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THERMOELECTRIC PROPERTIES OF THE CERAMICS BASED ON THE BARIUM – STRONTIUM PLUMBATES

The ceramics with $Ba_{1-x}Sr_xPb_{1+y}O_{3+2y}$ (x = 0.6; 0.8; y = 0.00; 0.10; 0.20) composition was prepared using solid-state reactions method and its phase composition, crystal structure, electrical conductivity, thermal conductivity and thermo-EMF was studied. The electronic and lattice parts of the thermal conductivity of ceramics were determined and its power factor (P) and figure-of-merit values (ZT) were calculated. It was found, that the best thermoelectric characteristics at high temperatures had the ceramics with composition $Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}$ ($P_{1000} = 1.36 \text{ mW/(m} \cdot \text{K}^2$), but near the room temperature – the $Ba_{0.2}Sr_{0.8}Pb_{1.2}O_{3.4}$ sample ($ZT_{423} = 0.033$). On the basis of $Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}$ (n-type conductor) and $Na_{0.55}Co_{0.9}Ni_{0.1}O_2$ (p-type conductor) ceramics the prototype of the thermoelectric module was produced and its working characteristics (open-circuit voltage and power) at different temperatures were determined.

Introduction. The heat, which evolved in environment during working of the factories and transport can be directly converted into electrical energy in the devices named thermoelectrogenerators (TEG). The prospective materials for creation of the high-temperature TEG are oxides, which thermally and chemically more stable in air than traditional thermoelectrics based on the lead, bismuth and antimony chalcogenides. The potential base for development of *p*-branches of such TEG are the layered sodium (Na_xCoO₂) or calcium (Ca₃Co₄O_{9+ δ}) cobaltites but for the *n*-branches the perovskite barium – strontium metaplumbates [1]. So, searching and preparation of thermoelectric materials based on these oxides as well as investigation of their physicochemical and functional properties represents great scientific and practical interest.

The authors of [2] are found that the best thermoelectric characteristics (power factor P and figure-of-merit ZT) in the $Ba_{1-x}Sr_xPbO_3$ system possess the Ba_{0.4}Sr_{0.6}PbO₃ and Ba_{0.2}Sr_{0.8}PbO₃ solid solutions ($P_{\text{max}} \approx 0.40 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at T = 700 - 100 mW900 K, $ZT_{\text{max}} \approx 0.13$ at T = 673 K) as well as SrPbO₃ ($P_{\text{max}} \approx 0.38 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at $T = 1,000 - 1000 \text{ m}^{-1}$ 1,050 K). According to the [3, 4], introduction of the lead oxide excess into ceramics based on the $Ba_{1-x}Sr_{x}PbO_{3}$ increases its sinterability as well as lead to the considerable increasing of its power factor (for Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2} and Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2} compositions at T = 700-750 K $P_{\text{max}} \approx 0.72 0.77 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ [3]) due to the formation the phase heterogeneity in it, which allow us to consider this approach as effective method of increasing the thermoelectric properties of the oxide ceramics.

In this work the influence of the lead oxide (PbO) excess on the phase composition, crystal structure, thermal expansion, thermal and electrical conductivity, thermo-EMF and thermoelectric characteristics of the ceramics based on barium–strontium plumbates (Ba,Sr)PbO₃ is studied. On the basis of Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2} (*n*-type conductor) and Na_{0.55}Co_{0.9}Ni_{0.1}O₂ (*p*-type conductor) ceramics

the prototype of the thermoelectric module was produced and its working characteristics (opencircuit voltage and power) at different temperatures were determined.

Experimental technique. For preparation of $Ba_{0.4}Sr_{0.6}Pb_{1+\nu}O_{3+2\nu}$ and $Ba_{0.2}Sr_{0.8}Pb_{1+\nu}O_{3+2\nu}$ ($\nu = 0.00$; 0.10; 0.20) ceramics we used the mixture of BaCO₃ (pure grade), SrCO₃ (pure grade) and PbO (pure for analysis), which was mixed in the mill Pulverizette 6.0 (Fritsch, Germany) (material of crucibles and grinding balls – ZrO₂), after that it was pressed into pellets having 25 mm diameter and 3–5 mm height under pressure of 0.26 MPa and annealed in air at 1,073 K during 12 h. Annealed in air samples were grinded in the agate mortar, after that again milled (with addition of ethanol) in mill Pulverizette 6.0 and pressed into bars with dimensions of 5×5×30 mm and pellets having 9 and 15 mm diameter and 2-3 mm height, which were then sintered in air during 26 h at 1,123 K. Sintered samples were processed to give them the correct geometrical shape.

Identification of the samples and determination of their lattice constants using X-ray diffraction analysis (XRD) (diffractometer D8 Advance Bruker AXS (Germany), CuK_{α}-radiation) and IR absorption spectroscopy (Furier-spectrometer Nexus ThermoNicolet) were performed.

Apparent density values (ρ_{exp}) of the samples were determined using their mass and geometrical dimensions. Thermal expansion, electrical conductivitiy (σ) and thermo-EMF (*S*) of ceramics were studied in air within 300–1,100 K using procedures described in [4, 5]. The values of the linear thermal expansion coefficient (LTEC) of the samples from linear parts of $\Delta l / l_0 = f(T)$ dependences were obtained. Thermal conductivity of the sintered ceramics (λ) in air within 298–423 K using thermal conductivity measurer IT- λ -400 was investigated. Lattice (λ_{lat}) and electronic (λ_{el}) parts of thermal conductivity were calculated using $\lambda = \lambda_{el} + \lambda_{lat}$, $\lambda_{el} = \sigma LT$ relations, where *L* is the Lorentz number ($L = 2.45 \cdot 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$). The power factor and figure-of-merit values of the samples were calculated using $P = S^2 \sigma$, $ZT = (PT) / \lambda$ equations. Thermoelectric module power (W) was determined from $W = U_0^2 / R$ relation, where U_0 is open-circuit-voltage of the module, and R is its resistance.

Results and their discussion. According to the XRD analysis and IR absorption spectroscopy results, the samples with $y \ge 0.1$ contained impurity – PbO, which amount increased with y increasing; the main phase of ceramics – barium – strontium metaplumbate – had the orthorhombically distorted perovskite structure with lattice constants of a = 0.5913-0.5957 nm, b = 0.5945-0.5954 nm, c = 0.8375-0.8418 nm (Table 1), which values did not changed practically at increasing of the (Ba,Sr) : Pb relation and decreased at increasing of substitution degree of barium by strontium (Fig. 1). Obtained by us values of the lattice constants of the barium – strontium plumbates solid solutions are in a good accordance with the data given in the [2, 5].

IR absorption spectra of the Ba_{0.4}Sr_{0.6}Pb_{1+y}O_{3+2y} powders contained one absorption band with extremum at 584–588 cm⁻¹, but ones of Ba_{0.2}Sr_{0.8}Pb_{1+y}O_{3+2y} powders – three absorption bands with extremes at 337–343 cm⁻¹, 395–397 cm⁻¹ and 570–574 cm⁻¹ and absorption band positions did not changed practically at *y* increasing.

Complication of a view of spectra at increasing of substitution degree of barium by strontium is due to the increasing of tetragonal distortion degree of the crystal structure of the samples (increasing of the c / a relation (Table 1)). So, results of the XRD analysis and IR absorption spectroscopy of the samples are in a good accordance with each other.

Apparent density of the sintered (Ba,Sr)Pb_{1+y}O_{3+2y} ceramics changed within 4.51–5.57 g/cm³ (Table 1) and, as a whole, increased at *y* increasing.

So, results obtained by us are in a good accordance with works [3, 4], in which was found that introduction into ceramics based on the barium – strontium plumbates the excess of lead oxide (PbO) improved its sinterability.



 $\begin{array}{l} Fig. \ 1. \ X\mbox{-ray powder diffractograms} \\ of the \ Ba_{0.4}Sr_{0.6}PbO_3\ ({\it I}), \ Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2}\ ({\it 2}), \\ Ba_{0.4}Sr_{0.6}Pb_{1.2}O_{3.4}\ ({\it 3}), \ Ba_{0.2}Sr_{0.8}PbO_3\ ({\it 4}), \ Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}\ ({\it 5}), \\ Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}\ ({\it 6}) \ samples, \ * - PbO\ phase \end{array}$

On the temperature dependences of the relative elongation of sintered ceramics the kink near $T^* = 730-770$ K was observed, which was accompanied with increasing of LTEC values of the samples up to 1.5–1.6 times (Table 2). According to the [5], this phenomenon take place due to the rearrangement of the oxygen sub-lattice of the samples as well as due to the beginning of so-called weakly-bonded oxygen evolution from their structure.

Table 1

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Composition	<i>a</i> , nm	<i>b</i> , nm	c, nm	V, nm ³	c / a	$\rho_{exp},g/cm^3$
$Ba_{0.4}Sr_{0.6}PbO_3$	0.5956	0.5954	0.8417	0.2984	1.4133	5.11
$Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2}$	0.5957	0.5952	0.8418	0.2985	1.4130	5.28
$Ba_{0.4}Sr_{0.6}Pb_{1.2}O_{3.4}$	0.5953	0.5952	0.8417	0.2982	1.4141	5.57
Ba _{0.2} Sr _{0.8} PbO ₃	0.5913	0.5945	0.8375	0.2943	1.4164	4.92
$Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}$	0.5913	0.5945	0.8375	0.2943	1.4164	4.95
$Ba_{0.2}Sr_{0.8}Pb_{1.2}O_{3.4}$	0.5919	0.5945	0.8379	0.2948	1.4156	4.51

EVALUATE: Unit cell parameters (a, b, c), unit cell volume (V), and c / a relation for the main phase as well as the apparent density (ρ_{exp}) of the (Ba,Sr)Pb_{1+v}O_{3+2v} ceramics

LTEC values for $Ba_{0.2}Sr_{0.8}Pb_{1+y}O_{3+2y}$ ceramics were smaller than for $Ba_{0.4}Sr_{0.6}Pb_{1+y}O_{3+2y}$ samples (Table 2) due to the amplification of the metal – oxygen interactions in the samples structure at increasing of the substitution degree of barium by strontium. The results of dilatometry accord with the XRD data, accordingly with the latter increasing of the strontium content in the samples lead to the shrinking of their unit cell).

Table 2

LTEC values (α) of the (Ba,Sr)Pb_{1+y}O_{3+2y} ceramics at different temperatures

Composition	$\alpha \cdot 10^6, \mathrm{K}^{-1}$				
composition	$T < T^*$	$T > T^*$	T^*, \mathbf{K}		
$Ba_{0.4}Sr_{0.6}PbO_3$	13.0 ± 0.7	20.6 ± 1.0	770		
Ba _{0.4} Sr _{0.6} Pb _{1.1} O _{3.2}	13.0 ± 0.7	19.7 ± 1.0	745		
Ba _{0.4} Sr _{0.6} Pb _{1.2} O _{3.4}	12.5 ± 0.6	19.9 ± 1.0	730		
$Ba_{0.2}Sr_{0.8}PbO_3$	11.3 ± 0.6	18.1 ± 0.9	750		
Ba _{0.2} Sr _{0.8} Pb _{1.1} O _{3.2}	11.9 ± 0.6	17.6 ± 0.9	770		

All the samples studied were the *n*-type semiconductors, which thermo-EMF values un-monotonously changed at temperature increasing and reached minima near 700–800 K (Fig. 2, *a*, *b*). Taking into account the results of [5], increasing of thermo-EMF of samples above 700–800 K may be explained with decreasing of oxidation degree of the lead cations from Pb⁴⁺ to Pb²⁺ in the surface layer of ceramics, which accompanied with evolution of the weakly-bounded oxygen from ceramics in the gas phase. The absolute values of electrical conductivity and thermo-EMF for the Ba_{0.2}Sr_{0.8}Pb_{1+y}O_{3+2y} samples were larger than for the Ba_{0.4}Sr_{0.6}Pb_{1+y}O_{3+2y} oxides and maximal value of σ and *S* were observed for the Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2} ceramics.

The power factor values of $Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}$ and $Ba_{0.2}Sr_{0.8}Pb_{1.2}O_{3.4}$ samples increased, but for other

samples un-monotonously changed at temperature increasing (Fig. 2, *c*), hereby maximal value of power factor was fixed for $Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}$ ceramics – 1.36 mW/(m · K²) at 1,000 K.

The results of measuring of thermal conductivity of (Ba,Sr)Pb_{1+y}O_{3+2y} ceramics are given in the Fig. 3. As can be seen, at temperature increasing thermal conductivity of Ba_{0.2}Sr_{0.8}Pb_{1+y}O_{3+2y} ceramics, as a whole, decreased, and for Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2} sample increased. λ values of ceramics considerably decrease at increasing of lead oxide content in it and, as a whole, do not depend practically on the Ba : Sr relation in the samples. Electronic part of thermal conductivity for Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2} ceramics was large than for Ba_{0.2}Sr_{0.8}Pb_{1+y}O_{3+2y} samples – $0.02\lambda < \lambda_{el} < 0.03\lambda$ and $\lambda_{el} \le 0.01\lambda$ respectively.

When temperature increased for all samples studied λ_{el} inappreciably and practically linear increased. So, by means of lattice vibrations (phonons) transfers practically all the heat in the Ba_{0.2}Sr_{0.8}Pb_{1+y}O_{3+2y} samples ($\lambda_{lat} \approx \lambda$) and its prevailing part in the Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2} ceramics (0.97 $\lambda < \lambda_{lat} < 0.98\lambda$).

On the base of the data obtained the values of figure-of-merit (Ioffe parameter) (*ZT*) the ceramics studied were calculated. As can be seen from the Fig. 4, *ZT* values of ceramics increase when temperature increases, hereby the maximal gain of the Ioffe parameter observes for the $Ba_{0.2}Sr_{0.8}Pb_{1+y}O_{3+2y}$ compounds. This fact, mainly, is causes by character of temperature dependence of the thermal conductivity of the samples. Within the temperature interval studied the maximal value of figure-of-merit possesses $Ba_{0.2}Sr_{0.8}Pb_{1.2}O_{3.4}$ ceramics: *ZT* 0.033 at 423 K.

On the basis of $Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}$ (*n*-type conductor) and $Na_{0.55}Co_{0.9}Ni_{0.1}O_2$ (*p*-type conductor) ceramics the prototype of the thermoelectric module was produced and its working characteristics at different temperatures were determined.



Fig. 2. Temperature dependences of electrical conductivity (*a*), thermo-EMF coefficient (*b*), power factor (*c*) of Ba_{0.4}Sr_{0.6}PbO₃ (*1*), Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2} (*2*), Ba_{0.4}Sr_{0.6}Pb_{1.2}O_{3.4} (*3*), Ba_{0.2}Sr_{0.8}PbO₃ (*4*), Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2} (*5*), Ba_{0.2}Sr_{0.8}Pb_{1.2}O_{3.4} (*6*) ceramics



Fig. 3. Temperature dependences of the total thermal conductivity (λ) (1) as well as of the lattice (λ_{lat}) (2) and electronic parts in it (λ_{el}) (3) of Ba_{0.2}Sr_{0.8}PbO₃ (a), Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2} (b), Ba_{0.2}Sr_{0.8}Pb_{1.2}O_{3.4} (c), Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2} (d) samples

For the module (Fig. 5, c) production firstly on the surface of non-conductive ceramics on the base of the lanthanum – calcium titanate – aluminate (8)with dimensions approximately of 0.5×1.0 cm the Ag-contacts (7) by means of annealing of silver paste ($T_{ann} = 1,073$ K, $t_{ann} = 15$ min) were formed. From the massive samples of thermoelectric ceramics $(Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3+\delta}(3)$ and $Na_{0.55}Co_{0.9}Ni_{0.1}O_{2}(4))$ the bars with dimensions approximately of $0.5 \times 0.5 \times 0.5$ cm everyone were cutted out. These bars connected with the contacts 7 by means of the silver paste with additions of ≈ 10 wt % of corresponding oxide (5 and 6 for $Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3+\delta}$ and Na_{0.55}Co_{0.9}Ni_{0.1}O₂ respectively) to decrease the contact resistance on the "Ag - oxide" grain boundary. The obtained product was seated in the electroheating furnace and annealed in it at 1,073 K to form the strong interphase contacts.



Fig. 4. Temperature dependence of the figure-of-merit of Ba_{0.2}Sr_{0.8}PbO₃ (*1*), Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2} (*2*), Ba_{0.2}Sr_{0.8}Pb_{1.2}O_{3.4} (*3*), Ba_{0.4}Sr_{0.6}Pb_{1.1}O_{3.2} (*4*) ceramics

The open-circuit-voltage of the module (U_0) was measured by means of the high-ohmic voltmeter when current in the circuit was absent; the resistance of the module (taking into account the external current wires) was determined using voltmeter – ampermeter method. Hot side of the module was put into electroheating furnace and the cold one was cooled using mixture of water with ice.

The module open-circuit-voltage (U_0) increases at temperature increasing (Fig. 5, *a*) and reaches the maximal value of $U_0 = 130$ mV at $T_h = 770$ K; it is necessary to note that this value corresponds to the expected one: $U_0 \approx (S_p - S_n)(T_h - T_c)$, where S_p and S_n are the average values of the *p*- and *n*branches of the module within $T_c - T_h$ temperature interval, T_c and T_h are the temperatures of the cold and hot sides of the module respectively.



Fig. 5. Dependences of the open-circuit-voltage (*a*) and power (*b*) of thermoelectric module versus temperature of the hot side (*I* – first cycle; 2 – second cycle), as well as schema of the module $(3 - Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2} \text{ ceramics}; 4 - Na_{0.55}Co_{0.9}Ni_{0.1}O_2$ ceramics; 5 – $Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}$ – Ag composite; $6 - Na_{0.55}Co_{0.9}Ni_{0.1}O_2$ – Ag composite; 7 – silver contacts; 8 – lanthanum – calcium titanate – aluminate ceramics; T_h and T_c – temperatures of the hot and cold side of the module respectively)

The module power un-monotonously changed when temperature increased and was maximal at $T_{\rm h} = 400-500$ K (370 µW) (Fig. 5, *b*), which corresponds to the specific power of the module of $315 \ \mu\text{W} \cdot \text{g}^{-1}$ or $1.2 \ \text{mW} \cdot \text{cm}^{-3}$. U_0 and W values of the module were reproduced at many-time thermocycling of the module (on Fig. 5 are given the data obtained during first and second heating – cooling cycles of the module); thus, produced by us prototype of thermoelectric module demonstrates stabile in time characteristics.

The small value of the module power is caused by the high values of its resistance, probably, due to the high values of the contact resistance of the "oxide – Ag" grain boundary. So, increasing of the working characteristics of the module one can reach by improving of the "oxide – metal" grain boundary morphology. This aim may be reached, for example, by means of changing of the contact layers 5 and 6 of the module (Fig. 5, c) or by means of changing of conditions of the grain boundary formation (temperature and time of annealing etc.).

Conclusion. By means of the solid state reactions method the $Ba_{0,4}Sr_{0,6}Pb_{1+\nu}O_{3+2\nu}$ and $Ba_{0.2}Sr_{0.8}Pb_{1+y}O_{3+2y}$ (y = 0.00; 0.10; 0.20) ceramics was prepared and its phase composition, physicochemical and thermoelectric properties were studied. The electronic and lattice parts of thermal conductivity of ceramics were determined and its power factor and figure-of-merit values were calculated. The influence of the substitution degree of barium by strontium as well as the amount of excessive lead oxide in the samples on the sinterability of ceramics and its characteristics was analyzed. It is shown, that the best thermoelectric characteristics have Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2} ceramics $(P_{1,000} = 1.36 \text{ mW}/(\text{m} \cdot \text{K}^2))$, but near the room temperature the Ba_{0.2}Sr_{0.8}Pb_{1.2}O_{3.4} sample ($ZT_{423} = 0.033$). On the basis of $Ba_{0.2}Sr_{0.8}Pb_{1.1}O_{3.2}$ (*n*-type conductor) and $Na_{0.55}Co_{0.9}Ni_{0.1}O_2$ (*p*-type conductor) ceramics the prototype of the thermoelectric module was produced and its working characteristics (open-circuit voltage and power) at different temperatures were determined.

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