

# Fast firing of lead zirconate titanate ceramics at low temperature

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## Abstract

A fast firing technique for densification of PZT (up to 97% of theoretical density) at a low temperature (950 °C) has been found out. A small amount of excess PbO (3–5 wt.%) and a fast firing schedule are required to achieve the desired sintering. The final composition of the sintered ceramics can be kept close to the morphotropic phase boundary by modifying the firing time and post-sintering annealing treatment at 800 °C. The  $g_{33}$  values of fast fired samples are comparable to those of conventionally sintered samples, though the  $d_{33}$  values are somewhat lower than those reported for conventionally sintered (at 1250 °C or above) samples.

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## 1. Introduction

Lead zirconate titanate (PZT) piezoelectric ceramics of composition  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ , which is close to the morphotropic phase boundary, find a host of applications in recent time [1,2]. Conventionally, PZT ceramics require a sintering temperature of 1250 °C or more. Such high temperature sintering is undesirable because of higher energy consumption and above all, volatilization of lead with consequent change in composition and deterioration of piezoelectric properties. To get around the problems, the common practice is to use controlled atmosphere sintering [2]. Probably, a better alternative is to use a sintering aid so as to get the desired densification exploiting the liquid phase sintering at a lower temperature. However, the selection of sintering aid is crucial because they should not degrade the piezoelectric properties of PZT. So far, a lot of sintering aids have been tried by different workers with varying success. Some examples [3–6] of sintering aids are  $\text{P}_2\text{O}_5$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cu}_2\text{O}$ – $\text{PbO}$ , etc. However, the incorporation of such extraneous components in PZT degrades the  $d_{33}$  and  $g_{33}$  values in most of the cases. As an alternative approach, there are a few reports of low temperature liquid phase sintering of PZT using excess

PbO as a sintering aid. Chiang et al. [7] could achieve full densification at 1200 °C using excess PbO. Garg and Agrawal [8] obtained good sintering of PZT at 1220 °C using excess PbO. Hansch et al. [9] succeeded to densify PZT, albeit in the fibre form, at a temperature of 900 °C using excess PbO and such low temperature sintering has been explained by considering the high surface area of the fibres.

In the present work, we report a technique of obtaining highly dense PZT ceramics of acceptable properties at a temperature of 950 °C by employing a fast firing schedule and using excess PbO as a sintering aid. The process is simple, economic and does not require any controlled atmosphere. The final composition of the sintered ceramics can be kept close to the morphotropic phase boundary by a post-sintering annealing treatment at a lower temperature.

## 2. Experimental

PZT powder of composition  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  was prepared by a mixed route of citrate–nitrate gel method followed by solid state mixing and calcination as described elsewhere [3]. The powder was characterized by XRD and the particle morphology was observed by a SEM (Leo 430i). The synthesized powder was then mixed with 0–7 wt.% PbO in an agate mortar and a pestle under acetone and after drying, pelletized

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at 64 MPa pressure. For fast-firing, the pellets were placed on either a platinum or dense zirconia plate and directly introduced inside a furnace already heated to 950 °C. They were kept there for 30–120 min and then allowed to cool slowly inside the furnace. The second important step was to anneal the sintered pellets at a lower temperature (800 °C) on a clean platinum or dense zirconia plate.

The bulk densities of the sintered pellets were measured geometrically and calculated with respect to the theoretical density of morphotropic PZT, ignoring the little excess or deficient lead content of the sintered samples. The microstructure of the sintered specimens after thermal etching at 950 °C for 1h was viewed in a SEM (Leo 430i).

The samples for electrical testing were polished and coated with silver paint and cured at 650 °C for 15 min. The samples were poled in silicone oil at a temperature of 120 °C at 3 kV mm<sup>-1</sup> field for 30 min. After poling, the dielectric studies were made using a Hioki 3532-50 LCR Hitester in the frequency range of 42 Hz to 4 MHz and the piezoelectric voltage constants ( $g_{33}$ ) were determined after measuring the piezoelectric strain constants ( $d_{33}$ ) using a  $d_{33}$  meter (Pennebaker 800  $d_{33}$  tester).

### 3. Results and discussion

Fig. 1 shows the X-ray diffractogram of the powder prepared by the mixed route of citrate–nitrate gel method followed by solid state mixing and calcination. The XRD peaks indicate phase purity (morphotropic phase boundary composition) of the synthesized powder (JCPDS File No. 33-784). The SEM photograph (Fig. 2) depicts the powder morphology and the particle size lies in the range of 200–400 nm.

Table 1 describes the sintering parameters used, the bulk densities achieved, the percent change in weight (measured as weight loss or gain) due to lead loss or presence of excess lead with respect to phase pure morphotropic PZT composition.

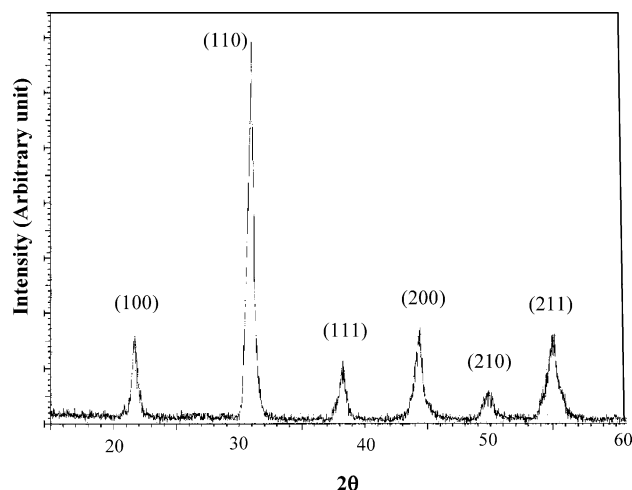


Fig. 1. X-ray diffractogram showing phase pure PZT.

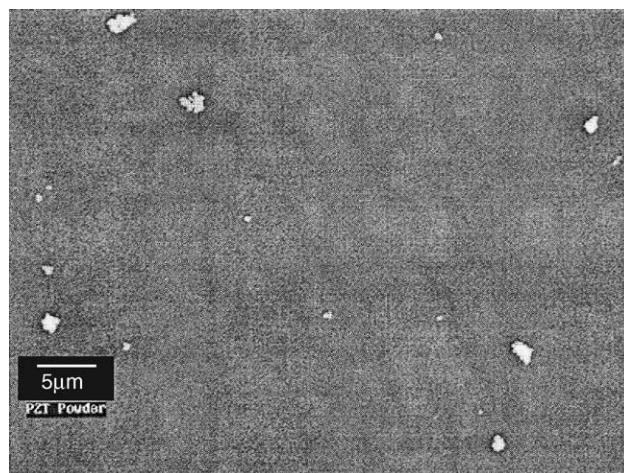


Fig. 2. SEM micrograph of synthesized powder.

It is evident from Table 1 that even at 950 °C, high sintered density can be achieved, provided excess PbO is added as a sintering aid and the fast firing schedule is employed. Also it can be noted that the final composition of the sintered body can be kept close to the morphotropic phase boundary (as evident from a little weight loss or gain with respect to starting PZT powder of morphotropic phase boundary composition) by modifying the firing schedule and or the amount of excess PbO addition. Because of the direct introduction of the samples to the furnace at 950 °C, all the excess PbO melts and forms a liquid phase in contrast to conventional slow heating where much less liquid is formed as some of the excess PbO volatilizes and some may go into solid solution [10]. The liquid phase formed during fast firing can produce enough capillary pressure [11] to allow marked particle rearrangements aiding in liquid phase sintering. Huppman [12] considered rearrangement densification as a function of force existing between two solid particles, which are connected by a melt bridge. He considered both rearrangement of initial particles and rearrangement of grains after particle disintegration. According to Huppman, the rearrangement shrinkage  $\Delta V/V_0$  is given by

$$\frac{\Delta V}{V_0} \sim (F - F_0) \quad (1)$$

where  $F$  is the interparticle force between two spherical particles connected by a liquid bridge. Only when  $F$  exceeds the weakest configuration intrinsic force  $F_0$ , particles rearrangement can take place. Hence, due to capillary pressure of the liquid phase, consolidation of the powder takes place, and in the process, some of the excess molten lead oxide is squeezed out and accumulated on the substrate at the bottom of the sample. Similar observation has earlier been reported [13] for fast firing of lead magnesium niobate. Such squeezing out of molten lead oxide gives rise to compositional gradient of PbO in the sample; especially, the surfaces of the pellets become richer in PbO. To homogenize the sample, a post-sintering annealing treatment at a lower temperature

Table 1  
Physical properties and sintering parameters of PZT samples

Sample code	Description of the samples	Sintering temperature/time	Annealing temperature/time	Bulk density (%)	Weight <sup>a</sup> change (%)
3Pb30	PZT + 3 wt.% PbO	950 °C/30 min	800 °C/4 h	94.320	+0.70
5Pb30	PZT + 5 wt.% PbO	950 °C/30 min	800 °C/4 h	97.220	+2.025
7Pb30	PZT + 7 wt.% PbO	950 °C/30 min	800 °C/4 h	95.500	+3.48
3Pb45	PZT + 3 wt.% PbO	950 °C/45 min	800 °C/4 h	94.965	−0.27
5Pb45	PZT + 5 wt.% PbO	950 °C/45 min	800 °C/4 h	95.870	+1.935
7Pb45	PZT + 7 wt.% PbO	950 °C/45 min	800 °C/4 h	96.095	+3.245
3Pb60	PZT + 3 wt.% PbO	950 °C/60 min	800 °C/4 h	95.805	−0.495
5Pb60	PZT + 5 wt.% PbO	950 °C/60 min	800 °C/4 h	95.615	+1.445
7Pb60	PZT + 7 wt.% PbO	950 °C/60 min	800 °C/4 h	97.290	+3.06
3Pb90	PZT + 3 wt.% PbO	950 °C/90 min	800 °C/4 h	95.225	−2.5
5Pb90	PZT + 5 wt.% PbO	950 °C/90 min	800 °C/4 h	95.610	−0.63
7Pb90	PZT + 7 wt.% PbO	950 °C/90 min	800 °C/4 h	95.720	+1.045
3Pb120	PZT + 3 wt.% PbO	950 °C/120 min	800 °C/4 h	94.065	−2.885
5Pb120	PZT + 5 wt.% PbO	950 °C/120 min	800 °C/4 h	95.185	−0.845
7Pb120	PZT + 7 wt.% PbO	950 °C/120 min	800 °C/4 h	95.860	−0.405
0Pb45	PZT + 0 wt.% PbO	950 °C/45 min	800 °C/4 h	80.130	−2.665

<sup>a</sup> (+) PbO excess, (−) PbO loss.

(800 °C) is required, which gives a uniform colour to the surface and interior of the samples. At the same time, the annealing treatment can be tailored to achieve the desired morphotropic composition by allowing controlled volatilization of lead oxide. From Fig. 3 it is evident that the volume shrinkage after fast firing at 950 °C remains more or less constant for soaking time beyond 45 min. From Table 1 and Fig. 3 it can be said that 3–5 wt.% excess PbO and soaking time of 45 min at 950 °C are the optimum for low temperature densification of PZT through fast firing route. For 7 wt.% excess PbO addition, the amount of excess PbO remaining in the sintered samples is quite high for low soaking periods. A typical micrograph of a fast fired sample has been depicted in Fig. 4.

As expected [14,15], the dielectric constant and dissipation factor of the PZT samples remain nearly constant (a slow decreasing trend) with frequency (Figs. 5 and 6). However, it is noteworthy that the dielectric constant ( $\epsilon$ ) of convention-

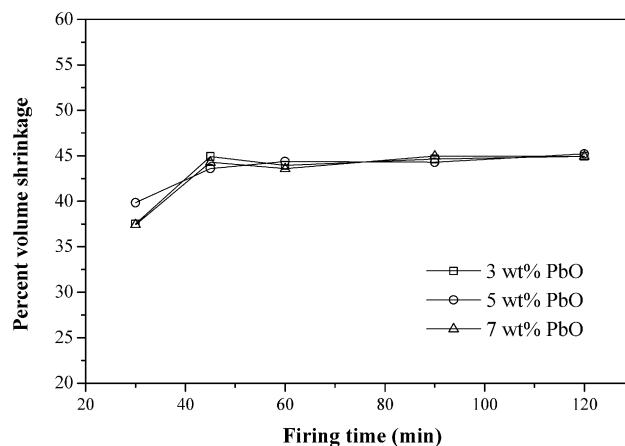


Fig. 3. Volume shrinkage with firing time for samples fast fired at 950 °C.

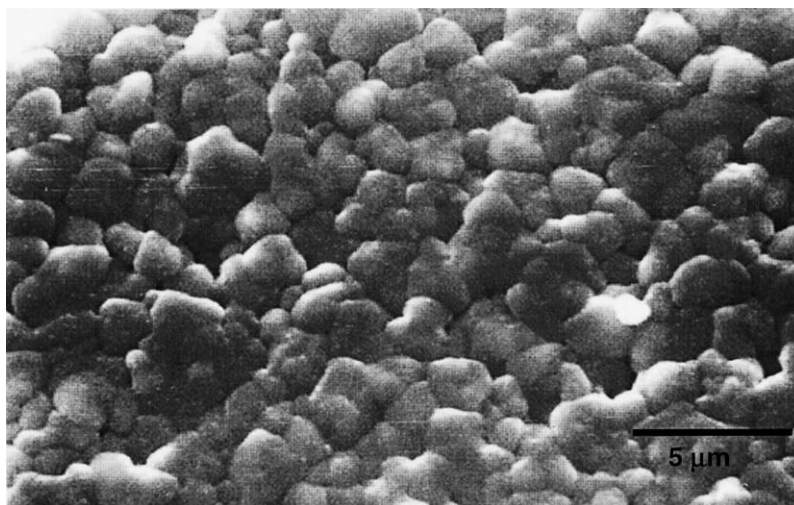


Fig. 4. SEM micrograph of a fast fired sample.

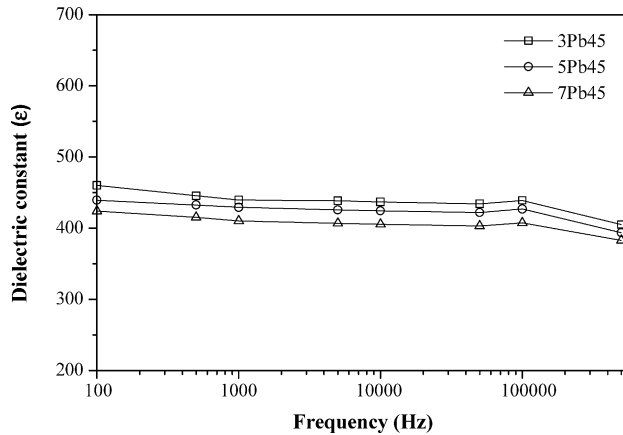


Fig. 5. Dielectric constant vs. frequency of some typical fast fired samples.

ally prepared (sintered at 1200 °C or above) sample is much higher ( $\sim 730$ , Ref. [10]) than the dielectric constant values we obtained for our fast fired samples. The lower  $\epsilon$  of the fast fired samples in comparison to that of conventionally prepared high temperature sintered samples may be understood by considering the presence of low  $\epsilon$  PbO rich grain boundaries in the former. The effective dielectric constant of a sample can be obtained by considering [16,17] the ceramic microstructure as parallel and series combinations of inter-granular boundaries. The series boundaries should dominate [17] the overall dielectric constant owing to the small volume fraction and low dielectric constant of the boundary region and the series mixing law is given by [17]:

$$\frac{1}{\epsilon_{\text{eff}}} = \frac{1}{\epsilon_g} + \frac{1}{R\epsilon_{\text{gb}}} \quad (2)$$

where  $R = \langle t_g \rangle / \langle t_{\text{gb}} \rangle$ ,  $\epsilon_{\text{eff}}$  is the effective dielectric constant,  $\epsilon_g$  and  $\epsilon_{\text{gb}}$  are the dielectric constants of the grain and grain boundary respectively,  $t_g$  the mean grain size, and  $t_{\text{gb}}$  is the mean grain boundary thickness. Low  $\epsilon_{\text{gb}}$  due to the presence of nonferroelectric PbO rich grain boundary leads to low  $\epsilon_{\text{eff}}$  for the fast fired samples.

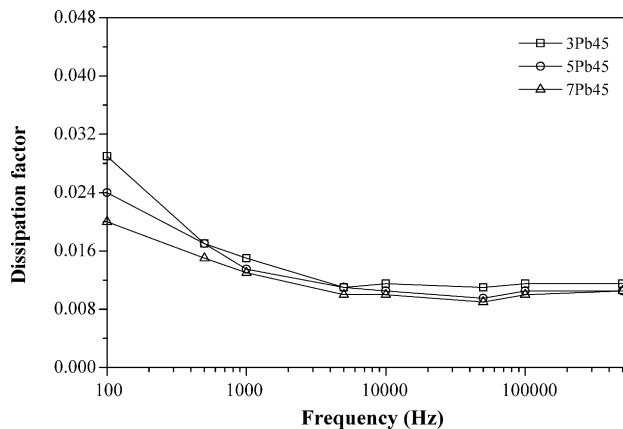


Fig. 6. Dissipation factor vs. frequency of some typical fast fired samples.

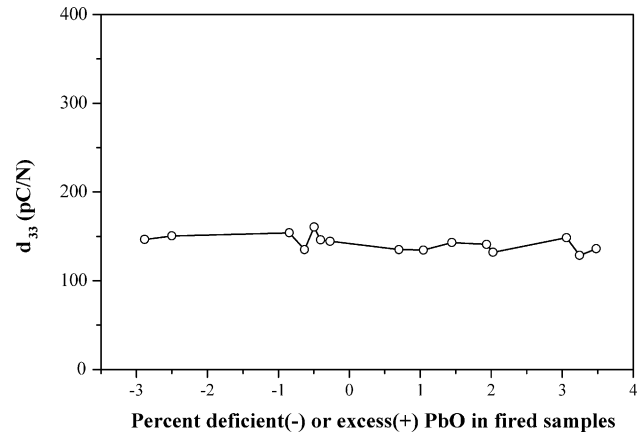


Fig. 7. Variation of  $d_{33}$  values with excess or deficient PbO content (with respect to morphotropic composition) in PZT samples fast fired with excess (3–7 wt.%) PbO at 950 °C (30–120 min) followed by annealing at 800 °C.

Fig. 7 depicts the trend of  $d_{33}$  values of the fast fired samples with respect to excess or deficient PbO content in the samples. A slight excess or deficiency in PbO does not affect the  $d_{33}$  values much indicating the flexibility of the process. However, the reported  $d_{33}$  values of conventionally sintered samples are higher ( $\sim 223$ , Ref. [10]) than those we obtained for the fast fired samples. The low  $d_{33}$  values in the present case may be due to the following reasons. Firstly,  $d$  quantifies the strain arising from the applied field  $E$  on the piezoelectric ceramics. It may be noted that in the present case the grains are piezoelectric, whereas the grain boundaries consist of a non-piezoelectric material (primarily PbO). The electric field, should be distributed on both the grains and grain boundaries, and the impressed field on the grain boundary should be proportional to  $t_{\text{gb}}/t_g \times \epsilon_{\text{gb}}$ . Though the grain boundary dielectric constant  $\epsilon_{\text{gb}}$  is an order of magnitude lower than that of the grain ( $\epsilon_g$ ),  $t_{\text{gb}}$  being at least two orders of magnitude lower than  $t_g$ , the contribution of the impressed field on the non-piezoelectric grain boundary should not appreciably offset the measured  $d_{33}$  values of the ceramics from the true  $d_{33}$  values arising from the piezoelectric grains. Probably, the low  $d_{33}$  values of the fast fired samples can be understood by accounting both the intrinsic and extrinsic contribution towards the resultant piezoelectric constant ( $d$ ) of a material [16]:

$$d = d_{\text{ex}} + d_{\text{in}} \quad (3)$$

where  $d_{\text{ex}}$  and  $d_{\text{in}}$  are the extrinsic and intrinsic contributions respectively. It may be noted that the domain wall dynamics mainly contributes towards  $d_{\text{ex}}$  and its contribution towards  $d$  can be 40–70% [18,19] of the total at room temperature. Due to strong coupling [16] between the domain walls and the grain boundaries, the domain wall dynamics should be appreciably dampened in case of fast fired samples, where the PbO rich grain boundary composition is quite different from the ferroelectric grain composition. The dampened domain wall dynamics should lead to lower  $d_{\text{ex}}$  and in effect should lower  $d$  in case of fast fired samples.



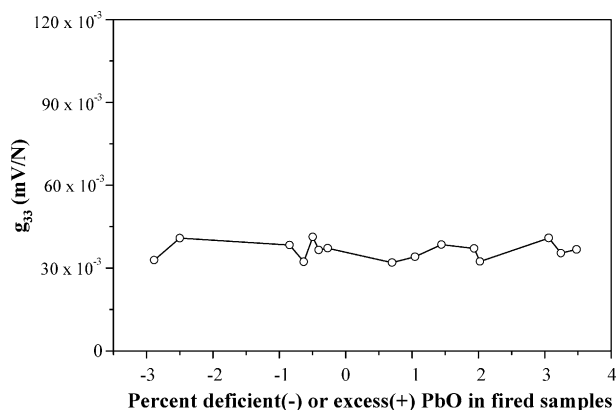


Fig. 8. Variation of  $g_{33}$  values with excess or deficient PbO content (with respect to morphotropic composition) in PZT samples fast fired with excess (3–7 wt.%) PbO at 950 °C (30–120 min) followed by annealing at 800 °C.

Interestingly, the  $g_{33}$  values of fast fired samples, calculated as  $d_{33}/\epsilon_0 \epsilon_{33}$ , show a similar trend (Fig. 8) to that of the  $d_{33}$  values with respect to excess or deficient PbO content in the samples. It is interesting to note that  $g_{33}$  values of fast fired samples are comparable to those of conventionally sintered samples because of lower  $\epsilon_{33}$  of the fast fired samples.

#### 4. Conclusion

Highly dense PZT samples can be obtained by fast firing technique at a temperature as low as 950 °C by adding a small excess of PbO. The final composition of the sintered samples can be kept close to the morphotropic phase boundary by modifying the firing time and post-sintering annealing treatment at 800 °C. The  $g_{33}$  values of the fast fired samples are comparable to those of the conventionally sintered samples. However, the  $d_{33}$  values of fast fired samples are somewhat lower than that of the conventionally sintered (at 1250 °C or above) samples.

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