Processes Occurring at Preparation of $Ca_3Co_4O_{9+\delta}$ Ceramics by Means of Different Solution Methods, and Its Properties

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By means of complex independent methods the processes occurring at preparation of $Ca_3Co_4O_{9+\delta}$ ceramics using solid-state reactions and different solution (citrate, polymeric and sol-gel) methods were investigated. The crystal structure and microstructure, oxygen stoichiometry, thermal expansion, electrical conductivity and thermo-EMF of the samples were studied and values of their power factor were calculated. It is shown that usage of solution methods let us obtain more dense and fine-grained ceramics, which is characterized with higher values of electrical conductivity and power factor.

1. INTRODUCTION

Layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$ has 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]. The functional properties of $Ca_3Co_4O_{9+\delta}$ ceramics obtained by means of solid-state reactions method is worth than for monocrystals, but can be improved at preparation of $Ca_3Co_4O_{9+\delta}$ by means of solution methods of synthesis [2, 3]. Taking it into account, investigation of processes occurring at formation of $Ca_3Co_4O_{9+\delta}$ ceramics during solution methods of synthesis as well as effect of preparation method on the microstructure and functional properties obtained hereby ceramics is actual problem which have great scientific and practical importance.

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

2. PREPARATION AND INVESTIGATION METHODS

At preparation of $Ca_3Co_4O_{9+\delta}$ ceramics using solid-state reactions method (SSRM) the $CaCO_3$ and Co_3O_4 (both pure grade) were used, which were mixed in the 9:4 molar ratio in Pulverizette 6 (Fritsch, Germany) planetary mill with addition of C_2H_5OH, 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 К, re-grinded in Pulverizette 6 planetary mill (with addition of C_2H_5OH), 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 citrate 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 (SGM) methods to the solution obtained the ethylene glycol solution was added $(n(C_2H_6O_2) = n(C_6H_8O_7))$. 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 °К on the magnetic stirrer with heating IKA RH basic 2 at 343–363 К 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.

Gels were dried at 383–403 K on the electroheating plate to form pink for citrate but dark-grey for polymeric and sol-gel methods xerogels, which were milled and dried on the electroheating plate at 433–453 K to form black powders. These powders were annealed in the muffle furnace during 4 h at 873 K, 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 is the X-ray wavelength, β is the reflex broadening, and Θ is the diffraction angle.

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 precursors at synthesis of $Ca_3Co_4O_{9+\delta}$ by CM, PM and SGM after drying at 403 K was conducted by means of the Mettler Toledo (Swiss) thermal analysis system in air within 298–1173 K temperatures at $10\,K \cdot min^{-1}$ heating rate. Microstructure of the sintered ceramics was studied using JSM-5610 LV (Japan).

Thermal expansion, electrical conductivity and thermo-EMF of ceramics was measured in air within 300–1100 K temperatures using methods described in

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[4]. Power factor values of ceramics were calculated using equations of $P = S^2\sigma$, where P is the power factor, S is the thermo-EMF, σ is the electrical conductivity. 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.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Absorption spectra of solutions used at synthesis of ceramics by means of solution methods during their evaporation did not change 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 solution pH, which must be thoroughly monitored, because at too small pH values hydroxide sol is not formed, but at too high pH in solution not sol but suspension is formed which particles rapidly precipitate to the bottom of the vessel. In our experiments, the precipitate formed at pH > 4,5 (these solutions also were used in preparation of ceramics the same way as in SGM and this preparation method in manuscript is named as precipitation method (PrM)) and increase of solutions pH was accompanied by a change of their color (fig. 1, a). Analysis of the literature data 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, $1 < pH < 4$) to $[Co(NH_3)_{6-n}(H_2O)_n]^{2+}$ (blue, $5 < pH < 8$).
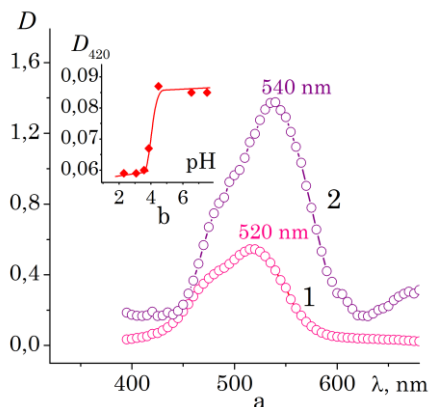

Fig. 1 – Absorption spectra of solutions with different pH values (a) and dependence of solution optical density at $\lambda = 540$ nm versus pH: *1* – pH = 1,3 (pink color); *2* – pH = 8,2 (violet color)

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. 1, b, increase of the optical density of solution due to 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 precursors are given in the fig. 2. As can be seen, thermogravimetric

curve (TG) of the mixture of $CaCO_3$ and Co_3O_4 powders (fig. 2, a, curve 1) may be divided in three stages and on the 1st–2nd stages mass of the sample decreased but on the 3rd stage mass increased.
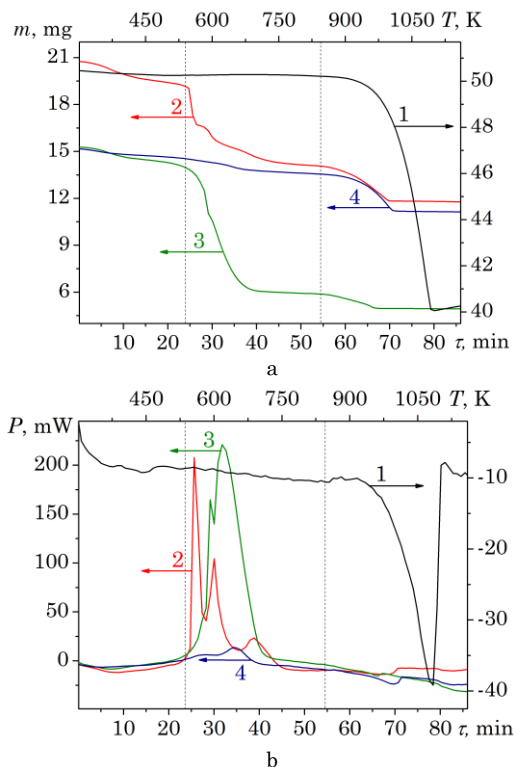

Fig. 2 – Results of the thermal analysis of the calcium carbonate $CaCO_3$ and cobalt oxide Co_3O_4 mixture (1) and $Ca_3Co_4O_{9+\delta}$ precursors prepared by citrate (2), polymeric (3) and sol-gel methods (4): a – TG, b – DSC curves

The mass loss of the sample on the 1st stage is small ($\approx0,58\%$ within 298–893 K temperature region) and occurs, 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. The intensive ($\approx20,06\%$ or $\approx10,12$ mg, which is close to the calculated mass loss $-\approx10,72$ mg) mass loss begins at 893 К. It follows by the large endothermic effect with extremum at 1083 K (fig. 2, b, curve 1) and corresponds to the $CaCO_3$ decomposition (according to [5], calcium carbonate decomposition in air begins near 900 K). On this stage forms the product of reaction – layered calcium cobaltite $Ca_3Co_4O_{9-\gamma}$.

Mass gain at the 3rd stage of the TG curve (1098–1197 K) ($\approx0,41\%$), which follows by the small and diffuse exothermic effect with extremum at 1110 K, took place due to the saturation of the calcium cobaltite with oxygen and formation of $Ca_3Co_4O_{9+\delta}$ final product.

Decomposition of the $Ca_3Co_4O_{9+\delta}$ precursors obtained by the CM, PM and SGM also occurs in three stages (fig. 2, a, b, curves 2–4), which, however, have somewhat different nature. On the 1st stage (298–≈530 К) the free and bonded water goes out of the samples, which contents in the precursors varies within 3,67–7,89%.

Mass loss of the precursors on the 2nd stage (≈530–≈850 К) is 7,51–53,54%, follows by the large exothermic effects at 558–687 K (CM), 634 K (PM), 574–649 K (SGM) and took place due to the oxidation of organic components of precursors into $CaCO_3$ and Co_3O_4 by the

atmospheric oxygen as well as by oxygen, which evolves at calcium and cobalt nitrates decomposes. 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 organic components (citric acid, ethylene glycol) of solutions used in CM and SGM during the evaporation partially evolves into gas phase (leaving the solution), but at heating of solution used in PM between these components the polycondensation reaction occurs, which results in formation of rather hard polymeric matrix.

Mass loss of precursors at 3rd stage (≈850–1173 К) is accompanied by the weak and diffuse endothermic effect at 997 (CM), 962 (PM) and 999 K (SGM) is 6,29–16,01% and corresponds to the calcium carbonate decomposition with formation of the reaction product – $Ca_3Co_4O_{9+\delta}$ [5, 6, 8]. Mass loss of all the precursors on the 3rd stage is about 20% from the final product mass, which means that after 2nd stage of decomposition of precursors the calcium 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. 3, the xerogel obtained by citrate method has a large-cell structure, in which the cells having dimension ≈40 μm 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 10–20 μm (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. 3); so, xerogels are polydisperse solid foams and polydispersity more pronounced for the xerogels obtained by means of sol-gel method and precipitation method), and in the nodes of PrM xerogel the paricles of $Ca(OH)_2$ with dimensions about 1–2 μm (fig. 3, d) are observed, which are more or less evenly distributed throughout the volume of xerogel.

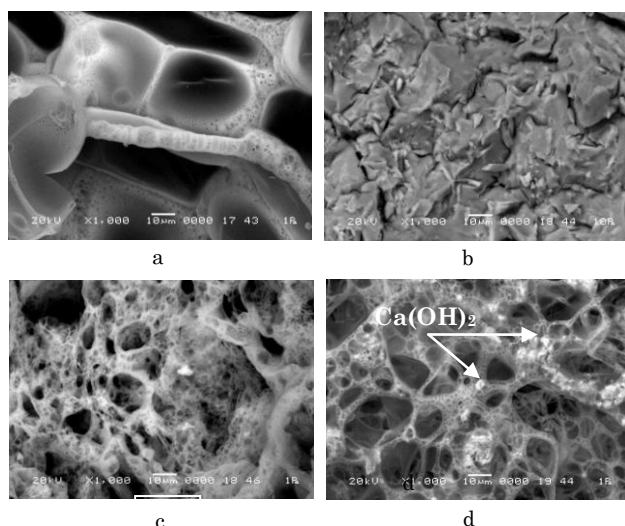**Fig. 3** – Microstructure of xerogels of $Ca_3Co_4O_{9+\delta}$ prepared by means of citrate (a), polymeric (b), sol-gel (c) and precipitation methods (d)

The cellular structure of xerogel obtained by polymeric method on the photo is not seen (fig. 3, 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 К). In the other words, due to the high strength of the framework of xerogel obtained by PM 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 samples after finishing of synthesis was, within XRD accuracy, monophase and was a calcium cobaltite $Ca_3Co_4O_{9+\delta}$, and its lattice constants were in a good accordance with the literature data: $a = 0,48376(7)$; $b_1 = 0,45565(6)$; $b_2 = 0,28189(4)$; $c = 1,0833(1)$ нм; $\beta = 98,06(1)°$ [6].

The formation of $Ca_3Co_4O_{9+\delta}$ in the samples obtained using solution methods begins at 873 K (when polymeric 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; on the diffractograms of the powders obtained by means of SGM 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 citrate method) and practically finishes after sample annealing during 4 h at 1123 K. So, usage of the solution methods allows us to decrease of temperature (for 50 K) and time of the synthesis (up to 3 times) of calcium cobaltite.

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 $Ca_3Co_4O_{9+\delta}$ [6] 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°. The value of oxygen nonstoichiometry index (δ) of the sample obtained by means of SSRM was 0,29, but for samples prepared using solution methods was slightly higher ($\delta = 0,35$–0,58) due to their heat treatment temperature was lower.

The CSA values of ceramics (corresponding to sizes of its individual grains) prepared using different methods were similar and equal about 40 nm (except sample obtained using SGM, which CSA values were slightly higher – ≈50 nm). 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 and was smallest for ceramics prepared using polymeric method.

The ceramics porosity determined using XRD and densitometry results was 30% for the sample prepared using SSRM and 14–17% for samples obtained using solution methods. So, 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 SSRM.

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. LTEC of ceramics prepared using PM and PrM methods were equal to
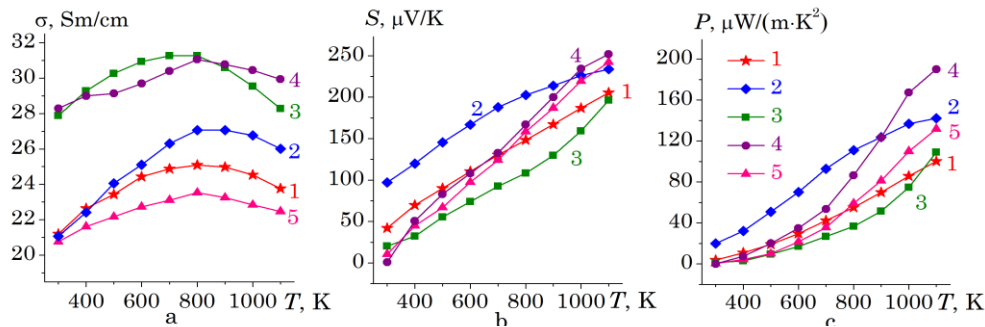
Fig. 4 − Temperature dependences of electrical conductivity (σ) (*a*), thermo-EMF (*S*) (*b*) and power factor (*P*) (*c*) of Ca₃Co₄O₉₊δ ceramics prepared using solid-state reactions (*1*), citrate (*2*), polymeric (*3*), sol-gel (*4*) and precipitation methods (*5*)

$(1,20\text{--}1,22)\cdot10^{-5}$ K⁻¹, which was lower than for than ceramic obtained using solid-state reactions method $(1,29\cdot10^{-5}$ K⁻¹) 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 Ca₃Co₄O₉₊δ ceramics prepared using different methods are given in the fig. 4. As can be seen, the materials synthesized are the *p*-type semiconductors ($\partial\sigma/\partial T > 0$, $S > 0$, fig. 4, *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 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 SSRM (fig. 4, *a*) and highest conductivity values was characterized the ceramics prepared using PM and SGM ($\sigma_{PM}/\sigma_{SSRM} \approx \approx \sigma_{SGM}/\sigma_{SSRM} \approx 1,25$), obviously, due to their lower porosity. The values of the samples E_A varied within 0,060–0,069 eV and for ceramics obtained using solution methods was slightly lower. So, we can conclude that use of solution methods at synthesis of 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 the fig. 4, *b*, thermo-EMF values of Ca₃Co₄O₉₊δ ceramics increased at temperature increasing and at high temperatures for ceramics synthesized using solution methods (except sample prepared using PM) 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. 4, *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 SGM Ca₃Co₄O₉₊δ ceramics − ≈190 μW/(m·K²) at 1100 K which more than two times higher than for ceramics synthesized by means of SSRM (≈90 μW/(m·K²) at the same temperature).

4. CONCLUSION

So, in this work using complex of independent methods the processes occurring at preparation of Ca₃Co₄O₉₊δ ceramics using solid-state reactions method and different solution methods were studied as well as effect of preparation method on the structure, microstructure, physicochemical and thermoelectric properties of Ca₃Co₄O₉₊δ ceramics was investigated.

By means of optical investigation methods selected pH interval in which formation of Ca₃Co₄O₉₊δ precursors goes through the stage of sol formation. Influence of preparation on the microstructure of xerogels which are precursors at synthesis of Ca₃Co₄O₉₊δ ceramics by means of solution methods is studied.

Decomposition of Ca₃Co₄O₉₊δ ceramics precursors prepared using different solution methods obey 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 2ⁿᵈ stage of precursor decomposition and to the formation of more fine-grained ceramic as than at using of citrate and sol-gel methods.

Precipitation of Ca(OH)₂ at synthesis of Ca₃Co₄O₉₊δ ceramics using sol-gel method did not prevent to obtain the monophase sample, which crystal structure, microstructure and thermo-EMF are practically the same as for sample prepared by means of SGM. It is established, that using solution methods 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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