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SOLUTION KINETICS OF La AND Sc IONS IN $PbTi_{.5}Zr_{.5}O_3$

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ABSTRACT

An investigation has been made of the extrinsic non-stoichiometry created in $PbTi_{.5}Zr_{.5}O_3$ at 1150°C by the solution of La^{3+}, Sc^{3+}, Nb^{5+}, and Bi^{3+}. Constant activity multi-phase (CAMP) PZT crucibles allowed a gravimetric study of the solution kinetics, as well as affording equilibrium atmosphere control and a simple processing technique.

Results indicate a lead vacancy defect structure is created by the substitution of 0.5, 1.0, and 2.0 mol% Bi^{3+}, Nb^{5+}, and La^{3+} in the PZT lattice, and an oxygen vacancy defect structure for 0.5, 1.0 and 2.0 mol% Sc^{3+}, obeying the rules of electroneutrality. The simple predictions of crystal chemistry were followed in all cases, with Bi^{3+} and La^{3+} substituting on the Pb^{2+} sublattice, Nb^{5+} and Sc^{3+} substituting on the $(Ti,Zr)^{4+}$ sublattice.

Multi-phase PZT crucibles or burial powders provided equilibrium PbO atmospheres which gave precise and reproducible results.

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I. Introduction

Small additions of oxides to lead zirconate-titanate have been reported to affect the electrical properties, sintering kinetics, and grain growth. Particularly, bismuth and niobium have been shown to act as sintering aids, and to improve the ferroelectric behavior. Lanthanum has markedly enhanced the sinterability of PZT ceramics. Haertling and Land,[1] incorporating lanthanum in the presence of a lead oxide liquid phase, have produced optically transparent material by hot pressing, while Snow[2] has achieved similar results by liquid phase sintering. Very interesting optical image storage devices have been produced from this material.[3-5] In addition, scandium can convert the ferroelectric characteristics of PZT to an anti-ferroelectric-like behavior.[6]

To generate commercially useful devices, reproducibility of results must be assured, which implies that the processing kinetics must be carefully controlled. It appears that to explain the reported results correctly, one must understand the kinetics of the incorporation of the Bi^{3+}, Nb^{5+}, La^{3+}, and Sc^{3+} ions into the perovskite lattice, their location in the lattice, and the defect structure that is generated.

Gravimetry has been employed to study the weight changes produced by the reactions of pure lead zirconate-titanate samples with its environment.[7] By maintaining proper atmosphere control, thermogravimetry may be used to study the continuous weight changes caused by the reaction between any oxide with lead zirconate-titanate. In this analysis, the number of titanium and/or zirconium ions distributed on the B-site of the perovskite lattice is constant due to the extremely low vapor pressure of these species. However, the lead ion concentration is free to adjust itself by means of equilibration with a surrounding lead oxide atmosphere. Hence, should a cation diffuse into the A-sublattice, some lead ions would be released, keeping the ratio of A-sites to B-sites at unity. If a cation diffused into the B-sublattice, the total number of B-sites would be increased, and additional lead ions would be obtained from the atmosphere, again holding the A/B site ratio at unity. This type of reaction weight-change analysis was first demonstrated by Weston et al.,[8] who determined the substitutional lattice site of Fe^{3+} in lead zirconate-titanate by weighing a sample containing iron oxide before and after a long high temperature firing.

This method has been further refined to reveal the valency of the substituted cation and the active charge compensation mechanism.[9] Also, thermogravimetry has the advantage of continuously recording both the weight-changes caused by the ionic substitution, including the development of any dominant, though transient, second phases, at the temperature of interest.

Thus, divalent ion substitutions on the A-sublattice and quatravalent ion substitutions on the B-sublattice of the perovskite require only equivalent amounts of PbO lost or gained from the original composition. However, trivalent ion substitutions on the A-sublattice and pentavalent substitutions on the B-sublattice require an additional mechanism to neutralize the charge imbalance created. This neutralization may be accomplished in several ways. Excess positive charge may be neutralized by:

(a) Creation of lead vacancies (reduction in the number of lead ions on lead sites);

(b) Reduction of Ti and/or Zr to trivalent species;

(c) Distribution of the substituting ions on both A and B lattice sites;

(d) Creation of B-site vacancies--theoretical number of B sites are increased with no change in the number of Ti and/or Zr ions.

The reduction of titania and/or zirconia may be dropped from further consideration as it has been shown that reduced lead titanate turns black and becomes a good semi-conductor; no color or conductivity change was observed in these experiments. If the ions to be investigated are selected such that their ionic radii closely match either the A or the B site radius, it should be unlikely that a distribution would result without grossly perturbing the perovskite crystal structure. Data of Shannon and Prewit[10] on ion in radii are presented in Table I.

Therefore, it is expected that either (a), the creation of lead vacancies, or (d), the creation of B-site vacancies, or some combination of these serve to neutralize the charge. These possibilities are analytically stated by Eqs. (1) and (2).

(1) The complete substitution of M^{3+} ions on the lead sublattice

$$\begin{tikzcd} & \text{(a)} \\ {[Pb(Ti,Zr)O_3 + xMO_{1.5}]} \arrow[ur] \arrow[dr] & \\ & \text{(b)} \end{tikzcd}$$

(a) $[(Pb_{1-1.5x}\Box_{.5x}M_x)(Ti,Zr)O_3] + 1.5x\ PbO_v$

lead vacancy charge compensation.

(b) $[(Pb_{1-.75x}M_x)(Ti,Zr\Box_{.25x})O_{3+.75x}] + .75x\ PbO_v$

(Ti,Zr) vacancy charge compensation.

(2) The complete substitution of M^{5+} ions on the (Ti,Zr) sublattice

$$Pb(Ti,Zr)O_3 + xMO_{2.5} + \begin{cases} (a) \\ (b) \end{cases}$$

(a) $+.5xPbO_v \rightarrow Pb_{1+.5x}\Box_{.5x}(Ti,Zr,M_x)O_{3+3x}$

lead vacancy charge compensation.

(b) $+1.25xPbO_v \rightarrow Pb_{1+1.25x}(Ti,Zr,M_x\Box_{.25x})O_{3+3.75x}$

(Ti,Zr) vacancy charge compensation.

Hence the final weight change observed will determine which model is more appropriate. The stoichiometric sample containing the trivalent substituent compatible with the lead sublattice will either show a weight loss corresponding to .75x moles of lead oxide or 1.5x moles of lead oxide. If a weight loss between these values is obtained, it is possible that both charge compensating mechanisms are operative. Similarly, samples containing the pentavalent B-site substituent should exhibit a weight gain of lead oxide of either .5x moles or 1.25x moles of lead oxide.

Another situation is created by the substitution of a trivalent ion on the (Ti,Zr) B-sublattice. In this case there is a deficiency of positive charge which must be neutralized. Neutralization may be accomplished by the removal of oxygen ions (i.e. the creation of oxygen vacancies), or by an increase in the lead ion concentration, reduction of lead vacancies. If an increase in lead ions is required to make up for the charge deficiency, a weight gain should be observed equal to 0.5 moles of PbO in addition to the x moles of PbO required by the direct substitution. When oxygen vacancies form, the sample weight gain of x moles PbO is the only change that will be detected. These changes are illustrated by Eqs. (3a) and (3b).

(3) The complete substitution of M^{3+} on the (Ti,Zr) sublattice

$$\mathrm{Pb(Ti,Zr)O_3} + x\mathrm{MO}_{1.5} \begin{cases} \longrightarrow (a) \\ \longrightarrow (b) \end{cases}$$

$$(a) + x\mathrm{PbO}_v \rightarrow \mathrm{Pb}_{1+x}(\mathrm{Ti,Zr,M}_x)\mathrm{O}_{3+3x-.5x}\emptyset_{.5x}$$

oxygen vacancy charge compensation.

$$\text{(b)} + \frac{3}{2}x\text{PbO}_v \quad \text{Pb}_{1+x+.5}\square_{I-.5x}(\text{Ti},\text{Zr},\text{M}_x)\text{O}_3$$

reduction of lead vacancies

I = the intrinsic vacancy concentration.

Gravimetric analysis in a controlled PbO atmosphere was made possible by the fabrication of constant activity multi-phase (CAMP) lead zirconate-titanate crucibles that establish an equilibrium lead oxide atmosphere and effectively isolate the sample being weighed. The crucible composition established the lead oxide activity and the sample's atmospheric environment. It is important that the weight changes measured are associated only with the reaction with the oxide addition. The intrinsic stoichiometry must not change during the experiment. This could be assured by fixing the stoichiometry of the lead zirconate-titanate sample prior to the addition of the dopant. This is illustrated in Fig. 1 for lead titanate, but the principle is applicable to any PZT composition.[7]

If a crucible was fabricated of a (PZT + Z + T) composition B, and a "stoichiometric" mixture of PbO, TiO_2 and ZrO_2 composition C, was placed in it, a high-temperature calcination would establish the equilibrium composition, E, for the powder. This is implied in Fig. 1(b) for $PbTiO_3$. If any further heat treatment of this powder is done within this same crucible, no PbO exchange would be expected for the powder with the atmosphere provided by the crucible.

Alternately, this experiment could be conducted with a crucible, or burial powder, which has the identical single-phase composition as the sample, composition C. However, as the crucible loses PbO and its composition changes, the weight change data would vary in an unpredictable manner.

II. Experimental

High purity PbO, TiO_2, and Hf-free ZrO_2 were homogeneously mixed in their stoichiometric proportions in the manner discussed in ref. 7. This powder was then divided into two portions: (a) to be fabricated into crucibles, and (b) to be fabricated into samples. The crucible fabrication and calcination techniques were identical to those discussed in ref. 7, and are summarized in Fig. 2. The sample powder was poured into the crucible, covered, enclosed within an outer platinum crucible, and calcined for 20 h at 850°C in air, followed by a 3 h soak at 1100°C, to achieve vapor phase equilibration with the atmosphere provided by the crucible. Then the sample powder of fixed stoichiometry was suitably modified with the oxide additions of interest. In this study, 0.5, 1.0, and 2.0 mol% quantities of $BiO_{1.5}$, $NbO_{2.5}$, $ScO_{1.5}$ and $LaO_{1.5}$ were chosen. In addition, samples containing excess PbO or $(Ti,ZrO)O_2$ were included.

It is critical that the samples contain as much open porosity as possible to assure rapid equilibration with the atmosphere. To achieve this result, approximately 7 wt% napthalene crystals were mixed into the sample. Pellets were cold-pressed in a 3/4" steel die. A 30 mil hole was drilled through each pellet to allow the suspension of the sample by a platinum wire. Alternatively, some samples were isostatically pressed about a platinum coil, as is shown in Fig. 3.

The pellets were then raised at 10°/min in air to 450°C, held there for 24 h, and furnace cooled to burn out all the napthalene.

The sample suspended from a gravimetric balance was then positioned within the same PZT crucible that was first used to calcine the powder, and heated to the desired temperature (1100°C).

The crucible cap was designed in such a way that cavities were available to enclose samples identical to the sample being weighed. Thus, at any time during the experimental run the furnace could be opened, and the extra sample removed for destructive analysis (X-ray diffraction, chemical analysis, microscopy, D.T.A. etc.) without interrupting the gravimetric experiment.

The experimental arrangement shown in Fig. 4 was identical to the one discussed for the measurement of the single-phase width (ref. 7).

III. Results and Discussion

(1) Bismuth and Niobium

The samples containing bismuth and niobium were selected as experimental controls. Crystal chemistry considerations present a strong case for assuming that trivalent bismuth will substitute for lead and pentavalent niobium will substitute for titanium/zirconium. Preliminary experiments[9] conducted using a burial powder of the same composition as the sample, confirm this hypothesis.

The present results are shown in Figs. 5(b) and 6(b) for 1.0 mol% additions of MO_x to samples of approximately the same weight. The equilibrium results clearly indicate total Bi^{3+} substitution for Pb^{2+} and Nb^{5+} substitution for $(Ti,Zr)^{4+}$ with both requiring lead vacancy charge compensation. However, in both cases, weight gains are observed which are significantly larger than reported in earlier experiments.[7]

This is particularly interesting for the case of Nb_2O_5 substitution. It is suggested that the refractory niobia particles (initially at $a_{PbO}=0$) reacts with the lead oxide obtained from the atmosphere (constant $a_{PbO}=0.280$), forming layers of complex lead niobates as equilibrium conditions are approached. No sample weight losses were observed until the sample had shown a 1.4 wt%* gain of PbO. At this point the Nb_2O_5-PbO composition is 83 mol% PbO, 17 mol% Nb_2O_5 which creates about 1.5 vol% second phase. From the PbO-Nb_2O_5 phase diagram[11] it may be seen that this composition at 1100°C a liquid phase may have formed.

Mechanistically, liquid formation is possible since the amount of Nb^{5+} ions that diffuses into the PZT lattice is at least partially controlled by the area of solid-liquid contact. Initially, the homogeneously dispersed refractory particulates have a very small contact area with the PZT particles. As these particulates gain PbO from the atmosphere, they increase in volume, but still exist primarily as solid particles. The surface contact area is still insufficient to observe signs of diffusion. When the liquid phase forms, it spreads out, covering large areas of PZT surface, and Nb^{5+} diffusion is enhanced. As Nb^{5+} leaves the liquid, its lead oxide activity is momentarily greater than that of the atmosphere. Hence, additional PbO leaves the liquid, and the partially open system. It should be re-emphasized that because the PZT sample powder particles are in equilibrium with the atmosphere as a result of the pretreatment described, no non-stoichiometry weight changes are expected. Therefore,

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* $\text{wt\%} = \dfrac{\text{PbO gain (grams)}}{\text{sample wt. (grams)}}$

only the niobia contributes to the observed weight changes.

A similar situation is observed in the bismuth modified system, except that the liquid phase forms from the outset (Bi_2O_3 melts at 825°C).[11] However, as the PbO dissolves, increasing the lead oxide activity of the liquid, the liquid volume increases while liquid viscosity may be decreasing. When about .615 vol% or .735 wt% liquid is attained, Bi^{3+} diffusion becomes apparent.

(2) Lanthanum and Scandium

This work was primarily undertaken to investigate the kinetics of solution of the lanthanum and scandium oxides. The reaction weight-change data is presented in Fig. 7(b) and Fig. 8(b) for data representative of 1.0 mol% $LaO_{1.5}$ and 1.0 mol% $ScO_{1.5}$ respectively.

For the lanthanum substitution, no initial weight gains are observed. However, the rate of equilibration is seen to be quite dependent upon the incorporation of a maximum amount of napthalene to control porosity. Figure 7(b) demonstrates this effect, where (b-dotted) describes the data of a sample which was sintered simultaneously without napthalene, and (b-solid) describes the data of an identical sample containing approximately 7 wt% napthalene. In addition, it was observed that the smaller the sample in volume, the more rapid the equilibration.

It is possible that the $PbO-La_2O_3$ liquid phase that forms (see the phase diagram[11]) is not as viscous as either the pure Bi_2O_3 liquid or its dilute solution with PbO. Hence, the lanthana liquid may be able initially to cover a much larger surface area, such that the diffusion of the La^{3+} ions into PZT can proceed at a greater rate. In addition, it is possible that the lead oxide activity in the $(La_2O_3+PbO)_{liq.}$

could be high enough so that it is initially nearly in equilibrium with the atmosphere. In either event, the diffusion of La^{3+} proceeds gradually until an equilibrium is reached corresponding to a total La^{3+} substitution for Pb^{2+} via a total lead vacancy charge compensation mechanism such as was detailed by Eq. (1a), for all doping levels studied.

As a result of study by a different technique, it has recently been reported[12,13] that for low doping levels, lanthanum ions substitute on the lead sublattice of lead titanate, and that charge compensation is accomplished by A-site vacancies. In addition, it was determined that for the higher doping levels[12] (greater than 5 mol%), while La^{3+} substitutes for Pb^{2+}, charge compensation is best explained by a distribution of A-site and B-site vacancies. The same workers have recently extended this analysis to $PbTi_{.5}Zr_{.5}O_3$ for the high doping levels.[14]

Finally, experiments were conducted to characterize the addition of Sc_2O_3. From crystal chemistry considerations it is deduced that scandium illustrates a trivalent substitution on the $(Ti,Zr)^{4+}$ sublattice, but that the substitution occurs with either decreased lead vacancy or increased oxygen vacancy charge compensation, as described in Eq. (3a). The data obtained supports this conclusion and indicate clearly that oxygen vacancies (3(a)) are formed to neutralize the charge. This is illustrated in Fig. 8.

In this case the initial weight gain is believed to occur in the manner described for niobia.

(3) Lead Oxide and $(Ti,Zr)O_2$

As an additional control, samples containing known excesses of either PbO or $(Ti,Zr)O_2$ were equilibrated with the atmosphere crucible at 1100°C.

The results were as expected: a sample containing excess lead oxide did not show any weight change when equilibrated in a crucible composition of PZT + PbO. A sample containing excess titania + zirconia also remained the same weight when equilibrated with a crucible composition of PZT + Z + T. However, when the excess quantities were below 1.0 mol% and were added to PZT powder slightly off stoichiometry and the crucibles were fabricated of a composition identical to the PZT sample powder, the samples lost the excess PbO or gained an amount of PbO to the excess $(Ti,Zr)O_2$.

(4) The Atmosphere

The method of equilibrium atmosphere control used in these studies is far more accurate and reproducible than the "disk" technique used by Weston et al.[8] after the earlier work of Jaffe et al.[15] Weston's samples were sintered in the presence of lead zirconate disks. It has been shown[16] that stoichiometric lead zirconate (PZ) maintains the highest lead oxide vapor pressure in the PZT system. Thus, a positive pressure is established between the surrounding atmosphere, determined by pure PZ, and the PZT sample, which results in misleading weight gains.

If large quantities of lead zirconate are provided, it is clear that there is no $PbTi_xZr_{1-x}O_3$ sample that can equilibrate with the atmosphere, unless a liquid is formed. This conclusion can be deduced from the isothermal (1100°C) ternary phase diagram,[17,18] drawn to include the experimentally determined lines of constant activity (see Fig. 9). A $PbTi_{0.5}Zr_{0.5}O_3$ sample, for instance, is constrained to alter its overall composition only along the lines of constant Zr/Ti=1 composition. Therefore, the sample will not achieve an activity balance with the atmosphere until the lead rich liquid phase is formed. While the kinetics of the system may not allow this result in practice, sizable weight gains are possible.

Additionally, it was established[16] that lead zirconate has a very wide range of non-stoichiometry with large variation in lead oxide activity (0.5 to 0.07). As the composition of a lead zirconate disk is altered by the evaporation of PbO from the system, the lead oxide activity of the atmosphere falls, creating additional weight changes that are not related to the ionic substitution mechanisms.

The actual magnitude of both of these unwanted weight changes is a function of time at temperature, the PbO loss character of the particular system, and the amount of lead zirconate used.

In the earlier studies of bismuth and niobium ionic substitutions in PZT,[9] the basic technique of Dungan et al.[19] incorporating a burial powder of the same composition as the sample was used. This technique was modified, however, by replacing the burial powder with a solid PZT crucible, either single-phase or multi-phase. There are several distinct advantages to this approach. First, experiments involving gravimetry may be performed. Second, PZT may be preprocessed as a powder in its own container, to firmly establish its exact stoichiometry and its homogeneity. In addition, the crucibles may be fabricated of most desired compositions facilitating experimentation, even when the crucible contains a reasonable amount of liquid phase. In a burial powder, the liquid phase encourages sintering, making for difficult sample removal.

While reasonable data was obtained using single-phase PZT crucibles, even this approach is subject to small inconsistencies which result from the changes in the composition of the crucible. However, it was found that smaller errors are observed with the crucible technique than with the burial powder, when precautions were taken to maximize the reproducibility. Specifically, the sample powder and crucible powder must come from the same batch, and the sample must be placed within the companion crucible during a common calcination. In addition, the atmosphere crucible may be used for only the single experiment.

While the results obtained employing either crucible technique were within sufficient range of the predictions of the proposed models, the deviation from theory were greater with use of single-phase crucibles than with the use of the low constant activity multi-phase (CAMP) crucibles. The incremental weight losses observed were in the direction expected to result from a decrease in lead oxide activity of the "stoichiometric" crucible, as a result of the evaporation of PbO. This loss is unrelated to the ionic substitution mechanisms. The differences are illustrated in Figs. 5, 6, 7, 8, where the (a) curves describe results obtained in the "stoichiometric" crucibles and the (b) curves correspond to results obtained in low CAMP crucibles.

IV. Conclusions

The nature of the extrinsic non-stoichiometry created in lead zirconate-titanate by the solution of La^{3+}, Sc^{3+}, Nb^{5+}, and Bi^{3+} ions has been characterized. The production of constant activity multi-phase (CAMP) PZT crucibles allowed a gravimetric study of the solution kinetics, as well as affording equilibrium atmosphere control and a simple processing technique.

Results indicated a lead vacancy defect structure created by the substitution of Bi^{3+}, Nb^{5+}, and La^{3+} in the PZT lattice, and an oxygen vacancy defect structure for Sc^{3+}, obeying the rules of electroneutrality. The simple predictions of crystal chemistry were followed with Bi^{3+} and La^{3+} substituting on the Pb^{2+}-sublattice, Nb^{5+} and Sc^{3+} substituting on the $(TiZr)^{4+}$-sublattice.

Multi-phase PZT crucibles or burial powders provided equilibrium PbO atmospheres that allowed for the most error-free and reproducible results.

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Table I. Ionic Radii[10]

Perovskite $A^{2+}B^{4+}O_3^{2-}$

Ion	C.N.	Effective Radius (Å)	Probable PZT Lattice Site
Pb^{2+}	12	1.49	A
Ti^{4+}	6	0.605	B
Zr^{4+}	6	0.72	B
Bi^{3+}	8*	1.11	A
Bi^{5+}	6	0.74	B
Nb^{3+}	6	0.70	B
Nb^{5+}	6	0.64	B
La^{3+}	12	1.32	A
Sc^{3+}	6	0.73	B

*Highest C.N. tabulated.

Table II. Possible Ionic Substitution Reactions

[PZT+.5y (metal oxide)] sample

Ion	Weight Change	Mechanisms
M^{2+}	$\ominus$ y PbO (loss)	A-site substitution
M^{3+}	$\ominus$ 1.5y PbO (loss)	A-site substitution lead vacancy charge comp.
M^{3+}	$\ominus$ y PbO (loss) ($\ominus$ .75y PbO vacancies)	A-site substitution B^{4+} reduction or B^{4+} vacancies
M^{3+}	$\oplus$ y PbO (gain)	B-site substitution oxygen vacancy charge comp.
M^{4+}	$\oplus$ y PbO (gain)	B-site substitution
M^{5+}	$\oplus$ .5y PbO (gain)	B-site substitution lead vacancy charge comp.
M^{5+}	$\oplus$ y PbO (gain) ($\oplus$ 1.25y PbO vacancies)	B-site substitution B^{4+} reduction or B-vacancies
M^{5+}	$\ominus$ 1.25y PbO (loss)	A-site substitution lead vacancy charge comp.

FIGURE CAPTIONS

Fig. 1. (a) $PbO-TiO_2$ phase diagram assuming a lead titanate region of non-stoichiometry.

(b) Activity of PbO vs mole fraction PbO at constant temperature (1100°C) for the lead titanate binary.

Points A and B designate the constant PbO atmospheres provided by the CAMP crucibles of these compositions; point C locates the composition and activity of the nearly stoichiometric single-phase compound, whereas D and E indicate the single-phase boundaries.

Fig. 2. Processing flow diagram for the study of the ionic substitutions in lead zirconate-titanate by gravimetry and vapor phase equilibration.

Fig. 3. Weight-change (CAMP) crucible for thermogravimetry.

Fig. 4. The experimental arrangement for the vapor phase equilibration experiments.

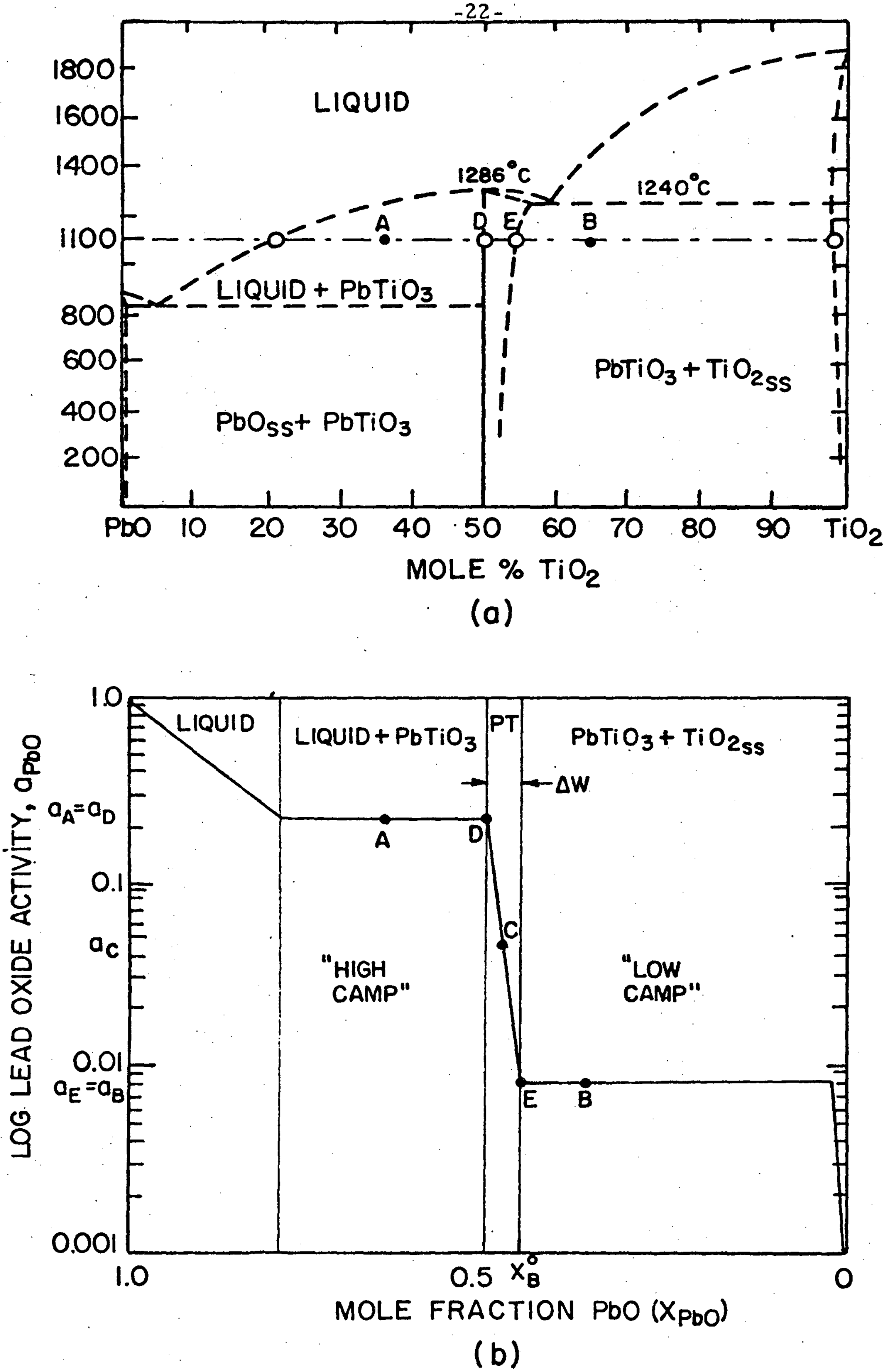
Fig. 5. Continuous weight change vs time at 1150°C of a $PbTi_{.5}Zr_{.5}O_3$ sample containing 1 mol% bismuth oxide ($BiO_{1.5}$): (a) lead oxide atmosphere provided by a stoichiometric $PbTi_{.5}Zr_{.5}O_3$ crucible, (b) lead oxide atmosphere provided by a low-CAMP crucible.

Fig. 6. Continuous weight change vs time at 1150°C of a $PbTi_{.5}Zr_{.5}O_3$ sample containing 1 mol% niobium oxide ($NbO_{2.5}$): (a) lead oxide atmosphere provided by a stoichiometric $PbTi_{.5}Zr_{.5}O_3$ crucible, (b) lead oxide atmosphere provided by a low-CAMP crucible.

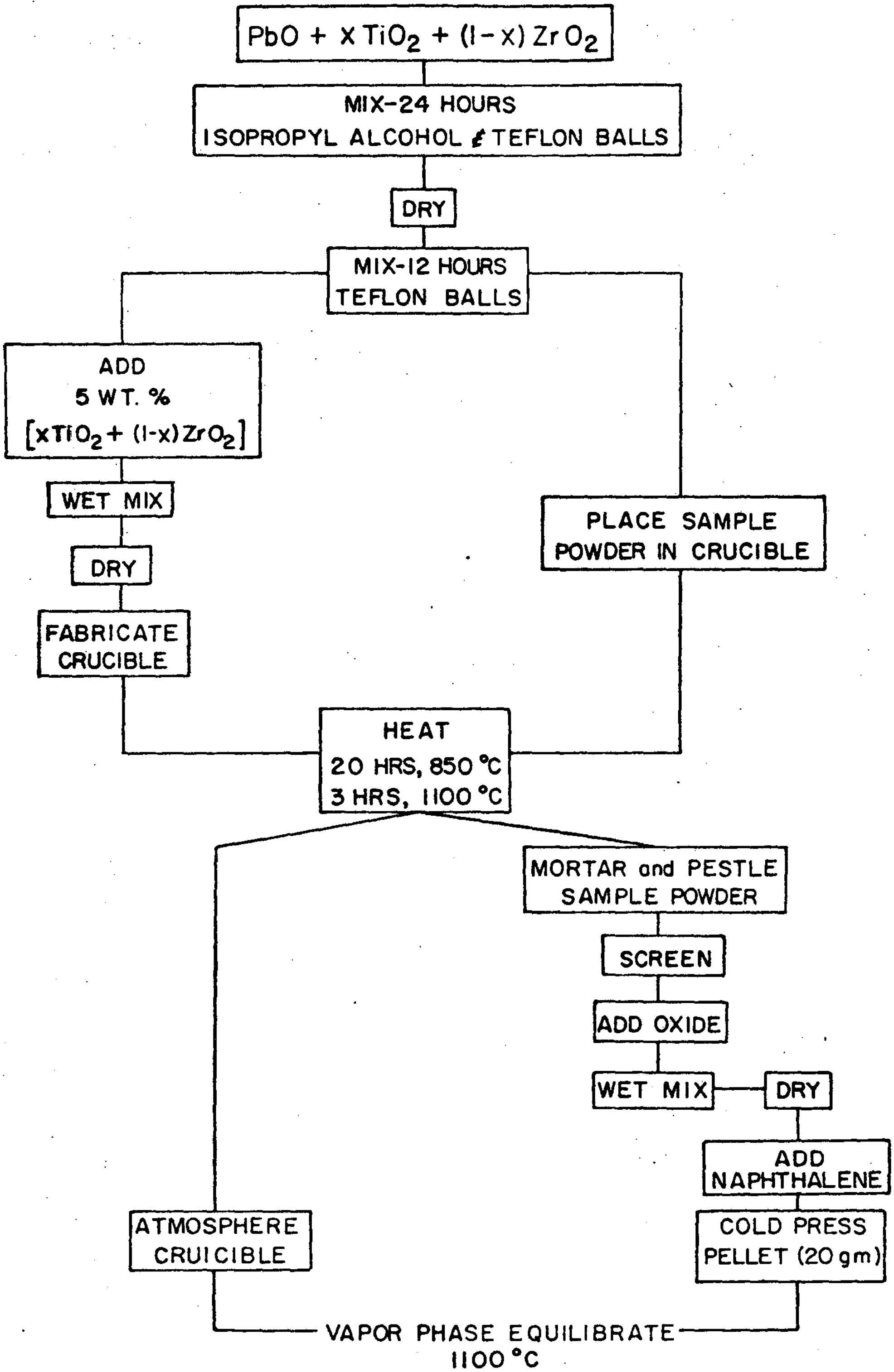
Fig. 7. Continuous weight-change vs time (hours) at 1150°C of a pre-treated $PbTi_{.5}Zr_{.5}O_3$ sample containing 1 mol% lanthanum oxide ($aO_{1.5}$): (a) lead oxide atmosphere provided by a stoichiometric $PbTi_{.5}Zr_{.5}O_3$ crucible, (b) lead oxide atmosphere provided by a low CAMP crucible (b-dotted) sample contained no naphthalene and shows the result of sintering at 1150°C.

Fig. 8. Continuous weight-change vs time (hours) at 1150°C of a pre-treated $PbTi_{.5}Zr_{.5}O_3$ sample containing 1 mol% scandium oxide ($ScO_{1.5}$): (a) lead oxide atmosphere provided by a stoichiometric $PbTi_{.5}Zr_{.5}O_3$ crucible, (b) lead oxide atmosphere provided by a low CAMP crucible.

Fig. 9. The $PbO-TiO_2-ZrO_2$ isothermal (1100°C) ternary phase diagram sketched to include the experimentally determined lead oxide isoactivity lines. The arrows indicate the compositional changes occurring in a $PbTi_{.5}Zr_{.5}O_3$ sample equilibrating with any $PbTi_xZr_{1-x}O_3$ + PbO mixture with x less than 0.5, or with pure lead oxide. The sample must transform totally to a liquid phase to achieve an activity balance with the atmosphere.

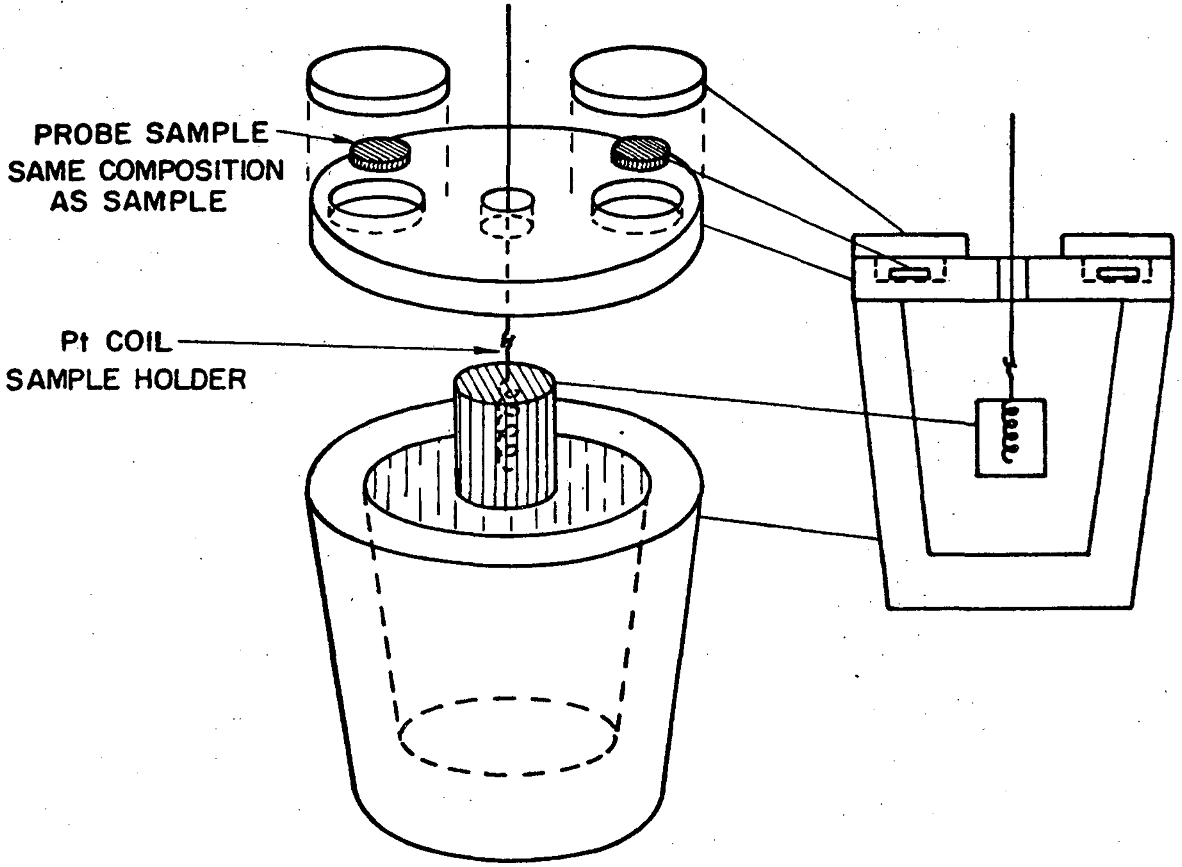

LIQUID
1286°C
1240°C
A
D
E
B
LIQUID + PbTiO₃
PbTiO₃ + TiO₂ss
PbOss + PbTiO₃
1800
1600
1400
1100
800
600
400
200
PbO
10
20
30
40
50
60
70
80
90
TiO₂
MOLE % TiO₂
(a)
1.0
LIQUID
LIQUID + PbTiO₃
PT
PbTiO₃ + TiO₂ss
ΔW
a_A=a_D
A
D
0.1
C
a_C
"HIGH CAMP"
"LOW CAMP"
0.01
a_E=a_B
E
B
0.001
LOG LEAD OXIDE ACTIVITY, a_PbO
1.0
0.5
X°_B
0
MOLE FRACTION PbO (X_PbO)
(b)

XBL 726-6447



XBL726-6459A

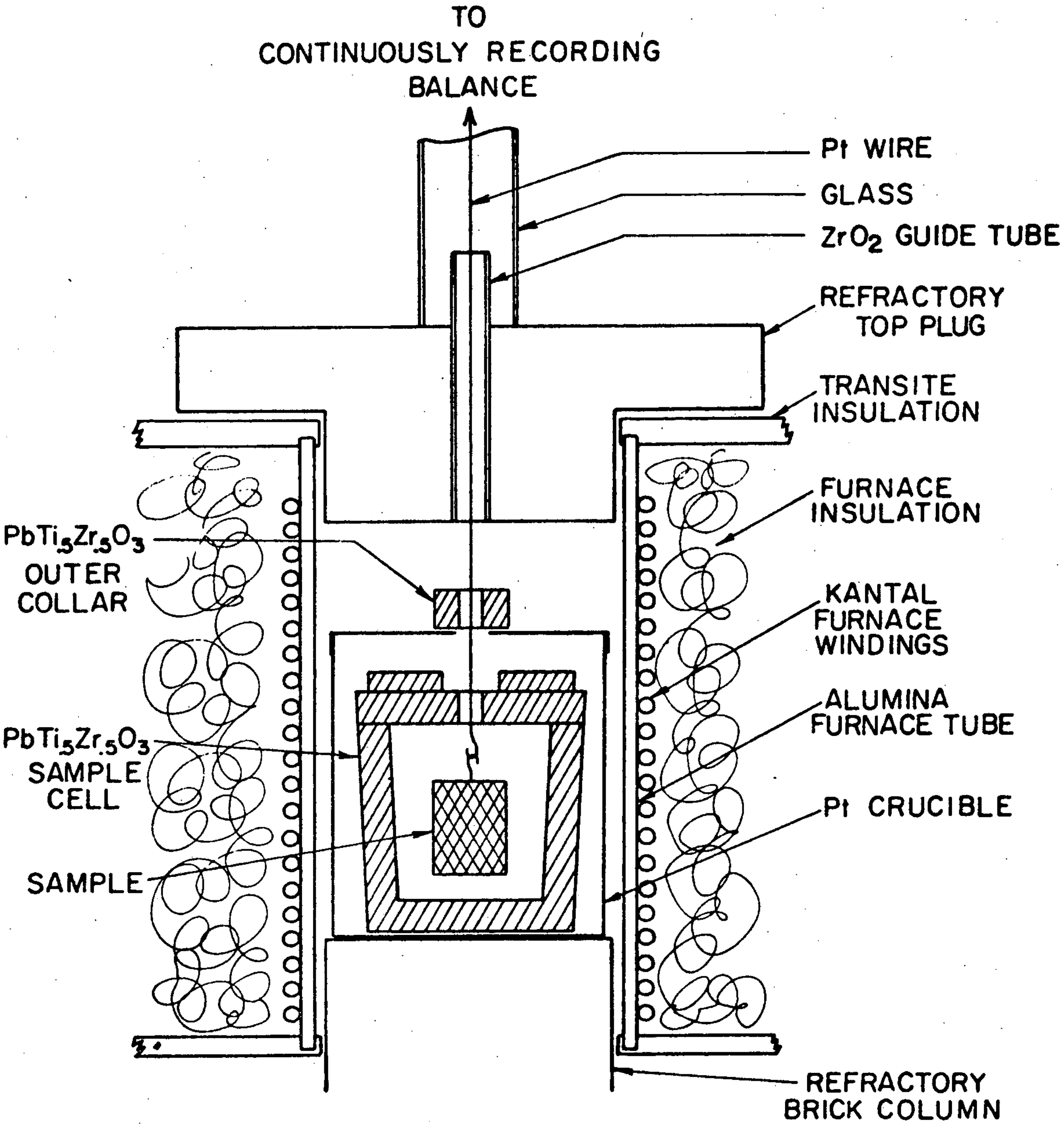
Fig. 2



TGA WEIGHT - CHANGE CELL

XBL 7010-6822

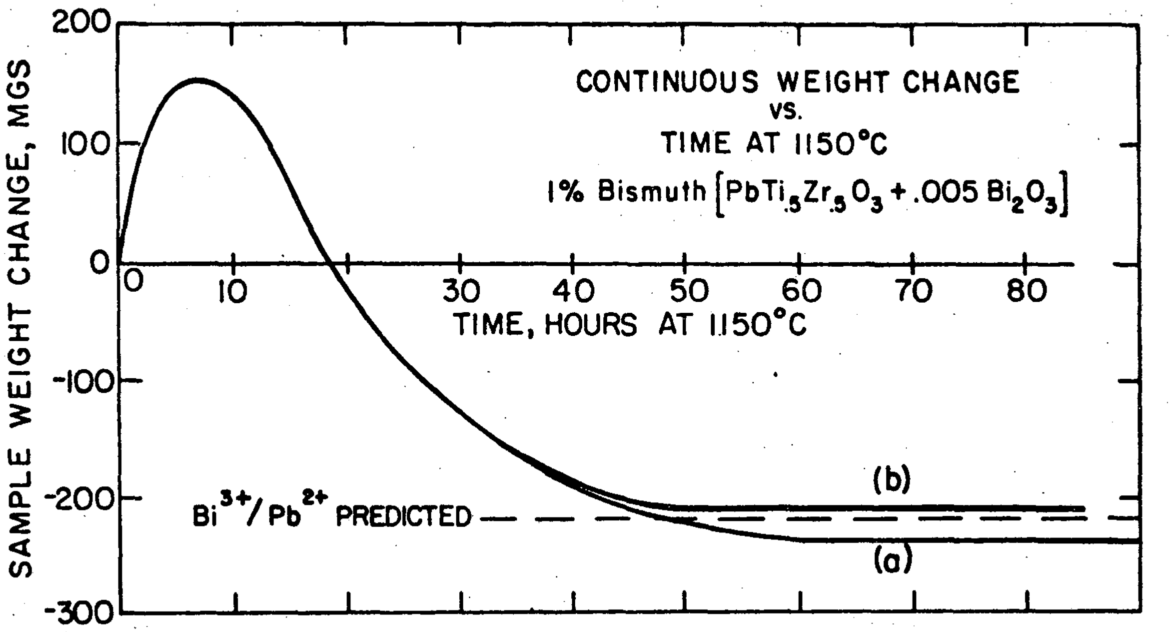
Fig. 3



EXPERIMENTAL ARRANGEMENT

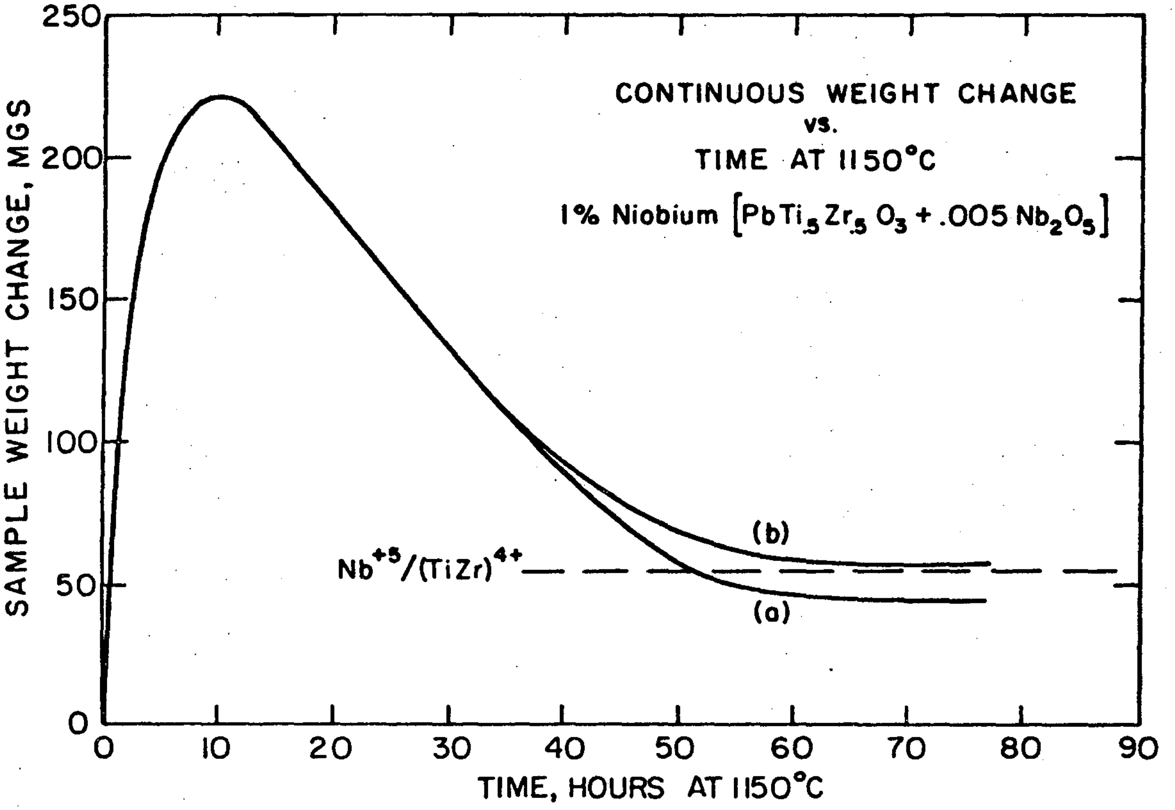
XBL 7010-6819

Fig. 4



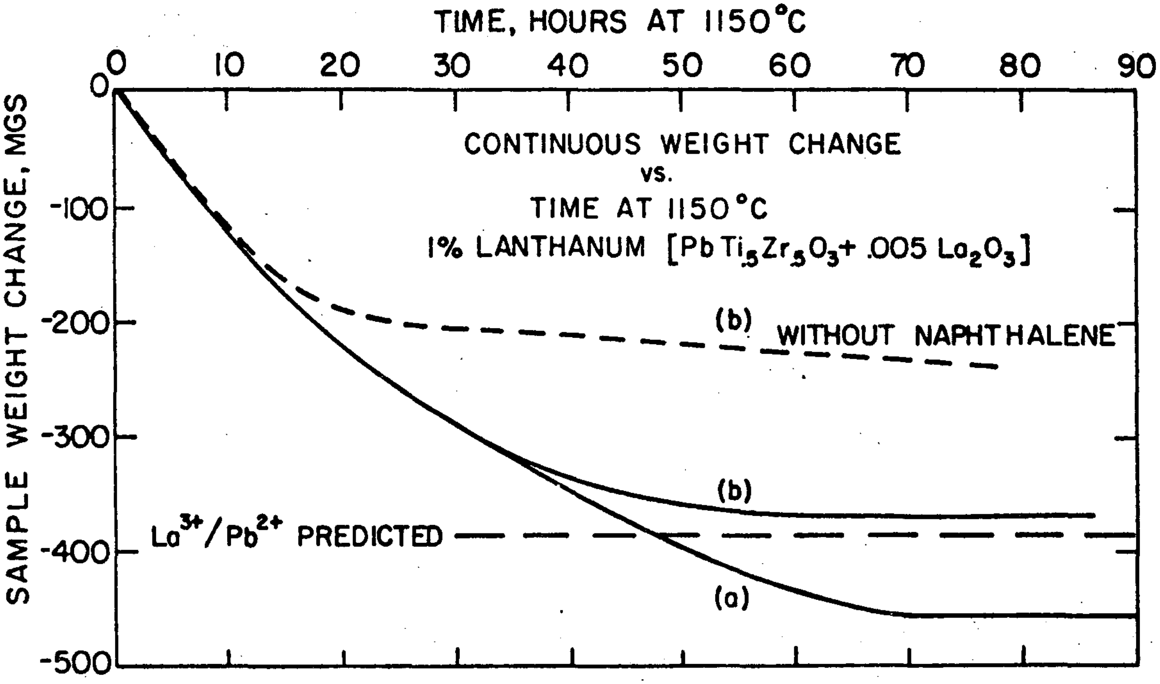
XBL 7010-6821 A

Fig. 5



XBL 7010-6825 A

Fig. 6



XBL 7010-6820B

Fig. 7

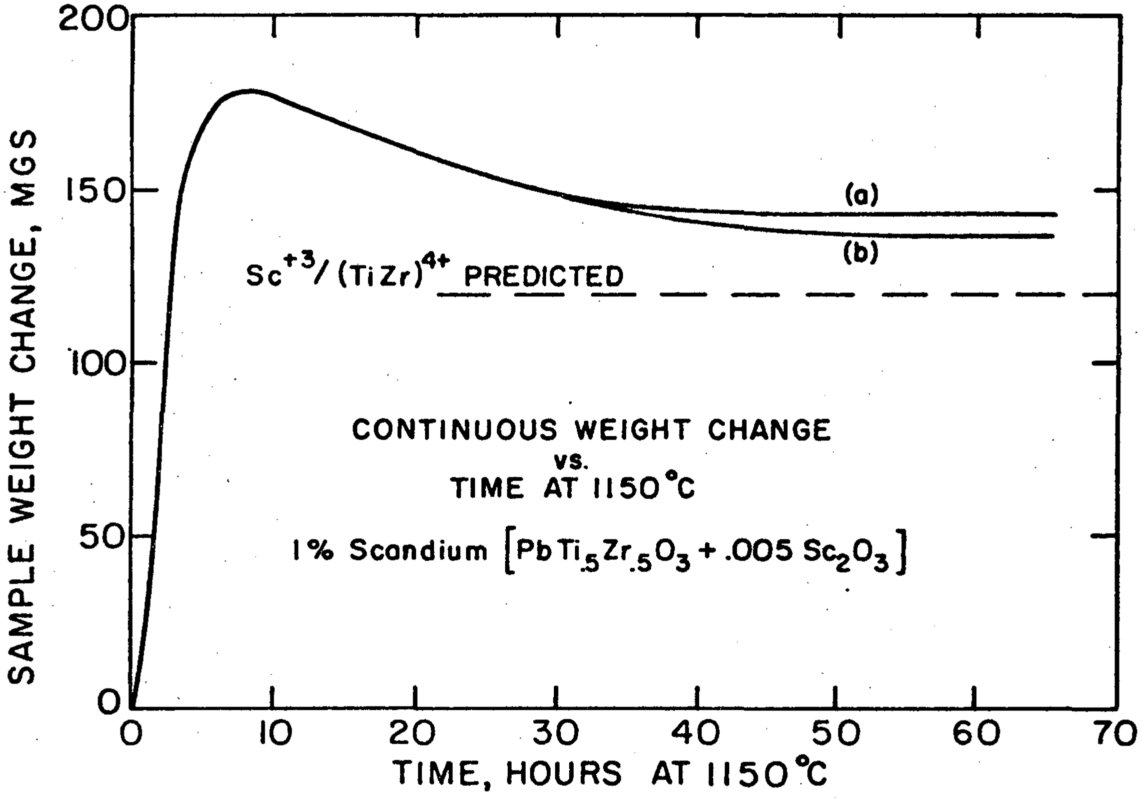


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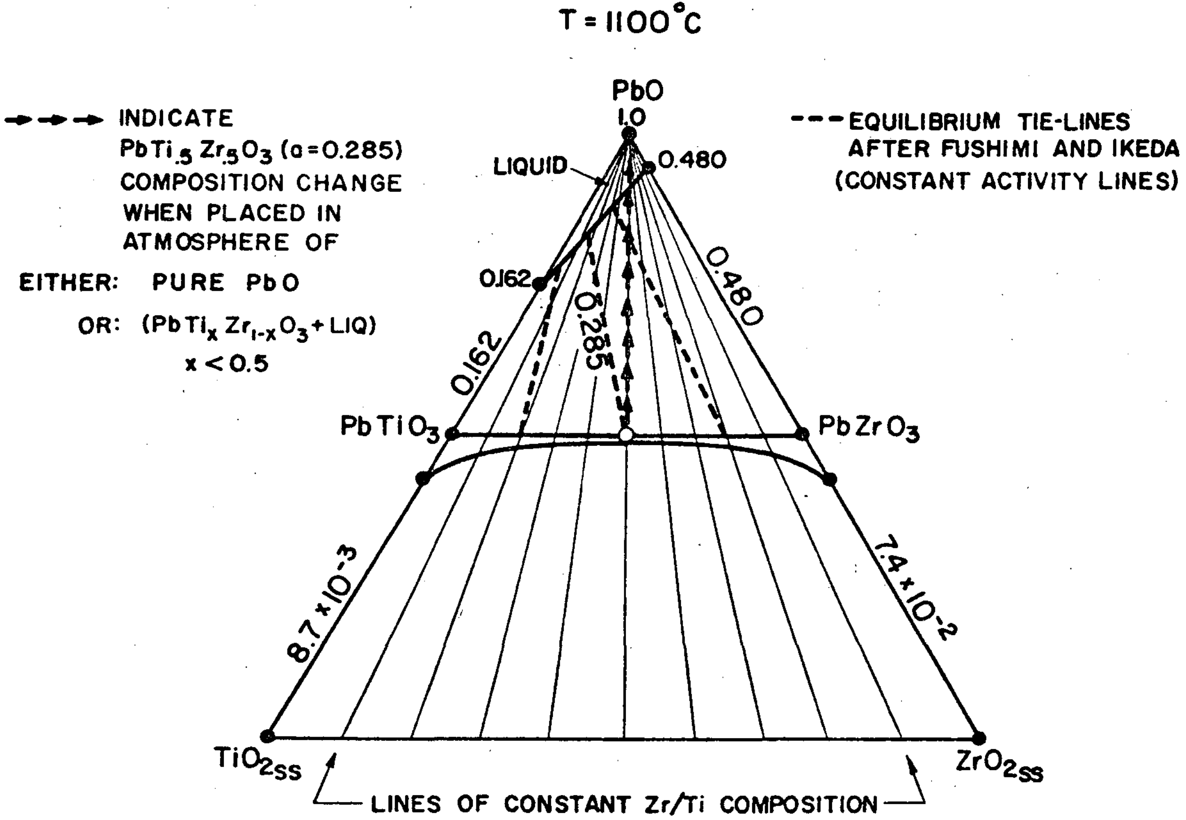
Fig. 8



XBL 726-6440

Fig. 9

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