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Sulfidation of Zinc oxide by interaction with Antimony sulfide

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The mechanism of interaction between ZnO and Sb_2S_3 in the temperature range of 500-700°C was studied. The methods of differential thermal analysis, X-ray diffraction, diffuse reflectance spectroscopy and IR transmission spectroscopy, as well as thermodynamic calculations established the exchangeable acid-base reaction mechanism with the removal of the most volatile of the products – Sb_2O_3. The final and only product of interaction in the system is ZnS of cubic modification (sphalerite) without phase impurities. Condensate mainly contains Antimony oxides of various compositions. In the same way, it is possible to remove oxygen-containing impurities (mainly ZnO) from zinc sulfide obtained by the method of self-propagating high-temperature synthesis.

Keywords: Zinc oxide, Antimony sulfide, acid-base interaction, sulfidation.

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Introduction

Zinc sulfide serves as the basis for creating a number of optical materials, in particular phosphors, materials for interference optics, pigments, etc. [1-3]. The product obtained by various methods, in addition to the main substance, contains (often in noticeable quantities) oxygen-containing impurities (zinc oxide, hydroxide, carbonate, sulfate, etc.). For various reasons, they are not standardized by product manufacturers. These impurities, in the case of using ZnS as a starting material for applying thin-layer coatings with a high refractive index by thermal evaporation in a vacuum, worsen the optical and operational parameters of interference optics. This is due to the possibility of reactions between the oxide impurity and the evaporator material (molybdenum) occurring in high vacuum and at high temperatures. The feasibility and necessity of removing or neutralizing the ZnO impurity in Zinc sulfide follows from the assumption of the possibility or impossibility of the interaction of both substances with the evaporator material.

The calculation of the thermodynamic functions of individual components and chemical reactions between them under standard conditions and high temperatures was carried out according to the standard method [4].

Calculated thermodynamic characteristics were obtained based on data for reactions at room temperature (298 K) and the conventional temperature of ZnS evaporation (1173 K). The equations of possible reactions have the following form:

$$2ZnO(s.) + Mo(s.) \xrightarrow{T} MoO_2(s.) + 2Zn(g.)\uparrow,\ \Delta G_r^\circ = –64{,}1\ kJ/mole; \quad (1)$$

$$2ZnS(s.) + Mo(s.) \xrightarrow{T} MoS_2(s.) + 2Zn(g.)\uparrow,\ \Delta G_r^\circ = +213.5\ kJ/mole. \quad (2)$$

As it follows from the calculations, both reactions are endothermic and also occur with an increase in entropy. However, the total balance of the enthalpy and entropy components of Gibbs energy (1173 K) leads to its negative value for reaction (1) and positive for reaction (2). Thus, ZnS practically does not react with Mo, and ZnO reacts with the formation of metallic zinc, which is volatile under these conditions. It condenses in the coating together with zinc sulfide, forming centers of optical absorption and scattering, and also causes mechanical stress on the coating. In addition, oxygen-containing impurities cause «dips» to appear in the region of 14-15 μm, which limits the transparency of ZnS-based ceramics [5-7].

Therefore, considerable attention has recently been paid to the maximum possible elimination of oxygen-containing impurities in ZnS. For this, a number of alloying additives have been developed – mainly lanthanide sulfides, which bind ZnO with the help of exchange reactions into a less reactive form – lanthanide oxosulfides [8-10]. At the same time, methods of complete removing oxygen-containing impurities from Zinc sulfide have not been developed to date. Moreover, this also applies to the quantitative assessment of impurity content.

The purpose of this work is to investigate the possibility of using Sb_2S_3 as a sulphiding agent with the simultaneous removal of volatile oxide compounds formed during the reaction, and to clarify its mechanism.

I. Experimental part

The following reagents were used: Zinc oxide (ZnO), obtained by calcination of Zinc hydroxycarbonate of composition $2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$ of special purity grade at 1250°C, followed by cooling in a desiccator over $CaCl_2$; Zinc sulfide (ZnS) and Antimony (III) sulfide (Sb_2S_3) produced by JV «New Materials and Technologies», Odessa (TU V3-639-88 and TU V3-613-84, respectively). Zinc sulfide was obtained using the technology of self-propagating high-temperature synthesis (SHS) [11], and Antimony sulfide was obtained by fusing the components in a vacuum ampoule. In terms of the content of chromophore impurities (Cu, Fe, Cr) – at the level of 10^{-3} wt. % – the substances correspond to the «special purity» qualification. The content of ZnO in ZnS is not standardized, but the synthesis method itself is from powders of sulfur and metallic zinc of the PT-1 brand, containing up to 4% by mol. ZnO – indicates the possibility of the presence of an oxide impurity – in the form of a separate phase of ZnO or a solid solution in ZnS. The formation of a solid solution is favored by the significant wurtzite content in the SHS product, since ZnO crystallizes in a similar (hexagonal) structure.

The ZnS sample contained both polymorphic modifications – sphalerite ($a = b = c = 5.407$ Å) and wurtzite ($a = b = 3.820$ Å, $c = 6.251$ Å). It should be noted that the authors of [11] denied the presence of significant amounts of ZnO impurities in the samples of the SHS method, which is clearly indicated by absorption bands in the IR spectra in the region ≈ 400-420 cm^{-1}. Most likely, an attempt to extract Zinc oxide embedded in the ZnS lattice during chemical analysis gave greatly underestimated results on its content. To substantiate the reasons for the sharp decrease in the ZnO content as a result of the SHS process, the authors point to the reaction of Zinc oxide with elemental sulfur allegedly occurring at temperatures above 800 K to form ZnS and SO_2. However, our thermodynamic calculations do not confirm this possibility.

A preliminary prediction of possible double exchange reactions was made using the concept of acidity-baseness. It is believed that they occur according to the scheme:

$$3ZnO(s.) + Sb_2S_3(l.) \leftrightarrow 3ZnS(s.) + Sb_2O_3(g.)\uparrow. \qquad (3)$$

It has been established that Zn^{2+} and Sb^{3+} ions belong to the group of acids of intermediate type, as well as O^{2-} and S^{2-} ions belong to hard and soft bases, respectively, in terms of softness and hardness according to Pearson [12]. Therefore, the exchange reaction has a little effect on the nature of the «soft-hard» combination. In this regard, we can use the electronegativity criterion we developed as a measure of acidity-basicity [13]. According to this criterion, the exchange reaction is possible if the electronegativity difference of the reaction products ($\Delta\chi_2$) is smaller than that of the starting reactants. Indeed,

$$\Delta\chi_1 = 2.47 - 1.59 = 0.88;$$
$$\Delta\chi_2 = 2.18 - 1.88 = 0.30,$$

i.e. $\Delta\chi_2 < \Delta\chi_1$, which indicates the fundamental possibility of an exchange reaction in the system under study.

The given prediction is confirmed by the data of thermodynamic calculations of the reaction. As can be seen from Table 1, the indicated reaction (3) is exothermic and proceeds with a negative change in entropy. It should be noted that the evaporation of Sb_2O_3 contributes to the shift of the equilibrium to the right side, and therefore to the increase of the efficiency of the process.

Heat treatment of the ZnO + Sb_2S_3 charge was carried out in an atmosphere of deeply purified argon in a high-temperature tubular (horizontal) furnace RHTC 80-450 manufactured by Nabertherm (Germany) with automatic temperature control with an accuracy of ±1°C. The choice of heat treatment mode follows from the need to take into account several factors: a) carrying out the process in the liquid phase region of one of the reagents, namely Sb_2S_3 (mp ~560°C); b) carrying out the interaction process at a minimum vapor pressure of Sb_2S_3 (less than 0.1 mm Hg) and a maximum ratio of the vapor pressure of one of the volatile reaction products Sb_2O_3 and Antimony sulfide (it should be noted that the volatility of ZnO and ZnS in this region is negligible); c) carrying out complete distillation of the volatile product, Sb_2O_3, in liquid phase mode (mp ~660°C).

As follows from the temperature dependences of the elasticity of the Sb_2S_3 and Sb_2O_3 vapor (Table 2), constructed according to data [14, 15], the most favorable ratio is in the temperature range of 500-800°C. The influence of temperature and duration of heat treatment on the degree of interaction between ZnO and Sb_2S_3 was also studied. To do this, well ground and pressed into tablets, samples of the charge, consisting of components taken in a stoichiometric ratio, were subjected to sequential stepwise heat treatment (for 2 hours at each stage) at temperatures of 500, 600 and 700°C. Next, heat treatment

Table 1.

Thermodynamic characteristics of the double ion exchange reaction (3) of ZnO sulfidation

Compound	ΔH°_T, kJ/mole		S°_T, J/mole·K		ΔH°_r, kJ/mole	ΔS°_r, J/mole·K	ΔG°_r, kJ/mole
	ΔH°_{298}	ΔH°_{873}	S°_{298}	S°_{873}			
ZnO	–350.5	–320.8	43.6	99.35			
Sb_2S_3	–205.0	–80.8	182.0	381.3			
ZnS (sphalerite)	–205.0	–172.7	57.7	112.7			
Sb_2O_3 (rhombic)	–708.6	–650.3	123.0	232.0			
The reaction (3), T = 873 K					–125.2	–109.3	–29.8

Table 2.

Temperature dependences of saturated vapor pressure of compounds

Compound / T, °C	ZnS	Sb_2S_3	Sb_2O_3	$\lg \frac{P_{Sb_2O_3}}{P_{Sb_2S_3}}$
	lgP (mmHg)			
400		–3.44 *s.*	–3.21 α	0.17
450		–2.485 *s.*	–2.14 α	0.34
500		–1.64 *s.*	–1.21 α	0.43
550		–1.23 *s.*	–0.39 α	0.84
600		–0.66 *l.*	0.30 β	0.96
650		–0.146 *l.*	0.91 β	1.06
700		0.31 *l.*	1.17 *l.*	0.86
750		0.725 *l.*	1.37 *l.*	0.64
800	–2.33 α	1.10 *l.*	1.545 *l.*	0.44

Note: *s.* – solid; *l.* – liquid; α, β – polymorphic modifications (α – low-temperature, β – high temperature).

temperatures of 600 and 700°C were selected, lasting 4 and 3 hours, respectively.

The thermograms of the sample were recorded on a computerized Derivatograph D 1000 device from MOM (Hungary) at temperatures from 20 to 750°C, at a speed of 5°/min. The sensitivity of the device is 0.25°. The sample was prepared by thoroughly grinding the starting components (ZnO and Sb_2S_3 in a ratio of 3:1 mole) in an agate mortar. The resulting mixture was placed in an ampoule made of quartz glass and dried under vacuum at 300°C. After cooling, the ampoule was evacuated and sealed. The obtained thermograms are shown in Fig. 1.

Identification of the synthesized samples was carried out by X-ray phase diffraction (XRPD) analysis on an automated DRON-3M installation (CuK_α radiation) according to standard methods.

Electronic diffuse reflectance spectra were recorded on a Lambda 9 spectrophotometer (Perkin Elmer, USA) in the visible and near-IR ranges of the spectrum (400-800 nm). Finely dispersed MgO served as a comparison sample. The spectral dependences of the Kubelka-Munk function were recorded:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s}, \qquad (4)$$

where: R is relative reflection; k, s – absorption and scattering coefficients, respectively.

IR transmission spectra in the range 4000-200 cm^{-1} were recorded on a Frontier Perkin Elmer (USA) spectrometer with Fourier transform. To record the spectrum, the samples were ground with CsI (Ukraine, Institute of single crystals, Kharkiv) high purity grade in a ratio of 1:20. The CsI sample was preheated at 180°C to remove residual moisture.

II. Experimental results and their discussion

In thermogram 1 (Fig. 1), in the range of 500-560°C, a double exothermic effect is observed with one unpronounced and a second pronounced maximum at 515 and 530°C, respectively. This effect corresponds to the primary stage of interaction of the initial components according to the scheme:

$$ZnO + Sb_2S_3 \rightarrow Sb_2S_2O + ZnS. \qquad (5)$$

Thus, an intermediate product called kermesite is probably formed [16].

Further, with increasing temperature, the endothermic effect follows with a minimum at 623°C, characterizing the process descripted by the general scheme:

$$3Sb_2S_2O \rightarrow 2Sb_2S_3 + Sb_2O_3. \qquad (6)$$

The minimum then changes to a maximum at 650°C, which is probably caused by the crystallization of Sb_2O_3.

After cooling, the sample in the ampoule changed color from black to light brown. During repeated second thermography (Fig. 1, curve 2), the interaction of intermediate components manifests itself as an extended exothermic effect with a plateau at temperatures of 440-480°C. These effects can be described by the following interaction:

$$2ZnO + Sb_2S_2O \rightarrow 2ZnS + Sb_2O_3. \qquad (7)$$

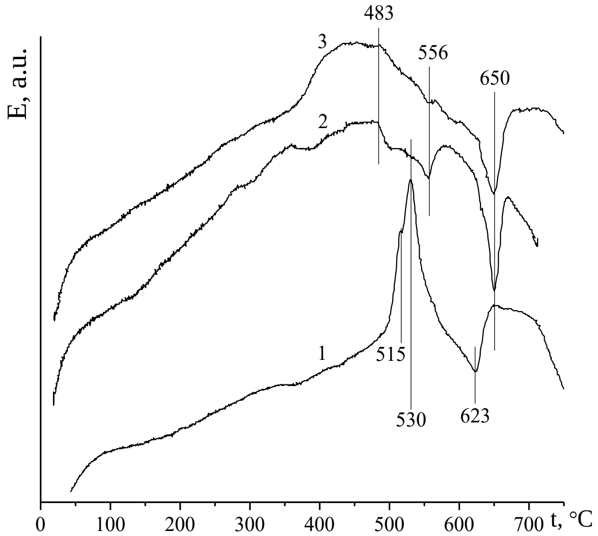

Fig. 1. Thermograms of the ZnO–Sb_2S_3(3:1) system at various records: 1 – the first; 2 – the second; 3 – the third. Each subsequent recording was carried out after complete cooling of the sample.

Endothermic effects with minima at 556 and 650°C can be explained by the melting of Sb_2S_3 and Sb_2O_3, respectively.

During the third recording of thermography (Fig. 1, curve 3), the intermediate products obtained during preliminary calcination finally interact, which is expressed by an extended flat exothermic effect in the range of 370-490°C.

The increasing endo effects at a temperature of 650°C are associated with the melting of the resulting Antimony oxide. Endothermic effects decreasing in area in the region of 550°C correspond to a decrease in the amount of Antimony sulfide in the initial mixture.

Thus, the process of interaction of the initial components is well controlled by changes in the color of the sample and the presence of distinct endo- and exothermic effects. In addition, after the third thermography, the mixture is not completely white, but slightly colored in a light brown color; this means that the reaction is not complete, but the main stages and temperature intervals are defined.

Since the reaction between ZnO and Sb_2S_3, as can be seen from the thermograms, begins at a temperature above 500°C, a sample of the system, which was calcined at the mentioned temperature, was investigated by the XRD method (Fig. 2). As expected, it turned out to be polyphasic and contained phases of both initial reactants (ZnO and Sb_2S_3) and reaction products (ZnS, sphalerite and α-Sb_2O_3), as well as $ZnSb_2O_4$. It should be noted that many of the diffraction peaks turned out to be such that it was impossible to assign them to any of the possible phases with a clear stoichiometry. This primarily concerns the phase attributed to the composition $SbO_{3.5}$ (card no. 96-901-5893 with reference to [17]). Due to the significant number of peaks for the compound Sb_2S_3, which, according to various data, coincide only partially, it turned out to be quite difficult to identify the phase for this compound compared to the phases of other components of the systems. However, the obtained data clearly confirm the course of the exchange reaction in the system. The final product of the heat treatment process at 700°C is ZnS, sphalerite without any impurity phase.

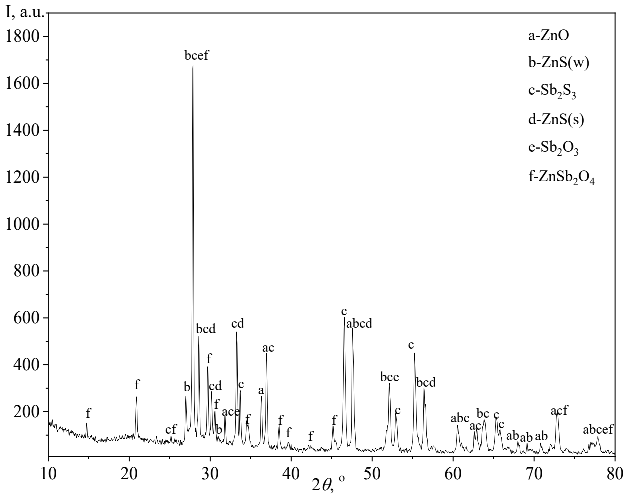

Fig. 2. Diffraction pattern of a sample of the ZnO–Sb_2S_3 system (3:1) after calcination at 500°C:
a – ZnO [$a = b = 3.22183$ Å, $c = 5.20337$ Å] (zincite);
b – ZnS [$a = b = 3.82068$ Å, $c = 12.5055$ Å] (wurtzite);
c – Sb_2S_3 [$a = 10.7563$ Å, $b = 4.10425$ Å, $c = 10.956$ Å] (stibnite); d – ZnS [$a = b = c = 5.40792$ Å] (sphalerite);
e – α-Sb_2O_3 [$a = b = c = 11.14$ Å] (senarmontite);
f – $ZnSb_2O_4$ [$a = b = 8.508$, c = 5.932 Å].

As can be seen from the diffuse reflectance spectra, ZnS and ZnO contain absorption bands with a weak «tail» in the visible region of the spectrum.

Antimony sulfide is opaque in the UV and visible spectral ranges (absorption band with a maximum at 740 nm, Fig. 3, curve 1) and transparent in the near IR interval of a spectrum.

On the basis of the diffuse reflectance spectra of the ZnO–Sb_2S_3 system, the integral intensities (the areas) under the bands corresponding to the absorption of Antimony sulfide (ZnO, like ZnS and Sb_2O_3, is known to have almost no absorption in the visible range) were determined. The relative integral intensity of Sb_2S_3 is taken as 1. The calculated values of the integral intensity (Table 3) and its relative values indicate the course of the process, which intensifies with increasing temperature and duration. The integrated absorption intensity drops sharply when mixing Sb_2S_3 with ZnO, which, as noted, does not contain absorption bands in the visible range. When this mixture (charge) is fired, the relative integral intensity further decreases, apparently due to the interaction of Sb_2S_3 with ZnO with the formation of colorless compounds (ZnS and Sb_2O_3). As the firing temperature increases, the drop in the integral intensity of absorption intensifies, especially at the transition from 500° to 600°C. After calcination at 700°C, the integrated intensity stops falling, apparently due to complete depletion of Sb_2S_3 in the reaction and accumulation of ZnS.

Long-term sequential heat treatment of a charge with a stoichiometric ratio of ZnO:Sb_2S_3 = 3:1 at 600 and 700°C ultimately leads to the production of a product consisting entirely of sphalerite (cubic modification of ZnS). It is worth noting that the loss of charge mass at the indicated temperatures (9.3 and 22.0 %, respectively) correlates with the values of Sb_2O_3 vapor pressure (Table

2). In the case of an insufficient amount of Sb_2S_3 ($ZnO:Sb_2S_3 < 3:1$), one of the end products of the reaction, in addition to ZnS, is a complex oxide of the composition $ZnSb_2O_4$. It should be noted that the color of the sublimate (white with a grayish tint) is similar to the color of the Sb_2O_3 sample obtained by burning Antimony sulfide in open air at 700°C.

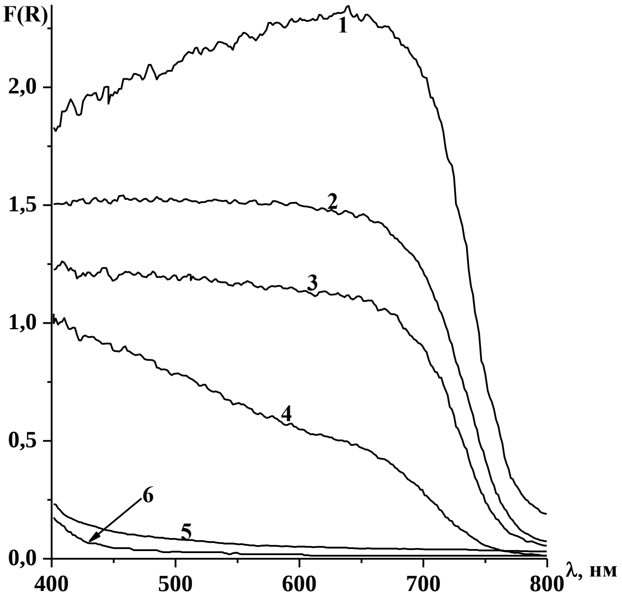

Fig. 3. Spectra of diffuse reflection in the visible and near-IR ranges of the spectrum of samples of the $ZnO–Sb_2S_3$ system (3:1): 1 – Sb_2S_3; 2 – initial charge $ZnO–Sb_2S_3$; 3 – charge after calcination at 500°C; 4 – the same at 600°C; 5 – the same at 700°C; 6 – ZnS.

In the IR spectrum of Antimony sulfide, no absorption bands in the region of 500-800 cm^{-1} corresponding to stretching vibrations of Sb–O bonds were detected (Fig. 4, curve 3). In the IR spectrum of the Sb_2O_3 sample (Fig. 4, curve 1), in addition to the bands of valence vibrations of Sb–O bonds, which are characteristic of it, there are also bands characteristic of SO_3 groups.

As can be seen from fig. 4, the IR spectrum of ZnO contains a broad band with a minimum in the range of 450-500 cm^{-1} with negligible transmittance in general. Instead, the IR transmission spectra of ZnS are curves with sharp minima near 300 cm^{-1}. Their position corresponds to lattice (valence) vibrations of Zn–S bonds. At the same time, the product of the SHS process has a more pronounced character, compared to the product of ZnO sulfidation, and also contains an additional peak at $\tilde{\nu} = 415$ cm^{-1}. The latter is most likely related to the oscillation of the Zn–O bonds of the ZnO impurity in the ZnS matrix. It should be recalled that the product of the SHS method contains both wurtzite and sphalerite modifications of ZnS, while the sulfurization product is single-phase (sphalerite).

The IR transmission spectra of both Sb_2S_3 and the sulphidation by-product, Sb_2O_3, have a completely different appearance compared to Zinc compounds. As can be seen from the table 4, the IR spectrum of the product of incomplete sulfidation contains a large number of absorption bands corresponding to different phases – both initial reactants (ZnO, Sb_2O_3) and reaction products (ZnS, sphalerite, and various Antimony oxides). Instead, the IR spectrum of the sublimate in the cold parts of the reactor contains only the absorption bands of volatile

Table 3.

Change in diffuse reflectance spectra in the $ZnO–Sb_2S_3$ (3:1) system

Spectral curve number	Sample composition and processing temperature	The area of the band under the curve	Ratio between areas
1	Sb_2S_3	736.42	1.000
2	Initial charge $ZnO–Sb_2S_3$	494.29	0.671
3	Charge after calcination at 500°C	378.02	0.513
4	the same at 600°C	209.03	0.284
5	the same at 700°C	26.95	0.037
6	ZnS	11.04	

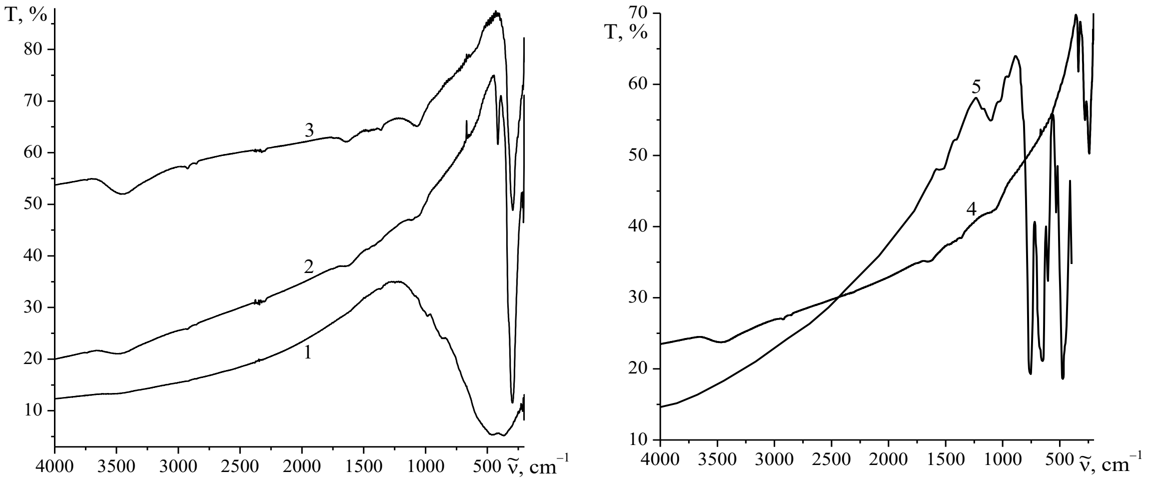

Fig. 4. IR transmission spectra of samples of the $ZnS(ZnO)–Sb_2S_3$ system: 1 – ZnO; 2 – ZnS (SHS); 3 – ZnS (made by sulfidation of ZnO); 4 – Sb_2S_3; 5 – Sb_2O_3.

Table 4.

The position of the absorption bands on the IR transmission spectra of the heat treatment products of the ZnO–Sb_2S_3 (3:1) system

Substance	The position of the absorption maximum, cm^{-1}
Product of incomplete interaction between ZnO and Sb_2S_3 (500°C). Phases are possible.	1101 710 624 601 493 430 339 292 246 227 209 SiO_2, ZnO, ZnS (sphalerite), Sb_2S_3, Sb_2O_3, Sb_2O_4, Sb_2O_5, x-phase
Sublimate on the cold parts of the reactor. Phases are possible.	1101 1032 953 733 612 559 474 453 430 386 343 320 291 257 214 202 SiO_2, Sb_2O_4, Sb_2O_5, x-phase

products (mainly various Antimony oxides, etc.). The presence of SiO_2 absorption bands is related to the reactor material (quartz glass), and the appearance of SO_3 absorption bands indicates the possible deep oxidation of sulfur by higher Antimony oxides.

Conclusions

The presence and negative influence of zinc oxide admixture in zinc sulfide on the performance parameters of the resulting coatings and the need for ZnO sulfidation were established.

Based on the concept of electronegativity and thermodynamic calculations, the possibility of an exchange reaction between Zinc oxide and Antimony sulfide is predicted. The course of the reaction in the temperature range of 500-700°C was confirmed by methods of thermal analysis (thermography), X-ray phase analysis and spectroscopic methods. The developed method of sulfidation of zinc oxide can be applied to the ZnO admixture in zinc sulfide obtained by the method of self-propagating high-temperature synthesis (SHS), as well as to material obtained by other methods.

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Сульфідування оксиду Цинку взаємодією із сульфідом Стибію

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Досліджено механізм взаємодії між ZnO та Sb_2S_3 в інтервалі температур 500-700°C. Методами диференціального термічного аналізу, рентгенівської дифракції, спектроскопії дифузного відбиття та ІЧ спектроскопії пропускання, а також термодинамічних розрахунків встановлено обмінний кислотно-основний механізм реакцій з видаленням найбільш леткого з продуктів – Sb_2O_3. Кінцевим і єдиним продуктом взаємодії в системі є ZnS кубічної модифікації (сфалерит) без фазових домішок. Конденсат містить переважно оксиди Стибію різного складу. Таким же чином можливо видалити оксигенвмісні домішки (переважно ZnO) із сульфіду цинку, отриманого методом самопоширюваного високотемпературного синтезу.

Ключові слова: оксид Цинку, сульфід Стибію, кислотно-основна взаємодія, сульфідування.