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Effect of oxygen on some reactions of ZnSe crystal surface interaction with H_2O vapors, CO_2, and CO

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Effect of oxygen on some interaction reactions of ZnSe crystal surface with water vapors, CO_2, and CO which result in release of hydrogen, and also carbon from a surface of crystals is discussed. Temperature dependences of equilibrium constants are calculated. It is found that participation of oxygen into the viewed processes of interacting results in sharp increase of probability and intensity of their actual behavior. It was shown that the essential contribution to these processes can be made by presence of antropogenic admixtures in air (water, hydrocarbons, CO_2, CO, engine exhaust fumes, etc.) which plays a critical part in pollution of ZnSe crystals surface by carbon.

Рассмотрено влияние кислорода на некоторые реакции взаимодействия поверхности кристаллов ZnSe с парами воды, CO_2, CO, которые приводят к выделению водорода, а также углерода на поверхности кристаллов. Рассчитаны температурные зависимости констант равновесия. Установлено, что участие кислорода в рассмотренных процессах взаимодействия приводит к резкому возрастанию вероятности и интенсивности их реального протекания. Показано, что существенный вклад в эти процессы может вносить наличие антропогенных примесей в воздухе (вода, углеводороды, CO_2, CO, выхлопные газы двигателей, др.), которое играет важную роль в загрязнении поверхности кристаллов ZnSe углеродом.

1. Introduction

Zinc selenide, and also substitutional solid solutions on its base demonstrate high reactivity against oxygen-containing atmospheric components. In particular, the research results for heat treatment (HT) process of ZnSe(X), $X = O_{Se}$, Te_{Se} crystals in boiling water vapors have been presented in [1]. Some reactions of interaction of ZnSe(X) crystals surface with H_2O which the product can be hydrogen have been viewed. It is shown that hydrogen released in these reactions diffuses into crystals ZnSe(X) and interacts with crystal components [1, 2]. This interaction results in changes of the physicochemical and optical (including luminescent) properties of the crystals. Character of hydrogen effect on these properties strongly depends on HT temperature in hydrogen. At HT temperatures close to 1200...1300 K irreversible changes of radioluminescence (RL) parameters occur. These changes in $ZnSe(O_{Se})$ crystals can lead even to their degradation. If HT temperature does not exceed 500 K, changes of RL parameters, in particular, RL spectra have reversible character. In [2] it has been shown that various character of hydrogen effect on RL parameters is related to differences in hydrogen interacting with radiative recombination centers (RRC) in ZnSe(X) crystals at various HT temperatures: at HT close to 1200...1300 K there is an irreversible conversion or RRC destruc-

Table 1. Reactions of ZnSe crystal interaction with the components of air

No.	The reaction equation	The temperature dependence lg K°	Values lg K°			
			300 K	375 K	400 K	500 K
1	$ZnSe + H_2O(g) \rightleftarrows ZnO + H_2 + Se(s)$	$-2919.19/T - 2.96$	−12.69			−8.8
2	$ZnSe + 2H_2O(g) \rightleftarrows Zn(OH)_2 + H_2 + Se(s)$	$-195.87/T - 11.20$	−11.85		−11.69	
3	$3ZnSe + H_2O(g) + O_2 \rightleftarrows 3ZnO + H_2 + 3Se(s)$	$16624.94/T - 13.53$	41.89			19.72
4	$3ZnSe + 4H_2O(g) + O_2 \rightleftarrows 3Zn(OH)_2 + H_2 + 3Se(s)$	$24794.91/T - 38.26$	44.38		23.73	
5	$3ZnSe + H_2O(g) + CO_2 \rightleftarrows 3ZnO + C + H_2 + 3Se(s)$	$-4027.66/T - 13.68$	−27.1			−21.74
6	$3ZnSe + 4H_2O(g) + CO_2 \rightleftarrows 3Zn(OH)_2 + H_2 + 3Se(s) + C$	$4142.30/T - 38.41$	−24.6		−28.05	
7	$5ZnSe + H_2O(g) + CO_2 + O_2 \rightleftarrows 5ZnO + C + H_2 + 5Se(s)$	$15516.47/T - 24.26$	27.46			6.77
8	$5ZnSe + 6H_2O(g) + CO_2 + O_2 \rightleftarrows 5Zn(OH)_2 + H_2 + 5Se(s) + C$	$29133.07/T - 65.47$	31.64		7.36	
9	$2ZnSe + H_2O(g) + CO \rightleftarrows 2ZnO + C + H_2 + 2Se(s)$	$1052.26/T - 12.93$	−9.42			−10.83
10	$2ZnSe + 3H_2O(g) + CO \rightleftarrows 2Zn(OH)_2 + H_2 + 2Se(s) + C$	$6498.9/T - 29.42$	−7.76		−13.17	
11	$4ZnSe + H_2O(g) + CO + O_2 \rightleftarrows 4ZnO + C + H_2 + 4Se(s)$	$20596.4/T - 23.5$	45.16			17.7
12	$4ZnSe + 5H_2O(g) + CO + O_2 \rightleftarrows 4Zn(OH)_2 + H_2 + 4Se(s) + C$	$31489.68/T - 56.47$	48.5		22.25	
13	$3ZnSe + H_2O(l) + CO_2 \rightleftarrows 3ZnO + C + H_2 + 3Se(s)$	$-6337.48/T - 7.46$	−28.58	−24.4		
14	$3ZnSe + H_2O(g) + CO_2 \rightleftarrows 3ZnO + C + H_2 + 3Se(glass)$	$-4884.06/T - 12.17$	−28.45			−21.94
15	$3ZnSe + H_2O(l) + CO_2 \rightleftarrows 3ZnO + C + H_2 + 3Se(glass)$	$-7193.87/T - 5.94$	−29.92	−25.1		

tion. At HT temperatures no more than 500 K such conversion is practically absent.

In [1] the analysis of chemical composition of ZnSe crystal surface layers after HT in boiling water vapors has been carried out by means of X-ray photoelectron spectroscopy method (XRPS-method) which has confirmed the fact of hydrogen release in reaction $ZnSe + H_2O \rightarrow ZnO + H_2 + Se(s)$.

However when carrying out the thermodynamic analysis both this and other chemical processes resulting in hydrogen release (see [1–3]) it has not been considered that in real conditions the viewed HT process in H_2O vapors has passed in usual air medium but oxygen, and also other chemically active components of air, for example, CO_2 and CO, should participate in these reactions.

The purpose of the study is to analyze the most probable chemical processes occurring on zinc selenide crystals surface under interaction with components of air (water vapor, oxygen, carbon dioxide, carbon monoxide) and to compare them with the experimental data. It is important with regard to explanation of causes of zinc selenide crystals' scintillation and optical parameters degradation over time.

2. Results and discussion

The chemical reactions examined by us are presented in Table 1. Temperature dependences lg K° of these reactions are given there too. A reaction balance equation is made with attraction of analytical computer system Wolfram Alpha. At the same time we paid special attention to the fact that those reactions should be analyzed which correlate with analytical results for ZnSe samples surface layers obtained by XRPS method [1], and also with the data of the study [4] in which results of research of actual ZnSe surface chemical composition are summarized.

Among the reactions shown in Table 1 reactions with oxygen participation (reaction (3), (4), (7), (8), (11), (12)) proposed by us are presented. Products of these reactions are the same as the products of analogous reactions without oxygen (reactions (1), (2), (5), (6), (9), (10)). It is possible to create the reaction balance equation shown in Table 1 on the basis of combinations from the simple reactions well-known in the literature [5–9] passing in the temperature interval considered. Let's show it by the example of reactions (1) and (3).

Reaction (1) is obtained combining following simultaneous reactions:

$$ZnSe + CO_2 \rightleftarrows ZnO + COSe, \quad (1a)$$

$$COSe + H_2O(g) \rightleftarrows CO_2 + H_2Se, \quad (1b)$$

$$H_2Se \rightleftarrows H_2 + Se(s) \quad (1c)$$

the resulting reaction:

$$ZnSe + H_2O(g) \rightleftarrows ZnO + H_2 + Se(s). \quad (1)$$

Analogously, reaction (3) can be featured as a result of competing processes

$$2ZnSe + O_2 \rightleftarrows 2ZnO + 2Se(s), \quad (3a)$$

$$ZnSe + CO_2 \rightleftarrows ZnO + COSe, \quad (3b)$$

$$COSe + H_2O(g) \rightleftarrows CO_2 + H_2Se, \quad (3c)$$

$$H_2Se \rightleftarrows H_2 + Se(s) \quad (3d)$$

the resulting reaction:

$$3ZnSe + H_2O(g) + O_2 \rightleftarrows \rightleftarrows 3ZnO + H_2 + 3Se(s). \quad (3)$$

Reactions (1a)...(1c), (3a)...(3d) have been considered in [5–9]; authors of these studies have found presence of the reagents participating in these processes and their products.

In [1] composition of ZnSe crystal surface layers before and after HT in H_2O vapors at $T \approx 370$ K in the air within 140 hours had been analyzed by XRPS method. Analysis of the results presented in [1] shows that on a surface of all samples there was observed carbon, apparently, related to hydrocarbonaceous pollutions; oxygen (up to 8 %) which content decreased to ≈ 2 % after ionic etching; redundant number of selenium in state Se^0 which decreased from 84 % on a surface to 5 % at depth of 40 nm. In the sample which was not exposed to specified HT, Se^0 excess in amount of 10 % was observed only superficially, and at depth of 3 nm Se^0 concentration was only 4 %. KLL-Auger spectrum of zinc looked like the characteristic spectrum for ZnSe with low ZnO impurities. Results of XRPS-analysis obtained in [1] bear witness to that reaction (1) and, especially, the reaction (3) presented in Table 1 really occur. The data of the study [4] also confirm that the reactions (1) and (3) take place on ZnSe crystals surface. In [4] it has been found that at exposure ZnSe in the air (i.e. with interference of H_2O and O_2) the part of oxygen transfers into a tightly bound state substituting selenium ions in ZnSe which, in turn, transfer in the adsorbed state. Such state of selenium conforms to Se^0 state [1].

As to ZnO definition as one of (1) and (3) reaction products, by results of XRPS it is impossible to state univocally what phase, ZnO or $Zn(OH)_2$, is formed as a result of HT in H_2O vapors in the air [1]. The analysis of zinc and oxygen spectra allows only supposing that there is either ZnO, or $Zn(OH)_2$, or an intermixture of these phases on ZnSe surface. The analysis of temperature dependence of lg K° carried out for reaction $ZnO + H_2O(g) \rightleftarrows Zn(OH)_2$ testifies that at temperatures near the room temperature simultaneous existence of these phases is practically equiprobable. This statement is consistent with the data well-known from the literature as for existence domain and the physicochemical properties of $Zn(OH)_2$ (see e.g. [10]), and also with the data [4] of mass-spectrometry of secondary ions of ZnSe crystals surface. According to [4], the intensive peaks of ions ZnO^+ and $ZnOH^+$ were observed in the spectra of secondary ions.

Therefore we considered reactions with formation both ZnO (reactions (1), (3), (5), (7), (9), (11), (13)–(15)), and $Zn(OH)_2$ (reactions (2), (4), (6), (8), (10), (12)) as one of the products. Thus it is possible to write down a resultant reaction balance equation where a product is not ZnO, but $Zn(OH)_2$, in the same way, combining simple known reactions. For example, reaction (2) is obtained combining following concurrent reactions:

$$ZnO + H_2O(g) \rightleftarrows Zn(OH)_2, \quad (2a)$$

$$ZnSe + CO_2 \rightleftarrows ZnO + COSe, \quad (2b)$$

$$COSe + H_2O(g) \rightleftarrows CO_2 + H_2Se, \quad (2c)$$

$$H_2Se \rightleftarrows H_2 + Se(s) \quad (2d)$$

the resulting reaction:

$$ZnSe + 2H_2O(g) \rightleftarrows Zn(OH)_2 + H_2 + Se(s). \quad (2)$$

Reaction (4) is a combination of the reactions:

$$3ZnO + 3H_2O(g) \rightleftarrows 3Zn(OH)_2, \quad (4a)$$

$$2ZnSe + O_2 \rightleftarrows 2ZnO + 2Se(s), \quad (4b)$$

$$ZnSe + CO_2 \rightleftarrows ZnO + COSe, \quad (4c)$$

$$COSe + H_2O(g) \rightleftarrows CO_2 + H_2Se, \quad (4d)$$

$$H_2Se \rightleftarrows H_2 + Se(s) \quad (4e)$$

the resulting reaction:

$$3ZnSe + 4H_2O(g) + O_2 \rightleftarrows \rightleftarrows 3Zn(OH)_2 + H_2 + 3Se(s). \quad (4)$$

All other complex reactions proposed by us (see Table 1) have been similarly analyzed and the substantiality of their passing is proved.

Given that there is always a significant amount of carbon on an analyzed surface, we have considered along with reactions in which H_2O and O_2 participate, reactions with participation of CO_2 and CO in which carbon can be a product besides H_2 and Se(s). These reactions are also shown in Table 1 (reactions (5)–(15)).

Temperature dependences of lg K° presented in Table 1 have been constructed using first Ulikh approximation [11, 12]:

$$\lg K^o = -\Delta H^o_{298}/(4.576T) + \Delta S^o_{298}/4.576. \quad (1)$$

Dependences lg K° on $1000/T$ are presented in Fig. 1. Thermodynamic data for calculations lg K° are taken from [12–14].

For reactions (3), (4), (7) (Table 1) values lg K° have been calculated according to second Ulikh approximation [11, 12] by the following formula:

$$\lg K^o = -\Delta H^o_{298}/(4.576T) + \Delta S^o_{298}/4.576 + \quad (2)$$
$$[2.3\lg(T/298) - (T - 298)/T] \cdot (\Delta C_p)_{298}/4.576.$$

In Table 2 results of the calculations of lg K° by formula (2) in comparison with the results obtained by formula (1) are given. From Table 2 it follows that in the considered interval of temperatures differences in values of lg K° calculated under formulas (1) and (2) is inappreciable. It has served as a substantiation of legitimacy of first Ulikh approach use for calculations of lg K°.

Let's analyze in more details results of temperature dependence lg K° calculation for the reactions considered.

The detailed analysis of the data presented in Table 1 and Fig. 1 testifies that the probability of passing the reactions (1) and (2) in a forward direction is by tens orders greater than the probability of passing the reactions in the opposite direction, if interaction of ZnSe with H_2O occurs with oxygen participation (reactions (3) and (4)).

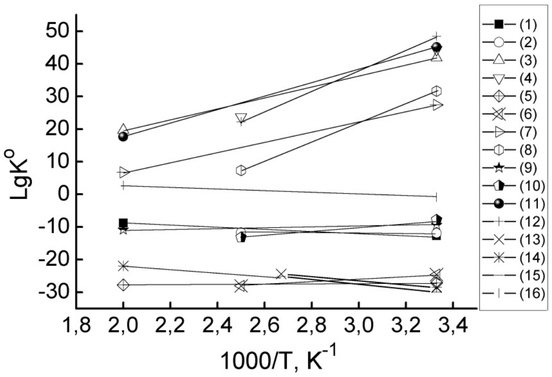

Fig. 1. Temperature dependences of lg K° (line numbers correspond to the numbers of chemical reactions in Table 1).

In real conditions of heat treatment of ZnSe crystals in H_2O vapors in the air the reaction volume represents open flowing system with constant inflow of oxygen and with good heat rejection. Group of thermodynamic and kinetic factors results in the reactions (3) and (4) pass under such heat treatment conditions. Let's note also, that various phase states of H_2O (a fluid or a vapor) and selenium (crystalline or vitreous) in the considered temperature interval does not have essential influence on the reactions behavior (compare reactions (5) and (13), (13) and (14), (13) and (15)).

As to reactions (5), (6), (9), (10), participation of oxygen in these processes also results in very high probability of their passing in a forward direction (reactions (7), (8), (11), (12)). Nevertheless, if to exclude in reference conditions the anthropogenic factors influencing composition of an environmental atmosphere, the share of reactions (7), (8), (11), (12) in processes of interaction of ZnSe crystals with H_2O should be inappreciable in view of smallness of CO and CO_2 content in atmosphere [15].

Table 2. Values of lg K° calculated according to first and second Ulikh approximations

Reaction No. from the Table 1	The temperature dependence lg K°	Values lg K°		
		300 K	400 K	500 K
3, first approximation	$16624.94/T - 13.53$	41.89	28.03	19.72
3, second approximation	$16624.94/T - 13.53 + 0.072$ (*for 500 K*)	41.89	28.05	19.79
7, first approximation	$15516.47/T - 24.26$	27.46	14.53	6.77
7, second approximation	$15516.47/T - 24.26 + 0.085$ (*for 500 K*)	27.46	14.56	6.86
4, first approximation	$24794.91/T - 38.26$	44.38	23.73	11.33
4, second approximation	$24794.91/T - 38.26 + 0.08$ (*for 500 K*)	44.38	23.76	11.41

However in certain conditions the probability of passing reactions (7), (8), (11), (12) can sharply increase. The data of XRPS-analysis from [1] testify that on a surface of ZnSe crystals both before, and after HT the significant amount of carbon related to hydrocarbonaceous pollution is always observed.

Various anthropogenic impurities, CO_2, CO, hydrocarbons, aldehydes, etc. [16], can be an essential source of carbon presence on ZnSe surface. Let's consider one of alternatives of interaction reaction between acetic aldehyde and ZnSe surface:

$$4CH_3CHO + 5ZnSe + 3O_2 \rightarrow$$
$$\rightarrow 5Zn(OH)_2 + 5Se + 3H_2 + 8C,$$

and also reaction

$$CH_3CHO + 2ZnSe + 3O_2 + H_2O \rightarrow$$
$$\rightarrow 2Zn(OH)_2 + 2Se + H_2 + 2C.$$

For both reactions lg $K^\circ > 100$ (on conversion to 4 molecules CH_3CHO) over the temperature range 300...500 K, i.e., probability of passing these reactions in a forward direction is very high.

There is one more source of pollution by carbon of ZnSe crystals, pores in the crystals containing COSe, CO_2, CO and C [5]. These pores are always present in ZnSe crystals which grow in compression furnaces by Bridgman method. In such furnaces basic parts are made of graphite. However from [1] it follows that the surface of the crystal which has not been exposed to HT in H_2O vapors after etching by the ionic gun contains carbon in 10 times less at depth of 3 nm than the initial surface. It means that effect of pores in ZnSe crystals plays a supporting role in processes of pollution of ZnSe crystals surface by carbon. The basic role in these processes is played by other sources including anthropogenic impurities. It should be considered at designing of technology for production of ZnSe crystals with severe requirements to surface cleanliness.

3. Conclusions

It is shown that probability and intensity of reactions of ZnSe crystal surface interaction with water vapor, CO and CO_2 in which hydrogen is released sharply increases if oxygen participates in these reactions. The essential contribution to these processes could be made by anthropogenic impurities in the air (hydrocarbons, CO, CO_2, engine exhaust fumes, etc.) which result in pollution of ZnSe crystal surface by carbon.

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Вплив кисню на деякі реакції взаємодії поверхні кристалів ZnSe з парою H_2O, CO_2 та CO

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Розглянуто вплив кисню на деякі реакції взаємодії поверхні кристалів ZnSe з парою води, CO_2, CO, які приводять до виділення водню, а також вуглецю на поверхні кристалів. Розраховано температурні залежності констант рівноваги. Встановлено, що участь кисню у процесах взаємодії, які розглянуто, приводить до різкого зростання вірогідності та інтенсивності їх реального протікання. Показано, що суттєвий внесок у ці процеси може внести наявність антропогенних домішок у повітрі (вода, вуглеводневі домішки, CO_2, CO, випускні гази двигунів тощо), яка грає важливу роль у забрудненні поверхні кристалів ZnSe вуглецем.