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AEROSOL DEPOSITION OF INTEGRATED CAPACITORS

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Component integration into a volumetrically efficient, robust package is necessary to meet the requirements for next generation technologies in both defense and hybrid vehicle applications. In this work, single and multilayer capacitors were fabricated directly on alumina substrates using an aerosol deposition technique. In this process, PLZT powder is dispersed into an ink, which is then sprayed onto the substrate using a pneumatically operated nozzle. As the ink typically contains less than 2 wt% binder, shrinkage due to organic burnout is minimized, enabling sintering of thick films on previously sintered substrates without cracking. Computer control of the deposition process allows for rapid fabrication of components, with the potential for scale-up to large quantity production. At present, a 1cm^2 x 50µm thick film can be deposited in under one minute. Integration of PLZT capacitors into a component package can be challenging; at typical sintering temperatures (1200 ºC – 1300 ºC) there is significant diffusion of lead into the alumina substrate. This can lead to poor adhesion of the capacitor to the substrate, as well as drastically reduced electrical properties. Techniques such as chemical processing of sub-micron precursor powders as well as liquid flux additives have enabled the sintering temperature to be reduced by several hundred degrees, minimizing lead diffusion. Using these materials and techniques, large area (15cm^2) thick film capacitors have been fabricated on alumina substrates. Capacitances in excess of 400 nF were achieved for devices having 50 micron thick layers sintered at 950ºC. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL8500.

Introduction

Capacitors suitable for use in applications such as dc bus inverters for fuel cell and hybrid vehicles, as well as pulse discharge defense systems must meet several stringent design requirements. These requirements include: field insensitive dielectric constant, high intrinsic breakdown strength, reliability, and stability over the device's operating temperature range. Additionally, volumetric efficiency and integration are of primary concern, as designers strive to achieve greater performance from smaller device packages. To realize these goals, advancements in both material properties as well as device fabrication are necessary. The work described in this paper seeks to address these requirements through the use of lanthanum modified PZT (PLZT) materials for these applications. Further, we demonstrate the development of an aerosol technique for depositing multi-layer ceramic capacitors directly onto alumina substrates.

Lanthanum modified PZT (PLZT) is a class of materials that has been shown previously to have very good dielectric properties [1]. These compositions are unique in that they are relatively field insensitive, making them ideally suited for high voltage applications. Integrating lead based materials into an electronic component package can be difficult to achieve, largely due to the high volatility of lead at elevated sintering temperatures. This can lead to loss of stoichiometric control as well as degraded electrical properties. It has been shown by Holc and coworkers [2] that these difficulties are magnified when attempting to fire PZT on alumina in the presence of Pt electrode materials. Undesirable phases form at the alumina-PLZT interface, causing poor or no adhesion of the capacitor material to the substrate. To produce a high quality device, it is necessary to address this issue. One possible solution is to lower the sintering temperature of the material. By doing this, the degrading effects of lead diffusion and volatility can be minimized. Several researchers have used liquid flux additives to successfully reduce the sintering temperature of PZT based materials to below 1000°C [3, 4]. In general, these methods utilize a small quantity (~3%) of an additive which forms a liquid phase at the early stages of sintering. This small amount of liquid allows for greater particle mobility, and material transport, enhancing densification.

Several techniques exist for rapid prototyping of ceramic materials including fused deposition [5], and robocasting [6]. In this work, we have chosen to use an aerosol deposition technique, as it has a number of possible advantages for fabrication of integrated capacitors. Using a spray technique, a large area can be deposited relatively quickly, allowing for rapid fabrication. Also, as relatively small quantities of organics are needed for this technique, there is little to no shrinkage due to binder burnout, allowing the material to be sintered directly on previously sintered substrates without cracking.

Procedures

The general equation used for batching our PLZT compositions is given by the formula:

$$Pb_{(1-x)}La_x(Zr_yTi_{(1-y)})_{1-x/4}O_3$$

This formula assumes lanthanum occupies a-sites, while b-site vacancies are created to maintain electroneutrality. Two percent lead excess was added to improve sintering behavior, as well as compensate for lead volatilization. PLZT compositions for this work were prepared using a chemical synthesis method [7]. Using this technique, lead and lanthanum oxides, and zirconia and titanium alkoxides are dissolved in acetic acid and mixed. The metal cation solution is then combined with an oxalic acid/propanol solution to precipitate the homogeneously distributed cation solution, which is then filtered, dried, and calcined to form the target PLZT composition. For this work, the PLZT composition 12/70/30 was chosen, as it has a high dielectric constant, as well as good field and temperature stability. When the liquid flux additive $PbGeO_3$ was used in this work, it was incorporated into the calcined PLZT powder as its constituent oxides, PbO and GeO_2. Appropriate quantities of each oxide were weighed, and placed into a nalgene bottle with the PLZT powder. The powder was then wet milled in ethanol for 24 hours.

Pellets used for the evaluation of bulk material properties were formed by uniaxially pressing 3 grams of powder in a 1cm diameter pellet die. Before pressing, a 3 wt% solution of polyvinyl alcohol and water was added to the powder as a binder. The powder was compacted under a pressure of 14 ksi. Following sintering the pellets were cut to a thickness of 0.5-0.75 mm using a diamond saw, and polished to a 1μm finish. Gold electrodes were then sputtered onto the pellets after sputtering a chrome adhesion layer. These layers were 150 nm and 20 nm, respectively.

To produce a thick film sample, the PLZT powder was combined with a solvent, dispersant, and binder to form an ink suitable for spraying. A two component solvent containing both isobutanol and terpineol was used in this work. These solvents were chosen primarily by their vapor pressures. The isobutanol has a relatively low vapor pressure and evaporates quickly, allowing the deposited layer to dry, while terpineol has a higher vapor pressure, and prevents the sprayed material from drying completely before it contacts the substrate. The binder and dispersant used for the ink were ethocel and solsperes, respectively. The quantities of each material used to formulate a typical PLZT ink are given in Table I.

Table I. Batch formula for a typical PLZT ink.

Constituent	Vol. %
Isobutanol	84.3
Terpineol	3.9
PLZT	9.5
Ethocel	1.9
Solsperes	0.4

The electrodes for the thick film samples in this work were platinum, and were sprayed using the same techniques as the capacitor layers. The ink used was DuPont 9894 fritless platinum thick film conductor composition, which was thinned using ethanol or terpineol to a viscosity suitable for spraying.

The aerosol spray apparatus consists of a nozzle, a delivery system for controlling the ink flow, and a series of linear stages to raster the substrate under the nozzle. The nozzle is pneumatically operated, and combines the ink with a stream of compressed gas to produce a fine mist. Ink is fed into the nozzle from a pressurized holding container, which is mounted onto a stirring plate to ensure suspension homogeneity. The ink flow rate is controlled by adjusting the pressure in the holding container.

The alumina substrate (Coors Suprasurf, 25 cm^2) is mounted onto a stage which is connected to two linear motion stages that control x and y positioning. The stages, as well as operation of the spray nozzle, are controlled using Labview software.

To achieve the desired fired thickness for a layer, it is necessary to know the deposition rate of the ink. Test pieces were deposited and weighed to determine this rate; once this was established, the mass of deposited material, the deposited area, and the sintered density of the material are used to calculate the fired layer thickness. It is assumed in this calculation that the material sinters to theoretical density. Adjustments to the deposition time can then be made to achieve the desired layer thickness.

Single layer capacitors were fabricated by first depositing a 50 μm PLZT buffer layer onto the alumina substrate. This layer was sintered at 1200ºC for two hours prior to depositing any further layers. After the buffer layer is fired, a Pt bottom electrode is deposited. To achieve the target fired thickness of 3-5 μm, 0.25 grams of platinum was deposited onto the buffer layer. An aluminum mask was used to define the electrode area. Following the bottom electrode, a PLZT capacitor layer is deposited. This was done using the same technique as for the electrode layer. Again, the mass of the deposited material was used to determine the fired layer thickness. For a 50 μm target thickness, 0.9 grams of PLZT was deposited onto an area of 25 cm^2. Multilayer capacitors are fabricated by simply repeating the deposition of alternating electrode – capacitor layers.

To prevent lead loss during firing, samples were fired in closed crucibles, on a bed of PZT 95/5 powder. Additional PZT powder was used to completely cover the samples. Firing was done at either 1100°C or 1200°C using a heating rate of 2°C/min and a cooling rate of 3°C/min.

Density as a function of temperature was determined by direct observation of the sample shrinkage during sintering. A sapphire window in the furnace allowed a camera directed at the sample to record linear shrinkage as the temperature was increased at a rate of 5°C/min. Theoretical density could then be determined from these data.

Capacitance and dissipation factor of our PLZT samples were measured using an HP 4842 precision LCR meter at frequencies ranging from 100 Hz to 1 MHz. For dielectric constant versus temperature measurements, samples were heated and cooled at a rate of 2°C/min using a Thermotron environmental chamber. Temperature and capacitance data were recorded using LabVIEW data acquisition software. Polarization versus electric field data were taken using a Radiant Technologies Precision Material Analyzer. Samples were tested at a frequency of 10 Hz, at 25ºC.

Results and Discussion

The densities for PLZT 12/70/30 pellets sintered at 1200°C, 1100°C, and 1000°C are given in Table II. From these data it can be seen that highest densities were observed at a sintering temperature of 1100°C. Sintering at 1000°C reduced the density to 91% theoretical; this is however a great improvement over samples produced from the traditional mixed oxide precursor route, where sintering at 1000°C yields densities on the order of 67% theoretical. Dielectric constant and dissipation factor as a function of temperature for these samples can be seen in Figure 1.

Table II. Densities of PLZT powders sintered at different temperatures.

Sintering Temperature (ºC)	Density (g/cc)	% Theoretical
1200	7.6	**95**
1100	7.9	**99**
1000	7.3	**91**

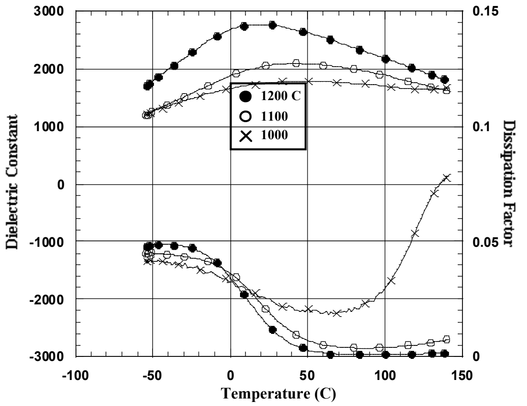

Figure 1. Dielectric constant vs. temperature for PLZT 12/70/30 bulk ceramics sintered at different temperatures.

A dielectric constant in excess of 2000 over the temperature range of -30°C to 100°C was observed for samples fired at 1200°C. For samples sintered at 1100°C and 1000°C, the dielectric constant was reduced somewhat. Interestingly, the sample sintered at 1000°C has a higher dielectric constant over the entire temperature range of -50°C to 150°C than the 1100°C bulk ceramic. SEM micrographs of these samples show very different fracture behavior, which can explain this behavior. At 1000°C, PbO rich pockets are evident, along with evidence of both transgranular and intergranular fracture, which would indicate some direct perovskite grain contact. At 1100°C, there is no evidence of PbO rich areas, and fracture is entirely intergranular, indicating a possible matrix phase and no direct perovskite grain contact. This would serve to lower the dielectric constant, and is consistent with the electrical data for these samples. By 1200°C, fracture is entirely transgranular, indicating good perovskite grain contact, and increased dielectric constant.

Theoretical density as a function of temperature for samples with both 2% and 4% $PbGeO_3$ added is given in Figure 2. Starting from a green density of 55%, the sample with 4% $PbGeO_3$ reached 98% theoretical density by 1000°C, and the 2% $PbGeO_3$ sample reached 87%. Samples containing 2% $PbGeO_3$ sintered at 950°C with a two hour hold at temperature have a density of 93% theoretical. Dielectric constant and dissipation factor for this sample is given in Figure3. A maximum dielectric constant greater than 3000 was observed at 90°C, the dissipation factor is below 0.05 over the temperature range -50°C – 150°C. these results compare favorably to samples sintered at 1200°C with no liquid flux additives.

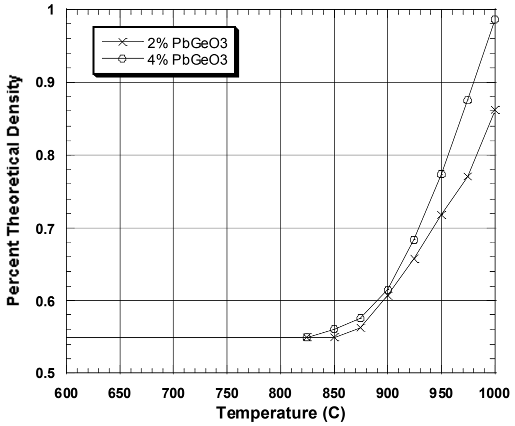

Figure 2. Theoretical density as a function of temperature for chemically prepared PLZT 12/70/30 powders with $PbGeO_3$ liquid flux additives.

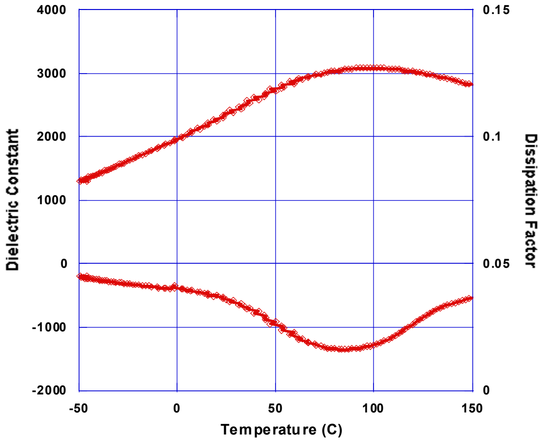

Figure 3. Dielectric constant and dissipation factor vs. temperature for a bulk PLZT 12/70/30 sample sintered at 950°C using liquid flux additives.

An SEM micrograph of an aerosol deposited PLZT 12/70/30 sample with no liquid flux additives is shown in Figure 4. This sample was sintered at 1200°C for two hours. In this micrograph evidence of a secondary phase at the PLZT/Alumina interface can be seen.

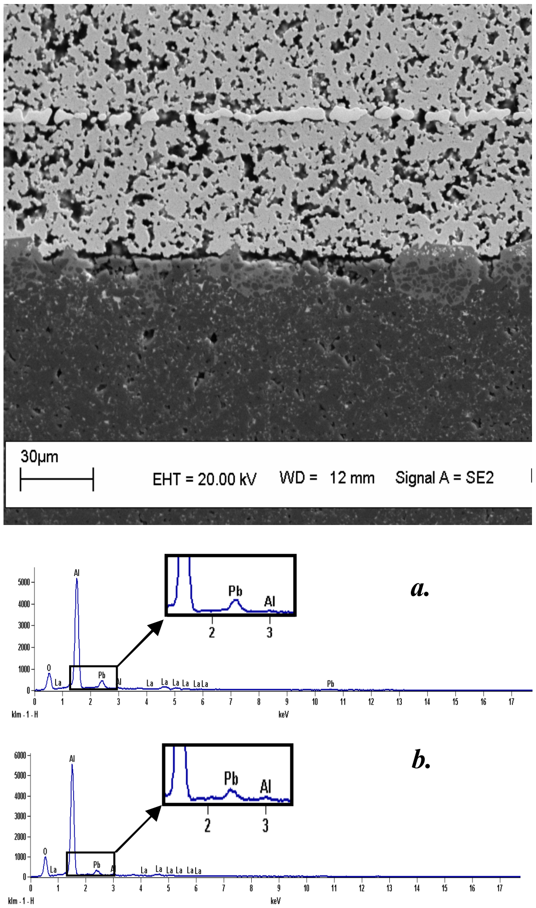

Figure 4. SEM micrograph and EDS spectra of a PLZT 12/70/30 thick film sample sintered at 1200°C. Spectra (a.) is from the PLZT – Alumina interface phase, and (b.) is taken several microns into the alumina substrate.

EDS spectra of this interfacial phase show both lead and aluminum constituents. Spectra taken further within the alumina substrate show significant diffusion of lead into the alumina. An SEM micrograph of an aerosol deposited PLZT 12/70/30 capacitor using 2% $PbGeO_3$ liquid flux sintered at 950°C is shown in Figure 5. Lower porosity is evident as compared to sample containing no liquid flux. Additionally, EDS spectra taken within the substrate shows no evidence of lead diffusion. Dielectric constant as a function of temperature for this single layer sample is given in Figure 6. As compared to a pressed pellet sample of the same material, the aerosol deposited thick film sample shows a slightly reduced dielectric constant over the entire temperature range. This may be caused by a slightly lower density of the thick film sample. From room temperature to 150°C, a dielectric constant in excess of 2000 and dissipation factor less than 0.04 was observed for the thick film sample. Polarization as a function of electric field for the thick film sample is given in Figure 7. For this sample, a maximum polarization of 21 μC/cm^2 is observed, and the breakdown strength is 220 kV/cm.

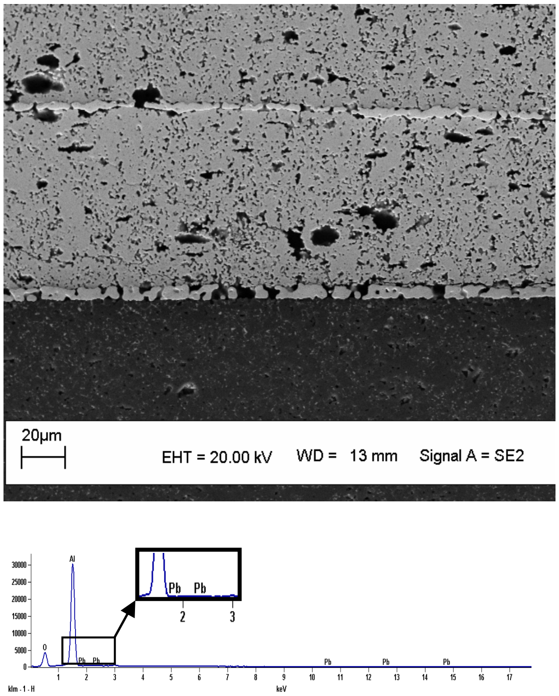

Figure 5. SEM micrograph and EDS spectra of a PLZT 12/70/30 thick film sample sintered at 950°C using liquid flux additives.

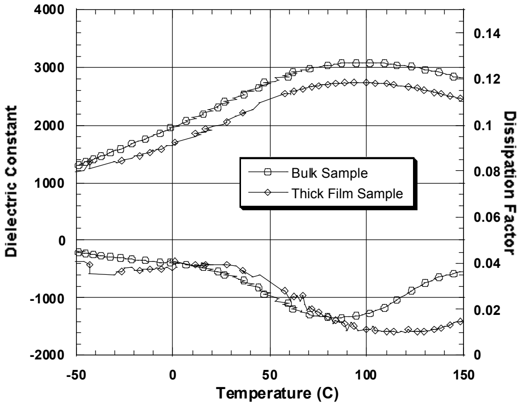

Figure 6. Dielectric constant and dissipation factor for a single layer, aerosol spray deposited thick film sample sintered at 950°C. Shown also for comparison is a bulk sample of the same material.

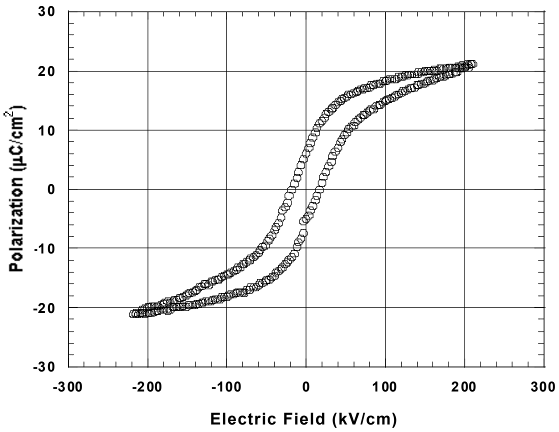

Figure 7. Polarization vs. electric field for a single layer aerosol spray deposited thick film sample sintered at 950°C.

Using aerosol spray deposition, a two layer multilayer sample was fabricated using PLZT 12/70/30 containing 2% $PbGeO_3$ liquid flux. This sample has an active capacitor area of 15 cm^2, and an individual layer thickness of 60 μm. This sample was sintered at 950°C for two hours. Dielectric constant and dissipation factor for this sample are given in Figure 8. A maximum dielectric constant of 2100 was observed at 60°C for this sample, and dissipation factor remained below 0.05 over the entire temperature range measured.

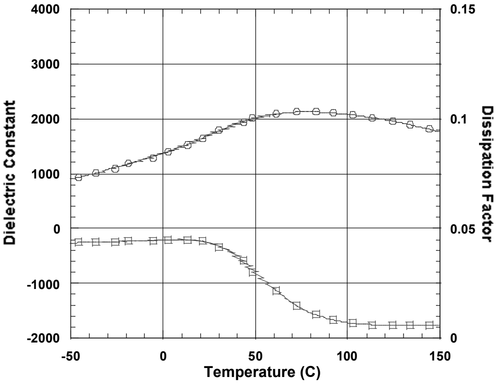

Figure 8. Dielectric constant and dissipation factor vs. temperature for a two layer aerosol spray deposited multilayer sintered at 950°C.

Conclusions

We have demonstrated that aerosol spray deposition is a feasible rapid process technique to produce large area multilayer capacitors. Control of lead loss through either diffusion into the substrate or volatilization during sintering is essential to producing high quality devices. This work has shown that by using advanced powder synthesis techniques, as well as liquid flux additives, the sintering temperature of PLZT dielectric materials can be reduced significantly. Consequently, lead loss can be minimized, yielding thick film capacitors with dielectric properties comparable to bulk samples.

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