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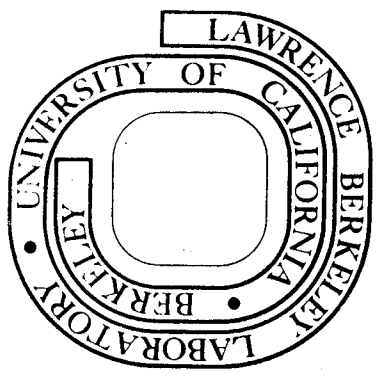
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## SINTERING OF Sc MODIFIED LEAD ZIRCONATE-TITANATE

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## ABSTRACT

Lead zirconate-titanate (PZT) is an important ceramic material widely used for piezoelectric devices.<sup>1,2</sup> Defect structures in PZT have been reported to affect the electrical properties, sintering kinetics, and grain growth.<sup>3-5</sup> It is apparent that understanding the behavior of defects in PZT is important in understanding the electrical properties. Many investigators tried to develop a desired defect structure extrinsically in PZT by intentionally doping. Scandium oxide is one of the materials that has received some attention as a dopant. Holman and Fulrath<sup>6,7</sup> determined that  $\text{Sc}^{3+}$  substitutes for (Ti, Zr) and creates oxygen vacancies in the perovskite structure. Lee and Fulrath<sup>8</sup> reported that Sc can convert the ferroelectric characteristics of PZT to an anti-ferroelectric-like behavior. The major problem in analyzing the Sc doped material is that the suppression of the rate of densification by the incorporation of Sc ions into PZT is so great that only very low density samples can be fabricated. The purpose of this study was to investigate the effect of PbO activity established by a packing powder during sintering on the densification of Sc doped PZT. A high density Sc doped sample was achieved.

A PZT composition of  $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$  was prepared from lead oxide powder, zirconium tetra-butoxide liquid and titanium tetra-butoxide liquid. 1 mole % scandium oxide ( $\text{Sc}_2\text{O}_3$ ) powder were used as a dopant.

Proper proportion of raw materials were mixed in a blender and then reacted and co-precipitated from solution when distilled water was added. The blended slurry was dried and calcined at 500°C for 24 hours. After calcining, the powder was milled for 4 hours in isopropyl alcohol and using  $ZrO_2$  as a grinding media. The powder was calcined again at 500°C for 8 hours. After the second calcination, 2.5 wt% or 5 wt% PbO was added to the powder. The PbO rich powder was milled again and then passed through a 325 mesh screen to complete the powder preparation process.

The powder was cold pressed at 10,000 psi in a 1 inch diameter steel die. The pressed pellets with green density about 2.6 gm/cc were sintered in a Pt crucible. The samples were always buried deeply into a packing powder with known PbO activity. The two compositions of the packing powder were lead zirconate-titanate plus 5 wt% PbO (PZT+P) and lead zirconate plus 5 wt%  $ZrO_2$  (PZ+Z). Either 1 atm oxygen or 1 atm helium was used as the sintering atmosphere. All sintering runs would begin by heating the furnace at constant rate of 300°C/hr to the sintering temperature 1200°C. The samples were held at temperatures for 16 hours and then allowed to cool at natural cooling rate of the furnace. Density of the sintered samples were measured by water displacement and also by geometric measurements. Theoretical density for PZT was taken as 8 gm/cc. X-ray diffraction was used to identify crystal phases present. The results are shown in Table I.

For a sample without excess PbO and using PZ+Z as the packing powder while sintering in 1 atm oxygen, the sintered density only reached 65% of the theoretical density. The density of a sample with

excess PbO can achieve 81% theoretical density. This is due to the excess PbO giving a liquid phase at high temperature to enhance sintering. If the PZT+P instead of PZ+Z is used as the packing powder, a completely dense sample is obtained. The X-ray diffraction pattern indicated that there was a trace of PbO in the sample. Recently, Holman and Fulrath<sup>9</sup> established the PbO activity above the  $\text{PbTiO}_3$ - $\text{PbZrO}_3$  system and determined the single phase width of the compounds in the system. It has been shown that PZT+P will provide a higher PbO activity than PZ+Z during firing. The PbO activity of PZ+Z is lower than that of the green compact. Therefore, the excess PbO in the sample is eventually lost to reach local atmospheric equilibrium with the PZ+Z packing powder. A high density sample can not be obtained. The high PbO activity established by PZT+P packing powder can suppress the PbO loss from the sample and lead to high density. The effect of environmental PbO activity on the sintered density is shown in Fig. 1. When 1 atm helium instead of oxygen was used during firing, the sintered density reached 95% theoretical density and no trace of a PbO phase was found in the sample. This shows that the lower the oxygen partial pressure in the sintering atmosphere the greater the PbO loss from the sample and the less effective is the liquid phase sintering process.

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TABLE I

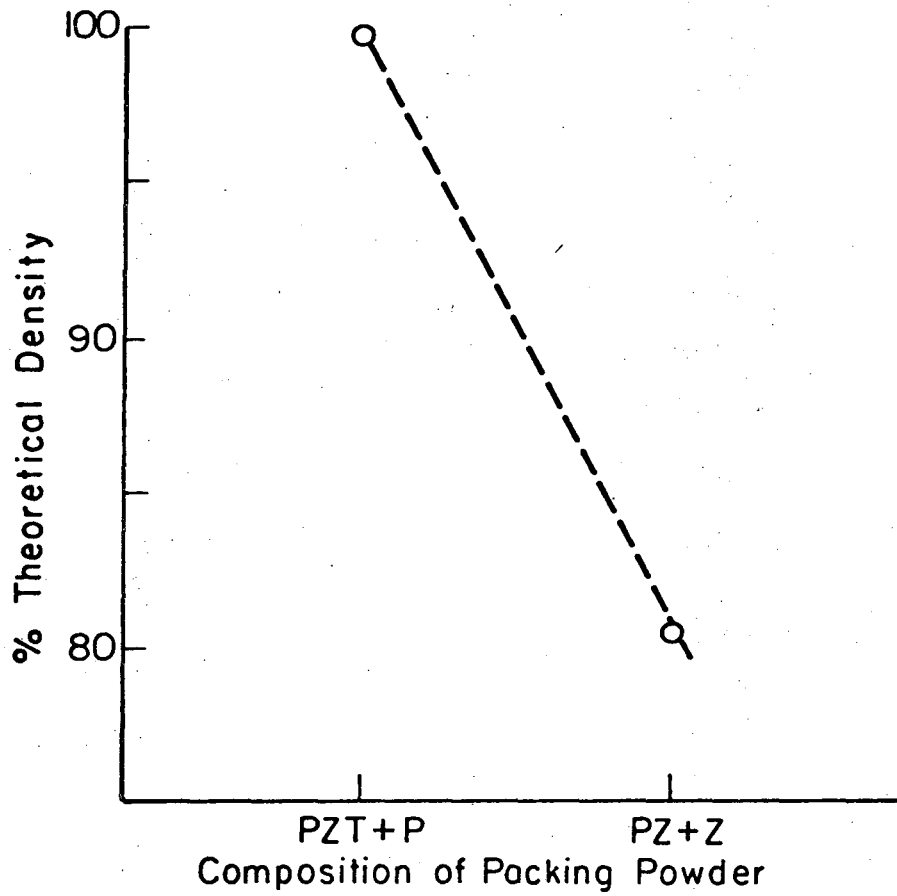
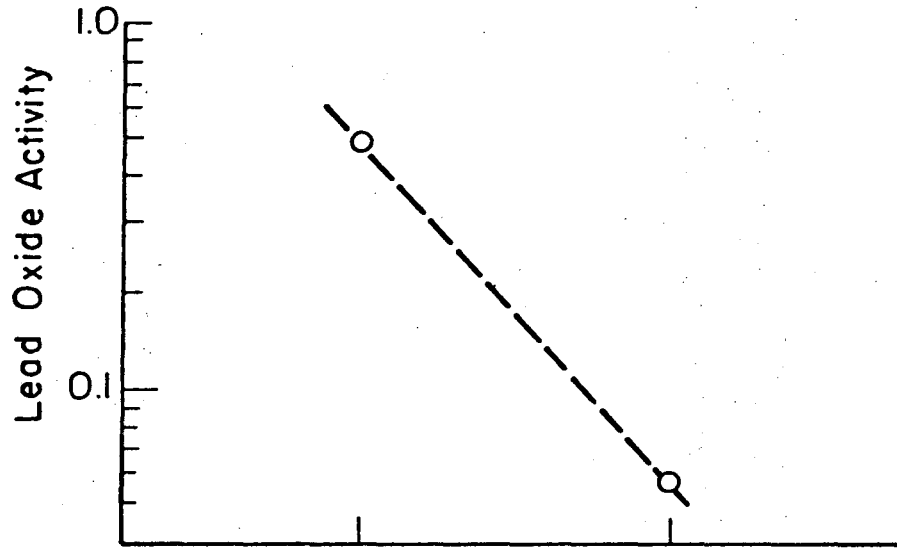
SINTERING PARAMETERS

Sample Compositions	Temperature (°C)	Time (Hour)	Atmosphere (1 atm)	Composition of Packing Powder	% Theoretical Density	X-ray Pattern
$\text{PZ}_{0.5}\text{T}_{0.5}$ + 2 mole% $\text{Sc}_2\text{O}_3$	1200	16	$\text{O}_2$	PZ+Z	65%	PZT
$\text{PZ}_{0.5}\text{T}_{0.5}$ + 2 mole% $\text{Sc}_2\text{O}_3$ + 2.5 wt%PbO	1200	16	$\text{O}_2$	PZ+Z	81%	PZT
$\text{PZ}_{0.5}\text{T}_{0.5}$ + 2 mole% $\text{Sc}_2\text{O}_3$ + 5 wt%PbO	1200	16	$\text{O}_2$	PZ+Z	85%	PZT
$\text{PZ}_{0.5}\text{T}_{0.5}$ + 2 mole% $\text{Sc}_2\text{O}_3$ + 2.5 wt%PbO	1200	16	$\text{O}_2$	PZT+P	99.9%	PZT+P
$\text{PZ}_{0.5}\text{T}_{0.5}$ + 2 mole% $\text{Sc}_2\text{O}_3$ + 2.5 wt%PbO	1200	16	He	PZT+P	95%	PZT
$\text{PZ}_{0.5}\text{T}_{0.5}$ + 2 mole% $\text{Sc}_2\text{O}_3$ + 5 wt%PbO	1200	16	He	PZT+P	96%	PZT

FIGURE CAPTION

Fig. 1. Effect of environmental PbO activity provided by a packing powder during sintering on the sintered density.





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Fig. 1

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