ISSN 2393-9850
GEM — Georgian Educational Mine
Interdisciplinary International Peer-Reviewed Research Journal
St. George's College Aruvithura, Kerala, India

Volume 3, Issue 1, 2023
Pages 1–7
gem.sgcaruvithura.ac.in

ORIGINAL RESEARCH ARTICLE

A Study on the Dielectric Properties of Sintered Titanium Dioxide

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Received: 20 October 2023 · **Revised:** 22 November 2023 · **Accepted:** 11 December 2023 · **Published:** 18 December 2023

Keywords: Solid state sintering; XRD; Dielectric constant; Dielectric loss; Porosity

Abstract

Dense samples of TiO_2 were prepared by the solid state sintering technique. The sintering temperature has been optimized by studying the variation of density with temperature. Phase identification has been performed with the help of the powder X-ray diffraction technique. The dielectric properties at radio frequencies were measured using an LCR meter by the capacitor method. It was observed that sintered TiO_2 has a high dielectric constant and a poor loss coefficient. The conductivity of sintered TiO_2 measured suggests that TiO_2 might be in the semiconducting state.

1. INTRODUCTION

Materials having different dielectric constant (ε_r) have a wide range of application in the field of wireless communication. Low dielectric constant materials are essential for substrate applications, whereas a very high dielectric constant is useful for applications as gate dielectrics and passive components in microelectronic technology [Kajfez and Guillon, 1986, Trinogga et al., 1991]. Medium dielectric constant materials are needed for dielectric resonators (DRs) for applications as filters, duplexers, oscillators and antennas in highly miniaturized electronic devices [Roberts et al., 1997, Kingon et al., 2000]. There are also other important parameters like the dielectric loss tangent ($\tan\delta$)

and the temperature coefficient of dielectric constant (τ_ε). The factor $\tan\delta$ indicates the energy loss in a dielectric medium when an alternating electric field is applied. The factor τ_ε indicates the variation of dielectric constant of the material with temperature [Sebastian, 2008, Joseph and Sebastian, 2010].

Several dielectric resonator materials containing Ti, such as $Ba_2Ti_9O_{20}$, $MgTiO_3$–$CaTiO_3$, $(Zr,Sn)TiO_4$ and BaO–PbO–Nd_2O_3–TiO_2, with ε_r values ranging from 20 to 150, have been developed for use in various applications [Sebastian, 2008]. Therefore TiO_2 is an important material in the field of the electronic and wireless communication industry. TiO_2 exists in three forms: rutile, brookite and anatase. Brookite and anatase convert irreversibly to rutile in the temperature range of 700–920 °C. Rutile has a tetragonal structure and is also a semiconductor under certain oxidation states. Sintering temperatures of up to 1500 °C are required to attain dense samples of rutile for powders with particle sizes of 0.2–3 μm, although lower sintering temperatures are possible in much finer powders. In this study, the sintering behaviour of TiO_2 is investigated along with its dielectric properties at the radio frequency range. If sintering occurs in an air atmosphere or under low oxygen partial pressure, a slight reduction of TiO_2 occurs. Problems that are associated with titanium-containing ceramics (including reduction) have been highlighted in various publications [O'Bryan et al., 1974, 1978, O'Bryan and Thomson, 1983, O'Bryan, 1987, Nomura et al., 1983, Negas et al., 1993].

2. EXPERIMENTAL METHODS

Dense samples of TiO_2 were prepared using the solid state sintering technique, starting from TiO_2 powder (Aldrich Chemicals). The powder was mixed with 6 wt% of PVA (molecular weight 22,000, BDH Lab Suppliers) and pressed into disks of about 11 mm in diameter and $\sim$1 mm in height under a pressure of about 100 MPa. The green compacts were initially fired at a rate of 3 °C/min up to 600 °C and then at a rate of 12 °C/min up to the sintering temperature. An intermediate soaking at 600 °C for 30 minutes was given to expel the binder. After cooling from the sintering temperature to 1000 °C at a rate of 2 °C/min, the ceramics were cooled inside the furnace naturally. The sintering was carried out at different temperatures in the range 800–1500 °C for 2 h in order to attain maximum density for all the pellets. The temperature corresponding to maximum density has been chosen as the optimized sintering temperature of the sample. The density of the samples was measured by the Archimedes method. The structure of the powdered sample was studied by X-ray diffraction using Cu Kα radiation (Philips X-Ray Diffractometer). The radio-frequency (up to 3 MHz) dielectric properties were measured by an LCR meter (Hioki 3532-50, Japan). This was done by the capacitor method, in which the sample is made into a parallel plate capacitor by pasting Ag on both sides and by connecting Cu leads.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern of TiO_2 is shown in Fig. 1. The diffraction pattern of TiO_2 is indexed based on ICDD file card no. 89-4920. All recognizable reflection peaks could be readily indexed to the tetragonal structure of rutile, having lattice parameters of $a = 4.584(2)$ Å and $c = 2.953(1)$ Å, and belonging to the space group $P4_2/mnm$ (136). Using the lattice parameters, the theoretical density can be calculated, which in this case is found to be $4.276\,\mathrm{g\,cm^{-3}}$. The most intense reflection is obtained from the (110) plane and the next one from the (211) plane.

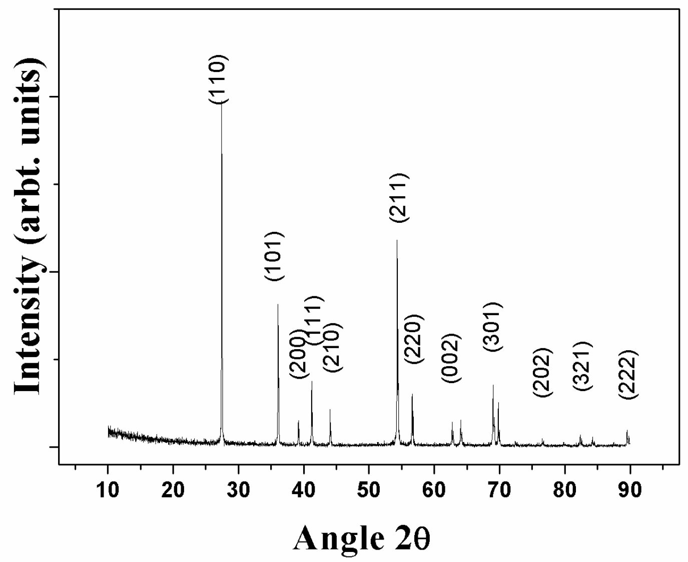

Figure 1. Powder X-ray diffraction pattern of heat-treated TiO_2.

Fig. 2 represents the optimization of the sintering temperature by studying the variation of the density with sintering temperature. The density of TiO_2 is found to increase with sintering temperature. The increase in sintering temperature enhances grain growth, which results in the elimination of porosity and hence an improvement in density. The highest density achieved for TiO_2 is 4.1159 g cm^{-3}, when sintered at 1450 °C/2 h. It corresponds to a densification of 96.25% of the theoretical value. A further increase in sintering temperature causes a decrease in the density of TiO_2.

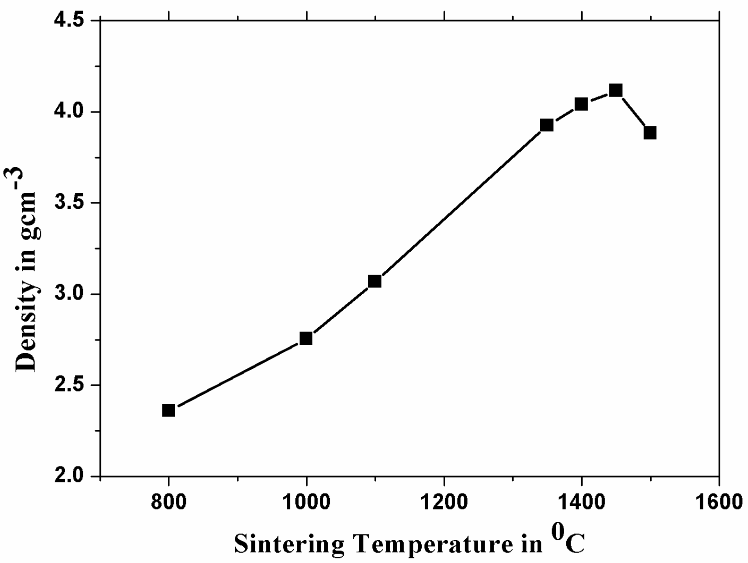

Figure 2. Variation of density of sintered TiO_2 with sintering temperature.

Fig. 3 shows the variation of porosity as a function of sintering temperature. The porosity in the material was calculated by the following expression:

$$\text{Porosity} = \frac{\rho_{th} - \rho_m}{\rho_{th}} \times 100,$$

where ρ_{th} and ρ_m are the theoretical and measured densities, respectively. The theoretical density of rutile TiO_2 is 4.276 g cm^{-3}. The porosity of TiO_2 decreases from 44.8% at 800 °C and reaches a minimum value of 3.74% at a sintering temperature of 1450 °C. Therefore, the optimized value of the sintering temperature of TiO_2 is 1450 °C/2 h. A further increase in sintering temperature, however, increases the porosity.

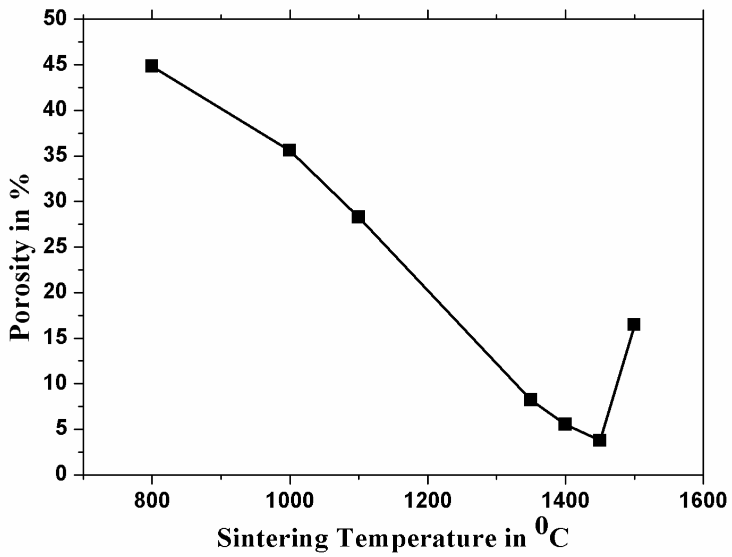

Figure 3. Variation of porosity with sintering temperature.

The dielectric constant of TiO_2 as a function of temperature is shown in Fig. 4. The dielectric constant increases with sintering temperature and reaches a maximum value of 154.3 at a sintering temperature of 1450 °C, and thereafter it decreases. The increase in the dielectric constant with sintering temperature can be related to the decrease in the porosity of the samples at 1450 °C. Air has $\varepsilon_r = 1$, which is very low compared to the dielectric constant of the TiO_2 phase. Therefore, the minimum value of porosity corresponds to the maximum value of dielectric constant. Usually, it is very difficult to obtain TiO_2 samples with 100% densification, and hence a correction for porosity is always necessary. Here it is assumed that the material consists of two phases (TiO_2 and air) with different values of dielectric constant. The following equation is used for the porosity correction of the dielectric constant of the material:

$$\varepsilon_m = \varepsilon_c \left[1 - 3P \frac{\varepsilon_c - 1}{2\varepsilon_c + 1} \right],$$

where ε_m is the measured ε_r, ε_c is the corrected ε_r and P is the fractional porosity [Penn et al., 1997]. The corrected value of dielectric constant at a sintering temperature of 1450 °C is 162.74.

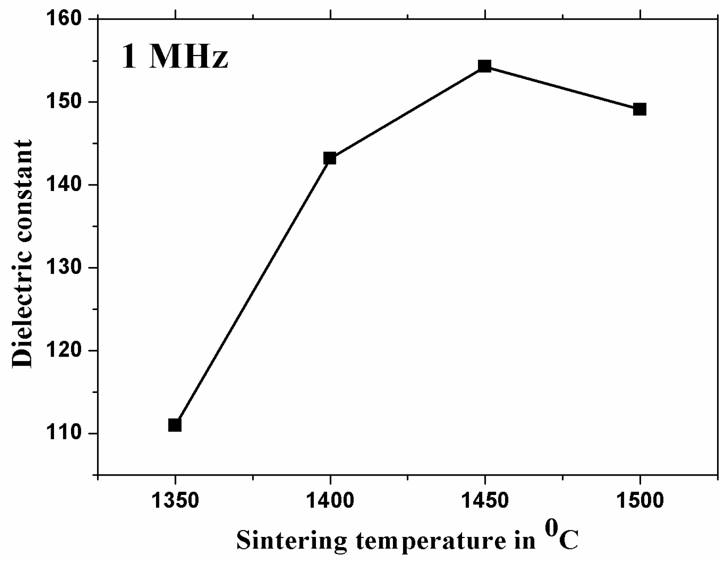

Figure 4. Variation of dielectric constant with sintering temperature.

The frequency dependence of the dielectric constant of sintered TiO_2 is shown in Fig. 5. The dielectric constant decreases with frequency as shown in the figure. Relaxation effects are associated with permanent and induced molecular dipoles. At low frequencies the field changes slowly enough to allow dipoles to reach equilibrium before the field has measurably changed. Hence the polarization, and the corresponding dielectric constant, will be high. For frequencies at which dipole orientations cannot follow the applied field due to the viscosity of the medium, the polarization will decrease, which decreases the dielectric constant. The absorption of the field's energy also leads to energy dissipation. The mechanism of dipoles relaxing is called dielectric relaxation and, for ideal dipoles, is described by the classic Debye relaxation. At low frequencies the effect of interfacial polarization is dominant, which is due to the polarization of free charges accumulated at the interfaces of the samples. As frequency increases, the effect of interfacial polarization decreases, leading to an overall degradation of the dielectric constant.

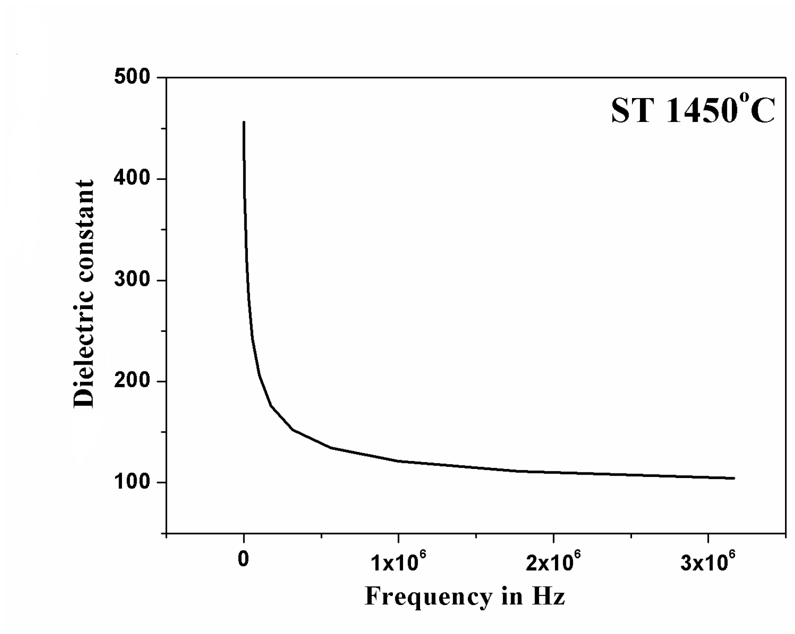

Figure 5. Variation of dielectric constant with frequency of the sample sintered at 1450 °C.

The dielectric loss tangent of the sample sintered at 1450 °C is found to be 0.13, whereas the loss tangent of dielectrics is of the order of $\sim 10^{-2}$ to 10^{-3}. The conductivity of TiO_2 sintered at 1450 °C is found to be 5.8×10^{-5} S cm^{-1}, which is of the order of semiconductors. If sintering occurs in an air atmosphere or under low oxygen partial pressure, a slight reduction of TiO_2 occurs. Using standard Kröger–Vink notation, this reduction can be described principally in terms of either the formation of oxygen vacancies (reaction (1)), Ti^{4+} interstitials (reaction (2)), Ti^{3+} interstitials (reaction (3)), or oxygen vacancies and Ti^{3+} species in octahedral lattice sites (reaction (4)):

$$2\,\mathrm{O_O^\times} \rightleftharpoons 2\,\mathrm{V_O^{\bullet\bullet}} + 4e' + \mathrm{O_2} \tag{1}$$

$$\mathrm{Ti_{Ti}^\times} + 2\,\mathrm{O_O^\times} \rightleftharpoons \mathrm{Ti_i^{\bullet\bullet\bullet\bullet}} + 4e' + \mathrm{O_2} \tag{2}$$

$$\mathrm{Ti_{Ti}^\times} + 2\,\mathrm{O_O^\times} \rightleftharpoons \mathrm{Ti_i^{\bullet\bullet\bullet}} + 3e' + \mathrm{O_2} \tag{3}$$

$$2\,\mathrm{Ti_{Ti}^\times} + \mathrm{O_O^\times} \rightleftharpoons 2\,\mathrm{Ti'_{Ti}} + \mathrm{V_O^{\bullet\bullet}} + \tfrac{1}{2}\mathrm{O_2} \tag{4}$$

Therefore the TiO_2 samples prepared in this case show the conductivity of semiconductors. It is reported that metal oxides, such as TiO_2, NiO and Cr_2O_3, have semiconducting properties [Kubaschewski and Hopkins, 1967, Birks and Meier, 1983].

4. CONCLUSIONS

The sintering temperature of TiO_2 was optimized to obtain a maximum density of 4.12 g cm^{-3}, which corresponds to a densification of 96.25%. The optimized sintering temperature was found to be 1450 °C/2 h. The X-ray diffraction pattern indicates that the material has a tetragonal structure of rutile and belongs to the space group $P4_2/mnm$ (136). The dielectric constant at 1 MHz has a maximum value of 154.3 at the optimized sintering temperature of 1450 °C/2 h. A correction for porosity has also been performed, which gives 162.7. This represents the dielectric constant of a 100% dense sample. The dielectric loss tangent of the sample at 1 MHz is found to be 0.13, which is quite unusual for a dielectric material. The conductivity of the sample measured suggests the possibility of a semiconducting phase formation.

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