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

Authors
Moon, Ronald L.
Fulrath, Richard M.

Publication Date
1970

Submitted as a Note to Journal
of the American Ceramic Society

UCRL-17545 Rev II
Preprint
c.2

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

Ronald L. Moon and Richard M. Fulrath

January 1970

AEC Contract No. W-7405-eng-48

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-17545 Rev II

DISCLAIMER

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

Ronald L. Moon* and Richard M. Fulrath

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

The phase equilibria of the $PbO-TiO_2-ZrO_2$ system above 900°C has been deduced solely from X-ray analysis of quenched samples.[1-3] Errors in the solidus temperature and in the phases detected can occur when using this technique. A higher solidus temperature will result if the liquid crystallizes rapidly to the solid during quenching. Even more important, the possibility of preferential nucleation of a non-equilibrium species possessing a lower surface energy than the equilibrium phase can lead to erroneous conclusions about the high temperature phases. These objections are overcome by analyzing the heating curves of homogeneous powders.

Based on a dissertation submitted by Ronald L. Moon in partial fulfillment of the requirements for the degree of Doctor of Philosophy in engineering science, University of California, Berkeley, California, May 1967.

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

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

* Now at Varian Associates, Palo Alto, California.

PZT (lead zirconate titanate) powders were prepared by mixing and pressing reagent grade PbO and TiO_2 and reactor grade ZrO_2 into pellets and calcining in a Pt crucible (along with a PZT pellet higher in $PbZrO_3$) at 800°C for approximately nine days. Compositions determined by standard wet chemical analysis[4] were compared to those obtained from the d spacing of the {321} and {211} X-ray diffraction lines. In order to achieve agreement with calculated d spacings[5] homogenization of the calcined powders by reheating to 1200°C in a closed Pt crucible was necessary (Fig. 1). Agreement between all methods was within 1 mole %. A conical Pt crucible charged with 30 gms of powder and sealed at the top with a welded Pt foil was used for thermal analysis (Fig. 2). Weight loss during the experiment was less than 1% of the total weight. Additional confirmation of the solidus temperatures was obtained by quenching sealed crucibles from a constant temperature and examining the contents for liquid formation as evidenced by shrinkage of the powder compact.

Tests performed below the solidus indicated only the solid solution cubic perovskite structure in agreement with observations between the Curie point and 900°C.[6] Given individual compositions quenched from just below the solidus temperature did not show a splitting in their X-ray diffraction peaks, verifying the continuous solid solution.[4] DTA of powders whose compositions were varied at 5% intervals between 0 and 52.5 mole % $PbZrO_3$ showed only the Curie and melting endotherms.[4] A 50-50 mole % mechanical mixture of powders of different compositions heated near the lowest solidus temperature of the two powders formed the final composition expected from such a combination.

The melting point of $PbTiO_3$ was found to be 1286°C ± 3°C. Confirmatory samples held for thirty minutes at 1280°, 1283° and 1286°C showed a sintered solid, slight liquid formation and complete melting, respectively. Similar experiments on $PbZrO_3$ were unsuccessful due to rapid deterioration of the Pt crucible at temperatures above 1500°C. Continuous heating of $PbZrO_3$ to 1550°C gave no indication of melting. $PbZrO_3$ held for several minutes at temperatures higher than 1520°C showed only a $PbZrO_2$ core surrounded by a white monoclinic ZrO_2 layer. The sudden onset of crucible attack could be explained by a reaction $PbO(vap) + Pt(s) \rightleftharpoons PtPb(s.s.) + 1/2\ O_2(g)$. A peritectic decomposition of $PbZrO_3 \rightleftharpoons liq + ZrO_2(s)$ would accelerate the previous reaction. In view of the incongruent melting of PZ[3] plus the above observations, the vertical section at 50 mole % PbO in the PbO-ZrO_2-TiO_2 composition-temperature diagram cannot be a quasi-binary.

Cooling curves in the system proved to be inaccurate because of compositional coring. For instance, at 25 mole % $PbZrO_3$ the last inflection point on cooling was 1290°C, whereas on heating, the first indication of melting was 1320°C. Furthermore, the temperature of the last cooling curve inflection point decreased as the cooling rate was increased.

X-ray analysis of the solid taken from the crucible after melting showed the following: (1) Charges containing 0, 5 and 10 mole % $PbZrO_3$ yield only the original composition. (2) 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. 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, or the non-equilibrium nucleation of ZrO_2 and PZT followed by solidification of the remaining PbO rich melt.

The first deviation in the heating curve represented the solidus temperature: the heat transfer along the Pt thermocouple well maintained that portion of the solid in the immediate vicinity of the thermocouple at the highest temperature. This was further assisted by the solids sintering and shrinking away from the sides of the crucible at temperatures greater than 800°C. As the furnace temperature continued to increase, the increased heat conduction of the liquid formed brought the remaining solid to the solidus temperature and resulted in an inflection point. The final inflection represented the liquidus temperature after which the melt temperature raised rapidly and establishing a heating rate similar to that of the furnace.

The heating curves support the proposal that a three-phase region (liquid + ZrO_2 + PZT) does exist at high temperatures. The results agree with those obtained from quenching techniques,[3] (Fig. 3). 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.

This study independently confirms the existence of a three-phase region in the $PbTiO_3$-$PbZrO_3$ system and definitely proves the system is not a quasi-binary section in the PbO-TiO_2-ZrO_2 composition-temperature diagram.

REFERENCES

1. T. Ikeda, T. Oakno, M. Watanabe, A Ternary System $PbO-TiO_2-ZrO_2$. Japan J. Appl. Phys. 1, 4, 218-222 (1962).

2. A. H. Webster, R. C. MacDonald and W. S. Bowman, The System $PbO-ZrO_2-TiO_2$ at 1100°C, J. Can. Ceram. Soc. 34, 97-102 (1965)

3. Shoichi Fushimi and Takuro Ikeda, Phase Equilibrium in the System $PbO-TiO_2-ZrO_2$, J. Am. Ceram. 50, 3, 129-132 (1967).

4. R. L. Moon, High Temperature Phase Equilibria in The Lead Titanate-Lead Zirconate System, Ph.D. Thesis, Univ. of California, Berkeley, May 1967 (UCRL-17545).

5. B. Jaffe, R. S. Roth, and S. Marzullo, Properties of Piezoelectric Ceramics in the Solid Series Lead Titanate-Lead Zirconate-Lead Oxide: Tin Oxide and Lead Titanate-Lead Hafnate, N.B.S. 55, 239-254 (1955).

6. Saburo Mori, Hironuchi Mitsuda, Kenju Date, Yashuhiro Hioki and Toshihiko Mizazawa, Study of Formation Process of $Pb(Ti,Zr)O_3$ solid solution with High Temperature X-ray Diffractometry and Differential Thermal Analysis, Matsushita Electrical Ind. Co., Nat. Tech. Report 10, 1, p. 32-40 (1964).

FIGURE CAPTIONS

Figure 1. X-ray back reflection lines of calcined powder and the same powder reheated for 1-1/2 hours at 1200°C

Figure 2. Platinum crucible geometry and positioning method used for heating curve analysis.

Figure 3. Comparison of the phase equilibrium diagram determined by analysis of heating and cooling curves (thermal analysis) and by quenching methods.[3]

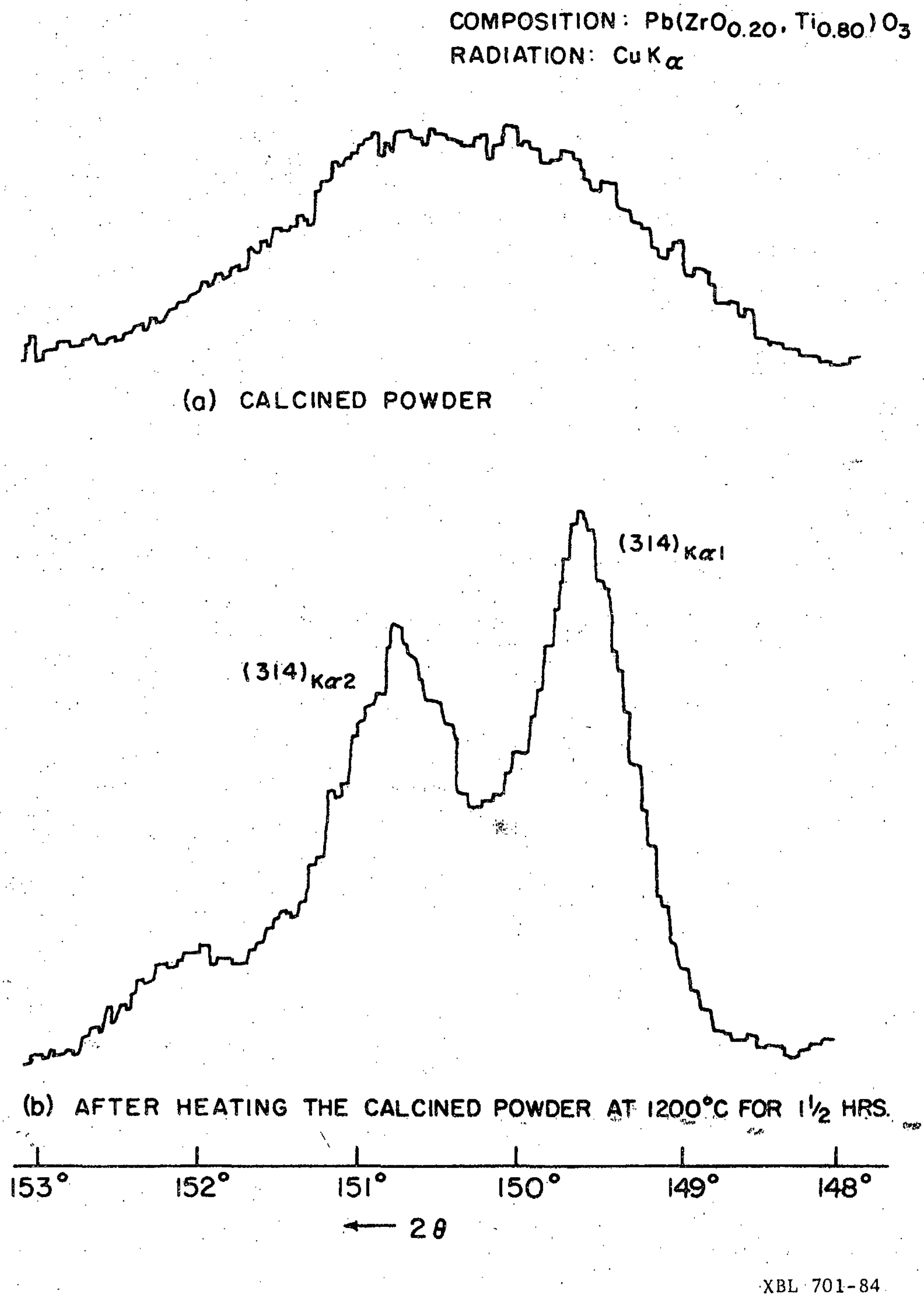

COMPOSITION: Pb(ZrO0.20, Ti0.80)O3
RADIATION: Cu Kα
(a) CALCINED POWDER
(314)Kα1
(314)Kα2
(b) AFTER HEATING THE CALCINED POWDER AT 1200°C FOR 1½ HRS.
153°
152°
151°
150°
149°
148°
← 2θ
XBL 701-84

Fig. 1

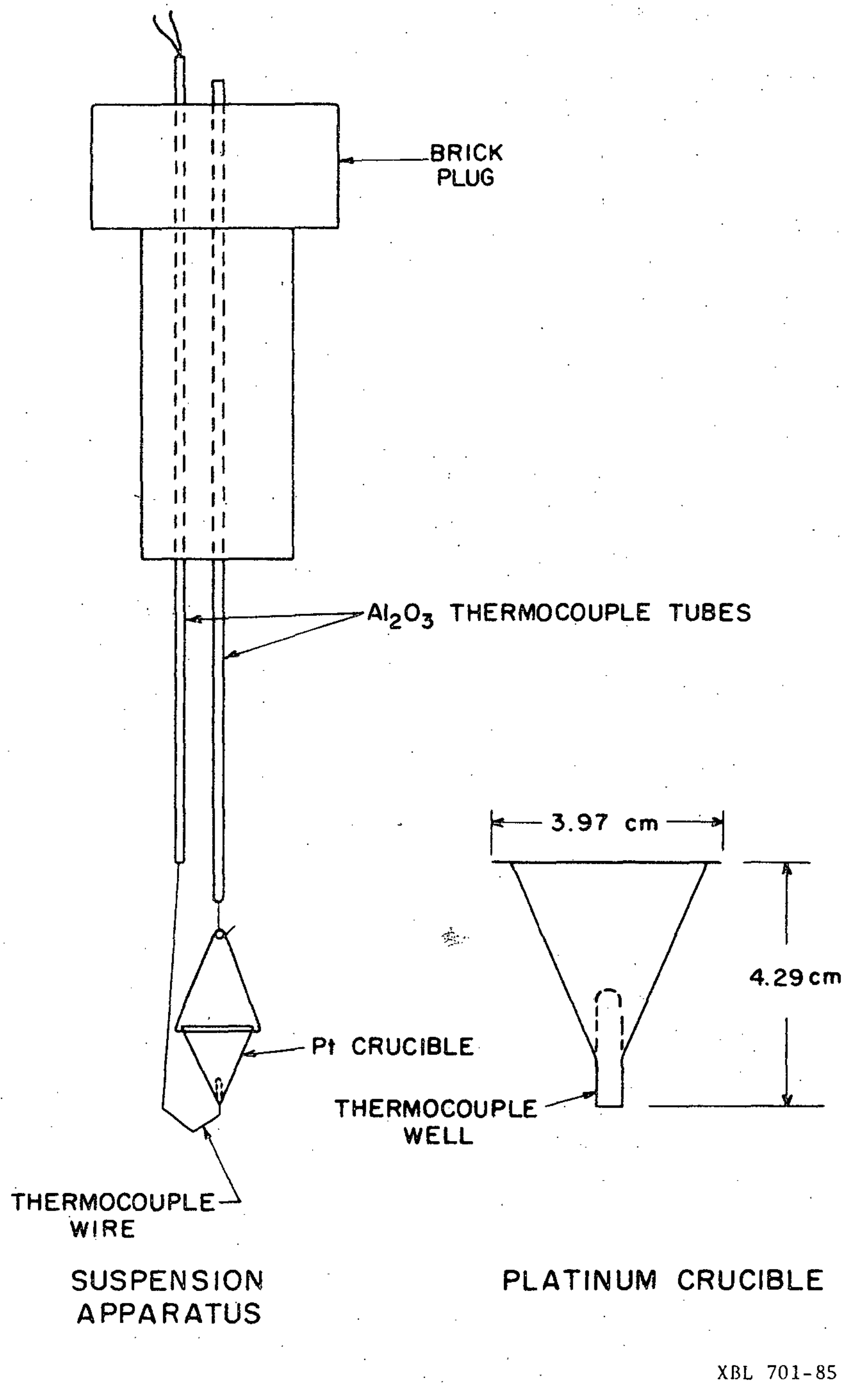
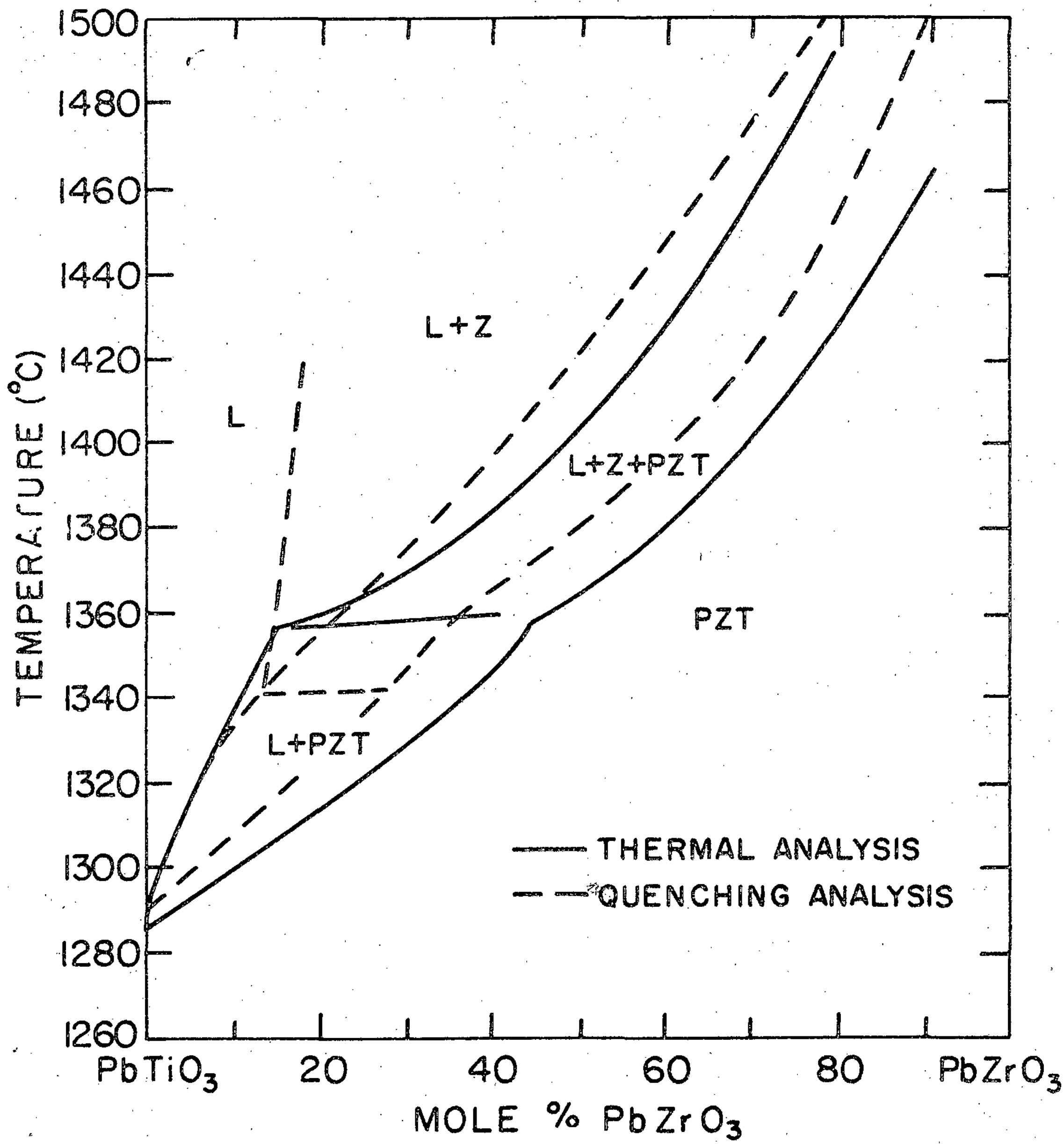

BRICK
PLUG
Al_2O_3 THERMOCOUPLE TUBES
Pt CRUCIBLE
THERMOCOUPLE
WIRE
SUSPENSION
APPARATUS
3.97 cm
4.29 cm
THERMOCOUPLE
WELL
PLATINUM CRUCIBLE
XBL 701-85

Fig. 2



L = LIQUID
Z = ZrO_2 RICH SOLID
PZT = LEAD ZIRCONATE TITANATE

XBL 701-86

Fig. 3

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