Effect of various sintering temperature of ceramic TiO₂ on physical properties and crystall structure

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Abstract. Titanium dioxide has been made by using sintering method with variation of temperature sintering. This method uses 100 % of Titanium dioxide powder as the raw material. The Titanium dioxide powder was pulverized by using High Energy Milling for one hour and continued with compacted to form a pellet by dry pressing with 8 tons force. Then the pellets were sintered by using electrical furnace with variation of temperature of 700°C, 850°C and 1000°C. The characterization of sintered samples includes measurement of density, porosity, hardness and XRD. The results show that the sintered 700°C sample has the smallest density of 1.94 g/cu.cm and the largest porosity 20 % and hardness 228 Hv. For the sintered 1000°C sample has greatest density of 2.38 g/cu.cm and smallest porosity of 15.9% and hardness 276 Hv. The results of the phase analysis with XRD show that the dominant phase is anatase and minor phase is rutile.

1. Introduction

Titanium dioxide has three forms of polymorph, they are anatase, rutile and brookite. The rutile phase is thermodynamically more stable and higher, the rutile structure appears to be thermodynamically stable under pellet conditions, based on thermodynamic experiments, it shows that above can be more stable than the rutile crystalline compilation only a few nano meters [1,2]. Anatase phase is form metastable, can transformed into rutile if it’s given heating treatment. At temperature and depressed room for macro crystalline systems, rutile phase thermodynamics are more stable than anatase and brookite, but thermodynamic stability depends on particle size which contributes to free energy face [3]. These compounds are used extensively in the upper fields as pigments, bactericides, toothpastes, photo catalysts and electrodes in solar cells [4]. One of its more well-known uses is as a photocatalyst [5]. Consequently, titanium finds applications mainly in high demanding sectors, such as the aerospace industry or to produce biomedical devices, where the final high cost is not the principal issue [6]. The mechanical properties of sintered products made using metal titanium powder are inferior to those of cast products. However, it is very cost-effective for non high-performance environments. In the process of producing of TiO₂ ceramics, there are important parameters that can influence the ceramic properties of TiO₂, namely the sintering temperature. The sintering temperature can have an effect on the level of density and strength of TiO₂ ceramics and changes in the TiO₂ crystal structure. The TiO₂ ceramics are said to have crystal structures at low temperatures and crystal structures at high temperatures. The application of TiO₂ ceramics is very broad, and is very dependent on the crystal
structure. Therefore, recent research has focused on improving the mechanical properties of sintered TiO$_2$ products [7]. Nowadays, little attention has been paid on dielectric properties of nanostructured TiO$_2$ ceramics. It is well known that the properties of electro ceramics are affected by their microstructural features (such as grain size, porosity, secondary phases) and defect structure (such as point and electronic defects) [5]. The purpose of this paper is to investigate the effect of sintering temperatures on density, porosity, hardness and crystal structure of TiO$_2$.

2. Experimental

Pure TiO$_2$ ceramic powder from E-Merck was used as raw material and the sample was milled by using the High Energy Milling for 1 hour and the mass ratio between the ball of milling and powder is 1:10. The sample is then separated from the ball mill by using a filter then weight the mass of powder. The fine powder was added a celuna binder (3 % of wt), then compacted with force of 8 tons to form a pellet. The pellet of TiO$_2$ was sintered with a temperature variation of 700°C, 850°C and 1000°C. The sintered pellets are then characterized such as: density, porosity and hardness vickers. The density was calculated using the equation [8]:

$$\rho = \frac{m}{V}$$  \hspace{1cm} (1)

where:
- $\rho$ = bulk density (g/cm$^3$)
- $m$ = mass of sample (g)
- $V$ = volume of sample (cm$^3$)

The measurement of porosity was conducted according Archimedes and calculated using equation [9]:

$$\varphi = \frac{m_w - m_0}{m_w - m_s} \times 100\%$$  \hspace{1cm} (2)

where:
- $\varphi$ = porosity (%)
- $m_w$ = mass of sample after soaking in the distilled water for 48 hours (g)
- $m_0$ = mass of dried sample (g)
- $m_s$ = mass of sample hanging in water (g)

Then the sample that has been calculated for density and porosity was tested for phase transformation by using XRD and analysis of XRD patterns were done by using match software. Then the hardness of the sample was measured by using Durometer with load 1000 g. Average values of hardness were calculated from three times repetition for each samples.

3. Result and Discussion

3.1. Density and Porosity

The pellet samples that have been sintered are measured to determine their density and porosity values. The results of density and porosity measurements can be seen in Table 1. Based on the Table 1, density and porosity are two material properties that influence each other, where if the porosity of a material is high, the density of the material will be lower but if the material has lower porosity it vice versa [10]

| Sintering Temperature (°C) | Bulk Density (g/cm$^3$) | Porosity (%) |
|----------------------------|-------------------------|--------------|
| 700                        | 1.94                    | 20           |
| 850                        | 2.268                   | 16           |
| 1000                       | 2.38                    | 15.9         |
The changes in the density and porosity values of Titanium Dioxide are shown in Figure 1 below. Figure 1 shows that the changes in density values is inversely proportional to the values of porosity. According Figure 1, the highest density value is achieved 2.98 g/cm$^3$ at a sintering temperature of 850°C, this value is certainly far enough with the theoretical density value of 3.95 g/cm$^3$ [10].

![Figure 1](image.png)

**Figure 1.** Graph of density and porosity of sintered TiO$_2$

While the smallest porosity value is achieved 15.90 % also at a sintering temperature of 850°C. The density value increased sharply from temperatures of 700°C to 850°C with value difference of 0.328 g/cm$^3$. While the increasing of density value from 850°C to 1000°C is not too sharp, but it is close to constant with value difference of 0.112 g/cm$^3$. The relationship of the bulk density value of ceramic material to porosity is inversely proportional, the higher the density, the cavity in the sample decreases, so the porosity value decreases. Similarly, the higher the sintering temperature, the density value tends to increase to the maximum limit. When the sintering process has been reached, the density tends to be constant. Based on the results of density and porosity measurements indicate that the achieved density value is still lower than the theoretical density, this is because the sintering temperature is still low or the grain size of the raw material is still not sufficiently fine.

### 3.2. Vickers Hardness

Likely density, temperature is directly proportional to the hardness of an object. This can be seen from the following Table 2. Based on the result of the measurement of hardness shows that with increasing sintering temperature, it will affect the hardness value of TiO$_2$ material. The higher sintering temperature, the greater the Vickers hardness. This can be linearly seen through the graph in Figure 2.

| Temperature (°C) | Hardness Vicker (HV) |
|------------------|----------------------|
| 700              | 228                  |
| 850              | 253                  |
| 1000             | 292                  |

Measurement of Vickers hardness values on the sintered samples are presented in Figure 2. It can be seen that the hardness value increases along its temperature increased. It correlated to the effect of density and porosity where it can be seen that the higher the density or the lower porosity (compare to Figure 1), then higher the hardness. The highest hardness at 1000°C temperature that is 292 HV and the lowest hardness is at 700°C that is 228 HV.
Figure 2. Graph of Hardness Vickers of TiO$_2$

3.3. **X-Ray Diffraction**

This XRD analysis uses 40 kV, 30 mA X-ray and CuK $\alpha$ wavelength 1.541862 Å. To find out the size of the crystal structure, the type of crystal and material phase can use a match application that will bring up specific peaks along with its miller index. The working system is a sample that wants to know the crystal structure and the phase analysis will be shot with X-rays in the 10-900 angle range. X-rays that affect the sample will be diffracted by the atoms making up the sample and will produce a certain diffraction pattern. Here are the results of X-ray diffraction tests on Titanium Dioxide samples on sintering temperature variations.

3.3.1. **XRD result of sintered 700 °C sample.** Based on the XRD test results in Figure 3 it can be seen that the sample with sintering temperature of 700°C has 18 peaks with the highest peak of 2θ at an angle of 25.27° with a crystal size of 011 which has an anatase phase.

There are 12 other peaks that have similar phases in these sample. This anatase phase has a tetragonal crystal type with a lattice parameter $a = 3.78500$ Å, $c = 9.51400$ Å. While the other five peaks were not detected as anatase phases with 2θ at angles of 27.39°, 31.38°, 36.09°, 41.41° and 66.42° with crystal sizes of 173, 77, 141, 56 and 80, respectively, indicating the presence of the VOTTDPz phase ($C_{16}N_{16}OS_{4}V$). This phase has a monoclinic crystal type with lattice parameters $a = 12.44900$ Å, $b = 6.86100$ Å, $c = 12.91600$ Å, and $\beta = 116.702^\circ$. From the results of the XRD analysis through the peaks in the graph (Figure 3), it has been shown that TiO$_2$ ceramic consists of two phases, namely the anatase phase and VOTTDPz ($C_{16}N_{16}OS_{4}V$) and does not indicate the presence of another phase in the
composite. Although there were no other ingredients doped on TiO$_2$ ceramics, other phases that emerged could be caused by technical errors during the research which caused the possibility of other ingredients being mixed through the tools used.

3.3.2. XRD result of sintered 850°C sample. Based on the XRD test results in Figure 4, the sample with sintering temperature of 850°C has 18 peaks with the highest peak of 2θ at an angle of 25.26° with a crystal size 244 which has an anatase phase. There are 12 other peaks that have similar phases in this sample. This anatase phase has a tetragonal crystal type with a lattice parameter $a = 3.78420$ Å $c = 9.51460$ Å. While the other four peaks were not detected as anatase phase with 2θ at angles of 27.41°, 36.04°, 41.26° and 43.93° with crystal sizes of 222, 226, 286 and 211, respectively, indicating the presence of the Bornite phase. This phase has a cubic crystal type with a lattice parameter $= 10.70000$ Å. Whereas one peak has a different phase with 2θ at an angle of 56.58°, with a crystal size of 224 which shows the presence of the Haycockite. This phase has an orthorombic crystal type with lattice parameters $a = 10.70500$ Å $b = 10.73400$ Å $c = 31.63000$ Å.

![Figure 4. Graph of XRD TiO$_2$ sintered at 850°C](image)

From the results of the XRD analysis above through the peak on the graph, it has been shown that TiO$_2$ ceramics consist of 3 phases, namely anatase phase, Bornite phase, and Haycockite, and bornite. Although the Haycockite and bornite phases are different names, but these crystals have the same elements (Cu, Fe and S), it’s just different formulas, the reason is caused by other ingredients are mixed through the tools used. At sintering temperatures of 850°C This, as well as a temperature of 700°C which both have an anatase phase as the major phase and has a value of 2 theta with peaks that are almost the same. Eventhough occurred the peak shifts, but the shift is not much different. This shows that at temperatures below 1000°C, the resulting phase is anatase.

3.3.3. XRD result of sintered 1000°C sample. Figure 5 shown that the temperature of 1000°C has 18 peaks with the highest peak of 2θ at an angle of 27.40° with a crystal size of 1285 which has a rutile phase. There are 17 other peaks that have similar phases in this sample. This rutile phase has a tetragonal crystal type with a lattice parameter $a = 3.78420$ Å $c = 9.51460$ Å. While one other peak was not detected as a rutile phase with 2θ at an angle of 25.16° with a crystal size of 47 indicating the presence of porphyrazine aluminium chloride phase. This phase has a cubic crystal type with a lattice parameter $= 10.70000$ Å.
Figure 5. Graph of XRD TiO$_2$ sintered at 1000°C

From the results above, TiO$_2$ ceramics consist of 2 phases, namely rutile and porphyrazine aluminium chloride phases and do not indicate the presence of other phases in ceramics. At sintering temperature of 1000°C phase changes occur. Different from the temperature of 700°C and 850°C. At sintering temperature 1000°C has a rutile phase and has a value of 2 theta with peaks that are different from the two previous temperatures. This shows that the rutile phase can be produced through high temperature sintering such as at a temperature of 1000°C.

4. Conclusions
This study demonstrated that through variation of sintering temperatures of Titanium dioxide, the increasing sintering temperature caused the increasing density values but decrease in porosity values. The TiO$_2$ sample which is sintered at 1000°C tends to produce a rutile phase. At a temperature of 700°C and 850°C, the anatase phase occurs while at a temperature of 1000°C transformation to the rutile phase occur.

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