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Synthesis and Properties of Na_xCoO_2 ($x = 0.55, 0.89$) Oxide Thermoelectrics

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Abstract—Na_xCoO_2 (x = 0.55, 0.89) sodium cobaltites have been prepared by solid-state reactions; their structural parameters have been determined; their microstructure has been studied; and their thermal (thermal expansion, thermal diffusivity, and thermal conductivity), electrical (electrical conductivity and thermoelectric power), and functional (power factor, thermoelectric figure of merit, and self-compatibility factor) properties have been investigated in air at temperatures from 300 to 1100 K. The results demonstrate that, with increasing sodium content, the electrical conductivity and thermoelectric power of the materials increase and their thermal conductivity decreases. As a result, the power factor and thermoelectric figure of merit of the $Na_{0.89}CoO_2$ ceramic at a temperature of 1100 K reach 0.829 mW/(m K^2) and 1.57, respectively. The electron and phonon (lattice) contributions to the thermal conductivity of the ceramics have been separately assessed, and their linear thermal expansion coefficients have been evaluated.

Keywords: oxide thermoelectrics, sodium cobaltite, power factor, thermoelectric figure of merit

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INTRODUCTION

Sodium cobaltite, Na_xCoO_2, first described by Jansen and Hoppe [1], is a bronze-type layered oxide consisting of $[CoO_2]$ layers (CdI_2 structure), with sodium atoms in between [2]. According to Viciu et al. [3], the oxygen vacancy concentration in the $[CoO_2]$ layers is negligible, so this compound can be thought of as having perfect oxygen stoichiometry, and the formal oxidation state of cobalt in it is only determined by the percentage of sodium. Na_xCoO_2 possesses unique electrical properties, which strongly depend on x. At low temperatures, sodium-poor cobaltites containing intercalated water, $Na_xCoO_2 \times yH_2O$ ($0.26 \leqslant x \leqslant 0.42$, $y = 1.3$), undergo a superconducting transition ($T_c \approx 4$ K) [4]. At a higher sodium content ($x \geqslant 0.5$), the Na_xCoO_2 layered oxides have a high thermoelectric power [2, 5], suggesting that they can be used as basic materials for designing new oxide thermoelectrics.

After the discovery that $NaCo_2O_4$ single crystals possess high thermoelectric efficiency [2], most research effort has been concentrated on this composition ($Na_{0.5}CoO_2$) [6, 7]. According to later results, however, the more sodium-rich cobaltites ($0.65 \leqslant x \leqslant 0.85$) have higher thermoelectric power [5, 8, 9]. Note that, as shown by Lee et al. [8, 9], the highest thermoelectric figure of merit at a temperature of 50 K ($Z \simeq 1.8 \times 10^{-3}$ K^{-1}) is offered by $Na_{0.88}CoO_2$ ceramics, which have a nearly critical doping level ($x_{cr} \simeq 0.85$). Thus, the sodium-rich ($x > 0.5$) layered cobaltites are of interest as new oxide thermoelectrics more efficient than the $Na_{0.5}CoO_2$ material.

There are only limited, and somewhat contradictory, data on the influence of sodium content on the properties of the Na_xCoO_2 cobaltites. In particular, according to Liu et al. [5] the thermoelectric power of the Na_xCoO_2 ($0.65 \leqslant x \leqslant 0.85$) materials increases monotonically with increasing x, whereas their electrical conductivity varies nonmonotonically, passing through a maximum at the composition $Na_{0.78}CoO_2$. According to Kawata et al. [10], the electrical conductivity of the Na_xCoO_2 ($0.55 \leqslant x \leqslant 0.70$) layered oxides increases monotonically with increasing x, whereas their Seebeck coefficient is essentially independent of sodium content. As shown by Baster et al. [11], both the electrical conductivity and thermoelectric power of the Na_xCoO_2 (x = 0.69, 0.72) materials increase with increasing x. Most research effort has been concentrated on the properties of the Na_xCoO_2 cobaltites below room temperature [8–12]. In the only report concerned with the electrical properties of the Na_xCoO_2 ($0.65 \leqslant x \leqslant 0.85$) materials at high temperatures (300–1100 K) [5], no thermal conductivity data are presented, which makes it impossible to evaluate the thermoelectric figure of merit of the samples and assess their potential for use in high-temperature thermoelectric conversion.

In this paper, we report the synthesis of Na_xCoO_2 layered cobaltites with different sodium contents ($x = 0.55$ and 0.89); describe their crystal structure, microstructure, physicochemical properties (microhardness, thermal expansion, thermal diffusivity, thermal conductivity, electrical conductivity, and thermoelectric power), and functional characteristics (power factor, thermoelectric figure of merit, and self-compatibility factor); and analyze the effect of sodium content on the structure and properties of the cobaltites.

EXPERIMENTAL

Ceramic samples of the Na_xCoO_2 ($x = 0.55, 0.89$) cobaltites were prepared by solid-state reactions between Na_2CO_3 (analytical grade) and Co_3O_4 (pure grade) at a Na : Co ratio of 1.2x : 1.0 (the excess of Na_2CO_3 in the starting mixture compensates for the Na_2O loss from the samples during heat treatment and makes it possible to obtain ceramics of controlled composition [12]).

After thorough mixing and grinding in an agate mortar, the mixture was pressed with ethanol at 40 MPa to pellets 25 mm in diameter and 5–7 mm in thickness, which were then fired at a temperature of 1133 K in air for 12 h. Next, the samples were crushed in an agate mortar, reground, and pressed at 110–130 MPa into rectangular parallelepipeds 5 × 5 × 30 mm in dimensions and into pellets 15 mm in diameter and 2–4 mm in thickness, which were then sintered in air at a temperature of 1203 K for 12 h. In electrical conductivity measurements, we used samples in the form of rectangular parallelepipeds 4 × 4 × 2 mm in dimensions (area-to-thickness ratio of $\simeq 8$), cut from the sintered ceramics.

The phase composition of the samples and the parameters of their crystal structure were determined by X-ray diffraction on a Bruker D8 XRD Advance X-ray diffractometer (CuK_α radiation). The crystallite size D in the ceramics was evaluated using the Debye–Scherrer equation: $D = (0.9\lambda)/(\beta\cos\theta)$, where λ is the wavelength of CuK_α radiation, β is the full width at half maximum of the reflection, and θ is the diffraction angle.

The IR absorption spectra of the powders were measured using pressed mixtures with reagent-grade KBr on a ThermoNicolet Nexus Fourier transform spectrometer in the frequency range 300–1500 cm^{-1}. X-ray diffraction data were used to determine the X-ray density (ρ_x) of the samples. The average oxidation state of the cobalt and the percentage of sodium in Na_xCoO_2 were determined by iodometric titration [12].

The microstructure of the ceramics was examined by scanning electron microscopy (SEM) on a JEOL JSM-5610 LV. The bulk density (ρ) of the samples was evaluated from their mass and dimensions. The porosity (Π) of the sintered ceramics was evaluated as $\Pi = (1 - \rho/\rho_x) \times 100\%$. The microhardness of the ceramics (H) was measured on a 401/402 MVD microhardness tester along ($H_\parallel$) and across ($H_\perp$) the compaction direction.

The electrical conductivity (σ) of the sintered samples was measured at dc ($I \leqslant 50$ mA) by the four-probe method (V7-58 and V7-53 digital voltmeters, B5-47 power supply unit) in air at temperatures from 300 to 1100 K in dynamic mode at a heating/cooling rate of 3–5 K/min [13, 14]. The thermoelectric power (S) of the ceramics was determined relative to silver (V7-65/3 digital voltmeter) in air at temperatures from 300 to 1100 K [15]. Prior to the electrical transport measurements, Ag electrodes were formed on the sample surfaces by firing silver paste at 1100 K for 15 min. The thermal expansion of the ceramics was investigated in air at temperatures from 300 to 1100 K in dynamic mode at a heating/cooling rate of 3–5 K/min [13, 14]. The linear thermal expansion coefficient (LTEC) α of the ceramics was evaluated from linear portions in plots of $\Delta l/l_0$ against T. The thermal diffusivity (η) of the ceramics was determined in a helium atmosphere in the temperature range 300–1100 K using a Netzsch LFA 457 MicroFlash laser flash apparatus, and their heat capacity (C_p) was measured with a Netzsch STA 449 F3 Jupiter simultaneous thermal analysis system. The thermal conductivity (λ) of the samples was calculated as $\lambda = \eta C_p \rho$. The lattice (λ_{ph}) and electron (λ_{el}) contributions to the thermal conductivity of the ceramics were evaluated using the relations $\lambda_{ph} = \lambda - \lambda_{el}$ and $\lambda_{el} = \sigma LT$, where L is the Lorenz number ($L = 2.45 \times 10^{-8}$ V^2/K^2).

The power factor (P), thermoelectric figure of merit (ZT), and self-compatibility factor (s) of the materials were evaluated as $P = S^2\sigma$, $ZT = (PT)/\lambda$, and $s = [(1 + ZT)^{0.5} - 1]/(ST)$ [16, 17].

RESULTS AND DISCUSSION

According to iodometric titration results, the compositions of the synthesized sodium cobaltites were $Na_{0.55}CoO_2$ and $Na_{0.89}CoO_2$ (the average oxidation state of the cobalt was +3.45 and +3.11, respectively). X-ray diffraction characterization (Fig. 1a) showed that they were isostructural with the hexagonal sodium cobaltite γ-Na_xCoO_2 [3, 4] and had the following unit-cell parameters: $a = 0.285(2)$ and 0.283(3) nm, $c = 1.12(2)$ and 1.09(1) nm, $V = 0.0785$ (20) and 0.0756(2) nm^3, $c/a = 3.93$ and 3.85, respectively. These data agree with previous results [3–6] and demonstrate that, with increasing sodium content, the unit cell of the samples decreases, predominantly in the c-axis direction (along the normal to the $[CoO_2]$ layers. The X-ray diffraction patterns (Fig. 1a) and IR absorption spectra (Fig. 1b) of the Na_xCoO_2 powders

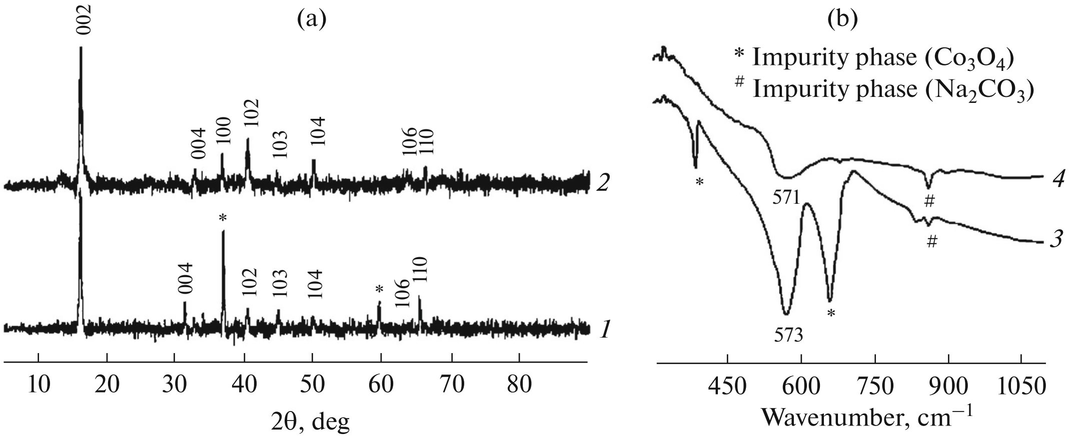

Fig. 1. (*1, 2*) X-ray diffraction patterns and (*3, 4*) IR absorption spectra of Na_xCoO_2 powders with x = (*1, 3*) 0.55 and (*2, 4*) 0.89.

contained peaks and absorption bands of impurity phases Na_2CO_3 and Co_3O_4), due to partial degradation of grain surfaces in the samples as a result of interaction with atmospheric CO_2 and H_2O according to the reactions

$$Na_xCoO_2 + x/2\ CO_2 \rightarrow x/2\ Na_2CO_3$$
$$+ 1/3Co_3O_4 + (1/3 - x/4)O_2,$$
$$Na_xCoO_2 + x/2\ H_2O \rightarrow x\text{NaOH}$$
$$+ 1/3\ Co_3O_4 + (1/3 - x/4)O_2.$$

The IR absorption spectra of the sodium cobaltite powders (Fig. 1b) contain a prominent absorption band of the major phase (Na_xCoO_2), centered at 571–573 cm^{-1}, which corresponds, according to Premila et al. [18], to vibrations of the Co–O bonds in the [CoO_2] layers. It follows from the present IR absorption spectroscopy results that the percentage of sodium in Na_xCoO_2 has little or no effect on the energy of the cobalt–oxygen interaction in the [CoO_2] layers of its crystal structure.

The bulk density of the Na_xCoO_2 ceramics was 3.65 and 3.38 g/cm^3, and its porosity was 17 and 28% at x = 0.55 and 0.89, respectively. This leads us to conclude that increasing the percentage of sodium oxide impairs the sinterability of the samples.

The ceramics consisted of platelike grains, which were partially aligned across the compaction direction. The grains were 1–10 and 10–30 μm in width and 0.5–1 and 2–10 μm in thickness in the $Na_{0.55}CoO_2$ and $Na_{0.89}CoO_2$ ceramics, respectively (Fig. 2), and were polycrystalline (according to X-ray diffraction data, the crystallite size in the ceramics was about 50 nm). The microhardness of the ceramics was found to decrease with increasing sodium content ($H_\parallel$ = 1.21 and 0.85 GPa and $H_\perp$ = 1.08 and 0.84 GPa for $Na_{0.55}CoO_2$ and $Na_{0.89}CoO_2$, respectively). Note that $H_\parallel > H_\perp$, which also indicates preferential alignment of the sodium cobaltite grains across the compaction direction, that is, partial texturing of the ceramics.

In the temperature range 300–1100 K, the relative length change $\Delta l/l_0$ of the samples was a linear func-

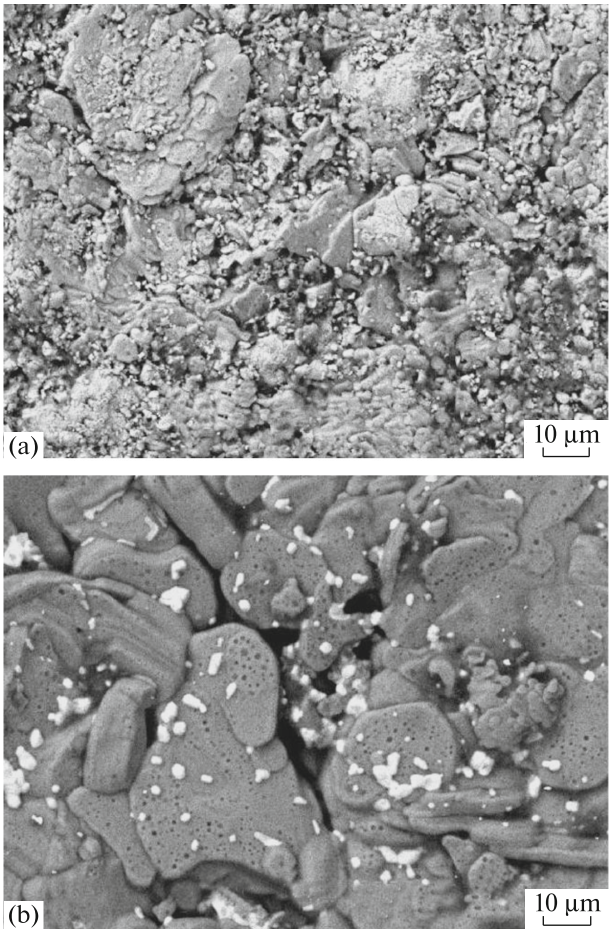

Fig. 2. Electron micrographs of fracture surfaces (normal to the compaction direction) for the Na_xCoO_2 ceramics with x = (a) 0.55 and (b) 0.89.

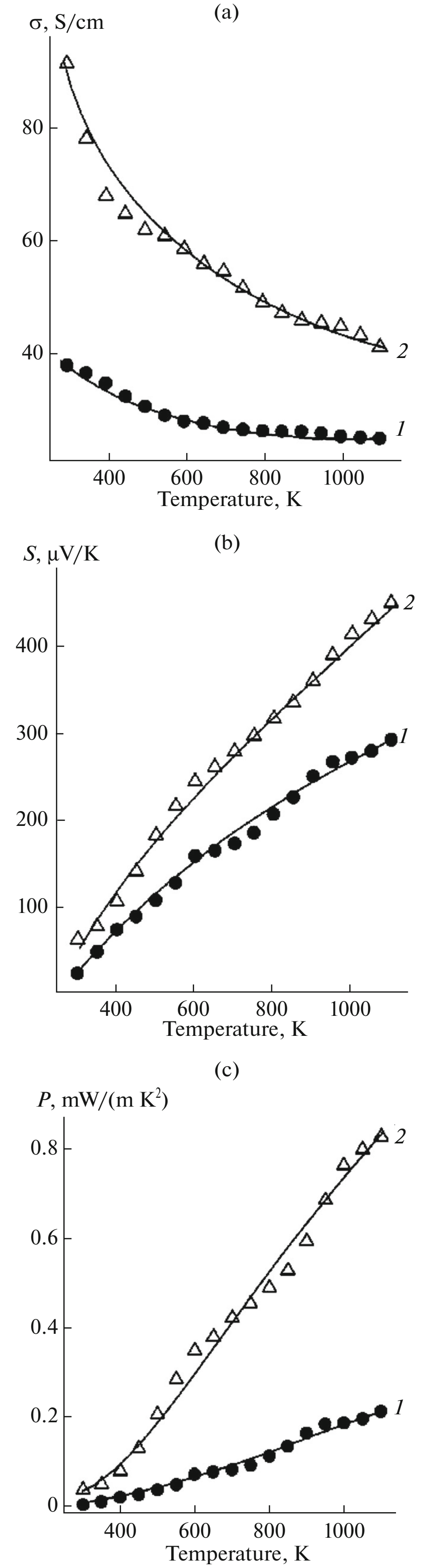

Fig. 3. Temperature dependences of the (a) electrical conductivity (σ), (b) thermoelectric power (S), and (c) power factor (P) for the Na_xCoO_2 cobaltates with x = (*1*) 0.55 and (*2*) 0.89.

tion of temperature. Therefore, the Na_xCoO_2 phases undergo no well-defined structural phase transitions in this temperature range. The sodium cobaltites differed little in LTEC ($\alpha = 12.2 \times 10^{-6}$ and 12.4×10^{-6} K^{-1} at $x = 0.55$ and 0.89, respectively). This correlates with the present IR absorption spectroscopy results, which suggest that the energy of interionic interactions in Na_xCoO_2 is essentially independent of sodium content.

As seen in Fig. 3, the Na_xCoO_2 cobaltites are p-type conductors ($S > 0$, Fig. 3b), and their electrical conductivity exhibits metallic behavior ($\partial\sigma/\partial T < 0$) and increases with increasing x (the two samples differed little in the temperature coefficient of electrical conductivity ($\partial \ln\sigma/\partial T$): -7.16×10^{-4} and -7.05×10^{-4} K^{-1} at $x = 0.55$, 0.89, respectively), which is due to the increase in the concentration of majority charge carriers (holes) in the samples with a decrease in the average oxidation state of the cobalt. The Seebeck coefficient of the sodium cobaltites under study was found to increase with increasing temperature and x. The latter finding can be understood based on previous results: as shown by Koshibae et al. [19], the high thermoelectric power of the layered sodium cobaltites is due to the degeneracy of the spin states of the cobalt ions (Co^{3+}, Co^{4+}) and strong correlation between their 3d electrons, and the S of these phases in the high-temperature limit is described by the Heikes equation

$$S = (k_B/e)\ln[(g_4[Co^{3+}])/(g_3[Co^{4+}])],$$

where k_B is Boltzmann's constant, e is the electron charge, g_4 and g_3 are the degeneracies of the spin states of the Co^{4+} and Co^{3+} ions, and $[Co^{3+}]$ and $[Co^{4+}]$ are their concentrations. With increasing sodium concentration in the Na_xCoO_2 materials, $[Co^{4+}]$ decreases and, according to the Heikes equation, their thermoelectric power rises.

The power factor of the ceramics was found to increase with increasing temperature and x (Fig. 3c), reaching the highest value (0.829 mW/(m K^2)) for the composition $Na_{0.89}CoO_2$ at a temperature of 1100 K.

As follows from the data presented in Figs. 4 and 5, the thermal diffusivity (η) and thermal conductivity (λ) of the Na_xCoO_2 ceramics decrease with increasing x and vary nonmonotonically with increasing temperature, passing through a broad minimum in the range 800–900 K, which is more prominent in the $\lambda(T)$ curve. As seen in Fig. 5, the electron thermal conductivity of $Na_{0.55}CoO_2$ is not very high (λ_{el} = (0.02–0.07)λ), whereas that of $Na_{0.89}CoO_2$ is considerably higher (λ_{el} = (0.07–0.21)λ). The largest contribution of λ_{el} to the total thermal conductivity of the ceramics is observed at $T > 800$ K. Lattice vibrations (phonons) account for most of the thermal conductivity of the $Na_{0.55}CoO_2$ cobaltite (λ_{ph} = (0.93–0.98)λ) and for a considerable fraction of the thermal conductivity of $Na_{0.89}CoO_2$ (λ_{ph} = (0.79–0.93)λ). Thus, the

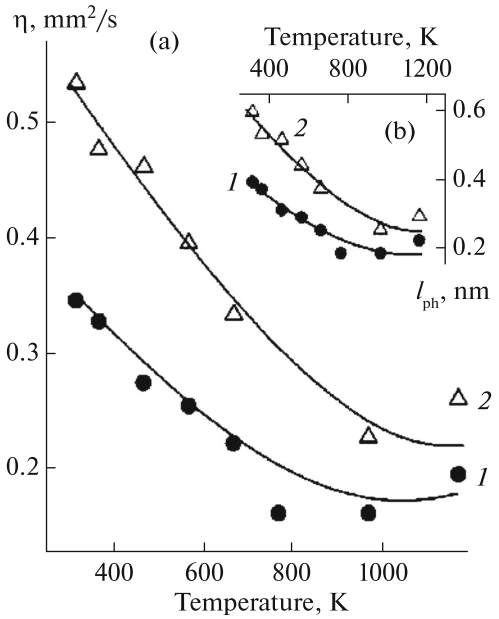

Fig. 4. Temperature dependences of the (a) thermal diffusivity (η) and (b) phonon mean free path (l_{ph}) for the Na_xCoO_2 ceramics with x = (*1*) 0.55 and (*2*) 0.89.

electron thermal conductivity of the Na_xCoO_2 sodium cobaltites increases with increasing x, whereas their lattice thermal conductivity decreases because of the stronger phonon scattering by the sodium atoms located between the $[CoO_2]$ layers in the crystal structure of the cobaltites.

Figure 4b shows the temperature dependences of the phonon mean free path (l_{ph}) in the materials under study, which was evaluated using the relation

$$\eta = \frac{1}{3} v l_{ph},$$

where v is the sound velocity [20].

The sound velocity was determined using the formula

$$\Theta = (hv(6\pi^2 N/V)^{1/3})/(2\pi k_B),$$

where Θ is the Debye temperature, h is Planck's constant, N/V is the number of atoms per unit volume, and k_B is Boltzmann's constant [20]. We used the Debye temperature reported by Ando et al. [21] for the $Na_{0.55}CoO_2$ sodium cobaltite: Θ = 354 K.

The cobaltites under study differ little in l_{ph}, which ranges from 0.23 to 0.61 nm (Fig. 4b). Therefore, phonon scattering by grain and crystallite boundaries is insignificant ($l_{ph} \ll D$), and the main phonon scattering centers in the layered sodium cobaltites are various structural distortions on the order of the lattice parameter in size. The phonon mean free path in Na_xCoO_2 is considerably smaller than the electron mean free path (l_{el}) (according to Terasaki et al. [2], l_{el} = 23 nm along the $[CoO_2]$ layers in $Na_{0.5}CoO_2$ at a temperature of 4.2 K), which suggests that the layered sodium cobaltite is a "phonon glass–electron crystal" material [22].

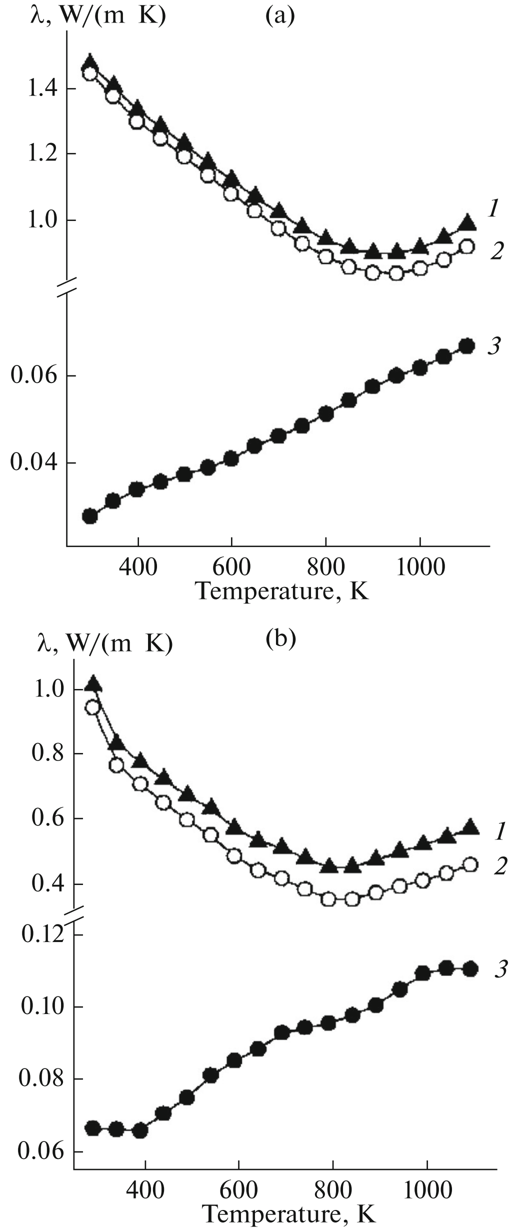

Fig. 5. Temperature dependences of the (*1*) total thermal conductivity (λ), (*2*) lattice contribution (λ_{ph}), and (*3*) electron contribution (λ_{el}) for the Na_xCoO_2 cobaltites with x = (a) 0.55 and (b) 0.89.

Thus, the η and λ of the Na_xCoO_2 cobaltites decrease with increasing temperature (for $T < 800$ K) because of the decrease in phonon mean free path, and the increase in the thermal conductivity of these materials in the temperature range 800–1100 K is mainly due to the increase in the electron contribution to their thermal conductivity.

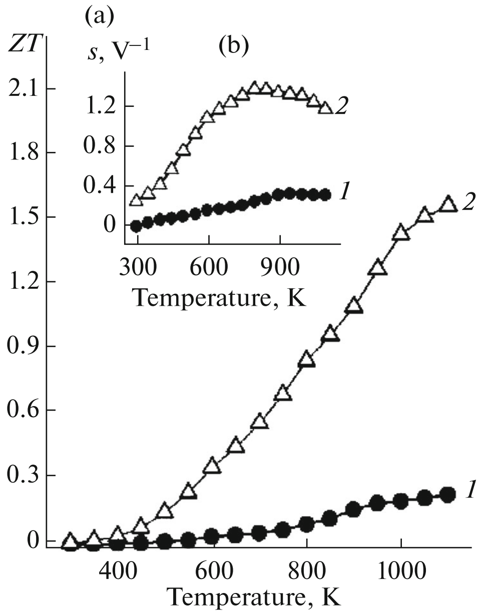

Fig. 6. Temperature dependences of the (a) thermoelectric figure of merit (*ZT*) and (b) self-compatibility factor (*s*) for the Na_xCoO_2 oxides with x = (*1*) 0.55 and (*2*) 0.89.

The dimensionless thermoelectric figure of merit of the ceramics increases with increasing x and temperature (Fig. 6a), reaching the highest value for the composition $Na_{0.89}CoO_2$: 1.57 at a temperature of 1100 K. This value exceeds the theoretical criterion ($ZT > 1$ [22]) that determines materials of practical interest for thermoelectric conversion, and suggests that this cobaltite is a potentially attractive material for *p*-legs of high-temperature thermoelectric power converters. In the temperature range 800–1100 K, the self-compatibility factor (s) of $Na_{0.89}CoO_2$ varies only slightly, between 1.2 and 1.4 V^{-1} (Fig. 6b), and the dimensionless relative self-compatibility factor $\Delta s = (s_{\max} - s_{\min})/s_{\max}$ [23] of this material is 14%, which is well below that of $Mg_2Si_{0.6-y}Sn_{0.4}Sb_y$ thermoelectric alloys (20–45%) [23] and confirms good self-compatibility of $Na_{0.89}CoO_2$ at high temperatures (800–1100 K).

CONCLUSIONS

Na_xCoO_2 (x = 0.55, 0.89) ceramics have been produced by solid-state reactions and their crystal structure, microstructure, thermal expansion, thermal diffusivity, thermal conductivity, electrical conductivity, and thermoelectric power have been studied. The electron and lattice (phonon) contributions to the thermal conductivity of the ceramics have been separately assessed, and their LTEC, power factor, dimensionless thermoelectric figure of merit, and self-compatibility factor have been evaluated.

The results demonstrate that, with increasing sodium content, the electrical conductivity and thermoelectric power of the materials increase and their thermal conductivity decreases. As a result, the power factor and thermoelectric figure of merit of the $Na_{0.89}CoO_2$ ceramic at a temperature of 1100 K reach 0.829 mW/(m K^2) and 1.57, respectively, and the relative self-compatibility factor of this cobaltite in the temperature range 800–1100 K is 14%. Therefore, this material is potentially attractive as a component of *p*-legs of high-temperature thermoelectric power converters.

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