Preparation Method on the Structure and Properties of the Layered Calcium Cobaltate**

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**Abstract** *By means of colorimetry, turbidimetry, thermogravimetry, differential thermal analysis, X-ray analysis and IR absorption spectroscopy the processes taking place at preparation of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics using solid-state reactions, citrate, polymeric and sol-gel methods were studied. The crystal structure and microstructure, thermal stability, thermal expansion, thermal conductivity, electrical conductivity and thermo-EMF of the samples were investigated and values of their power factor and figure-of-merit were calculated. It is shown that usage of solution methods let us obtain more dense and fine-grained ceramics, which characterizes more higher values of electrical conductivity and power factor.*

**Keywords:** Layered calcium cobaltate, preparation method, oxide thermoelectric, thermal stability, power factor.

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### **INTRODUCTION**

Layered calcium cobaltate  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  possesses high thermoelectric parameters, it is stable in air at elevated temperatures and has relatively low cost (in comparison with traditional thermoelectric based on the bismuth telluride), so, it can be considered as prospective material for high-temperature thermoelectroconversion [1]. It is well known, that functional properties of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics obtained by means of solid-state reactions method is worth than for monocrystals, but they can be improved by preparation of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  by means of «soft», solution methods of synthesis [2, 3]. Taking it into account, investigation of processes taking place at formation of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics during solution methods of synthesis as well as effect of preparation method on the microstructure and properties obtained hereby ceramics is actual problem which have great scientific and practical interest.

The aim of this work is the study of the processes occurring at synthesis of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics by means of solid-state reactions method and different solution methods (citrate, polymeric and sol-gel methods) as well as influence of preparation method on the crystal structure, microstructure, physicochemical and functional properties of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics.

## MATERIALS AND METHODS

At preparation of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics by means of solid-state reactions method (SSRM) the  $\text{CaCO}_3$  (pure grade) and  $\text{Co}_3\text{O}_4$  (pure grade) powders 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 and annealed during 12 h at 1173 K, re-grinded 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 than sintered during 4–20 h at 1193 K.

To synthesize the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  sample using citrate method (CM) we used the water solutions of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (pure for analysis) ( $C = 0,6 \text{ M}$ ),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (pure for analysis) ( $C = 0,8 \text{ M}$ ) and  $\text{C}_6\text{H}_8\text{O}_7$  (pure grade) ( $C = 0,5 \text{ M}$ ), 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 ( $n(\text{C}_2\text{H}_6\text{O}_2) : n(\text{C}_6\text{H}_8\text{O}_7) = 1 : 1$ ). 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  $\text{NH}_4\text{OH}$  (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 methodics. Obtained gels were dried at 383–403 K on the electroheating plate to form pink or dark-grey (for polymeric and sol-gel methods) xerogels, which were milled and then dried on the electroheating plate at 433–453 K to form black powders. The black powders obtained were annealed in the muffle furnace during 4 h at 873 K. The calcined powders were thoroughly grinded and pressed into disks and bars, which were than annealed during 10–12 h within 1123–1173 K with following sintering during 8 h at 1183 K.

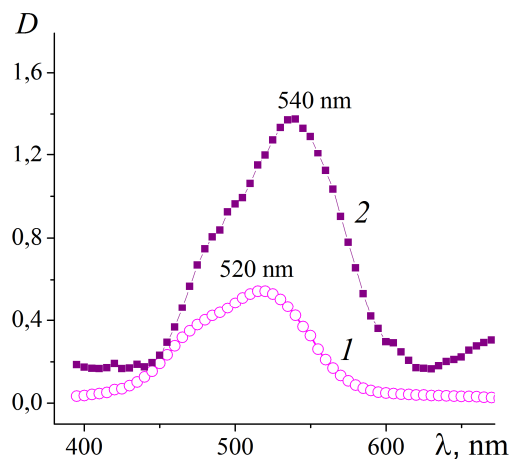
Identification of the samples and determination of their lattice constants using X-ray diffraction analysis (XRD) (diffractometer D8 Advance Bruker AXS (Germany),  $\text{CuK}_\alpha$  – radiation) were performed. The values of coherent scattering areas (CSA,  $t$ ) of ceramics were calculated using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

Thermal analysis of the  $\text{CaCO}_3$  and  $\text{Co}_3\text{O}_4$  powders mixture, the powders of precursors at synthesis of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  by citrate, polymeric and sol-gel methods after drying at 403 K as well as the obtained using different methods  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  powders 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) scanning scanning electron microscope. Apparent density of the samples ( $\rho_{\text{exp}}$ ) was determined using their mass and geometric dimensions. Thermal expansion, electrical conductivity ( $\sigma$ ) and thermo-EMF( $S$ ) of ceramics was measured in air within 300–1100 K temperature region using methods described in [5, 6]. Thermal conductivity of the sintered ceramics ( $\lambda$ ) in air within 298–423 K using thermal conductivity measurer IT- $\lambda$ -400 was investigated. Lattice ( $\lambda_{\text{lat}}$ ) and electronic ( $\lambda_{\text{el}}$ ) parts of thermal conductivity were calculated using  $\lambda = \lambda_{\text{el}} + \lambda_{\text{lat}}$ ,  $\lambda_{\text{el}} = \sigma LT$  relations, where  $L$  is the Lorentz number ( $L = 2.45 \cdot 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ ). Linear thermal expansion coefficient (LTEC,  $\alpha$ ) 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. Power factor and figure-of-merit values of ceramics were calculated using equations of  $P = S^2\sigma$  and  $ZT = PT/\lambda$ .

## RESULT AND DISCUSSION

Absorption spectra of the solutions used at synthesis of ceramics by means of citrate, polymeric and sol-gel 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.



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

One of the most important parameters at synthesis of oxide ceramics by means of sol-gel method is solution pH, 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<sup>1</sup> and increase of solution pH was accompanied by a change of their color (fig. 1). Analysis of the literature data [7] allows us to explain the change of solutions colors by changing in coordination environment of the cobalt cations from  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (pink,  $1 < \text{pH} < 4$ ) to  $[\text{Co}(\text{NH}_3)_{6-n}(\text{H}_2\text{O})_n]^{2+}$  (blue,  $5 < \text{pH} < 8$ ).

In contrast to the true solution sol (colloid solution) can scatter light so its formation process can be monitored by turbidimetry. 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  $\text{Ca}(\text{OH})_2$  particles. To avoid the formation of precipitate, the solution was acidified, bringing its pH to 2.5.

The results of the thermal analysis of precursors are given in the fig. 3 and in the table 1. As can be seen, thermogravimetric curve (TG) of the mixture of  $\text{CaCO}_3$  and  $\text{Co}_3\text{O}_4$  powders (fig. 3, a) may be divided in three parts (stages) and on the 1<sup>st</sup>–2<sup>nd</sup> stages mass of the sample decreased but on the 3<sup>rd</sup> stage mass increased.

<sup>1</sup> Solutions with precipitates also were used in preparation of ceramics according to the method applied in the solution methods (CM, PM and SGM). This ceramic preparation method in paper was named as precipitation method (PrM).

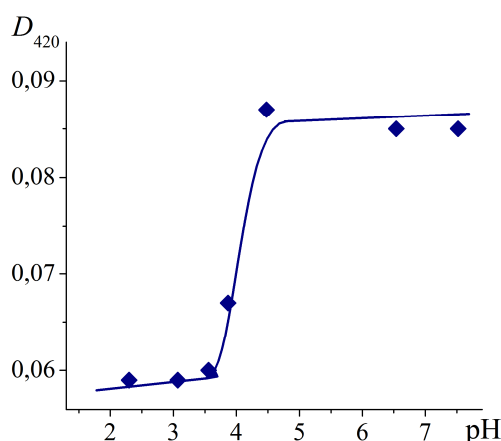


Fig. 2. Dependence of optical density of working solution versus its pH value

The mass loss of the sample on the 1<sup>st</sup> stage is small (0,37 и 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<sub>3</sub> particles having submicron size [8]. The intensive (20,06% or 10,12 mg, which is close to the calculated mass loss – ≈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<sub>3</sub> decomposition (according to [9], calcium carbonate decomposition in air begins near 900 K). On this stage forms the product of reaction – layered calcium cobaltate:

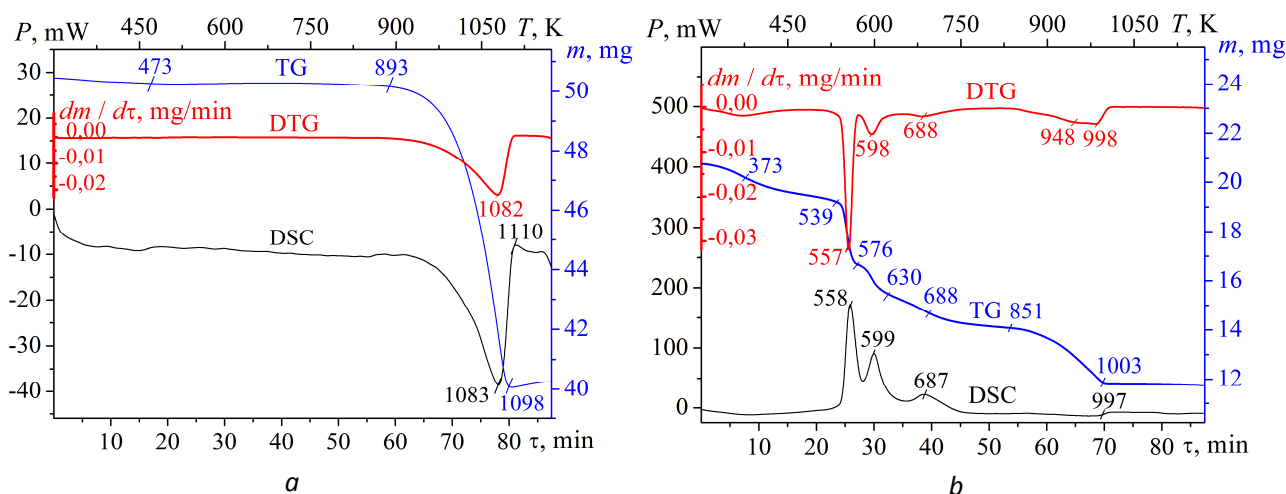
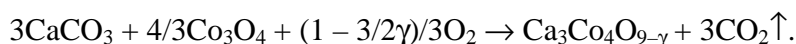
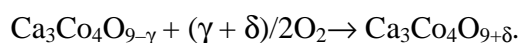


Fig. 3. Results of the thermal analysis of the calcium carbonate CaCO<sub>3</sub> and cobalt oxide Co<sub>3</sub>O<sub>4</sub> mixture (a) and Ca<sub>3</sub>Co<sub>4</sub>O<sub>9+δ</sub> precursor prepared by citrate method (b)

Mass gain at the 3<sup>rd</sup> stage of the TG curve (1098 < T < 1197 K) (0,41%), which follows by the small and diffuse exothermic effect with extremum at 1110 K, took place due to the saturation of the calcium cobaltate with oxygen:



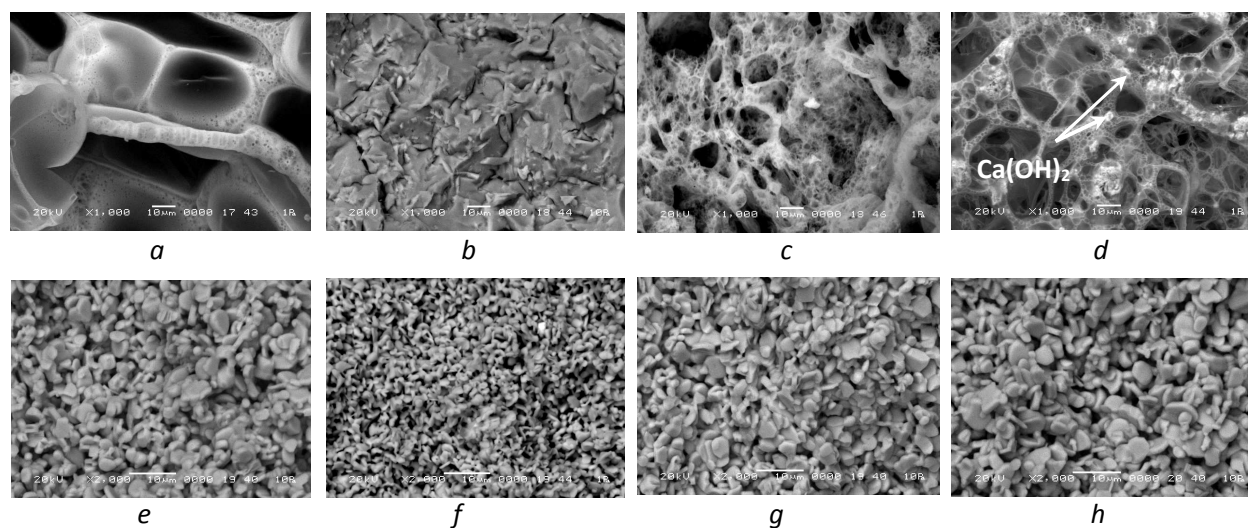
Decomposition of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  precursors obtained by the citrate, polymeric and sol-gel methods also occur in three stages (fig. 3, *b*, table 1), which, however, had somewhat different nature. On the first stage (298–530 K) the free and bonded water goes out of the samples, which contents in the precursors varies within 3,67–7,89%.

**Table 1****Processes occurred during heating of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  precursors prepared using solution methods**

Stage	Preparation method						Occuring processes
	Citrate		Polymeric		Sol-gel method		
	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 $\text{CaCO}_3$ , formation of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$

Mass loss of the precursors on the second stage (530–850 K) is 7,51–53,54%, follows by the large exothermic effects at 558–687 K (CM), 634 K (PM), 574–649 K (SGM) and takes place due to the oxidation of organic components of precursors into  $\text{CaCO}_3$  and  $\text{Co}_3\text{O}_4$  by the atmospheric oxygen as well as by oxygen, which evolves at calcium and cobalt nitrates decomposes [5, 6]. Interestingly, that mass loss of PM precursor is much higher than mass loss of other samples and it is accompanied by a very large heat evolution ( $P_{\max} \approx 225$  mW). This is caused, probably, due to the organic components (citric acid, ethylene glycol) of solutions used in citrate and sol-gel methods during the evaporation of solutions partially evolves into gas phase (leaving the solution), but at heating of solution used in polymeric method between these components the polycondensation reaction occurs, which results in formation of rather hard polymeric matrix.

Mass loss of precursors at third stage (850–1173 K) is accompanied by the weak and diffuse endothermic effect at 997 (CM), 962 (PM) and 999 K (SGM) is equal to 6,29–16,01% and corresponds to the calcium carbonate decomposition with formation of the reaction product –  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  [5, 6, 8]. Mass loss of all the precursors on the 3<sup>rd</sup> stage is about 20% from the final product mass, which means that after 2<sup>nd</sup> stage of decomposition of precursors the calcium in the samples is indeed in the form of carbonate ( $\text{CaCO}_3$ ) and not in the other form, such as oxalate ( $\text{CaC}_2\text{O}_4$ ) or hydroxide ( $\text{Ca(OH)}_2$ ).



**Fig. 4.** Microstructure of xerogels (*a – d*) and surfaces of cleaved ceramics (*e – h*) of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  prepared by means of citrate (*a, e*), polymeric (*b, f*), sol-gel (*c, g*) and precipitation methods (*d, h*)

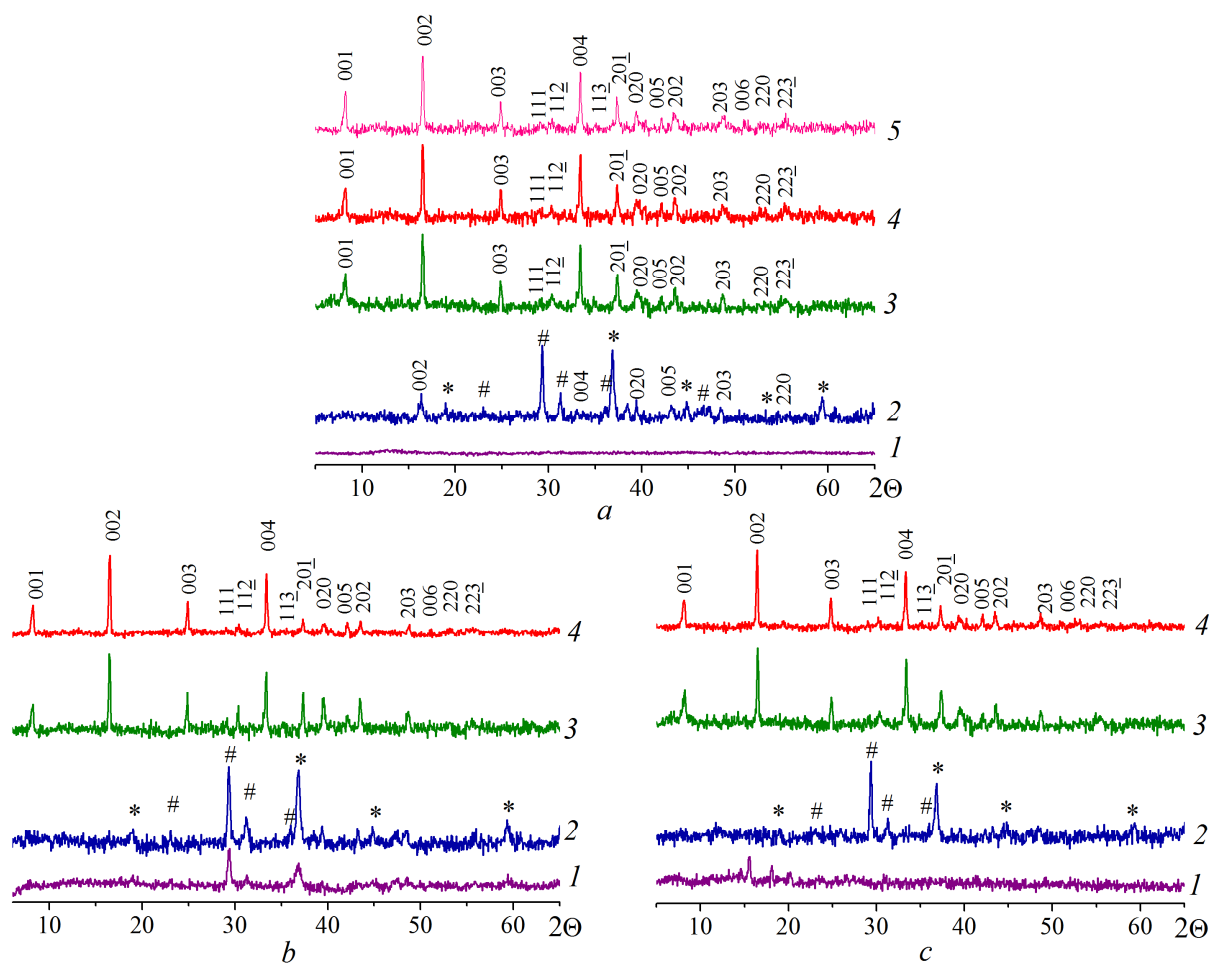
As can be seen from the fig. 4, the xerogel obtained by citrate method has a large-cell structure, in which the cells having dimension about  $40 \mu\text{m}$  separated by larger cavities; the structure of xerogels prepared by sol-gel and precipitation methods is also cellular and consists of cells (bubbles) having dimensions of the order of  $10\text{--}20 \mu\text{m}^2$ , and in the nodes of PrM xerogel the particles of  $\text{Ca}(\text{OH})_2$  with dimensions about  $1\text{--}2 \mu\text{m}$  (fig. 4, *d*) are observed, which are more or less evenly distributed throughout the volume of xerogel. The cellular structure of xerogel obtained by polymeric method on the microphotograph 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 ( $383\text{--}403 \text{ K}$ ). In the other words, due to the high strength of the framework of xerogel obtained by polymeric 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 SSRM sample after finishing of synthesis was, within XRD accuracy, monophasic and was a calcium cobaltate  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  (fig. 5, curve 5), and its lattice constants (table. 2) were in a good accordance with the literature data:  $a = 0,48376(7)$ ;  $b_1 = 0,45565(6)$ ;  $b_2 = 0,28189(4)$ ;  $c = 1,0833(1) \text{ nm}$ ;  $\beta = 98,06(1)^\circ$  [9].

As can be seen from the fig. 5, formation of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  in the samples obtained by means of solution methods begins at  $873 \text{ K}^3$  (curve 2) and practically finishes after sample annealing during 4 h at  $1123 \text{ K}$  (curve 3). So, usage of the citrate method allows us to essentially decrease of temperature (for  $50 \text{ K}$ ) and time of the synthesis (up to 3 times) of calcium cobaltate.

<sup>2</sup> In the solidified Plateau channels and nodes forming spatial framework of xerogels (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.

<sup>3</sup> When polymeric method of synthesis is used the most intensive reflexes of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  phase are seen after heat treatment of the sample at  $423 \text{ K}$  yet (fig. 5, *c*, curve 1). On the diffractograms of the powders obtained by means of SGM with the same thermal prehistory are seen pronounced reflexes of synthesis semiproducts ( $\text{CaCO}_3$  and  $\text{Co}_3\text{O}_4$  phases), which are absent in the powder obtained by citrate method (fig. 5, *b*, curve 1).



**Fig. 5.** X-ray diffractograms of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  powders obtained by means of solid-state reactions method (*a*, curve 5), citrate (*a*, curves 1 – 4), sol-gel (*b*) and polymeric 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 ceramic 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 cobaltate prepared using solution method were, within XRD accuracy, monophase and had  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  structure [10] with lattice constants of  $a = 0,4820\text{--}0,4835$ ;  $b_1 = 0,4554\text{--}0,4571$ ;  $b_2 = 0,2802\text{--}0,2885$ ;  $c = 1,085\text{--}1,088$  nm;  $\beta = 97,82\text{--}98,37^\circ$  (table 2). The value of oxygen nonstoichiometry index ( $\delta$ ) of the sample obtained by means of SSRM was 0,29, but for samples prepared using solution methods was slightly higher ( $\delta = 0,35\text{--}0,58$  (table 2)) due to their heat treatment temperature was lower. As can be seen from the data given in the table 2, lattice constants of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  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 which corresponded to sizes of their individual grains were similar and equal about 40 nm (except sample obtained using sol-gel method, which CSA values were slightly higher –  $\approx 50$  nm) (table 2). Considering the results obtained by means of XRD method we can conclude that preparation method of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics do not influence practically their structural characteristics.

The crystallites of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  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 polymeric method. The porosity of ceramics determined using XRD and densitometry results was 30% for the sample prepared using SSRM and 14–17% for samples obtained using solution methods (table 2).

**Table 2**

**Values of lattice constants ( $a$ ,  $b_1$ ,  $b_2$ ,  $c$ ,  $\beta$ ,  $V$ ,  $b_1/b_2$ ), LTEC ( $\alpha$ ), apparent activation energy of electrical conductivity ( $E_A$ ), oxygen nonstoichiometry index ( $\delta$ ), porosity ( $\Pi$ ) and coherent scattering areas ( $t$ ) of ceramics based on layered calcium cobaltite**

Preparation method	SSRM	CM	PM	SGM	PrM
$a$ , нм	0,4836(5)	0,4830(7)	0,4835(8)	0,4835(8)	0,4826(5)
$b_1$ , нм	0,4561(5)	0,4562(8)	0,4554(9)	0,4554(9)	0,4567(7)
$b_2$ , нм	0,2821(5)	0,2812(6)	0,2802(7)	0,2802(7)	0,2843(9)
$c$ , нм	1,083(1)	1,085(1)	1,088(1)	1,088(1)	1,084(8)
$\beta$ , °	98,19(5)	98,28(8)	98,37(9)	98,37(9)	97,88(6)
$V$ , нм <sup>3</sup>	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
$\delta$	0,29	0,35	0,56	0,58	0,57
$\alpha \cdot 10^6$ , K <sup>-1</sup>	12,9	12,8	12,2	13,1	12,0
$E_A$ , эВ	0,069	0,065	0,066	0,068	0,060
$\Pi$ , %	30	14	16	14	17
$t$ , нм	40,8	36,7	36,8	51,9	37,7

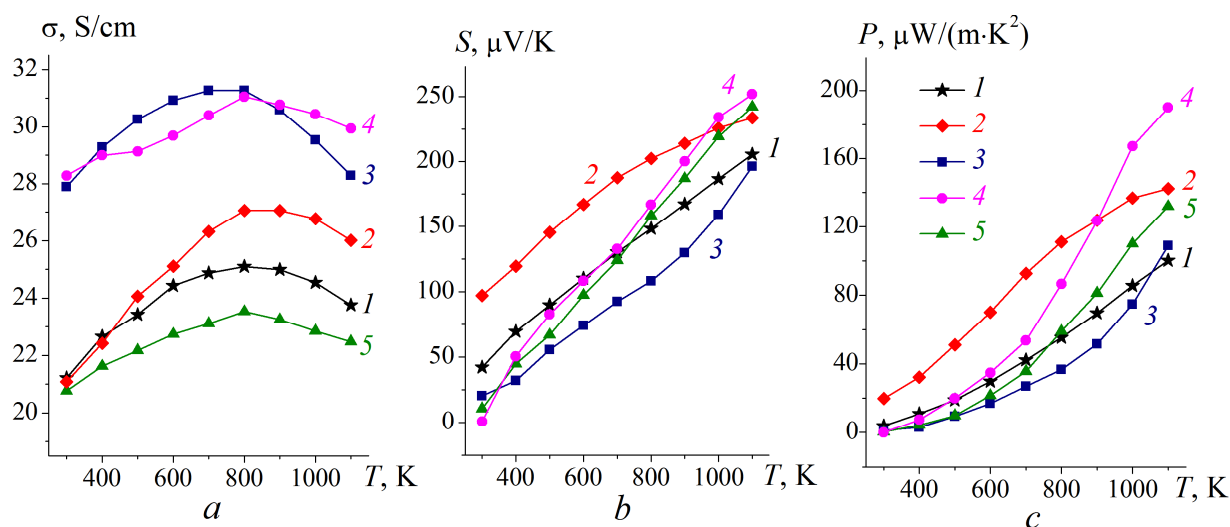
Comparing the results of X-ray analysis, porosity measurements, and electron microscopy, we can conclude, that using of solution method of synthesis let us obtain more dense and fine-grained ceramics with reduced energy consumption in comparison with solid-state reactions method.

The  $\Delta l/l_0 = f(T)$  dependences for the ceramics investigated were practically linear, which means, that in the temperature range 300–1100 K layered calcium cobaltate did not undergo the structural phase transitions. As can be seen from the data given in the table 2, LTEC of ceramics prepared using solution methods (except sample obtained by means of sol-gel method) is lower than for 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 electrotransport properties and power factor of the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  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 ( $\delta$ ) from the volume of ceramics to the environment.

Conductivity value of ceramics prepared using solution methods was larger (for ceramics synthesized using PrM was smaller) than for samples synthesized by means of the solid-state reactions method (fig. 6, *a*) and the ceramics samples prepared using polymeric and sol-gel methods by highest conductivity values was characterized ( $\sigma_{\text{PM}}/\sigma_{\text{SSRM}} \approx \sigma_{\text{SGM}}/\sigma_{\text{SSRM}} \approx 1,25$ ), 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 methods of synthesis of layered calcium cobaltate provides more electrical conductive ceramics in which the charge transfer occurs with lower energy difficulties.

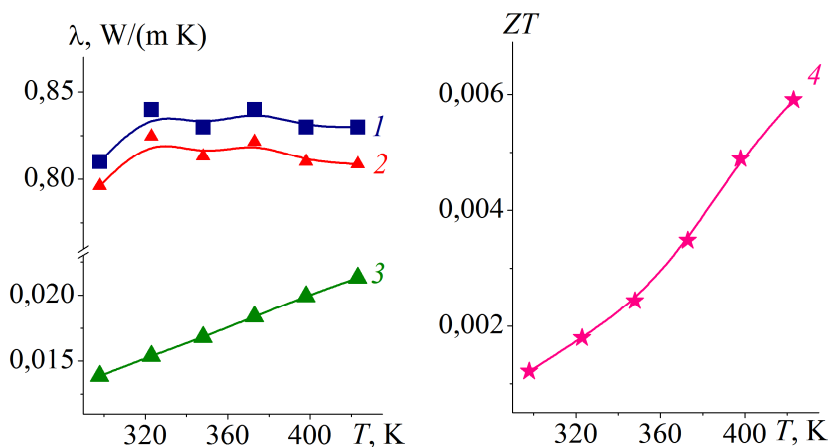


**Fig. 6.** Temperature dependences of electrical conductivity ( $\sigma$ ) (*a*), thermo-EMF ( $S$ ) (*b*) and power factor ( $P$ ) (*c*) of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics prepared using solid-state reactions (1), citrate (2), polymeric (3), sol-gel (4) and precipitation methods (5)

As can be seen from the data given in the fig. 6, *b*, thermo-EMF values of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics increased at temperature increasing and at high temperatures for ceramics synthesized using solution methods (except sample prepared using polymeric method) were slightly higher than for ceramic prepared by means of SSRM.

The power factor values for the ceramics studied also increased at temperature gain and at elevated temperatures for all samples prepared using solution methods was higher than for ceramics synthesized by means of SSRM (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 sol-gel method

$\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics  $-190 \mu\text{W}/(\text{m}\cdot\text{K}^2)$  at 1100 K which more than two times higher than for ceramics synthesized by means of SSRM ( $90 \mu\text{W}/(\text{m}\cdot\text{K}^2)$  at the same temperature).

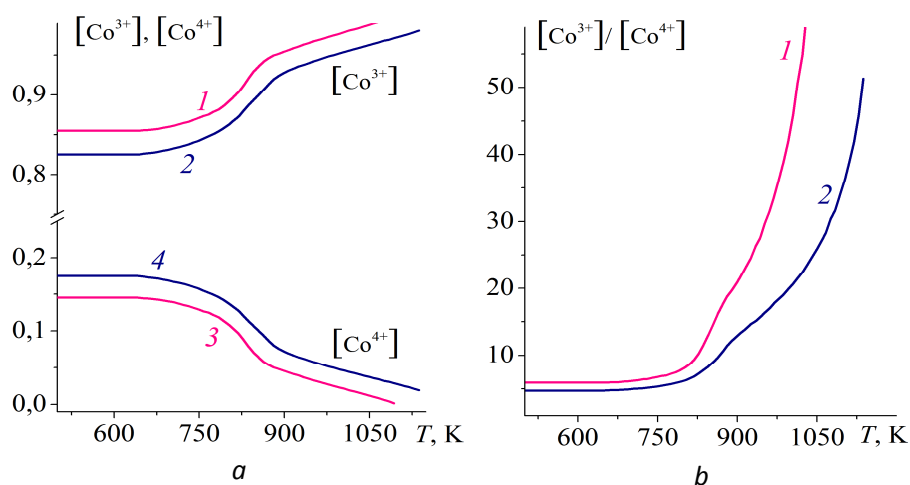


**Fig. 7.** Temperature dependences of total thermal conductivity (1) and its lattice (2) and electronic (3) parts as well as figure-of-merit (4) of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics

Thermal conductivity of the layered calcium cobaltate  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  prepared using SSRM within 298–423 K temperature region was 0,80–0,85 W/(m·K) and, in the whole, did not changed practically at temperature increasing (fig. 7, a). Electronic part of thermal conductivity of ceramics studied was small ( $\lambda_{\text{el}}/\lambda \approx 1-2\%$ ) and linearly increased at temperature increasing, but lattice part of thermal conductivity was dominated ( $\lambda_{\text{lat}}/\lambda \approx 98-99\%$ ) and did not depend on the temperature practically. As can be seen from the fig. 7, b, figure-of-merit of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  increased at temperature gain. Extrapolation of  $\lambda = f(T)$  dependence for  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  oxide to the high-temperature region and substitution of obtained results into equation for calculation of figure-of-merit gives us evaluated values of  $ZT_{1100}$  of this thermoelectric material equal to 0,093. It is close to the results of the work [11] in it which was found that figure-of-merit of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics prepared by means of solid state reactions method reached 0,11 at 1100 K. Evaluated value of  $ZT_{1100}$  for  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  oxide obtained using sol-gel method is 0,196, which is higher than for  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics prepared by means of solid-state reactions method in this work and in work [11].

According to the results of thermal analysis of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  powders synthesized using different methods, the intensive mass loss of the samples due to evolution of the weakly-bonded oxygen from their structure into environment, begins near 645 K and occurs in two stages. On the 1<sup>st</sup> stage within 650–900, 640–930 and 645–860 K for the samples prepared by means of SSRM, CM and PM the mass loss occurs more intensive and is equal to the 0,61, 0,73 and 0,32% respectively. Decreasing of oxygen content in the samples on the 1<sup>st</sup> and 2<sup>nd</sup> stages of mass loss is 1–2,5% and 0,9–1,6% respectively from its total content ( $9+\delta$ ) in the layered cobaltate  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ . On the fig. 8 the temperature dependences of concentrations of cobalt cations  $\text{Co}^{3+}$ ,  $\text{Co}^{4+}$  as well as  $[\text{Co}^{3+}]/[\text{Co}^{4+}]$  ratio in the layered  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  are given, which on the base the results of thermal analysis and iodometry were calculated. As can be seen, at  $T < 650$  K the concentrations of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  cations are 0,82–0,86 and 0,14–0,18 respectively and  $[\text{Co}^{3+}]/[\text{Co}^{4+}]$  ratio is close to the 5. At  $T > 650$  K due to the partial reduction of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$   $\text{Co}^{3+}$  content in it

increases and  $\text{Co}^{4+}$  content decreases.  $[\text{Co}^{3+}]/[\text{Co}^{4+}]$  ratio at temperature increasing exponentially increases and, particularly, for the  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics obtained using SSRM at 1000 K is 45,7.



**Fig. 8.** Temperature dependences of concentrations of  $\text{Co}^{3+}$ ,  $\text{Co}^{4+}$  cations (a) and  $[\text{Co}^{3+}]/[\text{Co}^{4+}]$  ratio (b) in the layered calcium cobaltate  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics prepared using different methods: 1, 3 – solid-state reactions method, 2, 4 – citrate method

## CONCLUSION

So, in this work using complex of independent methods the processes occurring at preparation of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics using solid-state reactions method and different solution methods (citrate, polymeric and sol-gel methods) were investigated as well as influence of preparation method on the crystal structure, microstructure, thermal expansion, thermal conductivity, electrotransport and thermoelectric properties of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics was studied.

By means of optical investigation methods (colorimetry and tyrbidimetry) pH interval was selected in which formation of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  precursors flows through the stage of sol formation. Influence of preparation method on the microstructure of xerogels which are precursors at synthesis of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics by means of solution methods is studied.

It was found that decomposition of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics precursors prepared using different solution methods obeys the general laws (particularly, occurs in three stages), but formation of polymeric matrix in the sample prepared by PM lead to the intensification of the 2<sup>nd</sup> stage of precursor decomposition and to the formation of more fine-grained ceramics than at using of citrate and sol-gel methods. It is shown, that precipitation of  $\text{Ca}(\text{OH})_2$  at synthesis of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  ceramics using sol-gel method did not prevent to obtain the monophasic 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 usage of solution methods let us obtain more dense and fine-grained ceramics of layered calcium cobaltate which characterizes higher values of electrical conductivity, power factor and figure-of-merit.

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