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Abstract

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Investigation of the Lead Selenite–Lead Oxide System

As a result of studying the process of interaction of lead selenide with oxygen ([1]), it was shown that at 500-600° the only oxidation product is lead selenite. At higher oxidation temperatures (700-900°), crystalline phases were found whose compositions are close to the oxyselenites $2PbO \cdot PbSeO_3$ and $4PbO \cdot PbSeO_3$. These same compounds and lead oxide were found in the products of thermal decomposition of lead selenite ([2]). In order to determine more precisely the composition and limits of existence of lead oxyselenites, we studied the system $PbSeO_3$–PbO by methods of thermal and X-ray phase analysis.

For preparing the mixtures, yellow lead oxide of chemically pure grade and lead selenite, obtained from selenious acid (chemically pure) and chemically pure lead nitrate, were used ([3]). The initial $PbSeO_3$ was analyzed for lead content by complexometric titration with the indicator 1-(2-pyridylazo)-2-resorcinol ([4]) and for selenium by the iodometric method ([5]). The positions and relative intensities of the lines on the X-ray pattern of the initial lead selenite agreed well with the literature data ([3], [6]).

Samples for thermal analysis were prepared by calcining thoroughly ground and mixed component mixtures in evacuated quartz ampoules. X-ray phase and thermal analysis of several samples obtained with different calcination times showed that, under our conditions, for obtaining equilibrium mixtures with a PbO content of less than 70 mole %, calcination for 20 hours at 560-570° was sufficient; for mixtures with a higher content of lead oxide, calcination for 40 hours at 630-650°* was required. We did not prepare samples by melting the components, because lead selenite melts with decomposition and evolution of selenium dioxide ([2]).

Differential thermal analysis was carried out on an N. S. Kurnakov PK-52 pyrometer with platinum-platinum-rhodium thermocouples. The temperature was determined with an accuracy of $±$5°. Aluminum oxide was used as the reference substance. The samples under investigation were placed in a platinum crucible. The usual sample mass was 0.8 g. Because of the pronounced supercooling of the melts and the change in the composition of mixtures upon melting, only heating curves were recorded. The average heating rate was 10-

Fig. 1. The PbSeO3—PbO system. a—heating rate 10-12 deg/min, b—heating rate 5-6 deg/min

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12 deg/min, and in individual cases 5-6 deg/min. Chemical analysis of several samples heated at a rate of 5-6 deg/min to complete melting and rapidly cooled established that the composition of the mixtures changed in this case by less than 1%.

X-ray patterns were obtained by the powder method using Fe—K radiation in RKD cameras 57.3 mm in diameter. For high-temperature X-ray photography, a "Unicam" camera ([7]) with a diameter of 190.05 mm was used. In all cases the substance was placed in capillaries made of Pyrex glass. The intensity of the lines of the X-ray patterns was estimated visually on a five-point scale.

* At higher temperatures the substances strongly corrode quartz.

The phase diagram of the system, obtained on the basis of thermal and X-ray phase analysis data for annealed mixtures, is shown in Fig. 1. The results of the X-ray phase analysis of the annealed mixtures are presented in Fig. 2.

The melting temperatures of the components determined by us—$PbSeO_3$ and PbO—proved to be 680 and 885°. Two compounds were found in the system—oxyselenites of the compositions $2PbO \cdot PbSeO_3$ and $4PbO \cdot PbSeO_3$.

The oxyselenite $2PbO \cdot PbSeO_3$ melts at 755° with decomposition:

$$2PbO \cdot PbSeO_3 \rightleftarrows \text{melt} + 4PbO \cdot PbSeO_3$$

and forms a eutectic with lead selenite at 605° and 33.3 mol. % PbO. The oxyselenite $4PbO \cdot PbSeO_3$ melts congruently at 805° and forms a eutectic with lead oxide (800°, 83.3 mol. % lead oxide).

Fig. 1. The $PbSeO_3$—PbO system.
a—heating rate 10-12 deg/min, *b*—heating rate 5-6 deg/min

In thermal analysis, in addition to effects definitely attributable to the decomposition or melting of the above-mentioned phases, a number of effects were found that could not be interpreted unambiguously. Thus, in the region of 45-63 mol. % lead oxide, at a heating rate of 5-6 deg/min, a series of endothermic effects appears (625, 650, and 710°); these are absent, or appear only as small inflections on the differential curves, at a heating rate of 10-12 deg/min. In addition, at slow

Fig. 2. Bar diagrams of annealed mixtures in the $PbSeO_3$—PbO system

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Figure 2: Fig. 2. Bar diagrams of annealed mixtures in the PbSeO3—PbO system

upon heating, the final melting temperatures of mixtures containing 55 and 60 mol.% PbO decrease from 750 and 755°, respectively, to 730°. The eutectic effect (605°) appears on the thermograms of all samples, regardless of the heating rate. It was not possible to determine the nature of these effects by comparing the magnitudes of the peaks of the differential trace and by visual observations. X-ray phase study of quenched samples of composition 1 : 1 showed that they consist only of two phases: $PbSeO_3$ and $2PbO \cdot PbSeO_3$. The use of high-temperature X-ray photography proved impossible, since we were unable to select a material for the capillary that would not interact with the substances at temperatures above 600°. It is possible that the indicated thermal effects are due to the formation and transformations of the unstable oxyselenite $PbSeO_3 \cdot PbO$.

Furthermore, on the thermograms of mixtures containing from 5 to 20 mol.% lead oxide, in addition to the eutectic effect, an endothermic effect appears at 625°, which is absent from the thermogram of pure lead selenite. The effect is reversible. In the Debyegram of a sample of composition 95 mol.% $PbSeO_3$ and 5 mol.% PbO, quenched from 640°, in addition to the principal lines of lead selenite, there are several lines that do not belong to $PbSeO_3$ or $2PbO \cdot PbSeO_3$. This effect may be attributed to a reversible polymorphic transformation of lead selenite stabilized by the oxyselenite $2PbO \cdot PbSeO_3$. The possibility is not excluded that the effect is due to melting of the eutectic of the compound $PbSeO_3 \cdot PbO$ assumed by us with lead selenite.

Effects that are not always reproducible at $275 \pm 10°$ and $370 \pm 10°$ are observed on the thermograms of mixtures containing 25-75 mol.% lead oxide. To establish the nature of the effects, we obtained X-ray photographs of a quenched mixture of composition 1 : 1 and of the oxyselenite $2PbO \cdot PbSeO_3$ at temperatures of 20, 320, and 450°. All three X-ray photographs of each sample are identical to one another. Thus, the observed transformations are not associated with the formation and decomposition of new crystalline phases and, possibly, are transformations of the second kind of the oxyselenite $2PbO \cdot PbSeO_3$.

X-ray phase analysis of the oxyselenites obtained showed that, in structure, they are identical to the crystalline phases previously found (^{1}) in the oxidation products of lead selenide. $2PbO \cdot PbSeO_3$ crystallizes in a tetragonal lattice with the parameters of the body-centered unit cell $a = 3.92$ kX, $c = 5.37$ kX; $4PbO \cdot PbSeO_3$—in a rhombic lattice with the parameters of the body-centered unit cell $a = 3.92$ kX, $b = 3.73$ kX; $c = 5.72$ kX.

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