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### Recommended Citation

W. Huebner et al., "A Study of the Sintering Mechanism of PZT-Based Piezoceramics," *Proceedings of the 9th IEEE International Symposium on Applications of Ferroelectrics*, 1994, Institute of Electrical and Electronics Engineers (IEEE), Jan 1994.

The definitive version is available at <https://doi.org/10.1109/ISAF.1994.522314>

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# A STUDY OF THE SINTERING MECHANISM OF PZT-BASED PIEZOCERAMICS

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## ABSTRACT

The densification behavior a PZT-based composition with additions of  $\text{BiFeO}_3$  as a flux was studied. Two different PZT powders were studied with varying initial particle sizes. Results clearly showed that  $\text{BiFeO}_3$  forms a low temperature liquid that aids in the densification behavior, with 3 mole% being optimum. Fine particle sizes substantially improved the density at low temperatures, with the net result that ceramics could be densified in air without the aid of a lead source. The corresponding electromechanical properties were typical of a hard PZT formulation.

## INTRODUCTION

One of the key parameters which affects the microstructural evolution and electromechanical properties of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) - based ceramics is control over the lead activity,  $a_{\text{Pb}}$ . It is well known that the vapor pressure of lead above PZT at temperatures well below the sintering temperature is high [1-4], and that the associated lead loss has a detrimental affect on the piezoelectric properties [5]. In practice, this problem is overcome by sintering in the presence of a lead source, such as  $\text{PbZrO}_3$ , which has a higher vapor pressure than the PZT, and also batching excess  $\text{PbO}$ . The latter dictates annealing of the PZT after sintering in order to remove any second phases in the grain boundary.

An effective strategy to minimize this problem is to lower the sintering temperature through the use of ultrafine powders [6], and/or liquid phase sintering. To obtain materials which retain good piezoelectric properties, a key step is to tailor the flux composition to produce densification with limited grain growth. During grain growth, dissolution of the additive ions from the flux into the ceramic is assisted by solution-reprecipitation processes, hence these additive ions should serve as the aliovalent or isovalent dopants desired to manipulate the piezoelectric properties. An additional requirement is for the flux to be either totally soluble in the piezoelectric, i.e. transient liquid phase sintering, or volatilize in order to minimize the presence of intergranular phases and porosity. Therefore the flux composition, melting temperature, reactions between the flux and the piezoelectric, and microstructural evolution during liquid phase sintering are all very important parameters to characterize and understand in any attempt to precisely control piezoelectric properties.

In this study we present results on the use of  $\text{BiFeO}_3$  as a sintering aid for a PZT-based composition.  $\text{BiFeO}_3$  was chosen on the basis of its incongruent melting temperature of  $\approx 930^\circ\text{C}$  [7], and since  $\text{Bi}^{3+}$  and  $\text{Fe}^{3+}$  are both soluble onto the lattice,  $\text{BiFeO}_3$  can yield desirable piezoelectric properties [8-10]. Additionally, the  $T_c$  for  $\text{BiFeO}_3$  is  $\approx 850^\circ\text{C}$ , and hence, in the interest of higher temperature piezoelectric applications, may increase  $T_c$  of the system [10].

## EXPERIMENTAL PROCEDURE

Figure 1 overviews in detail the processing steps used to prepare the following three compositions:

$$1-x (\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 - x \text{ BiFeO}_3$$
$$x = 0.01, 0.03 \text{ and } 0.05$$

Note that the mixed oxide approach was used to make the compositions, and that the PZT and BF were pre-calcined. Figure 2 shows the PZT powders calcined at  $780^\circ\text{C}$  and  $840^\circ\text{C}$  for 2 h. This  $60^\circ\text{C}$  difference made a large difference in the powder characteristics; the  $780^\circ\text{C}$  powder had a surface area of  $1.65 \text{ m}^2/\text{g}$ , and the  $840^\circ\text{C}$  powder  $0.47 \text{ m}^2/\text{g}$ . This corresponds to equivalent spherical diameters of  $0.47$  and  $1.69 \mu\text{m}$ , respectively. Both powders are equiaxed, and exhibit little aggregation. X-ray diffraction analyses on the pre-calcined PZT and BF verified the compositions.

All of the sintering studies were performed in air, without a lead source or excess  $\text{PbO}$  additions. Remember our goal is learn how to densify PZT ceramics without control over the lead activity.

Room temperature electrical measurements were performed on plane parallel disks approximately 1 to 2 mm thick. Gold electrodes were sputtered onto the surface in a vacuum through a mask. The dielectric properties were measured using a General Radio GR1689 RLC Digibridge. After poling, a Berlincourt  $d_{33}$  meter was used to measure the  $d_{33}$  coefficient, and resonance measurements were performed with an impedance analyzer (Hewlett-Packard 4194A

<b>Raw Materials:</b>	• $\text{PbO}$ 99%	• $\text{TiO}_2$ 99%
	• $\text{SrCO}_3$ 99.9%	• $\text{ZrO}_2$ 99%
	• $\text{Fe}_2\text{O}_3$ 99.8%	
<b>Mixing</b>		
	• Batch: $\text{ZrO}_2$ media:alcohol = 1:4:0.8	
	• Polyethylene jar	
	• 24 h	
<b>Calcination:</b>		
	• $\text{Bi}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ pre-calcined: $680^\circ\text{C}$ - 3h $\rightarrow \text{BiFeO}_3$	
	• $(\text{Pb}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ : $780^\circ\text{C}$ - 2h; $840^\circ\text{C}$ - 2h	
<b>Milling</b>		
	• Aggregates broken up with an agate mortar & pestle	
	• Milled again as above	
<b>Pressing:</b>		
	• 8 wt% of a 5% PVA solution	
	• Granulation	
	• Uniaxial pressing; $1000 \text{ kg/cm}^2$ [green density: 55% T.D.]	
<b>Sintering:</b>		
	• $650^\circ\text{C}$ - 4 h (binder burnout)	
	• Dilatometry: $10^\circ\text{C}/\text{min}$ to $1300^\circ\text{C}$	
	• Isothermal dilatometry: $850$ & $1100^\circ\text{C}$	

Figure 1: Overview of the processing steps used to prepare the PZT-BF ceramics.

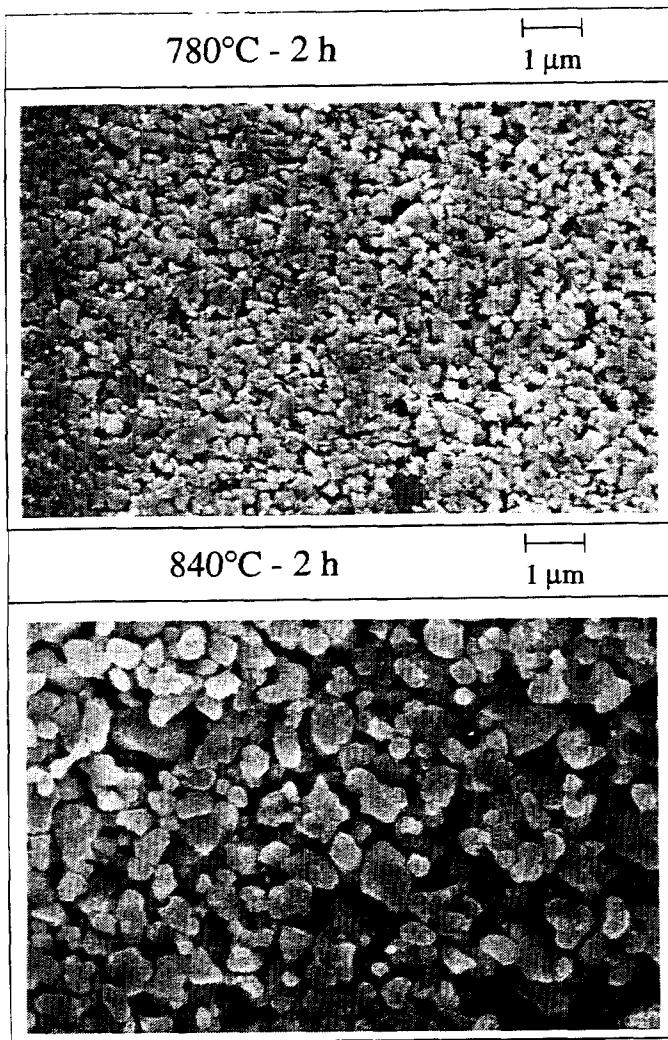


Figure 2: SEM micrographs of the PZT powder calcined at 780 and 840°C for 2 h.

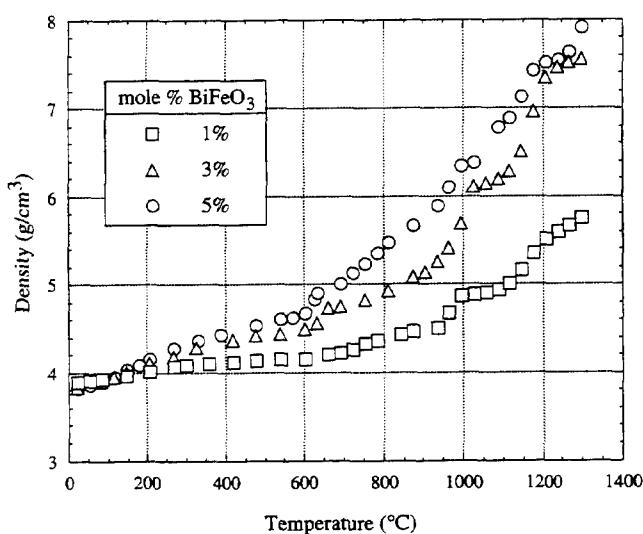


Figure 3: Densification behavior of the PZT-BF ceramics as a function of %BF.

Impedance Analyzer with a 41941A Impedance Probe and 16092A Test Fixture) to determine  $k_t$  and  $k_p$ .

## RESULTS AND DISCUSSION

The main results presented in this paper deal with the influence of starting powder characteristics and %BF on the densification behavior, coupled with electromechanical properties.

Figure 3 exhibits the influence of the %BF, in all three cases using the 780°C calcined powder. Clearly 1% additions are insufficient to densify the ceramic, resulting in  $\approx 73\%$  T.D. at 1300°C. Increasing to 3% BF improved the densification behavior, resulting in a density of 95% theoretical. Note in this behavior that the densification rate increases substantially at  $\approx 900^\circ\text{C}$ , which is close to the melting temperature of the BF. The situation is further improved by the addition of 5% BF, and the densification rate increases sharply at a lower temperature of 600°C. The density at 1300°C is similar to that of the 3% composition,  $\approx 95\%$  T.D.

Figure 4 exhibits fired surface SEM micrographs of the three compositions. The presence of a residual liquid phase is evident in the 5% BF composition. The grain sizes of all three were  $\approx 1\ \mu\text{m}$ . DTA analyses on both the 780°C and 840°C powders with 3% BF additions are shown in Figure 5. The low temperature exotherm is associated with alcohol removal. Only the 780°C powder exhibited a reaction at  $\approx 600^\circ\text{C}$ , which is 300°C lower than the temperature at which the densification rate changed sharply for this composition. The DTA curve for the 5% composition was nearly identical, hence it is likely that even though a liquid phase is forming in the 3% BF composition at  $\approx 600^\circ\text{C}$ , that the amount of the liquid phase is insufficient to result in significant particle rearrangement.

Using the 3% BF composition, further studies on the influence of the starting powder characteristics on the densification rate were performed. Figure 6 exhibits a comparison of the 780°C and 840°C powders. The impact of starting particle size is clear. Although the final density is nearly the same, the rate is substantially higher at low temperatures for the 780°C powder. The isothermal studies at 850°C and 1100°C shown in Figures 7 and 8 reinforce these results. Replotting this data with as a function of time $^{1/3}$  (indicative of a solution-reprecipitation mechanism) results in linear plots, but at this stage more data is needed to confirm the sintering mechanism.

The electromechanical properties of the PZT-3% BF ceramics after sintering at 1300°C are shown in Table I. Both ceramics exhibit behavior typical of a hard PZT ( $\text{Fe}^{3+}$ -doping), but the ceramics prepared using the 780°C powders are superior.

## CONCLUSIONS

The densification behavior of a PZT-based composition with additions of  $\text{BiFeO}_3$  as a flux were studied. Two different PZT powders were studied with varying initial particle sizes. Results clearly showed that  $\text{BiFeO}_3$  forms a low temperature liquid that aids in the densification behavior, with 3 mole% being optimum. Fine particle sizes substantially improved the density at low temperatures, with the net result that ceramics could be densified in air without the aid of a lead source.

### Acknowledgment

This work was sponsored by the Office of Naval Research under Grant N00014-92-J-1469.

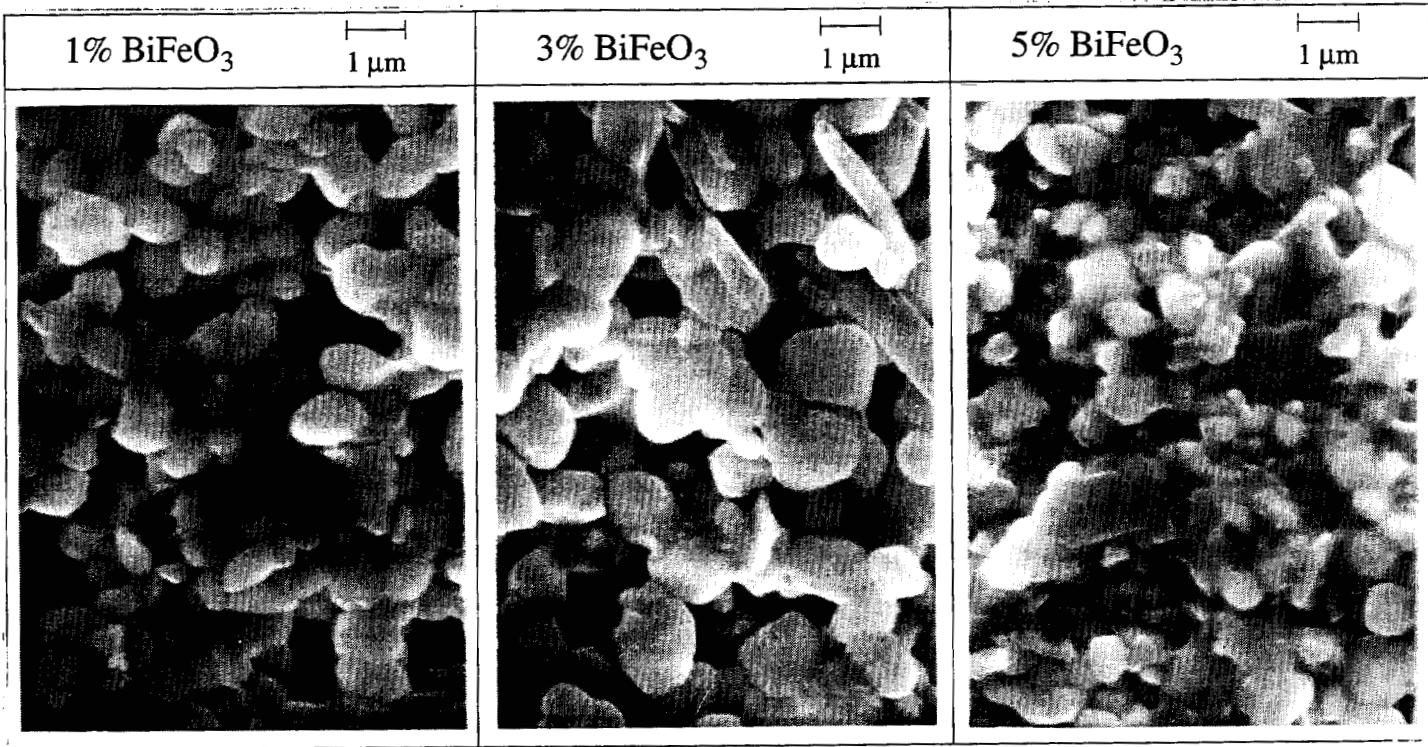


Figure 4: SEM micrographs of the PZT-BF ceramics after sintering to 1300°C.

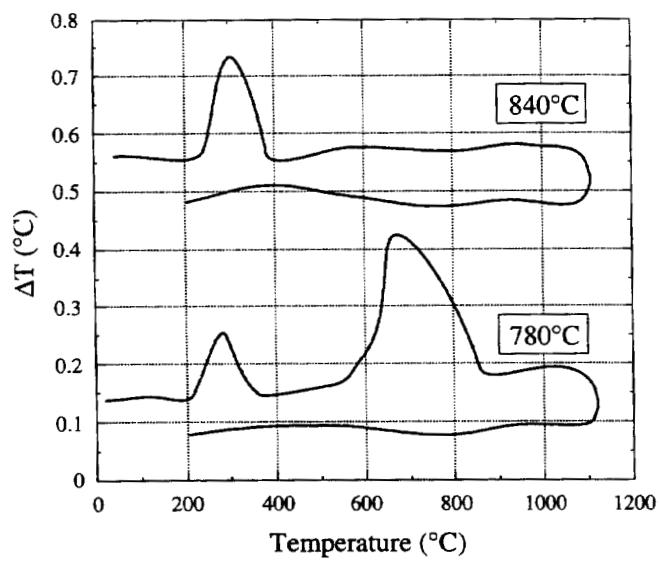


Figure 5: DTA analyses of the 780°C and 840°C powders with 3% BF additions.

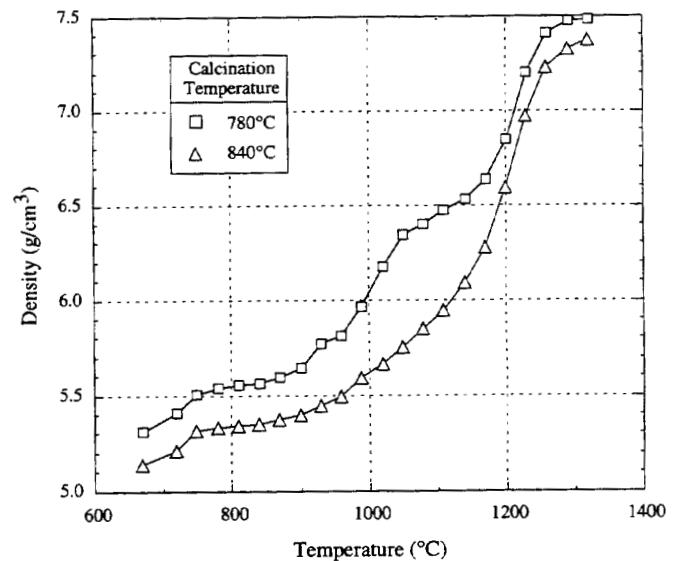


Figure 6: Densification behavior of the PZT-BF ceramics as a function of the powder calcination temperature.

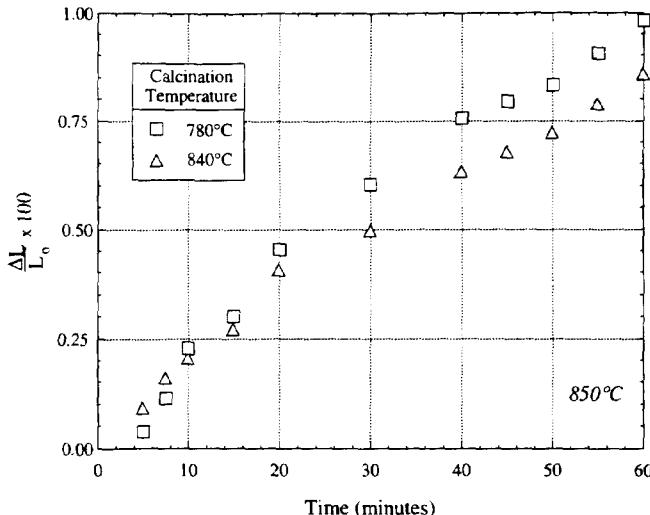


Figure 7: Isothermal shrinkage at 850°C of the PZT-3%BF powders calcined at 780°C and 840°C for 2 h.

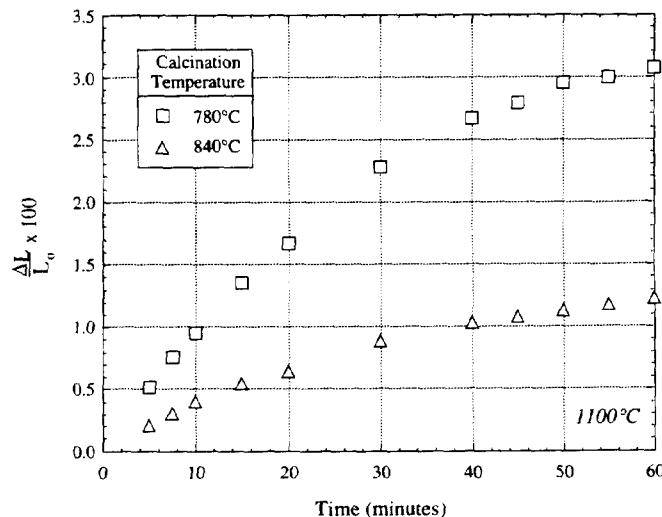


Figure 8: Isothermal shrinkage at 1100°C of the PZT-3%BF powders calcined at 780°C and 840°C for 2 h.

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TABLE I

EFFECT OF CALCINATION TEMPERATURE ON THE ELECTROMECHANICAL PROPERTIES OF PZT-3% BF

Property	780°C - 2 h	840°C - 2 h
$\epsilon_{33}/\epsilon_0$	1157	1325
$\tan \delta$ (%)	0.49	0.79
$d_{33}$ (pC/N)	285	256
$k_p$ (%)	54.1	48.7
$k_t$ (%)	47.3	41.4
$Q_m$	128	75