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PHASE EQUILIBRIA IN THE $\text{PbO-Al}_2\text{O}_3$ SYSTEM

Bob Ross Powell, Jr.
(Ph.D. thesis)

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PHASE EQUILIBRIA IN THE $\text{PbO-Al}_2\text{O}_3$ SYSTEM

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ABSTRACT

The use of the Knudsen effusion weight loss technique to measure the equilibrium vapor pressure of PbO in the $\text{PbO-Al}_2\text{O}_3$ system is described. The pressures are measured in two phase regions of the system to assess the applicability of this system as a packing powder to control the stoichiometry of lead zirconate-titanate ceramics during processing by fixing the PbO pressure in the sintering environment.

The need for revision of the current $\text{PbO-Al}_2\text{O}_3$ phase diagram is demonstrated and the revision is accomplished by calculating the decomposition temperatures of the three intermediate phases. The calculations combine the measured PbO pressures with estimated pressures along the high Al_2O_3 liquidus. The liquidus position and pressures are estimated using three approaches: the regular solution, the empirical and the modified ideal solution.

The Gibbs' free energies of formation of the intermediate phases are determined and the extent of nonstoichiometry is considered.

INTRODUCTION

Processing of PZT

The intent of this project is to determine the pressure of lead oxide that exists in equilibrium with aluminum oxide as a function of temperature and composition for ultimate application to the processing of PZT ceramics. PZT is a solid solution of lead zirconate and lead titanate that has good ferroelectric and piezoelectric properties and has a wide range of applications in transducer devices.¹ As with other electronic materials, the properties of PZT are very sensitive to processing parameters and much effort has been devoted to attaining an understanding of the influence of these parameters on the final properties of PZT ceramics.

The high temperatures (1200°C) required for sintering of PZT combined with the volatility of PbO make it difficult to prevent variation of the mole fraction PbO from one batch to another. The control of PbO vaporization has been studied in this laboratory.^{2,3} The approaches used have been based on the variation of PbO activity with composition.

An isothermal section of the PZT phase diagram⁴⁻⁶ and the compositional dependence of PbO activity for the $\text{PbO} - \text{ZrO}_2 \cdot \text{TiO}_2$ pseudo-binary at 1100°C are shown in Fig. 1.

The typical PZT composition used in electronic applications is $\text{Pb}(\text{Zr}_{0.52}, \text{Ti}_{0.48})\text{O}_3$ so that the activity-composition graph in Fig. 1 is an appropriate section for analysis. The standard state is chosen as the pressure of PbO that is in equilibrium with pure liquid PbO at the temperature of interest, in this case 1100°C. The activity of PbO decreases across single phase or two phase regions although it has been suggested⁷

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Fig. 1. (Top) $PbO-ZrO_2TiO_2$ isothermal section.⁴⁻⁶ The extent of nonstoichiometry of PZT was determined by Holman.³ (Bottom) Activity vs. composition for the $PbO-ZrO_2 \cdot TiO_2$ pseudobinary.

that the rate of activity decrease in the two phase regions is much less than in single phase regions. This is shown in the lower portion of Fig. 1. A sample of PZT will lose PbO during sintering and the composition of the remaining solid will move toward the $\text{ZrO}_2\cdot\text{TiO}_2$ edge of the diagram.

It is possible to prevent the loss of PbO by creating a PbO atmosphere around the sample. For example, suppose the initial PZT composition corresponds to that of point A in the figure. If the PZT is embedded in a "packing powder" of composition B, the PZT will lose PbO by vapor phase transport to the packing powder because of the higher PbO activity of the sample. If the packing powder and samples are in a closed isothermal volume, the activity of the packing powder increases. But the change in activity of the two phase packing powder is small.

When the PZT sample has lost enough PbO to change its composition to point B, it will have equilibrated with the packing powder and no further transfer of PbO will occur, the activity difference being zero.

An excess of a two phase packing powder with a PbO activity between points A and B will fix the composition of the PZT sample at that composition corresponding to that activity. It was predicted by Atkin and Fulrath² that a $\text{PbZrO}_2 - \text{ZrO}_2$ packing powder would accomplish this. Holman³ measured PbO pressures throughout the $\text{PbO}-\text{ZrO}_2\text{-TiO}_2$ system and verified their prediction. His data are presented in Fig. 2.

Because the function of the packing powder is to provide a PbO chemical reservoir, it is not necessary that the non-volatile component be ZrO_2 . Al_2O_3 is non-volatile relative to PbO and since Al_2O_3 is also present during sintering both as a container and as a structural element

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Fig. 2. Lead oxide activities in selected two phase regions of the PbO-ZrO₂-TiO₂ system.³

of the furnace, a knowledge of the activity of PbO in the $\text{PbO-Al}_2\text{O}_3$ system will make it possible to better understand the potential role of Al_2O_3 in the processing of PZT.

The $\text{PbO-Al}_2\text{O}_3$ System

Two studies of this system exist, Fig. 3. The early work of Bunting and Geller⁸ is limited to the PbO side of the diagram and is based on phase identification of quenched samples by x-ray diffraction and optical microscopy. Variations in the refractive indices of the crystal phases led them to suggest the existence of solid solutions. Torkar, et al.⁹ studied the entire diagram and determined diffraction patterns for three intermediate phases. Following their terminology, the compounds $\text{PbO} \cdot 6\text{Al}_2\text{O}_3$, $\text{PbO} \cdot \text{Al}_2\text{O}_3$ and $2\text{PbO} \cdot \text{Al}_2\text{O}_3$ will be referred to as lead β -alumina, the monoclinic phase and the cubic phase, or alternatively as PA_6 , PA and P_2A .

The diffraction pattern for the monoclinic phase agrees with that obtained by Bunting and Geller. Lead β -alumina has been studied by several workers¹⁰⁻¹² because of its possible electronic applications. The lattice parameters were determined by x-ray diffraction and transmission electron microscopy. Nonstoichiometry is suspected in this phase because the β -aluminas in general occur in all sorts of variable compositions.¹³ The single crystals grown by Comer, et al.¹⁰ had the formula $(1.03 \text{ PbO}) \cdot 6\text{Al}_2\text{O}_3$.

The decomposition temperatures for the three lead aluminates were determined in the study of Torkar, et al. using dynamic differential calorimetry (DDC). Since the construction of phase diagrams must be consistent with the laws of thermodynamics, their proposed phase

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Fig. 3. Proposed phase diagrams for the $\text{PbO}-\text{Al}_2\text{O}_3$ system.^{8,9}

diagram was compared with their DDC data. The DDC thermograms taken from their paper are shown in Fig. 4. Each was produced by heating (ten degrees per minute) an intimate mixture of PbO and η -Al₂O₃. The composition for each thermogram is labeled in mole percent PbO. The endotherm for fusion of pure PbO at 900°C was used to standardize the equipment.

As alumina content increases the temperature of the PbO branch of the liquidus decreases as would be expected. Below seventy mole percent PbO, exotherms at 800°C are observed. These exotherms were identified by Torkar, et al. as a consequence of the peritectic decomposition of the monoclinic phase. However, the principle of successive entropy states¹⁴ requires that peritectic decompositions be endothermic processes: an equilibrium transformation that occurs with increasing temperature must be accompanied by an entropy increase and consequently an increase in enthalpy.

Inasmuch as the starting materials were unreacted PbO and Al₂O₃, the exotherms at 800°C as well as those at 750°C can be attributed to the formation of the intermediate phases. Comer, et al. have stated that calcining mixtures of PbO and Al₂O₃ at temperatures between 500 and 700°C produced the monoclinic phase while calcining between 700 and 900°C results in the formation of lead β -alumina. Glasser and Glasser¹⁵ produced the monoclinic phase by calcining between 900 and 1100°C.

It is clear that the phase diagrams of Fig. 3 need to be reconsidered, particularly with respect to the decomposition of the monoclinic phase, PbO·Al₂O₃ and to the solution ranges of the intermediate phases. Investigation of these points became a second goal of

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Fig. 4. Dynamic differential calorimetry thermograms for the PbO-Al₂O₃ system taken from the work of Torkar, et al.⁹

this thesis. There is no quantitative information concerning the $\text{PbO-Al}_2\text{O}_3$ phase diagram above 1000°C , and no partial pressure measurements had been reported. The present study provides decomposition measurements and phase stability information to about 1100°C .

The $\text{PbO}\cdot\text{Al}_2\text{O}_3$ system is representative of a class of systems in which one component has a high vapor pressure, and this volatility makes it difficult to determine the phase stability at high temperatures. Each of the researchers referenced above has stressed the problem of PbO evaporation during calcining. To limit PbO loss the previous investigators wrapped the mixed oxides in platinum foil, but depending on the nature of the Al_2O_3 powder, reaction times varied from several hours to several weeks and PbO losses remained a significant problem at higher temperatures.

The Thermodynamic Approach

It is possible to use the high PbO vapor pressure to advantage. By containing the $\text{PbO-Al}_2\text{O}_3$ sample in a Knudsen effusion cell and letting the PbO evaporate in a "controlled" way, (the Knudsen effusion weight loss technique), the equilibrium vapor pressure of PbO throughout the system can be determined. When the PbO pressures are plotted with Arrhenius coordinates, a phase diagram results. Figure 5 shows the way Torkar's phase diagram would transform to the Arrhenius plot. The plot is schematic in that it includes hypothetical partial pressure curves (indicated by dotted lines) that would be consistent with the Torkar phase diagram. The line marked JANAF represents the vapor pressure of pure PbO as taken from the JANAF Thermochemical Tables.¹⁶ The melting

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Fig. 5. Arrhenius plot of PbO pressures based on the PbO-Al₂O₃ phase diagram of Torkar, et al.⁹

point of PbO, 888°C, is indicated by T_m in the figure. The PbO branch of the liquidus is represented by the line T_m -E on both Torkar's diagram in Fig. 3 and the schematic Arrhenius plot. This line shows the temperature dependence of PbO pressure in the liquid + PbO two phase region. Analogously, each line on the Arrhenius plot corresponds to a two phase region in Torkar's diagram; each area to a single phase region and each three line intersection to an invariant reaction line. But we are no longer using the condensed phase rule so that on the Arrhenius plot the three line intersections indicate four phase equilibrium. For example, the peritectoid reaction point at 800°C in Fig. 3 (point P_1 in Fig. 5) corresponds to the coexistence of lead β -alumina, $PbO \cdot Al_2O_3$, $2PbO \cdot Al_2O_3$ and a vapor phase (which contains an immeasurably small partial pressure of Al_2O_3 gaseous decomposition products). Four of these invariant points (three line intersections) occur on the Arrhenius plot just as four invariant reaction lines occur on Torkar's diagram.

Some of the lines in the Arrhenius plot are curved. Notice that these are found where one of two condensed phases is a liquid. As the temperature increases the position of the liquidus retreats from the PbO side of the diagram and this is reflected as a decrease in PbO pressure relative to the JANAF line on the Arrhenius plot.

Even though the partial pressures of Al_2O_3 vapor molecules can not be easily measured at these temperatures, through the use of the Gibbs-Duhem equation, the activity of Al_2O_3 can be calculated as can ultimately the free energy of formation of each intermediate phase. The necessary information is measured values of partial pressures of PbO to replace the hypothetical values of Fig. 5.

There are further applications for these thermodynamic data. As the study of electronic ceramics becomes more sophisticated and the availability of thermodynamic data increases, it will be possible to apply established thermodynamic models to the nonstoichiometric phases. Many ceramics are nonstoichiometric. In those in which the extent of nonstoichiometry is measurably large, much can be learned about the defect structure of the "compound" by interpreting the variation of the thermodynamic values across these regions.

In the simplest case each condensed phase can be treated as a solid solution of PbO and Al_2O_3 . The formation of intermediate PbO and Al_2O_3 phases implies that heats of reaction of PbO with Al_2O_3 are negative, or that the entropy of reaction is positive. The regular solution model of Hildebrand,¹⁷ in which a non-zero enthalpy of mixing is assumed but in which Pb^{+2} and Al^{+3} ions are assumed to mix randomly is an appropriate model for such a system.

Vacancies and interstitial or substitutional ions can be associated with each other throughout the solid solution lattice. In this case, the defects will be to some extent ordered and the entropy of mixing will be less than that in which defects are scattered at random throughout the lattice. Knowledge of the extent to which the compound conforms to the regular solution model will provide another step toward the understanding of the defect structure of nonstoichiometric materials. The $\text{PbO-Al}_2\text{O}_3$ system can be looked at in this manner.

PROCEDURES

Theory and Calibration

In 1882 Hertz¹⁸ showed that the vapor flux impacting on a unit area of surface obeys the relation,

$$j = \frac{P}{\sqrt{2\pi mkT}} \quad (1)$$

where P is the pressure of the vapor, m is the mass of a molecule of vapor and T is the absolute temperature and k is the gas constant. If cgs units are used for P, k, and m, j is the molecular flux and has units of molecules $\text{cm}^{-2} \cdot \text{sec}^{-1}$. When a vapor is in equilibrium with its condensed phase, equation (1) also describes the flux of molecules leaving the surface of the condensed phase, P being the equilibrium pressure of the vapor. When enclosed in an inert container with an orifice of area A_o , the rate of escape of molecules from the container can be written in units of mass flux, i.e. $\text{gm} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$, as

$$\frac{dw}{dt} \frac{1}{A_o} = P \sqrt{\frac{m}{2\pi kT}} \quad (2)$$

In this expression m is the mass of a molecule of the effusion vapor, and $\frac{dw}{dt}$ is the resulting decrease in mass of the vapor in the container. Thus, by determining the rate of loss of weight of the container, the pressure of the vapor in the container can be calculated. This technique is called the Knudsen effusion technique and the container is the Knudsen cell.¹⁹

There are several constraints inherent in this derivation. First, the orifice should in no way affect the motion of the vapor molecules in its vicinity. This condition can be met only if the diameter of the orifice is small in comparison to the mean free path of the vapor

molecules. Otherwise flow will depend more on intermolecular collisions than on the geometry of the orifice and the molecules near the orifice will develop a drift velocity in the direction of the orifice.²⁰ As a result, the measured flux will not be the flux corresponding to the equilibrium pressure of the vapor by equation (2). This kind of failure of equation (2) sets an upper limit to the pressures that can be measured by the Knudsen effusion method.

The second requirement is that the orifice either be ideal, i.e., none of the molecules that enter the orifice should return to the cell as a result of collisions with the orifice walls, or that the effect of the collisions with the orifice walls be measured or estimated. Since an infinitely thin walled orifice is not attainable, a correction for the fraction of the molecules that return to the cell, called the Clausing factor,²¹ must usually be included with A_o in equation (2). A tabulation of the Clausing factors for cylindrical and conical orifices and a description of the derivation and the assumptions implicit in the derivation can be found in the appendix of reference 21.

Molecules can also be returned to the cell following collisions with other vapor molecules. Effusion must be into a vacuum to prevent this effect. Although equation (2) implies steady state conditions, steady state is not required and the equilibrium pressure still can be calculated if 1) the reactions taking place in the cell are reversible and 2) the sample surface flux times the sample area is much greater than the product of the orifice area and the orifice flux. When these conditions exist, the pressure will build up in the cell to the equilibrium pressure and the measured flux will still be that of equation (2).

The problem of maintaining high enough ratios of sample area to orifice area will be discussed as it relates to single phase widths later.

When the above conditions are fulfilled, measurement of the rate of weight loss at a known temperature can be used to determine the equilibrium vapor pressure of the sample in the Knudsen cell. Sufficient experimental evidence that the constraints of this method are satisfied can be obtained by varying the orifice diameter and determining the dependence of the measured pressures on this diameter. When the calculated pressure depends on orifice area, the form of its dependence can be used to extrapolate to a zero diameter orifice, yielding the equilibrium pressure.

No orifice dependence of pressures was observed with lead oxide. The measured pressures from Pt cells are shown in Fig. 6. The solid line represents data taken from the JANAF Tables.¹⁶ The break at 888°C corresponds to the melting point of lead oxide. Lead oxide was chosen for calibration because its vapor pressure is known, and because PbO is the component of the lead oxide-aluminum oxide system which vaporizes under the conditions of this study.

The Knudsen Cell

Three designs for Knudsen cells are shown in Fig. 7. Two of the cells are platinum and the third is aluminum oxide. The "tapered" cell was machined with a five degree taper on the cap and in the cell body which made it possible to form a friction seal between the two pieces. This cell could be easily opened after each experiment and after smoothing the tapered surfaces with fine abrasive was ready for reuse. The "welded" cell required a lathe to remove the bead around the lid. The

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Fig. 6. PbO pressures measured by Knudsen effusion-weight loss technique in platinum cells, different orifice areas.

Fig. 7. Knudsen cells: left, tapered platinum cell; middle, welded platinum cell; right, aluminum oxide cell. Scale is in centimeters.

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orifices were drilled and then dimensions were measured with a calibrated optical microscope.

An alumina cell was used with powders that were in the alumina and the lead β -alumina two phase regions of the phase diagram. Although platinum is not expected to reduce lead oxide it was thought that a simple test for the influence of Pt on the PbO vapor pressure could be accomplished by measuring the PbO pressures in an alumina cell. It was assumed that for a thick walled cell, the diffusion of PbO through the walls would be slow enough to allow the measurement of PbO pressures. The PbO pressures measured in alumina did in fact agree with the pressures obtained with the Pt cells. Thus, the inertness of Pt is confirmed. The PbO pressures obtained with Al_2O_3 cells are labeled and included with the Pt cell data in a later figure.

Weight Loss Apparatus

The experimental equipment for Knudsen effusion-weight loss is shown in Fig. 8. A Knudsen cell is suspended by a platinum or molybdenum wire from one arm of a Cahn Model R-100 Electrobalance. Weight is monitored continuously and recorded on a Leeds and Northrup Speedomax Chart recorder.

The balance is mounted in a vacuum chamber that is maintained at pressures below 10^{-8} atmospheres by a four inch silicone oil diffusion pump and liquid nitrogen cold trap.

The furnace consists of a molybdenum mesh resistance heating element which is surrounded by an alternating series of Mo heat shields and Zircar insulating felt.* Two water cooled copper electrodes support

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* Zircar is the trade name of a 96 percent porous yttria-stabilized zirconia having a melting point of 2600°C.

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Fig. 8. Knudsen effusion-weight loss experimental apparatus.

the furnace assembly and are connected outside the vacuum chamber to a step-down transformer and a hydraulic lift assembly so that the furnace can be lowered for access to the Knudsen cell. When in the raised position, the furnace fits firmly against an insulating cap that is suspended from the top of the vacuum chamber. This cap has three holes to permit the passage of the Knudsen cell support wire and two Pt, Pt-10Rh thermocouples, one for temperature control and the other for temperature monitoring. There is no measureable horizontal thermal gradient above 700°C and the vertical gradient in less than 2°C per cm.

Sample Preparation and Data Analysis

Reagent grade orthorhombic lead oxide and 99.98 percent γ - Al_2O_3 were obtained from Baker Chemical Company and Atomergic Chemetals Corporation, respectively. Orthorhombic PbO also called Massicot, is the stable form of solid PbO above 500°C. The Al_2O_3 is a high surface area, 100m²/g, fumed alumina which is produced by oxidizing a form of AlCl_3 . Both chemicals absorb water and this water content was determined by Thermogravimetric Analysis so that allowances could be made for water in preparing samples of the desired initial PbO/ Al_2O_3 ratios.

The desired compositions were produced by mixing the appropriate ratios of PbO and Al_2O_3 which had been previously suspended in ethyl alcohol. Mixing was continued during evaporation of the alcohol to prevent settling and separation. The mixed powders were pressed into pellets and calcined in covered platinum crucibles until the reactions were complete. The high reactivity of the Al_2O_3 made it possible to obtain reaction at low enough temperatures (900°C to 1100°C) and short enough times (1 to 5 hrs) to prevent significant loss of PbO. Cooled

samples were crushed and analyzed by x-ray diffraction.

Vapor pressure vs. composition isotherms were obtained in the following way. A small amount of sample (100 to 500mg) was weighed and loaded into a Knudsen cell. The precise amount was recorded. The cell was sealed and suspended in the furnace. After evacuation, the furnace was heated to 700°C and allowed to stabilize for several hours. Then the temperature was increased to the desired level and maintained at that temperature until the PbO was evaporated completely from the cell. Weight was recorded continuously throughout. For example, an experiment using a starting composition of 90% PbO is shown in Fig. 9. Figure 9a plots the weight of the sample as a function of time. The weight of the platinum cell and the suspension assembly has been subtracted. Therefore, the weight remaining as $t \rightarrow 50$ is that of the Al_2O_3 and everything indicated as lost from the cell before $t=40$ is PbO.

This was confirmed by x-ray analysis of the Al_2O_3 . The amount of Al_2O_3 that is evaporated during an experiment is negligible. The slope of the weight vs. time graph is directly proportional to the vapor pressure of the PbO in the cell according to equation (2). Since the weight fraction of lead oxide can be transformed into the mole fraction, the resulting pressure vs. composition isotherm is derived, Fig. 9b.

The horizontal portions of the line in Fig. 9b correspond to two phase regions of the condensed phase diagram. They are separated by the single phase regions showing the compositional dependence of pressure. It is instructive to compare this line to the dotted line labeled Torkar, et al. That is the form of the isotherm that is expected from Torkar's phase diagram in which the compound corresponding to fifty mole

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Fig. 9. Comparison of weight of sample versus time (top) with PbO activity versus sample composition (bottom).

percent lead oxide is reported to decompose at 800°C.

In practice it was not necessary to hold the temperature constant. In a two phase region the pressure could be measured at one temperature and then measured again after changing temperature, and so on until the composition approached a single phase region. The interpretation of the pressure vs. composition data across a single phase region requires constant temperature.

RESULTS AND DISCUSSION

The measured pressures of PbO in the solid-solid two phase regions of the PbO-Al₂O₃ phase diagram are plotted in Fig. 10. The lines labeled JANAF are the pressures of pure PbO taken from the JANAF tables. Measured pressures are independent of effective orifice areas, which indicate that equilibrium was achieved in each two phase region. The data for each two phase region have been fit to straight lines. The results can be found in Table 1.

Before considering the phase diagram in detail, application of these results to the processing of PZT should be considered. Holman's results for the PZT system have been reproduced in Fig. 11. The PbO partial pressure line labeled PZ-ZrO₂ lies entirely in a range that makes some composition within the PZT single phase stable, and PZ+ZrO₂ is the currently used packing powder. For the PbO-Al₂O₃ system to provide a satisfactory packing powder, would require that two PbO-Al₂O₃ phases establish a PbO partial pressure at which PZT is stable. A suitable PbO pressure only occurs over a narrow temperature interval for the mixture of Al₂O₃ and lead β -alumina.

Although PZT sintering is accomplished in this temperature range, other problems exist. Lead oxide diffuses rapidly through polycrystalline Al₂O₃. Figure 12 is a scanning electron micrograph of a section of polycrystalline Al₂O₃ crucible that was heated at 1100°C in a PbO environment for five hours. Energy dispersive x-ray analysis shows that lead occurs only in the grain boundary phase. To confirm this observation, a single crystal of corundum was heated in pure PbO for twenty hours at 1100°C. No weight gain was observed. The rapid transport of

Table 1. Least Squares Analysis of Knudsen Effusion Data for the Lead Oxide - Aluminum Oxide System.

Phase(s) [*]	Range, °C	P_m , atm	H, $\frac{\text{kcal}}{\text{mole}}$	S, e.u.
A-PA ₆	990 - 1210	$\frac{-47397}{T} + 25.78$	94.19±2.80	51.23±2.04
PA ₆ -PA	870 - 1135	$\frac{-33875}{T} + 19.81$	67.32±1.97	39.37±1.76
PA-P ₂ A	820 - 980	$\frac{-31000}{T} + 18.19$	61.60±1.76	36.15±1.53
Liquidus	920 - 1080	$\frac{-22812}{T} + 11.58$	45.33±0.44	23.01±0.36
PbO liquid ^{**}	900 - 1200	$\frac{-26691}{T} + 15.05$	53.04	29.91

[*] A	$\alpha\text{-Al}_2\text{O}_3$
PA ₆	$\text{PbO} \cdot 6\text{Al}_2\text{O}_3$
PA	$\text{PbO} \cdot \text{Al}_2\text{O}_3$
P ₂ A	$2\text{PbO} \cdot \text{Al}_2\text{O}_3$

^{**} JANAF Tables

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Fig. 10. Measured pressures of PbO in various two phase regions of the PbO-Al₂O₃ system.

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Fig. 11. Activities of PbO in various two phase regions of the PbO-Al₂O₃ system.

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Fig. 12. Scanning electron micrograph of a polished section of a polycrystalline Al_2O_3 crucible wall. Magnification is 2000X.

PbO through the walls via the grain boundaries of the alumina container discourages the use of the $\text{PbO}\cdot\text{Al}_2\text{O}_3$ system in control of PZT stoichiometry.

Inspection of the results in Fig. 10 in comparison to the predicted Arrhenius diagram of Torkar, et al.⁹ confirms the stability of the monoclinic phase, $\text{PbO}\cdot\text{Al}_2\text{O}_3$ at temperatures well above 800°C. $\text{PbO}\cdot\text{Al}_2\text{O}_3$ should decompose peritectically at the temperature at which the PbO partial pressure for the lead β -alumina and $\text{PbO}\cdot\text{Al}_2\text{O}_3$ two-phase region equals that for the $\text{PbO}\cdot\text{Al}_2\text{O}_3$ -liquid two phase region, at about 1100°C. As will be shown, each of the intermediate phases melts incongruently.

The Arrhenius plot for the system is presented in Fig. 13.

The peritectic temperatures can be calculated, or in one case, observed. When one of the phases in the Knudsen cell is a liquid, temperature dependence of the pressure of that mixture will be affected by the curvature and slope of the liquidus. As the liquidus slope decreases the pressure over the mixture shows less of a pressure increase with temperature than would be predicted by the linear relation. In the $\text{PbO}\cdot\text{Al}_2\text{O}_3$ system this reduced dependence of pressure on temperature occurs because the liquid is decreasing in PbO content with increasing temperature. This departure from linearity can indicate the position of the peritectic although scatter in the data makes this method unreliable.

To determine the peritectic temperature of $2\text{PbO}\cdot\text{Al}_2\text{O}_3$ the pressure of PbO was measured in the $2\text{PbO}\cdot\text{Al}_2\text{O}_3$ -liquid region and the intersection of this line with that for the $\text{PbO}\cdot\text{Al}_2\text{O}_3$ - $2\text{PbO}\cdot\text{Al}_2\text{O}_3$ regions was found to occur at $965^\circ\text{C} \pm 10^\circ\text{C}$. The uncertainty is due primarily to the uncertainty in the $2\text{PbO}\cdot\text{Al}_2\text{O}_3$ -liquid two phase pressure measurements.

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Fig. 13. Arrhenius plot of PbO pressures in the $\text{PbO-Al}_2\text{O}_3$ system based on measured pressures from Knudsen effusion-weight loss technique.

Experimental difficulties prevented the extension of these measurements to higher temperatures in order to determine the peritectics of $\text{PbO} \cdot \text{Al}_2\text{O}_3$ and $\text{PbO} \cdot 6\text{Al}_2\text{O}_3$.

A third way of calculating the peritectics involves the free energy of formation of the phases and the estimated activities of the components of the liquid phase. The free energy of formation of each phase can be derived from the pressure vs. temperature relationships in Table 1.

For example, still using pure liquid PbO and pure solid Al_2O_3 as the standard states, the free energy of lead β -alumina can be written as the sum of three reactions:

in which $P_{\text{eq}}^{\text{A-PA}}_6$ is the pressure that was measured over the Al_2O_3 -lead β -alumina two-phase region and P° is the pressure of PbO in equilibrium with pure liquid PbO , which was also measured by Knudsen effusion and was in agreement with the tabulations in the JANAF Tables. Thus,

$$\Delta G_{\text{f-PA}_6}^\circ = -41.15 + .02 T \text{ kcal/mole.}$$

And since there are seven gram-molecules in one mole of lead β -alumina,

$$\Delta G_{\text{f-PA}_6}^\circ = -5.88 + .003 T \text{ kcal/gram molecule}$$

The same procedure yields for $\text{PbO} \cdot \text{Al}_2\text{O}_3$ and $2 \text{ PbO} \cdot \text{Al}_2\text{O}_3$

$$\Delta G_{\text{f-PA}}^\circ = -18.76 + .011T \frac{\text{kcal}}{\text{mole}} = -9.38 + .006T \frac{\text{kcal}}{\text{gram molecule}}$$

$$\Delta G_{\text{f-P}_2\text{A}}^\circ = -27.32 + .017T = -9.11 + .006T$$

There is a source of error in the above calculations that must be considered. Figure 14 shows the error that can result when the extent to which these phases are nonstoichiometric is large.

To calculate the free energy of formation of $\text{PbO} \cdot \text{Al}_2\text{O}_3$ from Al_2O_3 and PbO requires the free energy of formation at lead β -alumina. When lead β -alumina has a narrow range of composition as shown in the top of Fig. 14, the integral free energy of formation lead β -alumina will not change from the Al_2O_3 saturated side to the PbO rich side. In the lower portion of the figure the phases are drawn each having a significant phase width. If the free energies vary as illustrated in that figure, an error of 0.2 kcal would occur when the free energy of formation of lead β -alumina in equilibrium with Al_2O_3 is used to calculate the values for $\text{PbO} \cdot \text{Al}_2\text{O}_3$. This error is carried over to the calculations involving $2\text{PbO} \cdot \text{Al}_2\text{O}_3$.

The magnitude of error involved in assuming stoichiometric phases is uncertain in these studies because the uncertainties in the free energies as calculated from the experimental data using Gibbs-Duhem integration are also large.

These uncertainties also affect the analysis of nonstoichiometry in each of the intermediate phases of this system. During the course of several experiments the composition of the condensed phase(s) in the Knudsen cell passed through one of the single phase regions. This was evidenced by a decrease in the rate of weight loss as described in the procedural part of this paper. When the rate of weight loss again became constant the calculated pressure was found to be that characteristic of the appropriate two phase region. The transitions across

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Fig. 14. Free energy curves at 1293°K for $\text{PbO}-\text{Al}_2\text{O}_3$ system for cases of stoichiometric (top) and nonstoichiometric (bottom) phases.

$\text{PbO} \cdot \text{Al}_2\text{O}_3$ were relatively sharp corresponding to a narrow composition range. Two measurements of PbO pressure changes across the lead β -alumina phase were obtained which are of sufficient interest to discuss. The PbO activity changes across the lead β -alumina phase are shown in Figs. 15 and 16. The limiting values of activity correspond to the two phase regions on either side of the lead β -alumina single phase region.

By setting the activity of Al_2O_3 in equilibrium with lead β -alumina at an arbitrary value the activity of Al_2O_3 across the lead β -alumina region can be calculated. The procedure, described in Lewis and Randall²² and in a paper by Meschi and Searcy²³ is a Gibbs-Duhem integration. The activity of Al_2O_3 was assumed to be essentially unity at the alumina-rich boundary of the lead β -alumina phase because solubility of PbO in Al_2O_3 is believed to be low. The free energy of mixing can then be calculated using the relation

$$\Delta G^M = n_{\text{Al}_2\text{O}_3} RT \ln a_{\text{Al}_2\text{O}_3} + n_{\text{PbO}} RT \ln a_{\text{PbO}}$$

where, for example, n_{PbO} is the number of moles of PbO. If the phase were stoichiometric, then ΔG^M would correspond to the free energy of formation of the phase. The activity of PbO and ΔG^M calculated from the

PbO pressure measurements across lead β -alumina are plotted in Figs. 15 and 16 as functions of PbO mole fraction.

At 1020°C, Fig. 15, the most stable composition of lead β -alumina relative to solid Al_2O_3 and liquid PbO, i.e. the free energy minimum, occurs at .155 mole fraction of PbO. The apparent width of the phase is from $X_{\text{PbO}} = .125$ to .225. The word apparent is chosen because there are

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Fig. 15. Gibbs-Duhem analysis of $\text{PbO} \cdot 6\text{Al}_2\text{O}_3$ nonstoichiometry at 1020°C . Orifice area, $2.07 \times 10^{-4} \text{cm}^2$.

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Fig. 16. Gibbs-Duhem analysis of $\text{PbO} \cdot 6\text{Al}_2\text{O}_3$ nonstoichiometry at 1050°C . Orifice area, $5.17 \times 10^{-4}\text{cm}^2$.

reasons to suspect these values. First, a comparison of these results with those taken at a slightly higher temperature, Fig. 16, shows a large difference in the apparent width of the single phase region. The temperature difference is negligible compared to the orifice area change; $2.07 \times 10^{-4} \text{ cm}^2$ in Fig. 15 vs. $5.17 \times 10^{-4} \text{ cm}^2$ in Fig. 16. Doubling the orifice area nearly doubles the apparent width of the single phase region. In order to determine the true phase width it is necessary to vary the orifice area at constant temperature and extrapolate to an infinitely small orifice area. For example, if the position of the lead β -alumina - $\text{PbO} \cdot \text{Al}_2\text{O}_3$ boundary depends linearly on the orifice area and we ignore the thirty degrees difference in temperature then the true boundary would occur at $X_{\text{PbO}} = 0.178$. Correcting the measured pressure by the same linear relationship would result in a more accurate free energy of formation.

The precise value of the Gibbs-Duhem calculated free energy of mixing is very sensitive to the composition of the condensed phase in the Knudsen cell. Since there was difficulty in determining the actual composition after the termination of PbO versus composition experiments, it was decided that the precision of the calculations would not be sufficiently high to warrant the effort. Thus, a meaningful interpretation of the defect structure from configurational entropies was not obtained. However, it can be said with confidence that lead β -alumina does display significant nonstoichiometry at 1000°C , ranging over five mole percent.

To calculate the peritectic of $\text{PbO} \cdot \text{Al}_2\text{O}_3$, the free energies of formation of lead β -alumina in equilibrium with Al_2O_3 were used.

The peritectic decomposition of $\text{PbO} \cdot \text{Al}_2\text{O}_3$ will occur at the temperature at which the activity of PbO in this phase equals the activity of PbO in the liquid that is saturated with Al_2O_3 . The activity of PbO in lead β -alumina can be calculated from the measured pressure. When liquid PbO is the standard state the activity of PbO vapor is the ratio of the pressure of PbO at some temperature and composition to the pressure of PbO that is in equilibrium with pure liquid PbO at that same temperature. Using the data from Table 1, the activity of PbO at the Al_2O_3 side of PA_6 is

$$\exp \left(\ln P^{\text{A-PA}_6} - \ln P^\circ \right) = \exp \left(\frac{-20706}{T} + 10.73 \right) \quad (3)$$

In the same way the activities of PbO on the Al_2O_3 side of the $\text{PbO} \cdot \text{Al}_2\text{O}_3$ and $2\text{PbO} \cdot \text{Al}_2\text{O}_3$ are found to be

$$a_{\text{PbO}}^{\text{PA}_6} = \exp \left(\frac{-7184}{T} + 4.76 \right) \quad (4)$$

$$a_{\text{PbO}}^{\text{PA-P}_2\text{A}} = \exp \left(\frac{-4309}{T} + 3.4 \right) \quad (5)$$

The three relations yield PbO activities as function of temperature. The activity of PbO along the liquidus is more difficult to determine because the experimental data are not available above 1080°C . Thus, the activity must be extrapolated.

To accomplish the necessary extrapolations three approaches were used, the regular solution model, an empirical analysis and a modified ideal solution model. The concept of the regular solution in which a chemical interaction between the solution species occurs without ordering was first suggested in 1929 by Hildebrand.¹⁷ Starting with these

assumptions it can be shown that

$$\ln \gamma_{\text{PbO}} = \alpha x_{\text{Al}_2\text{O}_3}^2 \quad (6)$$

where γ is the activity coefficient of PbO and α is a constant.

Assuming the partial heat of solution of PbO to be independent of temperature it can also be shown that at a given composition

$$\ln \gamma_{\text{PbO}}^{T_2} = \frac{T_1}{T_2} \ln \gamma_{\text{PbO}}^{T_1} \quad (7)$$

The activities of PbO along the liquidus were measured in the range of 920 to 1080°C. In addition there is agreement concerning the position of the liquidus in the same temperature range in the studies of Bunting and Geller and Torkar, et al. The data can be combined to yield the activity coefficient of PbO. For activity, as before:

$$a_{\text{PbO}}^{\text{Liq}} = \exp \left(\frac{3879}{T} - 3.47 \right) \quad (8)$$

The liquidus position was approximated by a straight line

$$x_{\text{PbO}}^{\text{Liq}} = - 5 \times 10^{-4} T + 1.456 \quad (9)$$

where the temperature is in degrees Kelvin. The natural logarithm of the activity coefficient in the range of applicability of equations (8) and (9) is shown as the diagonal set of numbers in Table 2. Equation (7) was used to determine the activity coefficients of PbO at 1000°C, the midpoint of the data range.

Thus,

$$\ln \gamma_{\text{PbO}}^{1273} = - 7.88 (1 - x_{\text{PbO}})^2 \quad (10)$$

where the constant was determined by a best fit of the data to extrapolate the PbO activity to higher temperatures the position of the liquidus was determined at an arbitrary temperature via equation (8). The

Table 2. Activity Coefficients of PbO at 1000°C and Along the Liquidus as Functions of Mole Fraction PbO.

T°C	.781	.791	.801	.811	.821	.831	.841	.851	.861
920									-.069
940								-.111	
960							-.151		
980						-.189			
1000	-.378	-.341	-.303	-.265	-.226	-.186	-.146	-.106	-.065
1020				-.261					
1040			-.294						
1060		-.326							
1080	-.356								

activity coefficient at 1000°C was calculated using equation (10) and at the higher temperature through equation (7). For example, at 1473°K, $X_{\text{PbO}} = 0.720$ and $\gamma_{\text{PbO}} = 0.585$. The activities obtained in this way are plotted in Fig. 17. Included are the activities for each of the solid-solid two phase regions. The decomposition temperatures calculated from the intersections of the appropriate lines for $2 \text{ PbO} \cdot \text{Al}_2\text{O}_3$ and lead β -alumina are 958, 1068, and 1407°C.

The fit of the data at 1000°C to the regular solution model equation was not good. An empirical equation suggested by Marguiles²⁴ was tried. The result was an equation of the form

$$\ln \gamma_{\text{PbO}}^{1273} = -7.88 + 9.16 X_{\text{PbO}} + 7.06 X_{\text{PbO}}^2 - 8.34 X_{\text{PbO}}^3 \quad (11)$$

when the activity of PbO at higher temperatures was calculated substituting equation (11) for equation (10) the decomposition temperatures determined for $2\text{PbO} \cdot \text{Al}_2\text{O}_3$, $\text{PbO} \cdot \text{Al}_2\text{O}_3$ and lead β -alumina became 965, 1068, and 1407°C. This activity-temperature curve is also drawn in Fig. 17.

The third approach to the activity calculations was based on obtaining a more true temperature-composition relationship at temperatures above 1000°C. When the linear relation equation (9) is extrapolated to $X_{\text{PbO}} = 0$, the temperature is 2912°K. The melting point of Al_2O_3 is 2323°K. To test the effect of a different temperature-composition relation, a liquidus was derived from the ideal solution model.²⁵

When a solid component of a two component system is in equilibrium with the saturated solution (the liquidus) the activity of the solid phase equals the activity of that component in the solution. This

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Fig. 17. PbO activities versus temperature based on regular, empirical, and modified ideal solution models for the liquidus. Solid lines are measured two-phase activities.

activity can be calculated (relative to the pure liquid standard state) at any temperature assuming ideal solution using the relation

$$\ln a_A^T = \frac{-\Delta H_f}{R} \left(\frac{T_m - T}{T_m T} \right) \quad (12)$$

in which ΔH_f is the enthalpy of fusion of pure component A, R is the gas constant, and T_m is the melting temperature of pure component A. For an ideal solution, $a_A^T = X_A$ at temperature T, X_A being the position of the liquidus. There is considerable negative deviation of this calculated liquidus if the equation is applied to the lead oxide-aluminum oxide system. But it is assumed that the form of the equation is appropriate for our interests, it becomes

$$\ln (1 - X_{PbO}^T) = -a \left(\frac{2323}{T} - 1 \right) \quad (13)$$

The melting point of Al_2O_3 is 2323°K. To determine a, the value of X_{PbO} at the decomposition temperature of P_2A is used; 1238°K. Solving for a rearranging yields

$$X_{PbO}^T = 1.0 - \exp \left(2.07 - \frac{4808}{T^{\circ}K} \right) \quad (14)$$

Replacing equation (9) with equation (14) yields decomposition temperatures of 963, 1066 and 1359°C for P_2A , PA and PA_6 . The calculated activity vs. temperature curve using this "modified" ideal solution approach is also plotted in Fig. 17.

Having now considered several approaches to the problem of determining the decomposition temperatures (the regular solution, the empirical, and the modified idea) and shown that different approximations based on solution models have relatively little effect, the lead oxide-alumina oxide diagram can be completed (Fig. 18). The decomposition

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Fig. 18. Completed phase diagram of the $\text{PbO}-\text{Al}_2\text{O}_3$ system.

temperatures chosen are those that were calculated using the regular solution approach with the known low temperature liquidus and the measured activities in the same temperature range. There is an uncertainty of ± 10 degrees in these values.

CONCLUSIONS

The use of controlled vaporization of lead oxide from the lead oxide-aluminum oxide system as embodied in the Knudsen effusion weight loss technique has made it possible to measure the equilibrium partial pressures of lead oxide up to 1200°C. These data, coupled with calculations based on various solution models and empirical observations, have been used to complete the phase diagram and to determine the free energies of formation of the intermediate phases. These free energies of formation for lead β -alumina ($\text{PbO} \cdot 6\text{Al}_2\text{O}_3$), monoclinic $\text{PbO} \cdot \text{Al}_2\text{O}_3$ and cubic $2\text{PbO} \cdot \text{Al}_2\text{O}_3$ oxide are $-41.15 + .02T$, $-18.76 + .01T$ and $-27.32 + .017T$ kcal/mole, respectively.

There exists nonstoichiometry in this system, lead β -alumina ranging over 5 mole percent at 1020°C.

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