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High Energy Density Dielectrics for Symmetric Blumleins

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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 ($\geq$300 kV)
♦ High, nondispersive permittivity: $\approx$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 ($\geq$300 kV), a high, nondispersive permittivity ($\varepsilon \approx$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 $\approx$ 150 kV/cm, have a $\varepsilon \approx$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:
$L = \dfrac{c \cdot \tau}{2 \cdot \sqrt{K}}$	$w = \dfrac{2 \cdot V_{load}}{E\sqrt{K}}\left(\dfrac{Z_o}{Z_{load}} - \dfrac{\sqrt{K}}{2n}\right)$	$t = \dfrac{2nV_{TL}}{E}$
Energy density:	Line Volume:	$c =$ speed of light $\tau =$ voltage pulse width $K =$ relative dielectric permittivity $V_{load} =$ operating voltage $E =$ breakdown strength $Z_o =$ free space impedance (constant) $Z_{load} =$ load impedance $n =$ number of transmission lines $V_{TL} =$ voltage of transmission line
$\gamma = \dfrac{1}{2}K\varepsilon_o E^2$	$v = \dfrac{2\pi}{K}\left(\dfrac{Z_o}{Z_{load}} - \dfrac{\sqrt{K}}{2n}\right)\left(\dfrac{V_{load}}{E}\right)^2$	

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 $\varepsilon \approx$4000, which is strongly dependent on grain size and electric field, E. All samples evaluated in this study were prepared by doctor blade tape casting in a clean room environment. A slurry of 50 vol% BaTiO$_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

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	3.0×10^{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	3.6×10^{15}	769
Bi2 Glass	$0.4\ Bi_2O_3,SiO_2,B_2O_3$	400	670	13.5	5.7	6.94	36	5.3×10^{15}	
Ba1 Glass	$0.5\ BaO,\ SiO_2,B_2O_3$	520	820	11.4	8.3	4.30	13.8	5.8×10^{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 $11.7x10^{-6}/°C$

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 $\approx$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

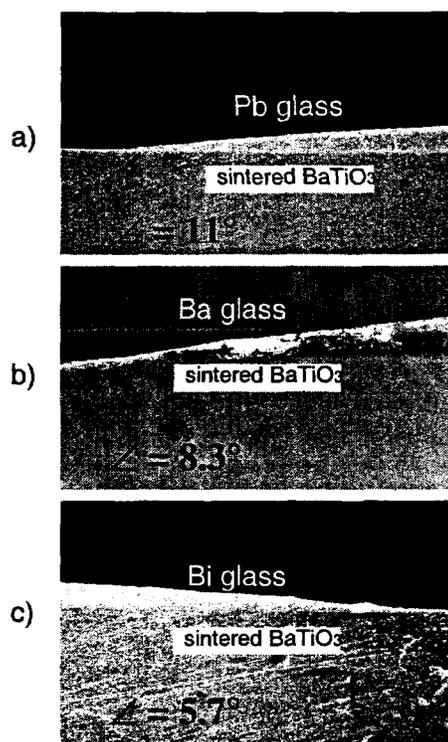Certainly the presence of a low K glass in the grain boundary will decrease the overall K, the extent of which

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:
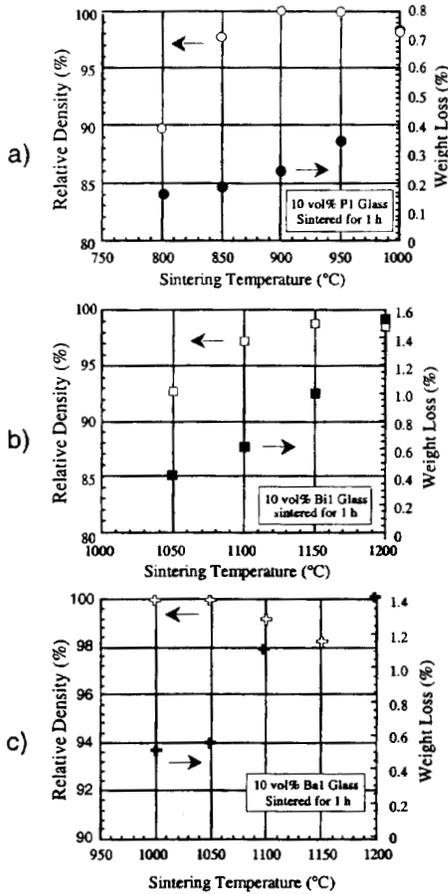
834

Fig. 3. Densification results and weight loss of the BaTiO$_3$-
a) Pb, b) Bi and c) Ba-based borosilicate glasses.
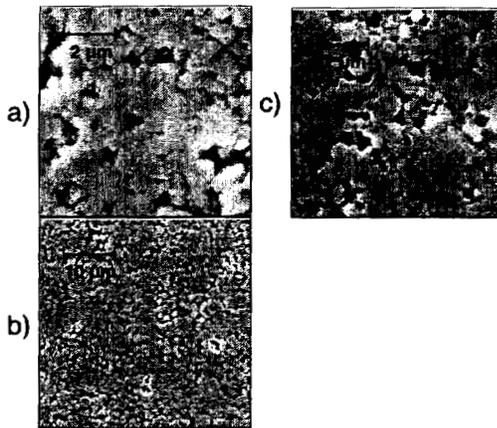

Fig. 4. Microstructures of the BaTiO$_3$- a) Pb, b) Bi and c) Ba-
based borosilicate glasses at the optimum sintering T/t.

♦ 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 (≈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
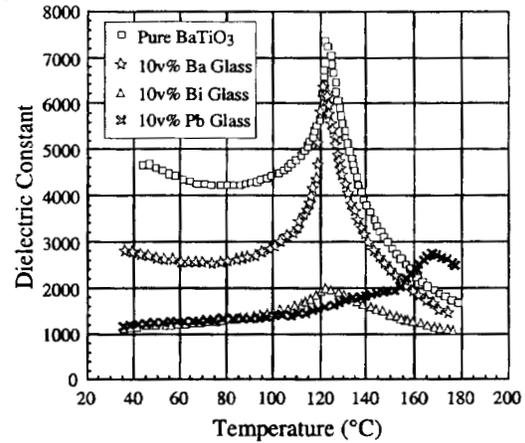resultant microstructures (which were similar between
specimens).

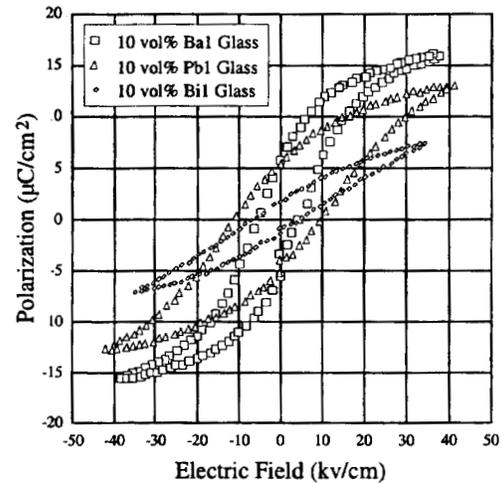Fig. 5 Dielectric properties of the BaTiO$_3$- glass composites.

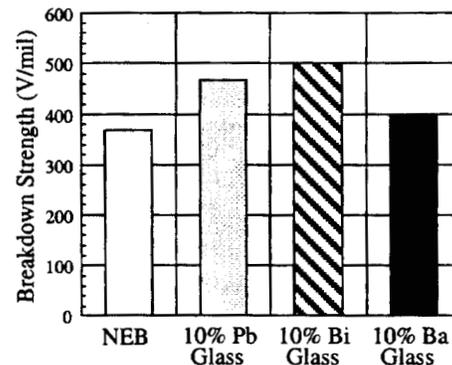Fig. 6 Hysteretic properties of the BaTiO$_3$- glass composites.

Fig. 7 Breakdown strength properties of the BaTiO$_3$- glass
composites.

835

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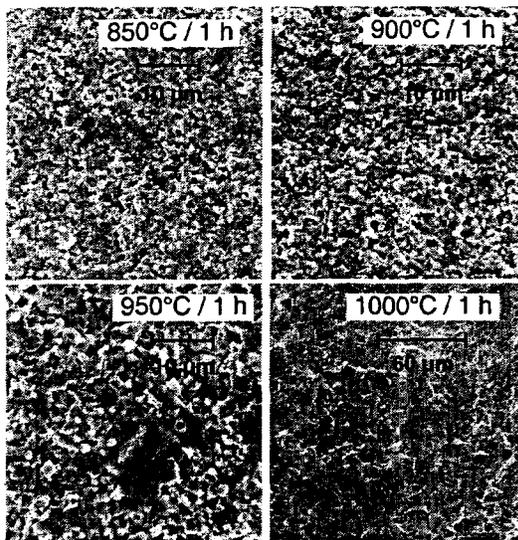
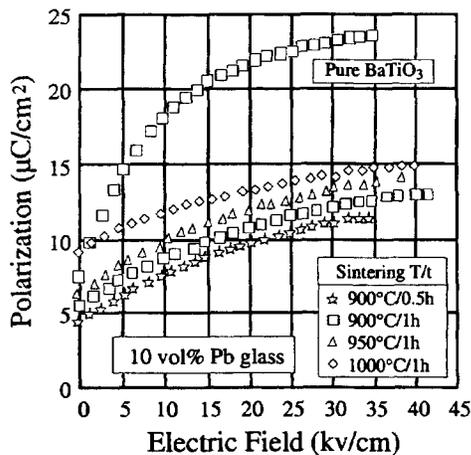Fig. 8 Microstructures of the Pb-glass composites sintered under various conditions.

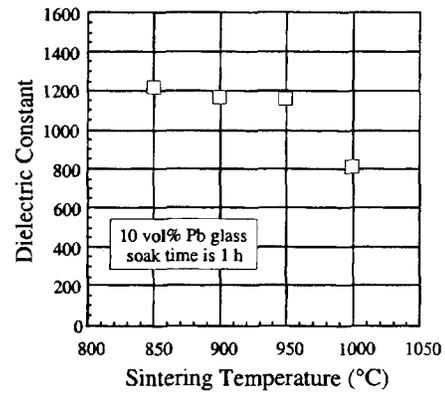Fig. 9 Hysteretic properties of the Pb-glass composites sintered under various conditions.

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

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