Materials Letters 200 (2017) 101–104

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

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

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ARTICLE INFO

Article history:
Received 3 February 2017
Received in revised form 9 April 2017
Accepted 23 April 2017
Available online 24 April 2017

Keywords:
Titanium oxide
Dielectrics
Microstructure
Electrical properties

ABSTRACT

The dielectic 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 tanδ and TCF and these models work well for intermediate porosity ranges (0.08 < Pore fraction < 0.4); however there were significant deviations at the high and low porosity ranges (Pore fraction < 0.08 and > 0.4). The deviations were attributed to local reduction of the rutile grains and grain boundaries.

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 (tanδ), 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 10–500 range [4].

2. Material and methods

Commercially pure TiO_2 (Alfa Aesar, 99.5%) powder was mixed with binder (Acryloid, Conservation Resources International, VA) and prepared into cylindrical green pellets. Then the pellets were sintered from 500 °C to 1550 °C for 60 min to obtain different porosities as determined from geometric density.

The TiO_2 ε_r and tanδ were obtained by the Hakki-Coleman method at frequencies between 4 GHz and 10 GHz. The TCF was obtained through a procedure outlined in Ref. [5]. The microstructures of cross sections of TiO_2 samples with different porosity were characterized by scanning electron microscopy (FEI NanoSEM 630). Multiple measurements were performed, which gave an average of coefficient of variation (standard deviation/mean × 100%) in the tanδ of 3%, 0.3% in ε_r, and 1% in density.

3. Results and discussions

The porosity (P) of the TiO_2 samples was calculated from the following equation

$$P = 1 - \frac{\rho_{measured}}{\rho_{theory}}, \quad (1)$$

where $\rho_{measured}$ is the experimental density; ρ_{theory} = 4.26 g/cm^3 is the theoretical density of rutile. The minimum P achieved in this study was 0.053 at a sintering temperature ($T_{sintering}$) of 1450 °C and maximum is 0.414 at 500 °C. The pore size, shape, and orientation also affects dielectric properties. But to simplify the analysis and to follow the method in Ref. [6], spherical pores were assumed here.

3.1. Microstructure in different porosity

The microstructures of rutile samples with different porosity and grain size were characterized by SEM (Fig. 1) and there is a general progression in grain size and a concomitant decrease in the

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http://dx.doi.org/10.1016/j.matlet.2017.04.113
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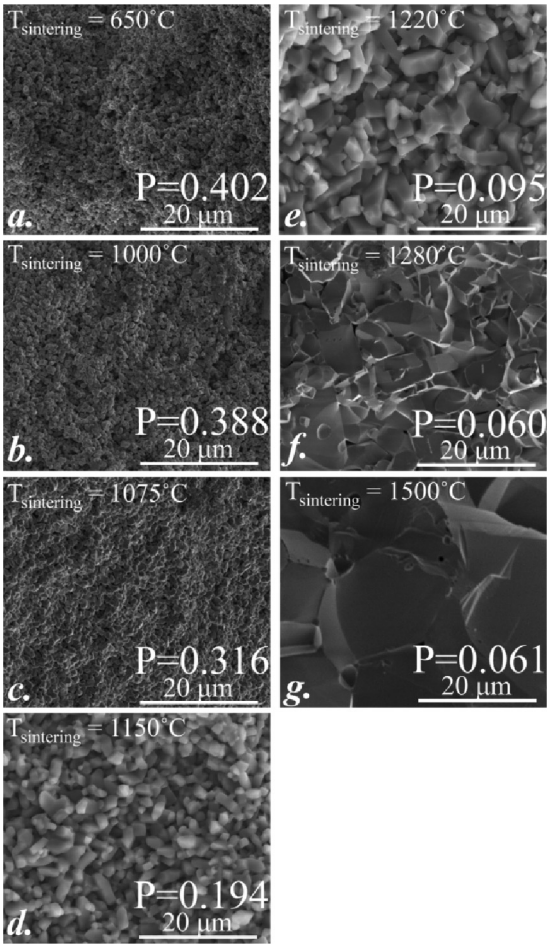

Fig. 1. Microstructures of TiO_2 samples with different porosity.

porosity as the $T_{sintering}$ increases. There is a monotonic increase in the grain size with $T_{sintering}$ and the grains are isometric. The transition from open porosity to closed porosity typically occurs at P = 0.1 as determined by gas permeability measurements [7].

3.2. Effect of porosity in dielectric properties

The porosity dependence on the dielectric properties showed in Fig. 2, and three ranges were observed. For P > 0.4 range, the samples are white with low mechanical strength making them difficult to handle. This observation is consistent with previous works showing a significant decrease in relative strength at a critical porosity volume [8]. The dielectric properties vary significantly over a narrow porosity range at P > 0.4 where the grain boundary contribution to permittivity and loss is significant. At 0.4 < P < 0.8, dielectric properties show clear trends, which are expected to be described by constituent mixing rules.

For P < 0.08, the dielectric properties are weakly correlated to the porosity. The values for ε_r, tanδ and TCF are 105.29 ± 1.96, 3.15 ± 1.00 × 10^{-4}, and 438 ± 1.96 ppm/°C, respectively. These values are comparable to the reported values in literature [8]. Higher $T_{sintering}$ did not necessarily result in a higher ε_r and lower tanδ. Instead, the tanδ is higher than the samples with 0.08 < P < 0.4. Rutile with $T_{sintering}$ > 1220 °C have a dark beige color and shiny surface. From both the sample color and the increased tanδ value, it is believed that the oxygen deficiency occurs in these samples. Generally, oxygen vacancy concentration increases at higher $T_{sintering}$ and the oxygen is reincorporated into the rutile structure

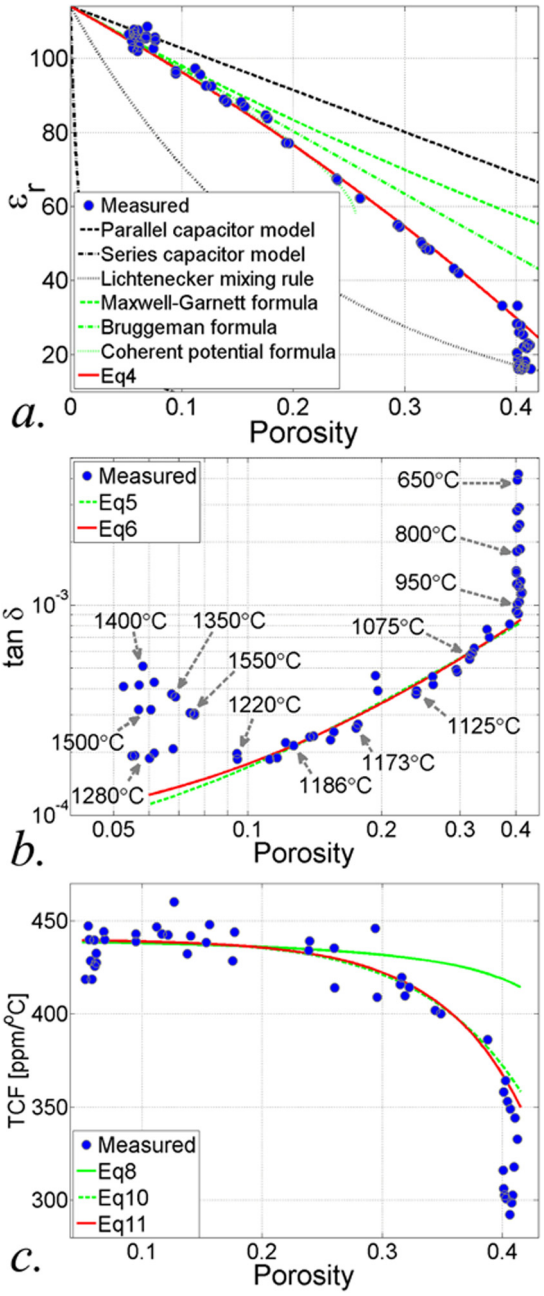

Fig. 2. The ε_r, tanδ, and TCF of TiO_2 samples in different porosities with sintering temperature labeled on selected data.

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. Previous reports on single-phase polycrystalline ceramics have shown that there is transition between open and closed porosity at P = 0.1, which is consistent with our data [7].

3.2.1. Predicting dielectric properties of rutile from constitutive mixing rules

The dependence of porosity on ε_r when 0.08 < P < 0.4 is examined by six generally accepted mixing rules, as shown in Fig. 2a. With the assumption of limited local electric field interaction between the pure polycrystalline rutile matrix (ε_{r1} = 114) and the spherical air inclusion (ε_{r2} = 1), the Maxwell–Garnett and