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Abstract

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STUDY OF THE INTERACTION OF LEAD SELENIDE WITH OXYGEN

In the present work the kinetics of the interaction of lead selenide with oxygen in the range 122–496°C has been studied; the composition of the oxidation products has been established by X-ray diffraction; and the surface area and specific resistance of lead selenide samples before and after oxidation have been determined. It was reported earlier that in the range 500–600° lead selenide is oxidized to lead selenite; in the range 600–800° to oxyselenite $2PbO \cdot PbSeO_3$; at 800–900° oxysalt $4PbO \cdot PbSeO_3$ is formed; and above 900° lead oxide is formed ([1,2]).

Experimental Part

A sample for study, thoroughly ground in an agate mortar, was prepared from single-crystal lead selenide synthesized by the vibration method ([3]) and sublimed in vacuum. After heating in vacuum at the temperature of the experiment, the surface area (S) of the samples was measured by the BET method ([4]). For this purpose the molar amount of krypton adsorbed on 1 g of PbSe (a) was measured at various ratios p/p_0 (p is the pressure of Kr in the system, p_0 is the vapor pressure of saturated liquid Kr at the temperature of the experiment ([5])). From graphs corresponding to the relation

$$\frac{p}{a(p_0 - p)} = \frac{1}{a_m \cdot c} + \frac{c-1}{a_m \cdot c}\frac{p}{p_0}, \tag{1}$$

where c is a constant ([4]), the number of moles of Kr required to form a monolayer (a_m) was determined. The adopted value of the effective area of krypton was $19.5 \cdot 10^{-16}$ cm^2 ([5]). The results of determining S are given in Table 1. Assuming that the powder consists of cubes with side x, and proceeding from the surface area of the powder (Table 1) and the pycnometric density of lead selenide $d = 8.30$ g/cm^3 ([6]), the most probable value was calculated as $x \cong 2$–$3\ \mu$. Electron-microscopic observation confirmed these calculations. The kinetics of the interaction of lead selenide with oxygen was studied in the range 122–496° on an apparatus consisting of: 1) torsion balances of G. Muttik' s design ([7]); 2) a vacuum post; 3) an oxygen purification system; 4) reservoirs for storing O_2, Kr, He, Ar (He and Ar for heating the sample in an inert atmosphere); 5) a system for heating, monitoring, and regulating the temperature.

The sensitivity of the balance was $2 \cdot 10^{-5}$ g, the load 10 g, and the temperature coefficient less than $2 \cdot 10^{-5}$ g when the thermostat temperature changed by 1°. The balance was placed in a glass jacket, to which a tube was sealed for the sample, placed in a container suspended from the beam by a metal thread. The container was made of three platinum dishes (diameter 1.8 mm, wall height 2.5 mm), placed one beneath another. During heating the entire container was in a zone of constant temperature. A vacuum of $2 \cdot 10^{-5}$–$6 \cdot 10^{-6}$ mm Hg was produced by VN-461 and MM-40A pumps. The pressure in the system was measured with U-shaped and compression mercury manometers, as well as with a VIT-1 vacuum gauge. Oxygen for oxidation was purified by passing it successively through H_2SO_4, $MgClO_4$, palladized asbestos heated to 450–500°, KOH, P_2O_5, and a trap, cool-

Table 1

Results of studying the interaction of PbSe + O_2

	122° before oxid.	122° after oxid.	275° before oxid.	275° after oxid.	317° before oxid.	317° after oxid.	496° before oxid.	496° after oxid.
Sample weight, g	8.94180	8.94395	8.93480	8.97530	9.93650	9.01395	2.59445	2.67550
Change in weight on degassing, in % relative to initial sample	0.043		0.008		0.038		0.15	
Surface area, cm^2	24500		18800	16300	32700	18800	3050	6600
Resistivity, ohm · cm	0.20	0.12	0.15	0.60	0.15	1.29	0.16	39

	122° before oxid.	122° after oxid.	275° before oxid.	275° after oxid.	317° before oxid.	317° after oxid.	496° before oxid.	496° after oxid.
Total amount of absorbed oxygen in % relative to initial sample		0.02		0.45		0.87		3.1
Reversible O_2 in % of total amount		35		0.4		0.6		0.37
Chemically bound O_2 in % of total amount		65		99.6		99.4		99.63
Amount of oxidized PbSe in % relative to initial sample		0.09		3.69		5.07		18.4

cooled with liquid nitrogen. Before admission into the storage reservoir, the oxygen was liquefied. The middle fraction of the gas evaporating from the trap was used for the work. The sample was heated by a TG-02 furnace supplied with voltage-stabilized current; the temperature was monitored potentiometrically with a XA thermocouple (R-307 potentiometer); heating was regulated by an EPV-01 potentiometer. The oxygen pressure in all experiments was 150 ± 1 mm Hg. Figure 1 shows the change in the amount of oxygen absorbed (Δm) with time (t). The initial rate of interaction is described by the parabolic equation

$$(\Delta m)^2 = kt. \tag{2}$$

From the temperature dependence of the rate constant $k = Ae^{-\Delta E/RT}$, where A is a constant, the activation energy was determined as $\Delta E = 15$ kcal/deg · mol, which agrees with the values obtained in works (^{8,9}). Table 1 gives data on “reversible”oxygen (removed by heating in vacuum) and “irreversible”(chemically bound) oxygen.

Fig. 1. Kinetics of oxidation of lead selenide by oxygen. *a*—122°, unit ordinate 0.01; *b*—275°, 0.25; *v*—317°, 0.25; *g*—496°, 10.

X-ray phase study of oxidized and unoxidized lead selenide samples was carried out with CoK and CuK_α (^{10}) radiation in RKU-86 and RKD-57 cameras with an asymmetric film loading. A flat germanium single crystal was used as monochromator, which made it possible to obtain sharp lines in the photographs. The principal product of oxidation of lead selenide by oxygen in the range studied is lead selenite, $\mathrm{PbSeO_3}$ (see Table 2), while in the samples, by X-ray analysis (photography with $\mathrm{Cu} = \mathrm{K}_\alpha$ radiation), up to 0.1 wt.% of oxidation product is detected. The lattice parameter a of PbSe upon oxidation does not change within the limits of measurement error and is $a = 6.114 \pm 0.001$ kX. The data obtained differ from the results of work (^{9}), in which the process of interaction of lead selenide with oxygen is considered as diffusion of oxygen into selenium vacancies of the lead selenide lattice without the formation of chemical compounds.

The rectilinear course (in the coordinates Δm—$\sqrt{t}$) of the initial portions of the ki-

Table 2

Results of X-ray phase analysis of the products of interaction of PbSe + $\mathbf{O_2}$

PbSeO$_3$: I; d, kX	PbSe: I; d, kX	122°, 6 h: I; d, kX	275°, 20 min: I; d, kX	275°, 6 h: I; d, kX	317°, 6 h: I; d, kX	495°, 6 min: I; d, kX	495°, 11 min: I; d, kX	495°, 4 h: I; d, kX
4; 4.15				0.1; 4.17	0.5; 4.18	0.8; 4.17	0.8; 4.18	2; 4.18
8; 3.41	2; 3.54	3; 3.56	2; 3.55	3; 3.56	3; 3.56	3; 3.55	3; 3.57	4; 3.55
9; 3.32		0.2; 3.32	1; 3.42	1; 3.42		1; 3.42	1; 3.44	3; 3.42
6; 3.16		0.2; 3.15	1; 3.32	1; 3.32	0.5; 3.34	1; 3.33	1; 3.35	3; 3.33
	10; 3.06	10; 3.07	1; 3.17	1; 4.17	0.5; 3.17	1; 3.17	1; 3.20	3; 3.17
2; 2.99		0.1; 2.99	10; 3.07	10; 3.07	10; 3.07	10; 3.07	10; 3.09	10; 3.07
10; 2.74		0.3; 2.75	2; 2.175	1; 2.75	0.2; 2.99	0.1; 2.99	0.5; 2.98	1; 2.99
2; 2.62		0.1; 2.59	—	—	1; 2.76	2; 2.74	2; 2.77	4; 2.75
1; 2.33		0.1; 2.35	—	—	0.2; 2.64	0.8; 2.63	0.8; 2.65	2; 2.63
4; 2.26		0.1; 2.22	1; 2.26	1; 2.26	0.1; 2.35	0.1; 2.33	0.1; 2.33	1; 2.33
0.5; 2.15	10; 2.165	10; 2.16	10; 2.166	10; 2.165	0.4; 2.26	0.8; 2.26	0.8; 2.27	2; 2.26
4; 2.103		—	—	—	10; 2.17	10; 2.166	10; 2.173	10; 2.166
5; 2.078		—	0.5; 2.084	0.5; 2.080	—	1; 2.084	—	3; 2.084
4; 2.025		—	0.5; 2.026	0.5; 2.025	1; 2.084	1; 2.026	1; 2.027	3; 2.026
2; 2.001		0.1; 2.00	0.5; —	—	—	1; —	—	2; 2.005
2; 1.964		—	—	—	—	0.5; 1.972	0.5; 1.973	2; 1.972
1; 1.946		—	—	—	—	—	—	2; 1.951
2; 1.895		—	—	—	0.4; 1.895	0.5; 1.897	0.5; 1.902	2; 1.897
	6; 1.846	4; 1.85	6; 1.847	4; 1.846	4; 1.845	3; 1.847	3; 1.847	5; 1.847
2; 1.788		0.1; 1.79	—	—	—	—	0.1; 1.796	1; 1.793

$PbSeO_3$: I; d, kX	PbSe: I; d, kX	122°, 6 h: I; d, kX	275°, 20 min: I; d, kX	275°, 6 h: I; d, kX	317°, 6 h: I; d, kX	495°, 6 min: I; d, kX	495°, 11 min: I; d, kX	495°, 4 h: I; d, kX
0.8; 1.763	7; 1.768	5; 1.77	7; 1.767	5; 1.767	4; 1.768	4; 1.767	4; 1.773	6; 1.767
1; 1.743		–	–	–	–	0.1; 1.745	–	2; 1.745
2; 1.713		–	–	0.2; 1.720	–	0.1; 1.720	–	2; 1.720
2; 1.693		–	–	0.2; 1.701	–	1; 1.697	1; 1.697	3; 1.701
1; 1.679		0.1; 1.65	–	–	–	0.1; 1.681	–	2; 1.681
2; 1.639		0.1; 1.63	–	–	–	0.5; 1.644	0.5; 1.646	2; 1.644
2; 1.585		0.1; 1.587	–	1.591	0.2; 1.586	1; 1.591	1; 1.591	3; 1.591
; 1.561		0.1; 1.549	–	1.562	–	1; 1.562	0.8; 1.563	3; 1.562
	6; 1.531	6; 1.430	6; 1.530	4; 1.528	4; 1.530	4; 1.518	3; 1.533	5; 1.528
; 1.494	–	–	–	–	–	0.2; 1.498	0.1; 1.498	2; 1.498
	–	–	–	–	–	–	–	1; –

···of the kinetic curves (Fig. 1) is connected with the diffusion of oxygen into anion vacancies (^{6}, ^{7}), with the formation and development of the oxide phase.

X-ray diffraction shows that lead selenide is detected in the samples under study both before and after the point in time corresponding to the break in the kinetic curves (see Table 2). By this time the portion of oxidized lead selenide is 0.07% at 122°, 2.01% at 275°, 3.6% at 317°, and 13.6% at 496°. It may be assumed that the break in the kinetic curves corresponds to the formation of such a thickness of oxide film that it becomes protective and, at the given temperature, sharply reduces the oxidation rate. The film completely covers the PbSe surface, since the specific molar volume of $PbSeO_3$ (v_1) is greater than the specific molar volume of PbSe (v_2) ($v_1 : v_2 \simeq 1.47$). In addition, $PbSeO_3$ is not a volatile compound (^{11}), and therefore the oxidation of lead selenide is associated with the growth of continuous surface layers of $PbSeO_3$ firmly bound to the underlying lead selenide layer. Calculation of the thickness ξ, carried out by the formula

$$\xi = \frac{\Delta m \cdot M_1}{M_x \cdot \rho_1} \tag{12}$$

(Δm is the change in sample weight, g/cm^2; M_1 and ρ_1 are the molecular weight and density of $PbSeO_3$; M_x is the weight of oxygen in 1 mole of $PbSeO_3$), shows that the limiting thickness of the oxide film, when the oxidation rate sharply decreases, is approximately 4 Å at 122°, 150 Å at 275°, 170 Å at 317°, and 700 Å at 496°. The course of the kinetic curves after the break is characterized by a noticeable decrease in the oxidation rate and is determined by the growth of the oxide phase, a decrease in surface area, and the appearance of mechanical defects. It is not possible to describe the oxidation kinetics unambiguously in this case.

To measure electrical conductivity, PbSe powders were pressed into cylindrical pellets (diameter 5 mm, length 8-10 mm) at a pressure of 50 kG/cm^2 on an LMZ press. The measurement method was compensating (^{13}). (When measuring the potential difference between the compensating electrodes, the error arising from the thermal emf of the PbSe—Ta pair was taken into account.) The results are presented in Table 1. It should be noted that the conductivity of sele-

lead selenide treated with oxygen at 122° increases; in all other cases, however, the conductivity falls as lead selenide accumulates in the initial sample.

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Note: Figure translations are in progress. See original paper for figures.