Effect of silver on thermal e.m.f. and electric resistance of La–Sr–Co–O ceramics

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The effect of silver on thermal e.m.f. and electric resistance of $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0; 0.15; 0.35) ceramic samples prepared by solid phase synthesis has been demonstrated. The thermoelectric characteristics of the ceramics become enhanced by the silver addition, the conductivity character remaining unchanged.

Продемонстрировано влияние серебра на термо-ЭДС и электрическое сопротивление керамических образцов $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0; 0.15; 0.35), полученных методом твердофазного синтеза. Установлено, что при введении серебра термоэлектрические характеристики керамик улучшаются. Характер проводимости при этом не изменяется.

Today, a considerable attention is given to studies of physical properties of a novel class of metal oxide compounds, the oxygen-deficient cobaltites $R_{1-x}A_xCoO_{3-\delta}$ (R = rare earth ion, A = alkali earth ion, $0 \le x \le 1$). The interest in investigation of those materials was initially caused by a large negative magnetoresistance in $La_{1-x}Sr_xCoO_{3-\delta}$ compound [1]. Another property of cobaltites, the high thermal e.m.f values, is ascribed usually to strong electron correlations, but its nature remains still unclear [2]. High thermal e.m.f. were reported for both undoped and strontium-doped $LaCoO_3$ [3]. The low conductivity values of those compounds may hinder the application thereof in thermoelectric converters. The addition of silver to complex oxides of other transition metals (cuprates and manganites) is known to enhance the conductivity [4, 5]. In those cases, silver may be present both in ionized state and as metallic clusters. Those compounds, like cobaltites, are systems with strong interelectron correlations. The physical properties thereof are similar to a great extent. To date, the effect of silver on physical phenomena in cobaltites was not studied. The aim of this work was to study the conductivity and thermal e.m.f. changes in undoped and strontium-doped lanthanum cobaltites caused by silver addition thereto.

The ceramic samples of initial $La_{1-x}Sr_xCoO_{3-\delta}$ composition (x = 0; 0.15; 0.35) were prepared using the standard solid phase technique. The CoO, La_2O_3, and $SrCO_3$ powders were mixed in the stoichiometric ratio and compressed at 100 MPa. The sintering was carried out in three staged for 2 h each, at temperatures 800°C, 900°C, and 1250°C, respectively, the sample being subjected to grinding and compression after each sintering stage. The samples were shaped as 2.5 cm long rectangular parallelepipeds of 0.2×0.55 cm^2 cross-section. The Ag containing samples were prepared in a similar manner, with $AgNO_3$ adding to the initial powder mixtures in

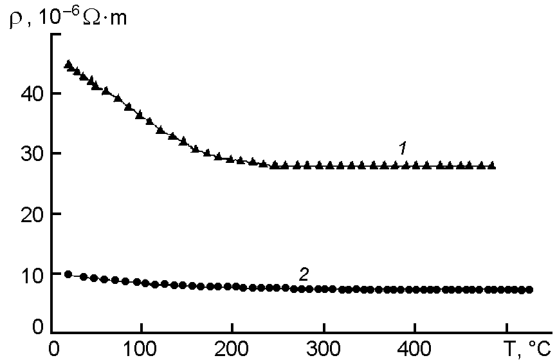

Fig. 1. Temperature dependences of specific electric resistance for $La_{0.85}Sr_{0.15}CoO_{3-\delta}$ (*1*) and $(La_{0.85}Sr_{0.15})_{0.75}Ag_{0.25}CoO_{3-\delta}$ (*2*) samples.

amounts corresponding to 5, 20, and 25 mol. % Ag for samples with $x = 0.35$, 0, and 0.15, respectively.

The Seebeck coefficient for the ceramics synthesized was determined by the integral method with copper as a reference. Indium applied by ultrasound soldering was used as the solder providing the ceramics/copper contact. The thermal e.m.f. was induced in the 20 to 400°C temperature range. The cold junction was thermally stabilized at 20°C. The hot junction temperature was measured using a copper/constantan thermocouple. The resistive measurements were carried out by dc four-probe technique. The measuring current was passed along the sample. The indium contacts were applied along the sample width using the ultrasound soldering. The distance between the potential leads was 10 mm. The measuring current did not exceed 50 mA. According to XPA data, the silver-containing samples consisted of a single phase of perovskite-like crystal structure with rhombohedrically distorted unit cell characterized by the cell parameters $a = b = 0.5376$ nm, $c = 1.34207$ nm for $La_{0.8}Ag_{0.2}CoO_{3-\delta}$ and $a = b = 0.53895$ nm, $c = 1.34294$ nm for $(La_{0.85}Sr_{0.15})_{0.75}Ag_{0.25}CoO_{3-\delta}$ samples.

The temperature dependences of specific electric resistance ρ and the changes therein due to silver addition to $La_{0.85}Sr_{0.15}CoO_{3-\delta}$ and $La_{0.65}Sr_{0.35}CoO_{3-\delta}$ are presented in Figs. 1 and 2, respectively. The $\rho(T)$ dependence for the $La_{0.85}Sr_{0.15}CoO_{3-\delta}$ sample is of semiconducting character; as x increases up to 0.35, the transition to metallic conductivity type takes place, in agreement with literature data [6]. The Ag addition causes the conductivity increase by a factor of 3 to 4, its character remaining unchanged. The temperature dependences of specific thermal

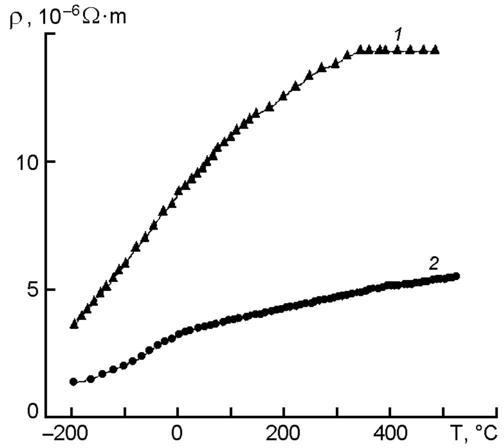

Fig. 2. Temperature dependences of specific electric resistance for $La_{0.65}Sr_{0.35}CoO_{3-\delta}$ (*1*) and $(La_{0.65}Sr_{0.35})_{0.95}Ag_{0.05}CoO_{3-\delta}$ (*2*) samples.

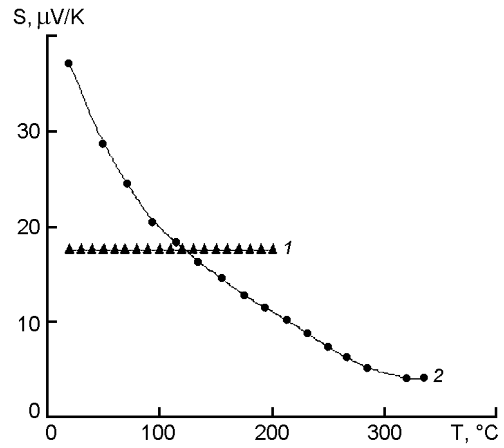

Fig. 3. Temperature dependences of Seebeck coefficient for $La_{0.85}Sr_{0.15}CoO_{3-\delta}$ (*1*) and $(La_{0.85}Sr_{0.15})_{0.75}Ag_{0.25}CoO_{3-\delta}$ (*2*) samples.

e.m.f. for the $La_{0.85}Sr_{0.15}CoO_{3-\delta}$ and $(La_{0.85}Sr_{0.15})_{0.75}Ag_{0.25}CoO_{3-\delta}$ ceramics is shown in Fig. 3. The Seebeck coefficient (S) for $La_{0.65}Sr_{0.35}CoO_{3-\delta}$ sample amounted 5.5 μV/K and was temperature-independent in the 20 to 200°C range. The addition of 5 % Ag did not cause any changes in S value. The charge carrier nature (holes) remained unchanged at Ag addition for the samples with both metallic and semiconducting conductivity types. The resistive and thermoelectric examination results for the $La_{0.8}Ag_{0.2}CoO_{3-\delta}$ ceramics were similar to the above ones. $LaCoO_3$ is well known to be a dielectric with a high Seebeck coefficient [7]. As 20 mol. % Ag were added to that compound, the conductivity increased by several orders (up to values typical of semiconductors), the high Seebeck coefficient being conserved.

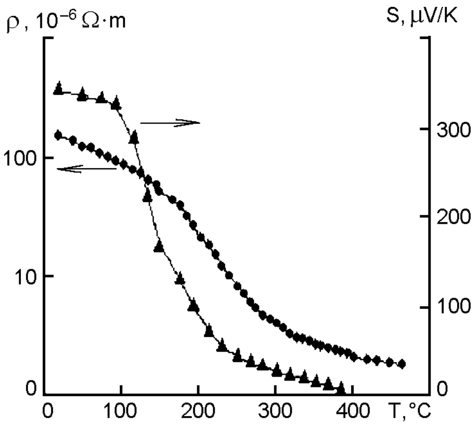

Fig. 4. Temperature dependences of specific electric resistance and Seebeck coefficient for $La_{0.8}Ag_{0.2}CoO_{3-\delta}$ ceramics.

Thus, the addition of silver to $LaCoO_3$ and La–Sr–Co–O ceramics enhances their thermoelectric properties, in particular, the electric resistance decreases and the high thermal emf values are kept. The conductivity character and charge carrier type remain unchanged. The S^2/ρ value for $La_{0.8}Ag_{0.2}CoO_{3-\delta}$ and $(La_{0.85}Sr_{0.15})_{0.75}Ag_{0.25}CoO_{3-\delta}$ samples at room temperature is about 10^{-4} W/(m·K^2), thus being close to thermoelectric efficiency of modern thermoelectric materials. This offers good prospects for practical application of cobaltites in thermoelectric converters.

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Вплив срібла на термо-ЕРС та електроопір кераміки La–Sr–Co–O

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Продемонстровано вплив срібла на термо-ЕРС та електричний опір керамічних зразків $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0; 0.15; 0,35), одержаних методом твердофазного синтезу. Встановлено, що при введенні срібла термоелектричні характеристики керамік поліпшуються. Характер провідності при цьому не змінюється.