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DENSIFICATION OF PZT CERAMICS WITH V205 ADDITIVE.(U)

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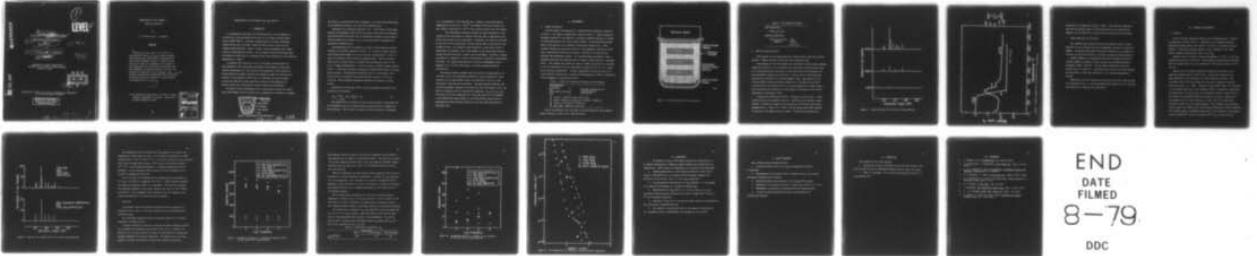
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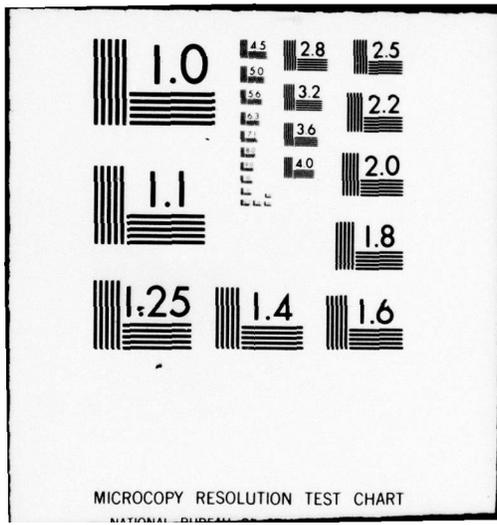
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DENSIFICATION OF PZT CERAMICS

WITH V_2O_5 ADDITIVE *

by

D. E. Wittmer and R. C. Buchanan

ABSTRACT

↓
Additions of V_2O_5 from 0.1 to 8.0 w/o to a coprecipitated $Pb(Zr_{.53}Ti_{.47})O_3$ ceramic promoted rapid densification below $1025^\circ C$, eliminating the need for PbO atmosphere control. Dielectric properties were found to be dependent on the amount of V_2O_5 added and on the microstructure developed, but were comparable to reported values for this PZT composition for additions of $V_2O_5 \leq 1.5$ w/o. The ϵ = indicated densification mechanism is one of activated sintering catalyzed by generation of oxygen defects on decomposition of the V_2O_5 . ↗

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Densification of PZT Ceramics with V_2O_5 Additive

I. INTRODUCTION

In conventional sintering of PZT ceramics, control of the atmosphere is critical due to the associated PbO activity at the normal sintering temperatures (1200°C-1350°C). Typically, packing powders or pellets containing excess PbO are used to provide a known PbO vapor pressure around the PZT ceramics during sintering. Figure 1 shows a typical arrangement used commercially for sintering PZT ceramics. The PZT samples shown had previously been hot-pressed at 1200°C prior to undergoing final stage sintering in the protective atmosphere at ~ 1320°C.

A technique that involves the use of a multiphase packing powder has been reported to give reproducible processing of PZT composites while maintaining stoichiometry.[1] More recently the preparation of PLZT powders by precipitation from organic solutions was reported to lower the sintering temperature of the compacts to 1120°C for 8 hr soak-time, but this technique required the addition of 10% excess PbO to allow for volatilization.[2] Precise control over stoichiometry therefore could not be maintained.

The object of this investigation was to explore ways in which the sintering of PZT ceramics could be carried out at temperatures low enough to eliminate

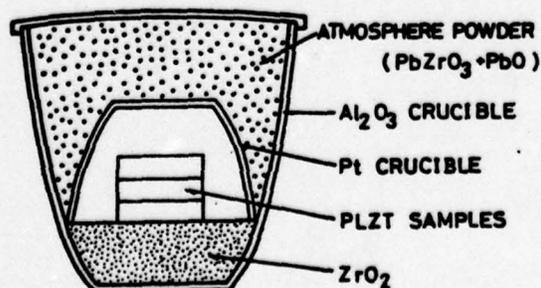


FIGURE 1 Physical arrangement for second stage sintering. [1]

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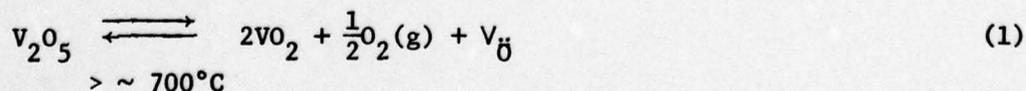
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the need for a controlled PbO vapor atmosphere, at the same time maintaining, or not adversely affecting, the electrical characteristics.

Lowering of the sintering temperature (to $< 1025^{\circ}\text{C}$ where the PbO vapor pressure is negligible) would provide for greater control over stoichiometry and microstructure and should lead to significant economies in processing of PZT and similar type ceramics, due to the expected faster throughput and simplified processing steps.

Approaches which were investigated in order to bring about the desired reduction in sintering temperature include: a) The use of highly reactive coprecipitated PZT powders; b) the use of small concentrations (< 2 w/o) of V_2O_5 as an additive, which typically decomposes above $\sim 700^{\circ}\text{C}$ to provide a ready source of oxygen defects to enhance the sintering rate; and c) The use of a higher concentration (> 3.0 w/o) of V_2O_5 to provide a highly reactive liquid $> \sim 850^{\circ}\text{C}$, which provides a mechanism for rapid densification via liquid-phase sintering. The distinction between (b) and (c) is not sharp, since oxygen defects are formed in both cases and play an active role in the sintering. Which mechanism predominates depends on the amount of liquid present.

Indications are that above 700°C , the V_2O_5 decomposes reversibly [3,4] according to the reaction:



The oxygen which is liberated in this reaction provides a ready means for pore elimination, while the oxygen vacancies generated serve to enhance the bulk diffusion. The net result of these activation processes or mechanisms

is an acceleration in the sintering rate leading to lower densification temperatures for the solid. The V^{4+} ions formed in the above reaction are most likely to substitute for Zr^{4+} in the B lattice sites of the PZT ceramics.

For liquid-phase sintering an amount of liquid sufficient to completely wet the solid phase is required, and there must be appreciable solubility of the solid in the liquid phase. In general, the lower the solubility of the solid in the liquid phase, the more liquid phase is required for this process to occur. For systems of high solubility, a much lower volume of liquid phase is necessary, since areas exposed to the liquid phase dissolve quickly and thus facilitate a greater rate of shrinkage. According to Cannon and Lenel,[5] a minimum of 5 vol% of liquid phase is required for liquid-phase sintering. For complete densification by particle rearrangement alone, a minimum of 25 to 35 vol% liquid phase is required (assuming spherical particles).[6]

Low-melting vanadate compounds have been used for fluxing glasses, for colorants, and in the liquid-phase sintering of zircon ceramics.[4] Since vanadium can form multivalent cations, the possibility of its use in PZT liquid-phase sintering was investigated. The phase diagrams indicated that low-melting vanadate compounds of zirconia and lead could possibly occur, and might be compatible with the selected PZT composition. $Pb_{1.0}(Zr_{.53}Ti_{.47})O_3$ was chosen as the base composition for this study because of its proximity to the morphotropic phase boundary in the $PbZrO_3$ - $PbTiO_3$ system (which is associated with high coupling coefficients) and the ready availability of literature data.

II. EXPERIMENTAL

1. Sample Preparation

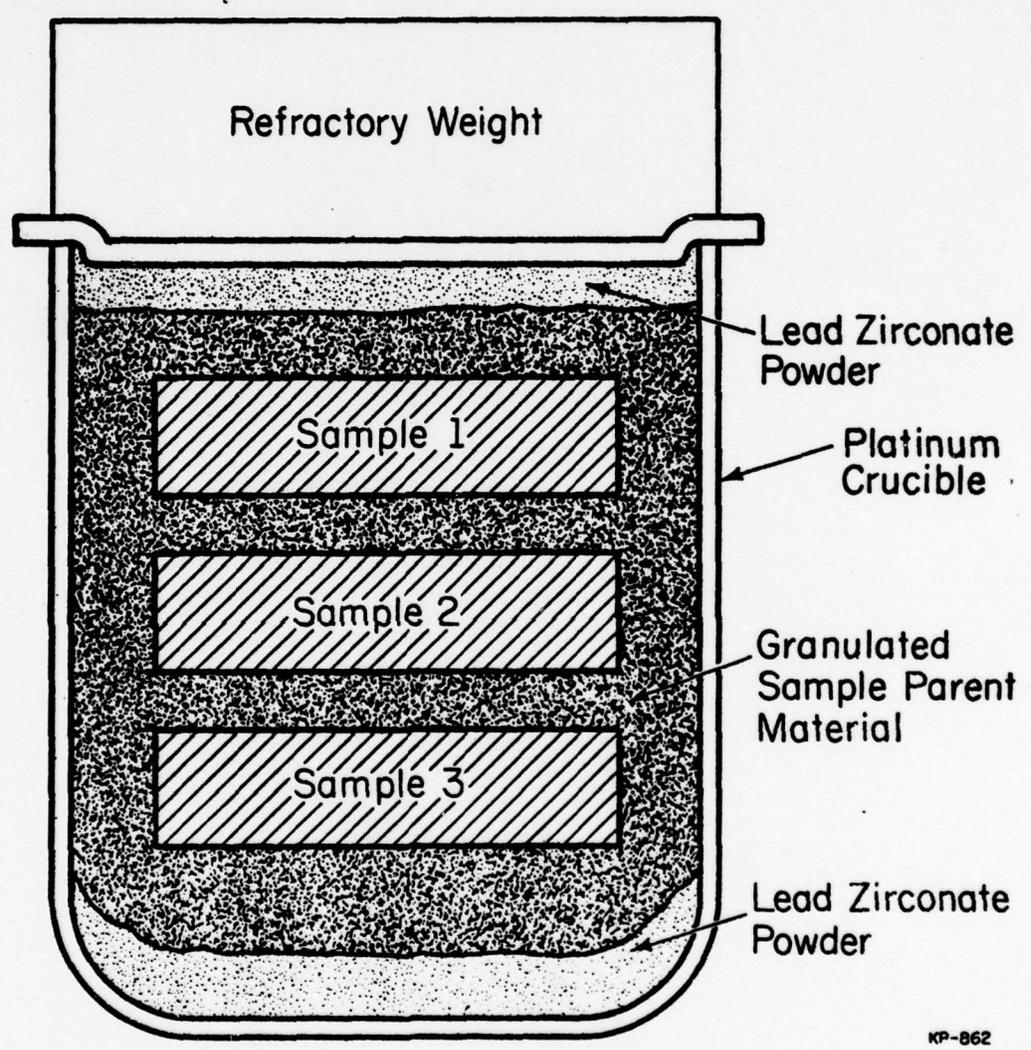
The PZT powders were prepared by a coprecipitation technique as indicated in Table 1. The range of compositions is given in Table 2. Sample preparation procedure consisted of the addition of electronic grade PbO and V_2O_5 to a blend of zirconium-n-butylate and tetra-n-butyl-titanate. Precipitation was brought about by the addition of an isopropyl alcohol-water mixture (2:1). After intimate blending the mixures were dried at room temperature and then at 150°C. After screening the batches were calcined ($\sim 550^\circ\text{C}/4$ hr) to drive off the butylates and carbonaceous residue. The calcined powder was ground to pass a 100-mesh screen and then dispersed with or without a binder (1% PVA or distilled water). Disc samples were pressed at 5,000 to 35,000 psi and were then sintered in air on a platinum foil in the range 890°C to 1025°C for 1/2 to 8 hrs depending on the V_2O_5 concentration. The base composition (no V_2O_5) was fired in a closed platinum crucible with a protective PbO atmosphere at 1280°C to 1300°C/4 hr.

This arrangement is illustrated in Fig. 2

Table 1. Outline of Preparation Procedure for PZT Ceramics

<u>PZT Preparation</u>	
Zr Butoxide	} Blend ① coprecipitate in isopropanol/water solution ② .
PbO	
Tetra-n-Butyl-Titanate	
V_2O_5	
③ Calcine $\sim 550^\circ\text{C}/1$ hr (Base $875^\circ\text{C}/1$ hr)	
④ Binder, disperse, screen, press (30,000 \pm 5,000 psi)	
⑤ Sinter in air 875°C to $1025^\circ\text{C}/2$ hr.	
⑥ Base comp: $1280^\circ\text{C}/4$ hr (Pb atm).	

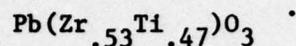
Density determination were then made on sintered samples by the suspended weight technique in water and by bulk measurement.



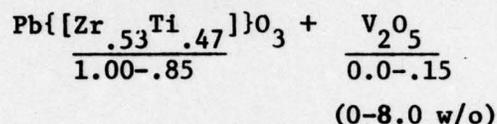
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Figure 2. Closed platinum cell for firing PZT.

Table 2. PZT Composition Ranges

 Base Composition:


Modified Composition:



2. Material Characterization

Dried powders for all compositions were characterized by XRD, TGA, and DTA analysis. Powders calcined at 550°C were also analyzed by XRD.

X-ray analysis of the dried powders were performed by powder camera technique using Cu-K α radiation. For all powders four faint lines were noted which could not be characterized and the absence of any back-scatter lines indicated that any crystallites present were very small. A "fuzzy halo" at low-diffraction angle was also indicative of a nearly amorphous state. XRD analysis of the calcined powders indicated definite formation of a PZT phase even at 550°C. A typical X-ray line pattern for PZT + 1.5% V₂O₅ composition is shown in Fig. 3. This illustrates the formation of the PZT phase on calcining at 550°C and its enhancement on sintering at 975°C.

A typical TGA and DTA plot for PZT + 3.0% V₂O₅ is given in Fig. 4. Both curves illustrate the pyrolysis effect at ~ 300°C due to the butylate decomposition. Virtually no weight loss is observed on the TGA after the initial decomposition at ~ 300°C up to ~ 960°C. Further heating above 960°C resulted in less than 0.13% weight loss up to 1000°C. The DTA curves indicate the

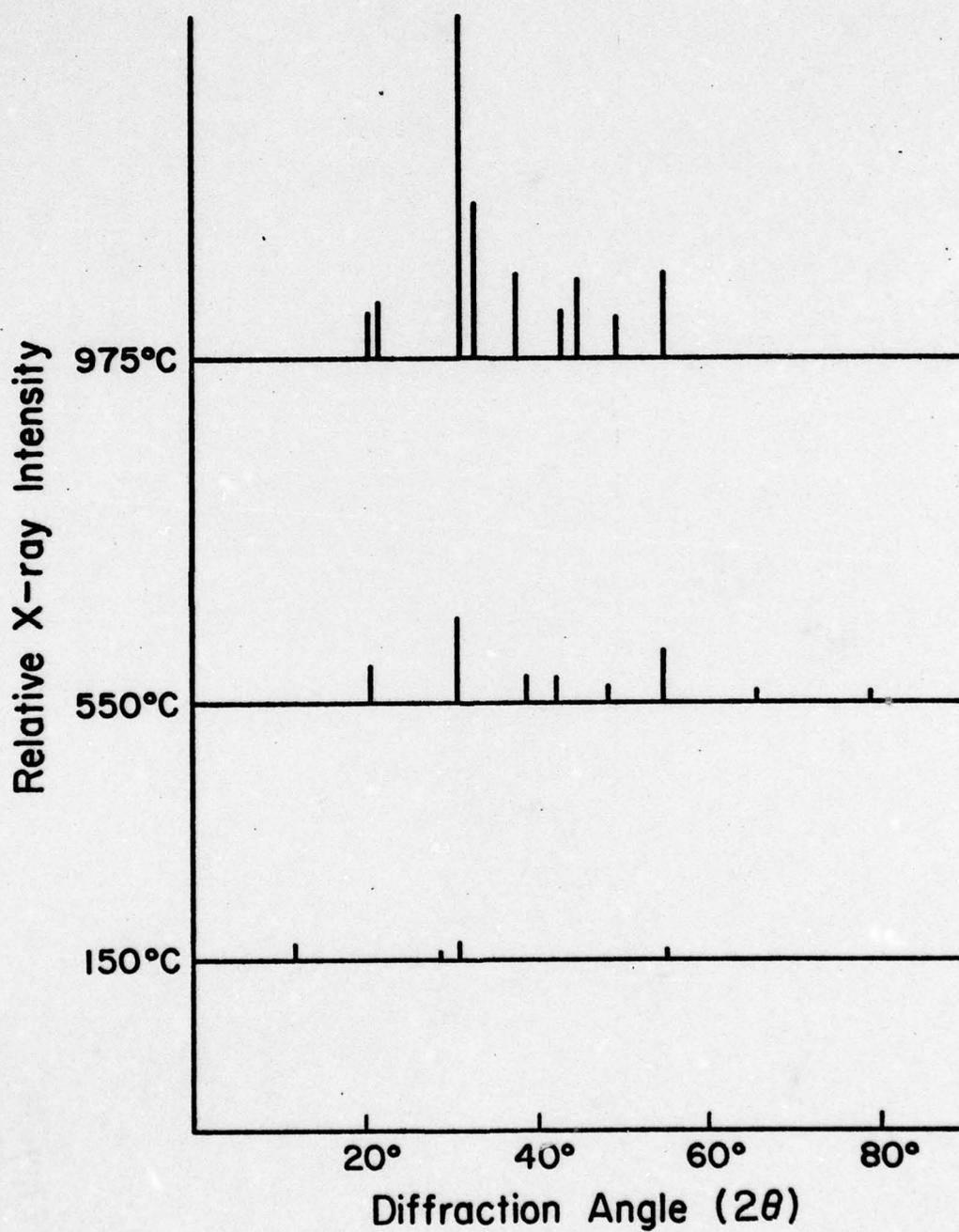


Figure 3. Typical XRD data for PZT with 1.5% V₂O₅ addition.

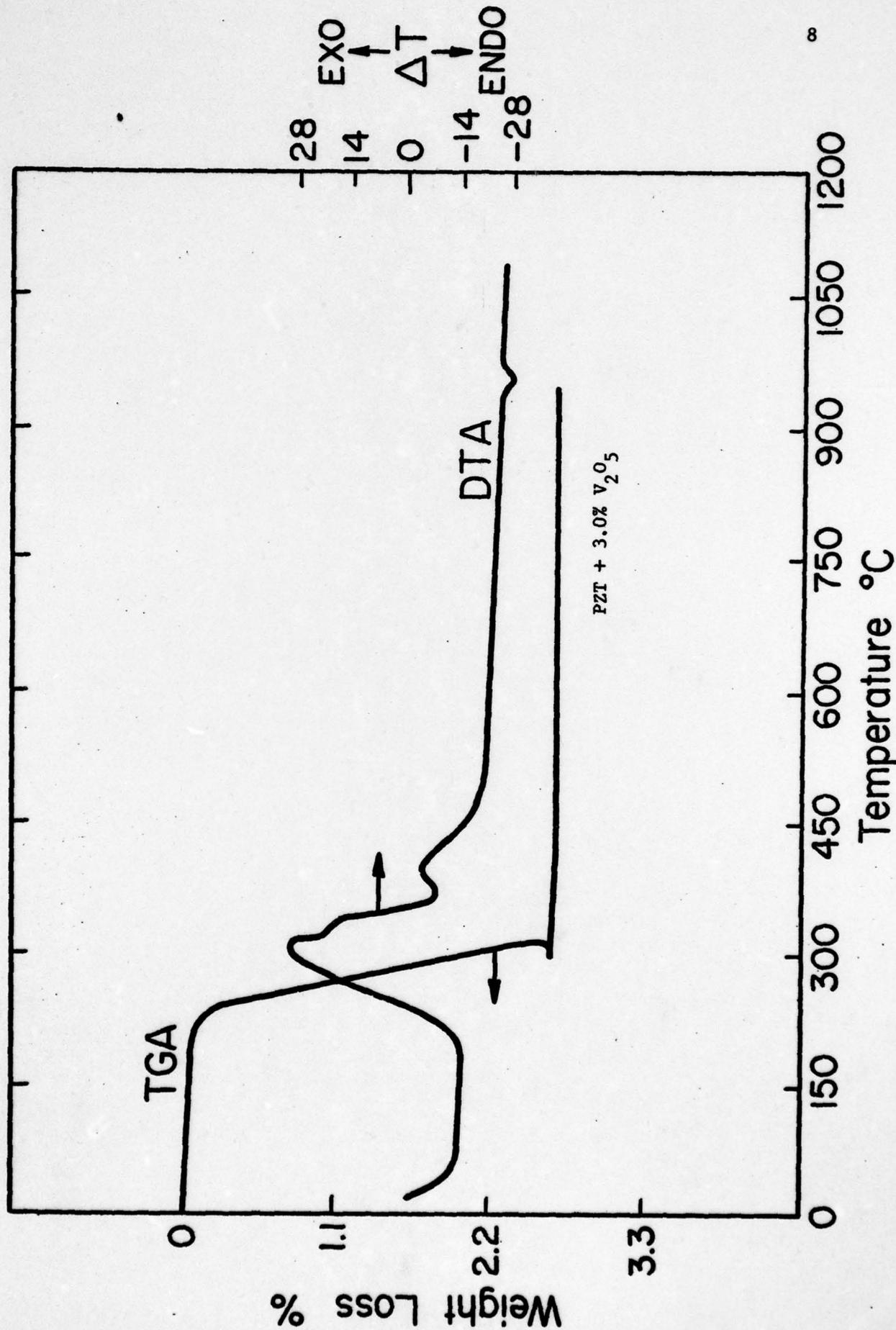


Figure 4. Typical thermal data for PZT with 3.0 w/o V₂O₅ addition.

initiation of an endothermic reaction $\sim 890^{\circ}\text{C}$. This coincides reasonably well with the observed onset of rapid densification of the sintered PZT compacts, and is indicative of the activation sintering process described.

3. Powder Compaction and Sintering

PVA, Carbowax 4000, and water were used at different times as binder additions to aid in pressing the dried, granulated, calcined, or uncalcined powders. The pressure was varied from 5,000 to 40,000 psi in increments of 5,000 psi to observe the effects of pressure on green and sintered density.

Optimum conditons for pressing were obtained by milling the dried or calcined powders in isopropyl alcohol, drying, and screening followed by pressing at $30,000 \pm 5,000$ psi. No real density differential was noted between 25,000 to 35,000 psi. Calcination was carried out by slowly heating the dry powders to 550°C . and holding for 4 hr to ensure decomposition of butylate.

Sintering of the base composition was carried out in the closed platinum cell indicated in Fig. 2. All other samples were sintered in air on platinum foil supported by stabilized ZrO_2 substrates.

III. RESULTS AND DISCUSSION

1. Sintering

A plot of percent theoretical density for all compositions as a function of temperature is shown in Fig. 5. Generally for all vanadium-containing compositions maximum density was realized $\sim 975^\circ\text{C}/2$ hr, the samples being air quenched. Slow furnace cooling resulted in some "puddling" of the liquid phase in samples containing more than 2.5 w/o V_2O_5 .

Figures 6 and 7 are typical fractured micrographs of a PZT + 0.1 w/o V_2O_5 composition sintered at $1025^\circ\text{C}/3$ hr. These samples were approximately 98% dense with the optimum density for this composition ($> 99\%$) being obtained at 975°C for 2 hr.

XRD data for the sintered compositions indicated the presence of the expected tetragonal phase for PZT (53-47). For the base composition and small additions of V_2O_5 the degree of lattice distortion is small. This is evident from the c/a ratio being near unity and the absence of specific diffraction lines, i.e., (001). Additions of V_2O_5 greater than 1.5 w/o resulted in a noticeable distortion of the tetragonal lattice, indicated by a splitting and slight shift of certain lines in the diffraction pattern shown in Fig. 8. The increase in tetragonal distortion (increased c/a ratio) is likely due to an elongation of the c axis resulting in a larger unit cell, hence lower theoretical density for the sintered samples. This elongation would indicate a shift towards the PbTiO_3 end of the PZT system indicating a relative depletion of the PbZrO_3 phase. A reasonable explanation of this behavior is the substitution of vanadium (V^{4+}) ions for zirconium (Zr^{4+}) ions in the PZT lattice.

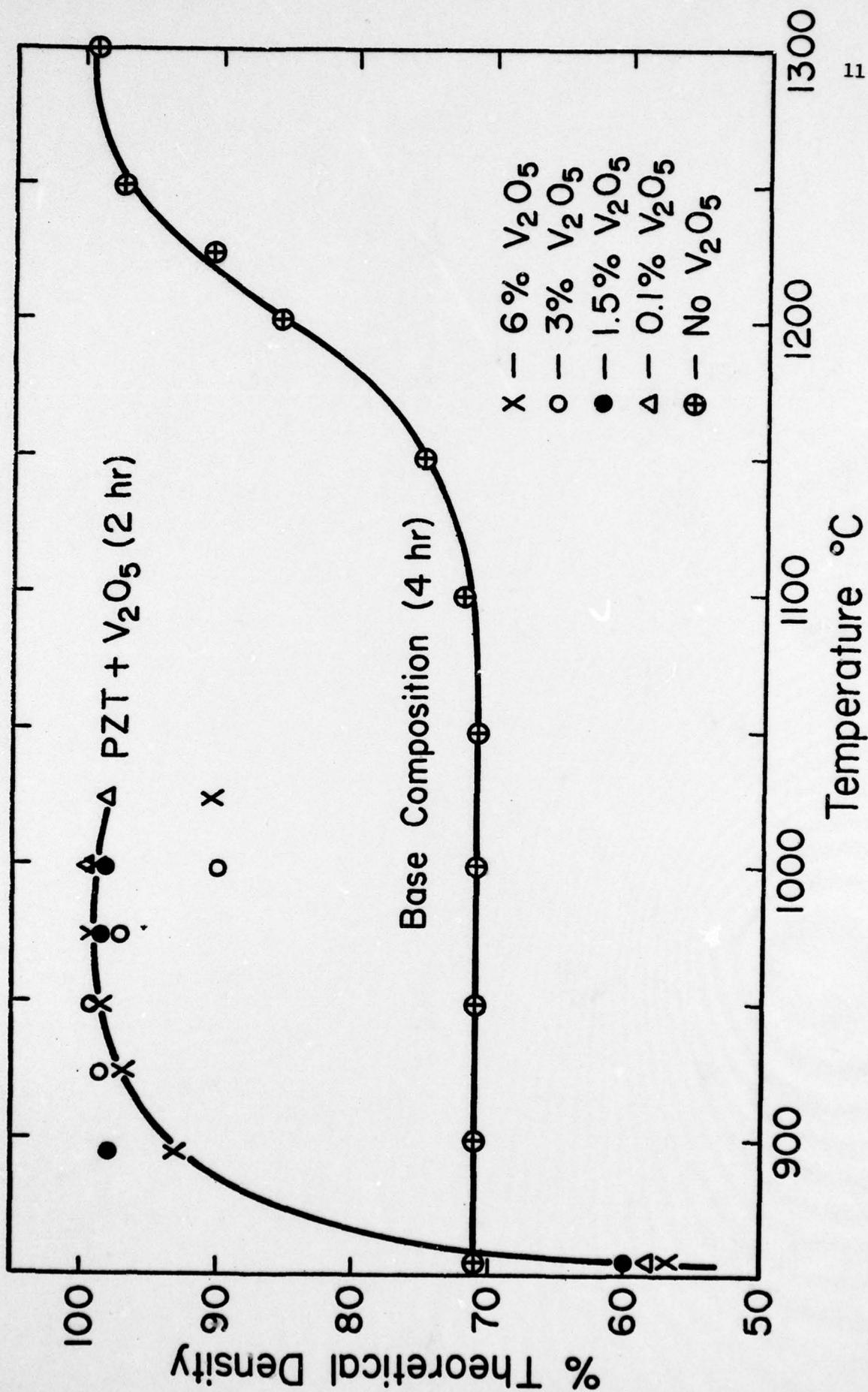
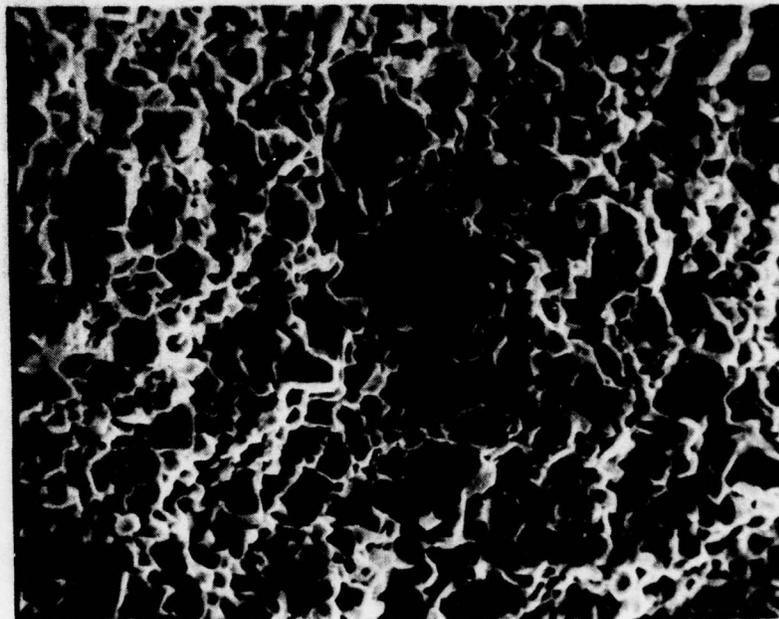
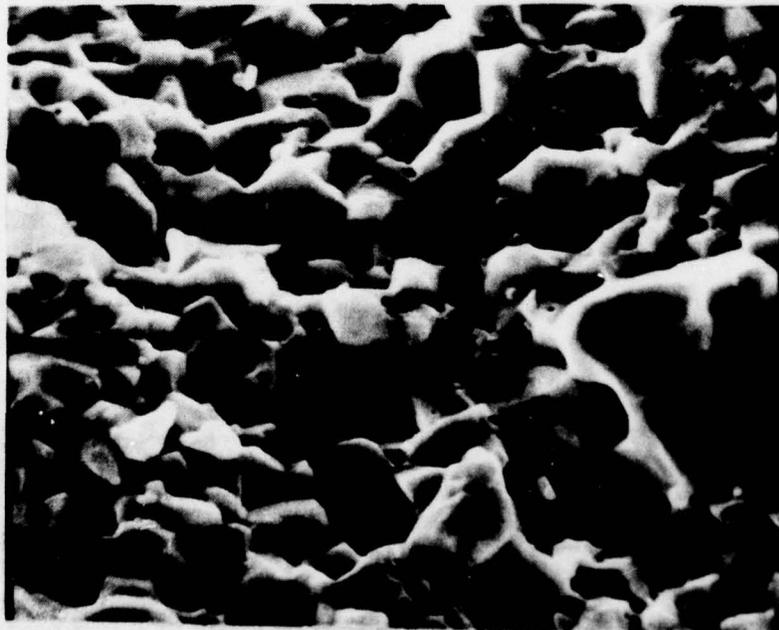


Figure 5. Percent theoretical density as a function of sintering temperature for PZT (53-27) ceramic.



1000X

Fig. 6. SEM micrograph of fracture surface for PZT (0.1 w/o V_2O_5) ceramic sintered at 1025°C/3 hr.



3000X

Fig. 7. Enlarged view of fracture surface in Fig. 6. (PZT 0.1 w/o V_2O_5 -- 1025°C/3 hrs).

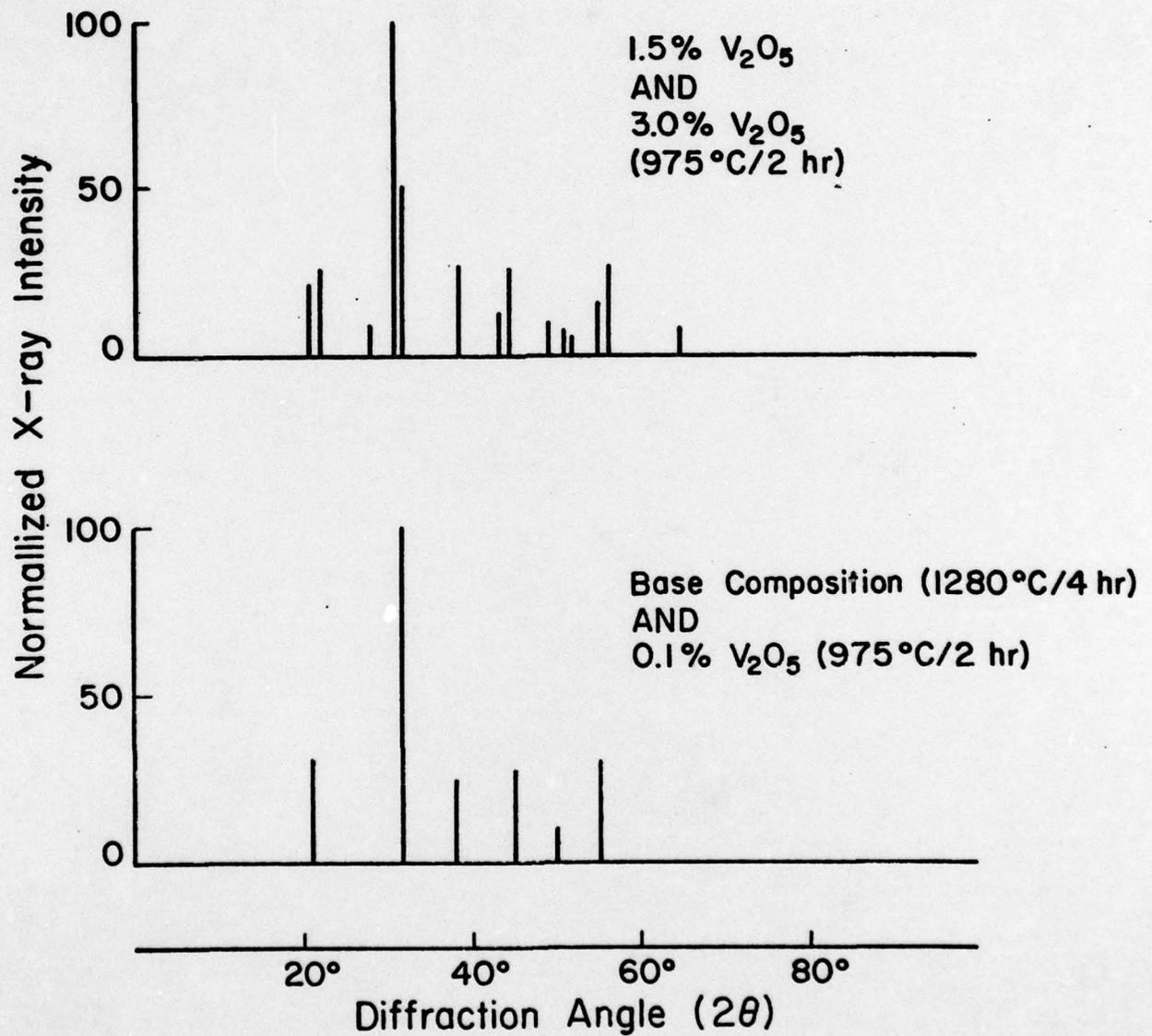


Figure 8. XRD data for sintered PZT with and without V_2O_5 additions.

The sintering of PZT with additions of V_2O_5 appears to be aided by the formation of a liquid phase for $V_2O_5 > 2.5$ w/o while the mechanism for densification below 2.5 w/o is likely to be by an activated sintering process catalyzed by the loss of oxygen from the V_2O_5 . This occurs on the change of valence ($V^{5+} \rightarrow V^{4+}$) with increasing temperature. A similar mechanism was noted by Kulikowski in the sintering of Ni-Zr ferrites,[7] and by Blackman in the sintering of magnesium ferrites.[8]

The use of V_2O_5 as a sintering aid was demonstrated by the addition of 0.03 V_2O_5 + 0.06 PbO to a commercial PZT (53-47). Normal blending techniques were used with isopropyl alcohol as a dispersant. After drying, screening, and pressing (15,000 psi), the ceramic compacts were fired to > 98% density at 975°C/2 hr. The recommended firing temperature for the commercial composition was 1230°C/4 hr in protective PbO environment.

2. Properties

The properties which were measured included dielectric constant (k'), dissipation factor ($\tan \delta$), electrical conductivity (σ), and piezoelectric coefficient (d_{33}).

The relationship observed between the measured values for k' and $\log f$ (frequency) is shown in Fig. 9.

A definite reduction in dielectric constant and greater frequency stability is apparent for additions of V_2O_5 greater than 1.5 w/o. Generally, an addition of 1.5 w/o V_2O_5 resulted in nearly the same dielectric constant and frequency dependence as the base composition. The addition of 0.1 w/o V_2O_5 appears to increase the dielectric constant and frequency sensitivity.

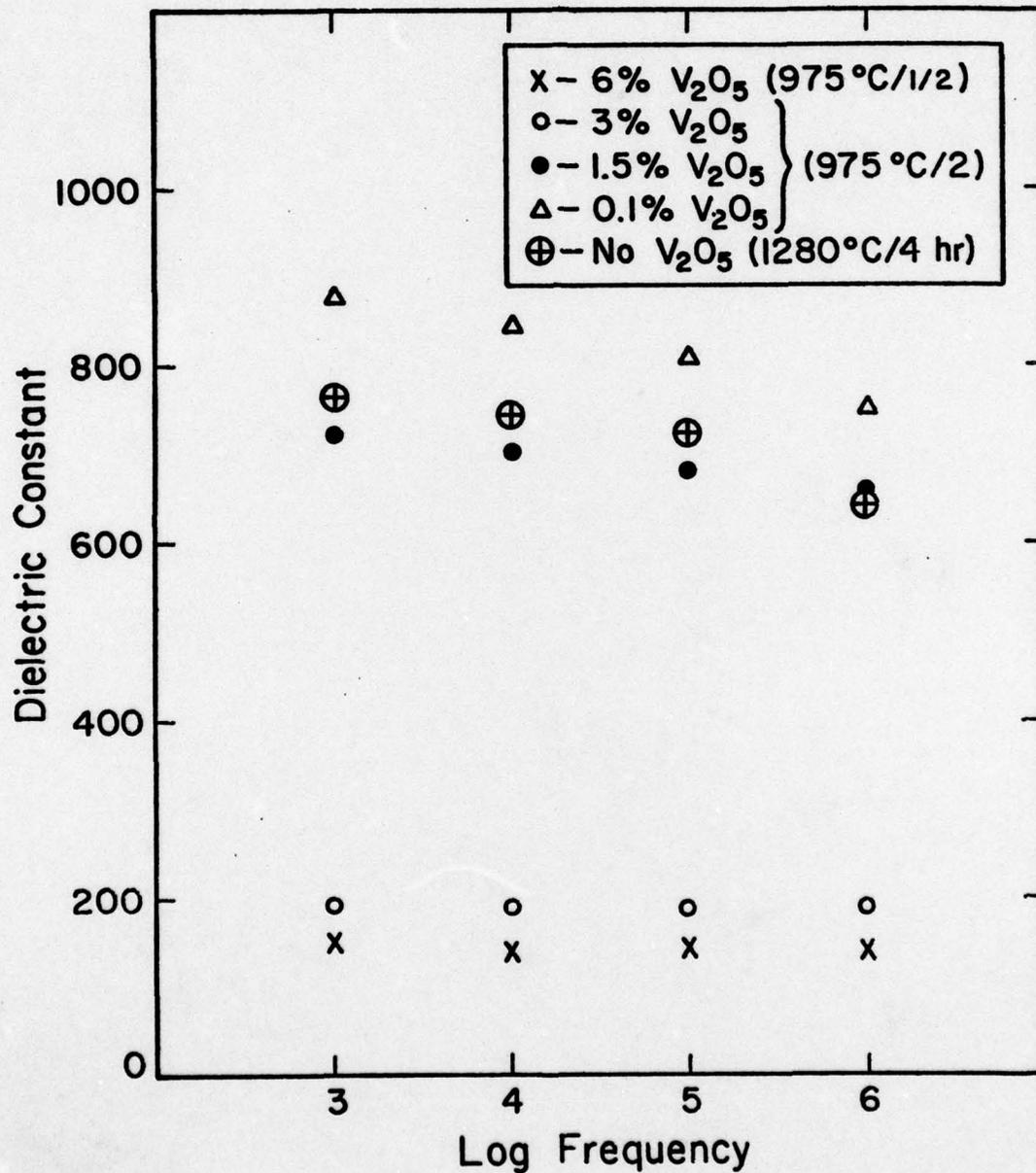


Figure 9. Dielectric constant as a function of frequency (log f) for PZT (53-47) with V_2O_5 additions.

This behavior could be related to the structure dependence on the amount of V_2O_5 additive and the amount of liquid phase present. The dielectric constant for the base composition and for the 1.5 w/o V_2O_5 addition (700-800) compares favorably with the value for k' (25°C, 1 KC) of 600-800 reported by Jaffe, Cook, and Jaffe.[9]

Figure 10 illustrates the relationship between dissipation factor and log frequency for the PZT composition investigated. Generally for V_2O_5 additions of 1.5 w/o and greater, $\tan \delta$ decreases as a function of frequency and for additions of V_2O_5 less than 1.5 w/o $\tan \delta$ increases as a function of frequency. This behavior may be due to a combined piezoelectric effect and a shift in the resonant behavior.

The dc conductivity relationship as a function of inverse absolute temperature is shown in Fig. 11 for V_2O_5 additions of 1.5-6.0 w/o and for PZT from Jaffe, et al.[9]. Generally, the conductivity at temperatures above 225°C exhibits similar behavior; indicating similarity in conduction mechanisms.

The piezoelectric coefficient, d_{33} , was measured for the base composition and for the 1.5 w/o V_2O_5 addition. Both were poled at 150°C and 100 V/mil with the field maintained while cooling to room temperature. The results shown in Table 3 indicate close agreement between d_{33} measured and d_{33} for PZT (53-47) reported by Jaffe, et al.[9]

Table 3. Piezoelectric Coefficient, d_{33}

	Composition		
	Base	1.5 w/o V_2O_5	PZT (53-47)[9]
$d_{33} (\times 10^{12} \text{C/N})$	160	130	180

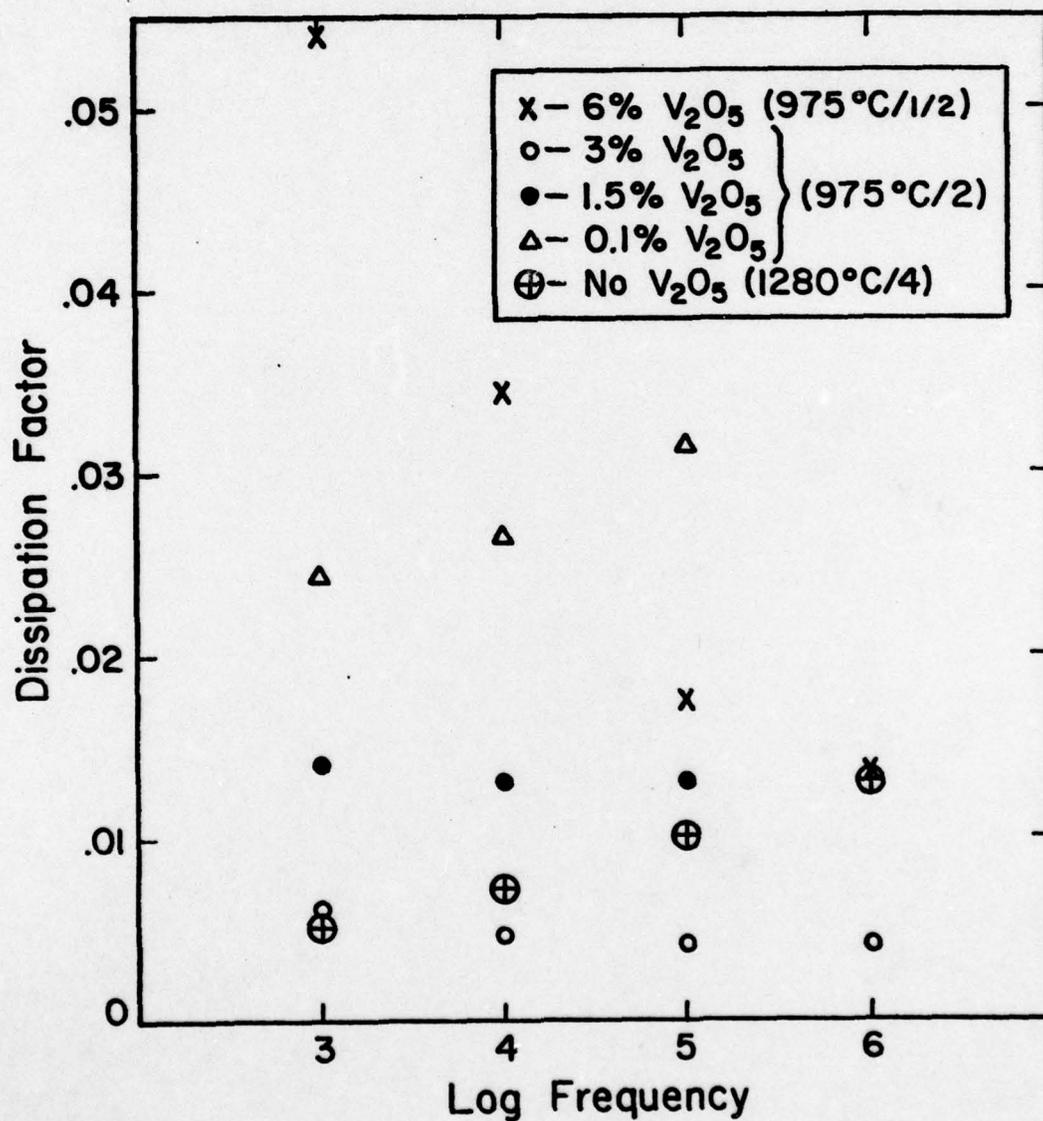


Figure 10. Dissipation factor as a function of log frequency for PZT (53-47) with V_2O_5 additions.

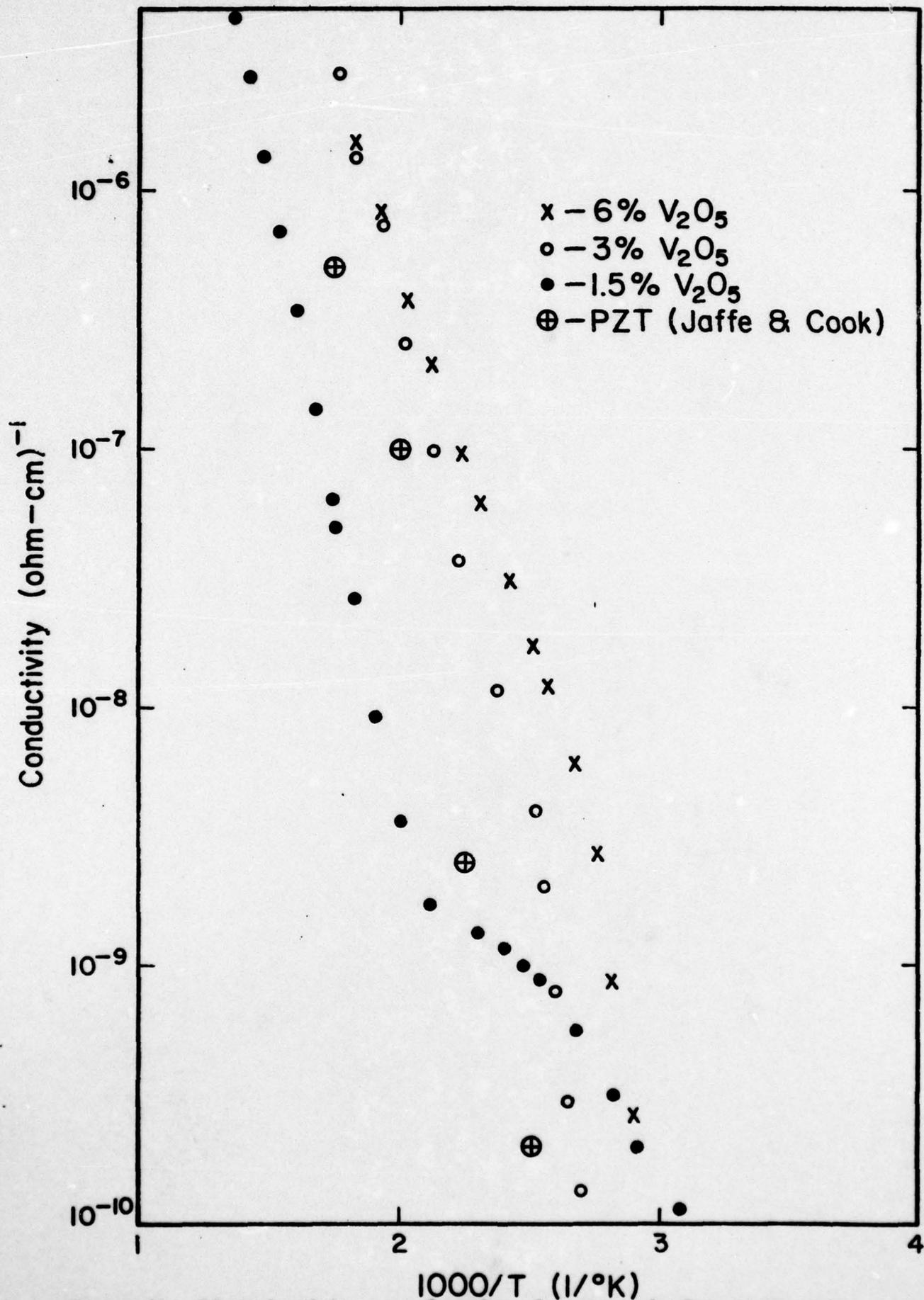


Figure 11. DC conductivity as a function of inverse absolute temperature.

IV. CONCLUSIONS

1. The addition of V_2O_5 to PZT powders prepared by coprecipitation or by regular blending with a commercial powder promoted rapid densification at temperatures $\leq 1025^\circ\text{C}$ without the maintenance of a protective PbO environment.
2. Optimum densification ($> 99\%$ theoretical density) for PZT (53-47) occurs at $1280\text{--}1320^\circ\text{C}/4$ hr in a protective PbO environment compared with $975^\circ\text{C}/2$ hr in air for PZT (53-47) + 1.5 w/o V_2O_5 composition.
3. The mechanism for densification for V_2O_5 additions > 2.5 w/o appears to be aided by the formation of a low-melting liquid phase.
4. Densification for V_2O_5 additive < 2.5 w/o is likely to be by an activation sintering process catalyzed by the loss of oxygen when V^{5+} goes to V^{4+} with increased temperature.
5. Additions of V_2O_5 near 1.5 w/o had only minor effects on the dielectric and piezoelectric properties measured.
6. The addition of V_2O_5 greater than 1.0 w/o results in distortion of the tetragonal lattice, corresponding to an increase in the c/a ratio.

V. WORK IN PROGRESS

Work currently being undertaken include:

1. A detailed study of the role of V_2O_5 on mechanism and kinetics of sintering.
2. Determination of the valence state of vanadium cations in the system from powder through sintered ceramics.
3. Detailed microstructural analysis of the sintered PZT ceramics.
4. Expansion of the composition matrix to include V_2O_5 from 0.1 to 1.5 w/o.
5. Measurement of piezoelectric coupling factors by resonant method.
6. A study of poling parameters and effect on polarization and piezoelectric behavior.

VI. FUTURE WORK

Work planned for the future include:

1. Application of V_2O_5 as sintering aid for other PZT systems. This would include the use of low-melting vanadates such as ZrV_2O_7 and $Ca_2V_2O_7$.
2. Effect of atmosphere on the sintering mechanism and kinetics of V_2O_5 modified PZT.

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