EFFECTS OF SINTERING CONFIGURATION AND OF LEAD TRANSPORT IN THE PROCESSING OF HIGH FIRE PZT.

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ABSTRACT

PZT 4S discs were sintered in covered boats without and with a PZ vapor source. XRF and weight loss, as well as d33 and K measurements indicated optimum performance with a lead loss near 1%. A semitransparent coating was seen on the grain surfaces in higher lead content samples.

I. INTRODUCTION

The lead in lead containing ceramics exhibits a substantial amount of volatility during sintering1,2, in particular when the atmosphere is oxygen deficient3. Weight loss can then commence at temperatures as low as 700°C and result in significant detrimental effects on the properties of the resulting ceramics.

The vehicle for this work is a modified PZT 4 formulation (PZT 4S3)*. This material was optimized to have a high d33 coefficient (350 pC/N), but it requires a high degree of control over lead stoichiometry.

II. EXPERIMENTAL

Discs were cold pressed from binder free PZT 4S powder at 5500 psi, to a diameter of 1.27 cm and a thickness of 0.29 cm. The samples were packed during heat treatment in 1mm zirconia beads in nested alumina boats (Fig. 1). The samples were sintered at 3° C/min to 1325° and held there for 10 min. Poling was at 2.4 KV/mm at 130°C.

III. RESULTS AND DISCUSSION

A) Lead loss and lead condensation.

Lead loss was determined from changes in weight during heat treatment and by X-ray fluorescence measurements. Fig 2 shows the relationship of the Pb/Zr fluorescence line amplitude ratios as obtained from the surfaces of the samples to the average weight losses of the sample groups they were in. The correlation between the two measurements is in excess of 0.95.

X-ray fluorescence showed a high sensitivity to lead content: The Pb/Zr count ratio was reduced nearly 50% with as little as 4% weight loss in the samples. This is due in part to the attenuation of the zirconia fluorescence by the lead in the matrix. No lead concentration gradients were found in the samples tested here.

Figure 2 contains data points from samples sintered with and without a lead zirconate (PZ) vapor source in the boats. The samples in each group that showed the highest lead content had been cooled from their peak sintering temperature at a faster rate, i.e. at 300°C/hour instead of 100°C/hour. The boat containing the sample with the highest lead content incorporated a PZ vapor source and had a 400 gr weight on its cover. It is speculated that the 400 gr weight prevents the lead vapor pressure from lifting the 50 gr cover, that otherwise would cause extra lead vapor to escape.

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Figure 3 shows that without a lead vapor source, and with only a single cover, the sample weight loss can be 1.3 to 1.7 times the loss by evaporation out of the boat. Samples in full boats with double covers and a PZ vapor source between the two covers also showed lead loss, even though the inside boat that contained the samples and its cover, actually gained weight. It appears that much of the lead lost from the samples is condensed on the insides of the boat covers.

These covers showed after sintering significant evidence of condensed material, often in the form of a yellow glaze. The consequent weight gains of the covers are the highest when there is a PZ vapor source, i.e., condensation is increased with enhanced vapor pressure inside the boat. On the other hand there was only a weak correlation of the amount of condensate to the evaporative weight loss. This can then create a condition where more lead from the samples recondenses inside the boat than what evaporates to the outside.

The lead lost to evaporation is reduced by as much as 40% when the cooling rate is increased from 100°C/h to 300°C/h. When a 400 gr weight is placed on the cover, the evaporative weight loss from a boat with a PZ source was reduced by a factor of two. It did not change significantly without PZ, implying an effective vapor pressure due to the PZ of more than 148 Pa (.0015 ATM).

B) Effects of Lead Stoichiometry on Electrical Properties

Effects of the lead content on the piezoelectric stress coefficient (d33) are shown in Fig. 4. There the average d33 values for each group of samples are plotted against the average weight loss in that group. In the present material the d33 is the highest (340 pC/N) when there is a 1-1.5% weight loss: It gradually drops with increasing weight loss. When a PZ vapor source is used to minimize the lead loss, lower rather than higher d33 values are observed. This is attributed to an intentional lead excess in the press powder, that in the absence of lead loss causes the formation of a glassy phase. This lead excess had been added to compensate for lead loss. This approach does not always give optimum performance, since the excess lead can form an intergranular phase that reduces the material's performance. The amount of intergranular phase left after sintering and the lead stoichiometry of the lattice at that time then become critical variables.

Figure 5 is a plot of the unpoled dielectric constant (K) versus weight loss. It peaks near 1250 with a weight loss of 1%. Similar to the behavior of the d33 coefficient, lower K values are observed when a PZ vapor source is used, even when this reduces the lead loss to 0.4%.

In the absence of a PZ vapor source the change in dielectric constant (ΔK) upon poling becomes generally larger (more positive) with higher unpoled K values, from +2% to +16%. This is shown in Fig. 6. The trend of the ΔK versus K curve is similar in samples sintered with a PZ vapor source except that in this case the K changes are up to 25% more negative. The occurrence of poling cracks in the high lead content samples could account for the two populations observed in this plot.

Figure 7 illustrates the effects of lead vapor pressure gradients within a boat. These are observed in PZT samples buried in setter sand and located at various distances (2cm to 5 cm) from a PZ vapor source. The XRF Pb/Zr amplitude ratios decrease by about 3.5% from 1.338 in the samples closest to the source, to 1.293 in samples at the 5 cm distance from it. This latter ratio is near the lead content where the d33, unpoled K and ΔK peak. As a result, increases are observed in the unpoled K and in the d33 in samples more distant from the vapor source.
The effects of the sample to vapor source separation are attributable to the sand slowing the diffusion of the lead vapor. This can also be expected to slow the lead evaporation from the samples when sintered without a lead source.

C) Microstructural Observations

As noted, reduction of the dielectric constant during poling implies poling cracks. This can be related to the presence of an intergranular phase, that appears to have formed a liquid before the samples are cooled. Figure 8 shows a sample fracture surface that appears to have a semitransparent coating over the grain surfaces and that has well rounded grain boundaries, both giving evidence of liquid phase formation during sintering.

SUMMARY

An investigation of the effects of lead loss in sintered PZT 4S samples showed that

1) Significant amounts of lead can condense on the insides of the boat covers.
2) There is more lead loss with slower cooling rates.
3) There is an optimum amount of lead loss in this material that maximizes the electrical properties.
4) A PZ vapor source causes an effective lead overpressure of >148 Pa (.0015 ATM) and reduces the lead loss in the samples.
5) Filling the boat with a coarse zirconia sand slows the amount of lead vapor transport.

REFERENCES


Figure 1

DOUBLE SEALED SINTERING CONFIGURATION
No PZ vapor source with samples in inside boat

SINGLE COVER CONFIGURATION - INSIDE BOAT ONLY

Figure 2: Pb/Zr XRF line amplitude ratio versus weight loss

Corr. coeff. = .974
Figure 3: Sample weight loss versus evaporative weight loss

Figure 4: $d_{33}$ versus sample weight loss

Figure 5: Unpoled $K$ versus weight loss
Figure 6: Change in dielectric constant upon poling at 2.4kV/mm versus dielectric constant.

Figure 7: Pb/Zr peak amplitude ratio versus distance from vapor source (samples fully embedded in sand).

Figure 8
PZT 4S - Fracture Surface