Synthesis of High-Purity α-and β-PbO and Possible Applications to Synthesis and Processing of Other Lead Oxide Materials

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ABSTRACT

The red, tetragonal form of lead oxide, α-PbO, litharge, and the yellow, orthorhombic form, β-PbO, massicot, have been synthesized from lead(II) salts in aqueous media at elevated temperature. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the size, morphology, and crystallographic structural forms of the products. The role of impurities in the experimental synthesis of the materials and microstructural variations in the final products are described, and the implications of these observations with respect to the synthesis of different conducting lead oxides and other related materials are discussed.

1 Introduction

Lead(II) oxide, PbO, is a member of the relatively small family of lead(II) binary oxides, which also includes PbO_2 and Pb_3O_4. Both PbO and PbO_2 are semiconducting metal oxides, being the subject of reports in the research literature involving their role in passivation layers [1] related to electrochemistry, oriented lead oxide on silica [2], high-pressure phase transformations and their mechanisms [3], lead oxide-matrix composites [4], nanorod formation of multiple phase lead oxides [5], and electrodeposition of lead oxides onto precious metals such as platinum [6]. Both α-PbO and β-PbO are photoactive semiconductors with bandgaps of 1.92 eV and 2.7 eV, respectively.

Over the years, quite a few different syntheses for the two forms (Fig. 1) of the divalent lead oxide, α-PbO and β-PbO, have been published. However, many of the literature syntheses lead to either impure products of the targeted lead oxide of interest, mixtures of products, or, in the worst case, a product different than the one reported. Additionally, because of the relatively high pH media in which some of the synthetic reactions are run, there is the possibility of hydrolysis products of the lead(II) reagents used as starting products. Also, the starting reagents must be pure, and the choice of reaction labware can play a role in what product is ultimately obtained at the end of the reaction sequence. Thus, in order to insure that a highly pure, single product is produced in any one given synthesis, it is necessary to follow very precise procedures.

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The present treatise describes methods for the syntheses of the two polymorphs of PbO, α-PbO and β-PbO, and discusses which of the various experimental aspects of the chemical syntheses effect which of the two forms is produced in a given chemical reaction. The phenomena which impact the resulting structural polymorphs are discussed, and various possibilities of these effects for new materials syntheses using different reaction approaches are presented.

1.2 *Experimental*

1.2.1 Synthesis of α-PbO, litharge. An almost boiling de-ionized water solution (50 mL) of 1.2 *M* $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ (Sigma Reagent Grade) was added to an aqueous solution of 50 mL of 19*M* NaOH (Aldrich) in a Teflon beaker with vigorous stirring. While adding the lead(II) acetate, the solution became cloudy, turned a light peach color, and then the deep red color of the final phase. Stirring was continued for about half a minute, stopped, and the supernatant was decanted. The red product was filtered on the bed of a Buchner funnel, washed with ice- cold de-ionized water, and dried overnight on the filter paper in a drying oven at ~ 90°C. After drying on the filter bed, the product was gently ground with a mortar and pestle. Gentle grinding gave a material that was X-ray crystallographically pure (Fig. 2).

1.2.2 *Synthesis of β-PbO, massicot.* The synthesis of the β-PbO phase may be made by the same procedure above, with the exception that *quartz glassware must be used in the synthesis* rather than the Teflon labware used for the α-PbO phase.

1.2.3 *Equipment.* A Siemens Model Daco-MP 5000 Diffraktometer using Cu Kα radiation from $2\theta = 10^o$ to 70° was used to obtain X-ray diffraction powder patterns, while the Siemens Diffract AT software Version 3.1 package was used for data treatment. An Inorganic Phases, Joint Committee on Powder Diffraction Standards (JCPDS)-International Centre for Diffraction Data, Newtown Square, PA, data base was used to identify the final products, while a ISI Model D130-C scanning electron microscope was used for studying the particle morphology of samples. X-ray powder diffraction patterns for the two newly synthesized PbO forms perfectly matched published diffractograms in the database.

1.3 Results and Discussion

The syntheses schemes presented here for obtaining α-PbO and β-PbO yield quite pure products that are isolable from their reaction solutions as very fine crystalline particles that are of mixed particle size. The top x-ray diffractogram in Fig. 2 represents freshly prepared litharge in which litharge is the exclusive, sole product formed (Fig.3). No evidence for any other complex lead(II) oxide hydrates such as $5PbO \cdot 2H_2O$ [7] or $3PbO \cdot H_2O$ (also formulated as $Pb_6O_8H_4$) [8] were observed in any samples that were obtained. The syntheses of α-PbO and β-PbO presented here have been shown to give reproducible, pure phases of each compound. In these syntheses using reagent grade starting materials, there is no need to painstakingly purify lead(II) salts as has been reported previously [9]. Also, as in some syntheses, there is no need to use ammonia. The critical factor with respect to obtaining either the α-PbO or β-PbO form is the amount of silicon leached from the reaction vessel during the reaction. Thus, one can control the exclusive phase by altering the trace amounts of silicon. Previous studies that looked at this reaction factor [9] focused only on the amount of trace elements in the reaction solutions that produced satisfactory, pure products; no systematic study of varying the dopants in order to look

at varying effects on products and yields was performed. This phenomenon of very slight concentrations of dopants in a reaction stream effecting a change in the chemistry of a material, its reactions relative to formation or chemistry to form new products, or its different structural phases is an excellent example of *fuzzy chemistry*. Other examples include the necessity of the presence of very slight amounts of the fluoride and/or chloride ions being present to form certain phases of hydrated iron oxide such as β-FeOOH (akagenite) in the FeOOH family [10].

The two structural phases of PbO present distinct differences in their overall bonding patterns [11]. In the case of α-PbO, the low/room-temperature phase, the structure exhibits a tetragonally distorted CsCl structure in which each lead atom is surrounded by four oxygen atoms in a square pyramid with a lead atom at the apex at each pyramid. Lead-oxygen distances are 0.232 nm. α-PbO is a layered structure. Oxygen atoms are found between two lead sublayers, with the distance between the lead atoms being 0.386 nm. β-PbO solidifies in the orthorhombic crystallographic structural system and is metastable at room temperature. Two oxygen sublayers are found between two lead sublayers; the layers form calliope (staggered) Pb-O chains with the lead exhibiting asymmetric square pyramidal coordination. The mean distance of the Pb-O bonds between and within the chains is 0.2358 nm, with the oxygen atoms found in the interior of the sheets in an asymmetric coordination. There is yet still a third phase of PbO, γ-PbO, which can only be made under non-solution, high-pressure conditions; it has an intermediate structure between those of α-PbO and β-PbO [12].

Previous research has shown that both the formation and interconversion of the two forms of PbO can be affected by extremely small experimental modifications related to a starting material, with many excellent examples of dramatic effects being reported. One study [13] showed the effect on the final structure of PbO synthesized by ball-milling Pb_3O_4 during decomposition to obtain the desired PbO product. Increasing the ball-milling time (which distorts the lattice) was found to effect a decrease in the temperature needed to preferentially obtain the massicot (β-PbO) form over the litharge (α-PbO) form. X-ray diffraction studies of different phases and mixtures in the reaction system showed that the PbO formed retained a "memory" of the lattice imperfections of the Pb_3O_4 being decomposed. Also observed was that a greater ball-milling time of the starting Pb_3O_4 resulted in a higher reactivity of the PbO to re-oxidize. A similar study by this same group [14] has shown that the "memory" concept also comes into play in the thermal decomposition of $PbCO_3$ to produce a reduction in the massicot/litharge ratio of products by increasing the grinding time of the starting $PbCO_3$ material.

A much more detailed---and also a really interesting--- study of the importance of different intermediate chemical species and phases to form a final desired product is that of the thermal decomposition of lead oxalate under a variety of gaseous atmospheres [15]. The end product is strongly affected by the atmosphere under which it is fired, with nitrogen giving a litharge-to-massicot phase change in the 525-575 ^{o}C temperature range. In air, litharge oxidizes to Pb_3O_4 on heating and rapidly reduces back to litharge on heating at higher temperature. Thus, in yet still another example, gaseous diffusion processes couple with different intermediate phases to produce the final product. This same identical reaction path and heating-rate/temperature phenomena for lead(II) hydroxycarbonate microwaved to form both phases of PbO have been reported in the literature [16].

Several other studies have been reported that indicate what massive changes can be made in the PbO phase system based on gaseous diffusion, autocatalysis of oxygen dissociation, temperature, and time of reaction during the formation of products. One study [17] showed that highly pure lead crystallites are extremely resistant to oxidation until nucleated by surface impurities, not unlike the necessity for silicon impurities needed to form β-PbO in the study here. The ultra-thin (~ 0.5 nm) coatings of oxide crystallites formed on the pure lead surfaces were thought to be the result of billions of surface chemical events. Continued oxide formation showed that, once nucleated, the grains of PbO catalyzed further oxidation. This study is one of the most detailed and thorough studies of the variable-temperature mechanism of the oxidation of lead to PbO, complemented by extensive high-resolution STM. Previous studies [18] had shown the importance of the oxygen sensitivity of the yellow form massicot to its change in electrical conductivity, with, again, also the importance of doped impurities such as potassium or bismuth.

While experimental data documenting the interconversion between the α-PbO and β-PbO forms are quite interesting, the interconversion is even more so from a visual standpoint. One can observe changes, for example, between the initially synthesized red litharge and its transition to massicot over a period of months (Fig. 2, bottom). With grinding, the massicot phase totally converts back to the red litharge phase. Other external experimental factors such as heat and light that very well may affect the phase transition were not studied here, but alone and in conjunction with one another, might prove to provide a multiplet of approaches to effect the transition. One other factor to consider would be the electrical properties [18] of both phases in conjunction with heat, light, and pressure, especially since grinding has been shown to have such a pronounced effect.

A consideration of the experimental aspects of the syntheses of the two forms of PbO described here lends itself to researchers devising new schemes to obtain additional information related to the formation of PbO, much of which can be used in other materials syntheses problems. In the study involving the effects of impurities [18], for example, the bismuth used as an impurity in the studies most likely exists as a bismuth(III) oxide species. Bismuth(III) and thallium(I) are isoelectronic with lead(II), all three having a formal electronic configuration of [Xe] $4f^{14}5d^{10}6s^2$. What effect would Tl(I) doping have on the formation of PbO, and which form would be produced? Since elemental bismuth forms an oxide species that is isolectronic with PbO, what would be the effect of doping lead metal with bismuth and synthesizing the lead(II) starting materials for the purpose of the PbO syntheses described above? How would this change the mechanism of formation of PbO? In another experiment, taking into account that ultra-trace levels of SiO_2 changes the structural form of PbO produced, what would be the effect of ultra-trace amounts of Al_2O_3 (isoelectronic with SiO_2) on the formation of PbO? Using an identical experimental approach with STEM as detailed in [17], what new intermediate phases might be observed by these isoelectronic ion substitutions?

The results observed here also can guide researchers in devising new schemes for the syntheses and processing of both PbO and other materials involving lead and lead-containing materials. One area would be making use of the different reaction conditions reported here for the two syntheses of PbO and their modifications for possibly making new mixed lead-metal ion oxides; the two reactions provide interesting possibilities for the study of the mechanisms of formation of the two lead(II) oxides as well as the formation of other mixed oxides. Another fertile area of research might be the effects of trace elements on the formation of the two lead

oxides here and mixed lead-metal ion oxides. Another area for investigation could possibly be that of lead oxide bulk and film composites with materials involving other elements and their reaction mechanisms, while another fruitful area might be that of oxidizing elemental lead films containing different dopant species in order to effect the formation of different phase nanoparticles of PbO on the surface of the film. Syntheses of materials containing mixed lead with other metal oxides might be conducted by modifying the present syntheses of PbO, both under ambient temperatures and at elevated temperatures in order to insure anhydrous products.

CONCLUSIONS

Rapid, reliably reproducible synthetic techniques for the preparation of the red tetragonal form of lead(II) oxide, α-PbO, litharge, and the yellow orthorhombic form, β-PbO, massicot, are reported in which the preparative routes resulted in highly-pure particles of variable size. The synthetic schemes used to make the two materials produced exclusively either the tetragonal α-PbO form or the β-PbO form with no detectable amount of alternate form present. Contaminant species such as residual lead(II) salt hydrates, lead(II) hydrolysis products, or other types of lead(II) complexes were not observed. Several other experimental schemes can be designed to look at the reaction mechanisms to form the two phases of PbO, along with possible schemes for the syntheses of other materials combining PbO with other elemental oxides.

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FIGURES

1. The schematic structural representations of (a) α-PbO (litharge) and (b) β-PbO (massicot) structural forms of lead(II) oxide

2. X-ray diffraction patterns of freshly prepared α-PbO, litharge (top) and α-PbO which has partially converted to β-PbO (bottom).

3. Scanning electron microscopic photograph of newly synthesized α-PbO.

FIGURE 1.

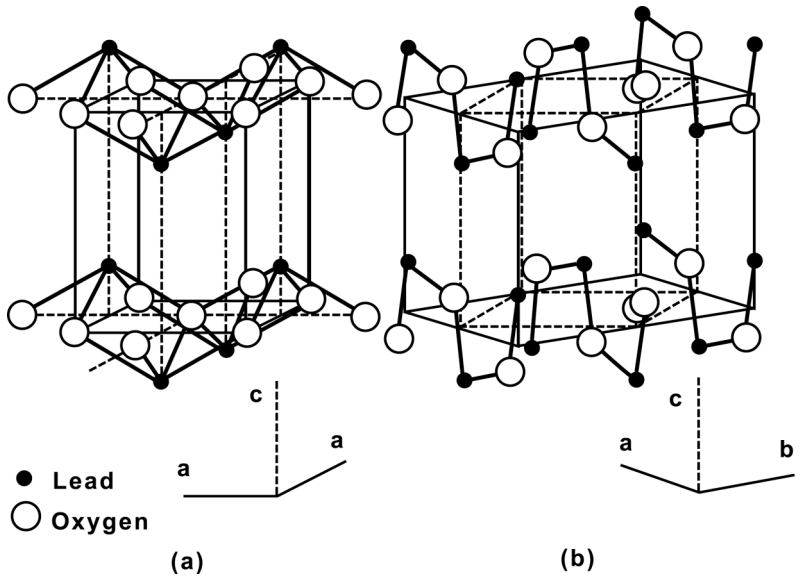
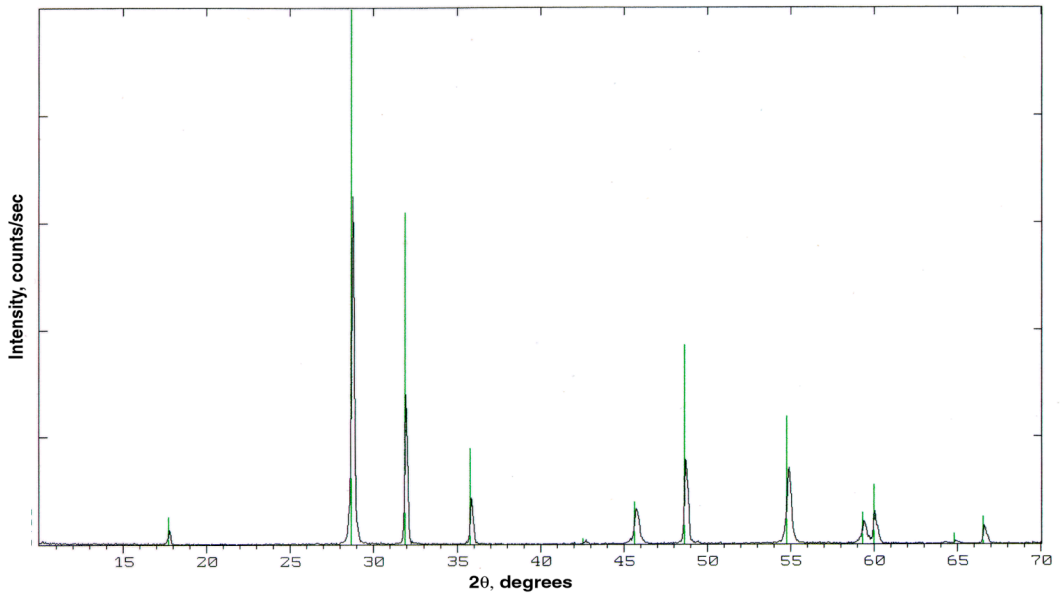


FIGURE 2.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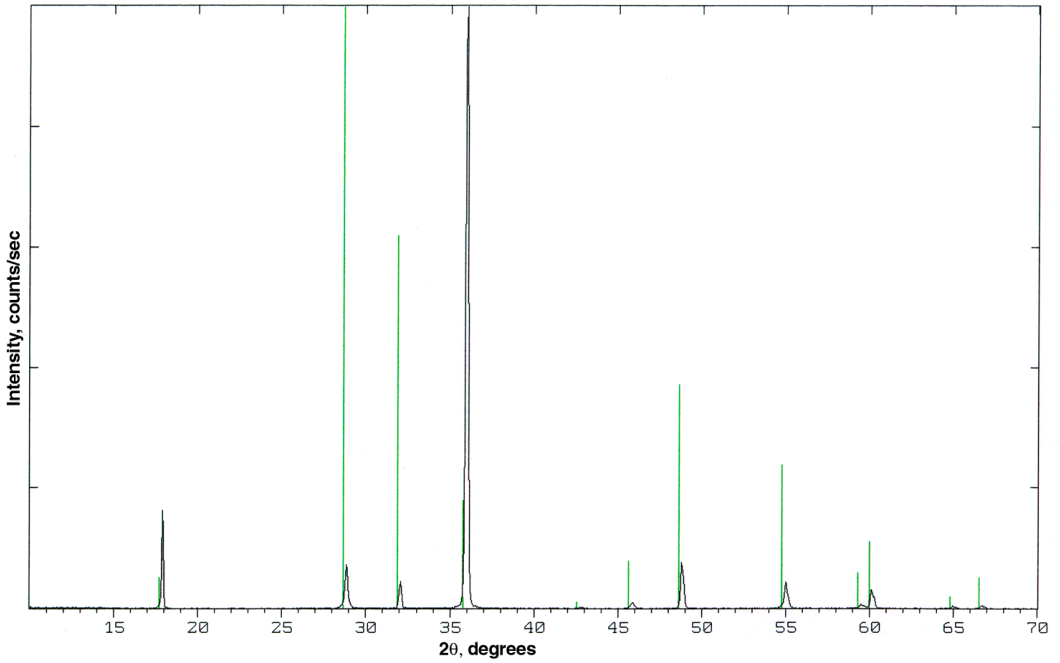
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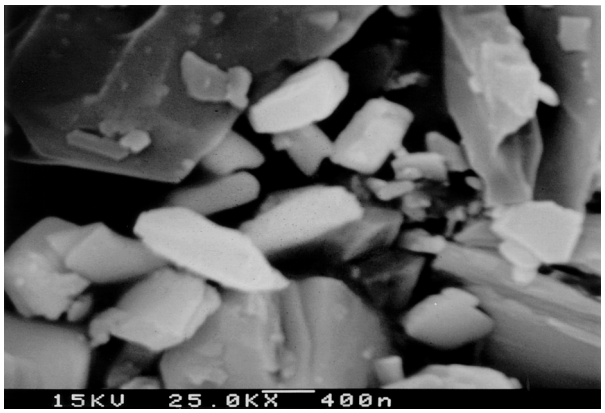
FIGURE 3.



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