

# INVESTIGATION OF THERMAL BEHAVIOR OF $\alpha$ -PbO AND $\beta$ -PbO IN O<sub>2</sub> ATMOSPHERE

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The compounds  $\alpha$ -lead oxide ( $\alpha$ -PbO) and  $\beta$ -lead oxide ( $\beta$ -PbO) were purchased from Merck co. and used for thermal investigations in laboratory. The compound was heated in a thermogravimeter at different temperature, from 25 to 400 °C. The used gas atmosphere was O<sub>2</sub>. The received products were investigated by X-ray diffraction (XRD) technique. The received product Pb<sub>3</sub>O<sub>4</sub> was confirmed by XRD. The textures of two different morphologies of  $\alpha$ -PbO,  $\beta$ -PbO and the product Pb<sub>3</sub>O<sub>4</sub> is investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM) techniques.

**Keywords:** lead (II) oxide, Pb<sub>3</sub>O<sub>4</sub>, thermal analysis, thermogravimetry, SEM-TEM.

## INTRODUCTION

Due to their chemical and physical characteristics, lead compounds are used in a wide variety of industries all over the world [1-6]. One of the most important characteristics of the lead concerns its reactions to acids and bases as well as to air, a process known as oxidation. Compounds like “lead (II) oxide,  $\alpha$ -lead oxide ( $\alpha$ -PbO) and  $\beta$ -lead oxide ( $\beta$ -PbO)” are the by-products of these reactions. Some are the end product of a desired process but most of them are undesired byproducts known as disturb compounds [7-9].

Lead(II) oxide [3,7] have two morphology known as  $\alpha$  and  $\beta$ . The present research intended to investigate the thermal properties of  $\alpha$ -lead (II) oxide under different temperature conditions. It is said that pure Pb<sub>3</sub>O<sub>4</sub> is the final product of the isothermal treatment process for compounds  $\alpha$ -PbO and  $\beta$ -PbO [10-11]. The morphology of these compounds was also studied [12]. The objective of this investigation are the study of thermogravimetry of  $\alpha$ -PbO and  $\beta$ -PbO in O<sub>2</sub> atmosphere.

## EXPERIMENTAL

### Materials and equipment

$\alpha$ -lead oxide ( $\alpha$ -PbO, artikel no. 7401, yellow, rhombic, massicot) and  $\beta$ -lead oxide ( $\beta$ -PbO, artikel no. 7405, red, tetragonal, litharge) were purchased from Merck AG Co., Darmstadt, Germany

TGA: Thermogravimeter, Mettler TG50, coupled with a TA processor.

XRD: X-Ray diffractometer D 5000, Siemens, Kristalloflex.

SEM: Scanning electron microscope, REM-JEOL (JXA-840), Japan.

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TEM: Transmission electron microscope, HITACHI, H-600, Japan.

### X-ray diffraction of $\alpha$ -PbO and $\beta$ -PbO

The  $\alpha$ -PbO and  $\beta$ -PbO samples were prepared in Bedacryl and exposed during two hours with CuK $\alpha$ 1 radiation. The received XRD diagrams of the compounds  $\alpha$ -PbO and  $\beta$ -PbO, which were confirmed by ASTM diagrams (ASTM: American Society for Testing and Materials).

### SEM and TEM sample preparation

The preparation of the samples for SEM was accomplished by gold coating its surface for 3 - 4 min. the morphology investigation of the  $\alpha$ -PbO and  $\beta$ -PbO samples was accomplished on a SEM instrument. The reseauable enlargement were 500 times for  $\alpha$ -PbO and 1000 times for  $\beta$ -PbO. The final photographs are shown in Figure 1.

The second series of electron microscopic investigation with TEM equipment were also accomplished. The sample was prepared as follows. The white powdery sample was coated first with a thin coal film. This film was than treated with HF acid from the surface and investigated in the TEM equipment. The applied enlargements were 6 000 to 8 000 (Figure 2).

### TGA (thermogravimetry analysis) and DTG (deviation of thermogravimetry analysis) of $\alpha$ -PbO and $\beta$ -PbO

It were weighed 47,022 mg  $\alpha$ -PbO in a standard container from corundum. Likewise were weighed 49,085 mg  $\beta$ -PbO in a standard container. This was heated up in the temperature range 25 – 450 °C. The heating rate was 1°C/min and the flow gas was O<sub>2</sub> (15

ml/min). Both TGA and DTG curves of  $\alpha$ -PbO and  $\beta$ -PbO are shown in Figure 3.

### Isothermal TGA and DTG analysis of $\alpha$ -PbO and $\beta$ -PbO

In the case of  $\alpha$ -PbO, the sample start with the absorption of O<sub>2</sub> from atmosphere and the weight of the sample began to increase. The temperature was kept constant. This was heated at the temperature range 400 °C. The heating time was 600 min and the flow gas was O<sub>2</sub> (15 ml/min) (Figure 4).

In the next case, the sample of  $\beta$ -BO start with the absorption of O<sub>2</sub> from atmosphere at 360 °C and the weight of the sample began to increase. The temperature was kept constant. This was heated at the temperature range 360 °C. The heating time was 600 min and the flow gas was O<sub>2</sub> (15 ml/min) (Figure 4).

## RESULTS AND DISCUSSION

### Crystal structure of lead (II) oxides

The structure consists of a chain in which each Pb atom is adjacent to two O atoms (Pb-O = 2,21 Å). These chains are weakly bound to layer of two Pb-O bonds (Pb-O = 2,49 Å). This layer is in the orthorhombic PbO, simply packed type of such tetragonal PbO, where four equivalent Pb-O bonds (2,30 Å) replace two shorter (2,31 Å) and two longer (2,49 Å) Pb-O bonds.

It will be pointed out that PbO can be detected as a defect fluorite structure in which every second layer of O atoms is located in the (001) direction. In the tetrahedral  $\beta$ -PbO, each Pb atom has four adjacent O atoms. The Pb<sup>2+</sup> and O<sup>2-</sup> ions form layers

### XRD results

The XRD results obtained in this work is in a good agreement with standard diagrams (ASTM 38-1477) for  $\alpha$ -PbO and (ASTM 5-561) for  $\beta$ -PbO. In the same way the obtained product was examined with XRD technique. The obtained results were in a good agreement with standard diagram (ASTM 38-1477) for Pb<sub>3</sub>O<sub>4</sub> (ASTM 8-19).

### SEM and TEM results

Figures 1 and 2 show the SEM and TEM electron micrographs of this compounds. These compounds consist of octahedral crystals, which are joined to produce large particles. The relative diameters of crystals are 1 to 50  $\mu$ m. The channel between particles lie in regular consequences and intervals, which makes a good flow of the electrolyte possible. The presence of this kind of "regular channels" causes good electrochemical contacts with the particles.

### Thermal investigations

Both TGA and DTG curves of  $\alpha$ -PbO and  $\beta$ -PbO are shown in Figure 3. The Both TGA and DTG curves look identical. A comparison of the curves would help an understanding of the rate of weight loss or gain at each stage and provide more information about rates of decomposition respective composition at each stage and possible interaction between two consecutive stages (Table 1).

In the top of the picture was shown the simple thermolyse (thermal decomposition). The vertical axis shows the decrease in weight and the axial shows the

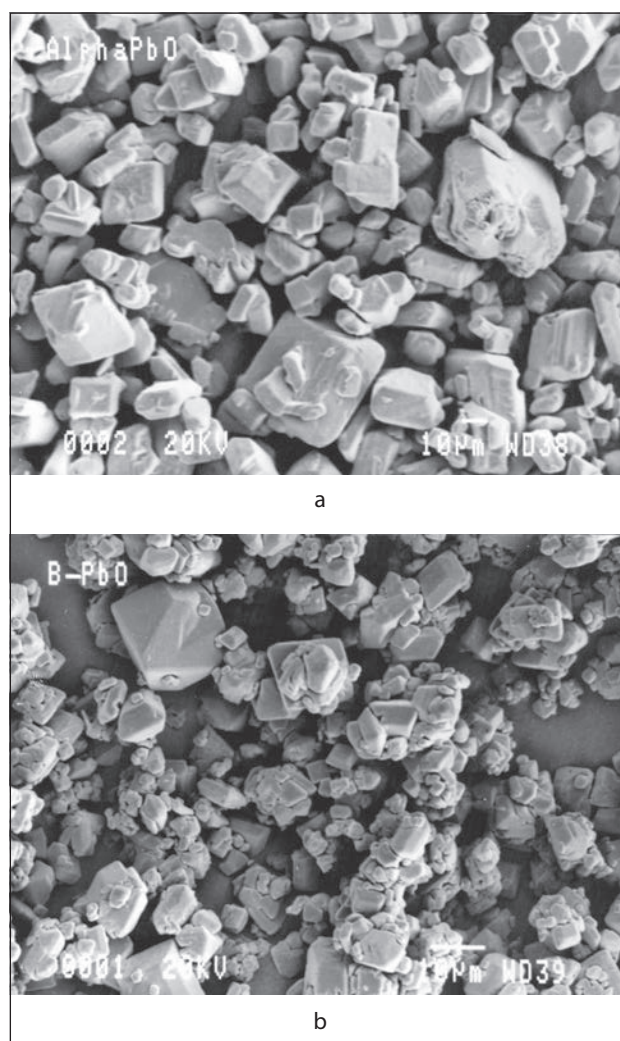


Figure 1 SEM of a)  $\alpha$ -PbO, 500 X and b)  $\beta$ -PbO, 1 000 X.

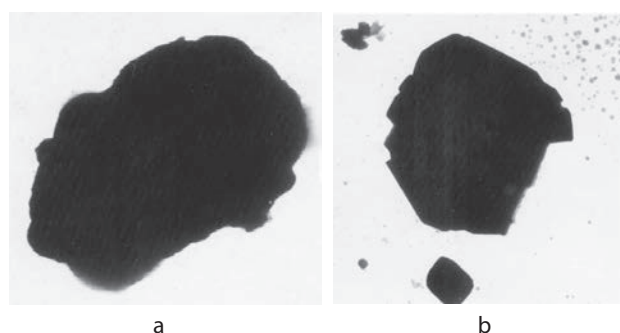
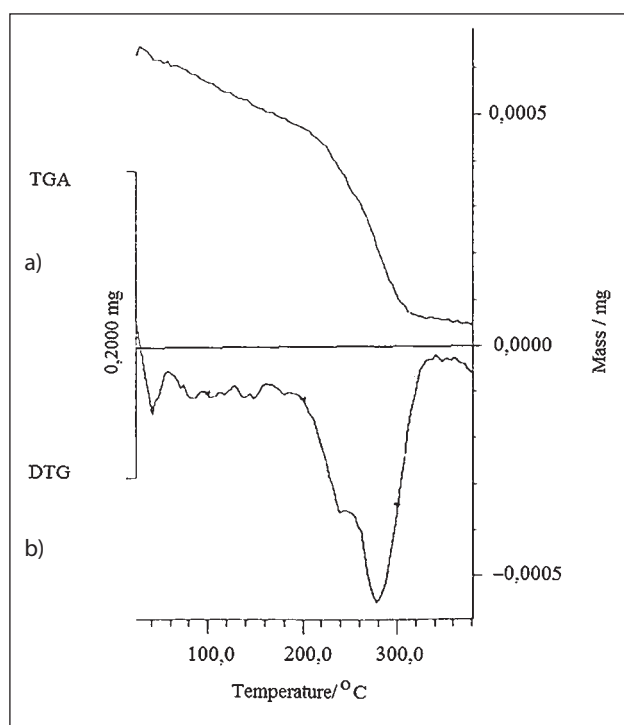
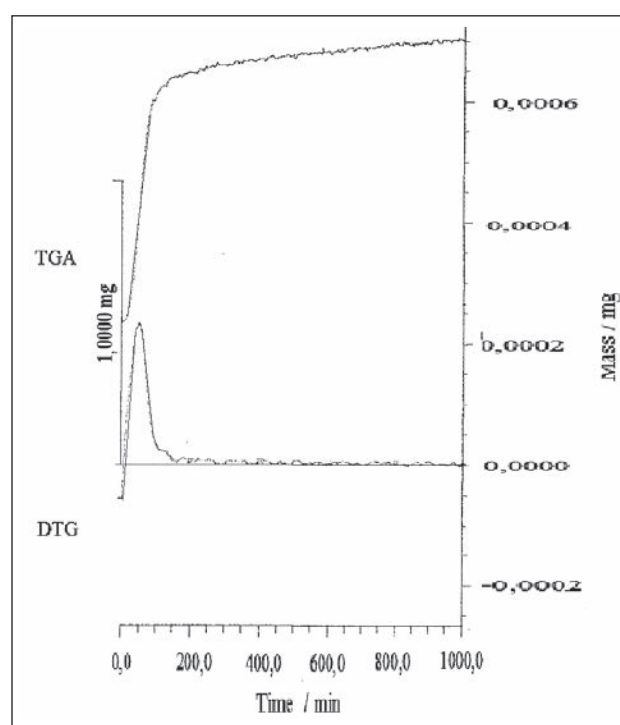


Figure 2 TEM of a)  $\alpha$ -PbO, 8 000 X and b)  $\beta$ -PbO, 6 000 X.



**Figure 3** TGA and DTG diagrams of a) orthorhombic  $\alpha$ -PbO and b) tetrahedral  $\beta$ -PbO.



**Figure 4** Isothermal TGA and DTG diagrams of  $\alpha$ -PbO and  $\beta$ -PbO under O<sub>2</sub> atmosphere, flow rate: 15 ml/min.

**Table 1 Results of the thermal investigations of  $\alpha$ -PbO and  $\beta$ -PbO in temperature range 25 – 400 °C.**

Compound	Start temp./ °C	Turning point/ °C	End temp./ °C	Weight decrease /mg	Weight decrease /%
$\alpha$ -PbO	25,0	280,8	381,7	-0,176	-0,37
$\beta$ -PbO	25,0	278,3	430,3	-0,196	-0,40

**Table 2 Results of isothermal TGA and DTG analysis of  $\alpha$ -PbO and  $\beta$ -PbO in constant temperature 400 °C.**

Compound	Start temp./ °C	Start time/ min	End time/ min	Weight increase /mg	Weight increase/ %
$\alpha$ -PbO	400,0	0,0	600,0	+0,208	+0,44
$\beta$ -PbO	400,0	0,0	1 000,0	+1,001	+2,04

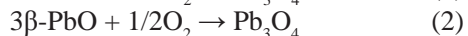
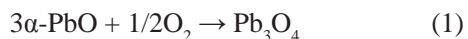
temperature changes. In the lower part of the picture was shown the first derivation of the thermolyse curve (DTG). So one can differentiate better between the stages of the thermal decomposition. From the results of the analysis of the thermal decomposition follows that this reaction consist of three stages. This was summarized in the table 1. It shows the results of the thermal decomposition of  $\alpha$ -PbO and  $\beta$ -PbO in the temperature range 25 - 400 °C. In the range 25 – 110 °C escapes the crystal water from the system. A standard crucified aluminum crucible was filled with 47,022 mg  $\alpha$ -PbO and placed in instruments. The sample was heated at a predetermined heating rate. When  $\alpha$ -PbO is heated up in the temperature interval 200 – 300 °C, a weight loss or an O<sub>2</sub> release is to be expected, whereby the sample loses about 0,4 % of its weight. After reaching the temperature point, the sample was heated further isothermally for 10 hours. Starting at 400 °C the compound O<sub>2</sub> begins to absorb. From this isothermal part of the TGA curve (Figure 4, Table 2), it can be seen that this oxidation of the sample involves a weight increase of 0,44 %. From our experience in this field we are aware that Pb<sub>3</sub>O<sub>4</sub> should form at 400 °C. The evaluation of the TGA results has shown that the following reaction has not been completed

completely. X-ray analysis showed the following. The TGA product consisted of a mixture of  $\alpha$ -PbO and Pb<sub>3</sub>O<sub>4</sub>. In this case we are concerned with the formation of  $\alpha$ -PbO, Pb<sub>3</sub>O<sub>4</sub>. Thermal decomposition of  $\beta$ -PbO<sub>2</sub> escapes O<sub>2</sub> and develops  $\alpha$ -PbO &  $\beta$ -PbO. This reaction take place at 492 °C. The XRD results confirmed the oxides  $\alpha$ - &  $\beta$ -PbO.

If we compare the TGA curves with each another we see that they are very similar. So that in the temperature range 25 – 400 °C a decrease (loss) of weight is to be observed. This decrease (loss) in weight is equal 2 %. The DTA picture, the first derivation of TGA curve is to be observed in the left side. The loss of weight is here good to observe. In the second phase, in the range 280 – 460 °C happens the second decrease in weight of 3.6 %. This part has a reminder (rest). This is apparent a further reaction, which overlaps with previous and represents together a large reaction. In the third phase, i.e. in the range 460 – 520 °C happens the last thermolyse reaction. In this reaction suffered the compound a decrease (loss) in weight of 2.6 %. The two last reactions are on the left side of fig. 3 to see, i.e. in DTA plot.

A comparison of the XRD results shows that both product are pure. The XRD analysis show good agree-

ment with standard diagram. The spectro-photometric analysis of the sample confirmed the purity of the product as well. For this reason we can define the following reactions:



The oxidation of PbO and its conversion into certain Pb oxide compounds with a higher oxygen content than PbO was interesting for us. This was achieved by increasing the temperature in the oxygen atmosphere. It has been reported that PbO<sub>2</sub> cannot be produced in this way. In this context, we were concerned about some such attempts to produce PbO<sub>x</sub> ( $2 > x > 1$ ) using thermogravimetry.

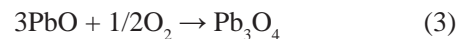
## CONCLUSION

X-ray diffraction patterns of the starting material, and final product have been obtained. These films have been compared with the data of standard known lead oxides compounds. The ASTM standard XRD diagram confirmed the received materials  $\alpha$ -PbO and  $\beta$ -PbO.

In the thermal investigations of  $\alpha$ -PbO and  $\beta$ -PbO we have shown that the particle size plays a very important role in the reaction rate or reactivity of these compounds. This fact can be explained as follows: In the case of coarse-particle solid substances, the conversion is large only at high temperatures at which the nucleation of stable phases is rapid and the diffusion rate is determined. With finely divided powders a high conversion takes place at low temperatures, the diffusion paths are short, and the nucleation takes precedence over the diffusion. The nucleation of the stable compounds is stable at low temperatures, and therefore metastable compounds may arise, or reactions may proceed as single-phase reactions. It is also important to ensure that the lattice defects are important for the reactivity of finely divided substances and can influence a reaction control. At low temperatures and only when a thin surface layer is being built, the reaction is carried out in a single-phase, diffusion-controlled manner.

The reaction speed follows the logarithmic law. At somewhat higher temperatures, the reaction is two-phase; the velocity is determined by the diffusion of the oxygen, by the layer of the reaction product. It follows the parabolic law.

With the help of different methods such as TGA and XRD was examined the thermal behavior of  $\beta$ -PbO<sub>2</sub>. One can as follows defining the thermal decomposition of  $\beta$ -PbO<sub>2</sub>:



The XRD results obtained in this work is in a good agreement with standard diagrams (ASTM 38-1477) for Pb<sub>3</sub>O<sub>4</sub> (ASTM 8-19).

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**Note:** The responsible translator for language English is R. Bahar – Sharif University of Technology Tehran, Iran.