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For $P < 0.08$, the dielectric properties are weakly correlated to the porosity. The values for ϵ_r , $\tan\delta$ and TCF are 105.29 ± 1.96 , $3.15 \pm 1.00 \times 10^{-4}$, and $438 \pm 1.96 \text{ ppm/}^\circ\text{C}$, respectively. These values are comparable to the reported values in literature [8]. Higher $T_{\text{sintering}}$ did not necessarily result in a higher ϵ_r and lower $\tan\delta$. Instead, the $\tan\delta$ is higher than the samples with $0.08 < P < 0.4$. Rutile with $T_{\text{sintering}} > 1220^\circ\text{C}$ have a dark beige color and shiny surface. From both the sample color and the increased $\tan\delta$ value, it is believed that the oxygen deficiency occurs in these samples. Generally, oxygen vacancy concentration increases at higher $T_{\text{sintering}}$ and the oxygen is reincorporated into the rutile structure during cooling. Both grain boundaries and pores act as fast diffusion paths for oxygen, so it is expected that samples with high density and large grain size will have a high oxygen vacancy concentration and a corresponding high dielectric loss.

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The dependence of porosity on ϵ_r when $0.08 < P < 0.4$ is examined by six generally accepted mixing rules, as shown in Fig2a. With the assumption of limited local electric field interaction between the pure polycrystalline rutile matrix ($\epsilon_{r1}=114$) and the spherical air inclusion ($\epsilon_{r2}=1$), the Maxwell-Garnett and Bruggeman formula fit well with the measured data only when $P < 0.18$. The coherent potential formula provides the best fitting up to $P = 0.26$, but it has no real solution beyond $P > 0.26$; hence we created an extrapolation of coherent potential formula from

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which is applicable beyond $P > 0.26$ under the condition that the permittivity of the ceramic is substantially higher than air. Based on the observation on Eq2 and Eq3, the difference between these two equations is the extra term of $-P(1-\epsilon_{r1})$ in the denominator. Normally, the removal of this term from Eq2 to Eq3 can be considered as an approximation when P is very small, which means very little porosity in the ceramic. But this term can be eliminated to emphasize of the effect of ϵ_{r2} . This also helps to extrapolate the coherent potential formula beyond $P>0.26$ from Eq2 and Eq3. Thus, the extrapolation is constructed as

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This extrapolation provided the best fitting to the measured ϵ_r for $0.08 < P < 0.4$ and it also an excellent match to the coherent potential formula even when $P < 0.26$ (Fig2a).

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As previously discussed, the $\tan\delta$ data in the range of $0.08 < P < 0.4$ has a very clear trend. Here, this trend can be found by using the method in Ref[6]. The linear-like behavior of the $\tan\delta$ data for $0.08 < P < 0.4$ in Fig2b suggests the porosity dependence can be obtain from the following formula

$$\tan\delta = \tan\delta_0 + A P^n. \quad \text{Eq5}$$

where $\tan\delta_0$ is the minimum loss of polycrystalline rutile and $A P^n$ is the loss contribution from the pores in the rutile. With $\tan\delta_0 = 8.9019 \times 10^{-4}$, $A = 1.5150 \times 10^{-4}$, and $n = 1.36$, Eq5 provided a good fit for the data (Fig2b). To explicitly show the P contribution on $\tan\delta$ from the effects of $\tan\delta_0$ and the pores size^[9], the final formula became

$$\tan\delta = (1 - P) \tan\delta_0 + PA \left(\frac{P}{1-P} \right)^{\frac{1}{3}}. \quad \text{Eq6}$$

This model provided a good fit to the measured $\tan\delta$ with $\tan\delta_0 = 7.609 \times 10^{-5}$ and $A = 2.219 \times 10^{-4}$. This $\tan\delta_0$ agrees well with the previously reported values^[10], where the low loss rutile is achieved by doping divalent and trivalent ions to limit the oxygen vacancies.

3.2.3 Effect of porosity in temperature coefficient of resonant frequency.

Figure 2: The ϵ_r , $\tan\delta$, and TCF of TiO_2 samples in different porosities with sintering temperature labeled on selected data.

The TCF values of the rutile in different porosity were shown in Fig2c. To find an expression that describes the porosity dependence on TCF within $0.05 < P < 0.4$, we can first start with the formula of TCF^[5],

$$\text{TCF} = -\left(\frac{1}{2}\tau_{\epsilon} + \alpha_L\right) \text{ and } \tau_{\epsilon} = \frac{1}{\epsilon_r} \frac{d\epsilon_r}{dT}, \quad \text{Eq7}$$

where τ_{ϵ} is the temperature coefficient of permittivity in the porous rutile and α_L is the linear thermal expansion coefficient. If the α_L is neglected and Eq4 is applied, the TCF for rutile with pores can be calculated as

$$\text{TCF} = \text{TCF}_{\text{TiO}_2} \left(1 - \frac{9 P \epsilon_{r1}}{[(2 \epsilon_{r1} + 1) + 4P(1 - \epsilon_{r1})][(2 \epsilon_{r1} + 1) + P(1 - \epsilon_{r1})]}\right). \quad \text{Eq8}$$

Eq8 only fits nicely to measured data with $\text{TCF}_{\text{TiO}_2} = 439 \text{ ppm}/^{\circ}\text{C}$ up to $P = 0.25$ (Fig2c). Even the fitted value of $\text{TCF}_{\text{TiO}_2}$ is comparable to literature values^[10], the mismatch for $P > 0.25$ indicates that the α_L cannot be neglected. And in here we assume that the α_L can be described as

$$\alpha_L = A P^n, \quad \text{Eq9}$$

and then

$$\text{TCF} = \text{TCF}_{\text{TiO}_2} \left(1 - \frac{9 P \epsilon_{r1}}{[(2 \epsilon_{r1} + 1) + 4P(1 - \epsilon_{r1})][(2 \epsilon_{r1} + 1) + P(1 - \epsilon_{r1})]}\right) - A P^n. \quad \text{Eq10}$$

With $A = 4278$, $n = 4.9139$, and $\text{TCF}_{\text{TiO}_2} = 439 \text{ ppm}/^{\circ}\text{C}$, Eq10 provides a nice fit to the measured TCF (Fig2c).

To explicitly show the effects of P and average pore size on α_L ^[9], the TCF becomes

$$\text{TCF} = \text{TCF}_{\text{TiO}_2} \left\{1 - P \left[\frac{9 P \epsilon_{r1}}{[(2 \epsilon_{r1} + 1) + 4P(1 - \epsilon_{r1})][(2 \epsilon_{r1} + 1) + P(1 - \epsilon_{r1})]} + \left(\frac{P}{1-P}\right)^3 \right] \right\}, \quad \text{Eq11}$$

Eq12 can give a good fit to the measured data with $\text{TCF}_{\text{TiO}_2} = 440 \text{ ppm}/^{\circ}\text{C}$ (Fig2c). In Eq11, the first and the second terms inside the brackets represent the effects in TCF from the change of ϵ_r and sample dimension due to temperature, respectively. And the second term shows a strong relationship between sample dimension and the pore size. When the porosity becomes very small, both effects will be suppressed by the factor P outside

the brackets and make the TCF toward $\text{TCF}_{\text{TiO}_2}$. All of these indicate that Eq11 is a logical and good model to represent the porosity dependence in TCF for the rutile samples.

4. Conclusion

The effect of porosity and microstructures in microwave dielectric properties of TiO_2 in rutile form was investigated. The ϵ_r , $\tan\delta$, and TCF within a range of porosity ($0.06 < P < 0.4$) have been shown. The $\tan\delta$ was found to be strongly affected by pore volume and ϵ_r has a relatively less effect by porosity. TCF was shown to be the least sensitive to pore volume. For each property, a simple constitutive model was provided to approximate its dependence on porosity with the assumption of spherical pores. A modified coherent potential formula was found to provide the best fit of the permittivity data over a broad porosity range. The process of ceramic sintering, grain growth and grain development was observed in the SEM images of the cross section of TiO_2 samples.

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Effect of porosity and microstructure on the microwave dielectric properties of rutile

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Abstract:

The dielectric properties of rutile were strongly affected by porosity and microstructure. The relative permittivity, loss tangent, and temperature coefficient of resonant frequency of titanium oxide in microwave frequency were explored over a broad density range which was controlled through sintering temperature. Permittivity values range between 15 and 115 as the sintering temperature increased from 500 to 1550°C. The measured permittivity were compared with several types of mixing rules which assumed titania and pores as the constituents. A Coherent Potential Formula was modified to produce the best fit over the largest porosity range. General constitutive formulas were also developed to describe $\tan\delta$ and TCF and these models work well for intermediate porosity ranges ($0.08 < \text{Pore fraction} < 0.4$); however there were significant deviations at the high and low porosity ranges ($\text{Pore fraction} < 0.08$ and > 0.4). The deviations were attributed to local reduction of the rutile grains and grain boundaries.

Keywords: Titanium Oxide, Dielectrics, Microstructure, Electrical properties

1. Introduction

The microwave (MW) dielectric properties of titanium oxide (TiO_2) have been extensively explored^[1-3]; however, no studies have correlated MW dielectric properties over a wide range of porosity. In this work, we present and discuss the porosity dependence and microstructure on relative permittivity (ϵ_r), loss tangent ($\tan\delta$), and temperature coefficient of resonant frequency (TCF) in MW frequency for undoped rutile.

Permittivity control in ceramics over a broad frequency range enables the precise control of electromagnetic response within a device which is critical for many applications. For example, metamaterials and magnetic resonance imaging applications require specific permittivity values in the 10 to 500 range ^[4].

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Figure 2: The ϵ_r , $\tan\delta$, and TCF of TiO_2 samples in different porosities with sintering temperature labeled on selected data.

The TCF values of the rutile in different porosity were shown in Fig2c. To find an expression that describes the porosity dependence on TCF within $0.05 < P < 0.4$, we can first start with the formula of TCF^[5],

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