

High Temperature, High Energy Density Dielectrics for Power Electronics Applications

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ABSTRACT

Mn and/or rare earth-doped $x\text{CaTiO}_3 - (1-x)\text{CaMeO}_3$ dielectrics, where $\text{Me}=\text{Hf}$ or Zr and $x=0.7, 0.8$, and 0.9 were developed to yield materials with room temperature relative permittivities of $\epsilon_r \sim 150\text{--}170$, thermal coefficients of capacitance (TCC) of $\pm 15.8\%$ to $\pm 16.4\%$ from -50 to 150°C , and band gaps of $\sim 3.3\text{--}3.6$ eV as determined by UV-Vis spectroscopy. Un-doped single layer capacitors exhibited room temperature energy densities as large as 9.0 J/cm^3 , but showed a drastic decrease in energy density above 100°C . When doped with $0.5\text{ mol\% Mn}$, the temperature dependence of the breakdown strength was minimized, and energy densities similar to room temperature values (9.5 J/cm^3) were observed up to 200°C . At 300°C , energy densities as large as 6.5 J/cm^3 were measured. These observations suggest that with further reductions in grain size and dielectric layer thickness, the $x\text{CaTiO}_3 - (1-x)\text{CaMeO}_3$ system is a strong candidate for integration into future power electronics applications.

To further improve the high temperature, high field reliability of these material systems, rare earth donor doping has been utilized. Initially, $1\text{ mol\%}$ doping with Dy, Gd, and Sm showed the most significant reduction in high temperature, high field conductivity. Further investigation of Dy co-doping with $0.5\text{ mol\% Mn}$, Mg, and (Mn+Mg) showed the most significant increase in $\text{Ca}(\text{Ti}_{0.8}\text{Hf}_{0.2})\text{O}_3$ resistivity from $4.61\text{ M}\Omega\cdot\text{m}$ with only Mn doping to $176\text{ G}\Omega\cdot\text{cm}$ with Dy and Mg co-doping. Material systems were characterized using capacitance and dielectric loss vs. temperature, current-voltage (I-V), UV-Vis spectroscopy for band gap determination, and polarization vs. field measurements.

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INTRODUCTION

Future technological advances in power electronics modules for renewable energy interfaces, hybrid/electric vehicles, and power distribution systems will depend on advances in dielectric materials with high energy and power densities. In state-of-the-art and emerging power electronics inverter modules, low permittivity ($\epsilon_r \sim 35$) NP0-type multilayer ceramic capacitors (MLCCs) are utilized, which reach operating temperatures of $> 260^\circ\text{C}$ [1]. While NP0 MLCCs provide precise capacitance control over a broad operating temperature range (commonly -50 to 150°C), the low permittivity of the dielectric limits the overall energy storage capabilities of the capacitors, thus limiting the efficiency of the module. Additionally, the operating temperatures are often well above the specifications of the capacitors themselves. One way to improve the efficiency of such power modules is to develop new materials for MLCC technologies that produce significantly higher energy densities at temperatures up to, and possibly above 300°C .

Recently, data on a new binary material system, $\text{Ca}(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3$ (CHT + Mn) was published that yielded energy densities of $> 6.0\text{ J/cm}^3$ at 300°C with large resistivity compared to its un-doped counterpart [2].

The maximum energy density ($U_{\text{max}}, \text{J/cm}^3$) of a material is defined in terms of its dielectric breakdown strength (E_b , kV/cm) and relative permittivity, as shown in Equation 1,

$$U_{\text{max}} = \frac{\epsilon_0 \epsilon_r E_b^2}{2} \quad (1)$$

where ϵ_r is the relative dielectric permittivity and ϵ_0 is the free-space permittivity ($8.85 \times 10^{-14}\text{ F/cm}$) [3]. There are several ways to experimentally determine the energy density of a material, which include using capacitance as a function of voltage and volume of material, and permittivity as a function of electric field as shown in Equation 1. Additionally, one can characterize energy density as a function of dielectric displacement and electric field using

polarization vs. field (PE) loops, as performed in this research and is quantified through Equation 2,

$$U_{\max} = \int E dP \quad (2)$$

where E is the electric field (kV/cm) and P is the polarization ($\mu\text{C}/\text{cm}^2$) [4]. A diagram of a typical P-E loop for a linear or paraelectric material of high vs. low permittivity is shown in Figure 1. The energy density in this case is referred to as the maximum recoverable energy density upon discharge of the capacitor.

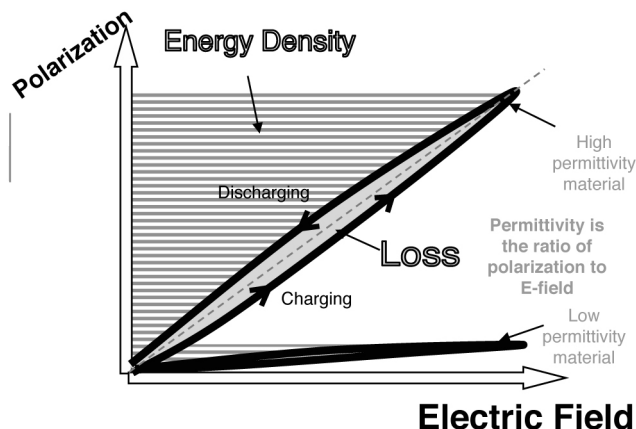


Figure 1. Diagram of polarization vs. field loop for linear/paraelectric material comparing one of high permittivity with low permittivity. The area within the loop is the dielectric loss ($\tan\delta$) and the total recoverable energy density is quantified as the lined area on the plot.

Equation 1 and Figure 1 show the basis for how high temperature, high energy density dielectrics are developed. The overriding goal is to optimize the balance between a material's relative permittivity, dielectric breakdown strength, and high temperature and field reliability. There are various types of dielectric compositions for high energy density applications including linear dielectrics, ferroelectrics, and antiferroelectrics. Despite having large permittivities ($\epsilon_r > 1000$), recoverable energy densities in ferroelectrics (e.g. BaTiO_3) are limited due to their hysteretic and non-linear behavior in which breakdown strengths are < 1 MV/cm and their large high field losses restrict their applicability here [3].

Antiferroelectrics (e.g. PbZrO_3), transform into a ferroelectric phase at high electric fields. A large polarization develops providing high energy density, but the relatively small number of antiferroelectric compositions available limits this class of materials. Additionally, regardless of having large permittivities ($\epsilon_r > 500$), the possible high field polarization dependence, high field losses due to hysteresis, strains as high as 0.6%, and commonly lead-based chemistries make them less attractive for these new opportunities, particularly above 200 °C [5].

Linear dielectrics (e.g. $0.8\text{CaHfO}_3 - 0.2\text{CaTiO}_3$) have a linear polarization-field dependence, moderate permittivities ($\epsilon_r \sim 30$ -300), and low losses ($\tan\delta < 0.001$) within the working temperature range [2]. In an ideal dielectric, the dielectric displacement increases linearly with increasing applied electric field, which allows for all stored energy to be recovered upon discharge while experiencing minimal dielectric loss as desired for these applications.

NP0-type materials have recently been shown to be competitive with polymer film capacitors, which together dominate the power electronics capacitor industry [6]. A typical NP0 composition is $0.8\text{CaZrO}_3 - 0.2\text{CaTiO}_3$ (CZT), which yields a relative permittivity of $\epsilon_r \sim 34$ -75, breakdown strengths of 0.65-1.75 MV/cm, thermal coefficient of capacitance (TCC) of 30 ppm/°C or 0.5 % from -50 to 125°C, and room temperature energy densities of up to 5 J/cm³ [6]. While the breakdown strength of this system is high, the low permittivity associated with CaZrO_3 limits the maximum recoverable energy density. In this work, the initial compositions investigated were $0.8\text{CaTiO}_3 - 0.2\text{CaZrO}_3$ (CZT) and $0.8\text{CaTiO}_3 - 0.2\text{CaHfO}_3$ (CHT) to emphasize the higher permittivity of paraelectric/incipient ferroelectric CaTiO_3 ($\epsilon_r \sim 171$ compared to 30 for CaZrO_3) and replace CaZrO_3 with CaHfO_3 to exploit the higher band gap of CaHfO_3 at 6.4 eV compared to 4 - 5.5 eV for CaZrO_3 to further minimize conduction [7,8,9,10,11].

After initial characterization revealed that high temperature breakdown strength was compromised in the base material, investigations into acceptor doping were made. Previous researchers have utilized Mn doping in order to improve insulation resistance in various material systems. Additionally, Mn doping has been used in both CZT and similar systems as a means to mitigate high temperature and high field losses that are often absent in room temperature measurements [2,12,13,14,15,16,17,18,19,20]. With 0.5 mol % Mn doping on the Ti site in CZT and CHT (CZT + Mn and CHT + Mn), significant improvements in high temperature breakdown stability, loss mitigation, and electrostatic energy densities have been observed in this work.

Based on success in similar perovskite systems by other researchers, in an attempt to further reduce high temperature conductivity in the CHT + Mn system, rare earth co-doping with Dy (donor doping, Ca-site) and Mg acceptor doping (CHT + Dy + Mg) has shown an increase in resistivity by an order of magnitude compared to only Mn doping [21,22,23,24]. This paper will describe a basic development template for engineering high temperature, high energy density ceramic materials from their basic perovskite or binary perovskite composition to their final, donor and acceptor doped composition as needed to create the optimum balance of high breakdown strength and polarization with high temperature, high field reliability. The most successful compositions to be discussed are $\text{Ca}(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Zr}_{0.2})\text{O}_3$

(CZT + Mn), $\text{Ca}(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3$ (CHT + Mn), and $(\text{Ca}_{0.99}\text{Dy}_{0.01})(\text{Ti}_{0.795}\text{Mg}_{0.005}\text{Hf}_{0.2})\text{O}_3$ (CHT + Dy + Mg).

EXPERIMENTAL

Powders for characterization of $\text{Ca}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ (CZT $x=0.8$), $\text{Ca}(\text{Ti}_x\text{Mn}_{0.005}\text{Zr}_{1-x})\text{O}_3$ (CZT + Mn, $x=0.7, 0.8, 0.9$), $\text{Ca}(\text{Ti}_{0.795}\text{Mn}_{0.005}\text{Hf}_{0.2})\text{O}_3$ (CHT + Mn), and $(\text{Ca}_{0.99}\text{Re}_{0.01})(\text{Ti}_{0.795}\text{X}_{0.005}\text{Hf}_{0.2})\text{O}_3$ CHT + Re + X where Re is Dy, Gd, or Sm and X is Mn or Mg were synthesized using solid state ceramic processing. Starting powders of CaCO_3 (Sigma-Aldrich, 99+% A.C.S. reagent), TiO_2 (Ishihara Sangyo Kaisha LTD., ultra high purity), HfO_2 (Alfa Aesar, tech.), ZrO_2 (MEL Chemicals, Flemington, NJ), MnO_2 (Cerac, 99%), Dy_2O_3 (Alfa Aesar, 99.9%), Gd_2O_3 (Alfa Aesar, 99.9%), and Sm_2O_3 (Alfa Aesar, 99.9%) were combined and ball-milled in ethanol for 24 hours. Powders were combined stoichiometrically. Powders were then dried, sieved, and calcined at 1100°C for 6 hours. To aid in densification, 1.5 wt.% borosilicate glass frits were added post-calcining and ball milled in ethanol for 6 hours. Final powders were dried and sieved.

To assess the high field behavior of the CZT and CHT systems, single layer capacitors with Pt internal electrodes were processed via tape casting. A general procedure for the ceramic slurry preparation, tape casting, and capacitor fabrication is described elsewhere [2,25]. Tape thicknesses after casting were 16-19 μm for active layers and 50-60 μm for bulk layers. To remove organic components, the capacitors were heated to 270°C at $0.5^\circ\text{C}/\text{min}$, then heated to 600°C at $0.5^\circ\text{C}/\text{min}$ while holding for 6 hours at both temperatures. Capacitors were sintered by heating at $10^\circ\text{C}/\text{min}$ to 800°C , held for one hour, then heated at $3^\circ\text{C}/\text{min}$ to 1200 to 1300°C and held for 3 hours. Final capacitor dimensions had thicknesses of $\sim 9\text{-}12\ \mu\text{m}$ and electrode areas of $\sim 3\ \text{mm}^2$. Silver ink (Dupont 6160, Dupont, Wilmington, DE) was applied to both ends of the samples as termination electrodes and fired on at 850°C for 30 minutes. Stacked and laminated tapes were also used to prepare sintered samples without electrodes to determine sintered phase purity and percent theoretical density (T.D.) as measured by the Archimedes method. For basic electrical characterization such as capacitance and loss vs. temperature and I-V, bulk layers of ceramic tape were stacked and laminated to form samples 0.5 mm thick after sintering. A Bal-Tec Sputter Coater SCD 050 (Capovani Brothers Inc., Scotia NY) was used to sputter 500 Å of Pt for electrodes.

X-ray diffraction (XRD) was performed on crushed, sintered, non-electroded ceramics using a PANalytical X'Pert Pro MPD θ/θ goniometer with Cu-K α radiation, and fixed slit incidence (0.5° divergence, 1.0° anti-scatter, specimen length 10 mm) and diffracted (0.5° anti-scatter, 0.02 mm nickel filter) optics. Samples were prepared by the back-loading method in which a powder sample is pressed into the cavity of a quartz low-background support. Data were collected at

45 kV and 40 mA from $10\text{-}70^\circ 2\theta$ using a PIXcel detector in scanning mode with a PSD length of $3.35^\circ 2\theta$, and 255 active channels for a duration time of approximately an hour. Resulting patterns were corrected for both 2θ position and instrumental peak broadening using NIST 640c silicon and analyzed with Jade+9 software (MDI, Livermore, CA). Scanning electron microscopy (SEM) was performed using a Hitachi S-3000N SEM (Tokyo, Japan) using secondary electron imaging at an operating voltage of 5 kV. Samples for SEM were polished to 1 μm using diamond slurry then thermally etched at 10% below the sintering temperature for 30 minutes. Grain size measurements were obtained using the line intercept method [25].

TCC measurements, which determine the percent the capacitance strays from the room temperature value, were made using a Hewlett Packard 4284A Precision LCR meter (HP, Santa Clara, CA) with a Hewlett Packard 3478A multimeter in Delta ovens (Delta Technologies, Conway, AR) with custom-designed multiple sample holders over the temperature range of 200 or 150 to -50°C with a $3^\circ\text{C}/\text{min}$ cooling rate at frequencies of 100 Hz to 1 MHz.

Current-voltage (I-V) measurements were performed on stacked, laminated and sintered Pt-electroded samples using a pA meter/DC voltage source HP-4140B (HP, Santa Clara, CA) and a Kepco bipolar power supply/amplifier model BOP 1000M (Kepco, Flushing, NY) in a custom-built high temperature box furnace at 250°C up to a maximum DV bias equivalent to 25 kV/cm. The steady state leakage current was measured after the sample was held at a constant bias for five minutes, permitting relaxation of the depolarization current. Samples had electrode areas of 3.5 to 6.6 mm^2 and thicknesses of 0.2 to 0.5 mm.

Polarization vs. field (P-E) loops were measured using a Labview-designed P-E program with a modified Sawyer-Tower circuit using a Trek model 30/20 $\pm 30\ \text{kV}$ (Medina, NY) voltage amplifier system in custom box furnaces at 25, 100, 200, and 300°C . The energy density was quantified as the area between the positive y-axis and the maximum polarization value on the discharge/decreasing field (E) portion of the unipolar curves according to Figure 1 and Equation 2, with the dielectric displacement approximated using polarization, P. Breakdown was quantified as the last field sustained before failure occurred. All values were obtained using a script written in Mathematica (Wolfram Research, Champaign, IL).

RESULTS AND DISCUSSION

CZT and CZT + Mn

Initial studies for the CZT system aimed at selecting the optimum composition of the CaTiO_3 -rich end of the binary, which included the $x=0.7, 0.8$, and 0.9 compositions. The XRD spectra for crushed, sintered samples of these compositions are shown in Figure 2. The main Bragg reflections in Figure 2 show slight splitting, indicating CZT