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 $\text{Pb}(\text{Ti}_{0.5}\text{Zr}_{0.5})\text{O}_3$

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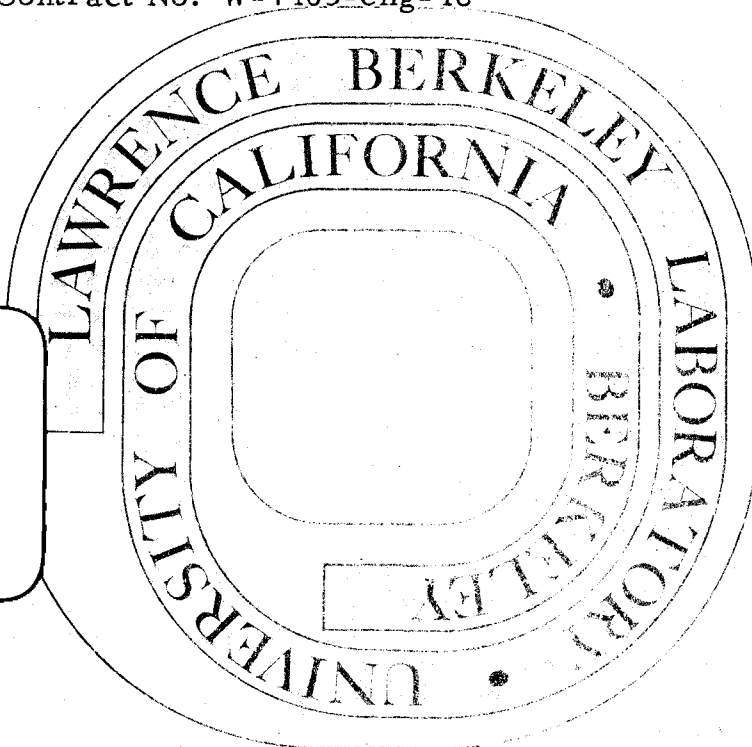
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INTRINSIC NON-STOICHIOMETRY IN SINGLE-PHASE
LEAD ZIRCONATE-TITANATE: I, $\text{Pb}(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_3$

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ABSTRACT

Two-phase crucibles made of lead zirconate titanate with small additions of either PbO or $(\text{Ti}_x\text{Zr}_{1-x})\text{O}_2$ can provide constant lead oxide activities, and permit studies to be made of intrinsic non-stoichiometry by thermogravimetric analysis. Alternate equilibration of a sample with high and low lead oxide activity crucible atmospheres allows a determination of the width of the single phase region. The width of the $\text{Pb}(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_3$ single phase region was found to be 2.48 mol% PbO at 1100°C .

I. Introduction

The attainment of a single-phase lead zirconate titanate with consistent dielectric properties requires a reproducible control of stoichiometry. Webster et al.¹ have observed that degrees of PbO deficiency effect the piezoelectric properties. And more recently, Atkin² observed a stoichiometry effect on the sinterability of $PbTi_{.5}Zr_{.5}O_3$ and suggested the existence of a rather wide single-phase region relative to the PbO content on the basis of reaction weight changes. To date, phase equilibria investigations in the lead zirconate-titanate system have not determined the width of $Pb(Ti_xZr_{1-x})O_3$ single-phase regions.

It has been shown recently³ that one can control the extrinsic stoichiometry of lead zirconate-titanate by controlling the lead oxide vapor pressure. This technique may be extended to determine the width of any $Pb(Ti_xZr_{1-x})O_3$ single-phase region, utilizing thermogravimetric analysis with atmosphere control. Thermodynamically, when a single-phase PZT sample has a different lead oxide activity than that provided by the atmosphere, reaction will occur until the sample and the atmosphere have the same PbO activity. If the sample is small, it will alter its stoichiometry, by either gaining or losing PbO, until an equilibrium activity balance is attained. The sample's composition will then remain fixed for as long as the atmosphere provides the constant lead oxide activity.

II. Experimental Procedure

(1) Technique

A single-phase, high purity and porous $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ sample is alternately "equilibrated" with the PbO vapor pressure established by PZT crucibles fabricated to give two-phase compositions that provide different constant lead oxide activities.

The general form of the PbO activity-composition diagram at a constant temperature (1100°C) is illustrated in Fig. 1, and applicable to analysis of all $\text{PbO}-(\text{Ti}_x\text{Zr}_{1-x})\text{O}_2$ "binaries." Composition A refers to a two-phase mixture of PZT with excess PbO . Composition B refers to a two-phase mixture of PZT with excess $(\text{Ti}_x\text{Zr}_{1-x})\text{O}_2$. Composition C designates the initial stoichiometry of a single-phase sample. The exact location of C is dependent upon the material's processing history.

The sample, activity C, is first equilibrated with the atmosphere provided by a crucible of composition A. The activity difference between the sample and the crucible, assisted by the high vapor pressure of PbO at temperature,* causes the sample to gain weight, PbO , until its activity is raised to equal that of the crucible of activity A. This is shown in Fig. 2a. Weight gain will stop at composition point D, fixing one side of the single-phase region. The sample will continue to maintain this weight for as long as the crucible is at the same constant activity.

Next, this sample, now with activity D, is "equilibrated" with a crucible of composition and activity B. The new activity difference

*The vapor pressure of PbO above $\text{PbTi}_{.5}\text{Zr}_{.5}\text{O}_3 + .02(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_2$ is approximately 5×10^{-4} atm at 1100°C .

causes the sample to lose weight to the atmosphere, until as in Fig. 2b, point E is attained. This point defines the low activity side of the single-phase region. Hence, the weight change (loss), D to E, should exactly correspond to the mole width of the single-phase region.

Reversibility is possible by replacing the sample at activity E, in the first crucible of high activity A, and returning, at temperature, to point D with the same weight change (gain) as before.

(2) The PZT Crucible

The desired crucible composition was obtained by homogeneously mixing correct proportions of the high purity oxides of lead, titanium and hafnium-free zirconium. Approximately 300 grams of the selected composition was isostatically pressed (30,000 psi) about a tapered stainless steel plug (1-3/4 in. x 7/8 in. dia.). Carefully sawing the top of the resultant shape allowed the removal of the steel plug, leaving a formed crucible and cap.

Crucibles containing excess PbO required further treatment since a liquid phase developed at firing temperatures, which aided sintering and resulted in densities such that PbO vapor transport was restricted. The addition of about 20 vol% of finely crushed naphthalene crystals provided ample controlled porosity after sintering. The naphthalene was slowly burned out at 250°C.

All crucibles were calcined for 30 h at 850°C in air, in clean, covered platinum crucibles. After this step, they were soft enough to "finish." The tops and bottoms of both the crucible and cap were ground flat by hand. A 1/8 in. hole was then drilled into the center of the cap, allowing access to the cavity for the platinum wire from a micro-

balance.

X-ray diffractometer analysis of the calcined crucibles revealed traces of the major lines of PbO or TiO₂ and ZrO₂ originally added in excess at 2 mol% to give the two phase compositions.

(3) Sample Fabrication

The homogeneously mixed oxides were combined with 30-40 vol% naphthalene crystals to provide controlled porosity and isostatically pressed (30,000 psi) around a clean platinum coil (shown in Fig. 3). The naphthalene was evaporated slowly (10°/min to 250°C, 12 h soak) in air. The pressed sample was then placed in a clean covered platinum crucible and calcined for 30 h at 850°C in air.

(4) The Weight-Change Cell and Apparatus

The positioning of the sample in the crucible is diagrammed in Fig. 3. Probe samples could be incorporated into the cap as shown, to be removed (at temperature), so as to provide additional information without interrupting the experiment. The TGA assembly, shown in Fig. 4, involved a vertically movable Kanthal wound furnace and a continuously recording microbalance. The sample was hung from the microbalance by an 8 mil dia. platinum wire with a short 16 mil dia. section in the hot-zone of the furnace.

The sample was always weighed, before and after each experiment, on a separate balance. The TGA platinum sample wire was weighed to determine the amount of PbO that condensed on it.

III. Results and Discussion

(1) Error Reduction and Experimental Control

The concept of using a PZT composition crucible as a controlled and constant source of PbO vapor, is subject to several apparent errors that must be either minimized or proved negligible.

First, the sample could lose weight via a "chimney effect" of PbO vapor diffusing out the hole provided in the crucible cap. This problem was shown to be negligible, providing the sample was placed deep enough within the crucible. A check was made by comparing the weight changes produced by heating of control samples equilibrated in both sealed and normal (1/8 in. dia. hole) crucibles. Identical results were obtained.

Also, at operating temperatures the PbO evaporation from the PZT of the crucible will condense on any surface whose temperature is below that of the furnace hot-zone. The platinum suspending wire, a good conductor of heat, allowed PbO vapor to condense on it, indicating an erroneous weight gain. The magnitude of this gain was measured for a platinum wire hanging into a typical PZT crucible. This error could be reduced to only 5 mg/experiment by minimizing chimney effects and using a thin platinum wire that had become saturated with PbO.

A final problem was encountered with the high PbO activity (PZT + PbO) crucible compositions. These cells were required to provide large amounts of PbO to the sample (typically 300 mg.). When this PbO transported from the crucible walls to the sample, it left behind a lead oxide depleted layer* providing a lowered lead oxide activity for the

*X-ray analysis revealed PZT + Z + T peaks.

sample. It was expected that the bulk material of the crucible's wall should immediately replace this PbO. However, the presence of the PbO liquid phase significantly enhanced the crucible densification, which in turn retarded vapor transport within the wall. The result was a degradation of the equilibrated sample's weight (weight loss) that increased with time. This error was significant, and could not be eliminated completely. However, control was managed by increasing the porosity of the crucible wall. This was accomplished, first by a naphthalene addition during fabrication, and then by painting a PZT and PbO suspended in isopropyl alcohol on the inner walls, prior to the experiment. Sample sizes were reduced such that weight gains of no more than 150 mg. would be expected. Under these conditions, the maximum usable length of a single run at 1100°C was found to be 15 h, with the cell maintaining "equilibrium" for 12 h before a slow sample weight loss (3 mg/h) could be detected.

By comparison, the low activity (PZT + ZT) crucibles showed no degradation after more than 1000 h at temperature (1100°C).

To provide a final check on the validity of this equilibration method, the solid state substitutions of bismuth and niobium ions in $\text{PbTi}_{.5}\text{Zr}_{.5}\text{O}_3$ were compared with earlier results obtained by a discontinuous weight change method.³ These experiments agreed with the previous results and provided additional data, previously unresolvable, on the initial reaction kinetics.

(2) The Single Phase Region - $\text{Pb}(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_3$

Experiments conducted to study the width of the single phase region

of $\text{Pb}(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_3$ indicated a width corresponding to 2.48 mol% PbO at 1100°C. This would imply a total weight change of about 150 mgs for a 10 gram sample. Several weight change cycles are shown in Fig. 5, illustrating the reversibility, and reproducibility of these experiments. The stoichiometric composition C is believed to be in its correct relation to the high and low lead boundaries. Equilibration was equally rapid for weight gains and losses, as long as the sample retained adequate porosity.

Only a minor temperature dependence of the overall width of the single phase region could be detected. As the temperature was raised to 1150°, the zone widened about .08 mol% PbO. At 1200°C a similar increase was found. Incremental temperature lowering narrowed the region. No change in the width was detected when temperatures fell below 870°C, probably due to the lowered lead oxide vapor pressure reducing mass transport to an immeasurable rate.

IV. Conclusions

These experiments indicate that two-phase lead zirconate-titanate crucibles may be successfully synthesized to maintain a constant "equilibrium" PbO atmosphere. These crucibles allow for the continuous weighing of specimens during their reaction with the pre-selected crucible atmosphere at temperature.

A width of the single-phase PZT region of 2.48 mol% PbO at 1100°C was determined for the $\text{Pb}(\text{Ti}_{.5}\text{Zr}_{.5})\text{O}_3$ composition by proper reaction with crucibles of different PbO activities.

Acknowledgment

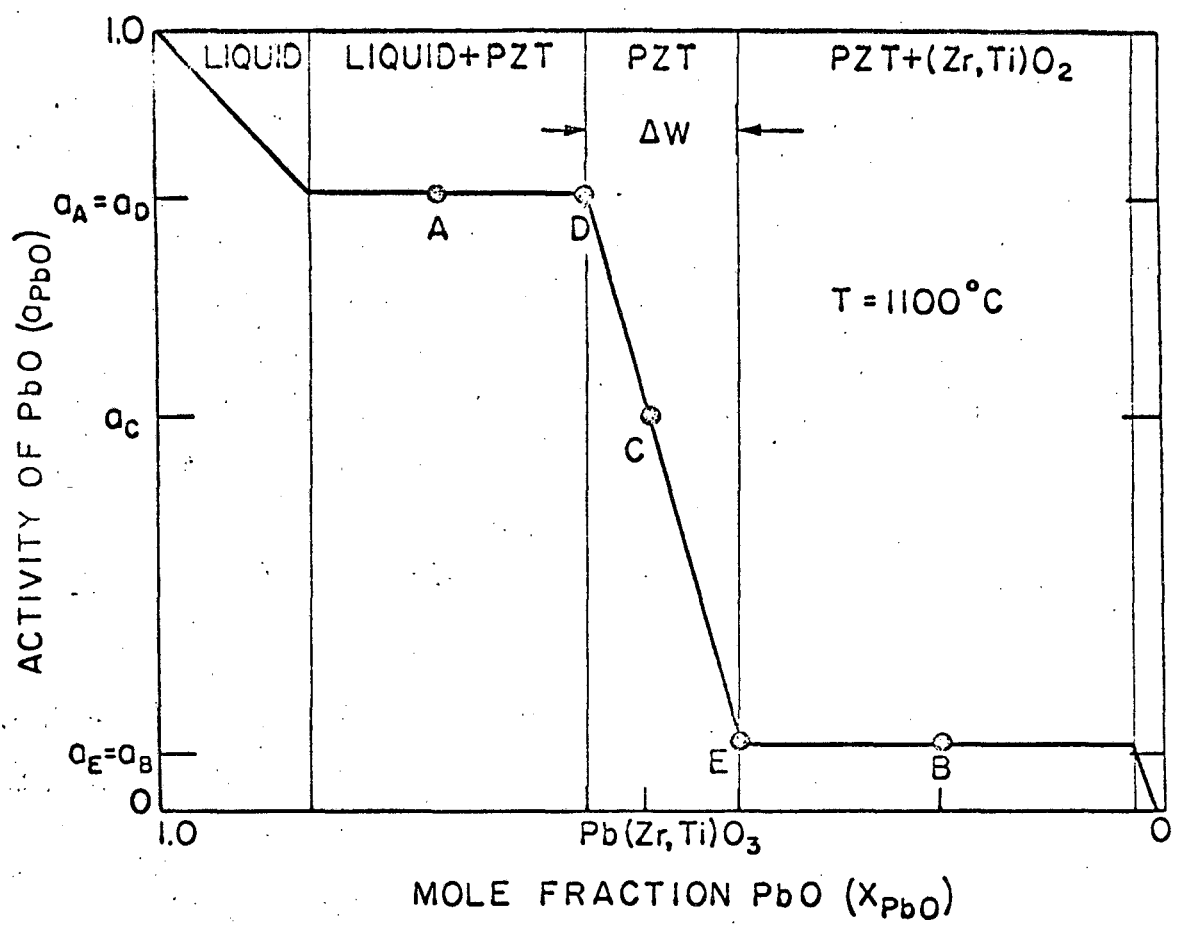
This work was done under the auspices of the United States Atomic Energy Commission.

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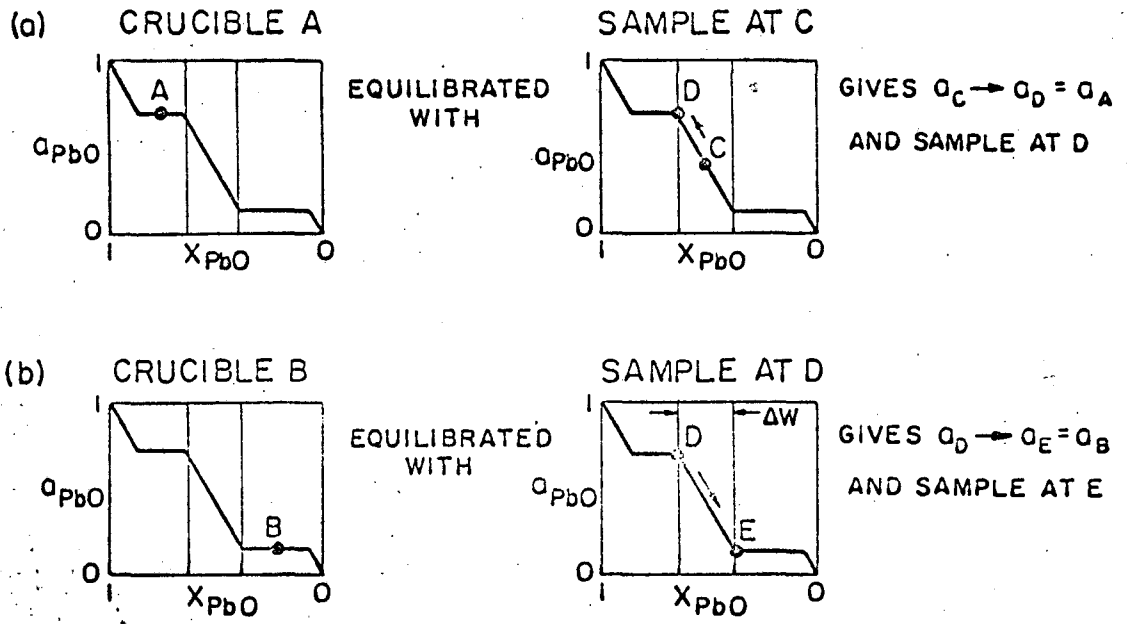
Figure Captions

- Fig. 1. Activity of lead oxide (a_{PbO}) vs. mole fraction of lead oxide (X_{PbO}) at constant temperature (1100°C) for any $\text{PbO}-(\text{Zr},\text{Ti})\text{O}_2$ binary. Points A and B refer to the constant lead oxide atmospheres provided by crucibles of these compositions. Point C locates the composition and activity of stoichiometric PZT, while D and E indicate the single phase extrema.
- Fig. 2. Activity (a_{PbO})-Composition (X_{PbO}) diagrams illustrating the two-step experiment to determine the width of any $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ single phase region.
- Fig. 3. TGA weight change crucible and sample.
- Fig. 4. Experimental arrangement.
- Fig. 5. Weight change vs. time at constant temperature (1100°C). These three experimental curves are placed together to show the determination of the single phase width (ΔW) and the reproducibility of the experiment.



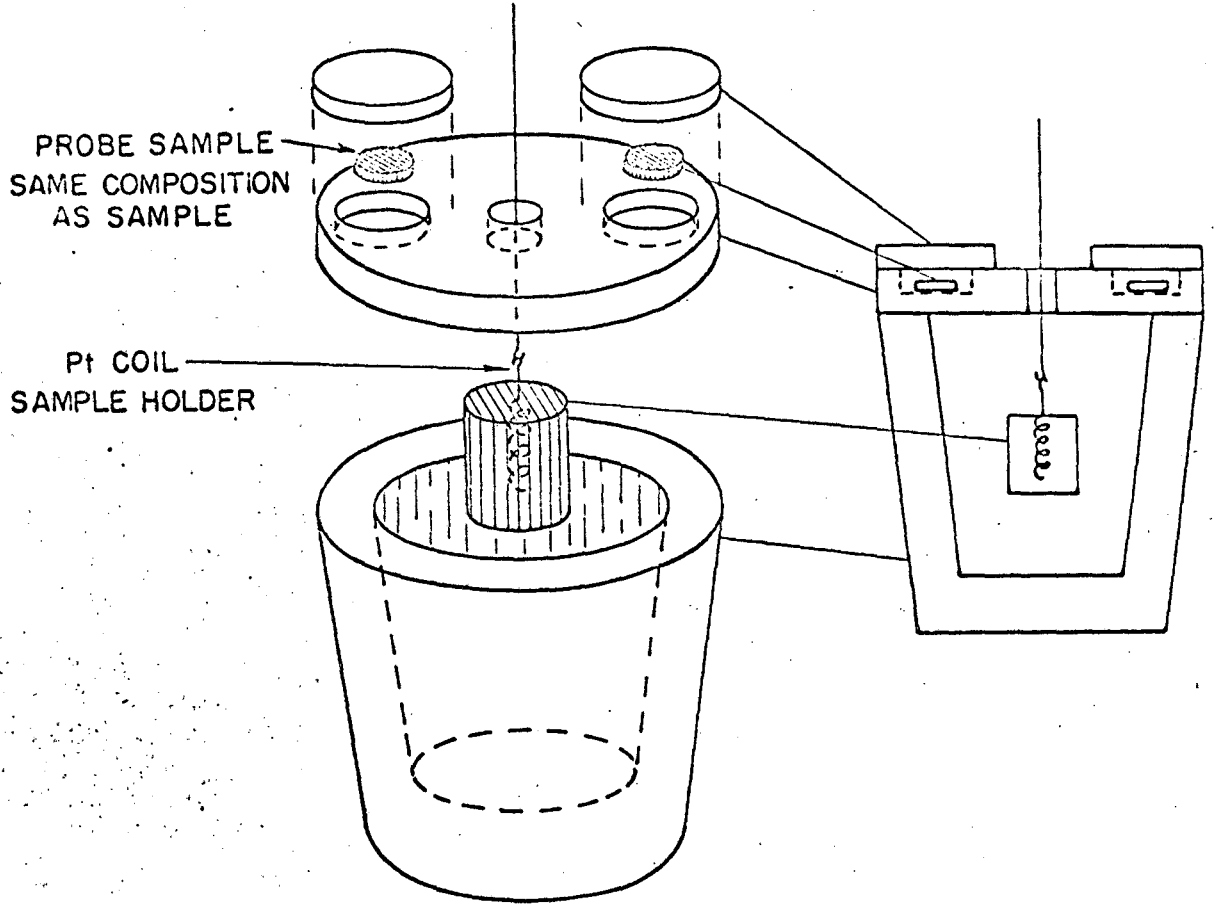
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Fig. 1



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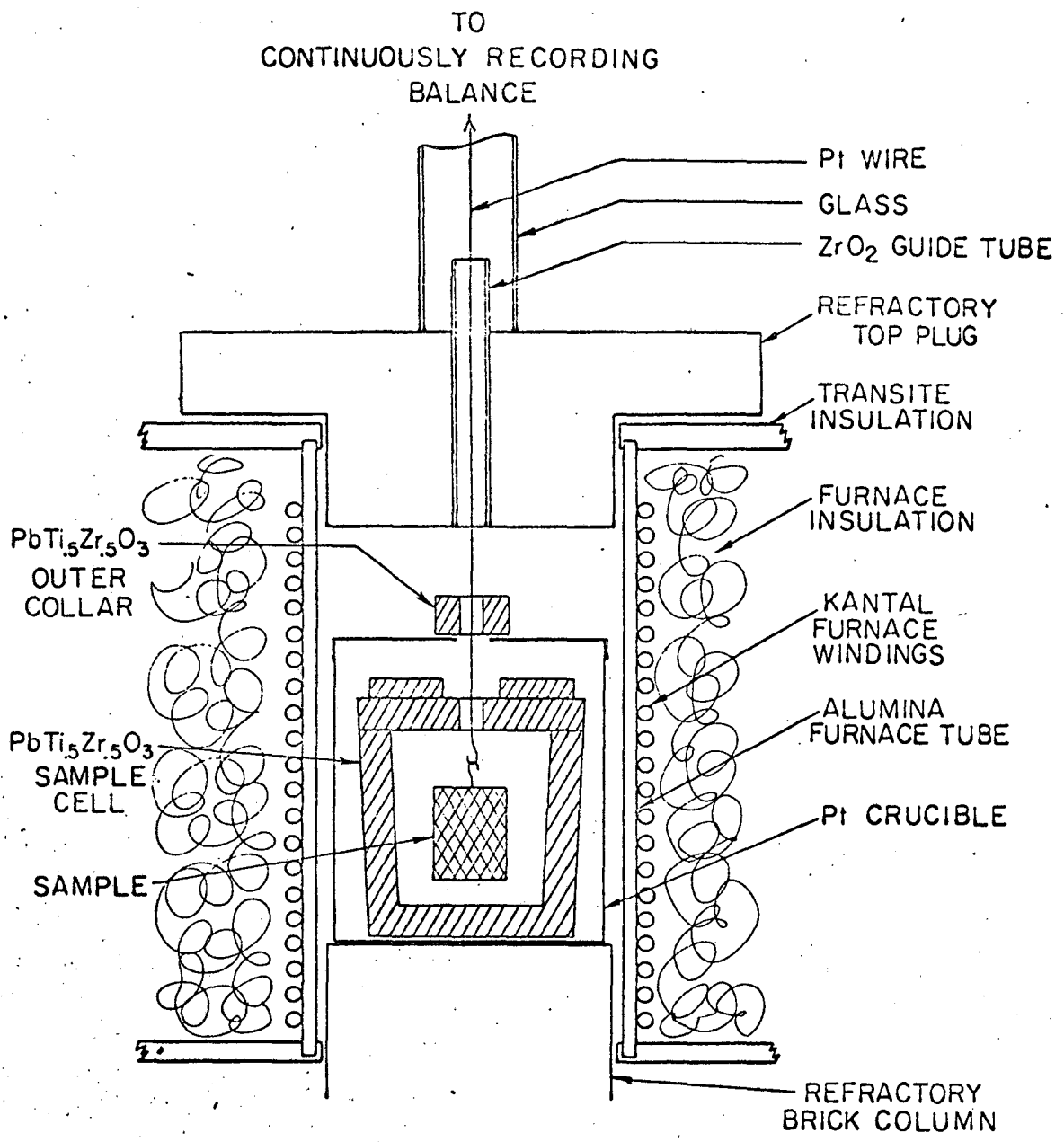
Fig. 2



TGA WEIGHT - CHANGE CELL

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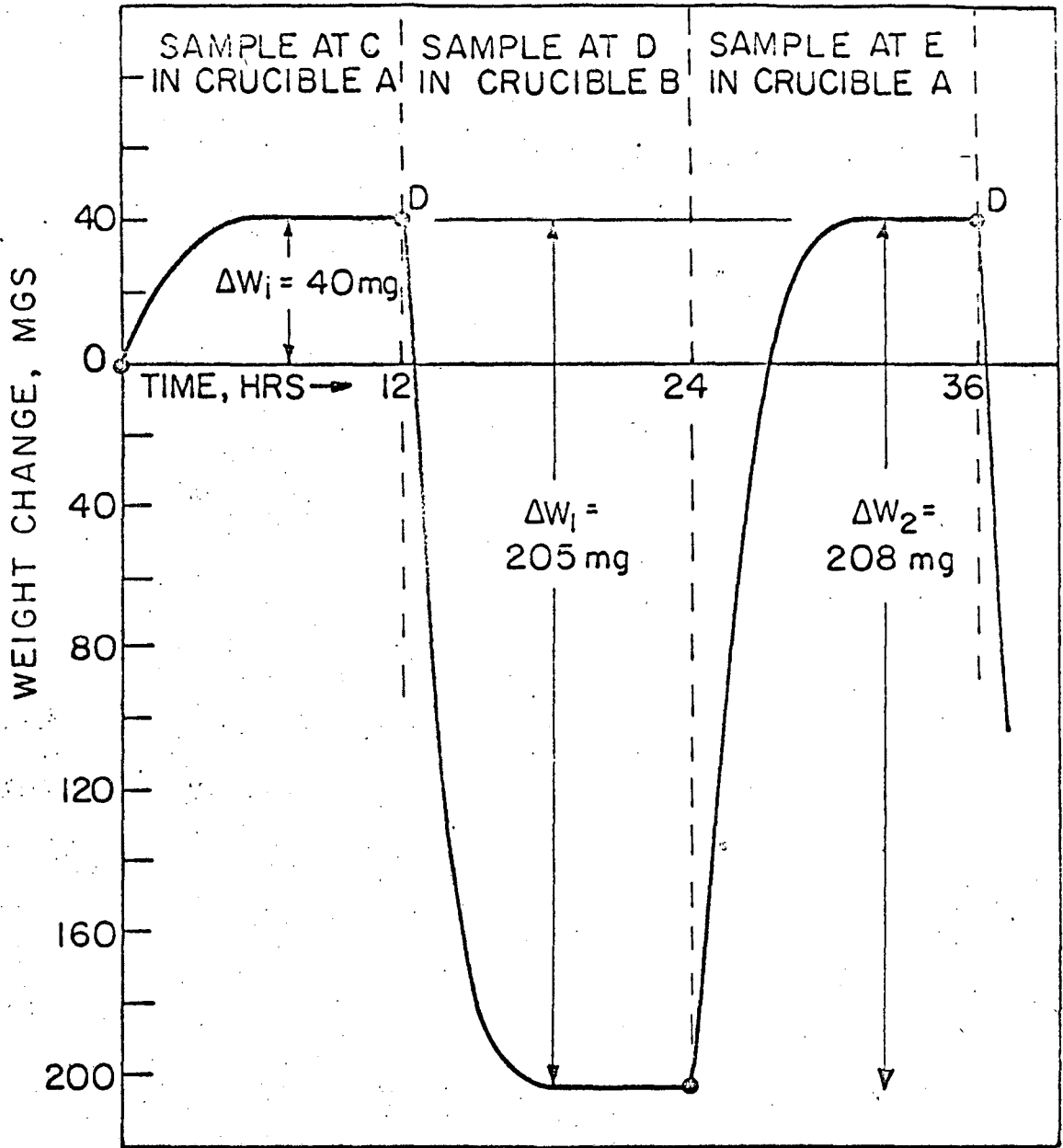
Fig. 3



EXPERIMENTAL ARRANGEMENT

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Fig. 4



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Fig. 5

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