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Effects of Yttria Concentration and Microstructure on Electric Breakdown of Yttria Stabilized Zirconia

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Abstract

Ceramic materials have great potentials for capacitor application. However, low breakdown strength of the materials remains a key challenge for development of high performance capacitors. In this study, yttria stabilized zirconia (YSZ) were fabricated and tested for breakdown strength. YSZ samples with 3, 8, and 10 mol% yttria were carefully processed to control grain size and porosity level. Experimental results revealed that breakdown strength as high as 2 MV/cm could be achieved. The breakdown strength was not significantly affected by porosity level, but it was by yttria concentration. Relationship among yttria concentration, residual porosity and breakdown strength is discussed in this study.

Key words : Yttria stabilized zirconia, capaitors, dielectric properties, breakdown strength, microstructure

Introduction

High dielectric constant and high breakdown strength of materials generally lead to enhanced energy storage capacity. In the case of linear dielectrics, the energy density is dependent on the square of the applied voltage. Therefore, linear-dielectric materials with high breakdown strength are greatly desired for capacitor application. Yttria stabilized zirconia (YSZ) is a ceramic material with various unique properties, including hardness. The attractive mechanical property of YSZ can be useful for fabrication of strong capacitors.

Breakdown strength of dielectric materials is affected by various intrinsic and extrinsic factors. Low values of dielectric breakdown strength are usually attributed to various types of defects which occurred during processing of polycrystalline dielectric materials.(1-2) It was reported that dielectric breakdown strength generally decreases with the increase of porosity, and increases as the grain sizes of the materials are refined.(3-8)

Significant reduction of breakdown strength in dielectric samples with presence of pores is attributed to the field enhancement effect in the materials. Field enhancement in porous materials is described as followed. The lower effective dielectric constant of the pore draws the field line into the dielectric, resulting in the increase of the field enhancement factor.(9) Relationship between grain size and the breakdown strength in dielectric materials was also investigated.(10) It has been reported that breakdown strength was proportional to the mean grain size to the power of n, where n is constant ranging from -3/4 to -2.(11-12)

In addition to minimizing porosity and grain size, an introduction of impurities or secondary phase particles in dielectric materials may be an effective route to the enhancement of electrical breakdown strength. The enhancement of the breakdown strength in binary system dielectric materials may be attributed to an increase in the path length of the breakdown or the change of the space charge distribution.(13-15) Charge localization or trapping effect of the additive is also documented as one of the main mechanisms related to enhancement of breakdown strength in the materials.(16-19)

The proposed experiments involve development of high electrical strength ceramics by introducing lattice defects into the materials. Yttria stabilized zirconia (YSZ) is examined in the study. YSZ with yttria concentrations ranging from 3 to 10 mol% in form of bulk materials is processed. Sintering conditions are monitored to control density and grain size. Microstructural characterizations along with measurements of electrical breakdown strength are conducted. Relationship among yttria concentrations, microstructure and the breakdown strength is presented.

Experimental Procedures

A. YSZ Sample Fabrication

YSZ powder with 3 mol% (Aldrich), 8 mol%, and 10 mol% (Tosoh, TZ-8YS) 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 240 MPa prior to the sintering process. Isothermal sintering, with the heating and cooling rates of 5 C°/min, was conducted at temperatures ranging from 1350 to 1500°C. Archimedes technique was employed in evaluation of the sintered density of the YSZ samples.

B. Microstructural Analysis

Microstructural analysis, specifically grain morphology and pore size of the sample, was conducted. A scanning electron microscope (Hitachi S4700-FESEM) was employed in the microstructure characterization. The sizes of grains and pores were analyzed using Scion Image Software. A minimum of 50 grains and pores was employed in the analysis to obtain the average grain and pore sizes.

C. Measurement of Breakdown Strength

Measurements of breakdown strength were carried out at room temperature in silicone oil. Since the breakdown strength strongly depends on the dimension and surface defects of the samples, sample thickness and surface roughness were controlled. All YSZ samples were ground to a thickness of less than 200 μm using silicon carbide sandpapers with 60, 120, 240, 400, 600, 800 and 1200 grit, respectively. The samples were painted with silver paste prior to the measurements.

Increasing dc voltage was applied to the sample at a rate of about 1 kV/s during the breakdown test. 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.

Results and Discussion

A. Density of YSZ Samples

Results from density measurement revealed that the sintered YSZ samples could achieve an average density higher than 94% of theoretical density when sintered at temperature 1350°C or higher. In general, high density could be observed in the samples containing lower yttria concentration or sintered at higher temperature. As shown in Figure 1, the samples with 3 mol% yttria could achieve an average density as high as 99.8% of theoretical density. For the samples with 8 mol% yttria, the average density values of the samples were in the range between 96.7 and 98.1 % of theoretical density. For the YSZ sample with 10 mol% yttria concentration, density values in range of 94.4 to 97.2 % of theoretical density could be attained.

The values of density obtained in this section were subsequently used in determination of sample porosity, which would be discussed with respect to breakdown strength of the samples in Section C.

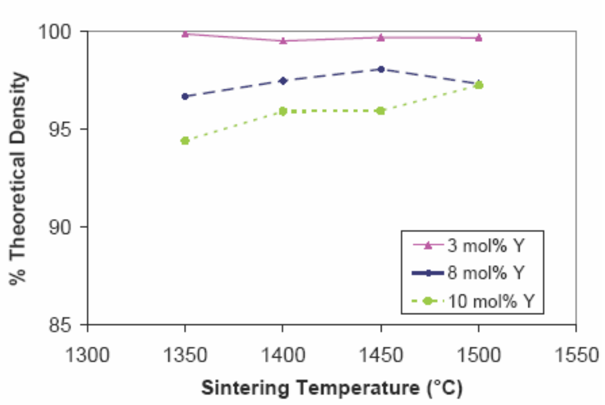

Figure 1. Average density of YSZ samples subjected to sintering at temperatures ranging from 1350 to 1500°C

B. Microstructural Examination of YSZ Samples

SEM micrographs of the surface of the YSZ samples revealed information related to grain morphology of the samples, as shown in Figures 2, 3 and 4. Small grains with average sizes in sub-micrometer range (0.23-0.28 μm) were observed in samples fabricated from the YSZ powder with 3 mol% yttria. For samples with 8 and 10 mol% yttria, average grain sizes in range of 0.8 to 1.0 μm were evident. No significant grain growth was observed in all samples as the sintering temperature increased, as shown in Figure 5. Microstructural analysis of the YSZ samples also indicated that pore sizes of the samples were very small. Average pore sizes of the samples were in the range of 0.1 to 0.2 μm, as shown in Figure 6.

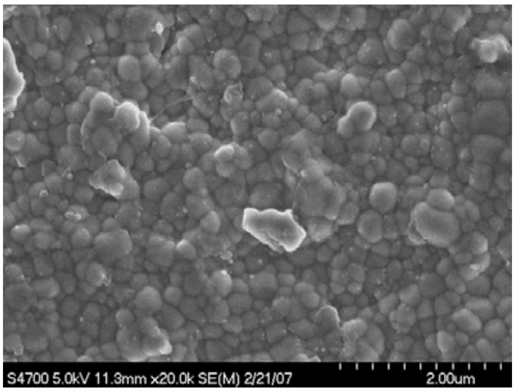

Figure 2. SEM micrographs of YSZ samples with 3 mol% yttria concentration, sintered at 1350°C

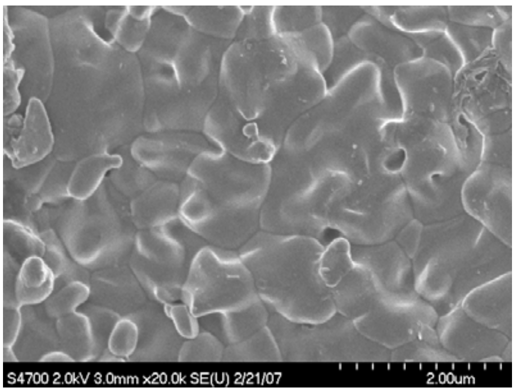

Figure 3. SEM micrographs of YSZ samples with 8 mol% yttria concentration, sintered at 1350°C

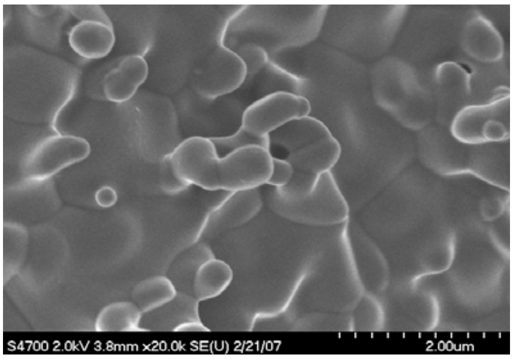

Figure 4. SEM micrographs of YSZ samples with 10 mol% yttria concentration, sintered at 1350°C

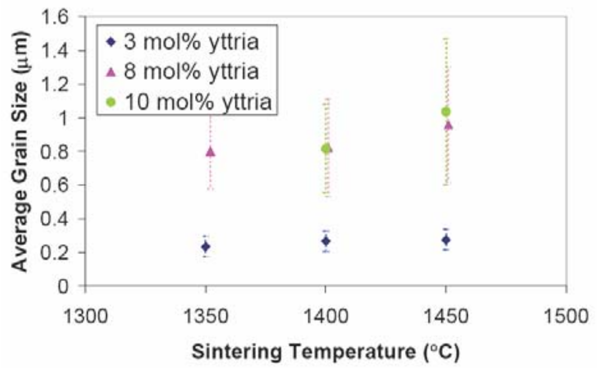

Figure 5. Average grain size of YSZ samples with 3, 8 and 10 mol% yttria as a function sintering temperature

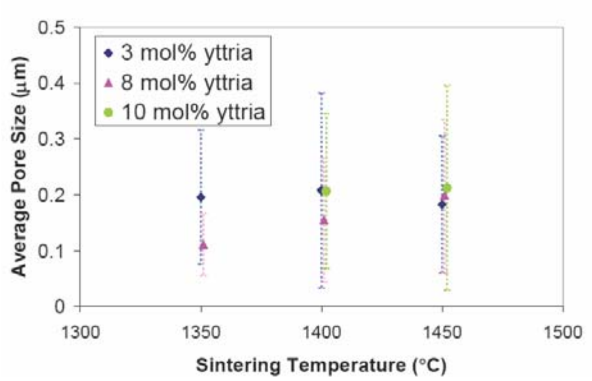

Figure 6. Average pore size of YSZ samples with 3, 8 and 10 mol% yttria as a function sintering temperature

C. Breakdown Strength of YSZ Samples

Measurements of dielectric breakdown strength were conducted on YSZ samples with 3, 8 and 10 mol% yttria concentration, sintered at temperatures ranging from 1350 to 1450°C.

Experimental results revealed that the YSZ samples with 3 % yttria had average breakdown strength of 1.29-1.34 MV/cm, while the breakdown strength values in the range of 1.64-1.71 MV/cm and 1.86-2.08 MV/cm were observed in the YSZ samples with 8 and 10% yttria, respectively. As shown in Figure 7, YSZ samples with higher yttria concentration tended to exhibit higher dielectric breakdown strength.

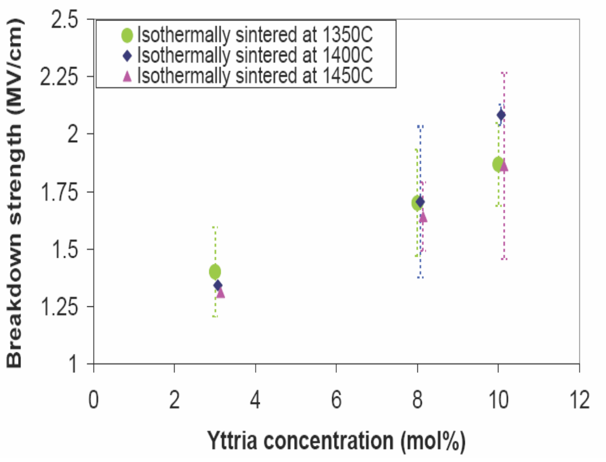

Figure 7. Breakdown strength of YSZ samples as a function of yttria concentration

It was generally accepted that porosity could result in reduction of dielectric breakdown strength in polycrystalline materials. However, experimental results from this study indicated that the amount of porosity did not have a significant detrimental effect on breakdown strength values of the samples, as shown in Figure 8. Deviation of the current results from the general understanding was explained in the following section.

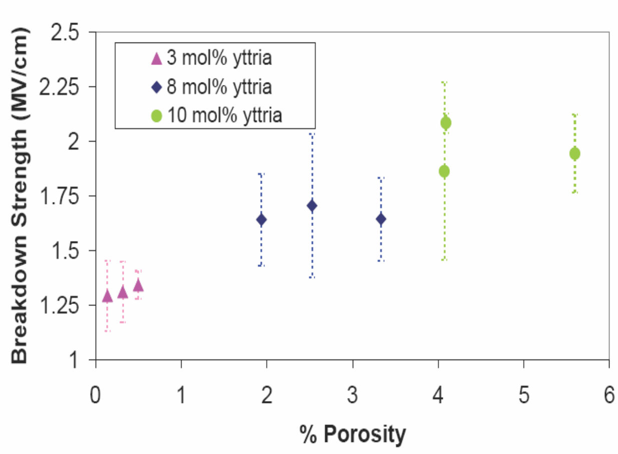

Figure 8. Dielectric breakdown strength of YSZ as a function of sample porosity

One of the widely accepted models related to effects of porosity on breakdown strength of porous ceramics was that of Gerson and Marshall. According to the Gerson-Marshall model, the measured dielectric strength in porous ceramics was dependent on the porosity and the pore size.[5] Experimental results and theoretical calculation from the report revealed that breakdown strength of ceramics could be reduced as much as 60% when the porosity reached 10%. However, the theory established has based on the samples with much larger pore sizes compared to those in the current study. For more precise comparison, experimental results from the Gerson-Marshall study were extrapolated. The extrapolated result indicated that as the pore sizes were reduced, a minimal effect on the breakdown strength of ceramics was observed. For the samples with pore size in the range of 100-200 nm and porosity not exceeding 5 %, a change of breakdown strength value of less than 5% could be observed, as shown in Figure 9.

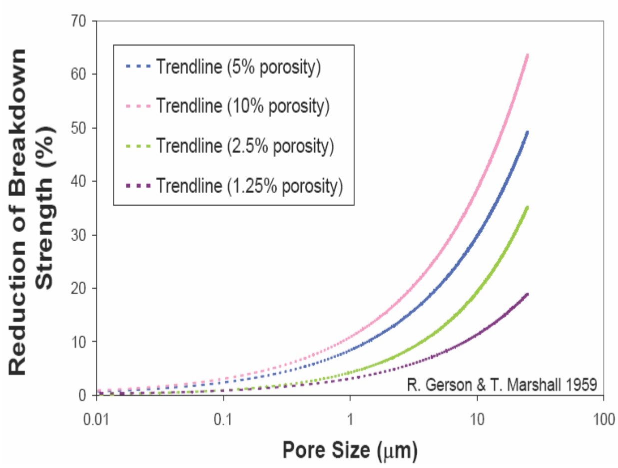

Figure 9. Effect of pore size on breakdown strength of ceramics, from ref.(5)

As shown in Figure 7, breakdown strength of YSZ sample depended on yttria concentration. The breakdown strength was considerably enhanced as the yttria content increased. Mechanism on enhancement of breakdown strength due to yttria has not been extensively investigated in this study. However, the study suggests that one of the possible explanations to the mechanism may 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.[20] 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 can be represented by following equation:

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

For the YSZ samples, concentration of oxygen vacancy depended on the yttria content. At optimum yttria content of 10 mol%, higher oxygen vacancy could be generated, according to the following defect chemistry:

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

Larger amounts of oxygen vacancy might result in more effective electron capturing, which potentially lead to enhancement of electrical breakdown strength in YSZ.

Summary

Porosity and grain size can be controlled by carefully monitoring the sintering process. Lower porosity could be achieved in YSZ samples with lower amount of yttria concentration and high sintering temperature, while small grains, with average sizes lower than 1 μm, were observed in all samples.

Porosity, previously reported to have a detrimental effect on breakdown strength of ceramics samples, was examined in this study. Experimental results and extrapolation of previous results indicated that small pores, with average sizes in the range of 100-200 nm, did not have significant effect on lowering breakdown strength of the samples.

Enhancement of breakdown strength, in range of 1.86-2.08 MV/cm, could be achieved in samples with 10 mol% yttria content. Results from this study revealed that breakdown strength was not significantly affected by porosity level. On the contrary, it was considerably affected by the concentration of yttria in YSZ samples.

Acknowledgement

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