

## Influence of $Ln_2S_3$ ( $Ln - Gd, Dy$ ) dopant on the crystal structure and optical properties of zinc sulfide

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**Data on the influence of the alloying dopants gadolinium or dysprosium sulfide on the crystal structure of ZnS prepared by self-propagating high-temperature synthesis (SHS) are presented. The dopants contribute to the removal of ZnO impurity from zinc sulfide by a reaction of double exchange resulting in the appearance of lanthanide oxysulfide,  $Ln_2O_2S$ . High-temperature annealing in deep vacuum produces significant changes in the crystal structure. Products of the reduction of  $Ln(III)$  were revealed by the presence of intense absorption bands in the UV range of the spectrum. Thin-film coatings on glass substrates have the character of a composite consisting of amorphous components and nanoparticles of the cubic modification of ZnS.**

### Zinc sulfide / Crystal structure / Dopant / Exchange reaction

#### 1. Introduction

It is well known that zinc sulfide (ZnS) obtained by synthesis in aqueous solutions crystallizes in two basic polymorphs (ZnS-3C / sphalerite, and ZnS-2H / wurtzite) [1]. It is possible to adjust the temperature of the phase transition  $ZnS-3C \leftrightarrow ZnS-2H$  by doping the zinc sulfide (introduction of additives) or by changing its stoichiometry. Vacuum has an influence on the phase transition as well, probably by producing a deviation from stoichiometry [1,2]. Zinc sulfide is traditionally used to obtain layers with a high refractive index ( $n = 2.25-2.30$ ) in interference coatings [3-6]. One of the main problems with ZnS is the presence of oxygen impurities in the form of ZnO or  $ZnSO_4$ , which causes light scattering of the layer and decreases its mechanical durability and adhesion to the substrate.

The last years, for ecological and technological reasons, the method of self-propagating high-temperature synthesis (SHS) has been widely applied for the preparation of zinc sulfide [7,8]. This method makes it possible to solve the problem of non-stoichiometry, however, questions concerning the presence of oxygen-containing impurities (introduced into ZnS as a superficial layer of ZnO with particles of metallic zinc) remain unsolved.

In previous works [9,10] we proposed to use lanthanide sulfides as dopants to improve the

properties of ZnS. However, the influence of these additives on the phase composition and crystal structure of zinc sulfide and other compounds (initial components and products of the interaction) remains unclear up to now.

#### 2. Experimental details

Zinc sulfide was prepared by the SHS method from zinc and sulfur powder of high purity. As during the high-temperature synthesis sulfur partially evaporates, an excess amount of 10 mass% was added. The reagents were ground and mixed in a ball mill. The mixture prepared in such a manner was submitted to a pressure of  $10^8$  Pa in cylinders of a diameter of 60 mm and a height of up to 200 mm. The samples were placed into a reactor, which was filled with compressed ( $\sim 1.5 \cdot 10^7$  Pa) inert gas (Ar). This procedure suppressed evaporation of the components (Zn and S) and, as a consequence, produced samples of ZnS with a composition close to stoichiometry. A ZnS sample synthesized this way is a melted bulk with zones differing slightly in phase composition (superficial, basic and central ones).

Additives of  $Ln_2S_3$  ( $Ln = Gd, Dy$ ) were obtained by traditional solid-state synthesis (SSS) [1]

**Table 1** Crystallographic data for ZnS–4H (SiC–4H type structure).

Atom	Position	x	y	z
Zn1	2b	1/3	2/3	0.452(2)
Zn2	2a	0	0	0.183(3)
S1	2b	1/3	2/3	0.244(5)
S2	2a	0	0	0.0
Space group	$P6_3mc$ (186)			
Lattice constants, Å	$a = 3.8220(2), c = 12.498(1)$			
Isotropic temperature factor, Å <sup>2</sup>	$B = 2.47(2)$			
Reliability factor	$R = 0.094$			

from elemental metals and sulfur of high purity. Samples containing 18.1 mass%  $Gd_2S_3$ , 18.5 or 5.0 mass%  $Dy_2S_3$ , respectively, were prepared by long sintering at ~900°C of freshly synthesized ZnS and  $Ln_2S_3$  in an inert atmosphere.

The structure and lattice constants of the phases, as well as their quantitative ratio, were determined by a technique developed by us [11] from data collected on an automated X-ray setup DRON 3 with filtered  $Cu K_\alpha$  radiation. The method for quantitative phase analysis is based on a mathematical algorithm considering simultaneous refinement of the crystal structure parameters (positional and thermal structure parameters, site occupancies, texture) for each phase. According to [12] the contribution of the  $i$ -th phase constituent to the peak intensity can be presented in the form:

$$I(hkl)^i = c_i Q_i \exp[-(\bar{\mu} - \mu_i) I_0] \quad (1)$$

where  $I(hkl)^i$  is the intensity of the reflection  $hkl$ ,

- $c_i$  is the volume content,
- $d_i$  is the mean particle size of the phase,
- $\mu_i$  is the linear absorption index,
- $Q_i$  is the reflectivity per volume unit,
- $\bar{\mu}$  is the average linear absorption index;
- $I_0$  is the intensity of the incident beam.

The reflectivity for the  $i$ -th phase constituent can be calculated from the equation:

$$Q_i = \frac{I(hkl)^{i0}}{V_i^2} \quad (2)$$

where  $I(hkl)^{i0}$  and  $V_i$  are the reflection intensity and unit cell volume for the  $i$ -th phase constituent, respectively.

A series of standard mixtures of various kinds (samples of known quantitative composition) were used to test the program system for quantitative phase analysis. The accuracy of the determination of the quantity of a phase constituent is better than 2 % when the sample is only weakly textured, the mean size of the particles is small (up to 1  $\mu m$ ), and the linear absorption indexes of the different phases are close to one another ( $\bar{\mu} - \mu_i \approx 0$ ). When at least one of these conditions is violated the correct determination of the grain sizes of the phase constituents (using optical microscopy, SEM, *etc.*) becomes of great importance. Some problems are also related with incorrect

consideration of texture, which may lead to a rise of the errors in the quantitative determination of the phase composition (up to 6 %).

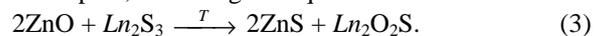
Diffuse reflectance spectra of the samples were recorded on a Perkin Elmer Lambda-9 spectrophotometer with smoked MgO as standard. The influence of thermal evaporation in vacuum on the structure and properties of the materials and coatings produced from them was investigated using a VU 1A vacuum setup.

### 3. Results and discussion

The X-ray study of the sample of zinc sulfide synthesized by the SHS method shows that it contains predominantly the phases ZnS–4H (new) and ZnS–3C. The polymorphic modification ZnS–4H (Fig. 1) crystallizes in the structural type SiC–4H. The refined values of the positional and thermal parameters of the ZnS–4H polymorph are presented in Table 1, and its structure is shown in Fig. 2 (for comparison, the structure of ZnS–2H is shown as well).

As follows from Table 2, the phase composition and lattice constants of the components of the systems ZnS– $Ln_2S_3$  have changed significantly in comparison with the initial samples. The content of the phases ZnS–3C and, particularly, ZnS–4H, has sharply decreased whereas an appreciable increase of the content of the phase ZnS–2H is observed. The lattice constants of the phases  $Gd_2S_3$  and  $Dy_2S_3$  have slightly changed; and significant amounts of a new phase – an oxysulfide  $Ln_2O_2S$  – have appeared. This new phase accounts for half or more of the dopant content, and, in the case of the sample with a small amount of dopant (5.0 mass%  $Dy_2S_3$ ), the initial sulfide  $Dy_2S_3$  has completely turned into  $Dy_2O_2S$ .

In our opinion, the oxysulfides appear due to an exchange reaction between zinc oxide impurities and the dopant, following the equation:



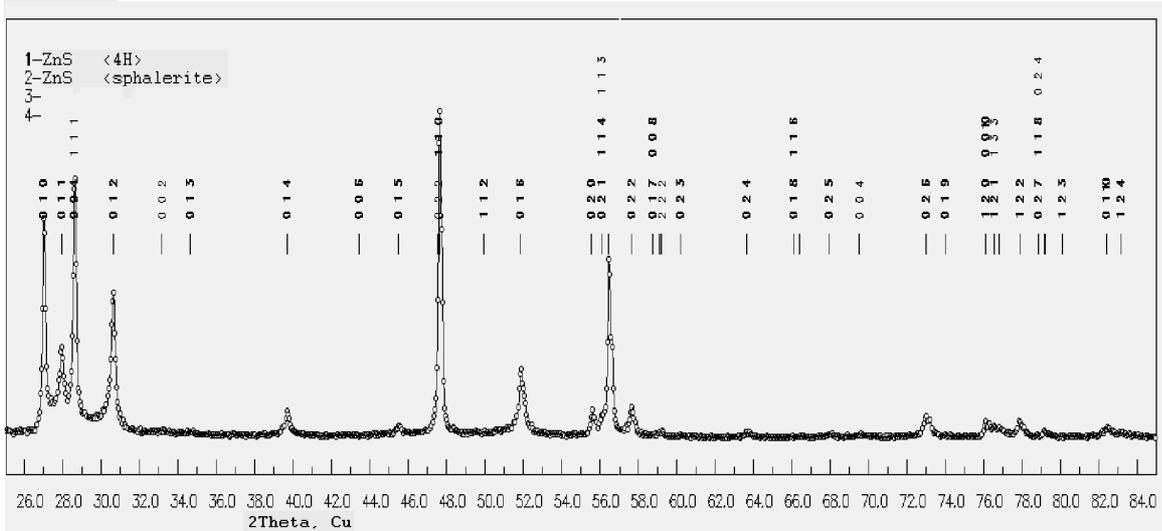
The content of ZnO in zinc sulfide is evaluated to be not less than 4 mass%. It may be mentioned that we did not observe the phases  $ZnLn_2S_4$  or  $ZnLn_4S_7$ , which were reported in [13,14].

**Table 2** Phase composition of specimens of the  $ZnS-Ln_2S_3$  systems,  $Ln = Gd, Dy$ , and lattice constants of the components.

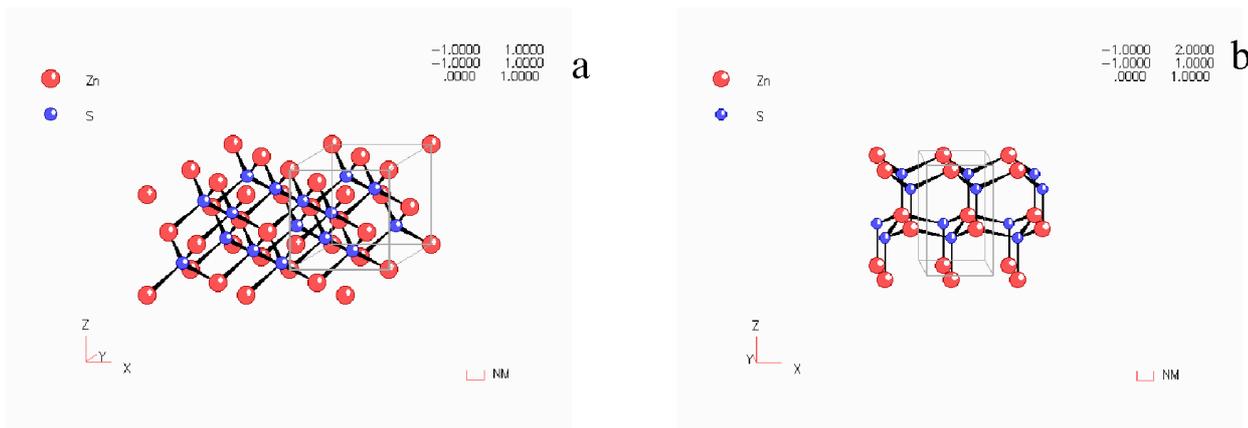
Chemical composition (mode of synthesis)		Color of the specimen	Phase composition (mass%)	Lattice constants, Å
ZnS (SHS)		White with yellowish tint	ZnS-4H (95) ZnS-3C (5)	$a=b=3.820(1), c=12.500(3)$ $a=b=c=5.406(1)$
$Gd_2S_3$ (SSS)		Brown-red	$\alpha$ - $Gd_2S_3$ , orth. (100)	$a=7.340(9), b=3.929(2),$ $c=15.286(5)$
$Dy_2S_3$ (SSS)		Red-brown	$\beta$ - $Dy_2S_3$ , orth. (100)	$a=7.270(1), b=3.871(1),$ $c=15.105(1)$
ZnS-Gd $_2$ S $_3$ (18.1 mass%)	Initial material (SSS)	Brown-red (light)	ZnS-2H (70) ZnS-4H (12) $\alpha$ - $Gd_2S_3$ , orth. (8) $Gd_2O_2S$ , hex. (10)	$a=b=3.822(1), c=6.254(9)$ $a=b=3.837(6), c=12.495(3)$ $a=7.333(9), b=3.935(8),$ $c=15.269(8)$ $a=b=3.850(9), c=6.651(0)$
	Residue (thermal evaporation in vacuum)	Brown-red (light) with dark inclusions	ZnS-2H (45) ZnS-3C (35) $\alpha$ - $Gd_2S_3$ , orth. (10) $Gd_2O_2S$ , hex. (10)	$a=b=3.821(3), c=6.251(8)$ $a=b=c=5.402(7)$ $a=7.335(9), b=3.930(7),$ $c=15.260(0)$ $a=b=3.852(4), c=6.628(9)$
	Coating (PVD on glass substrate)	Almost colorless (yellowish)	ZnS-3C	$a=b=c=5.379(4)$ X-ray amorphous component
ZnS-Dy $_2$ S $_3$ (18.5 mass%)	Initial material (SSS)	Red-brown (light)	ZnS-2H (82) $\beta$ - $Dy_2S_3$ , orth. (8) $Dy_2O_2S$ , hex. (10)	$a=b=3.821(7), c=6.266(1)$ $a=7.280(6), b=3.876(0),$ $c=15.173(4)$ $a=b=3.797(6), c=6.600(9)$
	Residue (thermal evaporation in vacuum)	Red-brown (light) with dark inclusions	ZnS-2H (80) $\beta$ - $Dy_2S_3$ , orth. (9) $Dy_2O_2S$ , hex. (11)	$a=b=3.821(4), c=6.258(4)$ $a=7.277(3), b=3.879(6),$ $c=15.142(0)$ $a=b=3.801(1), c=6.561(8)$
	Coating (PVD on glass substrate)	Almost colorless (yellowish)	ZnS-3C	$a=b=c=5.379(9)$ X-ray amorphous component
ZnS-Dy $_2$ S $_3$ (5.0 mass%)	Initial material (SSS)	White with grayish tint	ZnS-2H (85) ZnS-3C (10) $Dy_2O_2S$ , hex. (5)	$a=b=3.819(5), c=6.263(6)$ $a=b=c=5.404(5)$ $a=b=3.805(5), c=6.596(0)$
	Residue (thermal evaporation in vacuum)	White with dark inclusions	ZnS-2H (81) ZnS-3C (13) $Dy_2O_2S$ , hex. (5)	$a=b=3.817(3), c=6.260(0)$ $a=b=c=5.401(5)$ $a=b=3.807(4), c=6.599(7)$
	Coating (PVD on glass substrate)	Almost colorless (yellowish)	ZnS-3C	$a=b=c=5.441(3)$ X-ray amorphous component

Thermal evaporation in vacuum of the specimens of the systems  $ZnS-Ln_2S_3$  resulted in a change of their phase composition and lattice constants. The phase ZnS-4H (probably unstable at low pressure and high temperature) completely vanished, being replaced by ZnS-2H and ZnS-3C. Some change of the lattice constants of the basic phases of zinc sulfide ZnS-2H and ZnS-3C occurred.

A substantial part of X-ray amorphous components (Fig. 3) was in general present in the coatings. At the same time, reflections from the phase ZnS-3C are clearly seen, especially for coatings obtained from samples with greater dopant content. In the case of the specimen of composition ZnS-Dy $_2$ S $_3$  (5.0 mass%) an amorphous component prevails in the coating, and the diffraction peaks of the phase ZnS-3C are much



**Fig. 1** Diffraction pattern of zinc sulfide synthesized by the SHS method.

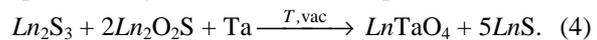


**Fig. 2** Crystal structure of the polymorphic modifications ZnS-4H (a) and ZnS-2H (b) of zinc sulfide.

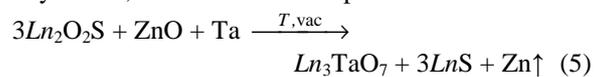
weaker. The lattice constants of a particular crystal phase in the coating are relatively close in the first two cases, *i.e.* for a high dopant content. In the case of the lower dopant content (5.0 mass%  $Dy_2S_3$ ), the lattice constant of the phase ZnS-3C shows a considerably larger value, both with respect to the other coatings, and with respect to the same phase in the initial material. This is probably caused by a deviation of the composition of the phase ZnS-3C from stoichiometry.

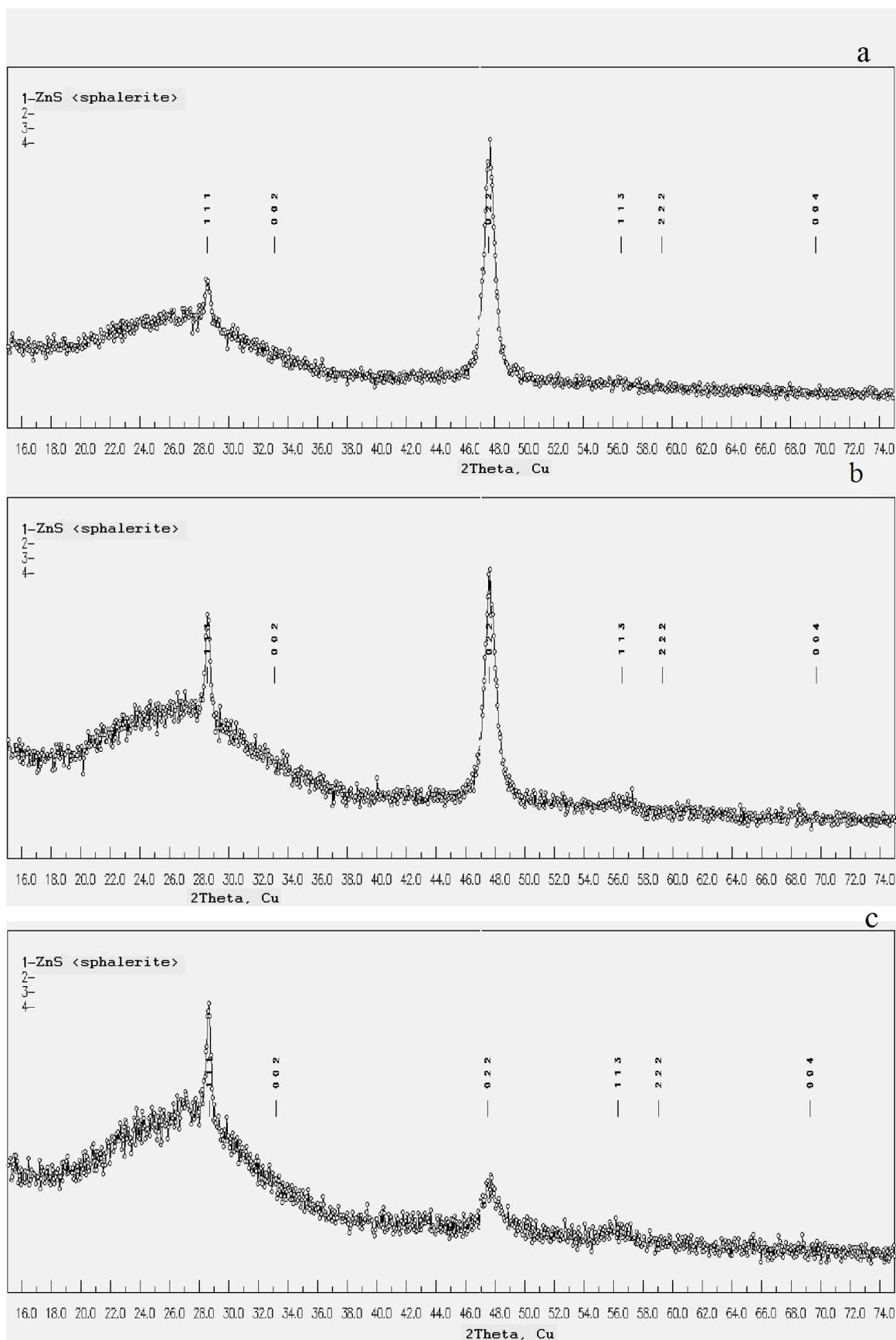
Additional data on the change of composition of the phases of the systems zinc sulfide –  $Ln_2S_3$  dopant induced by the heat treatment in vacuum were obtained by diffuse reflectance spectroscopy. Diffuse reflectance spectra (DRS) of powders of the systems ZnS- $Ln_2S_3$  (Figs. 4-6) in the UV range of the spectrum contain a wide absorption band of medium intensity characteristic of ZnS, caused by the charge transfer  $S^{2-} \rightarrow Zn^{2+}$ . Besides, in DRS of specimens with a large content of  $Ln_2S_3$ , a broad band of  $S^{2-} \rightarrow Ln^{3+}$

transitions is present in the visible range of the spectrum. In addition, the DRS of the samples ZnS- $Dy_2S_3$  contain narrow absorption peaks due to  $4f-4f$  electronic transitions in  $Dy^{3+}$  in the near IR range of the spectrum. Their intensity decreases with decreasing  $Dy_2S_3$  content in the specimen. The DRS of the specimens after thermal evaporation in vacuum (further on called “residues”) contain a characteristic band of rather high intensity in the UV range. This is, most likely, the result of partial reduction of the specimens by a material of the evaporator (tantalum):

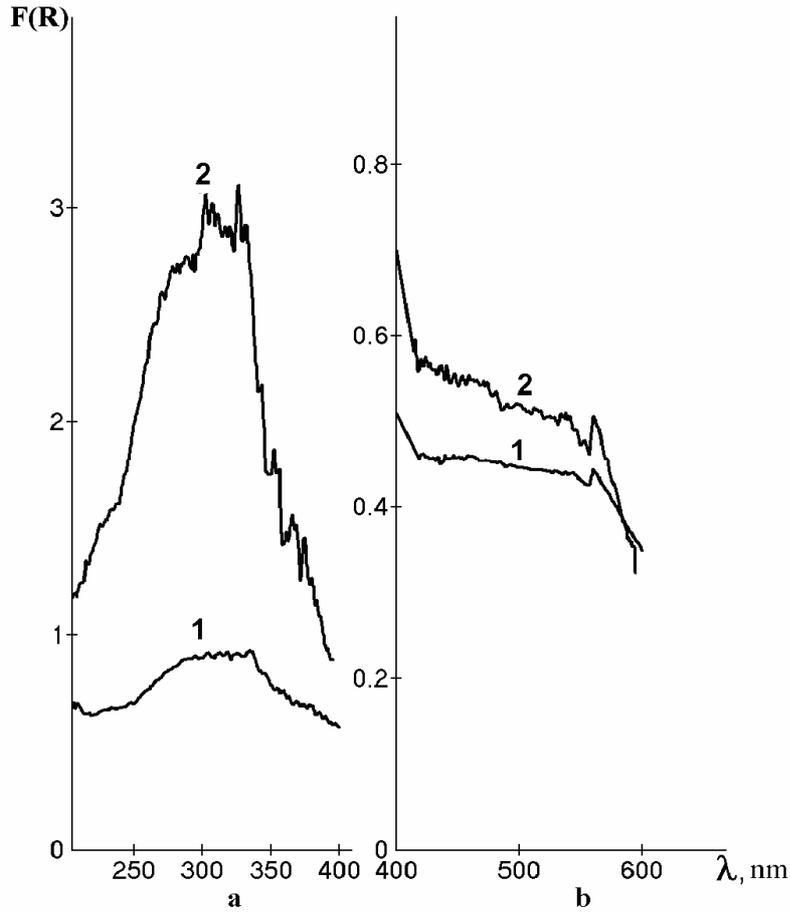


In the case of the specimen of the system ZnS- $Dy_2S_3$  with a low dopant content (5.0 mass%), in which ZnO is not completely transformed into oxysulfide, another reaction is probable:

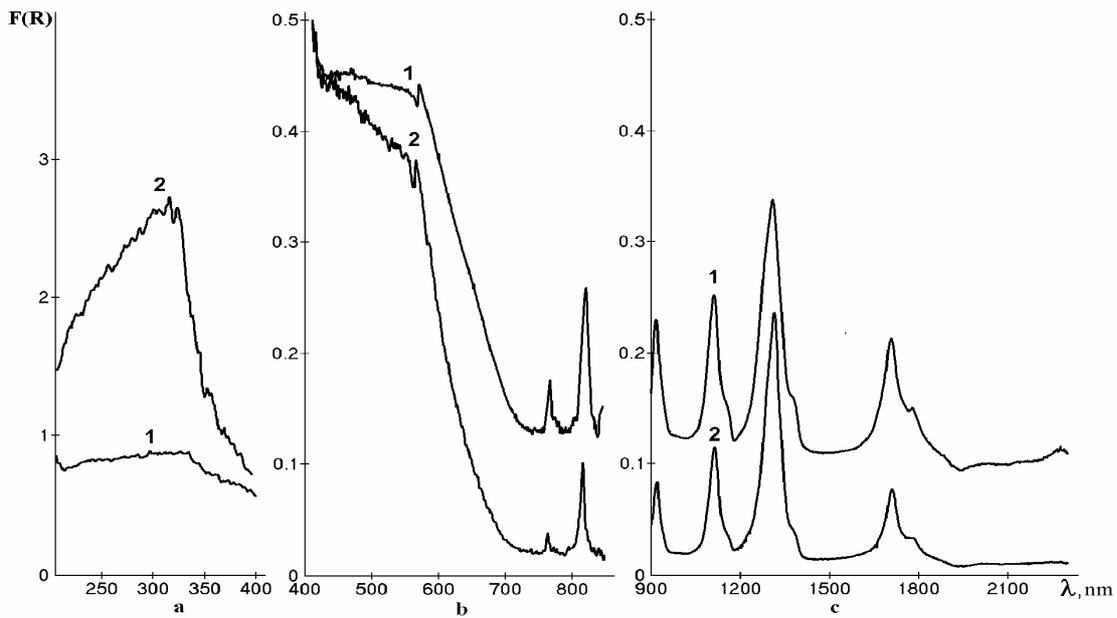




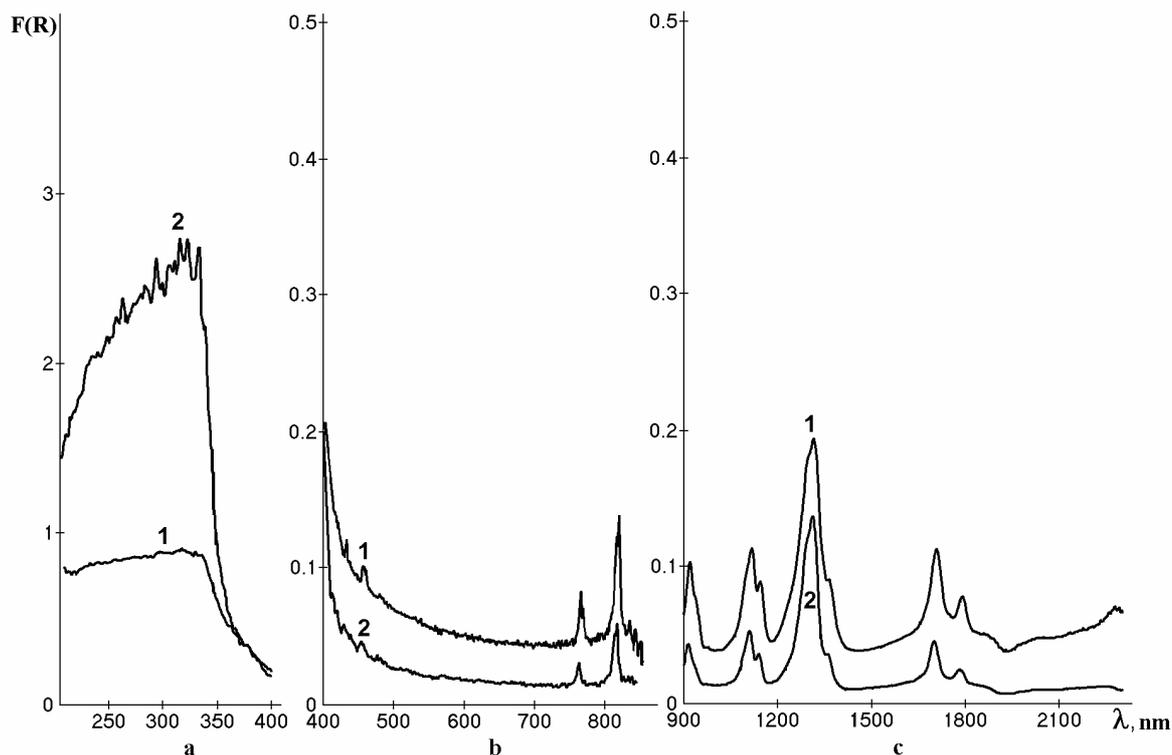
**Fig. 3** Diffraction patterns of coatings obtained from ZnS– $Ln_2S_3$  systems: (a) ZnS– $Gd_2S_3$  (18.1 mass%), (b) ZnS– $Dy_2S_3$  (18.5 mass%), (c) ZnS– $Dy_2S_3$  (5.0 mass%).



**Fig. 4** Diffuse reflectance spectra of the specimen  $ZnS-Gd_2S_3$  (18.1 mass%) in the UV (a) and visible (b) ranges of the spectrum: 1 – initial material, 2 – residue after evaporation.



**Fig. 5** Diffuse reflectance spectra of the specimen  $ZnS-Dy_2S_3$  (18.5 mass%) in the UV (a), visible (b) and near-IR (c) ranges of the spectrum: 1 – initial material, 2 – residue after evaporation.



**Fig. 6** Diffuse reflectance spectra of the specimen  $ZnS-Dy_2S_3$  (5.0 mass%) in the UV (a), visible (b) and near-IR (c) ranges of the spectrum: 1 – initial material, 2 – residue after evaporation.

Being volatile, metallic zinc will, most likely, cause a deviation of the composition of  $ZnS$  from stoichiometry in the coating and possible deterioration of its properties.

#### 4. Conclusions

The effect of  $Gd_2S_3$  and  $Dy_2S_3$  dopants on the phase composition and lattice constants of SHS zinc sulfide was studied. It was established that the  $ZnS-4H$  modification is unstable in the presence of the dopants, and at low pressure and high temperature. Thermal evaporation in vacuum resulted in a change of the crystal structure both of the residues and of thin-film coatings on glass substrates, where only  $ZnS-3C$  and X-ray amorphous components were detected. Diffuse reflectance spectra confirmed the occurrence of exchange and reduction reactions in the studied systems.

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