

Peculiarities of scintillation materials based on ZnS–ZnTe solid solutions

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The optimal conditions for obtaining and features of solid solution ZnS–ZnTe were defined taking into account the thermodynamic calculation of possible chemical reactions in ZnS–ZnTe–H₂–S in a wide temperature range (600–1400 K). It is shown that control of optical, scintillation and crystallographic characteristics of such materials can be performed by co-doping of rare earth elements and adding the nonstoichiometric sulfur in the initial mixture (improvement of the kinetic parameters), as well as by heat treatment in inert atmosphere (Ar) resulted in phase change of the crystal lattice, increasing the light output, and reducing the afterglow. The reasons of these changes are discussed.

С учетом термодинамического расчета возможных химических реакций в системе ZnS–ZnTe–H₂–S в широком температурном интервале (600–1400 K) рассмотрены оптимальные условия получения и особенности твердых растворов ZnS–ZnTe (ZnS_xTe_{1-x} (x < 1)). Показано, что управление оптическими, сцинтилляционными и кристаллографическими характеристиками в таких материалах может осуществляться как содопированием редкоземельными элементами и добавлением сверхстехиометрической серы в шихту (улучшение кинетических параметров), так и термической обработкой в инертной среде (Ar), что приводит к изменению кристаллической решетки, повышению светового выхода рентгенолюминесценции, уменьшению послесвечения. Обсуждаются возможные механизмы таких изменений.

Особливості отримання сцинтиляційних матеріалів на основі твердих розчинів ZnS–ZnTe. К.Катрунов, А.Лалаянц, В.Баумер, С.Галкін, Л.Гальчинецький, Е.Брильова.

З урахуванням термодинамічного розрахунку можливих хімічних реакцій у системі ZnS–ZnTe–H₂–S у широкому температурному інтервалі (600–1400 K) розглянуто оптимальні умови отримання і особливості твердих розчинів ZnS–ZnTe (ZnS_xTe_{1-x} (x < 1)). Показано, що управління оптичними, сцинтиляційними і кристаллографічними характеристиками у таких матеріалах може здійснюватися як содопювання рідкоземельними елементами і додаванням надстехіометричної сірки у шихту (поліпшення кінетичних параметрів), так і термічною обробкою в інертному середовищі (Ar), що призводить до зміни кристалічної ґратки, підвищенню світлового виходу рентгенолюмінесценції, зменшенню післясвітіння. Обговорюються можливі механізми таких змін.

1. Introduction

One of the most promising areas in the field of radiation instrumentation becomes a creation of the modern X-ray introsopic

systems. They are widely used in modern medical computer tomography (CT), customs examination equipment, technical radiography and provide information in real time and identify various objects, including or-

ganic substances with the close Z_{eff} . Detectors used in such equipment usually are scintillation detectors and most of them must have a high efficiency of absorption and conversion of radiation, the dynamic range of intensity more than 10^3 – 10^4 , low deviation of characteristics (0.1–0.5 %), a high-speed performance (10^{-4} – 10^{-5} s), minimal cross-influence between channels and high radiation stability [1].

Along with the alkali halide scintillators (NaI(Tl), CsI(Tl), CsI(Na)) and zinc and cadmium tungstate (CWO, ZWO) based scintillators widely used for these purposes, recently, a new class of scintillators based on compounds A^2B^6 is appeared, which is obtained by isovalent doping of ZnSe crystals. Such doping results in a formation of intrinsic defects in the associates that determines the optical properties of the fluorescent crystals. Chalcogenide scintillators (ZnSe (O, Al, Te)) ($Z_{eff} = 33$) have a high light output and low afterglow, but they are characterized by low transparency to its own radiation [2].

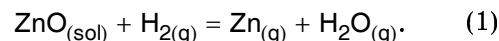
Extension of the class of scintillators for digital radiography is associated with other A^2B^6 compounds. In particular, double (ZnS–ZnSe, ZnS–ZnTe) or more complex (ZnS–ZnSe–ZnTe) solid solutions based on zinc sulphide could be the promising semiconductor materials [3]. First, they have a low effective atomic number $Z_{eff} = 24$, which could allow the reduction of the doses to patients under X-rays scanning in medical equipment. Second, such scintillation materials could be used in multi-energy X-rays detectors as a low-energy channel in them. Prospects for the use of such materials may be associated not only with their high quantum yield of luminescence, but also with possibility of varying their emission spectra and other output parameters in a wide range [4].

This work describes the features of production of materials based on solid solutions of $ZnS_{1-x}Te_x$ ($x < 0.1$). Also the ways of manipulating of their optical and scintillation properties have been proposed.

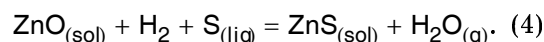
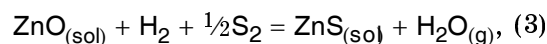
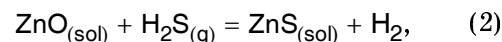
2. Experimental

The technological regimes of synthesis process and production of powdered samples of solid solutions of different compositions were determined with taking into account the thermodynamic calculations of possible chemical reactions in ZnS–ZnTe– H_2 –S system in a wide temperature range, a preliminary analysis of which was carried out in

[4]. From the analysis of the equilibrium constants values for the reactions in this system, it was shown that in addition to the main reaction of formation of solid solution probably there are a few more reactions in this temperature region. The first is the reaction of the oxide film ZnO reduction (1).



Passing of this reaction must have a positive effect on intensification of the process of ZnS and ZnTe sintering because it may unnecessarily destroy the oxide surface layer which is generally formed in these compounds at lower temperatures. There is a number of important reactions with high equilibrium constants else, which can take place under optimum sintering temperatures ($T = 1200$ – 1400 K). The reactions associated with the addition of one of the anionic components (S).



These reactions, as well as (1), may play a significant role in a formation of the solid solution, effectively restoring the oxidation layer that forms on the surface at lower temperatures. At the same time, the data of thermodynamic analysis showed that the reactions of dissociation, the reactions of ZnS and ZnTe with hydrogen and ZnS with Te can be neglected because they have a low probability of passing at sintering temperatures. The reactions of sulfur and tellurium with hydrogen can pass hardly for this reason, and because the area of the existence of H_2S and H_2Te is at much lower temperatures. Given the above analysis, determination of the necessary technological regimes of sintering ZnS and ZnTe was performed.

The temperature of synthesis was selected as 1200–1300 K, assuming that the sintering proceeds effectively at temperatures corresponding to (0.65±0.75) T_{mel} components ($T_{mel}(ZnS) = 2100$ K, $T_{mel}(ZnTe) = 1500$ – 1600 K) [5]. Synthesis time was $t = 3$ – 6 h. Solid phase synthesis of $ZnS_{1-x}Te_x$ was conducted in a reducing (H_2) medium in non-gradient zone of the muffle furnace in a special reactor. We used the following time regimes: heating to the desired temperature took 3 h, exposure — 5 h, cooling to room temperature — 16 h. ZnTe

concentration in the starting material was varied in the range of 0.5÷10 %.

To control the formation and to determine the composition of the solid solution the method of measuring the diffuse reflection spectra $R_{dif}(\lambda)$ (attachment PDO to the spectrophotometer) has been chosen. Its use is associated with the fact that the solid solutions based on A_2B_6 , including for $ZnS_{1-x}Te_x$, are characterized by a change of the band gap (E_g) depends on the composition. The value of the band gap can be estimated from the spectra $R_{dif}(\lambda)$ using the location of fundamental absorption edge [6]. The shape of the curve $R_{dif}(\lambda)$ can also characterize the completeness of the reaction. The phases content and the lattice parameters were determined by X-ray analysis using diffractometer Siemens D 500. The total weight content of Te was determined by a special technique using atomic emission spectroscopy with a spectrometer Trace ScanAdvantage Termo Jarrel Asc.

The X-ray spectra were measured by spectrophotometer KSVU-23 using X-ray source REIS-I with tube voltage up to 30 kV. Afterglow measurements $\eta(\%)$ were carried out by measuring and computing system for kinetic characteristics study (MCSKCS). The light yield was determined relatively to a reference sample in current regime under X-ray irradiation using Si-photodiode as a photodetector.

Additional doping with rare-earth elements was carried out on the samples with initial composition of $ZnS + 5\% ZnTe$ by introduction of ions Ho, Dy, Eu. Rare earth elements were introduced into the batch as presynthesized in hydrogen atmosphere at temperature of 950°C concentrate (ligatures), with high content of impurity ($ZnS + 10\% Ho_2S_3$, $ZnS + 10\% Dy_2S_3$, $ZnS + 10\% Eu_2S_3$). This concentrate added to the batch in the quantities necessary for the establishment of an appropriate concentration of the co-activator. This enabled us to obtain the material with a uniform distribution of the co-activator by volume.

Excess sulfur content in the samples was achieved by introducing elemental sulfur into the batch in amount of 10 %. Heat treatment was carried out in the vapor Zn ($T = 960^\circ C$, $t = 6\div 72$ h) and Ar ($T = 950^\circ C$, $t = 18\div 72$ h) in non-gradient zone of the furnace, in a special reactor.

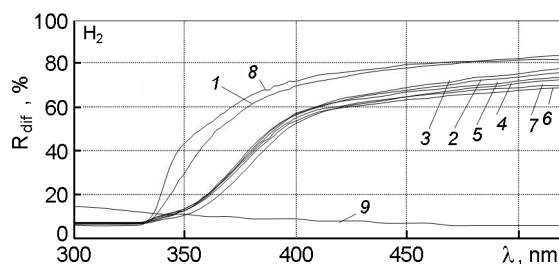


Fig. 1. Diffuse reflectance spectra of ZnS–ZnTe samples with different concentrations of ZnTe: 1 – 0.5 %, 2 – 1 %, 3 – 2 %, 4 – 3 %, 5 – 5 %, 6 – 7 %, 7 – 10 %, 8 – ZnS; 9 – ZnTe.

3. Results and discussion

Fig. 1 shows the diffuse reflectance spectra of the samples of ZnS–ZnTe with different content of ZnTe. We observe a shift of the absorption edge toward longer wavelengths compared to the original ZnS. The absorption edge shift, as well as the data about increase of XRD unit cell volume directly testifies to the passing of reaction of a solid solution formation in such system. Comparing the position of the absorption band edge with the data on changes in the band gap E_g [7] can be estimated from the composition of the real concentration of the solid solution ZnS–ZnTe. It should be noted that, from the concentration of about 2 % ZnTe in the starting material, the absorption edge shift remains practically unchanged, indicating about the achievement of Te solubility limit under sintering in such conditions. The data of atomic emission spectroscopy (AES) (Table 1) show greater tellurium content in the samples compared with the data on the diffuse reflection, especially, at high concentrations of ZnTe in the mixture. This can be explained by the fact that this method deter-

Table 1. AES data on tellurium concentration in the samples of ZnS–ZnTe

ZnTe concentration in the initial ZnS–ZnTe mixture, %	Mass fraction of tellurium in the sample, %
0.5	0.20
1	0.26
2	0.83
3	1.58
5	3.52
7	5.61
10	5.73

Table 2. Effect of rare earth elements and excess sulfur concentration on the value of afterglow in ZnS + 5 % ZnTe samples

Composition	Alloying impurity	Excess component	Afterglow	
			5 ms	20 ms
ZnS + 5 % ZnTe	–	–	25.89	19.56
ZnS + 5 % ZnTe	Ho ₂ S ₃ (0.5 %)	–	22.16	16.81
ZnS + 5 % ZnTe	Dy ₂ S ₃ (0.5 %)	–	21.61	16.46
ZnS + 5 % ZnTe	Eu ₂ S ₃ (0.5 %)	–	18.91	14.16
ZnS + 5 % ZnTe	–	S(10 %)	18.95	13.83
ZnS + 5 % ZnTe	Ho ₂ S ₃ (0.5 %)	S(10 %)	9.42	6.93
ZnS + 5 % ZnTe	Dy ₂ S ₃ (0.5 %)	S(10 %)	10.10	7.46
ZnS + 5 % ZnTe	Eu ₂ S ₃ (0.5 %)	S(10 %)	9.17	6.49

mines the total amount of tellurium in the sample, including tellurium, which is located in the other phases. We can assume that one of these phases is a solid solution of ZnTe–ZnS, is formed from ZnTe, the existence of which was confirmed by XRD. The presence of such phase results in additional absorption in the diffuse reflection spectra, which manifests itself in the reduction of $R_{dif}(\lambda)$ in the long wavelength region of the spectrum (see Fig. 1).

The X-ray luminescence spectra of ZnS–ZnTe solid solutions are the superposition of a number of bands, with the main ones being the bands with $\lambda_{max} = 460$ nm and $\lambda_{max} = 520$ nm. The intensity of these bands was slightly redistributed in such a way that intensity of long-wavelength band ($\lambda_{max} = 520$ nm) increases with increasing the tellurium concentration. In addition, at low concentrations of ZnTe (~0.5÷1.0 %) a shortwave band ($\lambda_{max} = 410$ nm) was observed. All these bands are described in the literature and relates to the so-called "self-activated" luminescence of ZnS [8].

Rare earth codopant elements, as well as the introduction of stoichiometric sulfur have a significant influence on the kinetic characteristics of the starting material. This is manifested in the reduction of afterglow. The most effective is the case in which there are two factors (Table 2). Reduction of the afterglow level in the system of ZnS–ZnTe with additional dopant of the rare earth elements (Ho, Dy, Eu), apparently, can be associated with the filling of traps equilibrium carriers, which have appeared in such doping. As a result, there is a partial or total shutdown of such traps from recombination process. A similar effect with the dopant of the rare-earth Re^{+3}

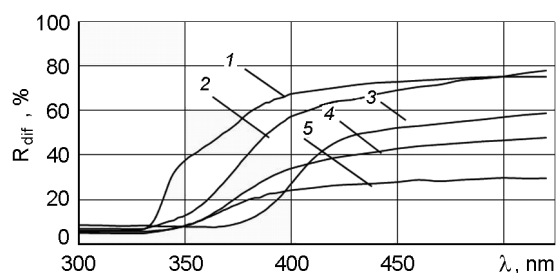


Fig. 2. Diffuse reflectance spectra of ZnS + 5 % ZnTe solution before and after thermal annealing: 1 — ZnS; 2 — before annealing, 3 — annealing in Ar (72 h), 4 — annealing in Zn (4 h), 5 — annealing in Zn (72 h).

ions has been observed for a number of other oxide and chalcogenide scintillation materials and has been described in [9, 10]. Reduction of the afterglow level in the system of ZnS–ZnTe with insertion of the excess elemental sulfur can be associated with a decrease of the number of sulfur vacancies, which act as additional trapping centers in the system.

Effect of heat treatment on optical, crystallographic, and scintillation characteristics was investigated on the samples of solid solutions with composition ZnS + 5 % ZnTe. The samples were annealed in an inert atmosphere (Ar) and Zn vapor at temperature of 950–1000°C. Long-drawn-out annealing in argon leads to rearrangement of the crystal lattice and as a result the sphalerite structure becomes predominant (Table 3), moreover, there is an additional shift of the absorption band edge to longer wavelengths, which is not observed upon annealing in zinc vapor (Fig. 2). This shift can be attributed to the transformation of the crystal lattice in sphalerite, band gap ZnS of which is less than wurtzite. Further-

Table 3. Scintillation and crystallographic data on ZnS–5 %ZnTe samples before and after thermal annealing

No.	Composition	Conditions of thermal annealing	Light output, relative units	Afterglow %, 5 ms	Percentage ratio of phases		Lattice volume, Å ³
					(S)	(W)	
1	ZnS	–	0.03–0.04	42.5	18.2	77.2	V(S) = 158.128
2	ZnS–5 %ZnTe	without thermal heating	0.08–0.1	19.5	20.0	77.6	V(S) = 158.628 V(W) = 79.287
3	ZnS–5 %ZnTe	Zn, 4 h, 950°C	0.1–0.12	26.5	–	–	–
4	ZnS–5 %ZnTe	Zn, 72 h, 950°C	0.15–0.15	15.7	40.8	21.1	V(S) = 158.504
5	ZnS–5 %ZnTe	Ar, 8 h, 950°	0.08–0.1	28.8	35.4	37.7	V(S) = 158.245
6	ZnS–5 %ZnTe	Ar, 48 h, 950°	0.8–0.85	3.7	87.5	9.7	V(S) = 158.961
7	ZnS–5 %ZnTe	Ar, 72 h, 950°C	0.85–0.87	2.9	91.8	8	V(S) = 158.954
8	ZnS–5 %ZnTe	Ar, 48 h, 950° + Zn, 4 h, 950°C	1	11.0	–	–	–

more, shift can be connected with additional entry unreacted Te in the sphalerite lattice.

Analysis of the X-ray luminescence spectra (Fig. 3) shows that the prolonged annealing in Ar leads to radical changes of optical, luminescence and scintillation properties. Band of luminescence is formed with $\lambda_{max} = 470$ nm, the emission intensity of the band under X-ray excitation is substantially (up to 20 times) higher than for the nonannealing samples. Furthermore, decrease of the afterglow is obtained (see Table 3). Follow-up the annealing (after annealing in argon) in zinc leads to further enhance the light output, however the level of afterglow increases insignificantly.

It can be assumed that one of the possible mechanisms of radiative recombination is the transfer with energy $E = 2.66$ eV from the conduction band or donor level to the acceptor level, which is a double complex level $(Te_S-V_S)^-$. The existence of such defect complex is thermodynamically favorable and can be explained by the following reasons. Under formation of a solid solution in the system of ZnS–ZnTe an occurrence of tellurium in interstitial position with preserving wurtzite lattice is the most probable.

Annealing in Ar leads to the transformation of the lattice, which is accompanied by a transition of tellurium from the interstitial position in the anionic sites of the crystal lattice (Te_S).

Situated in such sites Te (size larger than S) causes to burst the lattice and creates the additional elastic interactions. The presence of sulfur vacancies (V_S) near Te is thermodynamically favored, as it may

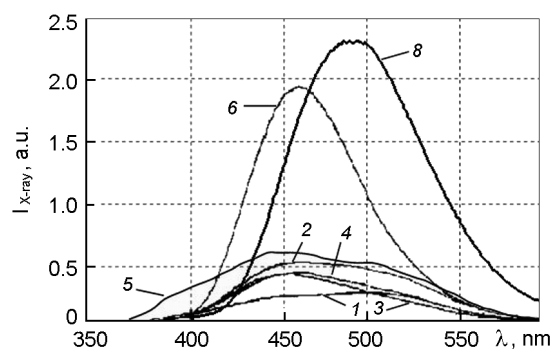


Fig. 3. X-ray luminescence spectra of ZnS–5 %ZnTe before and after different thermal annealing: 1 – original ZnS, 2 – before annealing, 3 – annealing in Zn (4 h, 950°C), 4 – annealing in Zn (72 h, 950°C), 5 – annealed in Ar (8 h, 950°C), 6 – annealing in Ar (48 h, 950°C), 7 – annealing in Ar (72 h, 950°C), 8 – annealing in Ar (48 h, 950°C) + Zn (4 h, 950°C).

weaken the elastic interaction. Zinc in interstitial position (Zn_i) could be a donor level.

For a final clarification of the luminescence nature further studies are necessary including the study of thermally stimulated luminescence.

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