Submitted to Journal of American
Ceramic Society

UCRL-19632
Preprint

c.2

RECEIVED
LAWRENCE
RADIATION LABORATORY
JUN 23 1970
LIBRARY AND
DOCUMENTS SECTION

IONIC SUBSTITUTIONS IN LEAD ZIRCONATE-TITANATE

R. B. Atkin, R. L. Holman, and R. M. Fulrath

May 1970

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

UCRL-19632 c.2

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

25

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

IONIC SUBSTITUTIONS IN LEAD ZIRCONATE-TITANATE

R. B. Atkin, R. L. Holman, and R. M. Fulrath

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
and Department of Materials Science and Engineering,
College of Engineering, University of California,
Berkeley, California

May 1970

ABSTRACT

The solid state substitutions of bismuth and niobium ions in the perovskite crystal structure of $Pb(Ti_{.47}Zr_{.53})O_3$, has been investigated by sample weight-changes that occur at temperature in an "equilibrium" lead oxide atmosphere. A model is proposed that includes the effect of charge neutralization, requiring weight losses for "A"- and weight gains for "B"-site substitutions. Experiments support the substitution of bismuth as Bi^{3+} on the Pb^{2+} "A" site and niobium as Nb^{5+} on the $(Ti,Zr)^{4+}$ "B" site of PZT. 1.5 moles of PbO are lost by specimens for each mole of $BiO_{1.5}$ added. For each mole of $NbO_{2.5}$ added, 0.5 moles of PbO are gained. These results are in agreement with both the proposed model and ionic size arguments. The weight changes were observed to be time dependent during the first 30-40 hours at temperatures (1150°C). This is accounted for by the formation of transient second phases.

This paper was presented in part at the 22nd Pacific Coast Regional Meeting, Seattle, Washington, October 15, 1969.

At the time this work was done the writers were, respectively, graduate research assistants (Atkin and Holman), and professor of ceramic engineering.

I. INTRODUCTION

The ferroelectric properties of lead zirconate-titanate (PZT) ceramics are quite sensitive to additions of trivalent and pentavalent oxides.[1,2] To understand this phenomena it must be known whether the dopant cations enter the "A" or "B" sublattices of the ABO_3 (PZT) perovskite crystal and their actual valence. If there is a valence discrepancy the charge balancing point defects should be identified.

Weston et al.[3] introduced a technique to establish that trivalent iron enters the "B" lattice sites in PZT, substituting for titanium or zirconium. They sintered PZT samples in a lead oxide atmosphere and observed weight gains corresponding to approximately two moles of PbO for each mole of Fe_2O_3 added. As iron entered the "B" lattice positions an equal number of lead atoms were obtained from the atmosphere filling the newly created "A" lattice sites. However, if the substitutional ion had entered the "A" sublattice it would displace lead causing the specimen to lose weight.

In addition, this technique may be adapted to reveal the valence of the substituted cation. When there is a valence discrepancy, anion or cation* vacancies will form to maintain electro-neutrality. The creation of these vacancies can be detected since the atoms initially occupying them must leave the sample, thereby decreasing its weight. For example,

---

* Only "A" site cation vacancies are expected as lead is less strongly bonded than either titanium or zirconium. The creation of electronic defects are rejected on the grounds that PZT is not semiconducting. However, charge compensation by either the formation of hydroxyl (OH^-) ions or reduced titanium ions, Ti^{3+}, is not considered because no weight change would be detected.

one oxygen vacancy will be formed for every two trivalent iron atoms that enter tetravalent lattice sites. The weight change due to the loss of oxygen is small but measurable, provided that the equilibration atmosphere has controlled the partial pressures of lead oxide and oxygen.

Accurate specimen weighing is required. The weight change resulting from the oxygen vacancies introduced by doping a 20 gram PZT specimen with 1 mole % iron is only 4.88 mg. However, this technique is far more sensitive for measuring lead vacancies because of the high atomic weight of lead: the weight change expected by a 20 gm PZT specimen with 1 mole % Nb_2O_5 is 69.5 mg.

The approximate chemical reactions for the ionic substitutions of trivalent ions on the "A" site and pentavalent ions on the "B" site in PZT are given by equations (1) and (2).

M^{3+} on the Pb^{2+} "A" site:

$$\left[ABO_3 + \frac{y}{2}M_2O_3\right] \rightarrow \left[\left(A_{1-y-\frac{y}{2}} \square_{\frac{y}{2}} M_y\right)(B)O_3\right] + \frac{3y}{2}\,PbO\ (\text{loss}) \qquad (1)$$

M^{5+} on the $(Ti,Zr)^{4+}$ "B" site:

$$\left[ABO_3 + \frac{y}{2}M_2O_5\right] + \frac{y}{2}\,PbO\ (\text{gain}) \rightarrow \left[\left(A_{1+y-\frac{y}{2}} \square_{\frac{y}{2}}\right)\left(BM_y\right)O_{3+3y}\right] \qquad (2)$$

The weight-change contribution of charge neutralization, for valence discrepancies of ±1, is always less than the substitution effect. Thus,

weight loss will be expected for "A" substitutions, and weight gains for "B" substitutions. The possible modification of the activity of lead by the presence of the dopant is assumed to have only a second order effect on the lead vacancy concentration and is not considered here.

In general, the experiment should be applicable to any A-B-O compound, provided that four requirements are satisfied at normal reaction temperatures:

1. The oxide vapor pressure of one cation must be high enough to permit transport.

2. The oxide vapor pressure of the other cation must be low enough to prevent vaporization loss.

3. An "equilibrium" atmosphere of the high vapor pressure oxide must be provided.

4. The high vapor pressure oxide must have a sufficient molecular weight to produce measurable weight changes.

The present work was undertaken primarily to determine the valence of bismuth in PZT. This has been a controversial subject. Haertling has suggested[2] on the basis of electrical resistivity measurement, that although added to PZT as Bi^{3+}, bismuth substitutes as Bi^{5+}. More recently, Atkin and Fulrath[4] have proposed a model suggesting Bi^{3+} substitution on the "A" sublattice, consistent with ferroelectric and sintering data, as well as ionic size arguments (Table 1).

The weight change method similar to Weston's has been employed with some modifications to study the valence and substitutional lattice sites of bismuth and niobium in PZT. Further, the experiments have provided an insight into reaction rates and mechanisms. The dopants were

added as oxides to a calcined PZT host composition, $Pb(Ti_{.47}Zr_{.53})O_3$.

II. EXPERIMENTAL PROCEDURES

(1) Materials Processing

Lead zirconate titanate, $Pb(Ti_{.47}Zr_{.53})O_3$, was obtained from high purity oxides of lead, titanium and hafnium free zirconium. The dry raw materials were weighed carefully into a low ash rubber lined ball mill containing clean teflon balls and isopropyl alcohol. The batch was roll-milled 48 hours. The alcohol was then evaporated at 85°C, followed by dry- roll-milling for 24 hours.

This homogeneously mixed material was separated from the milling media and pressed isostatically at 30,000 psi into 2 inch by 3 inch cylinders. The material was then calcined for 30 hours at 850°C in air, in a covered platinum crucible. No weight changes were detectable.

X-ray diffractometer analysis revealed completely tetragonal PZT, and indicated no unreacted oxides.

One portion of this material was lightly crushed and screened to provide several grades of coarse packing powder. The remainder was pulverized for 45 minutes in a lucite mortar and pestle. A heat treatment at 400°C for 24 hours was required to oxidize the acrylic pick-up during the grinding. An air permeation subsieve size analyzer recorded an average particle size of 2 microns.

Spectrographic analysis determined that processing to this point had not contributed any observable contamination. The major impurities were 0.03% Bi, 0.03% Al, 0.02% Si, 0.01% Fe, and 0.1% Nb (all as oxide weight percents).

(2) Sample Fabrication

The milled material was dried, and portions were doped with various amounts of dry reagent grade oxides of lead, titanium, bismuth and niobium. These doped, as well as undoped control batches, were then wet mixed in isopropyl alcohol for 24 hours. The alcohol was evaporated at 80°C using a teflon coated magnetic stirrer to minimize segregation. A short (6 hours) dry mixing step followed.

Specimens were pressed isostatically at 30,000 psi in clean, sealed rubber tubes, 3/4 inch in diameter. Each sample was hand smoothed with filter paper to remove sharp corners, rough surfaces, and loose powder.

The samples were dried for 24 hours at 110°C, cooled in a vacuum, and accurately weighed with minimal handling.

(3) The Weight-Change Cell

In each experiment, doped and appropriate control samples were positioned carefully in a clean platinum crucible, and surrounded with the PZT packing powder providing the "equilibrium" lead oxide atmosphere. Coarser powder was employed in the vicinity of each sample to minimize the degree of packing powder sintering, both to allow easy sample removal, and negate weight errors due to surface adhesion.

Experimental control was provided by including samples doped with PbO and TiO_2, as well as three strategically placed undoped specimens. The crucible was tightly capped, making a good seal. (Fig. 1)

The entire crucible was dried 24 hours at 110°C and weighed.

The crucible was heated slowly (200°C/hour) to a temperature of 1150°C, held for the required time, and allowed to furnace cool. The crucible weight, sample weight, and reaction time was recorded. The

cell was then repacked and refired. This procedure was repeated many times, thus allowing a monitoring of the weight change with time.

III. DATA AND DISCUSSION

Two types of experimental control specimens were employed. One type was to verify the stability of the lead oxide vapor pressure in the cell, while the other was to assure that lead oxide transport was rapid enough for equilibration.

Several undoped control samples were placed around the test specimens during each run. Their weights remained constant, indicating that the correct PbO partial pressure had been maintained. A lead oxide depleted layer was observed near the top of the crucible, but it did not penetrate far into the cell during any run. Control samples located in this layer lost substantial weight, while those farther down (near the test specimens) were unaffected.

The second type of control demonstrated the mobility of lead oxide in this system. Samples containing 0.5, 1.0 and 1.5 mole % PbO additions were run. The time required for the excess lead oxide to migrate out of the specimens increased with the amount of PbO added, but was never more than 20 hours (Fig. 2). Also, specimens with titania additions, (Fig. 3), showed that the cell atmosphere readily supplied lead oxide to the test specimens. Lead oxide vapor reacted with the added titania to produce $PbTiO_3$, which then formed a solid solution with PZT, eventually becoming $Pb_{1+y}(Ti_{.47}Zr_{.53})_1Ti_yO_{3+3y}$. The necessary amount of PbO was obtained from the atmosphere within 10 hours.

Bismuth doped specimens showed weight changes consistent with Eq. (1), indicating that Bi^{3+} substitutes for Pb^{2+} with lead vacancy

charge compensation. A weight gain was observed during the first 8 hours of reaction. After this, net weight losses occurred, approaching the equilibrium value in 30 to 40 hours. This behavior is believed to result from the transient appearance of a second phase. Bismuth is apparently slow to dissolve in PZT. The undissolved bismuth remains as a liquid phase (m.p. of Bi_2O_3 is 860°C) which picks up lead oxide from the atmosphere. This "pick-up" continues until the activity of PbO in the liquid is equal to that in the vapor. As diffusion of bismuth into the crystalline phase proceeds, the amount of lead oxide required to maintain the PbO activity in the liquid decreases and the excess PbO vaporizes. Eventually, all the bismuth dissolves in the PZT and the second phase disappears. The weight change-time relation is shown in Fig. 4 for a 1 mole % $BiO_{1.5}$ doping in relation to the other possibilities.

Niobium doped samples follow Eq. (2), Nb^{5+} substituting on the $(Ti,Zr)^{4+}$ "B" lattice site. All samples showed the appropriate weight gains. However, a weight greater than predicted by the model was observed during the first 10 hours of reaction. After this, samples began to lose weight, slowly approaching the predicted gain in about 30 to 40 hours. Figure 4 gives the results for 1.0 mole % of $NbO_{2.5}$.

It appears that PbO vapor is initially attacking the niobia particles, forming a second phase. Niobium ions then diffuse into the PZT, and this is accompanied by the simultaneous loss of the excess PbO.

The results are shown graphically in Figs. 2-4 for representative samples. Figure 4 includes normalized bismuth and niobium weight change results in comparison with the theoretical predictions. Table 2 summarizes all the experimental data. No dependence upon heating or

cooling rates, or upon the furnace atmosphere (O_2 or air) was observed.

IV. CONCLUSIONS

These experiments support the substitution of bismuth as Bi^{3+} on the Pb^{2+} "A" lattice site of PZT in agreement with the proposed model. Niobium dissolves as Nb^{5+} on the $(Ti,Zr)^{4+}$ sublattice of PZT, as would be expected. Both the bismuth and niobium data support a lead vacancy charge compensation mechanism and the solid solubility of each is greater than 2 mole %.

Although the high vapor pressure of lead oxide during reaction allowed lead to be lost or gained readily by the PZT samples, the reaction mechanism was complex due to the formation of temporary second phases.

ACKNOWLEDGMENTS

The authors sincerely appreciate the helpful discussions with Dr. Leon Brewer and Paul Jorgensen.

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

REFERENCES

1. Robert Gerson, "Variation in Ferroelectric Characteristics of Lead Zirconate Titanate Ceramics Due to Minor Chemical Modifications," Journ. App. Phys., 31 [1] (Jan. 1960).
2. Gene H. Haertling, "Hot Pressed Lead Zirconate-Lead Titanate Ceramics Containing Bismuth," Amer. Ceram. Bull., 43 [12] (1964).
3. T. B. Weston, A. H. Webster, V. M. McNamara, "Lead Zirconate-Lead Titanate Piezoelectric Ceramics with Iron Oxide Additions," J. Am. Ceram. Soc., 52 [5] (1969).
4. R. B. Atkin and R. M. Fulrath, "The Practical Aspects of Sintering," UCRL-18795, Feb. 1969, prepared for the International Conference on Interfaces, Melbourne, Australia, Aug. 1969.
5. R. D. Shannon and C. T. Prewitt, "Effective Ionic Radii in Oxides and Fluorides," Acta Crystallographia, Vol. B25 Part 5 (May 1969).

Table I. Ionic Radii ($A^{2+}B^{4+}O_3^{2-}$) (ref. 5)

Ion	C.N.	Effective Radius (Å)[5]	Probable Lattice Site
Pb^{2+}	12	1.49	A
Ti^{4+}	6	.605	B
Zr^{4+}	6	.72	B
Bi^{3+}	8*	1.11	A
Bi^{5+}	6	.74	B
Nb^{3+}	6	.70	B
Nb^{5+}	6	.64	B
O^{2-}	6	1.40	O

* Highest C.N. number tabulated.[5]

Table II. Experimentally observed weight changes in doped lead zirconate titanate

PZT Sample Doping	Sample Weight (gm)	Time (hrs) @ 1150°C	Weight Change Observed in %	Weight Change Predicted in %
0.5% PbO	34.813	11	-0.33 (-115)	-0.345 (-120)
1.0% PbO	35.783	19	-0.703 (-251)	-0.685 (-245)
1.5% PbO	12.879	20	-1.065 (-137)	-1.025 (-132)
0.5% TiO_2	35.273	10	+0.397 (+140)	+0.343 (+121)
1.0% TiO_2	38.356	7	+0.637 (+244)	+0.680 (+260)
0.5% $BiO_{1.5}$	35.413	24	-0.50 (-177)	-0.515 [1] (-182)
1.0% $BiO_{1.5}$	42.010	32	-1.02 (-430)	-1.03 [1] (-432)
2.0% $BiO_{1.5}$	39.214	41	-1.63 (-640)	-2.05 (-805) [1]
		60-70*	-2.04 (-800)	
0.5% $NbO_{2.5}$	16.705	20	+0.120 (+20)	+0.175 [2] (+29.3)
		29	+0.167 (+28)	
1.0% $NbO_{2.5}$	20.231	28	+0.376 (+76)	+0.344 [2] (+69.5)

* Extrapolated

( ) refers to actual weight change in mg.
[ ] refers to the equation by which calculation was made.

FIGURE CAPTIONS

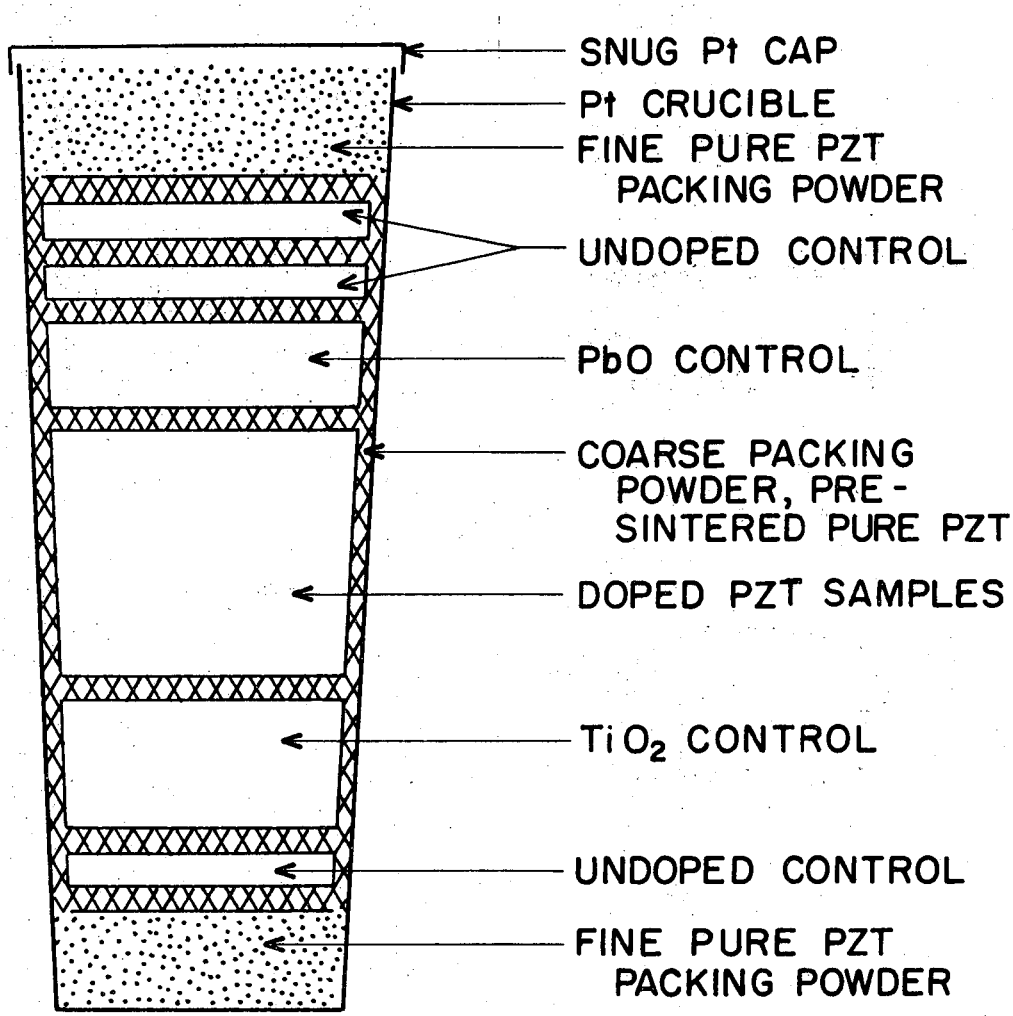
Fig. 1. Weight-change cell

Fig. 2. Sample weight-change (mg) vs. time at 1150°C (hours) for 0.5, 1.0, and 1.5 mole % PbO additions to PZT. Illustrates the mobility of lead oxide in leaving this system.

Fig. 3. Sample weight-change (mg) vs. time at 1150°C (hours) for 0.5 and 1.0 mole % additions of TiO_2 to PZT. Demonstrates the ability of the atmosphere to supply lead oxide when it is needed.

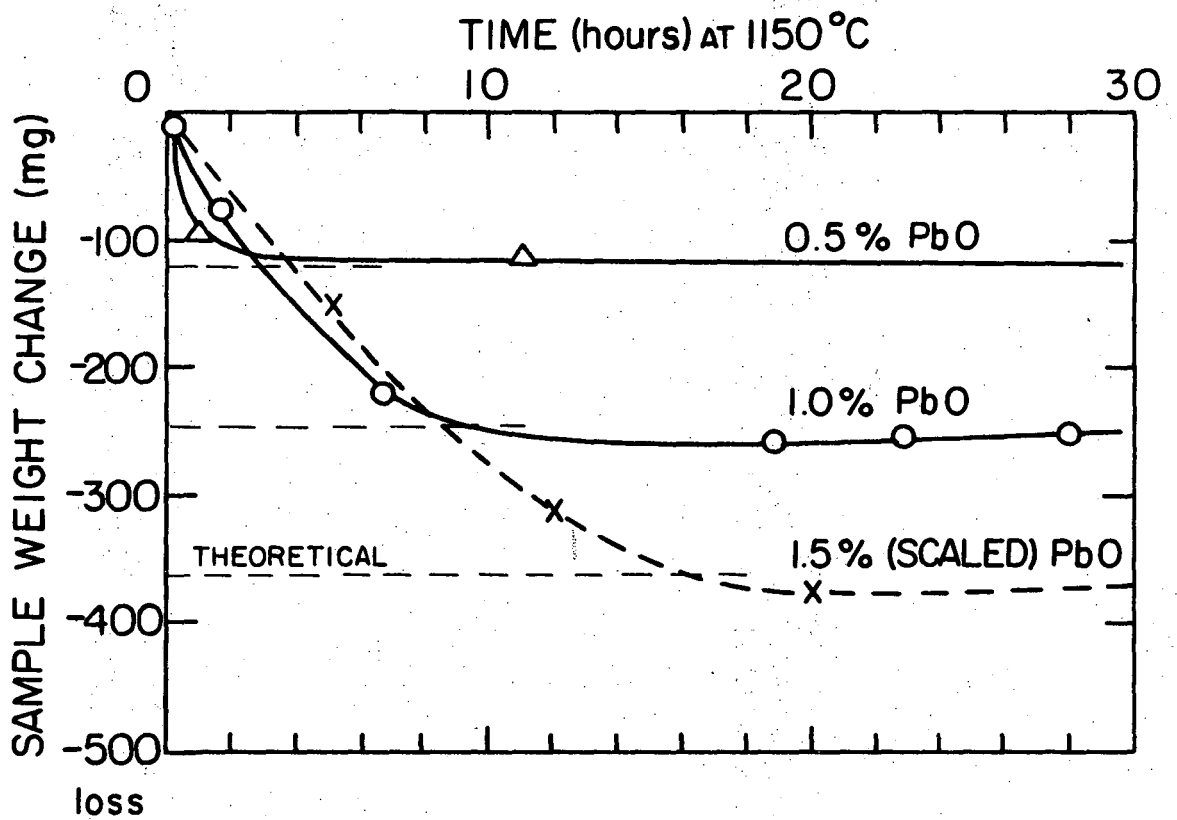
Fig. 4. A plot of bismuth and niobium weight change results in comparison with the predictions of the proposed model. Weight changes are in mgs and time is in hours at 1150°C. The data is normalized to 20 gram samples.

WEIGHT CHANGE CELL



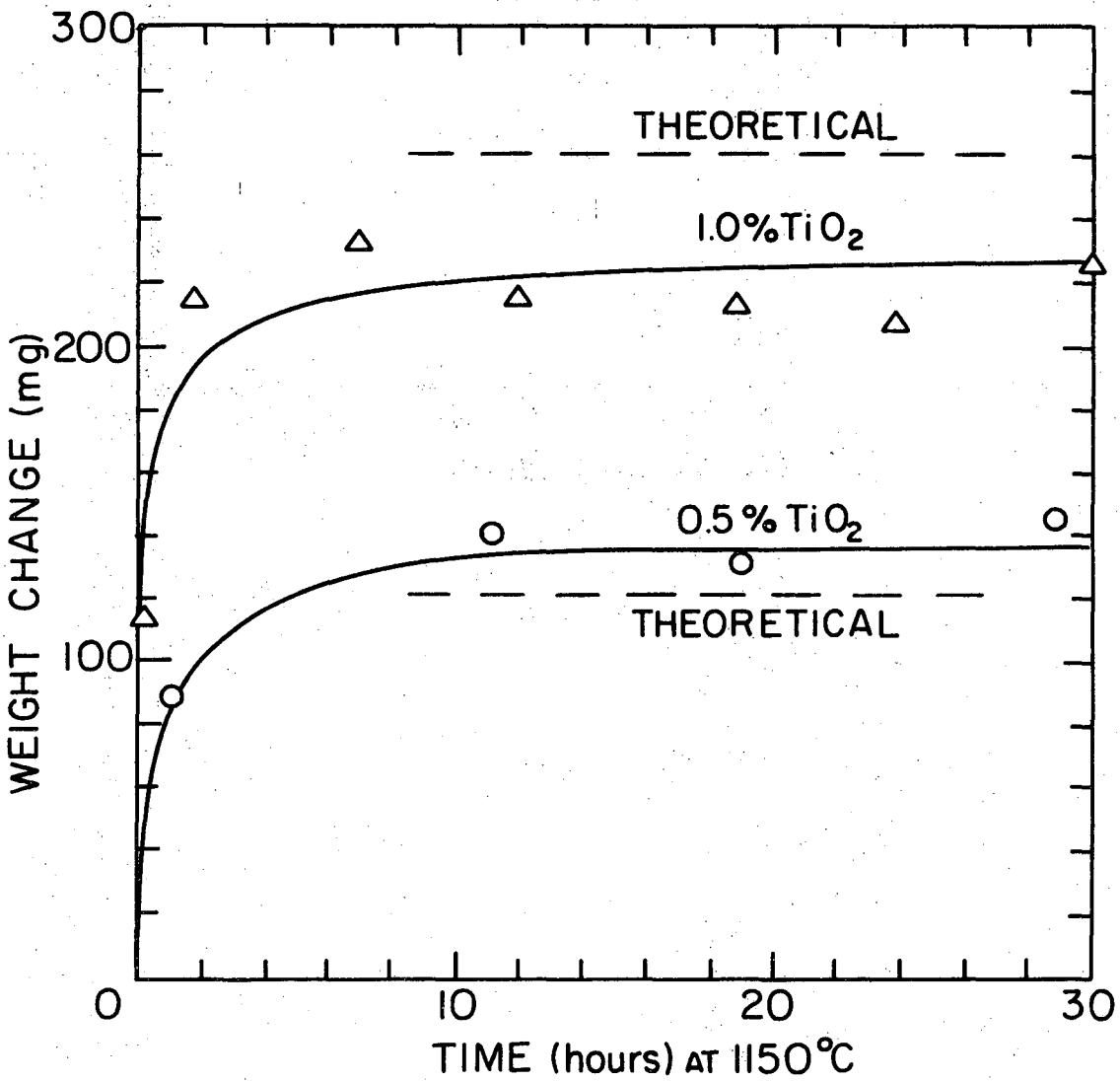
XBL 6910-5716

Figure 1



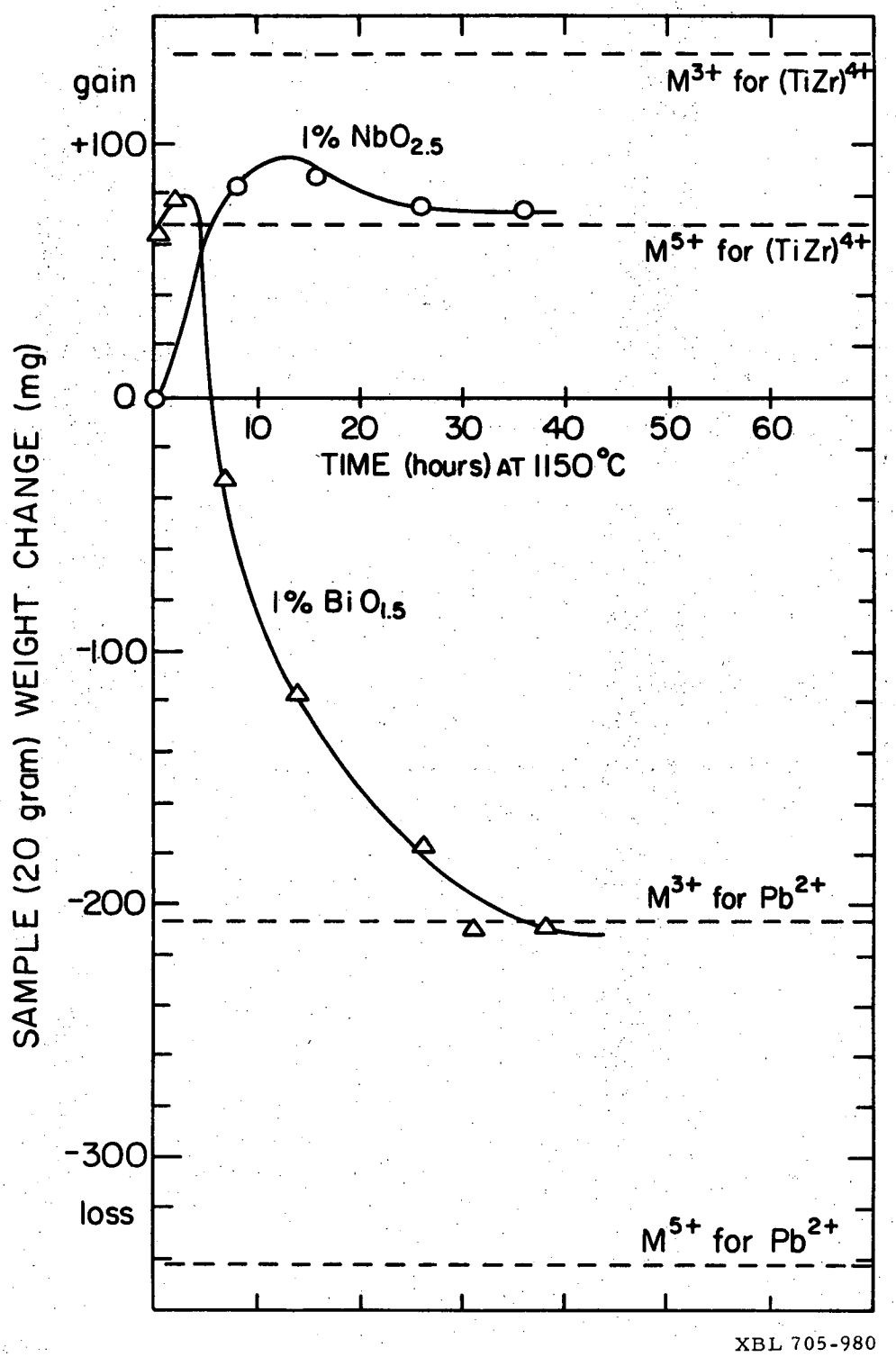
XBL 705-978

Figure 2



XBL 705-979

Figure 3



XBL 705-980

Figure 4

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720