Dielectric Loss in Porous TiO₂

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Abstract

The dielectric loss behavior of TiO₂ was characterized on samples of variable porosity and variable pore size. Pores were formed by two methods: varying the sintering temperature and by the addition of a spherical carbon porogen. Porosities varied from 5.9% to 59.3%. Dielectric loss increased with increasing pore volume in each case. However, dielectric loss increased at a slower rate for porogen induced pores. At equivalent pore volumes, pore surface area volumes were higher than those induced using the porogen. Dielectric loss behavior was shown to vary linearly with pore surface area. Our work demonstrates that large pores reduce free surface area and decrease dielectric loss when compared to similar samples with smaller pores. A new model of porous dielectric loss is proposed that characterizes materials based on generalized free surface area instead of porosity alone. Based on this model, we show that the relative loss of porous dielectrics depends critically on the pore surface area and the loss tangent of the parent dielectric.

Keywords:

TiO₂, Dielectric Properties, Porosity

1.0 Introduction

Earlier, we reported on the relative permittivity of titania and calcium magnesium titanates containing sufficient porosity to significantly change the permittivity [1]. In this paper we are concerned with dielectric loss in these porous dielectrics, as measured by the loss tangent ($\tan \delta$) or materials quality factor Q ($Q=1/\tan \delta$). Losses within the bulk of a dielectric are classified into intrinsic and extrinsic categories. Intrinsic losses depend on crystal structure and arise from the anharmonic interaction of the electric field and phonon system [2]. Typically, these losses are much lower than the actual losses in polycrystalline materials [3]. Porous materials with significant pore surface area can also have excess dielectric loss associated with the surfaces, both from surface defects and from species adsorbed onto the pore surfaces. Molla' et al. [4] showed that the dielectric loss of high purity alumina with 42 volume percent porosity was very sensitive to humidity in the air. Porosity distinctly increases the $\tan \delta$ of Al_2O_3 [5] and TiO_2 [6], which are otherwise quite low-loss materials. This paper presents the dielectric properties of porous TiO_2 and characterizes the $\tan \delta$ in terms of pore morphology and surface area.

2.0 Materials and Methods

Fabrication of samples is discussed in more detail elsewhere [1]. Briefly, the TiO_2 is a commercial powder consisting of 99.8% pure titanium dioxide (rutile) powder (203-4, Ferro Electronic Materials, Penn Yan, NY).

Porosity was introduced by three methods: 1) partial sintering at temperatures between 1100°C and 1350°C, to leave micropores 1-5 µm in size; 2) addition of spherical porogens to create 15 µm voids. Partially-sintered samples with porogens have both micro-and macro-porosity. Porosity was measured using Archimedes method. Pore sizes of partially sintered samples were determined by image analysis of polished cross sections. All samples were fired in air using a heating and cooling rate of 10°C/min and 1 hour dwell times.

Surface area was determined using multi-point BET (ASAP 2010, Micromeritics Instrument Corporation, Norcross, GA) All samples were degassed at 300°C for 2 hours.

Dielectric measurements (S_{21}) were performed using a resonant cavity that was approximately three times larger than the sample (Trans-Tech Inc, Adamstown, MD).

Testing was performed at room temperature in air under ambient conditions.

Atmospheric humidity was not recorded. Samples were excited to the ($TE_{01\delta}$) resonant mode. Q_L was found at 3 dB insertion loss down from the resonant peak on a network analyzer, where $Q=Q_L/(1-10^{-IL/20})$. Values obtained were normalized to 3 GHz using the expression $Qxf=constant$. It was estimated that the typical Qxf uncertainty was 1000 GHz. Values of $\tan \delta$ were obtained as $\tan \delta = Q^{-1}$.

Values obtained were consistent with initial measurements performed using a modified Courtney method at NIST-Boulder. The relative permittivity was obtained via numerical analysis of the resonant frequency and the sample geometry.

3.0 Results and Discussion

3.1 Porous TiO₂

The first data set consisted of partially sintered TiO₂ with “micro” porosity. Table 1 shows the properties of TiO₂ fired between 1100°C-1350°C.

Porosity varied from 5.9% to 40.6%. Samples fired at 1350°C had no measurable surface area because all porosity was closed. Therefore, the surface area was assumed to be zero. Reported values of $\tan \delta$ were normalized to 3 GHz (assuming Qxf was constant). In general, the normalized $\tan \delta$ increased with increasing porosity and increasing surface area. These values for $\tan \delta$ are comparable, although somewhat lower, than the Templeton data.

Figure 1 shows the fracture surfaces of a 1200°C sample and a 1350°C sample. The images show the grain growth and reduction in pore area at higher temperatures. Image analysis estimated the mean pore radius to be 0.3 μm and 0.5 μm at 1200°C and 1350°C, respectively.

The second data set included samples fired at 1350°C, but with varying fractions of porogen. The inclusion of porogens produced a similar range in porosities achieved via partial sintering. Table 2 shows the measured properties of titania samples fired at 1350°C with porogen.

Surface area determinations could only be measured on samples that contained more than 30% porogen. Below 30% porogen, a majority of the porosity remained closed. In

addition, the surface area at 59% porosity was much lower than partially sintered samples with a porosity of ~17%. This can be expected by the generation of comparatively larger pores. Overall, the loss tangent increased at a significantly slower rate with increasing porosity than that observed for the partially sintered samples. Figure 2 shows the fracture surface of a sample that contained 5 V% porogen. It is clear the 10-15 μm pores were well formed by the porogen.

3.2 Loss Vs. Porosity

Penn et al. [5] distinguished between the loss tangent for the pore-free bulk material ($\tan \delta_o$) and additional loss associated with pore surfaces. Using the relationship between pore volume fraction (P) and pore surface area that is expected for residual micropores in partially-sintered ceramics, they proposed Equation 1, below:

$$\tan \delta = (1 - P) \tan \delta_o + A' P \left(\frac{P}{1 - P} \right)^{2/3} \quad \text{Eqn. 1}$$

In Equation 1, A' is an empirical fit parameter. Penn et. al. could fit data for the loss tangent of sintered alumina using a value of $A' = 0.0093$. The Penn model also fits data reported by the same group for micro porous titania [6] at ~3 GHz. Templeton et. al. data for micro porous TiO_2 data is reproduced in Figure 3, showing the material $\tan \delta$ for titania plotted with a Penn model fit with $A' = 0.005$ and $\tan \delta_o = 7.44 \times 10^{-5}$.

The measured sample $\tan \delta$'s are plotted in Figure 3 in comparison to the literature values. All data sets show $\tan \delta$ increases with increasing porosity, but the three data sets are distinctly different. Literature values show equivalent pore volumes produce higher values of $\tan \delta$. A Penn model fit of the experimental data sets requires reducing the fit

parameter by nearly an order of magnitude for each data set. Values of $A'=0.0007$ and $A'=0.00009$ were required to fit the partially sintered and spherical porogen data sets, respectively.

Differences in $\tan \delta$ values between the literature values and the partially sintered data set could be due to differences in starting powders or environmental test conditions.

The measured porogen samples had $\tan \delta$'s that also increase with increasing porosity. However, the $\tan \delta$ values were significantly lower than observed for all other samples. Changing the pore morphology by increasing pore size (decreasing the surface-area / volume ratio) decreases the dielectric loss of TiO_2 at a fixed porosity. Thus, one must be careful when using porosity as an independent variable since the effect of pore morphology is significant.

Increasing pore size while maintaining a fixed porosity, has the effect of decreasing the amount of free surface area in a sample. This can be seen since the area/volume ratio for a sphere varies as $3/r$.

Equation 1 implies a relationship to pore surface area assuming McKenzie-Shuttleworth porosity (i.e., uniform, spherical pores are assumed) [7]. In doing so, information such as pore size, pore morphology, pore size distribution, pore surface area, and surface loss is lost. Therefore, Equation 1 must be modified to account for less ideal pore distributions and morphologies.

3.3 Loss Vs. Surface Area (SA)

In this section, we present a modified model to gain insight into the loss of porous dielectrics. This model will assume that the loss-porosity relationship is linear and that the change in loss is due to two factors. The first factor is the introduction of porosity (P). The second factor is due to the development of free surface area (S) with its own loss tangent ($\tan \delta_s$) and a specific thickness (t). Equation 2 proposes a model for dielectric loss based on these additional variables.

$$\tan \delta = (P) \tan \delta_p + (1 - P) \tan \delta_o + (S\rho t) \tan \delta_s \quad \text{Eqn. 2}$$

Pore volume is assumed loss-less ($\tan \delta_p = 0$). Therefore, Equation 2 can be simplified to:

$$\tan \delta = (1 - P) \tan \delta_o + (S\rho t) \tan \delta_s \quad \text{Eqn. 3}$$

Where ρ is density of the dense dielectric (e.g. $\rho = 4.25 \text{ g/cm}^3$ for TiO_2).

Figure 4 shows the experimental $\tan \delta$ values plotted against the measured surface area. The plot shows samples for both the partially sintered samples and the samples containing $15 \text{ }\mu\text{m}$ porogen. Overall, both data sets collapse to a linear relationship. The data was fit to a line using linear regression to determine the values in Equation 3.

The linear regression yields Equation 4.

$$\tan \delta = 0.00007 + 0.000157S \quad \text{Eqn. 4}$$

Using the values for micro porous TiO_2 (1350°C), $\tan \delta_o$ was determined to be 7.44×10^{-5} .

This allows for the loss tangent to be expressed directly as a function of both total porosity and surface area ($S = \text{m}^2/\text{g}$) in Equation 5.

$$\tan \delta = (1 - P)(7.44 \times 10^{-5}) + 0.000157 \times (S) \quad \text{Eqn. 5}$$

Using the experimentally determined porosity and surface areas, the model derived in Equation 5 was plotted against the experimental data sets (Figure 5). Unlike the Penn model which uses an empirical fit parameter, that must vary by orders of magnitude to describe dielectric loss behavior we observed, the new model fits both sets of experimental data using measurable physical parameters.

Previous work by Molla [4], has shown that humidity has a significant effect on measured properties of porous dielectrics. Changing the sample condition from moist air to dry nitrogen produced a reversible decrease ($\sim$ one order of magnitude) in dielectric loss tangent. This is not surprising since the $\tan \delta$ of water is very high ($\tan \delta_w \sim 0.2$ @ 3 GHz) [8-9]. It is proposed that the open pore surface areas in our test samples may absorb atmospheric moisture and contribute to the measured dielectric loss.

To determine the value for $\tan \delta_s$, the surface layer thickness (t) must be determined. Attempts were made to measure the amount of water on the surface of porous samples, but measurements were inconclusive. Therefore, the pore surface was assumed to be covered with a monolayer of water. A monolayer of adsorbed water is on the order of 0.4 nm thick [10]. Using the values $\rho=4.25$ g/cc (density of TiO_2) and $t=0.4$ nm, the value of $\tan \delta_s$ was estimated to be 0.096.

3.4 Relevance

The use of controlled porosity has been demonstrated previously as a method of tailoring the relative permittivity of dielectrics via effective medium theory [1]. If porous dielectrics are to be used in devices as demonstrated by Gong [11], then minimizing the development of excess surface loss is of utmost importance. Figure 6 shows a plot of $\tan \delta$ vs. relative permittivity (ϵ_r) for porous TiO₂.

Typically, porosity is considered undesirable in microwave dielectrics due to an increase in $\tan \delta$. Hence, one may be reluctant to exploit effective media concepts to change the relative permittivity of dielectrics via controlled pores. However, Figure 6 shows that modifying relative permittivity through controlled porosity does not necessarily lead to a $\tan \delta$ penalty. In the measured samples, spherical 15 μm pores maintained $Q_{xf} > 26,000$ at ~6-60% porosity with a wide range of $\epsilon_r \sim 20$ -100.

3.5 Mixing Behavior

A more general expression for the $\tan \delta$ behavior of porous dielectrics can be developed. Equation 3 can be normalized with respect to the $\tan \delta_o$ (Equation 6) of the base material and simplified to yield an expression for relative loss, R , shown in Equation 7.

$$R = \frac{\tan \delta'}{\tan \delta_o} = 1 + (Srt \frac{\tan \delta_s'}{\tan \delta_o} - P) \quad \text{Eqn. 6}$$

$$R = 1 + (Srt \frac{\tan \delta_s'}{\tan \delta_o} - P) \quad \text{Eqn. 7}$$

A parameter (α) is defined in Equation 8 that contains the relevant properties related to the bulk dielectric and surface species to yield:

$$\alpha = (Srt \frac{\tan \delta_s'}{\tan \delta_o}) \quad \text{Eqn. 8}$$

This allows the relative dielectric loss and impact of porosity to be expressed as:

$$R = 1 + (\alpha - P) \quad \text{Eqn. 9}$$

Equations 6-9 are important for understanding the mixing behavior that exists between the dielectric materials and pores. Pore volume (P) and SA are key components that dictate relative loss. For low loss dielectrics, the term α can be large and R will likely increase with porosity. This was observed to varying degrees in porous TiO_2 .

Minimizing surface area can mediate this effect.

However, the ratio of surface loss ($\tan \delta_s$) to the actual base material loss ($\tan \delta_o$) is also critically important to the final relative loss. If the quantity $(\alpha - P)$ is negative, R may decrease. This is most likely in porous dielectrics that have a high $\tan \delta_o$.

4.0 Conclusion

Pore morphology was shown to be an important factor when describing the dielectric loss of porous TiO_2 . For constant porosity, larger pores decrease dielectric loss compared to smaller pores. The reason for this behavior was attributed to the reduction of free surface area. Dielectric loss was shown to be well approximated by a linear function of surface area. The $\tan \delta_s$ of titania was shown to be ~ 0.092 (~ 3 GHz) which is on the same order as the $\tan \delta_w$ of water (0.2 at 3 GHz). If one is to incorporate porous dielectrics into low loss devices, one must consider pore size. A mixing model was developed that relates dielectric loss to porosity and free surface area.

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Figures

Figure 1: (Left) Fracture surface of 1350°C sample. (Right) Fracture surface of a 1200°C sample.

Figure 2: Fracture surface of a 1350°C TiO₂ with 5% porogen.

Figure 3: Measured $\tan \delta$ values for partially sintered TiO_2 compared Templeton et. al. [6]. Data was fit to the model in Equation 1 using a value of $\tan \delta_0 = 7.44 \times 10^{-5}$ and a fit parameter (A') of 0.005, 0.0007, and 0.00009 for Templeton, Partially Sintered, and Spherical, respectively.

Figure 4: Experimental $\tan \delta$ values for porous TiO_2 plotted versus measured surface area. The data suggests a linear dependence on surface area as shown by the regression line and equation.

Figure 5. Experimental $\tan \delta$ values for porous TiO_2 plotted versus measured porosity. The predicted values of $\tan \delta$ from Equation 5 are plotted using the experimental porosity and surface areas.

Figure 6: $\tan \delta$ vs. relative permittivity for porous TiO_2 . There is a significant $\tan \delta$ penalty for reducing permittivity using smaller pores.

Tables

Table 1. Measured properties of partially sintered TiO₂.

Temp (°C)	Porosity	SA (m ² /g)	tan δ (3 GHz normalized)
1350	5.9%	0.000	6.10 x 10 ⁻⁰⁵
1300	14.0%	0.095	8.39 x 10 ⁻⁰⁵
1275	17.1%	0.144	8.66 x 10 ⁻⁰⁵
1225	23.3%	0.382	1.18 x 10 ⁻⁰⁴
1175	31.9%	0.732	1.60 x 10 ⁻⁰⁴
1150	38.1%	0.780	2.16 x 10 ⁻⁰⁴
1100	40.6%	1.460	3.02 x 10 ⁻⁰⁴

Table 2: Measured properties for 15 μm pores in TiO₂.

Porogen (V %)	Porosity	SA (m ² /g)	tan δ (3 GHz normalized)
5	9.2%	N/A	5.99E-05
10	10.8%	N/A	6.12E-05
20	18.7%	N/A	6.65E-05
30	33.5%	0.025	6.90E-05
40	42.8%	0.046	7.31E-05
50	49.0%	0.087	9.40E-05
65	59.3%	0.112	1.16E-04