



## Effect of Cationic Nonstoichiometry on the Structure and Properties of the Barium and Strontium Metaplumbates

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### ABSTRACT

*The oxide ceramics with different barium (strontium) and lead ratio ( $0,77 \leq Ba (Sr) : Pb \leq 1,3$ ) had been prepared. Crystal structure, microstructure, thermal expansion, electrical conductivity and thermo-EMF of the materials prepared had been studied. It had been determined, that increasing of the lead oxide content in the samples led to the improving of their sinterability, decreasing of linear thermal expansion coefficient and increasing of the power factor of the sintered ceramics. The maximal value of the power factor have the  $SrPb_{1,2}O_{3+\delta}$  composition, that allow us to consider its as base for development of the new oxide thermoelectrics.*

**Keywords :** Barium (strontium) metaplumbate, cationic nonstoichiometry, electrical conductivity, thermo-EMF, power factor.

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### INTRODUCTION

Materials based on the perovskite barium and strontium meta plumbates have high electrical conductivity and thermoelectric power and low thermal conductivity, as well as are stable in air at high temperatures, which allows us to consider them as possible components of *n*-branches of high-temperature thermoelectro converters [1, 2]. It was shown in [3] that introduction of lead oxide excess into ceramics (Ba, Sr)PbO<sub>3</sub> increased the power factor of forming ceramics but did not reveal what was the reason for the improvement of their thermoelectric properties: the formation of vacancies in the barium (strontium) sublattice of (Ba, Sr)PbO<sub>3</sub> phases or appearance the phase in homogeneity in ceramic due to segregation of an excess PbO into a separate phase dispersed in the form of micro or nano particles by volume of (Ba, Sr)PbO<sub>3</sub> ceramics. To answer this question in the present study the influence of cationic nonstoichiometry on the phase composition, crystal structure, microstructure, thermal expansion and electro physical properties of ceramics based on perovskite barium and strontium metaplumbates was investigated.

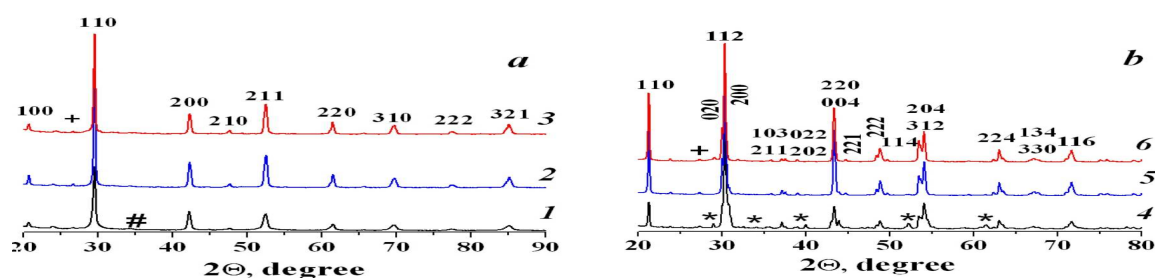
### MATERIALS AND METHODS

To obtain the oxide ceramics we used the mixture of BaCO<sub>3</sub> (pure grade), SrCO<sub>3</sub> (pure grade) and PbO (pure for analysis) powders, which were taken in different molar ratio (BaCO<sub>3</sub> : (SrCO<sub>3</sub>) : PbO = 1,3 : 1; 1,2 : 1; 1,1 : 1; 1,05 : 1; 1 : 1; 1 : 1,05; 1 : 1,1; 1 : 1,2; 1 : 1,3) and milled in Pulverizette 6.0 ball mill (Fritsch, Germany) with addition of ethanol (mortar and grinding balls material is ZrO<sub>2</sub>), then pressed into pellets at pressure of 0,26 MPa and annealed in air at 1073 K during 12 hours. Annealed samples were crushed in an agate mortar, milled in Pulverizette 6.0 ball mill, pressed into bars with dimensions 5x5x30 mm and sintered in air at 1123 K during 20–26 hours.

Identification of the samples was performed using X-ray diffraction analysis (XRD) (D8 Advance Bruker AXS X-ray diffractometer (Germany), CuK<sub>α</sub> – radiation) and IR-absorption spectroscopy (Nexus IR-Furier spectrometer (ThermoNicolet, USA)). The microstructure of the sintered ceramics was studied using scanning electron microscope JSM-5610 LV (Japan). Apparent density of the samples ( $\rho_{exp}$ ) was determined using their mass and geometrical dimensions. Thermal expansion, electrical conductivity ( $\sigma$ ) and thermo-EMF ( $S$ ) of ceramics prepared was investigated in air within 300–1100 K by methods described earlier [3, 4]. The power factor values of ceramics were calculated using equation  $P = \sigma \cdot S^2$ .

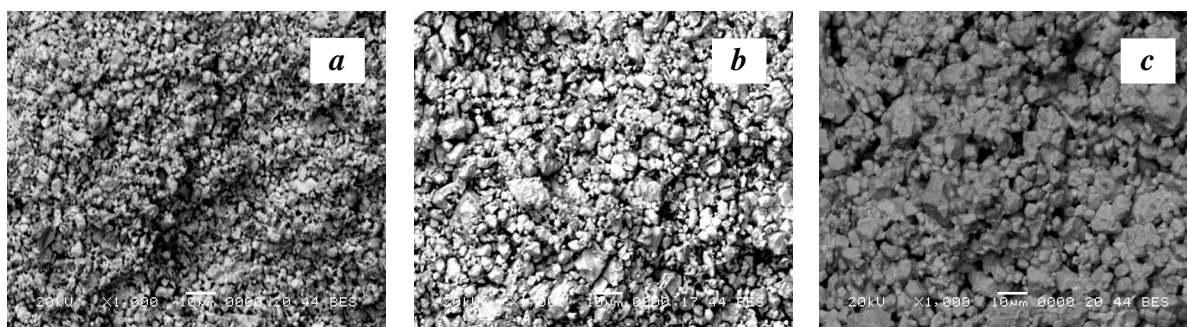
### RESULT AND DISSCUSION

After final stage of the synthesis the monophase were samples in which the ratio of alkaline-earth elements (AEE) and lead varied within limits of  $0,95 \leq \text{Ba}(\text{Sr}):\text{Pb} \leq 1,05$ . On the powder diffractograms of the samples with ratio of Ba(Sr) : Pb > 1,05 the additional reflexes were found, which corresponded to the impurity phases of Ba<sub>4</sub>Pb<sub>3</sub>O<sub>10</sub> or Sr<sub>2</sub>PbO<sub>4</sub> [5] (fig. 1) and intensity of which decreased at decreasing of AEE content in the samples. On the powder diffractograms of the samples with ratio of Pb : Ba(Sr) > 1,05 the additional reflexes of lead oxide (PbO) [5] were detected (fig. 1). So, monophase samples of metaplumbates of AEE (barium or strontium) are formed not only for stoichiometric composition (BaPbO<sub>3</sub>, SrPbO<sub>3</sub>), but for compositions with certain deficiency of barium (strontium) or lead oxides (Ba<sub>0,95</sub>PbO<sub>2,95</sub>, Sr<sub>0,95</sub>PbO<sub>2,95</sub>, BaPb<sub>0,95</sub>O<sub>2,90</sub>, SrPb<sub>0,95</sub>O<sub>2,90</sub>). The fact, that AEE plumbates have non-zero homogeneity region on the barium (strontium) and lead oxides, are in a good agreement with the literature data [6, 7], according that perovskite structure stored at formation up to 5–10% of vacancies in its different cationic sublattices. The main phase of ceramics had orthorhombically distorted perovskite structure with lattice constants of  $a = 6,015\text{--}6,027$  and  $5,813\text{--}5,861$  Å,  $b = 6,039\text{--}6,057$  and  $5,949\text{--}5,963$  Å,  $c = 8,513\text{--}8,520$  and  $8,319\text{--}8,328$  Å for barium and strontium metaplumbates respectively, which was close to the values obtained in [8] for BaPbO<sub>3</sub> and SrPbO<sub>3</sub> phases:  $a = 6,06370$  and  $5,86270$  Å,  $b = 6,02960$  and  $5,95440$  Å,  $c = 8,50840$  and  $8,32930$  Å respectively.



**Fig. 1.** X-ray powder diffractograms (CuK $\alpha$ -radiation) of the samples Ba<sub>1,3</sub>PbO<sub>3,3</sub> (1), BaPbO<sub>3</sub> (2), BaPb<sub>1,3</sub>O<sub>3,6</sub> (3), Sr<sub>1,3</sub>PbO<sub>1,3</sub> (4), SrPbO<sub>3</sub> (5) и SrPb<sub>1,3</sub>O<sub>3,6</sub> (6). The impurity phases Ba<sub>4</sub>Pb<sub>3</sub>O<sub>10</sub>, Sr<sub>2</sub>PbO<sub>4</sub> and PbO are designated with symbols (#), (\*) and (+) respectively.

On the IR-absorption spectra of strontium metaplumbates powders two pronounced absorption bands with extrema at 559–567 ( $\nu_1$ ) and 322–337  $\text{cm}^{-1}$  ( $\nu_2$ ) were observed, which were corresponded to the stretching ( $\nu_1$ ) and bending ( $\nu_2$ ) vibrations of Pb–O bonds in the structure of perovskite strontium metaplumbate [9]. The positions of absorption bands slightly altered at changing of Sr:Pb ratio in the samples studied. So, we can conclude, that formation of vacancies in the cationic sublattices of strontium or lead in the strontium metaplumbate structure do not influence on the value of interaction energy of lead cations and oxygen anions in the structure of this complex oxide.



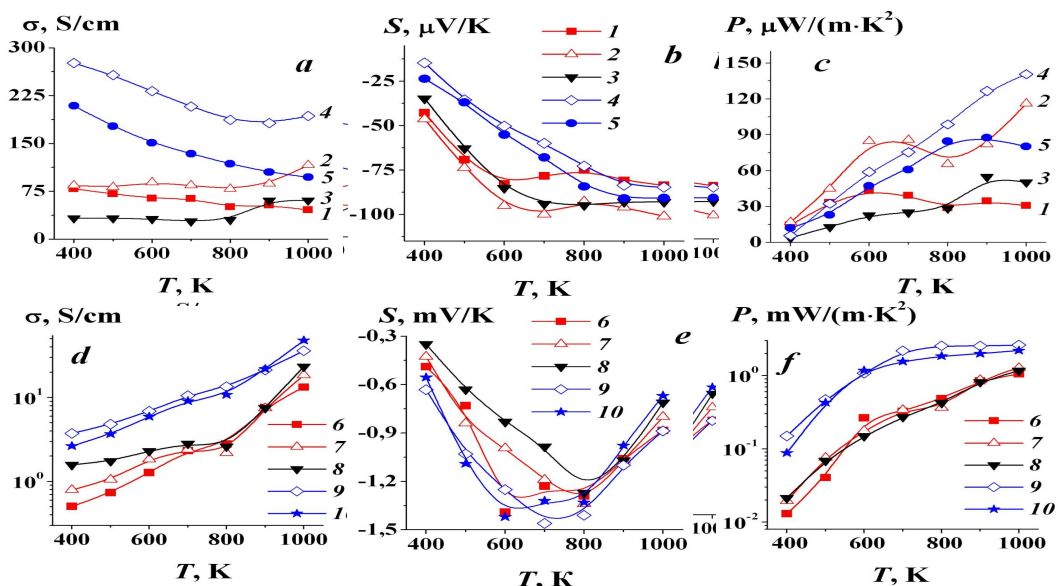
**Fig. 2.** Electronic microphotographs of the surfaces of cleaved ceramics Sr<sub>1,3</sub>PbO<sub>3,3</sub> (a), SrPbO<sub>3</sub> (b) and SrPb<sub>1,3</sub>O<sub>3,6</sub> (c) sintered at 1123 K.

Apparent density of the sintered ceramics varied within 3,94–7,42 and 4,38–6,62  $\text{g/cm}^3$  for metaplumbates of barium and strontium respectively and increased at increasing of Pb : Ba(Sr) ratio in the initial mixture. The highest values of apparent density were fixed for unmonophase samples which contained in addition to the main phase – barium or strontium metaplumbate – the lead oxide (PbO), which suggests that introduction of the PbO into ceramics based on BaPbO<sub>3</sub> or SrPbO<sub>3</sub> improves its sinterability. As can be seen from the fig. 2, the shape of the grains of ceramics was close to the isometric and the size of grains increased at increasing of the Pb : Sr ratio in the initial mixture and varied from 1–2  $\mu\text{m}$  for the samples which were rich of strontium oxide to the 10  $\mu\text{m}$  for the samples which were rich of lead oxide.

On the temperature dependence of the relative elongation of BaPbO<sub>3</sub> near 610 K the anomaly in a kink was observed, which was accompanied by an increase of linear thermal expansion coefficient (LTEC) of ceramics from  $13,6 \cdot 10^{-6} \text{ K}^{-1}$  to the  $15,7 \cdot 10^{-6} \text{ K}^{-1}$ . The our results are in a good accordance with the results of work [4], in which it was found that LTEC of BaPbO<sub>3</sub> increased from  $12,6 \cdot 10^{-6} \text{ K}^{-1}$  to the  $16,4 \cdot 10^{-6} \text{ K}^{-1}$  near 535 K.  $\Delta l/l_0 = f(T)$  dependences for the other samples studied were practically linear and their LTEC values within temperature interval studied were  $15,1 \cdot 10^{-6} \text{ K}^{-1}$  for the BaPb<sub>1,3</sub>O<sub>3,6</sub> samples and  $(11,6–14,5) \cdot 10^{-6} \text{ K}^{-1}$  for the ceramics samples of the strontium metaplumbate and for the latter, in the whole, decreased at increasing of the lead oxide content in the samples.

Temperature dependences of electrical conductivity of the samples studied had metallic character ( $\partial\sigma/\partial T < 0$ ) for the barium metaplumbates and semiconducting character ( $\partial\sigma/\partial T > 0$ ) for the strontium metaplumbates (fig. 3, *a, d*), and  $\sigma$  values of the samples increased at increasing of the lead oxide content in the samples and reached maximal values for the unmonophase ceramics, which contained in addition to the main phase – barium or strontium metaplumbate – the PbO impurity. Anomaly in the form of diffuse minima on the  $\sigma = f(T)$  dependence for the samples studied in the temperature range 700–800 K taking into account [4] can be explained by reduction of the parts of the lead cations from  $Pb^{4+}$  to  $Pb^{2+}$  in the surface layer of the grains of ceramics, which is accompanied by evolution of part of oxygen from the samples into gas phase. Values of activation energy of electrical conductivity of the strontium metaplumbates increased at temperature increasing and slightly changed at varying of the Sr:Pb ratio in the samples, from which it can be concluded that increase of electrical conductivity of ceramics at increasing of lead oxide content in it is not due to the change of the conductivity mechanism but due to the increasing of charge carrier (electrons) concentration.

Thermo-EMF of the barium and strontium metaplumbates within 300–1100 K temperature region was negative (fig. 3, *b, e*), from which we can conclude, that main charge carriers in these oxides are electrons, in other words, they are *n*-type conductors. On the  $S = f(T)$  dependences of the ceramics studied near 600–800 K the anomaly in a kink was observed. The nature of this anomaly is the same as for anomaly of electrical conductivity which was described earlier. The absolute value of *S* of ceramics slightly increased at increasing of barium and strontium oxides content in it, that is thermo-EMF of the samples changed antysymbatic to the electrical conductivity. So, results of the study of electrophysical properties of ceramics are in good accordance with each other: the increase of charge carrier concentration in the unipolar conductors leads to the increasing of their electrical conductivity and decreasing of their thermo-EMF. The *S* values of prepared in this work ceramics on the base of the strontium metaplumbate were (in absolute value) abnormally high due to its microheterogeneity.



**Fig. 3.** Temperature dependences of electrical conductivity ( $\sigma$ ) (*a, d*), thermo-EMF coefficient (*S*) (*b, e*) and power factor (*P*) (*c, f*) of metaplumbates of barium (*a–c*)  $Ba_{1,3}PbO_{3,3}$  (1),  $Ba_{1,1}PbO_{3,1}$  (2),  $BaPbO_3$  (3),  $BaPb_{1,1}O_{3,2}$  (4),  $BaPb_{1,3}O_{3,6}$  (5) and strontium (*d–f*)  $Sr_{1,3}PbO_{3,3}$  (6),  $Sr_{1,1}PbO_{3,1}$  (7),  $SrPbO_3$  (8),  $SrPb_{1,1}O_{3,2}$  (9),  $SrPb_{1,3}O_{3,6}$  (10).

The power factor values of ceramics investigated increased at increasing of temperature and lead oxide content in the samples (fig. 3, *c, f*).  $P$  values of unmonophase ceramics on the base of strontium metaplumbate, which contained as impurity phase the lead oxide above 600 K were high than  $1 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$  (fig. 3, *f*), hereby the maximal value of power factor demonstrated the sample with composition of  $\text{SrPb}_{1,2}\text{O}_{3,4}$  ( $2\text{--}3 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$  within 700–1000 K temperature range) due to high values of electrical conductivity and thermo-EMF (in absolute value) of its heterogeneous ceramics containing PbO micro-impurity.

### CONCLUSION

Thus, in this work the ceramics based on the barium and strontium metaplumbates with different barium (strontium) and lead ratio ( $0,77 \leq \text{Ba (Sr) : Pb} \leq 1,3$ ) was prepared and its structure, microstructure, thermal expansion, electrical conductivity and thermo-EMF were studied. It is shown, that perovskite barium and strontium metaplumbates have non-zero homogeneity region on the cations and can dissolve in itself up to 5 mol.% of AEE and lead oxides. Increase of the lead content in the samples leads to the improving of their sinterability, decreasing of their LTEC, and increasing of their electrical conductivity and thermo-EMF (in an absolute value). It is found, that thermoelectric properties of ceramics based on the metaplumbates of barium or strontium improve by introducing into it of lead oxide as a second (impurity) phase. The maximal value of power factor the ceramics of  $\text{SrPb}_{1,2}\text{O}_{3,4}$  composition is characterized, which allows us to consider it as a basis for development of the new oxide thermoelectrics, effective at higher temperatures.

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