01 Jul 2000

# High Energy Density Dielectrics for Symmetric Blumleins

Wayne Huebner
*Missouri University of Science and Technology*, huebner@mst.edu

Shi C. Zhang
*Missouri University of Science and Technology*, scz@mst.edu



## Recommended Citation

W. Huebner and S. C. Zhang, "High Energy Density Dielectrics for Symmetric Blumleins," *Proceedings of the 12th IEEE International Symposium on Applications of Ferroelectrics (2000, Honolulu, HI)*, vol. 2, pp. 833-836, Institute of Electrical and Electronics Engineers (IEEE), Jul 2000.
The definitive version is available at https://doi.org/10.1109/ISAF.2000.942447

# High Energy Density Dielectrics for Symmetric Blumleins

W. Huebner and S.C. Zhang
Department of Ceramic Engineering, University of Missouri-Rolla
222 McNutt Hall, Rolla, MO 65401 USA

*Abstract*

Multilayer, tape cast ceramics are being developed for use in large area, high voltage devices in order to achieve high specific energy densities (>$10^6$ J/m$^3$) and physical size reduction. In particular, symmetric Blumleins are desired with the following properties:

- High voltage hold off (≥300 kV)
- High, nondispersive permittivity: ≈100 to 900
- Ability to be fabricated into various shapes and sizes
- Surface flashover inhibition at the edge
- Ability to be triggered by surface flashover switching

The compositions being pursued are based on pure $BaTiO_3$ dielectrics. Our approach is to add glass phase additions which result in not only near theoretical densities, but also allow for fabrication of more complex geometries through high temperature creep. Variations in the volume fraction and connectivity of the glassy phase allow for direct control of the permittivity as well as energy density. Structures up to 5" in diameter have been fabricated and pulse-tested at field strengths over 300 kV/cm. A strong dependence of breakdown strength and permittivity has been observed and correlated with microstructure and the glass composition. This paper presents the interactive effects of manipulation of these variables.

## I. Introduction

Dielectrics for pulsed power applications need to satisfy several key material and processing parameters [1], including a high voltage hold off (≥300 kV), a high, nondispersive permittivity (ε ≈100 to 400), surface flashover inhibition at the edge, the ability to be triggered by surface flashover switching, and the ability to be fabricated into various shapes and sizes.

As can be seen by the equations given in Fig. 1, higher voltages and permittivities result in greater stored energy density and hence smaller systems. Current systems based on water dielectrics can hold off ≈ 150 kV/cm, have a ε≈80, and are self-healing [1]. Their replacement by a solid system such as a polymer or ceramic is highly desirable, but currently available systems based on polymers [2] or ceramics [3] are insufficient due to fundamental shortcomings.

This work focused on improving the microstructure and composition of ceramic-based systems, with particular emphasis on increasing the BDS and ε. The primary source of voltage failure for a ceramic is related to the presence of porosity [4,5], and the associated field/stress amplification. By adding a high BDS, low ε glass to a higher ε dielectric, the porosity can be virtually eliminated, and the BDS is increased. Here we report on studies on glass-loaded $BaTiO_3$ dielectrics, with additional improvements in processing methodology.

| Line Length: | Line Width: | Line Thickness: |
|---|---|---|
| $L = \frac{c \cdot \tau}{2 \cdot \sqrt{K}}$ | $w = \frac{2 \cdot V_{load}}{E\sqrt{K}}\left(\frac{Z_o}{Z_{load}} - \frac{\sqrt{K}}{2n}\right)$ | $t = \frac{2nV_{TL}}{E}$ |
| **Energy density:** | **Line Volume:** | $c$ = speed of light<br>$\tau$ = voltage pulse width<br>$K$ = relative dielectric permittivity<br>$V_{load}$ = operating voltage<br>$E$ = breakdown strength<br>$Z_o$ = free space impedance (constant)<br>$Z_{load}$ = load impedance<br>$n$ = number of transmission lines<br>$V_{TL}$ = voltage of transmission line |
| $\gamma = \frac{1}{2} K \varepsilon_o E$ | $v = \frac{2\pi c}{K}\left(\frac{Z_o}{Z_{load}} - \frac{\sqrt{K}}{2n}\right)\left(\frac{V_{load}}{E}\right)^2$ | |

Figure 1. Equations defining the physical dimensions of Blumleins.

## II. Experimental Procedure

In this work $BaTiO_3$ (NEB, Ferro, Niagara Falls, NY) was used as the base dielectric. At room temperature pure $BaTiO_3$ has a low field ε≈4000, which is strongly dependent on grain size and electric field, E. All samples evaluated in this study were prepared by doctor blade tape casting in a clean room environment. A slurry of 50 vol% $BaTiO_3$ & glass dispersed in a nonaqueous binder system (MSI Ferro, CA.) was used; individual tape layers were 0.20 mm thick. Structures were dried for 5 days at 140°C, and calcined at 450°C for 5 days (1°C/min heating rate). Sintering was performed at varying temperatures to vary the grain size and density.

The target microstructure of a glass composite has a 0-3 connectivity; i.e. a continuous, glassy grain boundary surrounding $BaTiO_3$ grains. A useful glassy phase needs to exhibit several key properties, including: a) the glass must "wet" the dielectric, but not react with it in a fashion detrimental to the electrical properties, b) the glass must result in higher densities, and c) the glass must exhibit a high electrical resistivity, as well as a high electrical

 0-7803-5940-2/01/$10.00 2001 IEEE.

Table I. Physical and Electrical Properties of the Candidate Glasses

| GLASS | Compositions | Tg (°C) | Tm (°C) | TEC* ($10^{-6}$/°C) | Contact Angle (°) | Density (g/cm$^3$) | K (1 kHz) | Resistivity ( Ω-cm) | BDS (V/mil) |
|---|---|---|---|---|---|---|---|---|---|
| Pb1 Glass | 0.5 $PbO,SiO_2,B_2O_3$ | 320 | 510 | 10.95 | 11 | 6.56 | 25.4 | $3.0 \times 10^{15}$ | 1075 |
| Pb2 Glass | 0.4 $PbO,SiO_2,B_2O_3$ | 370 | 540 | | 10 | 5.89 | 21.5 | $>10^{16}$ | 1141 |
| Pb3 Glass | 0.3 $PbO,SiO_2,B_2O_3$ | 415 | 560 | | 6.3 | 5.23 | 17 | $>10^{16}$ | 1570 |
| Bi1 Glass | 0.5 $Bi_2O_3,SiO_2,B_2O_3$ | 370 | 645 | | 7.6 | 7.51 | 39.5 | $3.6 \times 10^{15}$ | 769 |
| Bi2 Glass | 0.4 $Bi_2O_3,SiO_2,B_2O_3$ | 400 | 670 | 13.5 | 5.7 | 6.94 | 36 | $5.3 \times 10^{15}$ | |
| Ba1 Glass | 0.5 BaO, $SiO_2,B_2O_3$ | 520 | 820 | 11.4 | 8.3 | 4.30 | 13.8 | $5.8 \times 10^{15}$ | >1543 |
| Ba2 Glass | 0.5 BaO, $SiO_2,B_2O_3$ | 570 | 860 | 10.2 | - | 4.0 | 13.0 | $>10^{16}$ | |
| Ba3 Glass | 0.5 BaO, $SiO_2,B_2O_3$ | 620 | 880 | 9.8 | - | 3.77 | 12.6 | $>10^{16}$ | 1269 |

** The TEC of pure NEB sintered at 1260°C for 2 h is $11.7 \times 10^{-6}$/°C*

breakdown strength. Borosilicate glasses were chosen for these reasons [3]. Table I summarizes the composition and properties of glasses made by melt fining and quenching. Volume fractions of these glasses ranging from 5-20% were added to the $BaTiO_3$ by ball milling, and then microstructural evolution studies were performed on tape cast specimens to optimize the density and minimize the grain size.

The temperature-dependence of the dielectric properties was measured under low field conditions, with hysteresis loops measured to gain an understanding of higher field behavior. DC breakdown strength measurements were performed on tape cast structures with an active stressed volume of ≈10 cm$^3$, using sputtered Au electrodes.

## III. Results and Discussion

### 1) *Microstructural Evolution*

The ability to fabricate a dense, composite dielectric with a glassy grain boundary is predicated on the ability of the glass to wet the dielectric. Table I contains the contact angle of the various glasses on $BaTiO_3$ taken from the SEM micrographs such as those shown in Fig. 2. The Bi-based glasses wet the best, although their $T_m$ is higher than that of the Pb glasses. As shown in Fig. 3, all three were found to significantly reduce the sintering temperature, with optimum sintering temperatures and resultant microstructures shown in Fig. 4. All of these composites contained 10 vol% glass, which resulted in mostly discontinuous glassy grain boundaries. Significantly, the densification temperature of the Pb-based glass was 900°C, which is very low compared to the undoped conditions needed of ≈1325°C. The Bi-based glasses also resulted in larger grain sizes, which dilatometric and SEM studies showed was due to an enhanced grain boundary mobility.

### 2) *Electrical Properties*

Certainly the presence of a low K glass in the grain boundary will decrease the overall K, the extent of which

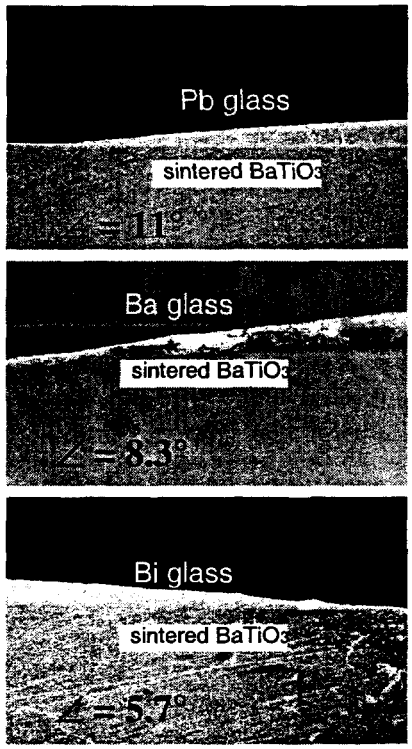


Fig. 2. Contact angles of the a) Pb, b) Ba and c) Bi-based borosilicate glasses on dense $BaTiO_3$.

will depend on the $V_f$ and thickness of the glassy grain boundary. Figs. 5 and 6 exhibits the variation in K and hysteretic properties of the glass systems illustrated in Figs. 3 and 4. As expected, all three systems decreased the ε, with the Bi and Pb-based glasses exhibiting the larger effects. These glasses had a more evident grain boundary phase, compared to the more discrete "pockets" of glass shown in the Ba-based glass. In addition, the Pb-based glass also exhibited some solubility in the $BaTiO_3$ as evidenced by the higher Curie temperature.

The ultimate purpose of this investigation was to study the influence of a glassy grain boundary on the BDS. Fig. 7 shows the results for all three glasses with 10 vol% glass additions; the complete set of data (not all shown here) can be summarized as:

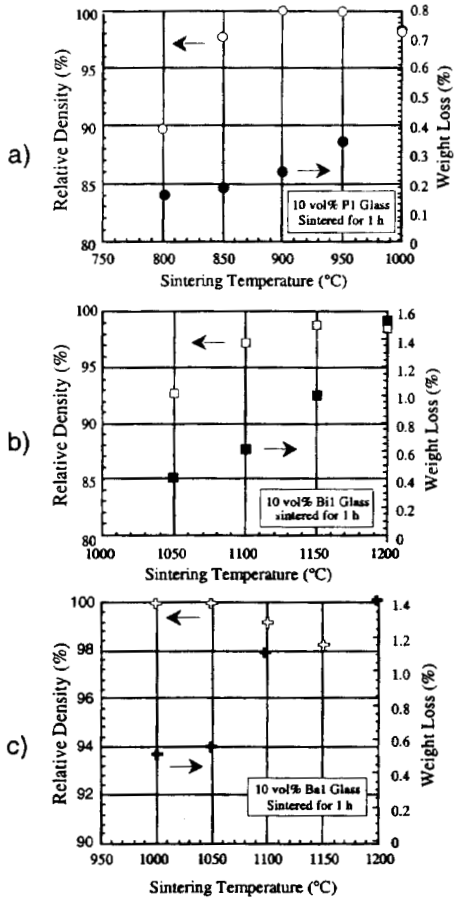


Fig. 3. Densification results and weight loss of the $BaTiO_3$- a) Pb, b) Bi and c) Ba-based borosilicate glasses.

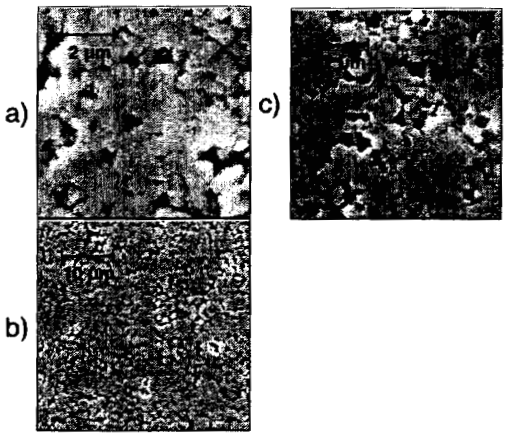


Fig. 4. Microstructures of the $BaTiO_3$- a) Pb, b) Bi and c) Ba-based borosilicate glasses at the optimum sintering T/t.

- Compared to pure $BaTiO_3$, all the glasses studied yielded higher BDSs. This is attributable to the higher densities which were achieved and the uniform microstructures.
- The BDS tracked closely with the density → higher densities yielded higher BDSs, although exceptions exist due to larger grain sizes. For the most part, the 10 vol% samples exhibited the highest BDS.
- In this study the Bi glass yielded the best properties, with a BDS ≈ 500 V/mil. Keep in mind these results are on large volumes of materials ($\approx 10\,cm^3$). This is very encouraging, and ongoing studies are focused on understanding why this composition yielded the highest BDS. This result cannot be explained on the basis of any fundamental glass properties or the resultant microstructures (which were similar between specimens).

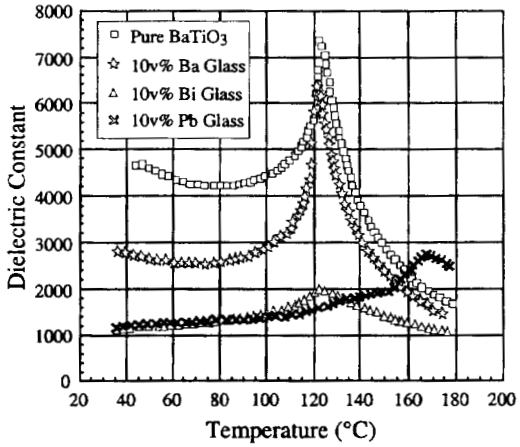


Fig. 5 Dielectric properties of the $BaTiO_3$- glass composites.

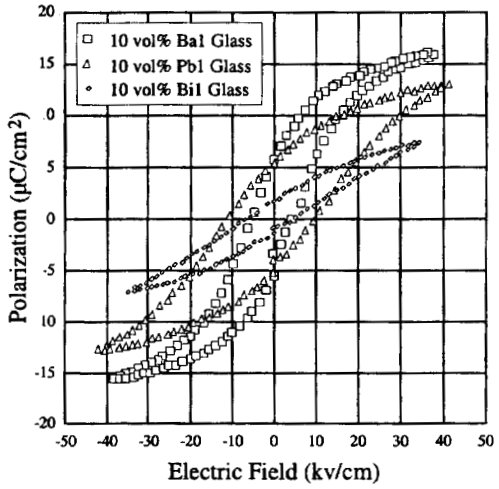


Fig. 6 Hysteretic properties of the $BaTiO_3$- glass composites.

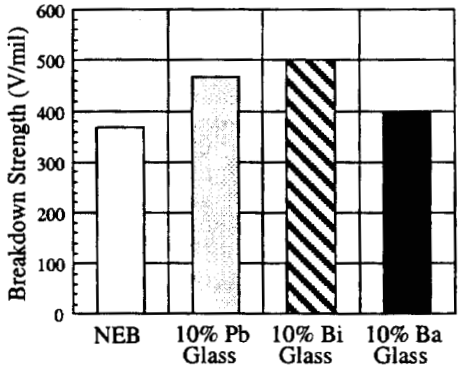


Fig. 7 Breakdown strength properties of the $BaTiO_3$- glass composites.

*3) Pb-based Glass Systems*

The significantly lower sintering temperature of the Pb-based glass systems prompted further studies. Fig. 8 illustrates the microstructures of this system sintered at temperatures ranging from 850 to 1000 °C. Coupled with the dielectric properties shown in Figs. 9 and 10, these results show that this system exhibits a broad processing window under which it can be processed and still retain a relatively high dielectric constant. The slope of the P vs. E loops shown in Fig. 9 reveal that the ε drops only ≈ 30% for fields up to 40 kV/cm. When sintered at 1000°C, the grain size becomes too large, with a resultant loss in the extrinsic contributions to the dielectric constant. This system may be advantageous for low-fire dielectric systems.

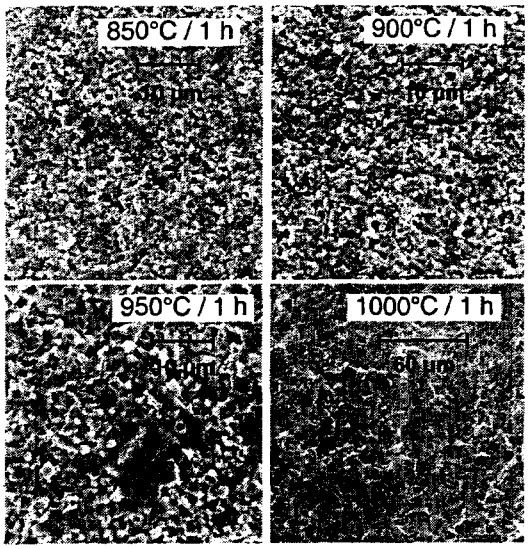


Fig. 8 Microstructures of the Pb-glass composites sintered under various conditions.

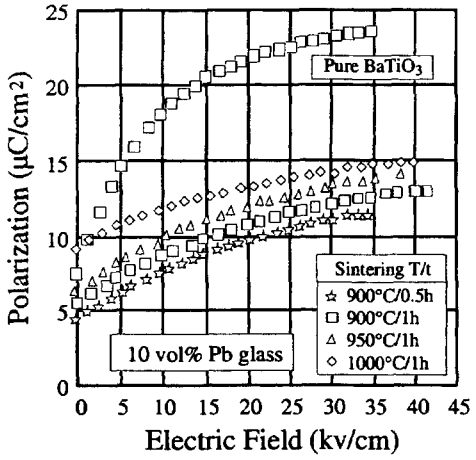


Fig. 9 Hysteretic properties of the Pb-glass composites sintered under various conditions.

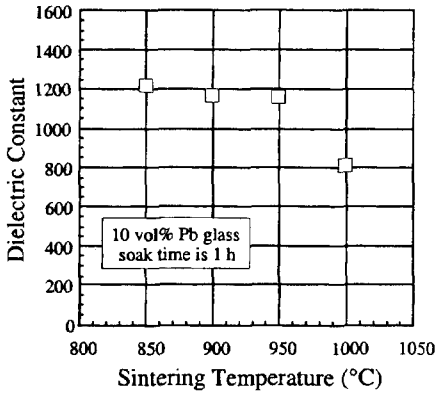


Fig. 10 Variation in the low field dielectric constant of the Pb-glass composites sintered under various conditions.

## IV. SUMMARY

Through modification of the microstructure with glass phase additions the bulk BDS of $BaTiO_3$ dielectrics has been substantially increased. The addition of glass increases the density, forms a continuous grain boundary phase, and allows for systematic control of the permittivity. The energy density of the best dielectrics studied here was on the order of 2 J/cm$^3$ for a stressed volume of 10 cm$^3$. As such these composite systems show great promise for compact pulsed power applications.

## V. REFERENCES


[1] S.T. Pai and Q. Zhang, Introduction to High Power Pulse Technology, World Scientific Publishing Co., Singapore.

[2] Z. Deheng and Y. Zhang, High Voltage Electrical Insulation, Tsinghua University Press, Beijing (1992).

[3] I.O. Owate and R. Freer, "Dielectric breakdown of ceramics and glass ceramics," in Proc. 6th Intl Conf. on Dielectric Materials, Measurements and Applications, 1992, p. 443.

[4] R. Gerson and T.C. Marshall, "Dielectric Breakdown of Porous Ceramics," *J. Appl. Phys.*, vol. 30, pp. 1650-1653, Nov. 59.

[5] G. Economos, "The Effect of Microstructure on the Electrical and Magnetic Properties of Ceramics," Ceramic Fabrication Processes, W.D. Kingery, Ed., New York, John Wiley & Sons, 1950, pp. 201-213.