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# Yttria Stabilized Zirconia as a Candidate for High Energy Density Capacitor

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## ABSTRACT

As one of the main components in power converters, dielectric capacitors can play crucial roles in facilitating power conversion in various applications, such as hybrid-electric and fuel cell vehicles. Capacitor reliability is a key challenge for development of high performance capacitors. In this study, yttrium stabilized zirconia (YSZ) with various yttria concentrations were fabricated and tested for dielectric properties, such as breakdown strength and dielectric loss factors. The results indicated that the breakdown strength as high as 2 MV/cm could be achieved in YSZ samples with 10 mol% yttria. In addition, the dielectric loss factors of the samples were lower than 0.4%. Superior breakdown strength and relatively low loss demonstrated that YSZ ceramics have high reliability, showing a great potential as candidates for high energy density capacitors.

**Key words:** yttria stabilized zirconia, dielectric, breakdown strength, capacitors

## INTRODUCTION

Dielectric capacitors are components used in various applications as energy-storage devices. In addition to storing electrical energy, capacitors can play crucial roles in facilitating power conversion in applications, such as hybrid-electric and fuel cell vehicles. Capacitor reliability is a key challenge for development of high performance dielectric capacitors. One of the primary objectives for fabrication of high-performance dielectric capacitors is to develop a material with enhanced energy storage capacity and low dielectric loss. High energy capacity in dielectric material can be achieved through the increase of the dielectric constant or the breakdown voltage. Since the energy density of linear dielectrics is dependent on the square of the applied voltage, material with high breakdown strength is greatly desired for practical applications.

Main factors that greatly affect the breakdown strength of dielectric materials are porosity, grain size and defect chemistry. It was reported that the dielectric breakdown strength generally decreases with the increase of porosity while increasing with the refinement of grain size (Gerson and Marshall, 1959). Hence, materials with low level of porosity and small grain size offer possibilities for enhancement of dielectric breakdown strength (Tunkasiri and Rujijanagul, 1996; Nagaya and Isibashi, 1997; Ye *et al*., 2003) In addition to minimizing porosity and grain size, an introduction of impurities, secondary phase particles or lattice defects in dielectric materials may be an effective route to the enhancement of electrical breakdown strength.

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The proposed experiments involve development of dielectric ceramics with high electrical strength and low loss factor by introducing lattice defects into the materials. Yttrium stabilized zirconia (YSZ) was examined in the study. Polycrystalline YSZ samples with yttria concentrations ranging from 3 to 20 mol% were processed. Measurements of electrical breakdown strength, along with dielectric loss factors, were conducted to determine the optimal concentration of yttria for enhancement of dielectric breakdown and minimization of dielectric loss.

## MATERIALS AND METHODS

Commercially available YSZ powder with 3 mol%, 8 mol%, 10 mol% and 20 mol% yttria concentrations were utilized in the sample preparation process. For samples employed in the breakdown strength measurements, the powders were uni-axially pressed in a 1.2 cm-diameter dimpled die. A flat-surface die with 2 cm-diameters was used to fabricate samples employed in other dielectric characterizations. In order to achieve high density, the samples were subsequently iso-statically pressed at 35,000 psi prior to the sintering process. Isothermal sintering, with the heating and cooling of 5°C/min, was conducted at 1350, 1400 and 1450°C. A schematic presentation of the sample preparation and characterization procedures is shown in Figure 1.

Measurements of dielectric breakdown strength of all samples were carried out at room temperature in silicone oil. The breakdown test apparatus is shown in Figure 2. During the breakdown test, an increasing dc voltage was applied to the sample at a rate of about 1 kV/s. The voltage was measured and recorded until dielectric breakdown occurred. Breakdown was defined as the maximum applied voltage value recorded before the onset of current of 200 mA was reached. A value of average breakdown strength, determined from measurements of three samples processed at the same condition, was used to represent each data point. The impedance/gain phase analyzer (Hewlett Packard, Model 4194A) was employed in analysis of dissipation factor of the samples sintered at 1350 and 1400°C. The dissipation measurements were conducted over the frequency ranging from 1 kHz to 1 MHz.

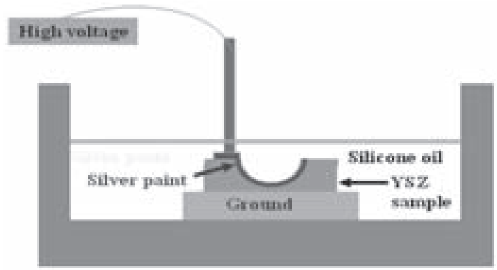


**Figure 2** Apparatus of the dielectric breakdown strength test.

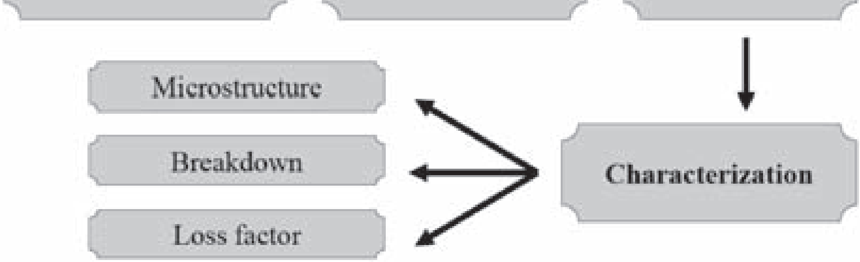


**Figure 1** Schematic presentation of sample preparation and characterization procedure.

## RESULTS AND DISCUSSION

Sintered YSZ samples were white in color and crack free, as shown in Figure 3. Geometry and density of the dimpled samples were examined. It was observed that the shrinkage of the samples was as high as 25 %. Densities of all samples were generally higher than 90% of theoretical density. Higher density could be attained in samples with lower yttria concentration.

As shown in Figure 4, SEM micrograph of YSZ sample revealed that average grain size was less than 2 micrometers. Small grain sizes of the samples indicated that the microstructure did not have a detrimental effect on breakdown strength of the samples.

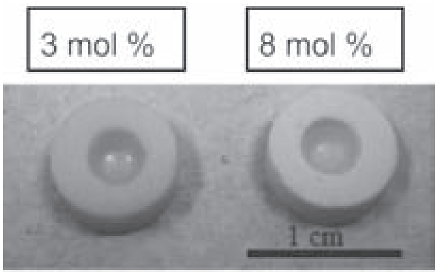


**Figure 3** YSZ samples with 3 mol % and 8 mol% yttria, sintered at 1400°C.

Experimental results from dielectric breakdown strength measurements revealed that the YSZ samples with 3 mol% yttria had average breakdown strength close to 1.4 MV/cm. The breakdown strength was enhanced as the yttria content increased up to 10 mol%. The values of average breakdown strength in the range between 1.6 to 1.7 MV/cm and 1.9 to 2.0 MV/cm were observed in the YSZ samples with 8 and 10 mol% yttria, respectively. For the samples with yttria content as high as 20 mol%, the breakdown strength, however, decreased abruptly, as shown in Figure 5.

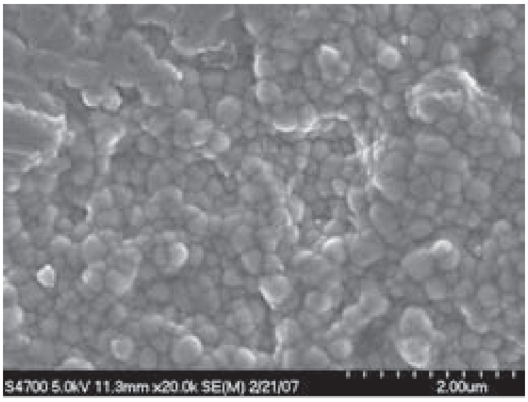


**Figure 4** SEM micrograph of YSZ sample with 3 mol% yttria concentration, sintered at 1350°C.

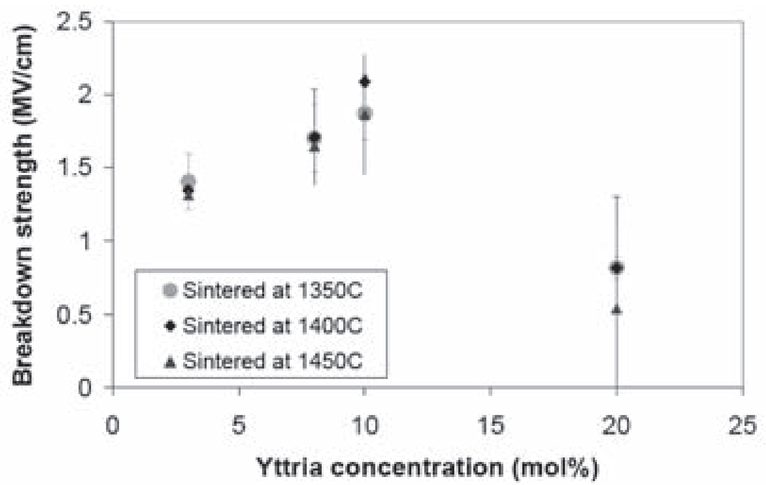


**Figure 5** Breakdown strength of YSZ samples as a function of yttria concentration.

It was evident that breakdown strength of YSZ samples was extensively dependent on yttria concentration. The highest breakdown strength could be achieved in the samples with the 10 mol% yttria content. Mechanism related to enhancement of breakdown strength due to yttria has not been well understood at this time. However, the study suggested that one of the possible explanations to the mechanism might be related to defect chemistry, charge mobility and space charge model.

It has been reported that introduction of extra electrons into YSZ led to segregations of these extra electrons into the space charge zone near grain boundaries (Lee *et al.,* 2006). An increase of electron concentration in the space charge zone offered high potential for the local dielectric breakdown to occur. It was therefore beneficial to minimize the local electron concentration in order to sustain high breakdown strength. Oxygen vacancy was believed to play a role in capturing the extra electrons in YSZ. The reaction could be represented by following equation:

$$^1/_2\, O_2 + V_o^{\bullet\bullet} + 2e^- \Rightarrow O_o$$

For the YSZ samples, concentration of oxygen vacancy was dependent on the yttria content. It has been accepted that at the optimum yttria content of 10 mol%, the highest oxygen vacancy could be generated in YSZ, according to the following defect chemistry:

$$Y_2O_3 \Rightarrow 2Y''_{Zr} + V_o^{\bullet\bullet} + 3O_o^x$$

The largest amounts of oxygen vacancy in the samples with 10 mol% yttria might result in the most effective electron capturing, which potentially lead to the maximum enhancement of electrical breakdown strength in YSZ.

In contrast to the breakdown strength, dielectric loss factors of the YSZ samples were not significantly dependent on the yttria content. Instead, they were dependent on the frequency. The dissipation factor measured at lower frequency range (10 kHz) was in the range of 0.1-0.2%. Higher loss, in the range of 0.3-0.4%, was observed at frequency ranging from 100 kHz to 1 MHz, as shown in Tables 1 and 2. In general, the results indicated that all samples had high dielectric breakdown strength and relatively low loss.

## CONCLUSION

Relatively high density and small grains could be observed in YSZ samples upon sintering under temperatures ranging from 1350 to 1450°C. High density and small sizes of grains did not have detrimental effects on dielectric breakdown of YSZ. Maximum enhancement of the dielectric

**Table 1** Dissipation factors of YSZ samples with 3, 8 and 10 mol% yttria, measured at 10 kHZ.

| Sintering temperature (°C) | Dissipation factor, measured at 10 kHz (%) | | |
|---|---|---|---|
| | YSZ with yttria 3 mol% | YSZ with yttria 8 mol% | YSZ with yttria 10 mol% |
| 1350 | 0.159 ± 0.04 | 0.143 ± 0.05 | 0.231 ± 0.06 |
| 1400 | 0.161 ± 0.04 | 0.197 ± 0.02 | 0.151 ± 0.04 |

**Table 2** Dissipation factors of YSZ samples with 3, 8 and 10 mol% yttria, measured at 1 MHZ.

| Sintering temperature (°C) | Dissipation factor, measured at 10 kHz (%) | | |
|---|---|---|---|
| | YSZ with yttria 3 mol% | YSZ with yttria 8 mol% | YSZ with yttria 10 mol% |
| 1350 | 0.281 ± 0.04 | 0.260 ± 0.01 | 0.362 ± 0.06 |
| 1400 | 0.243 ± 0.01 | 0.343 ± 0.01 | 0.353 ± 0.01 |

breakdown strength, with value as high as 2.08 MV/cm, could be achieved in the samples with 10 mol% yttria content. This may be attributed to the highest oxygen vacancy available in the samples with 10 mol% yttria, which may act as electron trapping sites. Dielectric loss factors of all samples were lower than 0.4%. Superior breakdown strength and relatively low loss demonstrated that YSZ ceramics could be potential candidates for materials used in fabrication of high energy density capacitors.

## LITERATURE CITED

Gerson, R. and T. Marshall. 1959. Dielectric breakdown of porous ceramics. **J. Appl. Phys**. 30: 1650-1653.

Lee, J. S., U. Anselmi-Tamburini, Z. A. Munir and S. Kim. 2006. Direct evidence of electron accumulation of yttria-doped nanocrystalline zirconia ceramics. **Electrochem. Solid-State Lett.** 9: J34-J36.

Nagaya, T. and Y. Isibashi. 1997. Dielectric breakdown in polycrystalline system. **Jap. J. Appl. Phys. Part I.** 36: 6136-6140.

Tunkasiri, T. and G. Rujijanagul. 1996. Dielectric strength of fine grained barium titanate ceramics. **J. Mater. Sci. Lett.** 15: 1767-1769.

Ye, Y., S. Z. Zhang, F. Dogan, E. Schamiloglu, J. Gaudet, P. Castro, M. Roybal, M. Joler and C. Christodulou. 2003. Influence of nanocrystalline grain size on the breakdown strength of ceramic dielectrics, pp. 719-722. *In* the **14th IEEE International Pulsed Power Conference**. Dallas, Texas.