

THERMOEMF AND ELECTRIC CONDUCTIVITY OF LANTANUM AND NEODYMIUM COBALTITES-GALLATES SOLID SOLUTIONS

N. N. Lubinsky, L. A. Bashkirov, G. S. Petrov, A. I. Klyndyuk
(Belarussian State Technological University,
Minsk, Belarus Republic)

- This paper gives the results of experimental research on thermoEMF and direct current electric conductivity of $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ and $\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$ solid solutions in the temperature range 300–1050 K. It is shown that temperature dependence of thermoelectric coefficient (S) is of a complicated nature. Thus, at room temperature in both studied systems at $0 \leq x \leq 0.3$ S has negative values. With increasing temperature, S grows, passes through zero at 435–530 K ($\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$) or 490–540 K ($\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$), reaches maximum values at 560–650 K ($\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$) or 560–705 K ($\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$) and then is reduced. It is shown that temperature dependence of electric conductivity (σ) for samples with low x values is S -like, during which for a series of samples at high temperatures a transition from semiconductor to metal conductivity type has been noted. The values of activation energy of electric conductivity (E) were calculated for different temperature ranges, dependence of E on temperature and composition of solid solution (x value) was analyzed. For both studied systems in the high-temperature region the areas were found where the relationship $S = C - A \cdot \ln \sigma$, valid for semiconductors with one type of current carriers, is satisfactorily met. Based on the resulting data for jumping electric conductivity mechanism, the share of Co^{3+} ions responsible for electric conductivity was assessed. Based on the calculated values of power factor (P), $\text{NdCo}_{0.8}\text{Ga}_{0.2}\text{O}_3$, $\text{LaCo}_{0.8}\text{Ga}_{0.2}\text{O}_3$ cobaltites were shown to be promising oxide thermoelectric materials.

Introduction

The recent years have seen a rekindled interest in the study of physicochemical properties of lanthanum cobaltites LaCoO_3 and other rare-earth elements, which is due to the presence in these objects of particular magnetic, electric properties, marked electrochemical and catalytic activity, owing to which they are widely used as electrode materials for galvanic elements with solid electrolyte for the manufacture of ceramic membranes in producing pure oxygen from the air, as well as in devices of new field of science and technology – spintronics [1–6]. In so doing, the overwhelming number of papers is dedicated to study of individual rare-earth element cobaltites LnCoO_3 , for which it is shown that their electrophysical properties are largely caused by the spin state of $3d^6$ -electrons Co^{3+} ions and the observed spin transition of Co^{3+} ions from the low-spin to intermediate-spin and/or high-spin state. Besides, for these cobaltites there is semiconductor-metal phase transition taking place in a wide temperature range [7–8]. Note that the results of physicochemical investigations by different authors not always are in good agreement. For solid solutions of the respective cobaltites the literary data on physics and chemical properties are practically absent.

The purpose of this paper is to study the influence of isovalent substitution in LaCoO_3 and NdCoO_3 of paramagnetic Co^{3+} ions with partially filled $3d$ -shell by diamagnetic Ga^{3+} ions with completely filled $3d$ -shell on the thermoEMF and electric conductivity of the resulting solid solutions of neodymium, lanthanum cobaltites-gallates $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ and $\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$.

Experimental procedure

Neodymium, lanthanum cobaltites-gallates $\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$, $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($x = 0 \div 1.0$) were produced by ceramic method from oxides of neodymium, lanthanum, cobalt (Co_3O_4), gallium. All reagents were qualified as “chemically pure”. The powders of original compounds taken in assigned polar ratios were mixed and ground in “Pulverizette 6” planetary mill with addition of ethanol. The resulting batch with addition of ethanol was compacted under pressure 50 – 75 MPa to pellets of diameter 25 mm and height 5 – 7 mm, and then annealed at 1523 K in the air for 4 hours. After preliminary annealing the pellets were ground, milled, pressed into bricks of length 30 mm and cross-section $5 \times 5 \text{ mm}^2$ that were annealed at temperature 1523 K in the air for 4 hours.

Electric conductivity of the resulting ceramic samples of neodymium, lanthanum cobaltites-gallates was measured on direct current in the air in the temperature range 300 – 1050 K by the four-probe method with the use of silver electrodes deposited as a thin layer on the end surfaces of samples of size $5 \times 5 \times 4 \text{ mm}^3$ by silver paste balking.

Thermoelectric coefficient (S) was determined for silver in the temperature range 300 – 1050 K in the air in dynamic mode with heating and cooling rate $(3 - 5) \text{ K} \cdot \text{min}^{-1}$ at temperature gradient 20 – 25 K on samples of size $5 \times 5 \times 27 \text{ mm}^3$.

Results and their discussion

X-ray phase analysis of the resulting samples of neodymium, lanthanum cobaltites-gallates showed that in $\text{NdCoO}_3 - \text{NdGaO}_3$, $\text{LaCoO}_3 - \text{LaGaO}_3$ systems there is formed a continuous series of solid solutions crystallized at $0 \leq x \leq 0.5$ in cubic perovskite structure, at $0.5 < x \leq 1.0$ – in the structure of rhombically (orthorhombically) distorted perovskite (for $\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$), in rhombohedral ($0 \leq x \leq 0.7$) and rhombic ($0.7 < x \leq 1.0$) structure of distorted perovskite (for $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$).

The results of measurements of electric conductivity of neodymium, lanthanum cobaltites-gallates samples are given in Fig. 1, 2 a, d.

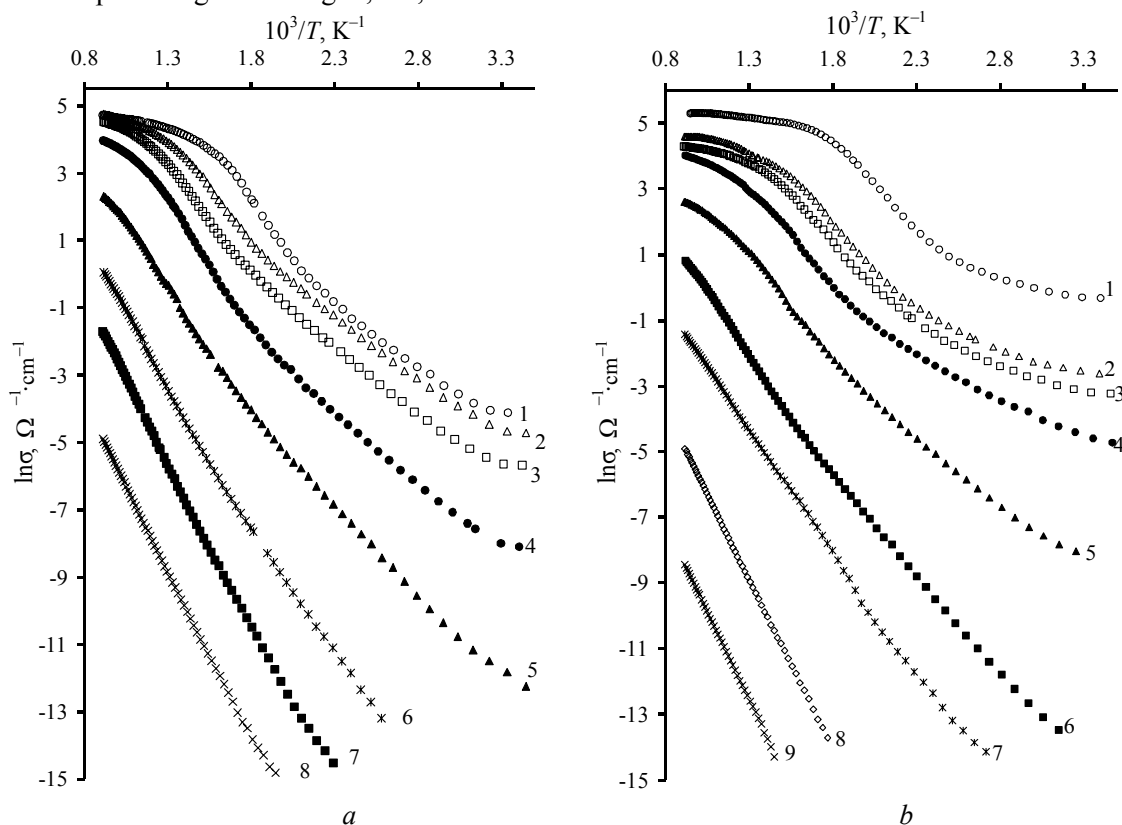


Fig.1. Dependence of $\ln \sigma$ on $1/T$ for $\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$ (a), $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ (b) for different values of x :

a) $x = 0$ (1); 0.1 (2); 0.2 (3); 0.3 (4); 0.5 (5); 0.7 (6); 0.8 (7); 0.9 (8);

b) $x = 0$ (1); 0.15 (2); 0.2 (3); 0.3 (4); 0.5 (5); 0.7 (6); 0.8 (7); 0.9 (8); 0.95 (9).

Electric conductivity of $\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$, $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ solid solutions with increased substitution degree x is gradually decreased by several orders, for example: for NdCoO_3 , LaCoO_3 at 950 K the electric conductivity is $\sigma = 100 \text{ } \Omega^{-1} \cdot \text{cm}^{-1}$, $\sigma = 200 \text{ } \Omega^{-1} \cdot \text{cm}^{-1}$, respectively, and with increased degree of Co^{3+} ions substitution by Ga^{3+} ions from 0 to 0.9 it is gradually reduced to values $1.70 \cdot 10^{-3} \text{ } \Omega^{-1} \cdot \text{cm}^{-1}$ – for $\text{NdCo}_{0.1}\text{Ga}_{0.9}\text{O}_3$ and $1.75 \cdot 10^{-3} \text{ } \Omega^{-1} \cdot \text{cm}^{-1}$ – for $\text{LaCo}_{0.1}\text{Ga}_{0.9}\text{O}_3$.

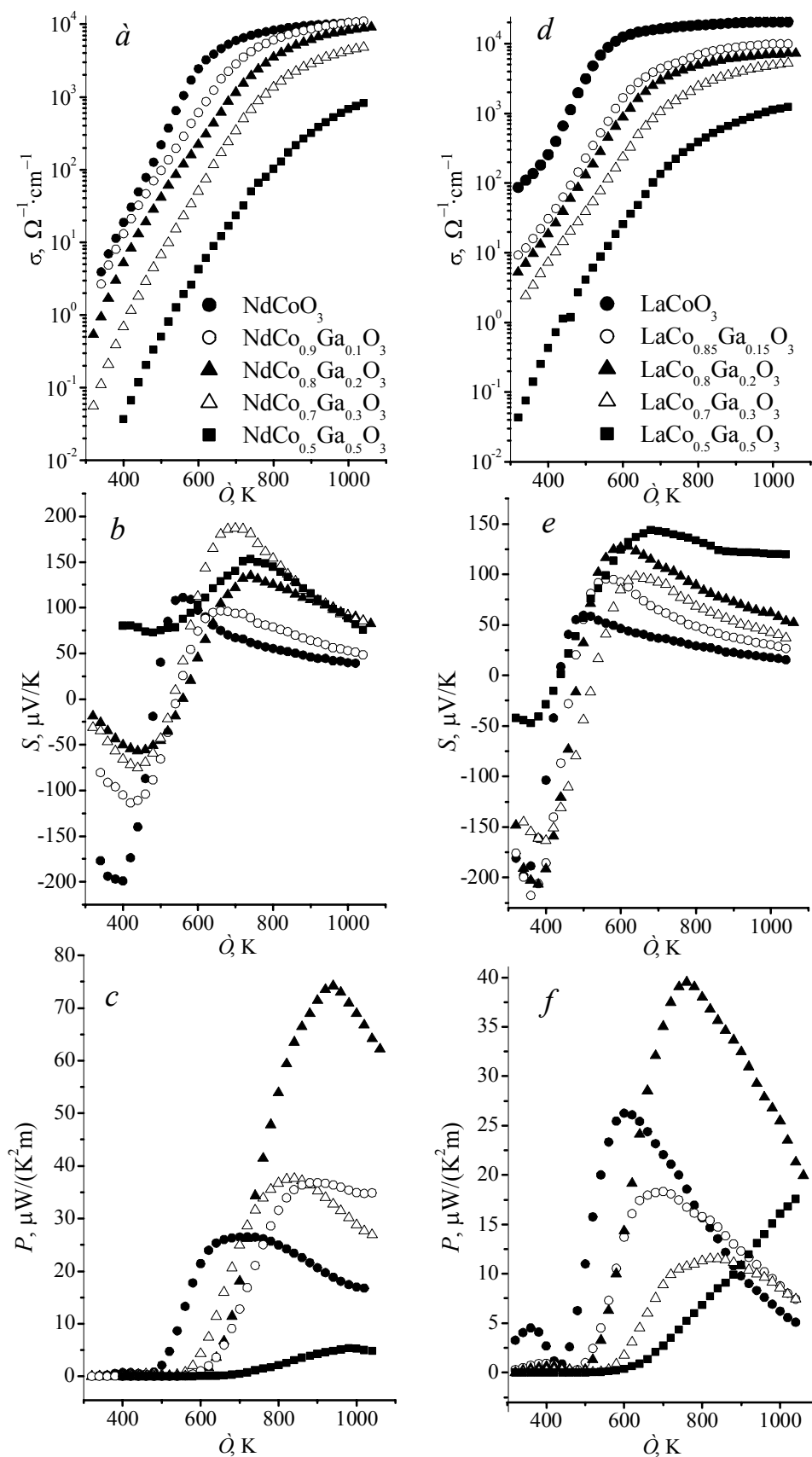


Fig. 2. Temperature dependences of electric conductivity σ (a, d), thermoelectric coefficient S (b, e) and power factor P , (c, f) for NdCo_{1-x}Ga_xO₃ (a – c), LaCo_{1-x}Ga_xO₃ (d – f).

Such considerable reduction of electric conductivity with increased degree of substitution x of Co^{3+} ions by Ga^{3+} ions is attributable to jumping (polaron) conductivity mechanism (increased screening effect by Ga^{3+} ions and reduced probability of electron jump from $(Co^{3+}\cdot e)$ pair to neighbouring cobalt ions in the presence of Ga^{3+} ions). The value of anomaly (jump) on the temperature dependence of electric conductivity of $NdCoO_3$, $LaCoO_3$, caused by the presence in the temperature range 550 – 950 K of smeared phase transition semiconductor-metal, is gradually decreased with increasing content of gallium ions, and at $x > 0.5$ it is practically absent.

For the samples of $NdCo_{1-x}Ga_xO_3$, $LaCo_{1-x}Ga_xO_3$ solid solutions with the values $x \leq 0.5$ on $\ln\sigma$ versus T^{-1} dependence one can observe three linear portions on each (Fig. 1). One of them (low-temperature portion) is located at the beginning of investigated temperature range 300 – 1050 K, another (high-temperature) – at the end of this investigated temperature range, and the third portion is located in the intermediate temperature range, wherein the largest increase in electric conductivity rate occurs with temperature change. Partial substitution of Co^{3+} ions by Ga^{3+} ions ($0 < x \leq 0.5$) results in a shift of temperature of transition to metal conductivity toward higher temperatures. For samples of solid solutions with high gallium content ($x > 0.5$) (Fig. 1) on dependences $\ln\sigma$ from T^{-1} there are only two or one linear portions and there is no high-temperature portion, testifying to the absence of semiconductor-metal phase transition in these solid solutions over the investigated temperature range. By the tangent of angle of slope of linear portions of $\ln\sigma$ dependence on T^{-1} , using the least-squares method, the activation energies of electric conductivity of neodymium, lanthanum cobaltites-gallates solid solution samples were calculated for the regions of low, intermediate and high temperatures (E_{A_1} , E_{A_2} , E_{A_3} , respectively) (Tables 1, 2).

Table 1

The values of activation energy of electric conductivity (E_A) in the region of low, intermediate, high temperatures (E_{A_1} , E_{A_2} , E_{A_3} respectively) for cobaltites-gallates $NdCo_{1-x}Ga_xO_3$, $LaCo_{1-x}Ga_xO_3$

Compound	E_A , eV			Compound	E_A , eV		
	E_{A_1}	E_{A_2}	E_{A_3}		E_{A_1}	E_{A_2}	E_{A_3}
$NdCo_{1-x}Ga_xO_3$				$LaCo_{1-x}Ga_xO_3$			
$NdCoO_3$	0.30	0.62	0.07	$LaCoO_3$	0.10	0.47	0.06
$NdCo_{0.9}Ga_{0.1}O_3$	0.31	0.56	0.11	$LaCo_{0.85}Ga_{0.15}O_3$	0.16	0.48	0.09
$NdCo_{0.8}Ga_{0.2}O_3$	0.34	0.59	0.16	$LaCo_{0.8}Ga_{0.2}O_3$	0.16	0.49	0.06
$NdCo_{0.7}Ga_{0.3}O_3$	0.36	0.67	0.24	$LaCo_{0.7}Ga_{0.3}O_3$	0.19	0.54	0.16
$NdCo_{0.5}Ga_{0.5}O_3$	0.51	0.67	0.39	$LaCo_{0.5}Ga_{0.5}O_3$	0.36	0.56	0.20
$NdCo_{0.3}Ga_{0.7}O_3$	0.62	0.76	–	$LaCo_{0.3}Ga_{0.7}O_3$	0.51	0.67	–
$NdCo_{0.2}Ga_{0.8}O_3$	0.85	–	–	$LaCo_{0.2}Ga_{0.8}O_3$	0.54	0.65	–
$NdCo_{0.1}Ga_{0.9}O_3$	0.87	–	–	$LaCo_{0.1}Ga_{0.9}O_3$	0.89	–	–
				$LaCo_{0.05}Ga_{0.95}O_3$	0.92	–	–

The data given in Tables 1, 2 show that with increasing substitution degree x from 0 to 0.3, the activation energy of electric conductivity E_{A_1} is increased only by 0.06 eV for $NdCo_{1-x}Ga_xO_3$ and by 0.09 eV for $LaCo_{1-x}Ga_xO_3$.

Further increase in the substitution degree x from 0.3 to 0.8 results in the increase of activation energy E_{A_1} by 0.51 eV for $NdCo_{1-x}Ga_xO_3$ and by 0.57 eV for $LaCo_{1-x}Ga_xO_3$. The activation energy of electric conductivity in the intermediate temperature region E_{A_2} is also gradually increased with increasing the substitution degree x , but to a lesser extent than in the low-temperature region.

Due to the fact that over the investigated temperature range 300 – 1050 K the activation energy of electric conductivity of neodymium, lanthanum is temperature dependent, in the paper from derivative $\frac{d \ln \sigma}{dT^{-1}}$ at certain temperature the temperature dependences of activation energy of electric conductivity E_A for $NdCo_{1-x}Ga_xO_3$, $LaCo_{1-x}Ga_xO_3$ were obtained (Fig. 3).

Table 2

Activation energy of electric conductivity (E_A) calculated from the values of derivative $\frac{d \ln \sigma}{dT^{-1}}$ for cobaltites-gallates $NdCo_{1-x}Ga_xO_3$, $LaCo_{1-x}Ga_xO_3$ at temperatures 400, 1000, $T_{E_{A,max}}$ K

Compound	E_A , eV			$T_{E_{A,max}}$, K
	400 K	$T_{E_{A,max}}$, K	1000 K	
<i>NdCo_{1-x}Ga_xO₃</i>				
<i>NdCoO₃</i>	0.34	0.70	0.06	565
<i>NdCo_{0.9}Ga_{0.1}O₃</i>	0.32	0.65	0.13	630
<i>NdCo_{0.8}Ga_{0.2}O₃</i>	0.35	0.69	0.16	670
<i>NdCo_{0.7}Ga_{0.3}O₃</i>	0.38	0.89	0.24	700
<i>NdCo_{0.5}Ga_{0.5}O₃</i>	0.47	1.03	0.50	755
<i>NdCo_{0.3}Ga_{0.7}O₃</i>	0.59	0.88	0.76	870
<i>LaCo_{1-x}Ga_xO₃</i>				
<i>LaCoO₃</i>	0.28	0.50	0.05	480
<i>LaCo_{0.85}Ga_{0.15}O₃</i>	0.24	0.55	0.06	560
<i>LaCo_{0.8}Ga_{0.2}O₃</i>	0.24	0.64	0.07	595
<i>LaCo_{0.7}Ga_{0.3}O₃</i>	0.24	0.66	0.17	620
<i>LaCo_{0.5}Ga_{0.5}O₃</i>	0.36	0.72	0.27	660
<i>LaCo_{0.3}Ga_{0.7}O₃</i>	0.52	0.73	0.59	810
<i>LaCo_{0.2}Ga_{0.8}O₃</i>	0.50	0.70	0.61	860

From Figure 3 it can be seen that dependences of E_A on T for $NdCo_{1-x}Ga_xO_3$, $LaCo_{1-x}Ga_xO_3$ with ($0 \leq x \leq 0.7$) have maximum the temperature of which ($T_{E_{A,max}}$) corresponds to the temperature of phase (electron) semiconductor-metal transition. It should be noted that this transition occurs not as a sudden change, but gradually. At higher than $T_{E_{A,max}}$ temperatures, the activation energy over a wide temperature range decreases monotonously, which is indicative of gradual increase of metal phase share. Probably, a change in the sign of temperature coefficient of electric conductivity from positive to negative will be observed at temperature when the semiconductor phase completely goes into metal phase.

Table 2 gives the values of activation energy of electric conductivity for $NdCo_{1-x}Ga_xO_3$, $LaCo_{1-x}Ga_xO_3$ at temperatures 400, 1000 K, $T_{E_{A,max}}$. The increase in degree of substitution of Co^{3+} ions by Ga^{3+} ions in $NdCo_{1-x}Ga_xO_3$, $LaCo_{1-x}Ga_xO_3$ systems results in gradual temperature shift of semiconductor-metal transition: from 565 K, 480 K for $NdCoO_3$, $LaCoO_3$ to 755 K, 660 K – for $NdCo_{0.5}Ga_{0.5}O_3$, $LaCo_{0.5}Ga_{0.5}O_3$, respectively.

Comparison of activation energy data given in Tables 1 and 2 shows that the values E_{A_3} are close to the values E_A at 1000 K, and the values E_{A_2} are somewhat lower than the values $E_{A_{\max}}$ for the respective cobaltites-gallates. The values E_A at 400 K are somewhat higher than the values E_{A_1} . The values $E_{A_{\max}}$, $T_{E_{A_{\max}}}$ are slightly different from the data given in paper [9].

The results of measuring thermoelectric coefficient of neodymium, lanthanum gallates in the temperature range 300 – 1050 K are given in the Fig.2 c,f. Thermoelectric coefficient S for neodymium, lanthanum cobaltites-gallates with $0 \leq x \leq 0.5$ at somewhat higher than room temperatures is negative, with temperature increase it passes through minimum, starts growing, passes through zero and reaches maximum value, following which it starts decreasing again. For examples, thermoelectric coefficient is equal to $S = -0.170 \text{ mV}\cdot\text{K}^{-1}$ at 335 K for NdCoO_3 , and $S = -0.166 \text{ mV}\cdot\text{K}^{-1}$ at 305 K for LaCoO_3 (Fig. 2 b, f).

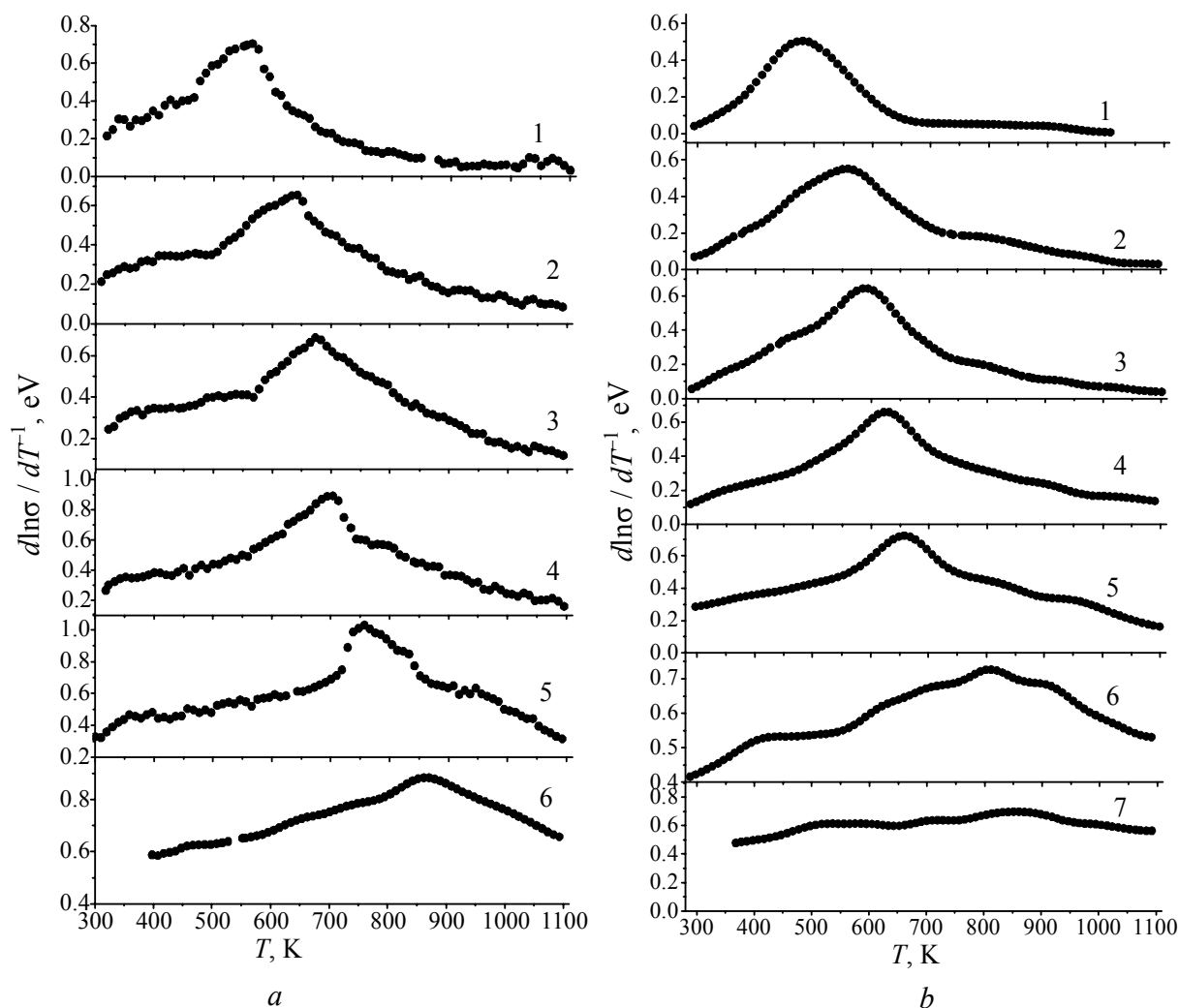


Fig. 3. Activation energy of electric conductivity (E_A), calculated by the values of derivative $d \ln \sigma / dT^{-1}$, for cobaltites-gallates $\text{NdCo}_{1-x}\text{Ga}_x\text{O}_3$ (a), $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ (b) for different x values:
 a) $x = 0$ (1); 0.1 (2); 0.2 (3); 0.3 (4); 0.5 (5); 0.7 (6);
 b) $x = 0$ (1); 0.15 (2); 0.2 (3); 0.3 (4); 0.5 (5); 0.7 (6); 0.8 (7).

With temperature increase to 396 K, 350 K S takes on minimum value ($-0.200 \text{ mV}\cdot\text{K}^{-1}$), ($-0.207 \text{ mV}\cdot\text{K}^{-1}$) – for NdCoO_3 , LaCoO_3 , respectively. With further temperature increase, S grows, passing through 0 at 490 K, 435 K, reaches maximum value at $\approx 560 \text{ K}$ ($S = 0.110 \text{ mV}\cdot\text{K}^{-1}$), $\approx 500 \text{ K}$ ($S = 0.060 \text{ mV}\cdot\text{K}^{-1}$), and then is gradually reduced for NdCoO_3 , LaCoO_3 , respectively. A similar

temperature dependence of thermoelectric coefficient for $LaCoO_3$ single crystal is also given in paper [10].

Partial substitution of Co^{3+} ions with Ga^{3+} ions leads to gradual increase of temperature whereby S changes its sign. In so doing, there is increase in maximum positive value S : from $0.110 \text{ mV}\cdot\text{K}^{-1}$ ($NdCoO_3$), $0.060 \text{ mV}\cdot\text{K}^{-1}$ ($LaCoO_3$) (Fig. 2 *b, e*) to $0.188 \text{ mV}\cdot\text{K}^{-1}$ ($NdCo_{0.7}Ga_{0.3}O_3$), $0.100 \text{ mV}\cdot\text{K}^{-1}$ ($LaCo_{0.7}Ga_{0.3}O_3$), as well increase in temperature at which S has maximum value: from 560 K, 500 K for $NdCoO_3$, $LaCoO_3$ to 705 K, 650 K for $NdCo_{0.7}Ga_{0.3}O_3$, $LaCo_{0.7}Ga_{0.3}O_3$, respectively. Here it should be noted that for cobaltites with $0 \leq x \leq 0.3$ the temperatures of maximum position on S versus T dependence are practically equal to temperatures at which maximum activation energy is observed for these cobaltites-gallates.

For both studied systems in the region of high temperatures the areas were found where the relationship $S = C - A \cdot \ln \sigma$, valid for semiconductors with one type of current carriers is satisfactorily met [11, 12]. Based on the resulting data for jumping electric conductivity mechanism, the share of Co^{3+} (y) ions responsible for electric conductivity was estimated by the formula

$$S = \frac{k}{e} \ln \frac{1-y}{y}, \quad (1)$$

where k is Boltzmann constant, e is elementary charge.

For solid solutions $NdCo_{1-x}Ga_xO_3$ with the values $x = 0.3$ and 0.5 temperature increase from 775 to 1050 K leads to growing share of Co^{3+} ions responsible for electric conductivity, from the values 13 and 15% to 25 and 30%, respectively. For lanthanum cobaltites-gallates $LaCo_{1-x}Ga_xO_3$ temperature increase from 700 to 1000 K results in certain increase of the share of Co^{3+} ions responsible for electric conductivity: by 5% for $LaCoO_3$ and by 9, 11, 12 % for samples with $x = 0.15, 0.20, 0.30$, respectively.

The resulting data show that not all cobalt ions Co^{3+} in solid solutions of neodymium, lanthanum cobaltites-gallates solid solutions are donors of current carriers (electrons, holes), and at temperatures of order 1000 K these do not exceed 40% (for $NdCo_{1-x}Ga_xO_3$), 45% (for $LaCo_{1-x}Ga_xO_3$) from the total number of ions in the respective solid solutions.

The results of measuring electric conductivity σ and thermoelectric coefficient S were used to calculate the values of power factor P by the formula

$$P = S^2 \cdot \sigma. \quad (2)$$

Temperature dependences of power factor are presented in Fig. 2 *c, d*. From Fig. 2 it is seen that, with increasing temperature, power factor is first increased, reaches maximum, and then is decreased. It should be noted that for cobaltites-gallates under study, with increasing degree of Co^{3+} ions substitution by Ga^{3+} atoms, maximum value of power factor is first increased, reaches maximum value at $x = 0.2$ ($P = 74 \mu\text{W} / (\text{K}^2\cdot\text{m})$) for $NdCo_{0.8}Ga_{0.2}O_3$ (Fig. 2*c*) and $P = 40 \mu\text{W} / (\text{K}^2\cdot\text{m})$ for $LaCo_{0.8}Ga_{0.2}O_3$ (Fig. 2*f*), and then decreased. Moreover, with increasing substitution degree x , there is increase in temperature at which maximum value of power factor is achieved: from 680 K, 600 K for $NdCoO_3$, $LaCoO_3$ to 980 K, 840 K for $NdCo_{0.5}Ga_{0.5}O_3$, $LaCo_{0.7}Ga_{0.3}O_3$, respectively (Fig. 2 *c, d*). The value of power factor of $LaCo_{0.5}Ga_{0.5}O_3$ solid solution over the entire temperature range under study is increased, without reaching maximum value. The values of power factor obtained for $NdCo_{0.8}Ga_{0.2}O_3$, $LaCo_{0.8}Ga_{0.2}O_3$ samples are considerably higher than for $LaCo_{0.8}Ti_{0.2}O_{2.86}$, $LaCo_{0.8}Ni_{0.2}O_{2.95}$ samples ($P = 28.2$ and $9.5 \mu\text{W} / (\text{K}^2\cdot\text{m})$), recommended by the authors of paper [12] for practical use, owing to which said solid solutions can be considered as promising oxide thermoelectric materials.

The results obtained in this paper can be used for creation of new functional oxide materials with assigned set of properties intended for manufacturing various electronic engineering devices.

Conclusions

It is shown that temperature dependence of thermoelectric coefficient S is of complicated nature. Thus, at room temperature in both studied systems, at $0 \leq x \leq 0.3$, S has negative values. With increasing temperature, S grows, passes through zero at 435–530 K (I) or 490–540 K (II), reaches maximum values at 560–650 K (I) or 560–705 K (II) and then decreases. It is shown that temperature dependence of electric conductivity σ for samples with low x values is S -like, and for a series of samples at high temperatures there was noted a transition from semiconductor to metal conduction type. The values of activation energy of electric conductivity E were calculated for different temperature intervals, dependence of E on temperature and composition of solid solution (x value) was analyzed. For both studied systems in the high-temperature region the areas were found where the relationship $S = C - A \cdot \ln \sigma$, valid for semiconductors with one type of current carriers is satisfactorily met. Based on the resulting data for jumping electric conductivity mechanism, the share of Co^{3+} ions responsible for electric conductivity was assessed. Based on the calculated values of power factor P , $NdCo_{0.8}Ga_{0.2}O_3$, $LaCo_{0.8}Ga_{0.2}O_3$ cobaltites were shown to be promising oxide thermoelectric materials.

References

1. Palguyev S.F., Gilderman V.K., Zemtsov V.I. High-temperature oxide electron conductors for electrochemical devices. – M.: Nauka, 1990. – 198 p.
2. Vashuk V.V. Synthesis and physicochemical properties of compounds with perovskite and perovskite-related structure based on cobalt and nickel oxides: DSc dissertation: 02.00.04. – Minsk, 2000. – 310 p.
3. Viswanathan B. Solid State and Catalytic Properties of Rare Earth Cobaltites – New Generation Catalysts // J. Sci. IND. Res. – 1984. – Vol. 4. – № 3. – P. 156-163.
4. Kharton V.V., Naumovich Ye.N., Zhuk P.P. Physicochemical and electrochemical properties of $Ln(Sr)CoO_3$ electrode materials // Elektrokhimiya. – 1992. – V. 28. – № 12. – P. 1693-1702.
5. Jakobs S., Hartung R., Mobius H.-H., Wilke M. Sauerstoffelectroden aus Mischoxiden mit Zirkondioxid und Cobaltaten der seltenen Erden // Rev. Chim. Miner. – 1980. – Vol. 17. – № 4. – P. 283-298.
6. Kharton V.V., Yaremchenko A.A., Naumovich E.N. Research on the electrochemistry of oxygen ion conductors in the former Soviet Union. II. Perovskite-related oxides // J. Solid State Electrochem. – 1999. – Vol. 3. – P. 303-326.
7. Rao C.N.R., Md. Motin Seikh, Chandrabhas Narayana. Spin-State Transition in $LaCoO_3$ and Related Materials // Top. Curr. Chem. – Berlin: Springer-Verlag, 2004. – Vol. 234. – P. 1-21.
8. Knižek K. Structural anomalies associated with the electronic and spin transitions in $LaCoO_3$ // The European Phys. Jour. B. – 2005. – Vol. 47. – № 2. – P. 213-220.
9. Yamaguchi S., Okimoto Y., Tokura Y. Bandwidth dependence of insulator-metal transitions in perovskite cobalt oxides // Phys. Rev. B. – 1996. Vol. 54. – № 16 – P. R11022-R11025.
10. Dordor P. Electrical properties of lead-doped $LaCoO_3$ single crystal // Phys. Status Solidi. – 1986. – Vol. 93 A. – № 1. – P. 321-329.
11. Metfessel Z., Mattis D. Magnetic semiconductors. – M.: Mir, 1972. – 405 p.
12. Robert R., Bocher L., Trottmann M., Reller A., Weidenkaff A. Synthesis and high-temperature thermoelectric properties of Ni and Ti substituted $LaCoO_3$ // J. Solid State Chem. – Vol. 179. – 2006. – P. 3893.

Submitted 10.02.09.