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HIGH TEMPERATURE PHASE EQUILIBRIA IN THE LEAD TITANATE-LEAD ZIRCONATE SYSTEM

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ABSTRACT

Phase relationships at elevated temperatures in the lead titanate-lead zirconate system were investigated by X-ray diffraction, thermal and differential thermal analysis. $PbTiO_3$ melts at 1286°C while $PbZrO_3$ appears to decompose before melting. Between 15 to approximately 40 mole % $PbZrO_3$ a peritectic reaction occurs at 1360°C. Compositions richer in $PbZrO_3$ directly decompose to the three phase region of liquid, zirconia and PZT on melting, whereas compositions lower than 15 mole % $PbZrO_3$ show solid solution behavior.

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At the time this work was done the writers were, respectively, research assistant and professor of ceramic engineering, Department of Materials Science and Engineering.

I. INTRODUCTION

Lead zirconate titanate is one of the leading materials used in the manufacture of transducers. Until recently, however, little information about the phase relationships existing at high temperatures was available. The purposes of this paper is to substantiate by an independent method the high temperature phases and to modify the transition temperatures proposed.

The region between room temperature and the vicinity of the Curie temperatures (490° and 210°C) for various ratios of $PbTiO_3/PbZrO_3$ has been fully investigated.[1,2,3] The phases are tetragonal, rhombohedral and orthorhombic with the morphotropic boundaries at 53 and 92 mole % $PbZrO_3$. At temperatures between the Curie point and 900°C, the lattice parameter vs $PbZrO_3$ content follows Vegard's Law with the structure being cubic perovskite.[4] Above 900°C sublimation of PbO causes compositional variations at the surface,[5] thus preventing further use of a high temperature X-ray camera. A PbO depleted layer which thickens with time has been observed for $Pb(Zr_{0.65}, Ti_{0.35})O_3$ heated in vacuum from 690° to 1130°C;[6] the rate of weight loss increases with an increase in $PbZrO_3$ content.[7] An isothermal reaction diagram for the ternary system $PbO-TiO_2-ZrO_2$ has been prepared by X-ray analysis of samples held at 1100°C for one hour followed by quenching to room temperature.[8,9] Of particular interest here is the section with a constant molar ratio of $PbO/(ZrO_2 + TiO_2) = 1$. The solid solution in this region extends from 0.96 to 1.08 indicating that a small loss in PbO will not cause a phase change. Using the same method Fushimi and Ikeda[10] determined the temperature-composition diagram for the $PbTiO_3-PbZrO_3$ binary. Between 0-14 mole % $PbZrO_3$ the behavior

resembled that of solid solution melting; above 14 mole% and temperatures above 1340°C the solid solution decomposed to liquid to ZrO_2 + $Pb(Zr,Ti)O_3$. Further heating caused the three-phase region to decompose to liquid + ZrO_2. The presence of a three-phase region in this binary demonstrated that the system $PbTiO_3$-$PbZrO_3$ must be treated as a vertical section in the ternary system PbO-ZrO_2-TiO_2.[10] This fact complicates the analysis of the PZT system because a greater reliance on the experimental data is necessary when the binary equilibrium conditions no longer apply.

Errors in the solidus temperature and in the phases detected can occur when quenching techniques are used to investigate a complex oxide system. Determination of the solidus temperature depends on the detection at room temperature of a new phase which is formed when the liquid resolidifies. If the liquid phase reacts rapidly with the solid phase during cooling, a greater amount of liquid is necessary before detection is possible by either optical or X-ray methods. The result is a higher solidus temperature. On cooling any complex melt, the possibility of preferential nucleation of a non-equilibrium species possessing a lower surface energy than the equilibrium solid can cause further complications. The solid then detected at room temperature will not be indicative of the high temperature equilibrium.

With a high temperature X-ray camera and vapor pressure studies ruled out, the most useful method of verifying the quenching results is thermal analysis. The previous objections to quenching procedures are overcome by using heating curves for the final temperature determination, provided the samples are properly homogenized.

II. EXPERIMENTAL TECHNIQUES

PZT powders of various composition were made by weighing the proper proportions of reagent grade PbO (Baker's), TiO_2 (Fisher's) and reactor grade ZrO_2 (Wah Chang) into a glass mixing jar, (Table I). The charge was mixed with isopropyl alcohol, vacuum-dried and pressed into pellets which were fired (along with a PZT pellet higher in $PbZrO_2$ content to prevent PbO loss) in a Pt crucible at 800°C for approximately nine days. Spectrographic analysis of the final pellets did not detect any impurity pickup by this procedure.

The final compositions were checked by wet chemical and X-ray methods. The wet chemical analysis for concentration determination utilized a spectrographic technique for Ti,[11] a thermogravimetric procedure for Zr[12] and an electrochemical method for Pb,[13] (Table II). For the X-ray determination of the compositions, the d spacings of the {321} and {211} lines were obtained and then compared to a d spacing calculated from lattice parameters.[14] The latter were assumed to vary linearly over the composition range and were fitted to a straight line by a least means square procedure, (Fig. 1 and Fig. 2). In order to obtain agreement with the calculated values, it was necessary to reheat the calcined powders at 1200°C for one hour in a closed Pt crucible. This treatment homogenized the powders. The effect of the treatment is illustrated in Fig. 3. A conclusion is that the uniformity of starting powders for various processing studies can be achieved only by reheating to higher temperatures; i.e., the common practice of calcining the mixed oxides for one hour at 800° to 900°C is insufficient for the attainment of reproducible powders.

Examination for phase changes taking place below the solidus temperature was by DTA[15] and X-ray diffraction. Thermal arrest experiments were conducted in a 48.2 cm x 82 cm water-cooled steel cylindrical furnace lined with fire bricks and heated with seven $MoSi_2$ elements. An Al_2O_3 muffle tube closed at both ends with removable bricks was placed down the centre of the furnace. The constant heating zone obtained was 6.4 cm long. Temperature control was regulated by a variable proportional drive controller which provided a linear rate of increase in temperature from room temperature to 1600°C.

A conical Pt crucible suspended from a Pt wire threaded through a thermocouple tube inserted in the upper brick plug served as the container, (Fig. 4). Powders of the composition to be tested were weighed (30 gm) into the Pt crucible and a 0.025 mm Pt foil was spot-welded over the top to reduce the vapor loss at high temperatures. A 0.20 mm Pt-Pt 10 Rh thermocouple insulated with a 0.64 mm Al_2O_3 tubing, notched and bound with Pt wire, was used as a temperature sensor. The thermocouple was inserted into the thermocouple well at the crucible's base and secured by pinching the well shut below the bound Pt wire. The thermocouple e.m.f. was monitored by a potentiometrically balanced strip chart recorder.

The system was calibrated with reagent grade $NaCO_3$ (mp. 854°C)[16] and $CaO \cdot B_2O_3$ (m.p. 1162°C)[17] which was obtained from the Bureau of Mines Pacific Experiment Station. Agreement was within 3°C. The melting point of $PbTiO_3$ was in excellent agreement with the published temperatures of 1281°C[18] and 1285°C[19] and was also used for calibration purposes. The sensitivity of the apparatus was demonstrated by its ability to detect

the Curie point transition of $PbTiO_3$. The weight loss during the experiment was less than 1% of the total weight.

Additional tests to confirm the solidus temperature were performed by placing a sealed 7 mm x 35 mm Pt crucible containing PZT powder into a furnace held at constant temperature. A thermocouple in contact with the outside of the crucible was used for temperature determination. The charge was examined for liquid formation after quenching in liquid nitrogen following a thirty-minute soak at a constant temperature.

III. RESULTS AND DISCUSSION

1. Investigations Below the Solidus Temperature

DTA of powders ranging in composition between 0 to 52.5 mole % $PbZrO_3$, taken at 5 mole % intervals, showed only the Curie point and melting point transition, (Fig. 5). These compositions seemed the most likely region for a high temperature phase in view of the cooling curve analysis (to be discussed later). Several tests in the composition region richer in $PbZrO_3$ demonstrated corresponding results. The high temperature X-ray camera cannot be used without substantial error above 800-900°C since the loss of PbO, combined with the high scattering ability of Pb and Zr ions, allows only the composition near the surface to be ascertained. If the X-ray technique recorded a phase change, the new phase could not unambiguously be assigned to a change in the bulk structure of the compact. To circumvent this problem, the following procedures were adopted:

(1) A 50-50 mole % mechanical mixture of powders of different compositions was heated near the solidus temperature of the lowest melting substance. If a high temperature phase does exist, a

compound not corresponding to that expected from the mechanical mixture should be observed.

(2) A sample of a particular composition was held for one hour below its solidus temperature and then quenched in liquid nitrogen. The presence of a new phase would be detected by splitting in the diffraction peaks.

In both cases the results gave no indication of a high temperature phase, (Table III). The failure of the above methods to detect a higher temperature phase--coupled with the fact that the lattice constants at 900°C follow Vegard's Law--indicates the solid solution region below the solidus is a substitutional cubic perovskite structure in all compositions.

2. Thermal Analysis of $PbTiO_3$ and $PbZrO_3$

The melting point of $PbTiO_3$ was found to be 1286°C ± 3°C by noting the temperature at which the horizontal plateau of the heating and cooling curve began. Confirmation of the melting temperature was accomplished by a quenching technique followed by visual observation. Samples held for thirty minutes at 1280°C, 1283°C and 1286°C showed a sintered solid, slight liquid formation and complete melting, respectively. Close examination of the heating curve showed a 3°C melting interval attributed to impurities. The report of a eutectic on both sides of $PbTiO_3$[19] and the absence of any compound formation other than $PbTiO_3$ in the PbO-TiO_2 system[20] negates the idea of a peritectic reaction and supports an impurity caused melting interval, although this seems large. $PbTiO_3$ is then a congruently melting compound.

Similar experiments on $PbZrO_3$ were unsuccessful due to rapid deterioration of the platinum crucible at temperatures above 1500°C. The

remaining solid was monoclinic ZrO_2 even though continuous heating of $PbZrO_3$ to 1550°C gave no indication of melting. In addition, several crucibles were placed in the furnace, held at temperatures higher than 1520°C for three to five minutes and then quenched. In this case liquid formation was not seen and the remaining solid consisted of a $PbZrO_2$ core surrounded by a white ZrO_2 layer. The onset of crucible attack appears very suddenly as the furnace temperature is raised above approximately 1520°C; this temperature could not be determined accurately. If the reaction $PbO_{vap} + Pt \rightleftarrows Pt$ (Pb solid solution) + 1/2 O_2 were taking place, it would be accelerated by an increase in the PbO concentration. A peritectic decomposition of the form $PbZrO_3 \rightleftarrows \begin{matrix} liq \\ or \\ vap \end{matrix}$ PbO + ZrO (s.s.) would cause such an increase. Any liquid PbO formed would probably be vaporized since PbO boils at 1472°C.[21] Reactions of these types would account for both the deterioration of the Pt crucible and the absence of any form of PbO in the remaining solid. The $PbZrO_3$ core that remained in the samples that were placed for one to two minutes in a constant temperature furnace is due to the radial temperature gradient that existed. Since the center was cooler than the exterior of the sample, decomposition had not occurred. The longer a sample was heated the greater the thickness of the white ZrO_2 layer and the smaller the diameter of the $PbZrO_3$ core.

Additional support for a decomposition reaction would be the absence of other intermediate compounds in the $PbO-ZrO_2$ system. To firmly establish whether $2PbO-ZrO_2$ exists, mixtures of 2 moles PbO and 1 mole ZrO_2 were heated at 800°C for a total of 54 hours. At eighteen hour intervals the sample was ground, analysed by X-ray diffraction, replaced and the heat treatment continued. The only phases detected were $PbZrO_3$ and

orthorhombic PbO. Other studies[8,22] have shown similar results. Heating a 20 mole % PbO-80 mole % ZrO_2 sample at 950°C produces only $PbZrO_3$ and tetragonal ZrO_2 which transforms to the monoclinic form on further heating.[23] From these observations the existence of two peritectic reactions at 910° and 1570°C (corresponding to $PbZrO_3$ decomposition) seems reasonable,[10] although the latter temperature is probably erroneous. As shown in this investigation $PbZrO_3$ cannot be contained in Pt above 1520°C.

In view of the incongruent melting of the $PbZrO_3$, the vertical section at 50 mole % PbO in the PbO-ZrO_2-TiO_2 composition-temperature diagram cannot be a quasi-binary.

3. Thermal Analysis of Lead Zirconate Titanate Mixtures

The final temperatures used for the phase diagram were obtained from data derived from heating curve analysis since supercooling, the possibility of preferential nucleation of a non-equilibrium solid and low diffusion rates in the solid appeared to be present. The cooling curves in this system proved to be inaccurate and were useful in indicating the general trend of events only.

As the melt was cooled the first inflection point, which is represented by the uppermost line in Fig. 6, showed distinct undercooling for compositions of $PbTiO_3$, $Pb(Ti_{0.95}, Zr_{0.05})\ O_3$ and $Pb(Ti_{0.90}, Zr_{0.10})\ O_3$. For compositions richer in $PbZrO_3$ the first point split into two inflection points. The temperature difference between the split points and their absolute temperature increases with increasing $PbZrO_3$ content. Since the lower point did not remain constant while the $PbZrO_3$ content was varied, a simple peritectic reaction could not be responsible. All

possible peritectic reactions could not be ruled out, however, because the cooling curve behavior was very much like that of a metal which undergoes a peritectic transformation; i.e. pronounced undercooling and a short isothermal arrest which slowly merges into the cooling rate of the furnace.[24] The temperature of the final inflection point, which could not be detected for samples exceeding 25 mole % $PbZrO_3$, was controlled by coring. Coring is particularly common when dendritic growth is present and results in a composition gradient through the dendrite. The melt of a given PZT composition (vertical line) will begin to solidify on reaching the liquidus temperature and deposit a solid with a composition in equilibrium with the liquid at that temperature. As the temperature is lowered the average composition of the solid is not that indicated by the solidus line due to slow diffusion in the solid, but is richer in $PbZrO_3$. The deviation from the equilibrium composition increases as the temperature is lowered. Upon reaching the equilibrium solidus temperature for the specific composition the average solid composition is still rich in $PbZrO_3$ and a liquid rich in $PbTiO_3$ remains. Cooling further, the average solid composition finally coincides with the original composition and the liquid rich in $PbTiO_3$ solidifies.

Support of this hypothesis is indicated by observation of dendritic growth which appeared to decrease with the addition of $PbZrO_3$ and by the different solidus temperatures obtained for different cooling rates. The faster the cooling rate, the shorter the period of time for solid state diffusion to take place; therefore, the larger the deviation of the average solid composition from equilibrium and the lower the final freezing temperature. Figure 6 shows the final inflection points of the 5.6°/min

cooled runs to be lower in temperature than the 2.8°/min runs.

Examination of the solid taken from the crucible showed the following: compositions containing 0, 5 and 10 mole % $PbZrO_3$ yield only the original composition as ascertained by X-ray analysis. At higher percentages of $PbZrO_3$, ZrO_2 (monoclinic) and PbO (orthorhombic and tetragonal) were present in addition to the PZT phase. The PZT phase was generally richer in $PbTiO_3$ than the original composition. A cross-section of a crucible containing a solidified melt whose original composition was greater than 15 mole % $PbZrO_3$ would have a greenish-white top layer followed by a gradual transition to a brownish-orange solid along the sides and bottom of the crucible. The phases present on the top layer are PZT and ZrO_2, while in the bottom the same species were detected with the addition of PbO. The solid at the bottom and sides of the crucible would be the phases to first solidify on cooling, while those at the top and center would be the last. The last liquid to solidify would be rich in PbO, the lowest melting component. The vapor pressure would be relatively high at these temperatures, accounting for the absence of PbO at the surface. The detection of PbO at the bottom and sides of the crucible could be explained by the PbO-rich liquid finally solidifying in the interstices between dendrites. The appearance of unreacted ZrO_2 in the presence of PbO seems strange considering the solid state reaction to form $PbZrO_3$ that takes place when powders of PbO and ZrO_2 are mixed and heated. The appearance of these three phases indicates the possibility of a three-phase equilibrium involving ZrO_2, PZT and liquid rich in PbO at some temperature above the solidus. On the other hand, since the

phases present do not react rapidly once in the solid state,* the same situation could be caused by non-equilibrium nucleation of ZrO_2 and PZT followed by solidification of the remaining melt.

From this discussion it is evident that the temperatures determined by cooling curve analysis must not be used because of undercooling and the inhomogeneity of the final solid caused by preferential nucleation of a non-equilibrium species or by the slow diffusion rates in the solid. Resolution of the question of whether three phases exist at high temperature or whether preferential nucleation causes the observation of PbO, PZT and ZrO_2 at room temperature can be solved only by heating curve analysis because nucleation and growth considerations are absent.

4. Heating Analysis

The thermocouple arrangement used here should be particularly sensitive to phase changes in powders. As heating proceeds, sintering takes place causing a shrinkage of the powder away from the crucible wall, demonstrated by the rattling of the unmelted charge in the crucible after heating near the melting point. The charge is then supported by the top of the thermocouple well and a break in the heating curve will result when the portion nearest the thermocouple melts. The unusual geometry employed causes the primary heat flow in this case to be through the Pt metal and not from the container wall through the vapor gap to the partially sintered mass of the original composition. The first inflection

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* If an equimolar mixture of ZrO_2 and $PbTiO_2$ is heated the resultant mixture is ZrO_2 containing a small amount of TiO_2 in solid solution and $PbTiO_3$ containing a small amount of $PbZrO_3$. Conversely, if a similar experiment is performed with TiO_2 and $PbZrO_3$, the $PbZrO_3$ will decompose leaving ZrO_2 and $PbTiO_3$ with 7 mole % $PbZrO_3$ in solid solution.[9]

point in the heating curve would thus represent the solidus temperature. This point was checked by inserting crucibles containing PZT into the furnace held at a constant temperature 3°-5°C above the first inflection point for that composition. Examination showed liquid formation.

Continued heating causes a second inflection which shows a larger heat effect. This is rationalized in the following manner: the sample sinters to a conical shaped solid supported by the thermocouple well and partially separated from the wall of the crucible. Heat transfer to the solid is by convection through the gas phase present in the crucible but primarily by conduction along the solid thermocouple well. The hottest point of the solid is the top of the thermocouple well because good contact between the sintered powder and Pt crucible is maintained in this region. After the first inflection point is reached the liquid formed in the vicinity of the thermocouple is very small and therefore shows a small heat effect. Further heating plus the added heat conduction effect of the liquid formed brings the remaining solid (major mass) to the solidus temperature or above it.

The last inflection on heating is the liquidus point. After reaching this temperature, the melt temperature rises very rapidly, due to the increased heat conduction in the liquid, to establish a heating rate similar to that of the furnace. A summary of results is in Fig. 7.

The heating curves show a trend that supports the idea that a three-phase region (liquid + ZrO_2 + PZT) does exist at high temperatures. The results agree with those obtained from quenching techniques, (Fig. 8). The major refinements to the quenching diagram are the lower solidus and liquidus temperatures due to greater sensitivity in detection, and the

determination of the peritectic temperature to be 1360° rather than 1340°C.

The establishment of a three-phase region in the $PbTiO_3$-$PbZrO_3$ system definitely proves the system is not a quasi-binary section in the PbO-TiO_2-ZrO_2 composition temperature diagram.

IV. CONCLUSIONS

A solid solution appears to exist in the region between the Curie and the solidus temperatures for all ratios of $PbZrO_3/PbTiO_3$. DTA and X-ray techniques failed to find a phase transition or any new phases.

The lowest temperature at which liquid is formed in this system is 1286° ± 3°C, the melting point of $PbTiO_3$. Increasing the $PbZrO_3$ to $PbTiO_3$ ratio increases the solidus temperature. The highest temperature, the melting point of $PbZrO_3$, could not be determined because the crucible rapidly deteriorated above 1500°C. $PbZrO_3$ appeared to decompose to PbO(vap) + ZrO_2(solid) before melting. Compositions between $PbTiO_3$ and 15 mole % $PbZrO_3$ showed a simple melting behavior characteristic of a solid solution. Between 15 mole % to approximately 40 mole % $PbZrO_3$ a peritectic reaction occurs at 1360°C. Above the peritectic temperature is a three-phase region with liquid, zirconia and PZT solid solution in equilibrium. Decomposition to three phases occurs directly at the solidus temperature for compositions richer in $PbZrO_3$ than 40 mole %.

The phase diagram determined here by thermal analysis is in basic agreement with that obtained by quenching methods and confirms the existence of a three-phase region.

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Table I. Semiquantitative spectrographic analysis of the oxides used. (Impurities reported as Wt. % of the oxide.)

	PbO (Baker's reagent grade)	TiO_2 (Fisher's reagent grade)	ZrO_2 (Wah Chang reactor grade)
Si	0.004%	0.2%	0.003
Mg	.005	.001	.002
Fe	<.002	.01	.01
Al	.002	.04	.005
Ca	.001	.002	.005
Cu	.0005	--	--
Ba	.002	--	--
Bi	.01	--	--
Hf	--	--	<.025%
Ag	<.0005	--	--
Nb	--	--	.05
Ti	--	--	.005
Y	--	--	.006

Table II. Chemical analysis of lead zirconate titanate powders

	Mole % PT											
	10	20	30	40	60	65	70	75	80	85	90	95
	Weight Percents											
% TiO_2	2.52	4.85	7.28	9.905	14.61	16.35	17.04	18.50	19.76	20.88	23.58	24.84
% ZrO_2	32.26	28.90	26.01	22.32	15.45	13.67	11.74	9.88	7.99	4.91	4.07	2.025
% PbO	66.1	66.0	66.6	67.5	69.8	70.55	71.1	71.95	72.25	72.53	72.9	73.45
Closure	100.9	99.75	99.9	99.73	99.9	100.6	99.9	99.8	100.0	98.3	100.6	100.3
Mole % PT*	10.74	20.56	30.16	40.64	59.33	64.85	69.13	74.29	79.23	86.77	89.94	94.99

Each percentage is the average of at least three separate determinations.

* Mole % $PbTiO_3$ calculated on the basis that all TiO_2 is combined in $PbTiO_3$ and all ZrO_2 is combined as $PbZrO_3$ and that their total = 100.0%.

Table III. Results of heating for 1 hour of equimolar mixtures of various compositions

Mixture 50/50 mole %	Temp	Resultant composition
$PbZrO_3+Pb(Zr_{0.80},Ti_{0.20})O_3$	1254°C	$Pb(Zr_{0.90},Ti_{0.10})O_3$
$Pb(Zr_{0.90},Ti_{0.10})O_3+Pb(Zr_{0.30},Ti_{0.70})O_3$	1281°C	$Pb(Zr_{0.60},Ti_{0.40})O_3$
$Pb(Zr_{0.60},Ti_{0.40})O_3+Pb(Zr_{0.10},Ti_{0.90})O_3$	1252°C	$Pb(Zr_{0.35},Ti_{0.65})O_3$
$Pb(Zr_{0.70},Ti_{0.30})O_3+PbTiO_3$	1254°C	$Pb(Zr_{0.35},Ti_{0.65})O_3$

FIGURE CAPTIONS

Figure 1. Interplaner spacing of the $(2\bar{1}1)$ and (211) planes for rhombohedral PZT.

Figure 2. Interplaner spacing of the (211) and $(1\bar{1}2)$ planes for tetragonal PZT.

Figure 3. Effect of thermal treatment on homogenizing calcined powders.

Figure 4. Suspension apparatus and crucible design used in thermal analysis.

Figure 5. DTA of lead titanate rich powders.

Figure 6. Phase diagram as determined by cooling curve analysis.

Figure 7. Phase diagram as determined by heating curve analysis.

Figure 8. Phase diagram as determined by thermal analysis (this investigation) and quenching methods.[10]

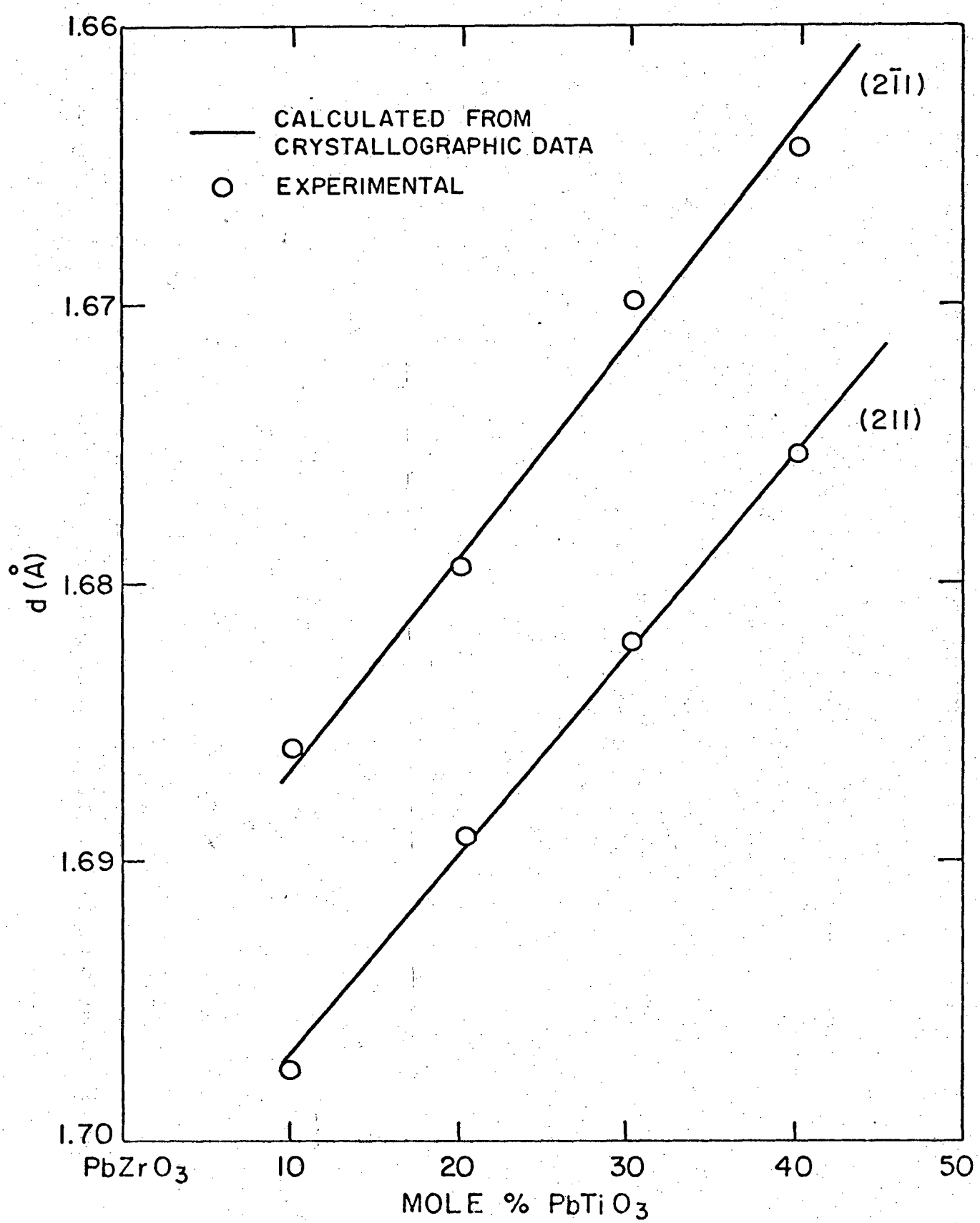

1.66
1.67
1.68
1.69
1.70
d (Å)
CALCULATED FROM
CRYSTALLOGRAPHIC DATA
EXPERIMENTAL
(2$\bar{1}$1)
(211)
PbZrO3
10
20
30
40
50
MOLE % PbTiO3

Fig. 1

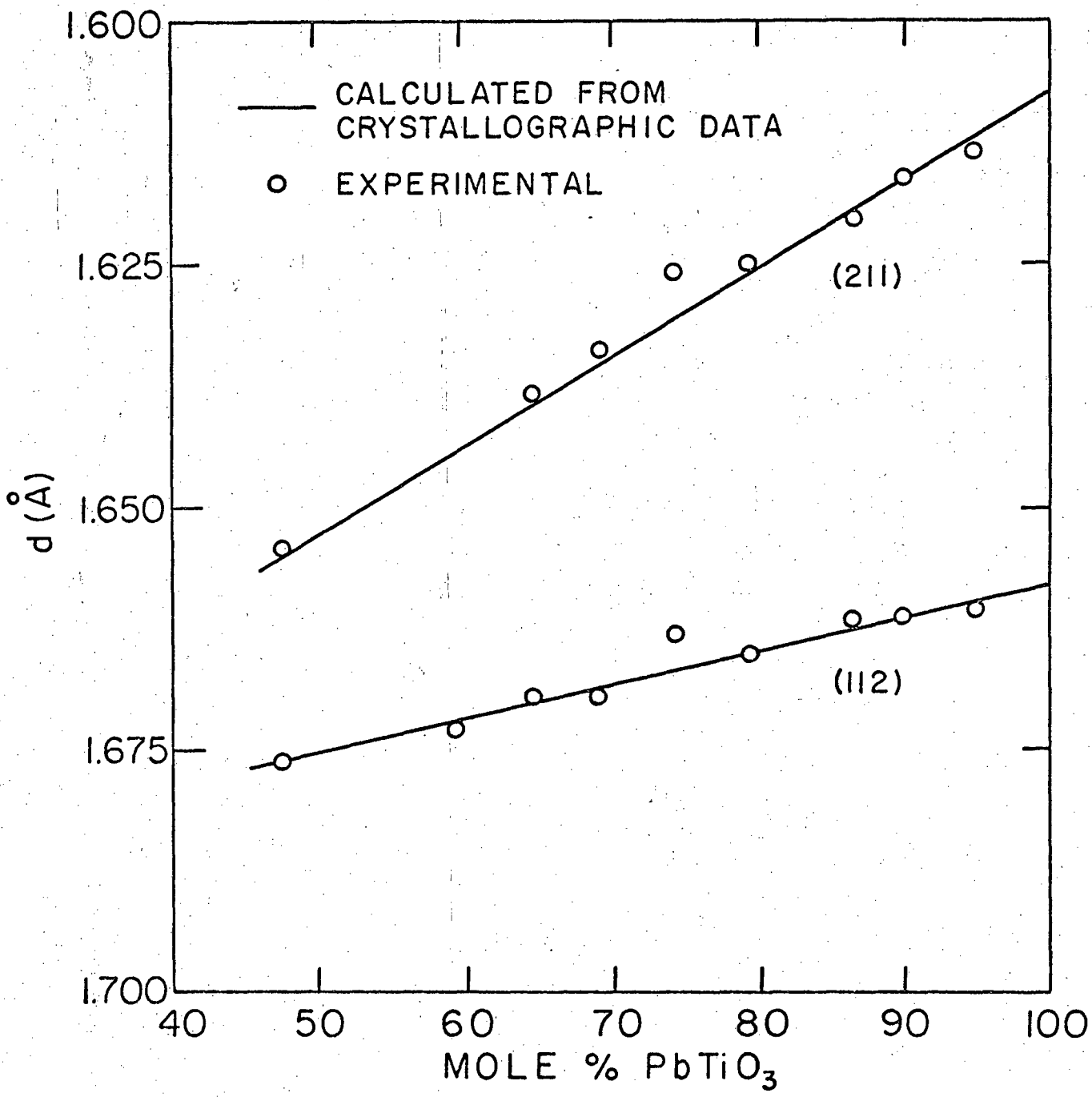
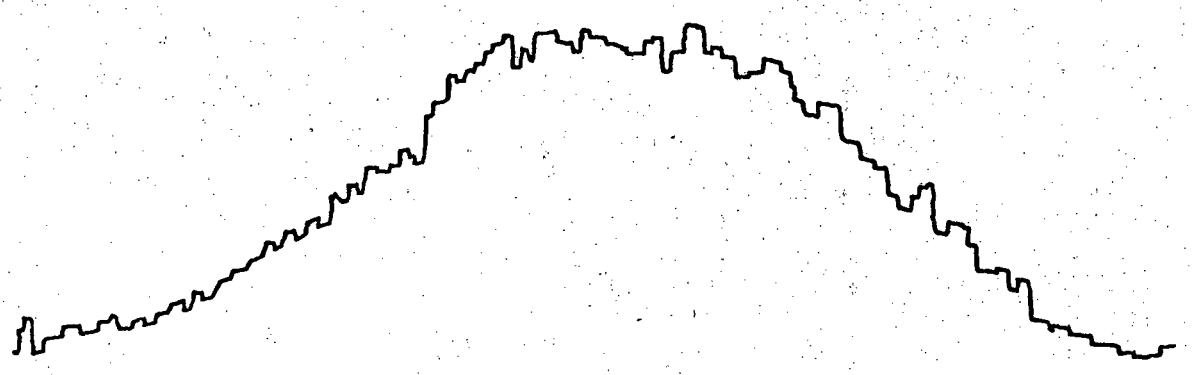
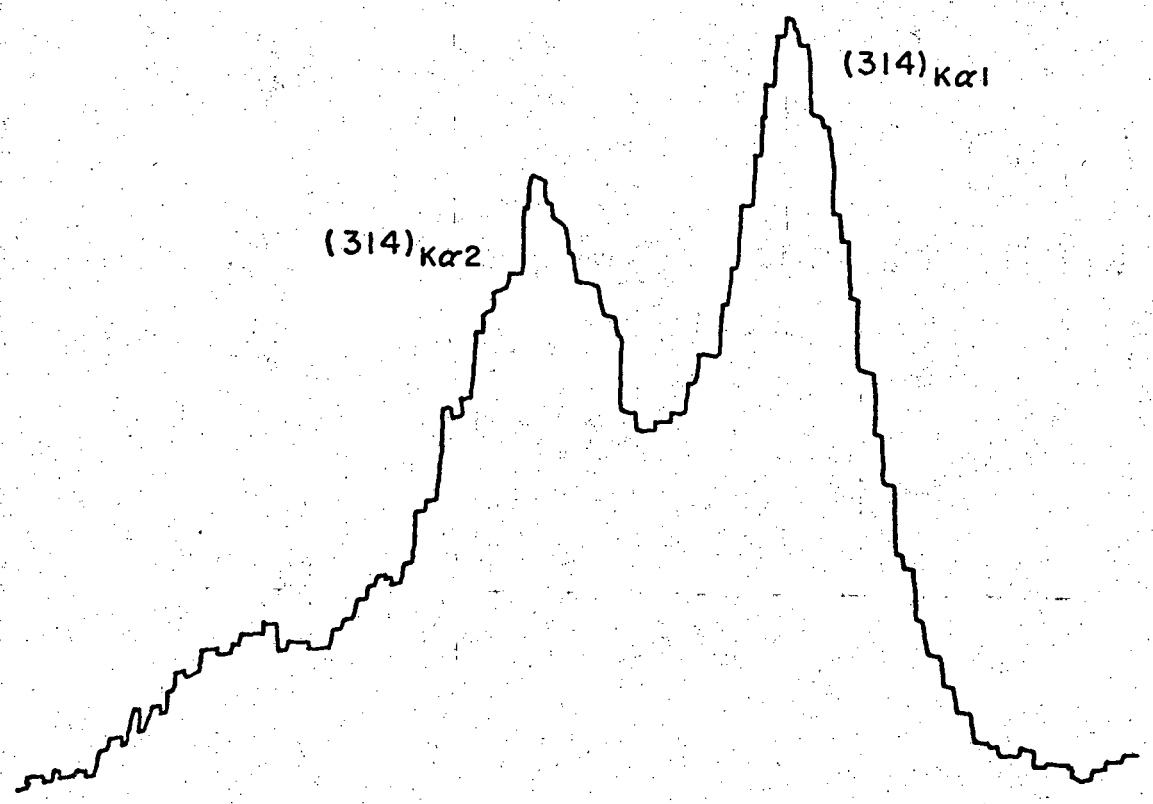

1.600
1.625
1.650
1.675
1.700
d (Å)
CALCULATED FROM
CRYSTALLOGRAPHIC DATA
EXPERIMENTAL
(211)
(112)
40
50
60
70
80
90
100
MOLE % PbTiO3

Fig. 2

COMPOSITION: $Pb(ZrO_{0.20}, Ti_{0.80})O_3$
RADIATION: CuK_{α}



(a) CALCINED POWDER



(b) AFTER HEATING THE CALCINED POWDER AT 1200°C FOR 1½ HRS.

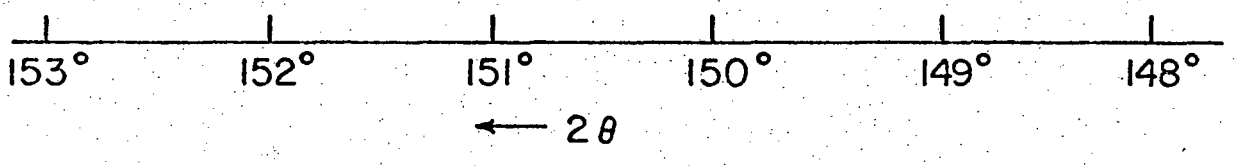


Fig. 3

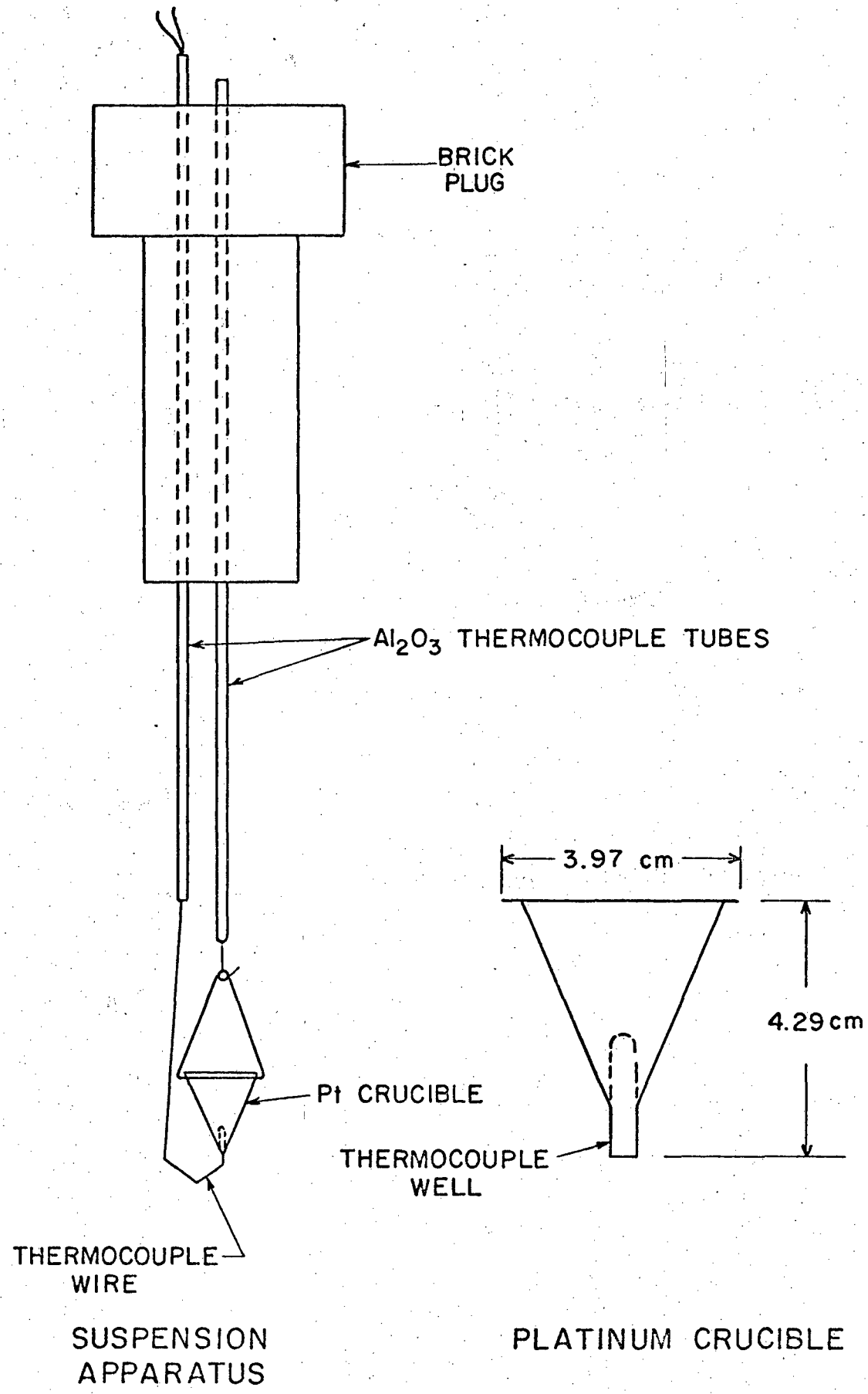

BRICK PLUG
Al_2O_3 THERMOCOUPLE TUBES
Pt CRUCIBLE
THERMOCOUPLE WIRE
SUSPENSION APPARATUS
3.97 cm
4.29 cm
THERMOCOUPLE WELL
PLATINUM CRUCIBLE

Fig. 4

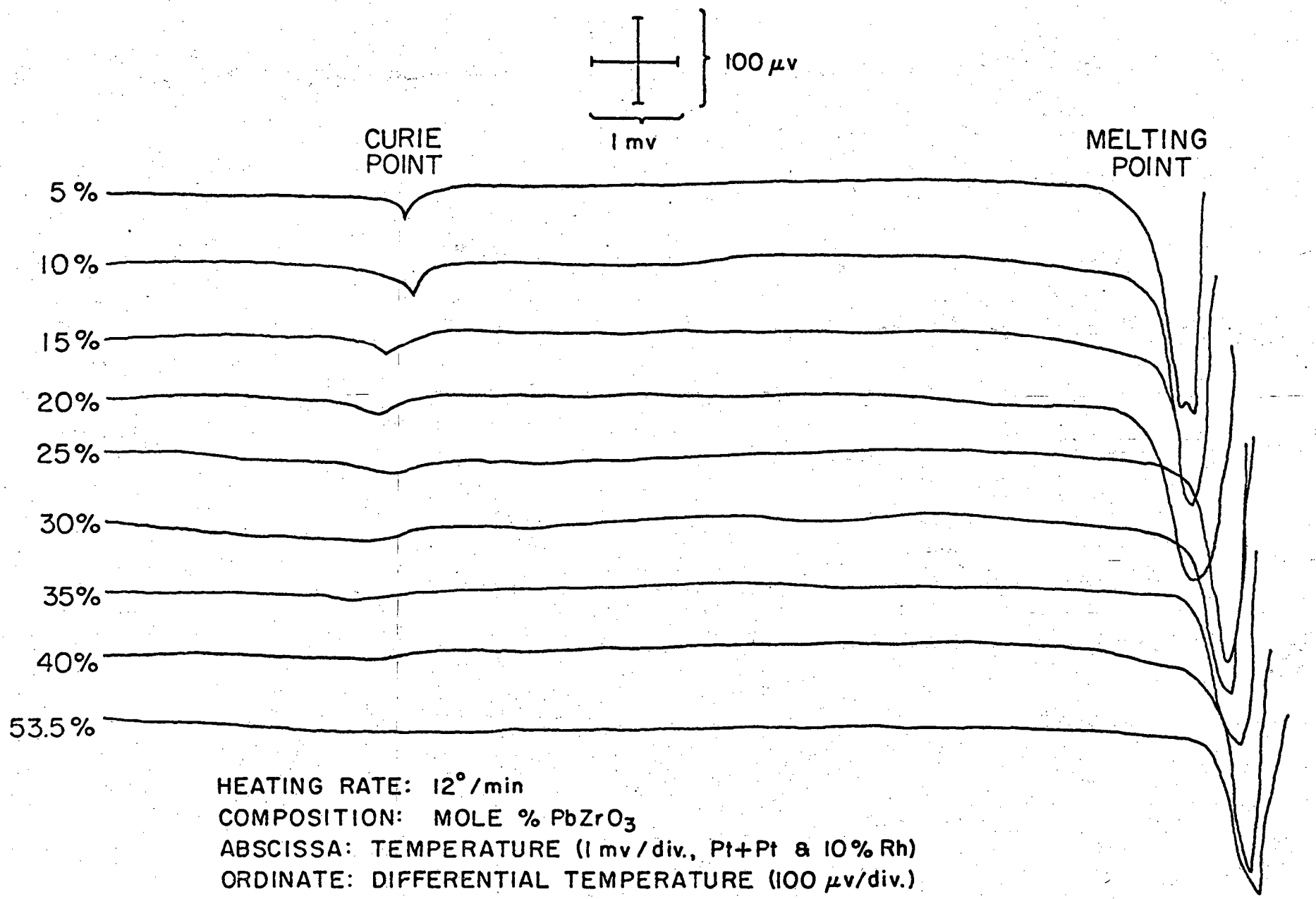

100 μv
1 mv
CURIE POINT
MELTING POINT
5 %
10 %
15 %
20 %
25 %
30 %
35 %
40 %
53.5 %
HEATING RATE: 12°/min
COMPOSITION: MOLE % PbZrO3
ABSCISSA: TEMPERATURE (1 mv/div., Pt+Pt & 10 % Rh)
ORDINATE: DIFFERENTIAL TEMPERATURE (100 μv/div.)

Fig. 5

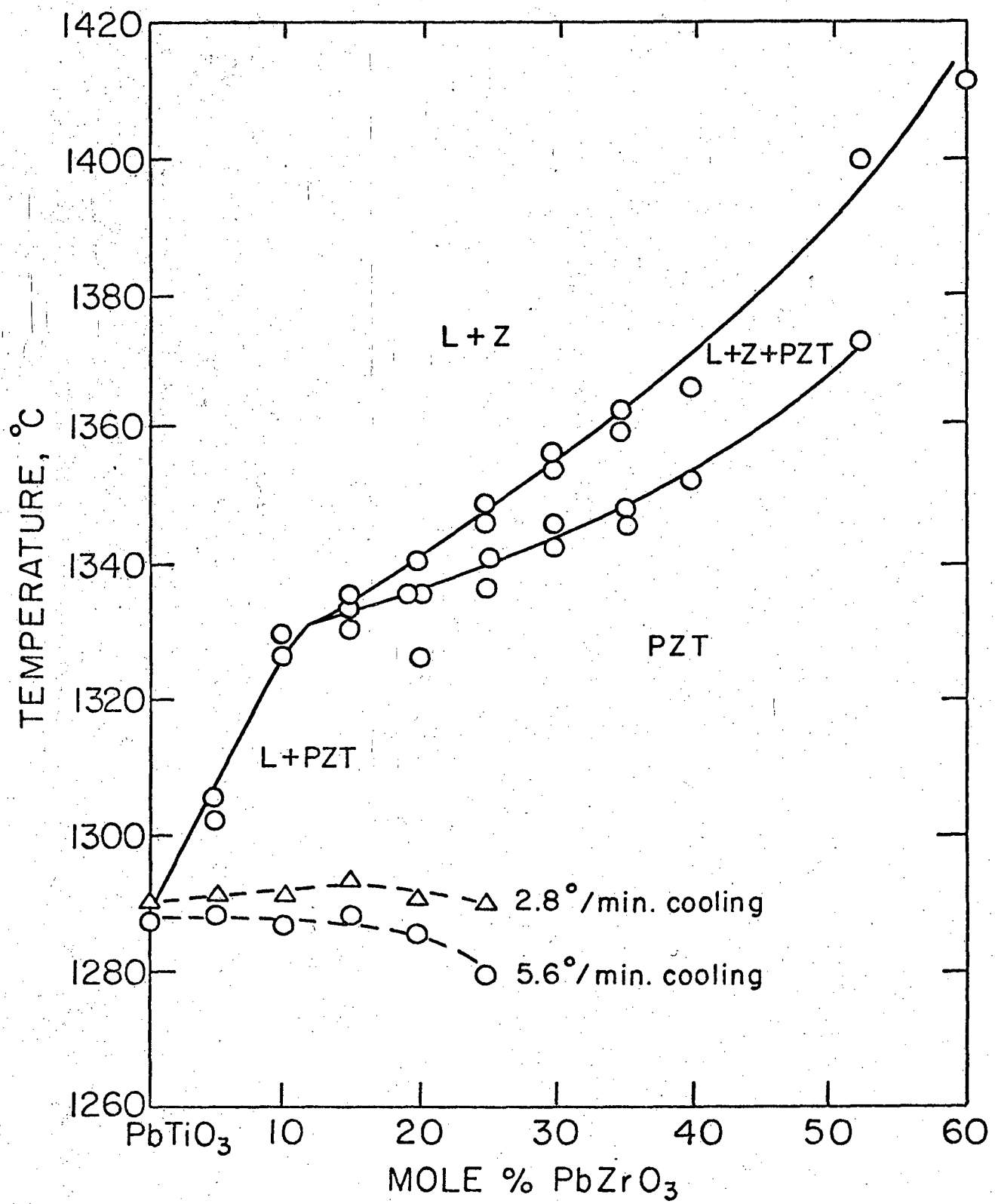
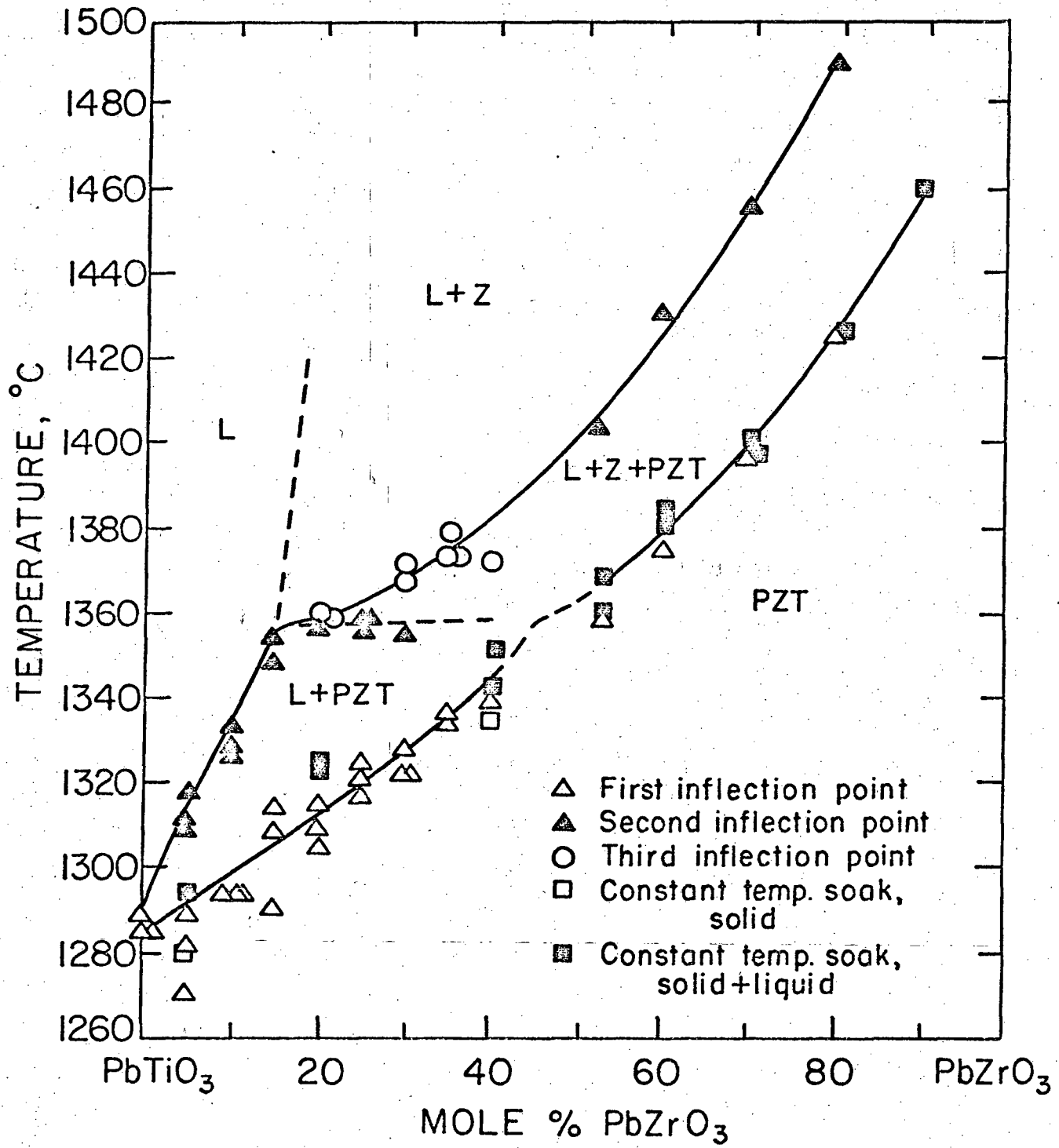

1420
1400
1380
1360
1340
1320
1300
1280
1260
TEMPERATURE, °C
L + Z
L+Z+PZT
PZT
L+PZT
2.8°/min. cooling
5.6°/min. cooling
PbTiO3
10
20
30
40
50
60
MOLE % PbZrO3

Fig. 6

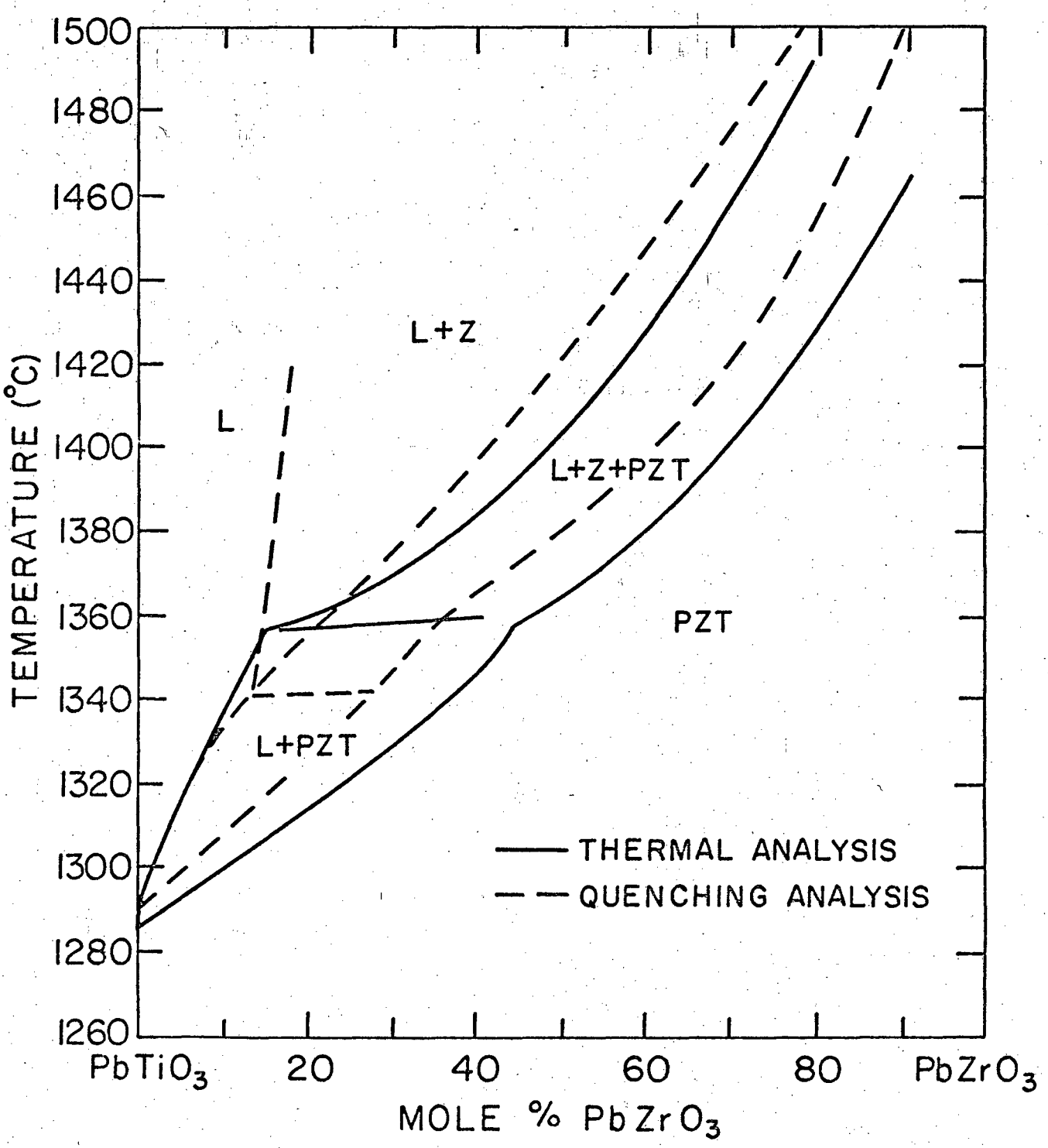


L = Liquid

Z = ZrO_2 Rich solid

PZT = Lead Zirconate Titanate

Fig. 7



L = LIQUID

Z = ZrO_2 RICH SOLID

PZT = LEAD ZIRCONATE TITANATE

Fig. 8

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