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## BARITE PHASE FORMATIONS DURING LEAD AND ZINC OXIDIZED ORES SINTERING

**Abstract:** The paper presents results of investigation of barite phase formation during the processing of the oxidized lead-zinc ores from the Alashpai ore deposit by the methods of the thiosalts metallurgy. The phase formations at sintering charge containing the mix of the oxidized lead-zinc barite ore, sodium sulfate and carbonaceous reductant were studied under the temperatures varying from 973 up to 1173 K with using X-ray phase analysis and electron probe screening in modes COMPO, EDS and WDS. The researched ore sample from the Alashpai ore deposit contains, in accordance with the X-ray fluorescent analysis, mass %: 6.158 Pb; 6.978 Ba; 0.016 Zr; 0.222 Zn; 0.063 Cu; 3.955 Fr; 0.603 Mn; 0.270 Ti; 0.265 Ca; 0.684 K; 1.226 S; 13.702 Si; 4.527 Al; 0.967 Mg; 0.244 Na, rest – oxygen and other. Phase formation at the temperature of 973 K combines transformations of two types: disordering of the cation sublattice and a change in the symmetry of the anion sublattice. Subsequently, the barium cations are distributed over the vacancies of the crystallographic positions. Based on the results of the X-ray phase analysis, barium silicates  $BaSiO_3$ ,  $Ba_4Si_6O_{16}$ , as well as an intermediate sulfate-sulfite complex  $Ba(SO_3)_{0.3}(SO_4)_{0.7}$  are presented in the cake sintered at 973 K. The research results substantiate formation within 1073 K temperature of the thiosalts of barium, i.e.  $BaCu_2SnS_4$ ,  $BaFe_2S_4$ ,  $Ba_3FeS_5$ ,  $Ba_9FeS_{15}$ , with concurrent formation of  $BaSiO_3$ ,  $Ba_2Si_3O_8$ ,  $Ba_5Si_8O_{21}$ ,  $Ba_4(Si_6O_{16})$ ,  $Ba_2(Si_4O_{10})$ ,  $BaFeSi_4O_{10}$ . In this sinters the cation of barium is an initiator of formation of thiosalts of the  $Ba_nMe_mS_x$  type. The rise in temperature up to 1173 K contributes to the destruction of barium compounds. Barium thiosalts decomposes with the formation of barium sulphide, the thiosalt crystal lattice breaks down into simpler structures. Solid solutions based on barium silicate also break down into constituent oxides of silicon and barium and further processes of formation of carbonates and barium sulphates take place.

**Key words:** barite, barium thiosalts, barium silicates, barium sulfide, sintering, phase formation, oxidized lead-zinc ore, Alashpai deposit, thiosalts metallurgy

**Introduction.** Development of raw materials resources base in the RK and emergence of new integrated technologies condition the need to further research the phase formation processes which occur during the processing of different materials.

High selectivity of breaking out of compound draw materials applying the methods used in metallurgy for the thiosalts of the nonferrous metals originates from the physical-chemical qualities of those compounds, formed during the pyro- and hydrometallurgical processing. Selectivity of breaking out patterns can be illustrated by an example of raw mix sintering in presence of sodium sulfate and carbonaceous reductant [1-3].

Previously studied physical-chemical properties, regularities of reactions displayed by the thiosalts of nonferrous metals as well as technologies that are based on the methods of thiosalts metallurgy, can be applicable if the thiosalts have the  $Na_nMe_mS_x$  structure, where Me stands for Cu, Zn, Pb, As, Ti, Mn, Al, Si, Ag, Re, Se, Te and other rare metals.

Currently, there come certain research matters that significantly differ in composition, for example, oxidized lead-zinc barite ores, which upon processing produce the thiosalts of barium. Anyway, the available data on the thiosalts of barium are limited and in most cases such research is targeted on the identification of the barium compounds which

possess unique properties of ionic conductivity.

There are references to certain data on drawing of T-x projection diagram of  $Cu_2S$ -BaS system status. Within the system, peritectic melting phases are formed, i.e.,  $BaCu_4S_3$  crystalizing into the rhombic syngony and  $BaCu_2S_2$  with 935 K melting temperature (“the  $T_{melt}$ ”), crystalizing into the tetragonal syngony with  $T_{melt}$  of 1035 K, the eutectic is formed between  $Cu_2S$  –  $BaCu_4S_3$  at 27 mole percent of BaS under  $T_{melt}$  of 910 K [4].

Based on the results obtained from melted and annealed samples, the applied series of physical-chemical analysis methods revealed the areas of homogeneity and heterogeneity in the BaS –  $Ga_2S_3$  system as well as their crystal-chemical properties. Annealed samples containing 16.66, 20, 25, 33.33, 50 and 66.66 mole percent of  $Ga_2S_3$  were single-phased and contained reflexes of  $Ba_5Ga_2S_8$ ,  $Ba_4Ga_2S_7$ ,  $Ba_3Ga_2S_6$ ,  $Ba_2Ga_2S_5$ ,  $BaGa_2S_4$  and  $BaGa_4S_7$  phases, respectively. The phases of  $Ba_5Ga_2S_8$ ,  $Ba_4Ga_2S_7$ ,  $Ba_3Ga_2S_6$ ,  $Ba_2Ga_2S_5$  and  $BaGa_2S_4$  melt incongruently. At initial ratio of sulfide mix being 1 BaS : 2  $Ga_2S_3$  the compound composition of  $BaGa_4S_7$  was formed, the existence of which proves single-phase nature of samples containing 66(6) mole percent of  $Ga_2S_3$  and annealed at 870 and 1070 K. The system also reveals presence of two eutectics between phases  $Ba_2Ga_2S_5$  and  $BaGa_2S_4$  and between phases

BaGa<sub>4</sub>S<sub>7</sub> and  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub>. The eutectics coordinates are 38 mole percent of Ga<sub>2</sub>S<sub>3</sub> and 72 mole percent of Ga<sub>2</sub>S<sub>3</sub>. Close to Ga<sub>2</sub>S<sub>3</sub> coordinate there was found a thin area of enclosed solid solution on basis of defect-structure of  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub>. Along with the temperature decrease, the span of the solid solution consistently decreases from 3 mole percent of BaS at temperature of 1070 K to 2 mole percent of BaS at temperature of 870 K [5].

The phase condition diagrams for systems BaS – Ln<sub>2</sub>S<sub>3</sub> (Ln = Sm, Eu, Er, Lu) are similar in qualitative terms and appear as systems with congruently melted compounds. Compound BaLn<sub>2</sub>S<sub>4</sub> (Ln = Nd, Lu) is isostructural. The span the solid solution building up on basis of BaSm<sub>2</sub>S<sub>4</sub> at 1720 K has concentration range of 50-56 mole percent of Sm<sub>2</sub>S<sub>3</sub>. The row from Sm to Gd is marked with decreasing solid solution on base of  $\alpha$ -Ln<sub>2</sub>S<sub>3</sub>, and the eutectic composition shifts towards composition of initial components. At 1820 K, about 15 mole percent of BaS is dissolved in  $\gamma$ -Sm<sub>2</sub>S<sub>3</sub> and 4 mole percent of BaS in  $\gamma$ -Gd<sub>2</sub>S<sub>3</sub>. The system of BaS – Er<sub>2</sub>S<sub>3</sub> produced two triple compounds Ba<sub>3</sub>Er<sub>2</sub>S<sub>6</sub> and BaEr<sub>2</sub>S<sub>4</sub>. The first one melted on peritectics at 2005 K, the second one melts congruently at 2040 K [6].

All of the BaLn<sub>2</sub>S<sub>4</sub> compounds are isostructural. Formation of compounds Ba<sub>3</sub>Ln<sub>2</sub>S<sub>6</sub> and BaLn<sub>2</sub>S<sub>4</sub> is characteristic for all systems in the row of BaS – Ln<sub>2</sub>S<sub>3</sub> (Ln = Tb-Er) with peritectics and congruent melting, respectively. It is determined that in systems BaS – Ln<sub>2</sub>S<sub>3</sub> (Ln = Tb-Lu) what is formed are the incongruently melting compounds compositions of Ba<sub>3</sub>Ln<sub>2</sub>S<sub>6</sub> with rhombic distorted structure and duplicated cell properties in three directions and regularly ordered distribution of Ba, Ln ions and vacancies on crystallographic cationic positions of basis structure. With the decrease of radius of the Ln (Ln = Tb-Lu) there is increase in melting temperature and the tendency of decrease in values of micro-hardness of compounds of type of Ba<sub>3</sub>Lu<sub>2</sub>S<sub>6</sub>. Within the BaS – Lu<sub>2</sub>S<sub>3</sub> system, the formation of three compounds is observed, namely of Ba<sub>3</sub>Lu<sub>2</sub>S<sub>6</sub> with incongruent melting at 2035 K, BaLu<sub>2</sub>S<sub>4</sub> with congruent melting at 2105 K, and BaLu<sub>8</sub>S<sub>13</sub> with congruent melting at 2060 K. In eutectic points with 34 mole percent of Lu<sub>2</sub>S<sub>3</sub> the melting temperature is 1995 K, with 68 mole percent of Lu<sub>2</sub>S<sub>3</sub> melting temperature is 2015 K, with 90 mole percent of Lu<sub>2</sub>S<sub>3</sub> under 1950 K. The obtained compound of BaLn<sub>8</sub>S<sub>13</sub> (Ln = Tm, Yb, Lu) has rhombic structure and grid parameters, like, a = 1.196 nm, b = 1.033 nm, c = 1.400 nm [7].

During the processing of the complex polycrystalline raw materials, containing barite using

the methods of thiosalts metallurgy in parallel with the formation of thiocompounds, the significant portion comes to phase formation of oxide compounds of barium, which display high mobility towards fast oxygen exchange on the surface [8-10].

Previous research of the oxide barium systems are relevant for the prospective development of crystal glass ceramics for obtaining of the new materials. As illustrated by the diagrams of compounds condition, within the system of BaO and oxides (Al, Si) there are compounds with such properties as high density, temperature stability, and that have dielectric parameters which allow to use them in production of resonators, filters, microwave-devices [11]. In particular, we obtained celsian glass ceramics on basis of hexagonal modification of the compound BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> at the synthesis and burning temperature of 1723 and 1773 K, respectively. With usage of DTA and temperature measurements of the dielectric properties for samples, the temperature of structural shift from Alpha-hexagonal modification to Beta-hexagonal modification was set to fall within the interval from 553 to 593 K.

One of the intensively researched classes of compounds are perovskite-like phases, mobile oxygen vacancies in them are created by lower-valent replacement in cationic subgrids [12-14]. Cationic replacements bring in the structural disorder preventing the movement of oxygen ions, because of which ionic conductivity may be not high enough. Oxygen mobility can be increased when the structural fragments are spatially divided. Such division of the structural fragments can be achieved by cationic ordering in perovskites R<sub>0.5</sub>Ba<sub>0.5</sub>MO<sub>3- $\sigma$</sub>  (R = Y, Ln. M = Mn, Co), that turns them into the laminate phases of RBaM<sub>2</sub>O<sub>6- $\sigma$</sub>  (R112). Ion-conducting properties are discovered in the laminate compounds of RBaCo<sub>4</sub>O<sub>7+ $\sigma$</sub>  (R114), the usage of R114 phases is possible in the temperature range of  $\leq 673$  K.

Processes of phase formation in the systems R<sub>2</sub>O<sub>3</sub> – BaO – CoO = 0.5:1:4 (R=Y, Gd-Lu) are studied in temperature area of 1173-1373 K. The optimal mode of solid phase synthesis of the phase RBaCo<sub>4</sub>O<sub>7+ $\sigma$</sub>  (R114) was identified and single-phase samples for R = Y, Dy, Ho, Er, Tm, Yb, Lu were obtained. Certain specific ways of the R114 (R = Y, Dy, Lu) samples reactions during the thermal cycling and oxygen saturation [15] were studied also.

Then, the uninterrupted row of solid solutions was found in the system containing oxide of barium and dioxide of silicon. The compounds 2BaO·SiO<sub>2</sub>, BaO·SiO<sub>2</sub>, 2BaO·3SiO<sub>2</sub> and BaO·2SiO<sub>2</sub> were identified. Further, the compound of 3BaO·SiO<sub>2</sub> and 3BaO·5SiO<sub>2</sub>, 5BaO·8SiO<sub>2</sub> were found when the elements reacted in their solid state. During

the study of the crystal structure of  $\text{Ba}_2\text{Si}_3\text{O}_8$ , which does not have an analogue amongst other groups of silicates of alkaline and alkaline earth metals, we identified three barium silicates, i.e.  $\beta\text{-BaSiO}_2$ ,  $\text{Ba}_2\text{Si}_4\text{O}_{10}$  and  $\text{Ba}_2\text{Si}_3\text{O}_8$ . Research results state the presence of the new type of silicon-oxygen belt  $\text{Si}_6\text{O}_{16}^{8-}$ , formed by polarization of three links of the structural type  $\text{BaSiO}_3$  inside of this silicate.

It was shown that two groups of solid solutions were formed, those based on  $2\text{BaO} \cdot 3\text{SiO}_2$  and based on the high-temperature modification  $\alpha\text{-BaO} \cdot 2\text{SiO}_2$ . For the disilicate of barium, two polymorph variations were found, i.e., low-temperature  $\beta\text{-BaSi}_2\text{O}_5$  and  $\alpha\text{-BaSi}_2\text{O}_5$ . Mutual transition of these modifications happens at the temperature of 1623 K. The study of the  $\text{BaO-SiO}_2$  system brought us to the conclusion that there is metastable liquation where the crystal point has temperature of 1703 K [16-18].

**Experimental.** The subject under this research represents the oxidized lead-zinc barite ore produced at the Alashpai deposit. The chemical reagents include sodium sulfate, carbonaceous reductant. The methods of analysis included spectral, X-ray, X-ray fluorescence, atomic-adsorption chemical, and electron probe microanalysis. The utilized equipment was electric resistance furnace chamber laboratory SNOL 12/16.

The experimental trial procedure was as follows, the ore from the deposit Alashpai was crushed, then placed in a mortar to prepare a mix by

adding anhydrous sodium sulfate and carbonaceous reductant in quantities predetermined by the stoichiometric ratios. The mix was put in the reaction vessel closed with the graphite lid with the aim to create a reducing environment above the mix surface and to prevent penetration of oxygen from ambient air getting into the zone of formation of the nonferrous metals thiosalts.

The sintered mix contained chemically pure sodium sulfate (98 %  $\text{Na}_2\text{SO}_4$ ) and carbonaceous reductant in form of activated carbon containing, in %, 74.3 C; 0.16 S; 0.025 P; 1.12 Fe; 0.93  $\text{SiO}_2$ ; 1.56  $\text{Al}_2\text{O}_3$ .

The mix sintering in compliance with above procedure was carried out under temperature range 973-1173 K with the optimal composition of mix being 25 % of  $\text{Na}_2\text{SO}_4$ , 15 % carbonaceous reductant; sintering duration lasted 2.5 hours.

The subject of the research was the ore sample taken from the Alashpai ore deposit. It contained, in accordance with the X-ray fluorescent analysis, mass %: 6.158 Pb; 6.978 Ba; 0.016 Zr; 0.075 Sr; 0.222 Zn; 0.063 Cu; 3.955 Fr; 0.603 Mn; 0.270 Ti; 0.265 Ca; 0.684 K; 0.138 Cl; 1.226 S; 0.258 P; 13.702 Si; 4.527 Al; 0.967 Mg; 0.244 Na; 0.104 F; 59.594 O.

X-ray phase analysis allowed to determine the presence of barite  $\text{BaSO}_4$ , cerussite  $\text{PbCO}_3$ , montmorillonite  $(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_2\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , muscovite  $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH}, \text{F})_2$ , quartz  $\text{SiO}_2$  (Figure 1).

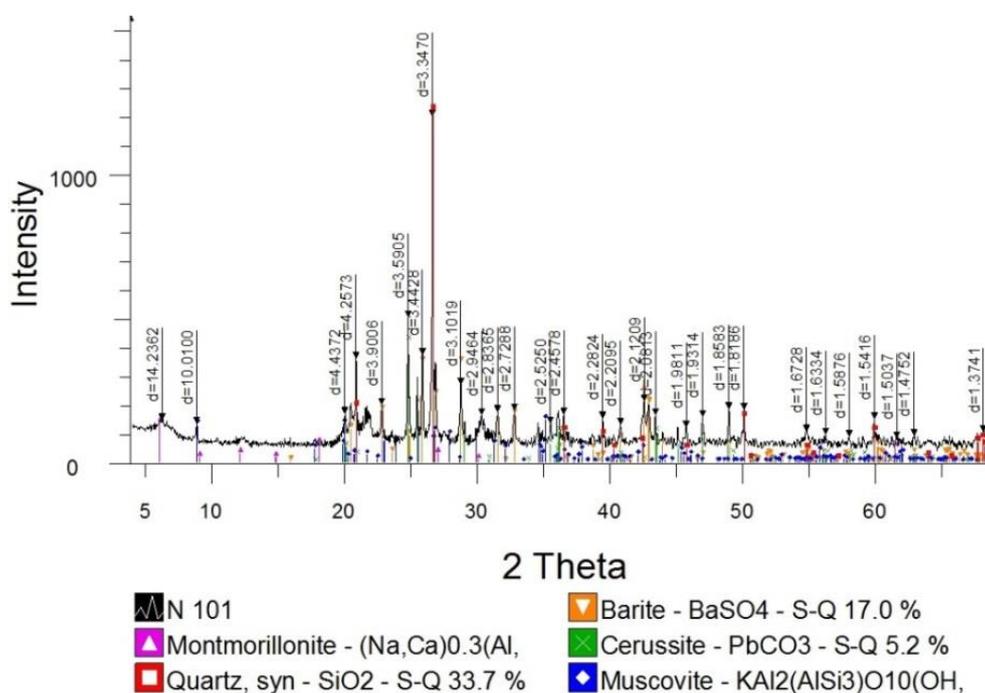
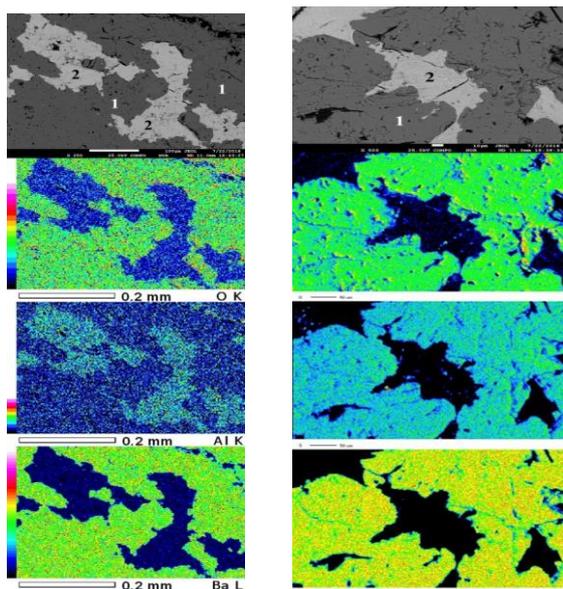


Figure 1 – X-ray diffraction pattern of the ore sample from the Alashpai ore deposit



a – cerussite  
 b – barite  
 1 – barite; 2 – gold-containing cerussite  
 (COMPO, ×250, ×500)

Figure 2 – SEM images of the ore sample from the Alashpai deposit with concentration of the elements in cerussite and barite (EDS, WDS, x500)

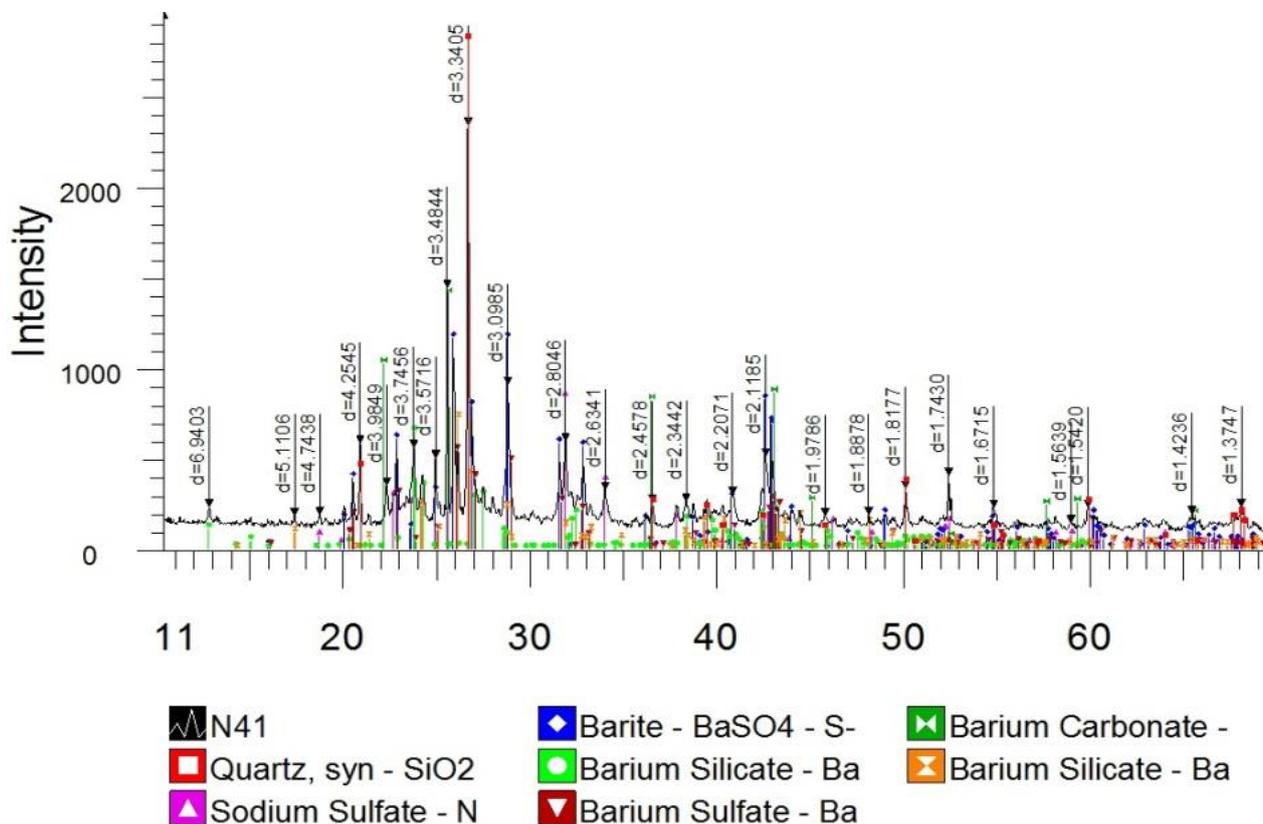
Electron probe screening of the ore sample performed in modes COMPO, EDS and WDS (Figure 2 a, b).

The composition of sinters obtained at temperatures range from 973 to 1173 K is shown in table.

Table - Chemical composition of sinters by main components

T, K	Content, %												
	Ba	Fe	Cu	Zn	Pb	Mg	Al	Si	Ca	Ti	Mn	Na	S
973	7.10	4.06	0.070	0.24	8.3	1.04	4.60	13.9	0.29	0.23	0.65	8.5	7.0
1073	7.21	4.10	0.077	0.25	8.5	1.05	4.78	14.2	0.37	0.24	0.70	8.6	7.1
1173	7.32	4.30	0.090	0.27	8.6	1.06	4.60	14.0	0.35	0.26	0.75	9.9	8.0

The accomplished sintering of the oxidized ores from the Alashpai deposit at 973 K testifies significant phase formation in systems containing barium. The XRD pattern of the sinters sample synthesized at 973 K is shown at Figure 3.



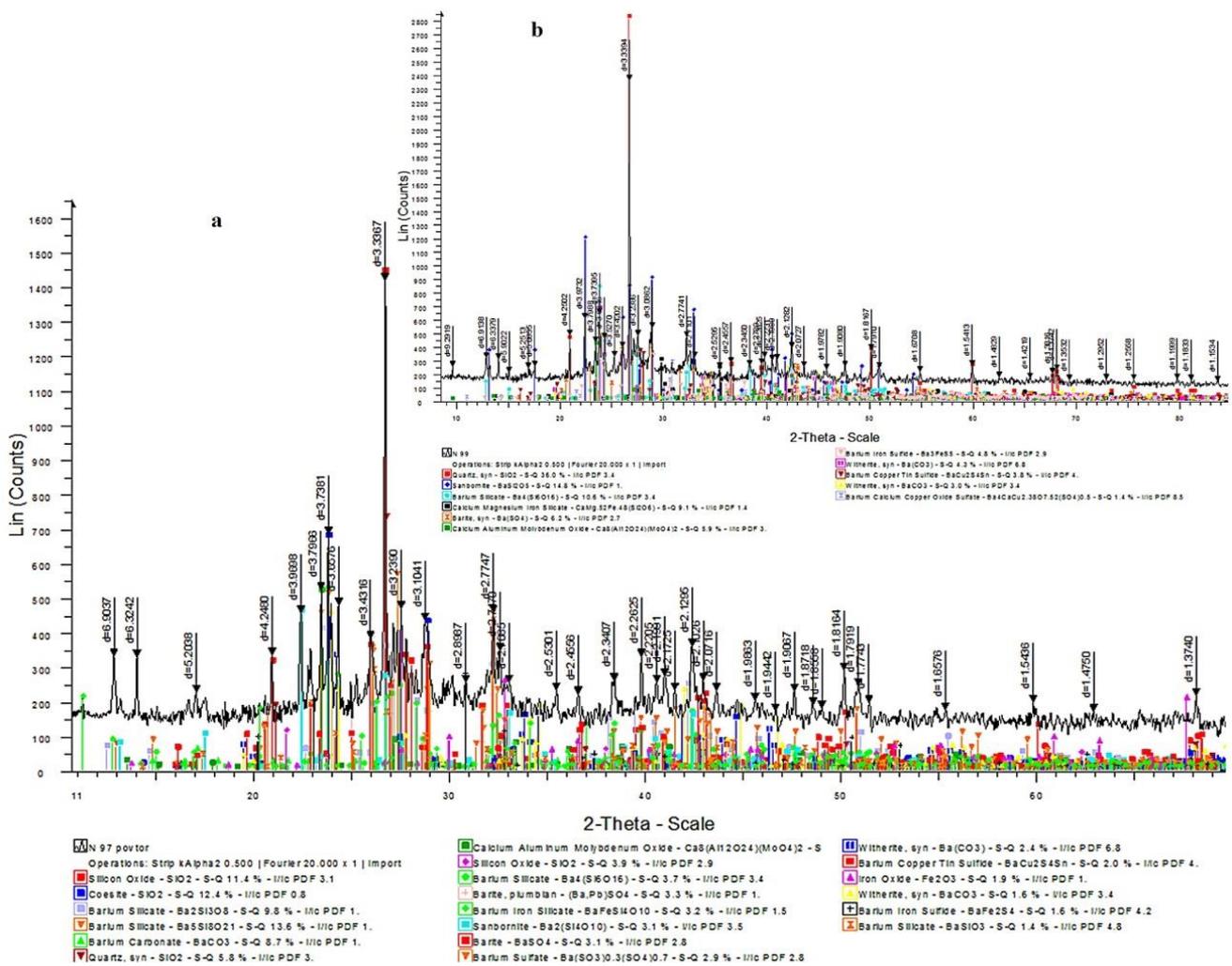
Phases of SiO<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, BaSO<sub>4</sub>, Ba<sub>4</sub>Si<sub>6</sub>O<sub>16</sub>, Ba(SO<sub>3</sub>)<sub>0.3</sub>(SO<sub>4</sub>)<sub>0.7</sub>, BaCO<sub>3</sub>, BaSiO<sub>3</sub>

Figure 3 - X-ray diffraction pattern of the sinter obtained at 973 K.

The sinter displayed the presence of the metasilicate of barium ( $BaSiO_3$ ) and of the compound  $Ba_4Si_6O_{16}$ , which is a part of solid solutions group. What is typical, is that as sintering progresses the formation of the barium silicates starts at the lower temperatures as compared to the data from diagram of the system  $BaO-SiO_2$  standing, which is attributed to activation and ongoing renewal of the surface of solid phases, elimination of the diffusion obstacles related to the inhibitory effect of the reaction products. Apart from that, another finding in the studied sinter revealed the presence of the intermediate sulfate-sulfite compound  $Ba(SO_3)_{0.3}(SO_4)_{0.7}$ ,

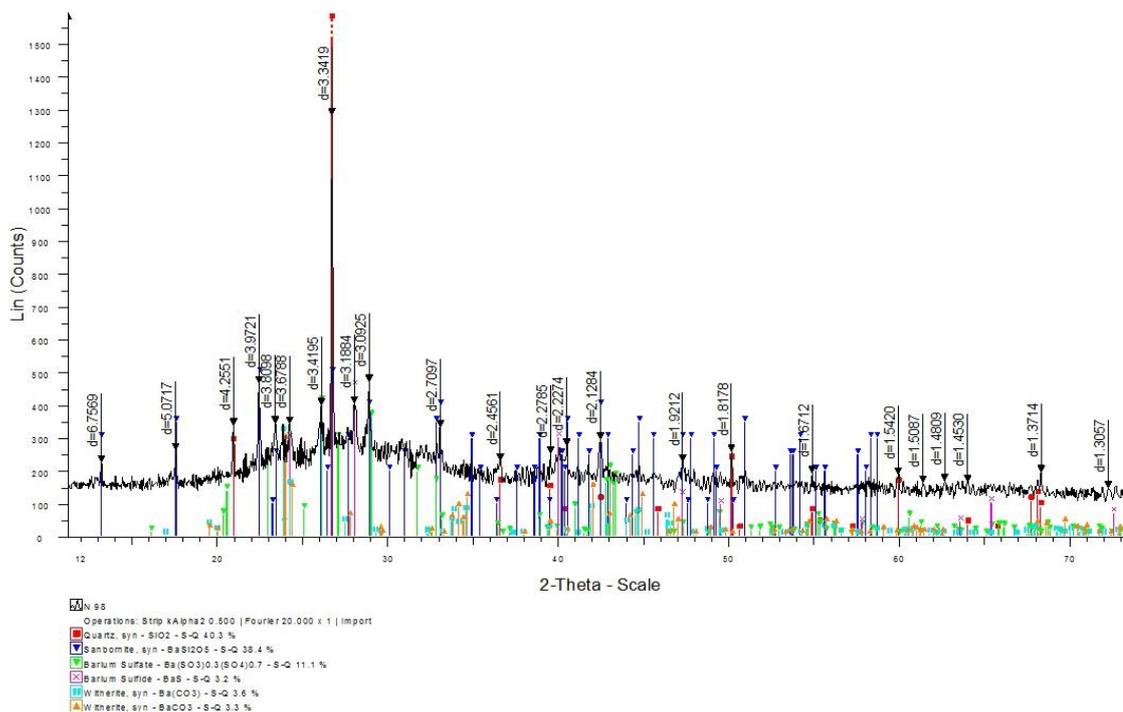
which has transitional nature during the formation of the sulfide compounds of barium.

Reviewing the results of x-ray phase analysis of the sinter synthesized at 1073 K allows to state that besides solid solutions on  $BaO$  and  $SiO_2$  on base, the destruction of the crystal grid of barite is coming along with the formation of sulfate-sulfite compound. The sinter also displays the presence of barium thiosalts, where cation of barium is an initiator of formation of thiosalts of the  $Ba_nMe_mS_z$  type presence of thiocompounds of  $BaCu_2SnS_4$ ,  $Ba_3Fe_5S_5$ ,  $BaFe_2S_4$ ,  $Ba_9Fe_4S_{15}$ . Parameters of these compounds are shown on the XRD pattern (Figure 4 a, b).



Phases are  $SiO_2$ ,  $Ba_2Si_3O_8$ ,  $Ba_5Si_8O_{21}$ ,  $BaCO_3$ ,  $Ca_8(Al_{12}O_{24})(MoO_4)_2$ ,  $Ba_4(Si_6O_{16})$ ,  $(Ba,Pb)SO_4$ ,  $BaFeSi_4O_{10}$ ,  $Ba_2(Si_4O_{10})$ ,  $BaSO_4$ ,  $Ba(SO_3)_{0.3}(SO_4)_{0.7}$ ,  $BaCu_2SnS_4$ ,  $Fe_2O_3$ ,  $BaFe_2S_4$ ,  $BaSiO_3$  (a);  $SiO_2$ ,  $BaSi_2O_5$ ,  $Ba_4(Si_6O_{16})$ ,  $CaMg_{5.2}Fe_{4.8}(Si_2O_6)$ ,  $Ba(SO_4)$ ,  $Ca_8(Al_{12}O_{24})(MoO_4)_2$ ,  $Ba_3Fe_5S_5$ ,  $Ba(CO_3)$ ,  $BaCu_2SnS_4$ ,  $BaCO_3$ ,  $Ba_4CaCu_{2.38}O_{7.52}(SO_4)_{0.5}$ ,  $Ba_9Fe_4S_{15}$ ,  $Fe_2O_3$  (b).

Figure 4 - XRD pattern of the mix sinter, containing 25%  $Na_2SO_4$  and 15% C, obtained at temperature of 1073 K



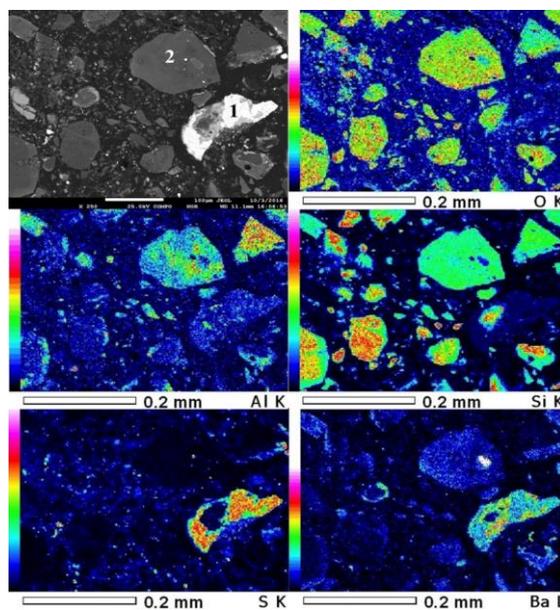
Phases are SiO<sub>2</sub>, BaSi<sub>2</sub>O<sub>5</sub>, Ba(SO<sub>3</sub>)<sub>0.3</sub>(SO<sub>4</sub>)<sub>0.7</sub>, BaS, BaCO<sub>3</sub>.

Figure 5 - XRD pattern of the mix sinter, containing 25% Na<sub>2</sub>SO<sub>4</sub> and 15% C, obtained at temperature 1173 K

The XRD pattern of the sinter synthesized at the temperature of 1173 K, traces sulfide of barium that is a sign of the processes of decomposition of unstable compounds (Figure 5).

The EPMA scanning of the sinter showed the presence of secondary minerals of complex composition, i.e. of leadhillite Pb<sub>4</sub>(SO<sub>4</sub>)(CO<sub>2</sub>)(OH)<sub>2</sub> and hyalophane (K, Ba)[Al(Si, Al)Si<sub>2</sub>O<sub>8</sub>] (Figure 6).

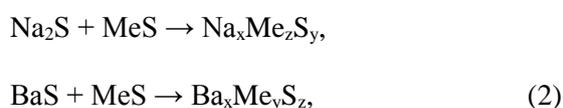
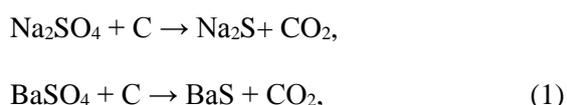
**Results and Discussion.** The process of sintering of the oxidized lead-zinc barite ore sample in presence of the sodium sulfate and carbonaceous reductant at temperature range of 973-1173 K performed with activated interaction of solid-phase components starts with the transformation of the crystal grid of the barite and leads to the formation of sulfides of sodium and barium, and formation of oxidized thiocompounds. Transformations conditioned by the loss of ordered structure of one of the crystal subgrids happen due to the high mobility of ions forming the sub-grids. The barium sulfates present in system are characterized by the high symmetry of the crystal grid, since the anions



1 – leadhillite Pb<sub>4</sub>(SO<sub>4</sub>)(CO<sub>2</sub>)(OH)<sub>2</sub>; 2 – hyalophane (K, Ba)[Al(Si, Al)Si<sub>2</sub>O<sub>8</sub>] (COMPO, ×250).

Figure 6 – Sinter. Coupling of barite with lead apposition with concentration of elements in minerals (EDS, ×250)

are regularly located and cations are scattered between positions in disorder. When exposed to the low-temperature synthesis, the transformation of the low-symmetry crystal grid occurs with the formation of the anion sub-grid. Cation sub-grid is prone to significant positional disorder, which is accompanied by changes in enthalpy, entropy. These transformation processes occur in several steps with gradual removal of the oxygen from the crystal grid, where the aggregate processes can be described with following reactions:

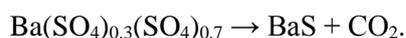


where  $n = 1-5$ ,  $m = 1-8$ .

Depending on the ratio of  $\text{BaO} : \text{SiO}_2$  content, certain main types of the polymer radicals of barium silicates are formed. These transformations go in parallel with the formation of the barium thiosalts. EPMA scanning state the new formation of the artificial mineral phases of barium, in particular, hyalophane  $(\text{K},\text{Ba})[\text{Al}(\text{Si},\text{Al})\text{Si}_2\text{O}_8]$ , which is related to the subgroup of potassium-barium feldspar. Presence of the K, Al, Si components found in the oxidized lead-zinc ore from the Alashpai deposit exposed to the solid-phase sintering is the condition for the possibility of formation of grains of hyalophane, crystalized in monoclinic crystal system. Proximity of the ionic radiuses of cations  $\text{K}^+$  and  $\text{Ba}^{+2}$  ensures the equivalent swap in crystal grid, similar is the swap in  $\text{Si}^{+2}$  and  $\text{Al}^{+3}$ .

Formation of the series of double solid solutions on  $\text{BaO} \cdot \text{SiO}_2$  bases in the batch under study sets forth the conditions for the new formation and appearance of more complex tripled solid solutions, as a results of which new artificial mineral phases are formed.

Formation of the barium sulfide takes place through the intermediate sulfite-sulfate bond following the scheme:



Next, barium sulfide forms similar thiosalts with copper and ferrum, such as  $\text{BaCu}_2\text{SnS}_4$ ,  $\text{Ba}_3\text{FeS}_5$ ,  $\text{BaFe}_2\text{S}_4$ ,  $\text{Ba}_9\text{Fe}_4\text{S}_{15}$  under the temperature of 1073 K. Increase of the temperature up to 1173 K leads to the destruction of the barium's thiocompounds with release of BaS in the a separate phase.

Phase formations occurring under the temperature 973-1173 K in presence of the carbonaceous reductant proceed in the solid phase because of the activation of the sodium and barium sulfates, which, as it is known, possess an imperfect structure, abundant of dislocations and inter-block boundaries, the impact of which is more significant as the sintering temperature gets higher. Under sintering conditions, sulfates convert into sulfides, which are characterized by the abnormally high mobility of cations, even under moderate heating temperatures. The dominating mechanism of the mass transfer in the interaction of barium sulfate with the reductant (1), in our opinion, is the formation of uninterrupted layer of BaS product and simultaneous transfer of the oxygen through the gas phase. Formation of the thiosalts of barium (2), most likely, is determined by the combination of two mechanisms, i.e. opposite diffusion of cations and migration of ions through the layer of product.

The dominating mechanism in processes of barium silicates formation (3), most probably shall be attributed to opposite diffusion of cations in the rigid oxygen frame being limited by the diffusion of  $\text{Si}^{+4}$  ions.

Process of phase formation during the sintering in solid phase, as it appears, combines transformation of two types, i.e. transformation of the first type that reflects the processes of the disordering of the cations sub-grid, and transformation of the second type that is caused by the changes in symmetry of the anion sub-grid. During the low temperature synthesis of the oxidized ores from the Alashpai deposit, the barium sulfate, contained in them, undergoes the change of the crystal grid related to the break in symmetry in cation and anion sub-grids. Sintering process of the oxidized ores at the temperatures of  $1073 \pm 323$  K leads to the ordered distribution of barium cations and vacancies throughout the crystallographic cation positions.

**Conclusion.** Researching of the barite phase formation processes during the sintering of the mix containing oxidized lead-zinc ore from the Alashpai deposit, sodium sulfate, carbonaceous reductant was carried out within the temperature interval of 973-1173 K. It was found that at the temperatures of 973, 1073 K decomposition of the barite crystal lattice occurs with the release of intermediate sulfate-sulfite complex of  $\text{Ba}(\text{SO}_3)_{0.3}(\text{SO}_4)_{0.7}$ . In presence of

SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> there is formation of metasilicate of barium BaO-SiO<sub>2</sub>, and of characteristic for the series of solid solutions, such compounds as Ba<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, Ba<sub>5</sub>Si<sub>8</sub>O<sub>21</sub>, Ba<sub>4</sub>(Si<sub>6</sub>O<sub>16</sub>), Ba<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>), BaFeSi<sub>4</sub>O<sub>10</sub>, BaSi<sub>2</sub>O<sub>5</sub>, in addition there is observation of the new formations of the artificial mineral phase of barium like hyalophane (K, Ba)[Al(Si, Al)Si<sub>2</sub>O<sub>8</sub>]. In parallel, the process results in phase formation of barium thiosalts, i.e. BaCu<sub>2</sub>SnS<sub>4</sub>, BaFe<sub>2</sub>S<sub>4</sub>, Ba<sub>3</sub>FeS<sub>5</sub>, Ba<sub>9</sub>Fe<sub>4</sub>S<sub>15</sub>. It is noted also that under the temperature of 1173 K, the sublimation process with the obtaining of nonferrous metals' sulfides get intensified; the sinters show the presence of barium sulfide (BaS); solid solutions get decomposed with the formation of silica dioxide, barium sulfate and barium carbonate.

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## ТҮЙІНДЕМЕ

Алашпай кенорнының тотыққан қорғасын-мырышты баритті кендерін, натрий сульфатын, көмір құрамды тотықсыздағыш, 973-1173 К температура аралығында рентгенфазалық және электрлі-зондты анализдерін қолдана отырып, барит қождамасын күйдірудің фазқұрылымы зерттелді. Зерттеу нысаны ретінде Алашпай кенорны кендерінің сынамасы алынды, рентген-флюоресценттік анализдердің нәтижесі бойынша құрайтын салмағы. %: 6,158 Pb; 6,978 Ва; 0,016 Zr; 0,222 Zn; 0,063 Cu; 3,955 Fe; 0,603 Mn; 0,270 Ti; 0,265 Са; 0,684 К; 1,226 S; 13,702 Si; 4,527 Al; 0,967 Mg; 0,244 Na, қалғаны – оттегі және тағы басқалары. Фазқұрылым 973 К температурасында екі түрдің араласуын қатыстырады: бір реттік тура тор асты катионы және анион тор астының симметриясының өзгеруі. Ары қарай жалғасуымен барий катионы кристаллографиялық бағытының бос қалуымен бөлімденеді. 973 К температурасында алынған күйінің рентгенфазалық анализдерінің нәтижесінде, барий силикаттарының болуы ВаSiO<sub>3</sub>, Ва<sub>4</sub>Si<sub>6</sub>O<sub>16</sub>, сонымен қатар аралық сульфатты-сульфидті жиынтық Ва(SO<sub>3</sub>)<sub>0.3</sub>(SO<sub>4</sub>)<sub>0.7</sub>. 1073 К температурасында барий тиотұзының пайда болатыны анықталған ВаCu<sub>2</sub>SnS<sub>4</sub>, ВаFe<sub>2</sub>S<sub>4</sub>, Ва<sub>3</sub>FeS<sub>5</sub>, Ва<sub>9</sub>FeS<sub>15</sub>, сонымен бірге пайда болатын ВаSiO<sub>3</sub>, Ва<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>, Ва<sub>5</sub>Si<sub>8</sub>O<sub>21</sub>, Ва<sub>4</sub>(Si<sub>4</sub>O<sub>10</sub>), ВаFeSi<sub>4</sub>O<sub>10</sub>. Осы күйінің ішінде барий катионы тиотұзының құрылуының бастамашысы болып табылады Ва<sub>n</sub>Me<sub>m</sub>S<sub>z</sub>. Температураны 1173 К дейін көтерген кезде барий қосындысының бұзылуы көрінеді. Барий тиотұзы барий сульфидінің пайда болуымен жалғасады, тиотұздың кристалдық торының неқұрлым оңай құрылымға өтеді. Барий силикатының негізіндегі қатты ерітінділер өзгеріске түсу жағдайы өтеді және сонымен қатар кремний оксидін құрайтын заттарға ауысады, барий және ары қарай барий сульфаттары және карбонаттарының құрылу процестері жүреді.

**Түйін сөздер:** барит, барий тиотұздар, барий силикаттар, барий сульфиді, күйежентек.

## РЕЗЮМЕ

Представлены результаты работы по изучению фазообразования барита при переработке окисленных свинцово-цинковых руд месторождения Алашпай методами металлургии тиосолей. Фазообразование барита при спекании шихты, включающей окисленную свинцово-цинковую баритовую руду месторождения Алашпай, сульфат натрия, углеродсодержащий восстановитель исследованы в интервале температур 973-1173 К с использованием рентгенофазового и электронно-зондового анализов. В качестве объекта исследований взята проба руды месторождения Алашпай, содержащая по данным рентгенофлюоресцентного анализа, мас. %: 6,158 Pb; 6,978 Ва; 0,016 Zr; 0,222 Zn; 0,063 Cu; 3,955 Fe; 0,603 Mn; 0,270 Ti; 0,265 Са; 0,684 К; 1,226 S; 13,702 Si; 4,527 Al; 0,967 Mg; 0,244 Na, остальное – кислород и прочие. Фазообразование при температуре 973 К совмещает превращения двух типов: разупорядочение катионной подрешетки и изменение симметрии анионной подрешетки. Впоследствии катионы бария распределяются по вакансиям кристаллографических позиций. По результатам рентгенофазового анализа в спеке, полученном при 973 К, присутствуют силикаты бария ВаSiO<sub>3</sub>, Ва<sub>4</sub>Si<sub>6</sub>O<sub>16</sub>, а также промежуточный сульфатно-сульфитный комплекс Ва(SO<sub>3</sub>)<sub>0.3</sub>(SO<sub>4</sub>)<sub>0.7</sub>. Установлено, что при температуре 1073 К образуются тиосоли бария ВаCu<sub>2</sub>SnS<sub>4</sub>, ВаFe<sub>2</sub>S<sub>4</sub>, Ва<sub>3</sub>FeS<sub>5</sub>, Ва<sub>9</sub>FeS<sub>15</sub>, параллельно образуются ВаSiO<sub>3</sub>, Ва<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>, Ва<sub>5</sub>Si<sub>8</sub>O<sub>21</sub>, Ва<sub>4</sub>(Si<sub>4</sub>O<sub>10</sub>), Ва<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>), ВаFeSi<sub>4</sub>O<sub>10</sub>. В этих спексах катион бария является инициатором образования тиосолей типа Ва<sub>n</sub>Me<sub>m</sub>S<sub>z</sub>. Повышение температуры до 1173 К способствует разрушению соединений бария. Тиосоли бария разлагаются с образованием сульфида бария, кристаллическая решетка тиосоли распадается на более простые структуры. Твердые растворы на основе силиката бария претерпевают изменения и также распадаются на составляющие оксиды кремния, бария и далее происходят процессы образования карбонатов и сульфатов бария.

**Ключевые слова:** барит, тиосоли бария, силикаты бария, сульфид бария, спекание, фазообразование, окисленные свинцово-цинковые руды, месторождение Алашпай, металлургия тиосолей

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