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SYNTHESIS AND THERMOELECTRIC PROPERTIES OF $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V - Zn$) SOLID SOLUTIONS PREPARED BY CITRATE GEL METHOD

Citrate gel method was used to synthesize $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V - Zn$) solid solutions, to investigate their structure and microstructure, thermoEMF, electric conductivity and thermal expansion. Processes occurring in the preparation of $Ca_3Co_4O_{9+\delta}$ ceramics by citrate gel method were studied. It was established that the resulting materials are p-type semiconductors. The influence of partial substitution of cobalt cations by 3d-metal cations on the physical-chemical and thermoelectric properties of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ceramics was analyzed. Maximum values of power factor are demonstrated by $Ca_3Co_{3.85}Fe_{0.15}O_{9+\delta}$ and $Ca_3Co_{3.85}Ni_{0.15}O_{9+\delta}$ solid solutions, namely 153 and 152 μW/(m·K^2) at 1100 K, which is a factor of 1.5 greater than for unsubstituted calcium cobaltite $Ca_3Co_4O_{9+\delta}$.

Key words: layered calcium cobaltite, citrate gel method, electric conductivity, thermoEMF, thermal expansion, power factor.

Introduction

A problem of scientific significance and practical importance lies in development of new thermoelectric materials efficient at elevated temperatures and resistant under these conditions to oxidation by atmospheric oxygen. Such properties are exhibited by layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$ characterized by sufficiently high values of power factor and thermoelectric figure of merit at high temperatures [1, 2]. Functional characteristics of ceramics based on $Ca_3Co_4O_{9+\delta}$ can be improved using "soft", low-temperature synthesis methods instead of solid-phase one [3-6], as well as through chemical modification of layered calcium cobaltite and, specifically, with a partial substitution of cobalt cations by 3*d*-metal cations [7-12].

In this work, $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ (M – 3*d*-metal) ceramics was prepared by citrate gel method, and influence of partial substitution of cobalt cations by 3*d*-metal cations on crystalline structure, thermal expansion, electrophysical and thermoelectric properties of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ phases was studied. It is shown that thermoelectric properties of layered calcium cobaltite are improved on introducing cobalt-substituting 3*d*-metal, and power factor attains its maximum value in the case of $Ca_3Co_{3.85}Fe_{0.15}O_{9+\delta}$ and $Ca_3Co_{3.85}Ni_{0.15}O_{9+\delta}$ solid solutions – 153 and 152 μW/(m·K^2), respectively, at 1100 K.

Experimental

For synthesis of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V$, Cr, Mn, Fe, Ni, Cu, Zn) samples the following solutions were prepared: $Ca(NO_3)_2{\cdot}4H_2O$ (analytical grade) ($C_1 = 0.6\ M$), $Co(NO_3)_2{\cdot}6H_2O$ (analytical grade) ($C_2 = 0.8\ M$), $Cr(NO_3)_3{\cdot}9H_2O$ (analytical grade), $Fe(NO_3)_3$ (chemically pure), $Ni(NO_3)_3{\cdot}6H_2O$ (analytical grade) (nitrate solutions of the rest of 3d-metals were prepared by dissolving oxides VO_2 (pure), Mn_2O_3 (pure), CuO (pure), ZnO (analytical grade) in concentrated nitric acid) ($C_3 = 0.8\ M$) and $C_6H_8O_7$ (pure) ($C_4 = 0.5\ M$), that were mixed in the ratios (of mole components) 3 : 3.85 : 0.15 : 15. The resulting solutions were boiled out at 343 K to produce viscous violet gel which was dried at 383 to 393 K on electric stove to form a caramelized mass. The mass was crushed and further dried in a muffle furnace for 2 hours at 423 K with subsequent grinding. The resulting dirty pink powder was annealed for 4 hours at 873 K. The black powder obtained was thoroughly ground and pressed as pellets and bars that were further annealed for 5 hours at 1123 K with subsequent sintering for 8 hours at 1183 to 1193 K.

Samples identification and determination of their crystalline structure parameters was performed with the aid of X-ray phase analysis (X-ray diffractometer Bruker D8 XRD Advance, CuK_α-radiation, exposure range: 5 – 100° 2Θ with a step 0.05°, exposure conditions: 40 kW/40 mA) and IR absorption spectroscopy (Nexus Fourier spectrometer by ThermoNicolet company, frequency range 300 to 1500 cm^{-1}). Index of oxygen nonstoichiometry (δ) in $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V – Zn$) was found using iodometric titration. The apparent density of samples (ρ_{exp}) was found by their mass and geometry.

Thermal analysis of precursor powder at synthesis of $Ca_3Co_4O_{9+\delta}$ by citrate gel method on drying at 403 K was performed using thermal analysis system Mettler Toledo (Switzerland) in the air in the temperature range of 298 to 1173 K at heating rate 10 K·min^{-1}.

The microstructure of sintered ceramics was studied through use of scanning electron microscope JSM-5610 LV with chemical analysis system EDX JED-2201 JEOL. Thermal expansion, electric conductivity and thermoEMF of sintered ceramic samples were studied in the air in the temperature range of 300 to 1100 K according to procedures described in [13-15]. The values of power factor (P) were calculated by the formula:

$$P = S^2 \cdot \sigma, \tag{1}$$

where S is thermoEMF, σ is electric conductivity.

The values of apparent activation energy of electric conductivity E_A and linear thermal expansion coefficient α of samples were found from linear parts of dependences $\ln(\sigma{\cdot}T) = f(1/T)$ and $\Delta l/l_0 = f(T)$, respectively.

Discussion of results

Decomposition of $Ca_3Co_4O_{9+\delta}$ precursor obtained by citrate gel method is a complicated procedure: TG curve in this case consists of eight parts (Fig. 1 a). During the first two process stages the loss of mass is ≈ 2.72 % ($298 < T < 373$ K) and ≈ 4.83 % ($373 < T < 539$ K), which corresponds to separation from the sample of free and bound water, respectively [4]. Reduction of powder mass during the third-sixth stages (≈ 11.95 % at $539 < T < 576$ K, ≈ 6.03 % at $576 < T < 630$ K, ≈ 2.92 % at $630 < T < 688$ K and ≈ 3.79 % at $688 < T < 851$ K) accompanied by pronounced exothermal effects with extremes at 588, 599 and 687 K, occurs due to stepwise oxidation of calcium ($Ca_3[C_3H_4(OH)(COO)_3]_2$) and cobalt citrates ($Co_3[C_3H_4(OH)(COO)_3]_2$) to $CaCO_3$ and Co_3O_4 [4, 5] according to reactions

$$Ca_3\left[C_3H_4(OH)(COO)_3\right]_2 + 9O_2 \rightarrow 3CaCO_3 + 9CO_2\uparrow + 5H_2O\uparrow, \tag{2}$$

$$Co_3\left[C_3H_4(OH)(COO)_3\right]_2 + 9.5O_2\uparrow \rightarrow Co_3O_4 + 12CO_2\uparrow + 5H_2O\uparrow \tag{3}$$

by atmospheric oxygen, as well as oxygen released at decomposition of calcium and cobalt nitrates:

$$Ca(NO_3)_2 \rightarrow CaO + 2NO_2\uparrow + {}^1\!/_2\,O_2\uparrow, \tag{4}$$

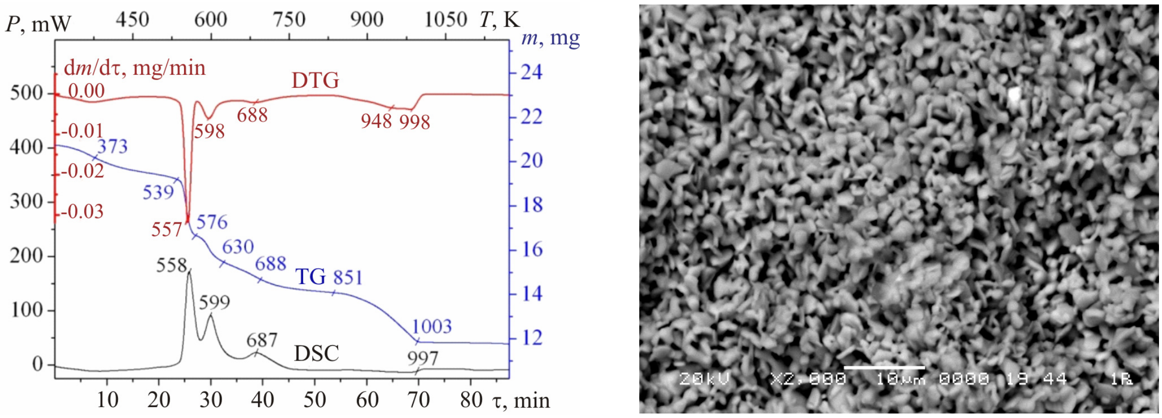
$$3Co(NO_3)_2 \rightarrow Co_3O_4 + 6NO_2\uparrow + O_2\uparrow. \tag{5}$$

The loss of mass during the seventh stage (≈ 10.70 % at $851 < T < 1003$ K) is accompanied by fuzzy endothermic effect with extreme at 997 K and corresponds to calcium carbonate decomposition with formation of reaction product $Ca_3Co_4O_{9+\delta}$ [4, 5]:

$$3CaCO_3 + {}^4\!/_3\,Co_3O_4 + ({}^1\!/_3 + {}^\delta\!/_2)O_2 \rightarrow Ca_3Co_4O_{9+\delta} + 3CO_2\uparrow. \tag{6}$$

Mass reduction during the eighth stage is not large (≈ 0.39 % at $1003 < T < 1197$ K) and corresponds, apparently, to completion of $Ca_3Co_4O_{9+\delta}$ reaction formation.

Crystallites $Ca_3Co_4O_{9+\delta}$ had the shape of plates with the average dimensions 2.5 × 1.7 × 0.5 μm; in so doing, the plates were oriented with their broad side perpendicular to compaction axis (Fig. 1 *b*), which points to partial texturing of the obtained ceramics.



a) *b)*

Fig. 1. Results of thermal analysis of $Ca_3Co_4O_{9+\delta}$ precursor (a) and micrograph of cleavage surface (perpendicular to compaction axis) of $Ca_3Co_4O_{9+\delta}$ ceramics (b) obtained by citrate gel method. (DTG) differential thermogram, (TG) thermogram, (DSC) differential scanning calorimetry curve.

After the final synthesis stage, samples of calcium cobaltite $Ca_3Co_4O_{9+\delta}$ and $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V – Zn$) solid solutions were single-phase, within the accuracy of *X*-ray phase analysis, and had the structure of layered calcium cobaltite [16] (Fig. 2, curves 1 – 4). Parameter values of crystalline structure of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ phases are given in Table 1. Parameter values of unit cell $Ca_3Co_4O_{9+\delta}$ within the limits of claimed error coincide with the results [16] according to which for layered calcium cobaltite $a = 0.48376(7)$; $b_1 = 0.45565(6)$; $b_2 = 0.28189(4)$; $c = 1.0833(1)$ nm; $\beta = 98.06(1)°$.

As is evident from the data represented in Table 1, the volume of unit cell and disproportion parameter (b_1/b_2) of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ solid solutions decrease from $M = V$ to $M = Zn$, which is mainly due to reduction of b_1 parameter of their crystalline structure.

IR absorption spectra of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V – Zn$) powders comprised two distinct absorption bands with extremes at $\nu_1 = 563 – 573$ cm^{-1} and $\nu_2 = 726 – 733$ cm^{-1} (Fig. 2, curves 5 – 9), corresponding, according to [17], to valence vibrations of $Co(M) – O$ (ν_1) and $Ca – O$ (ν_2) bonds in the structure of these oxides. The band ν_1 of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ solid solutions, as compared to unsubstituted phase $Ca_3Co_4O_{9+\delta}$, is displaced toward larger wave numbers, indicating to energy increase of cobalt-oxygen interactions in the structure of layered calcium cobaltite with partial substitution of cobalt cations by cations of other 3*d*-metals.

Table 1

The values of crystalline structure parameters (a, b_1, b_2, c, β, V, b_1/b_2) and oxygen nonstoichiometry index (δ) of layered cobaltites $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$

M	*a*, nm	b_1, nm	b_2, nm	*c*, nm	β, °	*V*, nm^3	b_1/b_2	δ
V	0.4839(7)	0.4591(7)	0.2837(9)	1.085(1)	98.23(6)	0.2386(9)	1.618	0.37
Cr	0.4838(7)	0.4595(8)	0.2841(9)	1.085(1)	98.20(7)	0.2387(9)	1.617	0.42
Mn	0.4830(6)	0.4561(7)	0.2819(9)	1.090(1)	98.26(8)	0.2377(9)	1.618	0.44
Fe	0.4868(5)	0.4557(5)	0.2843(6)	1.089(1)	100.3(1)	0.2378(6)	1.603	0.35
Co	0.4830(7)	0.4562(8)	0.2812(6)	1.085(1)	98.28(8)	0.2365(9)	1.622	0.35
Ni	0.4827(5)	0.4561(6)	0.2839(9)	1.084(1)	98.08(7)	0.2363(9)	1.607	0.35
Cu	0.4838(7)	0.4540(8)	0.2823(9)	1.081(1)	98.16(8)	0.2349(9)	1.608	0.55
Zn	0.4832(6)	0.4544(7)	0.2824(9)	1.083(1)	97.97(7)	0.2354(9)	1.609	0.48

The apparent density of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ solid solutions varied within 2.64 to 3.16 g/cm^3 (Table 2) and was somewhat lower than that of basic calcium cobaltite (3.18 g/cm^3), from which it can be concluded that partial substitution of cobalt by other 3*d*-metals impairs sintering behaviour of ceramics based on layered calcium cobaltite.

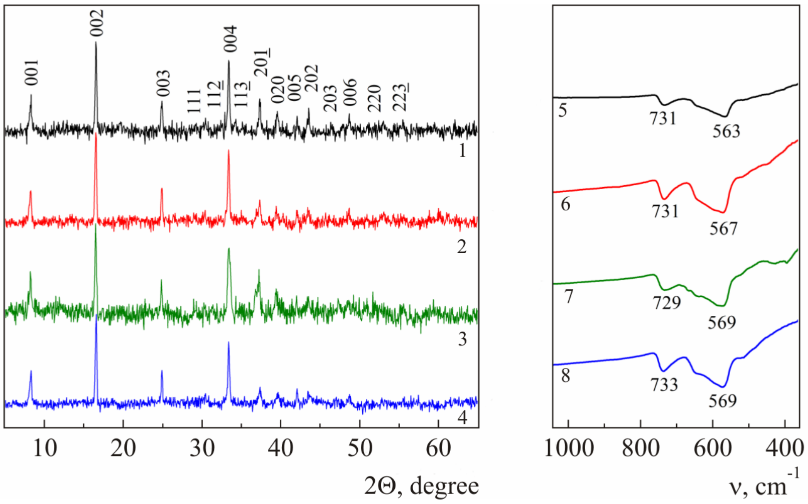


Fig. 2. Powder diffraction patterns (1 – 4) (CuK$_\alpha$-radiation) and IR absorption spectra (5 – 8) of $Ca_3Co_4O_{9+\delta}$ calcium cobaltite (1, 5) and solid solutions on its basis $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$: M = Ni (2, 6), Fe (3, 7), Mn (4, 8).

The temperature dependences of relative elongation of all investigated samples in the temperature range of 300 to 1100 K were linear, from which it follows that in this temperature range $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ phases do not experience any structural phase transitions. The value of linear thermal expansion coefficient of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V – Zn$) oxides varied within $(1.20 – 1.31)\cdot10^{-5}$ K^{-1} (Table 2), and for all solid solutions (except for $Ca_3Co_{3.85}Ni_{0.15}O_{9+\delta}$ phase) it was lower than for basic calcium cobaltite. The dilatometry results are in good agreement with the data of IR absorption spectroscopy, according to which partial substitution of cobalt by other 3*d*-metals increases the energy of ionic interaction in the structure of $Ca_3Co_4O_{9+\delta}$ phase.

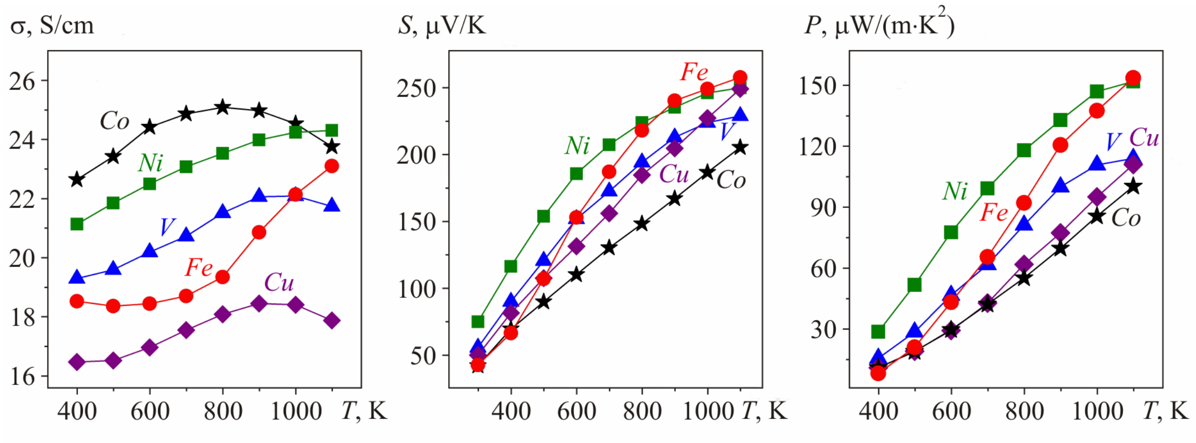
Table 2

The values of apparent density (ρ),linear thermal expansion coefficient (α), apparent electric conductivity activation energy (E_A), electric conductivity(σ_{1100}), Seebeck coefficient (S_{1100}) and power factor (P_{1100}) of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ceramics

M	ρ, g/cm^3	$\alpha\cdot10^5$, K^{-1}	E_A, eV	σ_{1100}, S/cm	S_{1100}, μV/K	P_{1100}, μW/(m·K^2)
V	3.02	1.22	0.075	21.7	229	114
Cr	2.86	1.25	0.099	13.7	242	79.8
Mn	2.64	1.21	0.075	7.73	278	59.8
Fe	3.09	1.20	0.068	23.1	258	153
Co	3.18	1.28	0.065	23.8	206	100
Ni	3.12	1.31	0.073	24.3	250	152
Cu	3.01	1.25	0.077	17.9	249	111
Zn	3.16	1.21	0.072	6.28	295	54.7

All materials investigated in this work were *p*-type semiconductors ($S > 0$, Fig. 3 *a*, *b*) whose conductivity in the temperature range of 800 to 1000 K varied from semiconductor to metal (Fig. 3 *a*), which is caused by partial reduction of samples due to partial oxygen release from their volume to the environment. The electric conductivity values of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V – Zn$) solid solutions were, on the whole, lower, and the value of apparent electric conductivity activation energy was higher than for the unsubstituted phase (Table 2, Fig. 3 *a*).

ThermoEMF of investigated cobaltites increased with a rise in temperature (Fig. 3 *b*) and for $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V – Zn$) solid solutions it was higher than for $Ca_3Co_4O_{9+\delta}$ calcium cobaltite, the highest thermoEMF values being observed for $Ca_3Co_{3.85}Mn_{0.15}O_{9+\delta}$ and $Ca_3Co_{3.85}Zn_{0.15}O_{9+\delta}$ solid solutions (Table 2).



a) b) c)

Fig. 3. Temperature dependences of electric conductivity σ (a), thermoEMF S (b) and power factor P (c) of $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ (M = V, Fe, Co, Ni, Cu) ceramics.

The values of power factor of oxide ceramics increased with a rise in temperature and for $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ solid solutions they were considerably higher than for the unsubstituted phase $Ca_3Co_4O_{9+\delta}$ (Fig. 3 *c*), with the highest *P* values demonstrated by $Ca_3Co_{3.85}Fe_{0.15}O_{9+\delta}$ and $Ca_3Co_{3.85}Ni_{0.15}O_{9+\delta}$ solid solutions, namely 153 and 152 μW/(m·K^2), respectively, at 1100 K, which is mainly due to high thermoEMF values of these oxides.

Conclusions

Citrate gel method was used to synthesize $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ ($M = V - Zn$) oxide ceramics, to study its crystalline structure and microstructure and to investigate in the air at above room temperatures its thermal expansion, electrophysical and thermoelectric properties. Processes occurring in the preparation of calcium cobaltite by citrate gel method were studied. The values of linear thermal expansion coefficient of samples were calculated that made $(1.20 - 1.31)\cdot10^{-5}$ K^{-1}. It was established that $Ca_3Co_{3.85}M_{0.15}O_{9+\delta}$ solid solutions are *p*-type semiconductors whose conductivity is lower and thermoEMF is higher as compared to basic calcium cobaltite $Ca_3Co_4O_{9+\delta}$. The highest values of power factor of the investigated compositions are possessed by $Ca_3Co_{3.85}Fe_{0.15}O_{9+\delta}$ and $Ca_3Co_{3.85}Ni_{0.15}O_{9+\delta}$ phases, namely 153 μW/(m·K^2) and 152 μW/(m·K^2), respectively, at a temperature of 1100 K.

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