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В сборнике опубликованы доклады, представленные на Международной научной конференции по актуальным проблемам физики твердого тела. В нем изложены результаты новейших исследований по проблемам физики магнетизма, полупроводников, диэлектриков и сегнетоэлектричества. Значительное число докладов посвящено вопросам практического применения разработанных материалов, технологий и устройств.

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DTA STUDIES OF FORMATION OF $BaPbO_{3-\delta}$ FROM OXALATES

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Introduction. The $BaPb_{1-x}Bi_xO_3$ solid solutions, including $BaPbO_{3-\delta}$ and $BaBiO_3$ ternary compounds, can be considered as the precursor material of high temperature oxide superconductors. While $BaPbO_{3-\delta}$ with an empty Pb 6s band is metallic, $BaBiO_3$ is a semiconductor although it has a half-filled Bi 6s band. For $x<0,3$ metallic and superconducting properties have been observed [1]. Neutron powder diffraction [2] indicates that in $BaBiO_3$ Bi-ions exist in a mixed valence state, which can be represented as $Ba_2Bi^{3+}Bi^{5+}O_6$. Bi ions occupy two crystallographically nonequivalent sites with significantly different Bi-O lengths [3]. Since the ionic radius of Bi^{3+} is considerably larger than that of Bi^{5+}, the oxygen octahedral surrounding the Bi ions are alternately expanded and compressed (the so-called breathing displacement). This leads to the larger monoclinic lattice in comparison with other perovskite-type compounds. There are a lot of contradictory information about the crystal structure of $BaPbO_{3-\delta}$ in the literature – from cubic [4] to tetragonal [5], rhombic [2], and monoclinic structure [6]. Such inconsistency of the obtained results can be explained by a number of reasons, among which the possibility of obtaining of $BaPbO_{3-\delta}$ compound with the varied value of δ at usage of different methods of obtaining is selected. The double valence Pb^{2+}-Pb^{4+} fluctuations might occur in oxygen deficient samples of $BaPbO_{3-\delta}$. The second reason can be the polymorphism of $BaPbO_{3-\delta}$. The detailed structural study of powder samples $BaPbO_{3-\delta}$ has been carried out in the temperature range 27 - 727 °C using neutron powder diffraction technique in order to characterize the temperature–induced phase transformations and the structures of different phases (from monoclinic to cubic) were refined by Rietveld method. In this connection very actually there is a problem of development of new methods of obtaining of $BaPbO_{3-\delta}$ with possibility to obtain this compound with the same composition (reproducible composition). It is known that the sol-gel method is superior to the conventional solid state reaction because in the former it is possible to mix the starting materials at the molecular level and the resulting product is expected to be homogenous. The formation of $BaPbO_{3-\delta}$ by decomposition of barium and lead oxalate up to 850 °C is significantly faster compared to conventional high temperature solid state reactions of oxide compounds [7].

This paper describes the formation of $BaPbO_{3-\delta}$ perovskite-type compound from the equimolar physical mixture of the previously prepared fresh corresponding oxalates $Ba(COO)_2\cdot 0,5H_2O$ and $Pb(COO)_2$ and studies of the thermal decomposition of the Barium Oxalate Hydrate $Ba(COO)_2\cdot 0,5H_2O$ and Lead Oxalate $Pb(COO)_2$.

Sample preparation and techniques of investigation. The aim of the coprecipitation is to prepare multicomponent ceramic oxides through the formation of the intermediate precipitates, usually hydrous oxides or oxalates, so that an intimate mixture of the components is formed during precipitation, and chemical homogeneity is maintained on calcinations. The solution method utilized the reaction of $(COOH)_2\cdot 2H_2O$ with $Ba(OH)_2\cdot 8H_2O$ and $Pb(NO_3)_2$ solutions (both in a 1:1 molar ratio) under controlled conditions of pH, temperature and reactant concentration. This procedure results in the immediate precipitation of finely powdered aggregates. After filtering a slow evaporation at room temperature of mother liquors of the previous preparation was made.

The equilibrium of the $Ba(OH)_2 \cdot 8H_2O$, $Pb(NO_3)_2$, $Ba(COO)_2 \cdot 0{,}5H_2O$, $Pb(COO)_2$, and $BaPbO_{3-\delta}$ compounds were determined by X-ray powder diffraction (XRPD). XRPD was used also to establish the chemical formula of the obtained in these ways materials and the ones prepared by heat treatment at the corresponding temperatures. Diffractometers SIEMENS D5000 and DRON-4 (filtered copper radiation) were used.

The thermal behaviour was studied using differential thermal analysis (DTA). The DTA measurements were performed by means of the apparatus specially constructed and suited for the measurements up to temperatures of 1300 °C. The presence of phase phenomena and their temperatures were determined from DTA with the accuracy of phase transition temperature determination of 2 °C. Powdered samples (typical weight 1 g) were placed in non-evacuated silica capsules. Al_2O_3 was used as reference material. The identity of the thermal conditions of the sample and reference material was reached by their placing into a high-temperature steel clamp. DTA was run on samples that were heated at the constant rate of 2-3 °C/min. The temperature of the sample and that the reference materials were determined with Pt/90%Pt-10%Rh thermocouples. The difference signal between temperatures of the sample and reference material was amplified and registered on computer together with the temperature signal itself. For each peak in the difference signal, a phase transition temperature was determined from the baseline intercept of the tangent to the leading edge of peak. Calibration of the temperature scale was achieved by recording the solid-state phase transitions and the melting points K_2SO_4 (585 and 1069 °C), NaCl (801 °C), and Na_2SO_4 (884 °C).

Thermal decomposition of oxalates and formation of $BaPbO_{3-\delta}$.

Decomposition of $Ba(COO)_2 \cdot 0{,}5H_2O$. The decomposition of $Ba(COO)_2 \cdot 0{,}5H_2O$ occurs in some complex stages. The first stage is the loss of H_2O at 198-216 °C. The second stage at 386-498 °C is complex and consists of the decomposition of $Ba(COO)_2$ to $BaCO_3$, and part decomposition of $BaCO_3$ to BaO_2. The third stage is the decomposition of BaO_2 in BaO at 805 °C and at the higher temperatures there is a mixture of BaO and $BaCO_3$. It is confirmed by results of XRPD of powder of $Ba(COO)_2 \cdot 0{,}5H_2O$, heated to the temperatures higher than the temperature of the corresponding thermal effect.

Decomposition of $Pb(COO)_2$. It was established that the decomposition of $Pb(COO)_2$ to PbO occurs in 3 stages. The first stage starts from 315 °C and finishes at the temperature of the minimum of the first endothermic peak of 365 °C. At the temperature of 340 °C there is a mixture of Lead Pb, Lead Oxide Carbonate $Pb_3O_2CO_3$, and rest of Lead Oxalate $Pb(COO)_2$. Additionally to XRPD results the repeated DTA of $Pb(COO)_2$, previously heated to 340 °C and then quenched to the room temperature shows clearly the presence of $Pb(COO)_2$ (beginning of the thermal peak from 315 °C) and Pb in this mixture (the weak peak of melting of Pb at 327 °C). X-Ray diffraction patterns for $Pb(COO)_2$ oxalate, heated up to 390°C and then quenched to the room temperature, shows that the result of the first stage of decomposition of $Pb(COO)_2$ is the mixture of Pb and $Pb_3O_2CO_3$. The result of the second endothermic peak of decomposition of $Pb(COO)_2$ is the mixture of Pb and violet-red PbO in litharge structure, that is confirmed by XRPD experiments for $Pb(COO)_2$ oxalate, heated up to 430 °C and then quenched to the room temperature. At 450-550 °C the interaction of Pb and O_2 takes place with the formation of PbO (the broad exothermic peak) and transformation of PbO from the litharge structure to the massicot one, there is a mixture of PbO with the structure of litharge (red PbO) and massicot (orange-yellow PbO) at 500 °C. XRPD confirms orange-yellow PbO with the massicot structure as the only detectable phase in the residue at the 570 °C. The temperature of 700 °C is the upper limit of usage of guartz vessels for Pb-containing compounds as at higher temperatures the reaction of PbO and SiO_2 takes place and Lead Silicate Pb_4SiO_6 is formed. The formation of Lead Silicate existing as γ-Pb_4SiO_6 at room temperatures was confirmed by results of XRPD of $Pb(COO)_2$ oxalate heated in DTA quartz crucibles up to 970°C. High-temperature DTA investigations (up to 970 °C) also confirmed the interaction of PbO and SiO_2 as they showed the phase transitions (β-Pb_4SiO_6 + PbO) $\rightarrow$ (α-Pb_4SiO_6 + PbO) and (α-Pb_4SiO_6 + PbO) $\rightarrow$ (PbO + L) at 712 °C and 733 °C, respectively.

Formation of $BaPbO_{3-\delta}$. Figure 1 gives the DTA curve of heating in air for the equimolar physical mixture of $Ba(COO)_2{\cdot}0{,}5H_2O$ and $Pb(COO)_2$ oxalates that was used to the formation of the ternary compound $BaPbO_{3-\delta}$. The last thermal endothermic peak (5-endo) ending up at 875°C is attributed to the melting of PbO. The extensive formation of $BaPbO_{3-\delta}$ ternary compound starts after the melting of PbO and is stimulated by the oxygen atmosphere because at these temperatures the decomposition of BaO_2 takes place. Nevertheless to the beginning of formation of $BaPbO_{3-\delta}$ the oxidation state of Pb in the Pb-containing compound (PbO) is 2+ and it leads to the deviation of the obtained ternary compound from the ideal perovskite ABO_3 formula concerning to the oxygen content. Using these results and to prevent the losses of content of Pb at the temperatures above the melting point of PbO the temperature of the formation of $BaPbO_{3-\delta}$ from the equimolar physical mixture of the corresponding oxalates was estimated being 850°C and a single-phase compound was prepared by calcinations in alumina vessels. It was found that $BaPbO_{3-\delta}$ is crystallized in the monoclinic structure with the lattice constants ***a***, ***b***, ***c*** being 6,021(5), 8,497(5), 6,031(5) Å, respectively, and ***β*** being 90,01.

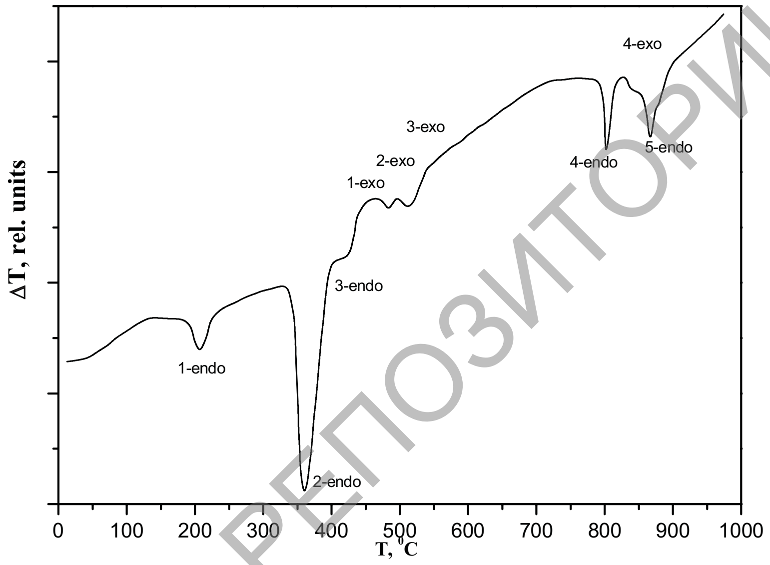

Figure 1 - DTA curve of heating in air for the equimolar physical mixture of $Ba(COO)_2{\cdot}0{,}5H_2O$ and $Pb(COO)_2$ oxalates

Conclusions. The decomposition of $Pb(COO)_2$ occurs in three complex stages - the first stage at 315 - 390 °C is the decomposition of $Pb(COO)_2$ to mixture of Lead Pb and Lead Oxide Carbonate $Pb_3O_2CO_3$. The result of the second decomposition's stage at 400 - 430 °C is the mixture of Pb and violet-red PbO in the litharge structure. At 450 - 550 °C the reaction of interaction of Pb and O_2 takes place with the formation of PbO and transformation of PbO from the litharge structure to the massicot one. The temperatures of the formation of $BaPbO_{3-\delta}$ was estimated being 850 °C and the single-phase compounds in the monoclinic structure with the lattice constants ***a***, ***b***, ***c*** being 6,021(5), 8,497(5), 6,031(5) Å, respectively, and ***β*** being 90,01 was prepared by calcination.

[1] A.W. Sleight, J.L. Gillson, P.E. Bierstedt, Solid State Commun. **17**, 27 (1975)
[2] D.E. Cox, A.W. Sleight, Solid State Commun. **19**, 969 (1976)
[3] G. Thornton, A.J. Jacobson, Acta Crystallogr. **B34**, 351 (1978)
[4] R. Hoppe, K. Blinne, Z. Anorg. All. Chem. **293**, 251 (1958)
[5] K. Kakimura, K. Fueki, Solid State Commun. **105**, 173 (1998)
[6] E.T. Shuvaeva, E.G. Fesenko, Kristallographiya **15**, 379 (1970)
[7] A. Franz, D. Klimm, W. Schmitz, I. Haferkorn, K. Bente, Cryst. Res. Technol. **46**, 906 (2011)