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VAPORIZATION AND SURFACE PHASES IN THE
LEAD ZIRCONATE-LEAD TITANATE SYSTEM

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Several papers on the vaporization of PbO from lead zirconate titanate (PZT) have shown a depletion layer to form as a result of the sublimation.¹⁻⁵ A layer deficient in PbO implies a compositional change at the surface of the specimen, resulting in the appearance of new crystalline phases as dictated by the PbO-TiO₂-ZrO₂^{6,7} phase relations. This has been suggested by Northrup's microprobe analysis of the surface of Pb(Zr_{0.65}Ti_{0.35})O₃ specimen following a Langmuir evaporation experiment.⁵ In addition the same study showed a parabolic weight loss below 50 tons and a linear weight loss about 150 tons at 1020°C. The effect that different ambient pressures have on the rate of weight loss may be influenced by the phases detected at the surface.

This investigation examined the phases appearing at the surface of a PZT compact, ranging in composition from a PT/PZ ratio of 95/5 to 30/70, following weight loss in air and vacuum at 1050°C.

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The microbalance was situated above a copper tee which connected to the vacuum system and to a mullite tube sealed at the bottom. The vacuum at temperature was 10^{-4} to 10^{-5} torr. Detection of the crystallographic phases present at the surface was achieved by removing the sintered specimen from its Pt suspension pan and placing it in an X-ray holder of a diffractometer.

In Table I, the phases detected after vaporization in vacuum at 1050°C for various PZ/PT ratios are summarized. The importance of the surrounding atmosphere is illustrated in Figs. 1 and 2. For example, if approximately 1% of the total weight is lost in air the PZT phase is still present on the surface, but for the same percentage loss in vacuum additional phases appear (Fig. 1). Also, if a sample previously heated in vacuum, resulting in the appearance of new phases, was reheated in air, the PZT phase would reappear, providing the weight loss had not been too large (Fig. 2).

A tentative explanation for this phenomena follows: As PbO is lost from the surface, the composition of the surface will move along a line of constant mole ratio of $\text{ZrO}_2/\text{TiO}_2$ towards the $\text{TiO}_2\text{-ZrO}_2$ binary on the ternary diagram, assuming that PbO is the only vapor species.

The phases present will depend upon whether a depletion layer is formed. If the diffusion of PbO to the surface is slow, the phases detected by X-rays will be mainly those lying off the line of 50 mole % PbO since the composition of the surface would rapidly lose PbO and other phases would appear. In vacuum the rate of PbO loss from the surface is fast, whereas in air the rate of removal of PbO vapor from the sample is much slower due to the presence of a gas above the surface.

Therefore, the time required to lose a given weight in vacuum is shorter than the time necessary to lose the same amount in air. The longer time in air allows diffusion to replenish the surface with PbO and yields a surface that more nearly reflects the average composition of the solid; new phases are not detected until a larger percentage of PbO is lost. Treating a vacuum sample in air allows the PbO to redistribute in the solid. For the surface, this means moving on a line of constant Zr/Ti ratio towards the PbO vertex of the ternary diagram. A sufficient amount of PZT will reform, by reaction of the PbO with the TiO₂ and ZrO₂ present at the surface, and be detected again by X-ray analysis.

The effect air has on the sample could also be explained by the oxidation of the divalent lead ion to its tetravalent state. As a result, a lead ion vacancy would be created. This would enhance the lead ion mobility in an air atmosphere. In vacuum the vacancy concentration would decrease and a depletion layer would form. The reaction $2\text{Pb}^{2+} + 1/2 \text{O}_2 \rightarrow \text{Pb}^{4+} + \text{PbO} + \square$ has been reported to take place in the PZT system.⁸ In either case, the results are explained by a deficiency of PbO near the surface which results in the appearance of other phases.

ACKNOWLEDGMENT

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Table I. Phases detected after sublimation of
lead oxide in vacuum at 1050°C

Mole % PbTiO ₂	Phases present after wt. loss in vacuum	Approximate % loss
95%	Anatase, TiO ₂ , rutile, TiO ₂ , 95% PZT	5%
90%	Anatase, TiO ₂ , rutile, TiO ₂ , 95% PZT	3%
85%	ZrO ₂ •TiO ₂ , rutile, PZT	7.6%
85%	Trace ZrO ₂ ?, ZrO ₂ •TiO ₂ , rutile, PZT	20%
85%	(cooled in vacuum)	
	ZrO ₂ ?, ZrO ₂ •TiO ₂ , rutile, PZT	18%
75%	ZrO ₂ •TiO ₂ , PZT	--
47.5%	ZrO ₂ , rutile, ZrO ₂ •TiO ₂ , PZT	21%
30%	ZrO ₂ , PZT tetrag. (ZrO ₂ •TiO ₂ or PZT rhomb)	23%

FIGURE CAPTIONS

- Figure 1. Comparison of X-ray diffractometer patterns between samples which lost weight in air and in vacuum. /
- Figure 2. X-ray patterns showing effect of air treatment to a sample previously heated in vacuum.

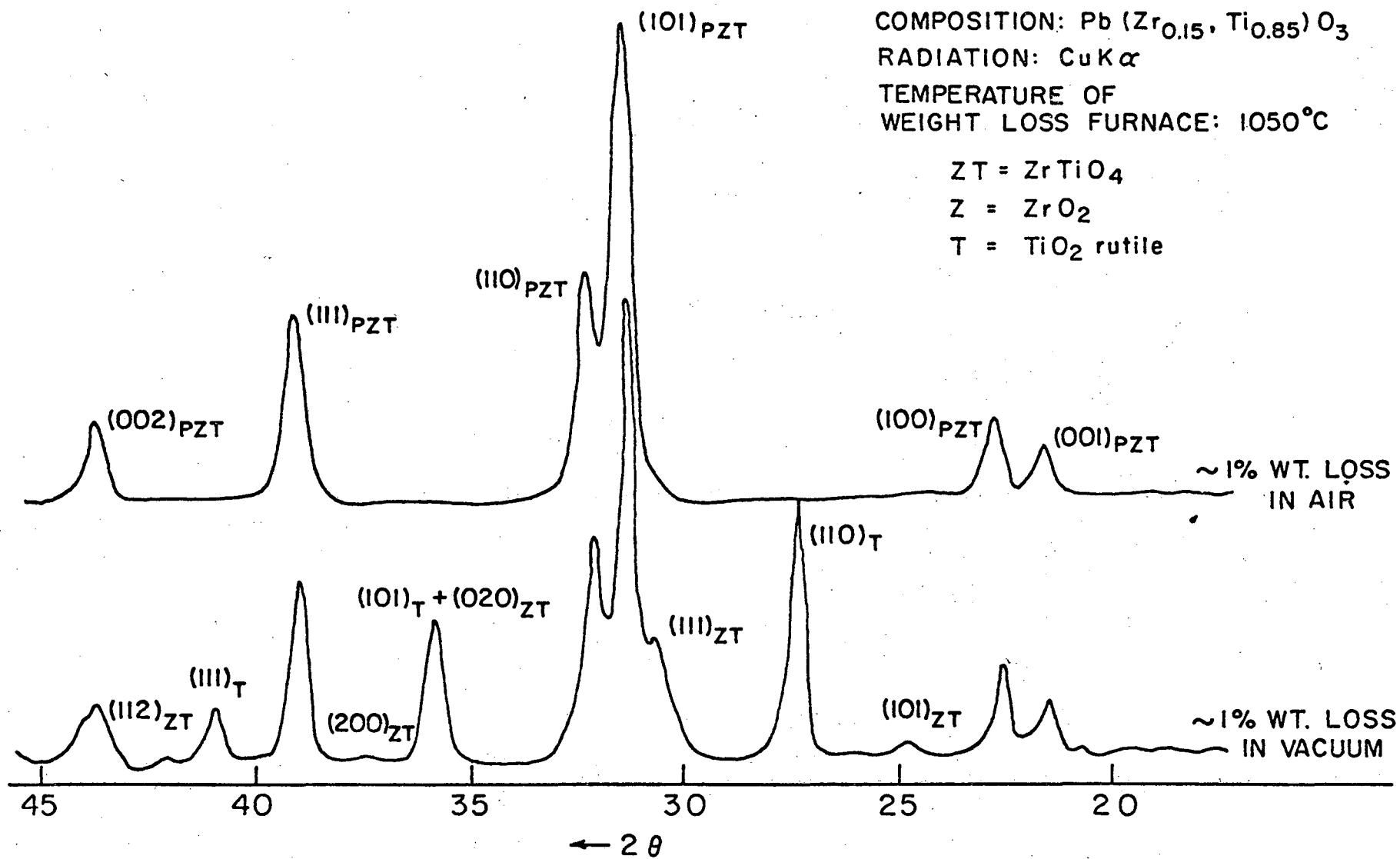


Fig. 1

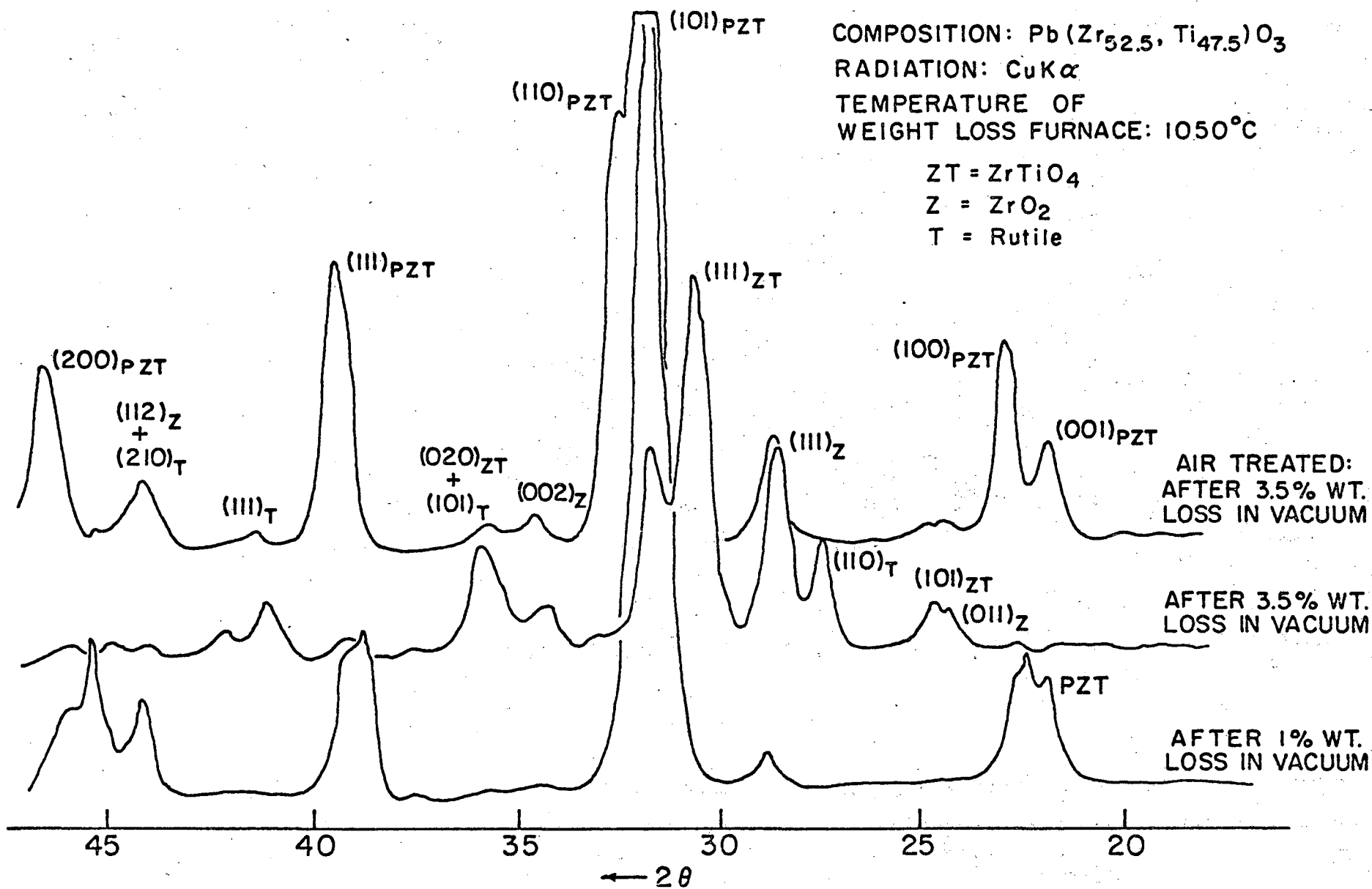


Fig. 2

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