

OBSERVED PHASE TRANSFORMATIONS OF OXALATE-DERIVED LEAD MONOXIDE POWDER

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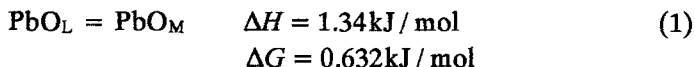
The purpose of this study is to elucidate the nature of the phase transformations of lead monoxide powder. Lead monoxide is prepared by calcination of a lead oxalate precursor salt, and its phase transformations are studied using X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TG). Analysis reveals that the phase transformations observed for oxalate-derived lead monoxide powder are highly dependent on the firing atmosphere. In nitrogen, as the temperature is increased 1 deg/min from room temperature, lead monoxide undergoes a reconstructive litharge-to-massicot phase transformation in a temperature range of 525–575°C. In air, litharge, metastable at room temperature, slowly oxidizes to the Pb₃O₄ phase at a temperature of 350°C and rapidly reduces to litharge at 560°C. At temperatures greater than 560°C, litharge converts to massicot. With heating rates of 10 deg/min or higher, formation of Pb₃O₄ is not observed.

Introduction

Lead monoxide has been used in a variety of applications such as electrochemistry, lubrication, film sensitizing, and ceramics [1]. In all of these applications, phase purity determines the usefulness of lead monoxide. For instance, for the high-temperature solid state synthesis of multicomponent ceramics, phase purity controls the thermodynamic driving force, reaction mechanism, and reaction kinetics [2, 3].

Lead monoxide exists in two crystalline forms, litharge (PbO_L) and massicot (PbO_M). The low-temperature polymorph litharge has a tetragonal crystal structure, while the high-temperature polymorph massicot has an orthorhombic structure [1]. The two components are easily distinguished in their pure crystalline phases, with litharge possessing a dark red color and

massicot a bright yellow color. The reported thermodynamic phase transition temperature is 489°C, although temperatures ranging from 475° to 585°C have been reported [3–5]. Given the small enthalpies and free energies for the phase transformation throughout the temperature range, the thermodynamic driving force to form either phase is small. At room temperature, for example, using the thermochemical database of Barin [6]:



Massicot can exist in a metastable state at room temperature. Impurities such as small as 50 ppm can enhance the stability of massicot [7], while factors such as silicon, antimony and molybdenum in concentrations as relative humidity can transform massicot to litharge [8, 9]. Sorrell has proposed several mechanisms for the observed transformation, one of which is that the incorporation of hydroxyl ions into the massicot lattice destabilizes the phase and renders the oxide oxygen-rich. Wet or dry ball-milling has also been shown to cause massicot to transform to litharge [5, 10–13].

The nature of the litharge-to-massicot phase transformation is not well understood. Many assume that this phase transformation is entirely reconstructive. Based on observations of color changes, it has been determined that litharge transforms to massicot at 489°C in vacuo [4]. However, recent research has revealed that this method of phase identification is not always reliable [14].

Furthermore, thermal analysis studies have suggested that litharge oxidizes in air to form the Pb₃O₄ phase and subsequently reduces to form the massicot phase at 532°C [15]. However, no X-ray diffraction analyses were conducted to verify either of the proposed phase sequences. The purpose of this paper is to elucidate the nature of the litharge-to-massicot phase transformation.

Experimental

The nature of the lead monoxide phase transformation was studied using a lead oxalate calcinate precursor. A single batch of lead oxalate was prepared by a precipitation from homogeneous solution (PFHS) technique after the method of Gordon *et al.* [16]. Solutions containing 0.2 M Pb(OOCCH₃)₂ (Fisher Scientific, Springfield, NY) and 0.365 M diethyl oxalate (Eastman Kodak, Rochester, NY) were dissolved in a solution containing

15 vol%^a water in 85 vol% acetic acid solution (Fisher Scientific). The solution was magnetically stirred at 90°C and precipitate became visible within 2 min after the solution reached 90°C. The suspension was aged for 1 h, after which the precipitate was recovered by centrifugation and subsequently washed twice with distilled-deionized water, followed by a final wash with acetone (Fisher Scientific). The resulting oxalate was dried in air at 90°C for 24 h.

All litharge samples used in this work were derived from the same batch of oxalate. The samples of litharge were obtained by calcining ~ 2 g lead oxalate at 380°C for 1 h in a porcelain crucible in static air in a box furnace (Lindberg, Watertown, WI) ramped to a temperature of 380°C in less than 5 min. Samples were removed at 380°C and quenched in air. To study the calcination of larger PbC₂O₄ samples under isothermal conditions, 5 g lead oxalate powder was calcined as above. Annealing studies were conducted by inserting samples into a furnace preheated at the temperatures and times listed in Table 1 and rapidly quenching the samples in air.

Table 1 Isothermal heating of oxalate-derived litharge powder in air

Firing*	Temperature /°C	Time /h	Phase composition
–	25	–	PbC ₂ O ₄
2	380	1.0	PbOL
1	380	4.0	PbOL–PbO _{1.37} (minor)
1	440	4.0	Pb ₃ O ₄ –PbOL
1	650	0.75	PbOL–PbOM (trace)
1	650	4.0	PbOM

*1 = 5 g batch of oxalate, 2 = 2 g batch of oxalate

The physicochemical nature of the precipitated oxalate and the resultant oxide were studied using a variety of characterization tools. The particle morphology and size were characterized using scanning electron microscopy (Amray, Model 1200, Brockton, MA). X-ray photosedimentation particle size analysis was used to determine the equivalent spherical diameter (Sedigraph 5000D, Micromeritics Instrument Corp., Norcross, GA), with *n*-butanol (Fisher Scientific, Springfield, NY) employed as the liquid medium due to the high density (5.3 g/cm³) of PbC₂O₄. Chemical characteristics were determined with X-ray diffraction (XRD), combustion analysis, thermal gravimetric analysis (TG), and differential scanning calorimetry (DSC). XRD analyses were conducted using a scan rate of 1 deg/min with Ni-filtered Cu-K_α radiation (Philips, Mount Vernon, NY). Joint Committee Powder Dif-

fraction Standards (JCPDS) powder diffraction files were consulted for all phase analyses. Combustion analysis for carbon, hydrogen and nitrogen concentrations was conducted using Oneida Research Services (Whitesboro, NY). TG studies were conducted on both oxalate and litharge powders in both high purity nitrogen (10.5 ppm) and air (Matheson Gas Products, East Rutherford, NJ) using a flow rate of 50 ml/min. All samples were heated in open pans to 600°C, with a heating rate of 10 deg/min (platinum pan, 17–20 mg sample, Perkin-Elmer TGA-7, Norwalk, CT) for oxalate samples and a heating rate of 1 deg/min (alumina pan, 155–170 mg sample, Netzsch STA 409, Exton, PA) for oxide samples.

Isothermal TG studies of oxide samples were conducted using a heating rate of 10 deg/min to a temperature of 500°C (Perkin Elmer TGA-7). DSC analyses (Perkin Elmer DSC-7) were conducted on litharge samples (~10 mg) in a sealed aluminum pan using a heating rate of 1 deg/min, with zirconia (99+ %, Alfa Products, Danvers, MA) as the reference material.

Results and discussion

(a) Characteristics of PFHS-derived PbC₂O₄ and resultant oxide

Chemical characterization of the PFHS-derived precipitate indicated that the salt was lead oxalate. XRD analysis of the precipitate indicated that the powder was single-phase lead oxalate, and combustion analysis showed an 8.21 wt% carbon (8.13 wt% theoretical) content, with negligible amounts of hydrogen and nitrogen. The results of TG performed on PbC₂O₄ samples in flowing air and N₂ atmospheres are given in Fig. 1. The loss on ignition (LOI) obtained in air, 24.4 wt%, corresponds to the following decomposition reaction:



The results obtained in N₂, 26.3 wt%, correspond to the following reaction, which indicates the formation of elemental Pb:



Small round 'balls' of Pb were visibly noted in samples calcined in N₂. This decomposition mechanism has been noted by Morsi for PbC₂O₄ calcined under vacuum [17]. The formation of Pb is attributed to the reduction of some PbO by CO. To avoid the formation of Pb, litharge samples used to study the transformation were obtained by calcining PbC₂O₄ in air at 380°C. These

samples were found to contain 0.11 wt% carbon, which corresponds to a residual lead oxalate content of 1.35 wt% or an expected weight loss of 0.330 wt%.

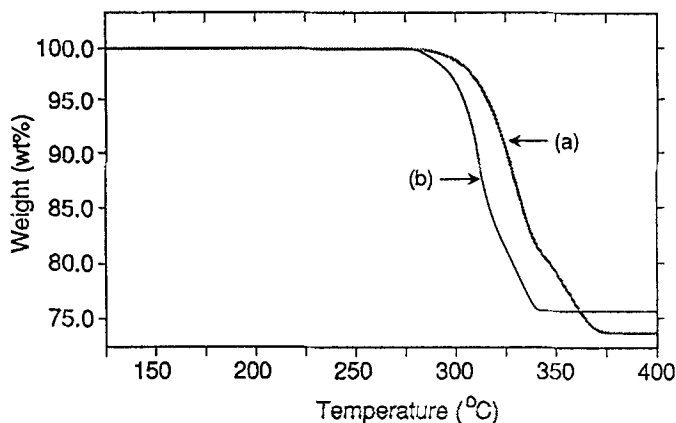


Fig. 1 TG traces of lead oxalate powder using a heating rate of 10 deg/min in flowing (a) nitrogen and (b) air

Physical characteristics of the lead oxalate are shown in Fig. 2. In general, the plate-like powder was found to aggregate as the powder underwent a phase transformation from litharge to massicot [18]. The equivalent spherical diameter (ESD) increased from 1.1 to 2.5 μm as the phase transformation

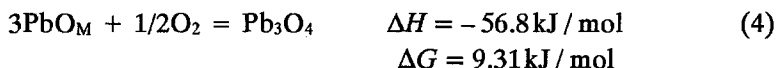


Fig. 2 SEM micrograph of PFHS-derived lead oxalate

progressed. However, a powder free of aggregation could be obtained if the oxalate was converted solely to the litharge phase. On the basis of XRD and TG data, for samples heated at a rate of 10 deg/min in air, Pb_3O_4 was never observed as the powder converted from litharge to massicot.

(b) Phase stability of PbO

Experiments first were directed toward determining whether the lead monoxide phase transformation was reconstructive or oxidative-reductive. A DSC trace of litharge (Fig. 3) exhibited a broad exotherm centered at 510°C , characteristic of a slow reaction, followed by a sharp endotherm, centered at 580°C , characteristic of a rapid reaction. These results are in reasonable agreement with previous work [15] where oxidation was reported to occur from 435° to 532°C (with a 491°C peak) and reduction from 532° to 578°C (with a 560°C peak). Thermochemically, at 527°C (800 K) lead monoxide oxidation is highly exothermic, as shown below [6]:



Furthermore, litharge has been observed to oxidize at 470°C when heated in air for 24 h [19]. Thus, it is likely that the DSC trace is characteristic of slow litharge oxidation followed by rapid Pb_3O_4 reduction.

The DSC data contradicted our earlier experimental observations regarding Pb_3O_4 formation. To analyze this phase transformation more closely, TG and XRD studies were conducted using flowing air and nitrogen atmospheres and various heating schedules. A TG study in nitrogen at a heating rate of 1 deg/min (Fig. 4a) revealed a 2.0 wt% weight loss at temperatures less than 400°C , which was characteristic of residual oxalate in terms of the observed temperature range but greatly in excess of the amount estimated from combustion analysis. At temperatures above 400°C no further weight losses were observed. A sample removed from the thermal analyzer at 600°C and quenched to room temperature was found to contain a mixture of approximately 50 wt% litharge and massicot. When a TG study was conducted in air using the same heating rate (Fig. 4b), a weight loss characteristic of residual oxalate and semi-quantitative evidence of reaction 4 were observed. A weight gain of 1.6 wt% was observed in the range of 350° to 550°C followed by a more rapid 2.2 wt% weight loss over a 10°C temperature range. Since reaction 4 represents a net weight gain of 2.39 wt%, this thermogram was suggestive of oxidation-reduction. X-ray diffraction of this powder after heating

to 600°C and quenching to room temperature in air indicated the presence of litharge and a trace of massicot.

To confirm this metastable behaviour, a powder sample was isothermally heated to 650°C for 0.75 h. XRD revealed the same phase assemblage as that obtained when heated in the TGA. To isolate and identify the Pb_3O_4 phase, a powder was heated in air at 1 deg/min to a temperature of 540°C, which was within the temperature range of oxidation indicated in Fig. 3. As expected, XRD indicated the formation of Pb_3O_4 under these conditions.

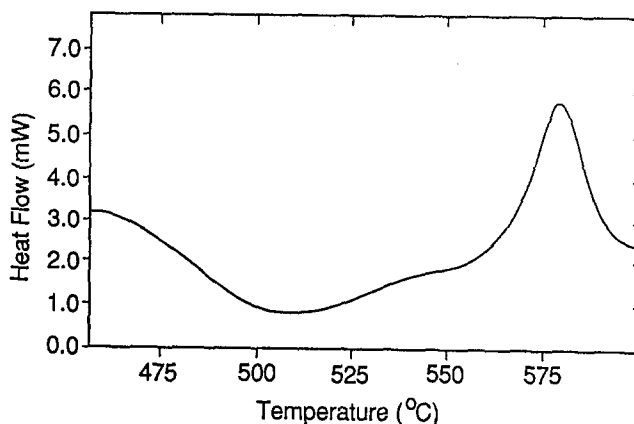


Fig. 3 DSC trace of litharge powder using a heating rate of 1 deg/min

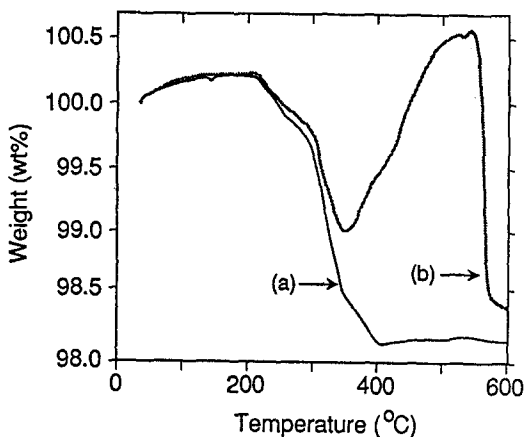


Fig. 4 TG trace of litharge heated at 1 deg/min in flowing (a) nitrogen and (b) air

Isothermal anneals were conducted in air to examine the kinetics of Pb_3O_4 formation in greater detail (Table 1). Below 400°C, PbO_L was observed to

convert to a mixture of litharge and PbO_{1+x} (where x ranges from 1.33 to 1.41). PbO_{1+x} , a metastable hexagonal nonstoichiometric oxide with the corundum structure, is known to exist in this temperature range and to decompose at 351°C to Pb_3O_4 under lengthy 451 h heat treatments [20]. However, the coexistence of PbO_{1+x} and Pb_3O_4 was not observed in this study. Instead, under a 4 h isothermal soak at 440°C , Pb_3O_4 was found to coexist with PbO_L . Considering the differences in annealing conditions, it is plausible that PbO_{1+x} reduces to Pb_3O_4 while coexisting with unreacted PbO_L . The oxidative kinetics are illustrated by Fig. 5, which shows a TGA trace of litharge heated in air at a rate of 10 deg/min and soaked at 500°C . A weight loss of 2.3 wt% occurred in the early stages of heating, which was characteristic of residual oxalate. Subsequently, a weight gain of 2.3 wt% was observed, indicating the formation of Pb_3O_4 from PbO (reaction 4, 2.39 wt% theoretical). Over 90 wt% of the conversion was accomplished in 250 min.

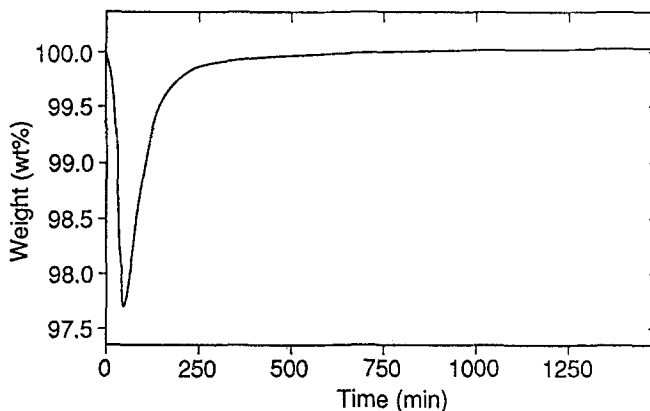


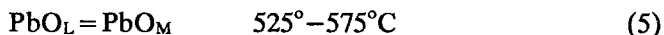
Fig. 5 TG trace of litharge heated at 10 deg/min and soaked at 500°C in flowing air

The sluggish nature of the oxidation reaction as PbO converts to Pb_3O_4 suggests that rapid heating (10 deg/min) as performed in earlier experiments completely circumvents the oxidation, resulting in reconstruction of PbO_L into PbO_M . Thus, the failure of earlier researchers to observe Pb_3O_4 can be explained on the basis of kinetics. Slower heating rates (1 deg/min) allow the oxidation reaction to proceed, and the formation of Pb_3O_4 appears to delay the formation of massicot still further. Powders heated in a thermal gravimetric analyzer at 1 deg/min to a temperature of 600°C in nitrogen contained substantially more massicot than those heated in air.

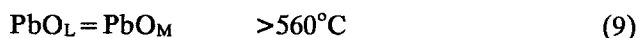
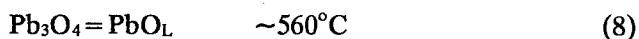
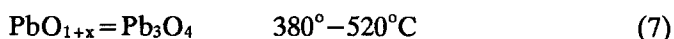
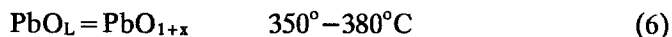
The complete phase progression in air was further confirmed using isothermal soaks in a box furnace (Table 1). These data show that massicot

nucleates and grows from the litharge phase and not from the Pb_3O_4 phase as reported earlier [15]. The reaction sequences observed are summarized as follows:

Nitrogen



Air



(c) Phase transformation thermodynamics

The nature of the lead monoxide phase transformations can be better understood by referring to the PbO_2 vs. $1/T$ plot shown in Fig. 6. Depending on the thermodynamic database consulted, Pb_3O_4 appears to be the most stable phase in air from 25°C (298 K) to a temperature lying in the range of $366^\circ - 384^\circ\text{C}$ (639–657 K) [6, 21–24]. At higher temperatures, lead monoxide is the most stable phase with a very small, if not immeasurable driving force favoring litharge over massicot at temperatures below 489°C (762 K). Thus, under conditions of equilibrium, Pb_3O_4 should transform to litharge prior to converting to massicot.

These data indicate that PbO is metastable at room temperature. Therefore, as suggested experimentally, oxidation kinetics must be limiting the minimum temperature at which Pb_3O_4 forms. Most likely, the rate-limiting step for this kinetic process is oxygen diffusion. The appearance of metastable PbO_{1+x} with litharge signifies that, at some point in the process, portions of the powder have O/Pb ratios equalling or exceeding that of Pb_3O_4 (O/Pb = 1.33). The oxygen-rich regions, most likely in the form of product layers, nucleate and grow the metastable PbO_{1+x} phase. Higher temperatures promote more rapid oxygen diffusion and lattice rearrangement to permit the thermodynamic and kinetic conditions suitable for crystallization of the more stable Pb_3O_4 phase.

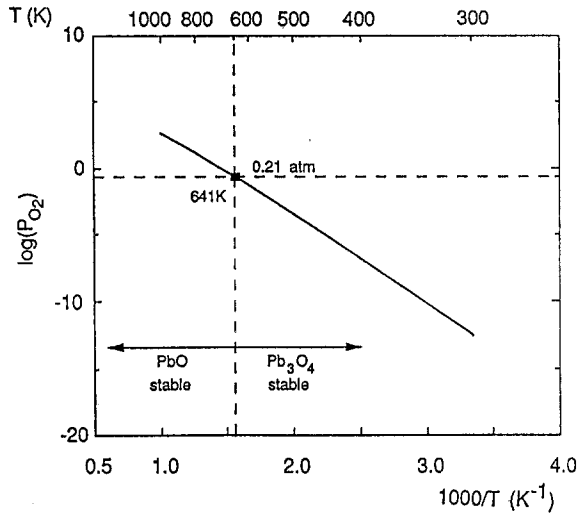


Fig. 6 Thermodynamic conditions favoring the formation of PbO or Pb₃O₄

The upper limit for Pb₃O₄ existence is governed by thermodynamics, which, above $\sim 400^{\circ}\text{C}$ ($\sim 673\text{ K}$), requires oxygen partial pressures exceeding those found in air. One possible explanation for the presence of Pb₃O₄ at higher recorded temperatures is that the endothermic nature of the reduction reaction and sluggish heat transfer kinetics may be lowering the sample temperature significantly below the temperature of the furnace, resulting in a recorded temperature exceeding what is thermodynamically possible. Alternatively, extending the ideas of Sorrell [9], the reduction of Pb₃O₄ to PbO may render the PbO lattice oxygen-rich, stabilizing the litharge phase for higher temperatures.

Conclusions

The phase transformations observed for oxalate-derived lead monoxide powder are highly dependent on the firing atmosphere. In nitrogen, as temperature is increased from room temperature, lead monoxide undergoes a reconstructive litharge-to-massicot phase transformation in a temperature range of $525\text{--}575^{\circ}\text{C}$. In air, litharge, metastable at room temperature, slowly oxidizes to Pb₃O₄ at a temperature of 350°C and rapidly reduces to litharge at 560°C . At temperatures greater than 560°C , litharge converts to massicot.

With heating rates of 10 deg/min or greater, formation of Pb_3O_4 is not observed.

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Zusammenfassung — Zweck dieser Untersuchung ist, das Wesen der Phasenumwandlungen von Bleimonoxidpulver zu ergründen. Bleimonoxid wird durch Calzinierung von Bleioxalat hergestellt und seine Phasenumwandlungen wurden mittels Röntgendiffraktion, DSC und

TG untersucht. Die Analyse zeigt, daß die für das aus Oxalat erhaltene Bleimonoxidpulver beobachteten Phasenumwandlungen stark von der Heizatmosphäre abhängen. Wird die Temperatur ab Raumtemperatur mit einer Aufheizgeschwindigkeit von 1/min erhöht, geht Bleimonoxid in Stickstoff im Temperaturbereich 525°-575°C eine rekonstruktive Bleiglätte-Massicot-Phasenumwandlung ein. In Luft wird die bei Raumtemperatur metastabile Bleiglätte bei 350°C langsam zu Pb_3O_4 oxidiert und dann bei 560°C schnell zu Bleiglätte reduziert. Bei Temperaturen über 560°C wird Bleiglätte in Massicot umgewandelt. Bei Aufheizgeschwindigkeiten von über 10/min kann keine Bildung von Pb_3O_4 beobachtet werden.