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The PbO_2 – Pb – MoO_3 System in air

M.A. Eissa^a, M.A.A. Elmasry^b, S.S. Younis^a

^a Chem. Eng. Dept., Cairo Univ., Giza, Egypt

^b Metallurgy Dept., Nuclear Research Center, Atomic Energy Authority, Cairo, Egypt

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Abstract

The ternary isobaric diagram, (PbO_2 – Pb – MoO_3), system in air has been drawn to determine the suitable conditions for the preparation of PbMoO_4 . Starting with PbO_2 instead of PbO , it was possible to prepare PbMoO_4 and Pb_2MoO_5 at 405 and 430°C, respectively, instead of 650 and 760°C [7,8].

Keywords: Lead molybdate; Ternary system; Thermal analysis; Thermal decomposition

1. Introduction

Lead molybdates have a wide scope of applications in solid state laser engineering for resonance and emission studies [1–3], microwave, optical maser devices [2], as well as for acousto-optical purposes [4,5]. It is necessary to understand the solid state reactions taking place during the fabrication of this type of ceramics by investigating the equilibrium relationships in the ternary system PbO_2 – Pb – MoO_3 in order to determine the best conditions for their preparation in a reproducible way as a first step in studying their physical characteristics.

There are two lead molybdates reported in the literature, these are PbMoO_4 and Pb_2MoO_5 . The PbMoO_4 , wulfenite, occurs naturally in lead veins with other ores of lead and can be prepared by precipitation from an acetic acid solution of ammonium molybdate using a 4% solution of $(\text{CH}_3\text{COO})_2\text{Pb}$ and calcination [6] or by solid state reaction between PbO and MoO_3 [7,8]. Single crystals of PbMoO_4 are now produced from Pb_3O_4 and MoO_3 melt [9]. Pb_2MoO_5 was prepared from PbO and PbMoO_4 as reported by Jaeger and Germs [10].

* Corresponding author.

The binary system Pb–O was established by Abadir et al. [11], and the equilibrium relationships existing between 0.21 to 1 bar O_2 were determined. From the results of the previous investigation it was concluded that the system Pb–O contains four intermediate compounds these are PbO_2 , PbO_x (with x between 1.41 to 1.58), Pb_3O_4 and PbO .

The phase diagram for the Mo–O system was established by Phillips and Chang [12], by determining the phase relations between 600 and 1700°C. According to this diagram the stable intermediate phases MoO_2 , Mo_4O_{11} , Mo_9O_{26} , and MoO_3 , were identified. No evidence of solid solutions was found between any of these oxides.

The system PbO – $PbMoO_4$ was investigated by Jaeger and Germs [10]. Normal molybdate, $PbMoO_4$, and the basic salt, Pb_2MoO_5 , melting at 1065 and 951°C, respectively, are the only compounds shown on this diagram. Two eutectics at 762 and 933°C corresponding to 87.5 and 40 mol% PbO are depicted in this diagram.

Kunев et al. [6] investigated the system MoO_3 – $PbMoO_4$ and established an equilibrium diagram from which they noted that above 800°C, it was difficult to record the heating curves due to the volatility of MoO_3 and the rapid change in composition of the initial mixture which leads to a sharp rise in liquidus temperature. At 49 mol% $PbMoO_4$ and 670°C the system has a eutectic point. It was reported also that $PbMoO_4$ melts without decomposition [6]. A molybdenum compound having the formula Pb_5MoO_8 was obtained by Doyle and Forbes [13] and investigated structurally by Mentzen et al. [14].

2. Experimental

The lead dioxide used was extra pure, imported from “VEB” Laborchemie Apolda, Germany. It was dried at 120°C in a drying oven, cooled and kept in a desiccator until it was used. MoO_3 was prepared by the decomposition of ammonium paramolybdate at 690°C for 6 h in a muffle furnace. Cooling of the product was carried out in the furnace down to 100°C, at which it was transferred to a desiccator to keep it dry. The ammonium para molybdate was imported from E. Merck AG, Darmstadt, Germany. The raw materials, (PbO_2 and MoO_3), with the required composition were intimately mixed in an agate mortar and held in the thermobalance at 120°C until all moisture has gone off, then subjected to equilibrium heating in air. The isothermal kinetics were followed by equilibrium heating in a thermobalance fitted with an on-off control device. The temperature was recorded using a Pt/PtRh(10%Rh) thermocouple. The maximum error in temperature recording was found to be $\pm 5^\circ\text{C}$. By the use of thermobalance the change in weight was calculated by subtracting the weight reached from the original weight and transferring it into atoms from which the O/Pb ratio was calculated.

3. Results and discussion

Since only subsolidus reactions are of interest in the Pb–Mo–O ternary system, the temperature was not allowed to exceed 700°C. A blank curve for the volatilization of

MoO_3 was performed up to 700°C . The maximum loss was 0.93 wt% at 700°C . The weight loss of MoO_3 was taken into consideration in the preparation of the compositions investigated. Mixtures of PbO_2 and MoO_3 were prepared as described before. The molar ratios in these compositions were 19:1, 9:1, 4:1, 3:1, 3:2, 1:1, 2:3, 1:2, 3:7, 1:3, 1:4, and 1:9, PbO_2 to MoO_3 . The dissociation curves for these compositions, and also for pure PbO_2 were followed using the thermobalance. It was found that for all ratios the state of valency of Mo is not changed. For each mixture at each temperature the O/Pb ratio was calculated and plotted against temperature to obtain the dissociation curves. The dissociation curves, corresponding to 70, 50, 40, 20, 10, and 0 mol% MoO_3 are shown in Figs. 1, 2 and 3. These figures show the behavior of the mixtures when heated in the thermobalance in air. From the thermal analyses of the PbO_2 – MoO_3 mixtures the following results are drawn.

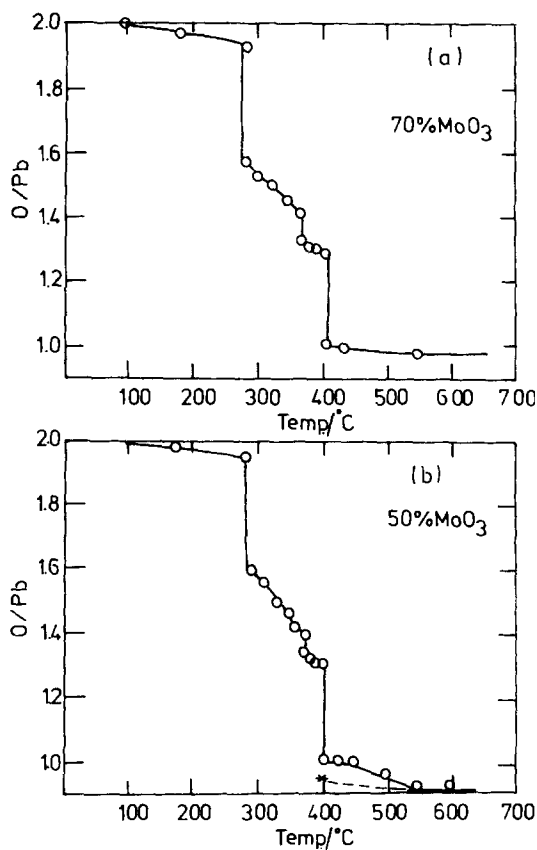


Fig. 1. Dissociation curves of PbO_2 – MoO_3 mixtures. a. 70 mol% MoO_3 b. 50 mol% MoO_3 .

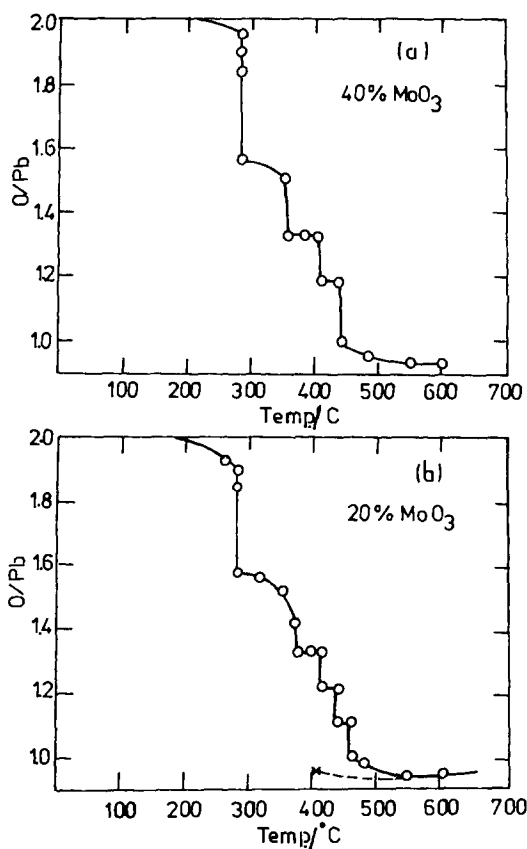
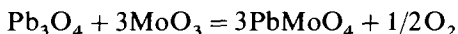


Fig. 2. Dissociation curves of $\text{PbO}_2\text{-MoO}_3$ mixtures. a. 40 mol% MoO_3 . b. 20 mol% MoO_3 .

3.1. Dissociation curves for mixtures containing more than 50 mol% MoO_3

The dissociation curve of the 70 mol% MoO_3 sample, Fig. 1a represents the behavior of this group. In this mixture a progressive loss of oxygen occurred from PbO_2 causing nonstoichiometry up to about 280°C. At this temperature an isothermal step occurs, giving $\text{PbO}_{1.58}$. From 280 to 370°C oxygen is lost progressively till the O/Pb ratio becomes 1.41. At 370°C the latter phase dissociates isothermally to Pb_3O_4 . The occurrence of these transitions at the same temperatures as published by Abadir et al. [11], suggests that PbO_2 , PbO_x and Pb_3O_4 did not dissolve MoO_3 into a solid solution. A slight oxygen loss occurred at 370°C up to 405°C at which isothermal dissociation takes place and the O/Pb ratio reaches unity due to destabilization of Pb_3O_4 according to the reaction:



At 550°C the O/Pb ratio decreases to 0.99. No further oxygen loss takes place at higher temperatures.

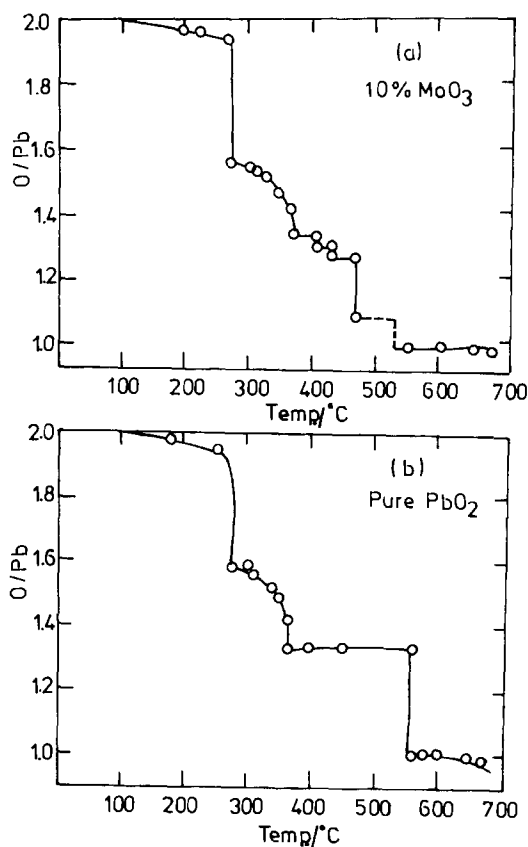


Fig. 3. Dissociation curves of $\text{PbO}_2\text{-MoO}_3$ mixtures. a. 10 mol% MoO_3 . b. Pure PbO_2 .

The behavior of the mixture containing initially 50 mol% MoO_3 is shown in Fig. 1b. It is up to 405°C is nearly the same as that for the 70 mol% MoO_3 mixture. On continued heating there was a slight loss of oxygen from 405 up to 550°C at which the O/Pb ratio reaches 0.96 and remained constant. This loss is partially reversible as is shown in Fig. 1b, indicating the presence of an oxygen deficient lead molybdate, which agrees with the results of Ninomiya [5]. It was also reported that this is the reason why PbMoO_4 , when used as a semiconductor, changes the conductivity type from P to N [7].

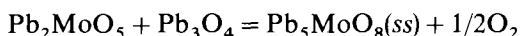
3.2. Dissociation curves for mixtures containing initially more than 33 and less than 50 mol% MoO_3

This category is represented by the mixture containing initially 40 mol% MoO_3 , Fig. 2a. The main features observed for the previous mixtures up to 405°C, are also observed. At the end of the isothermal step at 405°C, unlike the aforementioned mixtures the O/Pb ratio did not reach unity but decreased to about 1.17, indicating the

existence of PbMoO_4 in equilibrium with Pb_3O_4 . The weight remains constant up to 430°C at which an isothermal step takes place and the O/Pb decreases to reach unity. At 550°C the O/Pb ratio decreased down to 0.96.

3.3. Dissociation of mixtures containing less than 33 and more than 15 mol% MoO_3

The behavior of these mixtures is represented by the dissociation curve Fig. 2b, for the 20 mol% MoO_3 mixture. As it may be observed from this figure, the same behavior, described earlier up to 405°C for the other mixtures, is observed. At 405°C the O/Pb ratio is 1.25 and the mixture consisted of PbMoO_4 and Pb_3O_4 . At 430°C the O/Pb ratio decreased to 1.15 due to the formation of Pb_2MoO_5 . At 460°C oxygen loss took place isothermally shifting the O/Pb ratio to unity due to the reaction:



3.4. Dissociation behavior of mixtures containing less than 15 mol% MoO_3

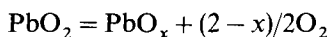
These mixtures are represented by the sample containing 10 mol% MoO_3 . As it is shown in Fig. 3a, the same steps were observed up to 460°C at which the O/Pb ratio reached 1.09 and not unity, presumably due to the formation of Pb_5MoO_8 [14]. It is believed that a further rise in temperature to about 560°C would reduce the O/Pb ratio to unity due to the transformation of the remaining Pb_3O_4 to PbO (shown dotted in Fig. 3a). This means that it is assumed that Pb_3O_4 dissociates to PbO at its normal decomposition temperature of 560°C .

The decomposition curve for pure PbO_2 is shown in Fig. 3b, for comparison with other curves obtained for the mixtures.

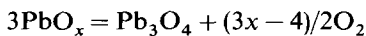
From the plottings of compositions reached at the beginnings and ends of vertical isothermal steps it is evident that:

(a) The following monovariant reactions occur:

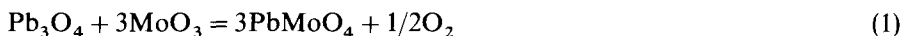
(i) at 277°C where PbO_2 (ss), PbO_x , MoO_3 , and O_2 coexist in equilibrium according to the reaction:



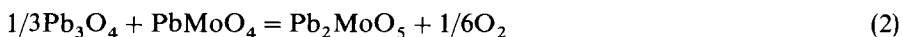
(ii) at 370°C , where PbO_x (ss), Pb_3O_4 , MoO_3 , and O_2 coexist in equilibrium according to the reaction:



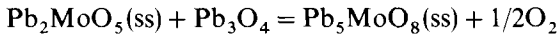
(iii) at 405°C where PbMoO_4 , Pb_3O_4 , MoO_3 , and O_2 coexist according to the reaction:



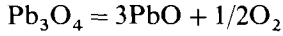
(iv) at 430°C where PbMoO_4 , Pb_2MoO_5 , Pb_3O_4 , and O_2 coexist according to the reaction:



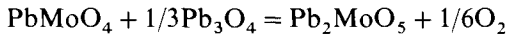
(v) at 460°C where Pb_2MoO_5 , Pb_5MoO_8 , Pb_3O_4 , and O_2 coexist according to the reaction:



(vi) at 560°C, where Pb_3O_4 , PbO , Pb_5MoO_8 and O_2 coexist, Pb_3O_4 dissociating to PbO according to the reaction:



(b) PbMoO_4 is stable between 405 and 430°C after which Pb_2MoO_5 is the stable phase [16], formed by the reaction:



The formation of PbOMoO_4 at 550°C was confirmed by X-ray analysis of the sample prepared and quenched at 570°C.

3.5. Ternary diagram MoO_3 – PbO_2 – Pb

From the dissociation curves of selected compositions, the ternary diagram MoO_3 – PbO_2 – Pb , Fig. 4, was constructed. The compositions reached on the dissociation curves at selected temperatures were calculated and plotted on the horizontal thin lines

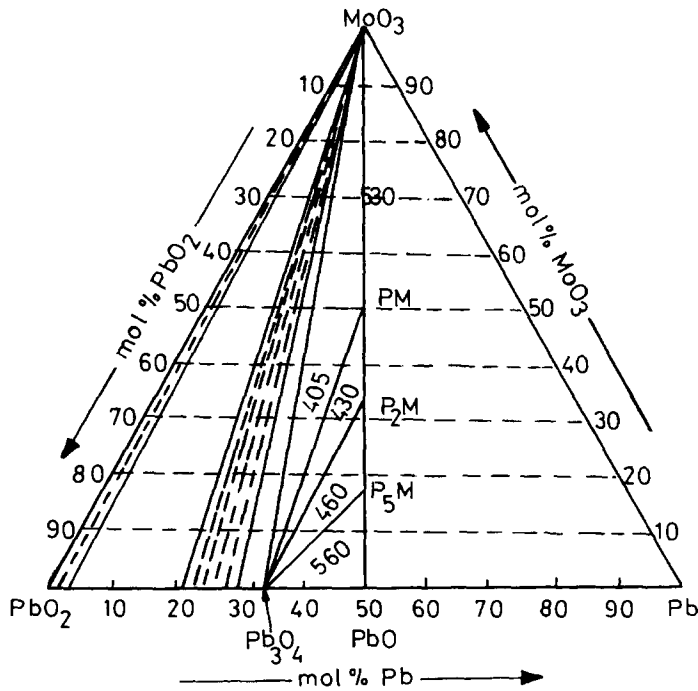
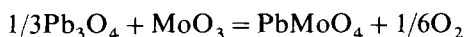
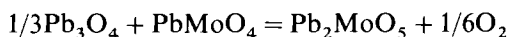


Fig. 4. The ternary system Pb – Mo – O in air.

which represent the dissociation paths. The isothermal triangles shown on the diagram represent monovariant situations appearing as vertical steps on dissociation curves appearing as vertical steps on dissociation curves. Compositions on the curved parts of the dissociation curves represent regions on the ternary diagram where a solid solution is in equilibrium with solid phase and oxygen. Straight lines represent tie lines joining two condensed phases in equilibrium with O_2 , while the triangles join three condensed phases in equilibrium with O_2 . In all mixtures a progressive loss of O_2 , from PbO_2 causing nonstoichiometry, occurred up to $280^\circ C$ at which an isothermal step occurs giving $PbO_{1.58}$. From 280 up to $370^\circ C$ oxygen is lost progressively up to a composition corresponding to $O/Pb = 1.41$. At $370^\circ C$ isothermal dissociation takes place giving Pb_3O_4 . At the end of this step all compositions consist of MoO_3 and Pb_3O_4 . Above $370^\circ C$ a slight oxygen loss occurred which increases as mole fraction of MoO_3 in the original mixture increases. Near $405^\circ C$ an isothermal triangle exists due to the reaction:



At $430^\circ C$ another isothermal triangle exists due to the formation of Pb_2MoO_5 according to the reaction:



At the end of this step mixtures containing initially less than 33 mol% MoO_3 , consist of Pb_3O_4 and Pb_2MoO_5 . Mixtures, containing more than 50 mol% MoO_3 , consist of

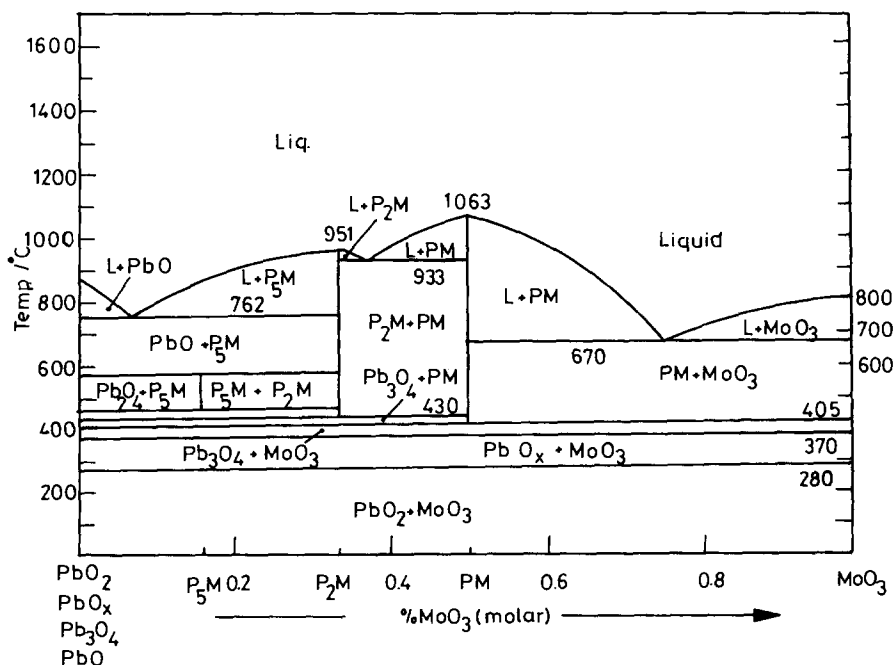


Fig. 5. Lead oxide – Molybdenum trioxide section in the system Mo–Pb–O in air.

PbMoO₄ and MoO₃. Above 430°C oxygen is lost progressively indicating the formation of a solid solution. The reversible loss of oxygen observed above 560°C shows that the O/Pb ratio decreases below unity, presumably due to the formation of an oxygen deficit PbMoO₄, the volatility of PbO or MoO₃ being negligible below 700°C. The melting behavior was not investigated due to the volatility of MoO₃ above 700°C [17].

From the ternary diagram it is noted that starting with PbO₂ instead of PbO, it was possible to prepare PbMoO₄ and Pb₂MoO₅ at 405 and 430°C respectively instead of 650 and 800°C.

3.6. Binary projection

To facilitate following up the phase changes that take place in the ternary system MoO₃–PbO₂–Pb a binary projection has been drawn by projecting the composition isopathes on a binary diagram as it is shown in Fig. 5. The data used were taken from the ternary diagram Fig. 6, and the liquidus curves are taken from the results of Jaeger and Germs [10], and Kunev et al. [6].

Conclusions

1 Starting with PbO₂ instead of PbO to prepare the molybdates, it was possible to prepare PbMoO₄ and Pb₂MoO₅ at lower temperatures, i.e. 405 and 430°C instead of 650 and 800°C.

2 PbO exists over a range of solid solution extending from a value of O/Pb ratio slightly higher than unity to values lower than unity.

3 The ternary diagram PbO–MoO₃–PbO₂ was established in air and the different phases occurring are shown with their regions of stability.

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