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Thermoelectric Properties of a Phase-Heterogeneous Ceramic Based on $Ca_3Co_4O_{9+\delta}$, Prepared by Hot Pressing

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Abstract—A phase-heterogeneous ceramic based on layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$ was prepared by solid-phase reactions followed by hot pressing. The phase composition, microstructure, electrical conductivity, and thermoelectromotive force (thermo-emf) of the ceramic were studied, and the power factor (P) was calculated. Hot pressing allows preparation of a high-density ceramic with high electrical conductivity, and the phase heterogeneity considerably increases its thermo-emf coefficient, which in total can be considered as a procedure for preparing a ceramic with improved thermoelectric characteristics. The ceramic of the nominal composition $Ca_3Co_{4.4}O_{9+\delta}$, containing an impurity Co_3O_4 phase, has the highest power factor (P_{1100} = 427 μW m^{-1} K^{-2}), which is 1.5 times higher than that of $Ca_3Co_4O_{9+\delta}$ (P_{1100} = 280 μW m^{-1} K^{-2}) and more than 4 times higher than that of the low-density ceramic $Ca_3Co_4O_{9+\delta}$ prepared by the traditional solid-phase method.

Keywords: thermoelectric ceramic, $Ca_3Co_4O_{9+\delta}$, phase heterogeneity, hot pressing, power factor

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The heat released into the environment in the course of operation of industrial enterprises, transport vehicles, and various devices and machines can be converted directly to electric power using thermoelectric generators. Their fabrication requires materials (thermoelectrics) combining high levels of electrical conductivity (σ) and thermoelectromotive force (thermo-emf) (S) with low thermal conductivity [1]. Traditional thermoelectrics are bismuth, antimony, lead, and tin chalcogenides and solid solutions based on them [1–3], which are characterized by high values of the power factor (P) and figure-of-merit (ZT) and are widely used in various thermoelectric devices. The drawbacks of these materials are high content of toxic and expensive components and low resistance to oxidation with atmospheric oxygen at high temperatures. Oxide thermoelectrics, including layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$, which is considered today as a promising base for the development of p-branches of high-temperature thermoelectric generators, are free of these drawbacks [4].

The functional (thermoelectric) characteristics of the ceramic based on $Ca_3Co_4O_{9+\delta}$ can be improved by the use of "mild" low-temperature synthesis procedures [5–8] instead of traditional ceramic procedure, by the use of special procedures in the course of ceramic sintering such as hot pressing [6] or spark plasma sintering [7, 9, 10], by partial replacement of calcium ions in $Ca_3Co_4O_{9+\delta}$ by bismuth [11, 12] or rare earth element ions [13, 14] or of cobalt ions by transition or heavy metal ions [15, 16], and by creation of chemical [17] or phase heterogeneity [18, 19] in the ceramic.

In a ceramic based on layered calcium cobaltite, the phase heterogeneity can be created both by introducing a second impurity phase into the charge in the synthesis

Table 1. Nominal and real (found from the results of EDX microanalysis) composition of the ceramic based on layered calcium cobaltite

Sample	Nominal composition, mol %		Real composition, mol %	
	CaO	CoO_y	CaO	CoO_y
$Ca_3Co_{3.6}O_{9+\delta}$	45.45	54.55	46.24	53.76
$Ca_3Co_4O_{9+\delta}$	42.86	57.14	41.95	58.05
$Ca_3Co_{4.4}O_{9+\delta}$	40.54	59.46	41.08	58.92

step [20–22] and by varying the cationic stoichiometry of the initial charge so that the target composition be beyond the $Ca_3Co_4O_{9+\delta}$ homogeneity area (self-doping) [23] (according to [24], layered calcium cobaltite exists in air in the composition range $Ca_3Co_{3.87}O_{9+\delta}$–$Ca_3Co_{4.07}O_{9+\delta}$), and also by annealing the ceramic at temperatures exceeding the temperature of the peritectoid decomposition of $Ca_3Co_4O_{9+\delta}$ (T_p = 926°C [24]) by the reaction $Ca_3Co_4O_{9+\delta} \leftrightarrow Ca_3Co_2O_6 + (Co,Ca)O$.

In this study, we examined the possibility of improving the functional (thermoelectric) characteristics of the ceramic based on layered calcium cobaltite by making it phase-heterogeneous via self-doping combined with hot pressing.

EXPERIMENTAL

Powders of the compositions $Ca_3Co_{3.6}O_{9+\delta}$, $Ca_3Co_4O_{9+\delta}$, and $Ca_3Co_{4.4}O_{9+\delta}$ were prepared by solid-phase reactions from $CaCO_3$ (analytically pure grade) and Co_3O_4 (pure grade), taken in the corresponding stoichiometric ratios, in air at 1173 K for 12 h as described in [12, 18]. The sintered ceramic in the form of pellets 20 mm in diameter and 2–5 mm thick were prepared by hot pressing with a DSP-507 installation (Dr. Fritsch, Germany) under argon at 1173 K under a pressure of 167 MPa for 5 min. After hot pressing, the samples were additionally annealed in air for 14 h at 973 K. Specimens in the form of rectangular parallelepipeds of size 4 × 4 × 7 and 4 × 4 × 20 mm were cut from the sintered ceramic for measuring the electrical conductivity and thermo-emf, and Ag electrodes were formed on the end faces of these specimens [25].

The phase composition of the samples and the parameters of the crystal structure of the major phase were determined by X-ray diffraction (XRD) analysis with an STOE Theta/Theta diffractometer (Germany) (Co_{K_α} radiation) and an RTP X-ray diffraction table processor [26]. The microstructure of the sintered ceramic and its chemical composition were studied by scanning electron microscopy (SEM) with SEM 7500F Jeol and JSM-5610 LV scanning electron microscopes equipped with an EDX JED-220 chemical analysis system (Tokyo, Japan).

The apparent density (ρ_{app}) of the sintered ceramic was determined from the sample weight and size. The sample porosity was calculated by the formula $\Pi = (1 - \rho_{app}/\rho_{XRD}) \times 100\%$, where ρ_{XRD} is the X-ray diffraction density of the sample ($\rho_{XRD} = 4.677$ g cm^{-3} [27]).

The electrical conductivity and thermo-emf of the materials were determined in the direction perpendicular to the pressing axis in air in the temperature interval 300–1100 K by the procedures described in [25]. The activation energy of the electrical conductivity (E_a) of the samples was determined from the linear portions of the dependences $\ln(\sigma T) = f(1/T)$. The power factor of the thermoelectrics was calculated by the formula $P = S^2\sigma$ [4].

The temperature conductivity (η) of the $Ca_3Co_{3.6}O_{9+\delta}$ and $Ca_3Co_4O_{9+\delta}$ samples was measured in the direction parallel to the pressing axis at 299 K by the laser flash method with a Linseis LFA 1000 installation (Germany). The thermal conductivity (λ) of the samples was determined by the equation $\lambda = \eta\rho_{app}c_{sp}$ from the experimentally determined values of the temperature conductivity and apparent density; the specific heat capacity (c_{sp}) was calculated using data from [24]. The phonon (λ_{ph}) and electron (λ_e) contributions to the thermal conductivity of the ceramic was calculated using the relationships $\lambda = \lambda_{ph} + \lambda_e$, $\lambda_e = \sigma LT$, where σ is the specific electrical conductivity of the ceramic, L is the Lorenz number ($L = 2.45 \times 10^{-8}$ V^2 K^{-2}), and T is the absolute temperature. The quantity ZT was found using the equation $ZT = (PT)/\lambda$ [2, 4].

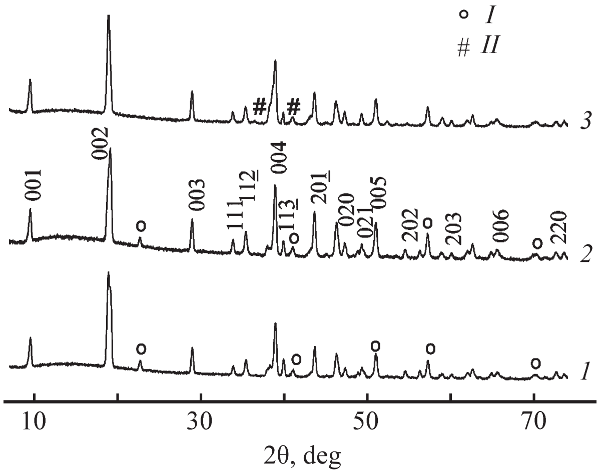

Fig. 1. Powder X-ray diffraction patterns of (*1*) $Ca_3Co_{3.6}O_{9+\delta}$, (*2*) $Ca_3Co_4O_{9+\delta}$, and (*3*) $Ca_3Co_{4.4}O_{9+\delta}$. Phase: (*I*) $Ca_3Co_2O_6$ and (*II*) Co_3O_4.

RESULTS AND DISCUSSION

Analysis of the elemental composition of the ceramic (Table 1) shows that the composition of the heat-treated samples corresponded to the preset nominal composition of the charge within the error of the EDX microanalysis.

After the synthesis completion, the ceramic, according to the XRD data, was not single-phase. The powder X-ray diffraction patterns (Fig. 1) contained, along with pronounced reflections of the major phase, layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$ [28], also the reflections of impurity phases: $Ca_3Co_2O_6$ [29] for the samples of the composition $Ca_3Co_{3.6}O_{9+\delta}$ and $Ca_3Co_4O_{9+\delta}$; Co_3O_4[1] for the sample of the composition $Ca_3Co_{4.4}O_{9+\delta}$.

The crystal lattice parameters of the major phase ($Ca_3Co_4O_{9+\delta}$) in ceramics of different compositions are close (Table 2) and agree with the published data, according to which for $Ca_3Co_4O_{9+\delta}$ $a = 0.48376(7)$ nm, $b_1 = 0.45565(6)$ nm, $b_2 = 0.28189(4)$ nm, $c = 1.0833(1)$ nm, and $\beta = 98.06(1)°$ [28]. At the same time, a slight increase in the parameters a and β of layered calcium cobaltite on deviation of the Ca : Co ratio from the stoichiometric value (3 : 4) should be noted.

The apparent density of the ceramics prepared by hot pressing was 4.215, 4.308, and 4.130 g cm^{-3} for samples of the compositions $Ca_3Co_{3.6}O_{9+\delta}$, $Ca_3Co_4O_{9+\delta}$, and $Ca_3Co_{4.4}O_{9+\delta}$, respectively, which corresponds to the porosity of 9.9, 7.9, and 11.7%. The results obtained allow two conclusions: firstly, the use of hot pressing allows preparation of a low-porosity ($\Pi \sim 10\%$) thermoelectric ceramic based on layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$; second, creation of the phase heterogeneity in the material by self-doping impairs, though not very significantly, its sinterability.

The ceramics of the compositions $Ca_3Co_{3.6}O_{9+\delta}$ and $Ca_3Co_4O_{9+\delta}$ had layered microstructure and consisted of well crystallized plates (flakes) of 8–10 μm size with a thickness of approximately 1 μm, partially aggregated in stacks and oriented predominantly in the direction perpendicular to the pressing axis (Figs. 2a, 2b). The anisometric shape of the crystallites of the major phase (layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$) in the ceramic of the nominal composition $Ca_3Co_{4.4}O_{9+\delta}$ was less pronounced (Fig. 2c); the crystallite size varied in a wide range, and the crystallites were partially aggregated in stacks near which small (of approximately 1 μm size) almost isometric particles of the impurity phase, cobalt oxide Co_3O_4 [18], could be seen. The $Ca_3Co_{4.4}O_{9+\delta}$ sample had a large number of pores (Fig. 2), in agreement with the results of determining the apparent density of the ceramic.

At temperatures close to room temperature, the ceramic exhibited the metal conductivity ($\partial\sigma/\partial T < 0$), which changed to semiconductor conductivity ($\partial\sigma/\partial T > 0$) at approximately 500 K (Fig. 3a); the activation energy of the electrical conductivity in the temperature interval 600–1100 K was 0.054(2), 0.051(1),

Table 2. Parameters of the crystal structure of the major phase ($Ca_3Co_4O_{9+\delta}$) in the phase-heterogeneous ceramic based on layered calcium cobaltite

Composition	a, nm	b_1, nm	b_2, nm	c, nm	β, deg
$Ca_3Co_{3.6}O_{9+\delta}$	0.4846 ± 0.0009	0.4540 ± 0.0010	0.2807 ± 0.0008	1.083 ± 0.002	98.45 ± 0.01
$Ca_3Co_4O_{9+\delta}$	0.4827 ± 0.0005	0.4541 ± 0.0007	0.2815 ± 0.0005	1.084 ± 0.001	98.09 ± 0.01
$Ca_3Co_{4.4}O_{9+\delta}$	0.4834 ± 0.0006	0.4542 ± 0.0007	0.2812 ± 0.0005	1.085 ± 0.001	98.26 ± 0.01

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[1] Powder Diffraction File, Swarthmore: Joint Committee on Powder Diffraction Standard, card no. 00-042-1467.

and 0.044(2) eV for the $Ca_3Co_{3.6}O_{9+\delta}$, $Ca_3Co_4O_{9+\delta}$, and $Ca_3Co_{4.4}O_{9+\delta}$ samples, respectively, which well agrees with the value of $E_a \sim 0.05$ eV, found by Zhou et al. [23] for the ceramic of the composition $Ca_3Co_{4\pm x}O_{9+\delta}$ (x = 0–0.4). The close values of E_a for the materials that we studied suggest a common mechanism of the electrical conductivity, determined by the charge transfer within the major phase, layered calcium cobaltite. The specific electrical conductivity of the ceramic was considerably higher [$\sigma_{300} \sim 45$–111 S cm^{-1} (Fig. 3a)] than that of the materials prepared by the common solid-phase or citrate method ($\sigma_{300} \sim 20$–25 S cm^{-1} [8, 12, 14, 16, 18]), which is caused by its low porosity; the conductivity strongly increased with an increase in the cobalt oxide content (in particular, the electrical conductivity of the phase-heterogeneous ceramic of the composition $Ca_3Co_{4.4}O_{9+\delta}$, containing cobalt oxide Co_3O_4 as an impurity phase, throughout the examined temperature interval was 40–60% higher than that of the base compound, layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$) (Fig. 3a).

The thermo-emf coefficient of the materials studied was positive ($S > 0$); this means that the main charge carriers in them are holes. This coefficient increased with temperature also for the samples containing an excess amount of calcium or cobalt oxide relative to the stoichiometry, being appreciably (by 5–20%) higher than that for $Ca_3Co_4O_{9+\delta}$ (Fig. 3b). Thus, creation of the phase heterogeneity in the ceramic based on layered calcium cobaltite (in particular, owing to introduction of less conducting phases, $Ca_3Co_2O_6$ or Co_3O_4) allows its

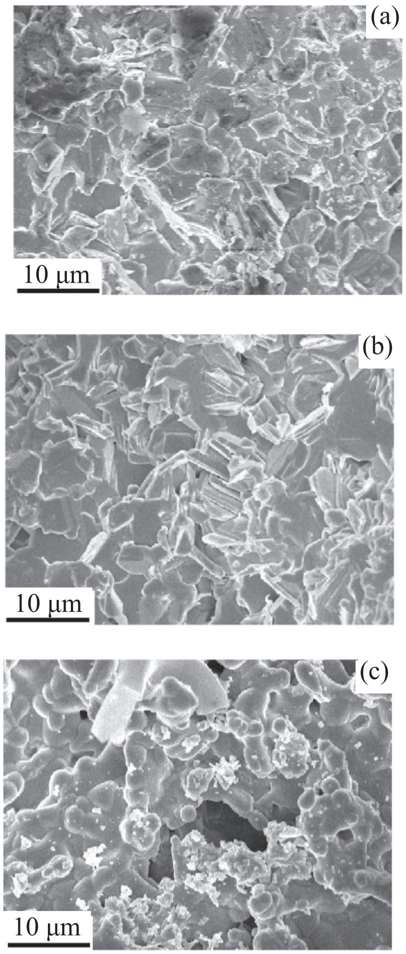

Fig. 2. Electron micrographs of chips of (a) $Ca_3Co_{3.6}O_{9+\delta}$, (b) $Ca_3Co_4O_{9+\delta}$, and (c) $Ca_3Co_{4.4}O_{9+\delta}$.

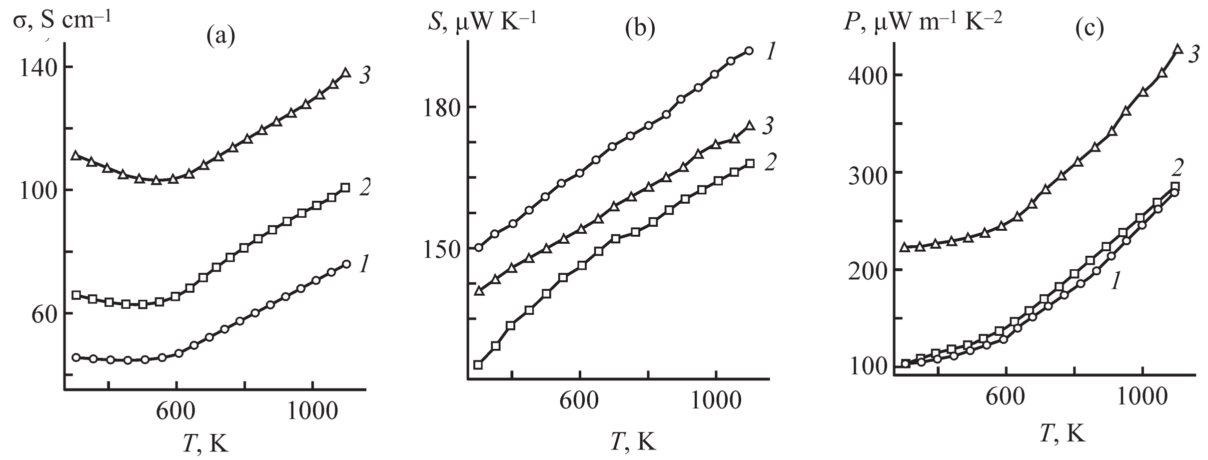

Fig. 3. Temperature dependences of the (a) electrical conductivity, (b) thermo-emf coefficient, and (c) power factor of samples of the composition (*1*) $Ca_3Co_{3.6}O_{9+\delta}$, (*2*) $Ca_3Co_4O_{9+\delta}$, and (*3*) $Ca_3Co_{4.4}O_{9+\delta}$.

thermo-emf coefficient to be appreciably increased.

The power factor of the ceramics studied increased with temperature. It was close for the $Ca_3Co_{3.6}O_{9+\delta}$ and $Ca_3Co_4O_{9+\delta}$ samples and appreciably higher for $Ca_3Co_{4.4}O_{9+\delta}$ (Fig. 3c), which is due to high values of its specific electrical conductivity and thermo-emf coefficient. The highest power factor was observed for the phase-heterogeneous ceramic of the composition $Ca_3Co_{4.4}O_{9+\delta}$ ($Ca_3Co_4O_{9+\delta}$ + Co_3O_4): P_{1100} = 427 μW m^{-1} K^{-2}, which is 1.5 times higher than for the ceramic $Ca_3Co_4O_{9+\delta}$ prepared by the same method (P_{1100} = 285 μW m^{-1} K^{-2}) and more than 4 times higher than for the low-density ceramic $Ca_3Co_4O_{9+\delta}$ prepared by the traditional solid-phase method (P_{1100} = 100 μW m^{-1} K^{-2} [16]).

The temperature conductivity of the $Ca_3Co_4O_{9+\delta}$ and $Ca_3Co_{3.6}O_{9+\delta}$ samples at 299 K was 7.69×10^{-7} and 8.93×10^{-7} m^2 s^{-1}, respectively, and the thermal conductivity values calculated on their basis are 3.22 and 3.66 W m^{-1} K^{-1}. Such values are characteristic of high-density (low-porosity) ceramic based on layered calcium cobaltite [8]. Because the $Ca_3Co_4O_{9+\delta}$ sample is characterized by higher apparent density (lower porosity) than the $Ca_3Co_{3.6}O_{9+\delta}$ sample, higher values of the temperature and thermal conductivity of the latter sample are probably due to the presence of the impurity $Ca_3Co_2O_6$ phase. The electronic contribution to the thermal conductivity of the ceramics $Ca_3Co_4O_{9+\delta}$ and $Ca_3Co_{3.6}O_{9+\delta}$ was 34.36 and 12.31 mW m^{-1} K^{-1}, and the phonon contribution, 3.18 and 3.64 W m^{-1} K^{-1}, respectively. That is, the electronic constituent of the thermal conductivity is low (λ_e/λ = 0.3–1.1%) and the phonon conductivity prevails (λ_{ph}/λ = 98.9–99.7%), which is characteristic of materials of this type [12, 14].

The figure-of-merit of the sample with excess calcium oxide, $Ca_3Co_{3.6}O_{9+\delta}$, at 299 K was 0.00836 and was lower than for the base compound, layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$ (0.00955), which is caused by lower specific electrical conductivity and higher thermal conductivity of this material.

CONCLUSIONS

The creation of the phase heterogeneity in a ceramic based on layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$ by self-doping allows the thermo-emf coefficient of the materials to be appreciably increased. The quantity S for the samples self-doped with calcium oxide ($Ca_3Co_2O_6$ impurity phase) increases to a greater extent than in self-doping with cobalt oxide (Co_3O_4 impurity phase). Hot pressing allows preparation of a ceramic exhibiting low porosity (Π = 8–12%) and therefore increased electrical conductivity. Joint use of self-doping and hot pressing leads to the formation of a ceramic with improved functional (thermoelectric) characteristics. For example, among the samples studied, the phase-heterogeneous ceramic of the composition $Ca_3Co_{4.4}O_{9+\delta}$, containing cobalt oxide Co_3O_4 as an impurity phase, has the highest power factor, 427 μW m^{-1} K^{-2} at 1100 K, which is 1.52 times higher than for the $Ca_3Co_4O_{9+\delta}$ sample (P_{1100} = 280 μW m^{-1} K^{-2}) and 4.27 times higher than for the low-density (Π = 25%) ceramic $Ca_3Co_4O_{9+\delta}$ prepared by the common procedure (P_{1100} = 100 μW m^{-1} K^{-2} [16]).

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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