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# Effect of Thermal Treatment on Nanosized Brookite-to-Rutile $TiO_2$ Phase Transformation Prepared by Sol-Gel method

**Majida A. Ameen[1], Asmaa J. Kadhim Al kinani[2]**

[1]Sulaimany University, College of Education, Department of physics, Kurdistan Regional, Iraq

[2]Baghdad University, College of Science for Women, Department of physics, Baghdad, Iraq

**Abstract:** ***This paper describes heat treatment temperature effect on the phase transformation of titanium dioxide ($TiO_2$) prepared using metal organic precursors as starting materials. X-ray diffraction (XRD) was used to investigate the structural properties of as prepared $TiO_2$ powder and calcined at different temperatures (100, 300, 500, 700) ℃. the results showed that the prepared and 100 ℃ treated samples were amorphous, and have typical peaks of $TiO_2$ polycrystalline brookite nanopowders after calcined at (300 ℃), which confirmed by (111), (200), (040), and (231) diffraction peaks. Also, XRD pattern showed the presence of crystallites of anatase with low proportion of rutile phase reaches (27.3%) weight fraction where calcined at (500 ℃). With further increase in the calcination temperature, i.e. to (700 ℃), formation of complete rutile phase has been observed. The crystallite size of $TiO_2$ nanopowders was calculated by Scherer's formula and showed that the crystallite size decreased and then increased with increasing the annealing temperature.***

**Keywords:** Thermal treatment, Phase transformation, $TiO_2$ powders, sol-gel

## 1. Introduction

Nanostructured materials have attracted wide attention due to their special optical, electronic, magnetic, chemical, and mechanical characteristics that cannot be achieved using their bulk form [1]. Nanocrystalline titanium dioxide ($TiO_2$) is a well-known multifunctional nanoparticle because of its abundance, stability, non-toxicity, low cost, easy handling, and resistance to photochemical and chemical erosion [2]-[4]. These advantages make $TiO_2$ a material in solar cells, chemical sensors, hydrogen gas evolution, optical filters, antireflection coatings, catalysts, and used in pigments, self-cleaning surfaces, and environmental purification applications [4], [5].

Controllable crystalline structure of nanosized $TiO_2$ represents some of the key subjects in its applications. Titanium dioxide exists in both crystalline and amorphous forms and mainly exists in three crystalline polymorphous, including; rutile and anatase have a tetragonal structure, whereas brookite has an orthorhombic structure [3], [6], [7]. All crystallographic phases of $TiO_2$ have different physical properties, which in turn, are the basis of many applications [8]. Rutile phase employed in pigments, paints, and ultraviolet absorbents, because of its highest refractive index and ultraviolet absorptivity, while the anatase phase is chemically and optically active, it is suitable for catalysts and supports [9]. Because of its difficult preparation, brookite is seldom studied and rarely used [10], [11]. Rutile is the stable phase, whereas anatase and brookite are metastable phases and are readily transformed into rutile when the sample is calcined at higher temperatures [9], [12]. This transformation does not have a unique temperature [11] and its possible sequences among three $TiO_2$ main polymorphs can be described as anatase to rutile, anatase to brookite to rutile, brookite to rutile, and brookite to anatase to rutile. These transition sequences is dependent on the experimental conditions and the properties of the prepared sample, including; particle size, starting material, initial phase, and annealing temperature [8].

Since nanosized $TiO_2$ efficiency in the specific application depends on its physical, chemical and phtochemical characterization which in turn are dependent on the manufacturing method, sol-gel process is one of the most common method for preparing nanocrystalline metallic oxide material (such as $TiO_2$) at a laboratory scale, due to its advantages such as high purity, good uniformity of the microstructure, low processing temperature, and easily controlled reaction condition [13]. Generally, in a conventional sol-gel process, a colloidal suspension or a sol is formed due to the hydrolysis and polymerization reactions of the precursors, which on complete polymerization and loss of solvent leads to the transition from the liquid sol into a solid gel phase. The wet gel can be converted into nanocrystals with further drying and hydrothermal treatment [14].

In this paper, phase transformation for different annealing temperatures of $TiO_2$ nanopowder prepared by the sol-gel method using titanium tetraisopropoxide, were investigated and reported.

## 2. Materials and Methods

### 2.1 Chemical Materials

Tetra (IV) Isopropoxide ($Ti(OC_3H_7)_4$); (TTIP) (≥ 98%) was used as a starting material and supplied by Fluka company. Ethanol ($C_2H_5OH$, 99.9%) from GCC acts as a solvent, and hydrochloric acid (HCl, 34.5%) from BDH as a catalyst. Deionized water was used to hydrolyze (TTIP) and preparation of $TiO_2$ sol. All regents were used as received.

### 2.2 Preparation of the samples

The preparation of $TiO_2$ powder by the sol-gel technique was performed as follows:

**i)** A mixture of ($6.895\times10^{-3}$ mol) of deionized water and (2.02 ml) of ethanol containing hydrochloric acid (0.06 ml) was added, dropwise into a premixturer of ($6.895\times10^{-3}$ mol) of $Ti(OC_3H_7)_4$ and (2.02 ml) of ethanol at temperature of (11 °C) under stirring for (20 min). A clear yellow sol was obtained.

**ii)** A homogeneous $TiO_2$ sol was transformed into gel after dried at (54 °C) for (1:15 hr) in an open vessel. The gel was broken into small pieces after drying in air, then heated at (100 °C) for (1 hr) to remove physically adsorbed water and residual ethanol. After that, the sample was placed in dense alumina crucible and carried to annealing process at (300, 500, 700) °C in an ambient atmosphere.

### 2.3 Characterization of $TiO_2$ Nanopowder

The crystal structure and crystallinity of $TiO_2$ nanopowder were examined by an x-ray diffractometer (Shimadzu Japan, XRD-6000) using the (Ni-filtered) monochromatic with Cu-Kα crystal radiation (λ=1.5406 Å). The detection range was (20°-60°) with the step size of 5° ($2\theta/\text{min}^{-1}$). The peak width at half height in the x-ray diffraction (XRD) pattern has been used to calculate the crystallite size by following Scherer's equation [15]:

$$t = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

Where:
t is the crystallite size (in nm), K (=0.9) is the Scherer's constant, λ is the x-ray wavelength, β is (FWHM) (in radian) and θ the Bragg's diffraction angle (in degree).

The mass fraction of rutile ($x_r$) in the crystal lattice can be calculated based on the relationship between the integrated intensities of anatase (1 0 1) and rutile (1 1 0) peaks by the following equation developed by Spurr and Myers [16].

$$X_{rutile} = \frac{1}{1+k\left(\frac{I_A}{I_R}\right)} \qquad (2)$$

Where:
X: mass fraction of rutile in the powders.
$I_A$: X-ray integrated intensity of the strongest peaks of anatase ($2\theta = 25.489^o$, (101) plane).
$I_R$: X-ray integrated intensity of the strongest peaks of rutile ($2\theta = 27.654^o$, (110) plane).
The empirical constant k was determined via an XRD analysis of powders of known proportions of pure anatase and pure rutile $TiO_2$, and is equal to 0.79 [17].

The $TiO_2$ anatase and rutile unit crystal are tetragonal, with lattice constants 'a' and 'c', whereas for brookite is orthorhombic with 'a', 'b', and 'c'.

For the anatase and rutile crystal system 'a' and 'c' were determined from two appropriate reflections (hkl) using the following formula [15]:

$$\sin^2\theta = \frac{\lambda^2}{4}\left(\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right) \qquad (3)$$

And for brookite 'a', 'b', and 'c' were determined from two appropriate reflections (hkl) using the following formula [15]:

$$\sin^2\theta = \frac{\lambda^2}{4}\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right) \qquad (4)$$

## 3. Result and Discussion

The purity and the crystal structure of $TiO_2$ nanocrystalline powder were analyzed by XRD, the peak location and relative intensities for $TiO_2$ are cited from the JCPDS data base. The influence of the thermal annealing temperature on the structure of $TiO_2$ nanopowder was study using different temperatures (100, 300, 500, and 700) °C.

XRD pattern of the uncalcined titania powder, (as prepared powder), indicating its amorphous nature. The amorphous phase could be hydrous $TiO_2$, (i.e. $TiO_2\ nH_2O$). The $TiO_2$ nanopowder remains at its amorphousity after treatment at 100 °C, as shown in figures (1) and (2) respectively.

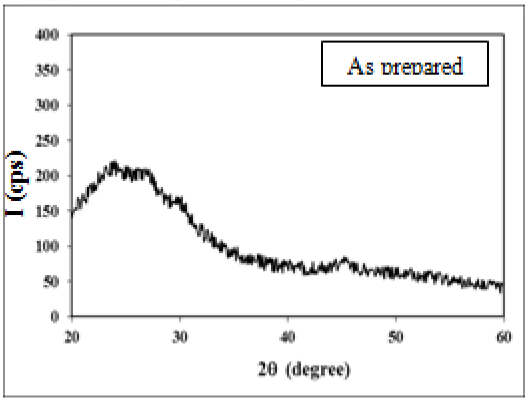

**Figure 1:** The XRD pattern of as prepared $TiO_2$ powder

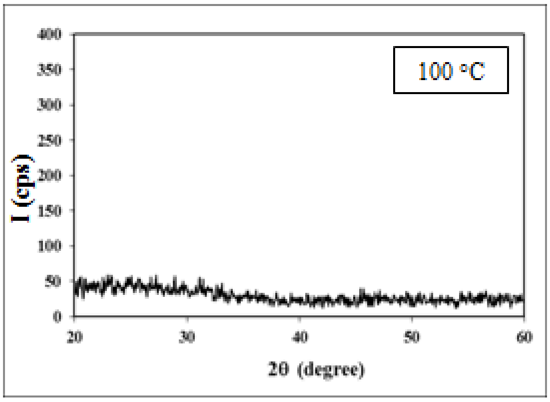

**Figure 2:** The XRD pattern of $TiO_2$ powder annealed at 100 °C.

Nanosize $TiO_2$ powder prepared by sol-gel method is yellow in color which converted to black when is annealed at (300 °C), indicate to yield brookite $TiO_2$ phase. Figure (3) shows the XRD pattern for these samples. The peaks located at "d spacing" values (3.456, 2.888, 2.727, 2.491, 2.365, 2.343, 2.304, 1.896, 1.862 and 1.599) nm respond to the (111), (121), (200), (012), (131), (220), (040), (231), (132) and (232) of the brookite titania phase, respectively.

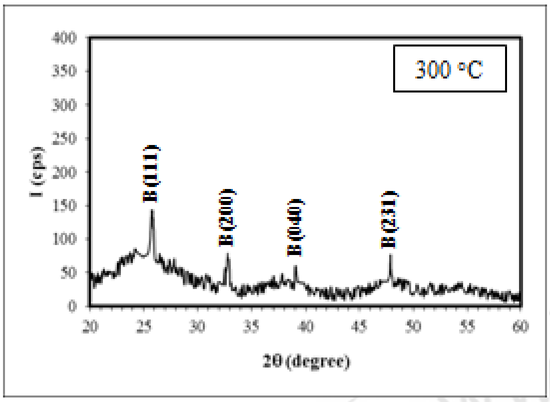

**Figure 3:** The XRD pattern of $TiO_2$ powder annealed at 300 °C

After annealing at (500 °C); a changed result, being not accordance with that at (300 °C), was obtained, identifying that the powder became white in color and the peaks characteristic of brookite were disappeared and new peaks corresponding to anatase structure with a small proportion of a coexisting rutile structure, as shown in figure (4). The peaks located at (25.489°, 36.186°, 37.81°, 48.129°, 54.426° and 55.326°) respond to the (101), (103), (004), (200), (105) and (211) of the anatase phase, respectively. And the peaks located at (27.654° and 41.532°) are respond to the (110) and (111) of the rutile phase, respectively, and its amount was calculated about (27.3%) according to eq.(2).

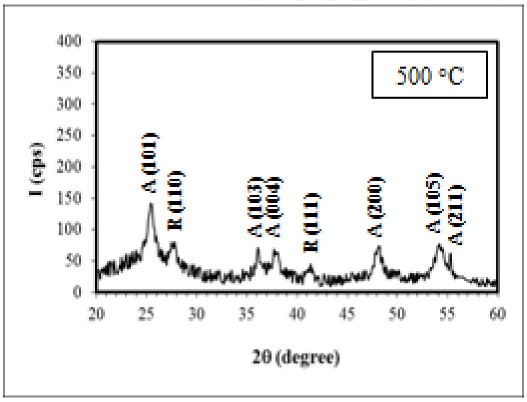

**Figure 4:** The XRD pattern of $TiO_2$ powder annealed at 500 °C.

At annealing temperature (700 °C) only the peaks for rutile were observed, indicating that anatase completely transformed to rutile through heat treatment. The polycrystalline rutile structure was confirmed by (110), (101), (111), (211) and (220), as shown in figure (5). From these results, it can be said that brookite is directly not transformed to rutile but to rutile via anatase. The results are consistent with the observation of Bakadjieva et al. [6] and Lee et al. [18] who claimed that $TiO_2$ brookite transforms to rutile via anatase.

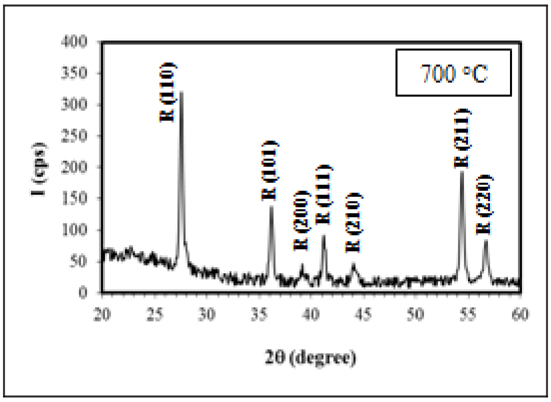

**Figure 5:** The XRD pattern of $TiO_2$ powder annealed at 700 °C.

The crystallite size of the all anatase $TiO_2$ samples were estimated from XRD patterns using Scherer's equation with their strongest brookite (111), anatase (101) and rutile (110) peaks. All $TiO_2$ samples have dimensions on the nanometer range, varying from (15.97 nm) for brookite ($TiO_2$ annealed at 300° C) to (9.53 nm) for anatase and (8.92 nm) for rutile at (500 °C) which increases to (40.79 nm) when annealed at (700 °C).

The obtained data showed that the synthesis of ultrafine titania resulted in anatase and brookite, which on coarsening transformed to rutile after reaching a certain particle size [19], dependent on the experimental conditions. And at (500 °C) the anatase can grow to a size larger than rutile, so the crystallization of rutile is not as well as that of anatase because the relative intensity of rutile phase is lower than that of anatase. This result may be attributed to suppose that anatase may nucleate and grow at the expense of brookite matrix. Based on these result, also the annealing of $TiO_2$ powder at (700 °C) causes an increasing in the rutile crystallite size; this is coming from the fact that the thermal annealing improves the crystallinity of the particles by rearrangement phenomenon and the increase of the $TiO_2$ crystallite size.

These results can be interpreted as follows:
According to the temperature, the anatase-rutile transformation is related to some extent with the degree of packing of the particles, since the transformation begins with the nucleation of rutile on anatase and the rutile nuclei grow throughout the anatase particle until completion.

The tetragonal Bravais lattice type of the polycrystalline anatase and rutile $TiO_2$ nanopowder structure, and orthorhombic of brookite $TiO_2$ was verified by lattice constants calculated from diffraction peaks in figures (3-5)). Based on the peaks of the anatase (101) and (200), rutile (110) and (111), and brookite (111), (200), and (040) reflections, the lattice constants were calculated via equations (3) and (4). The data were collected and summarized in table (1).

**Table 1:** Summary of the properties of $TiO_2$ nanopowder

| *Annealing temperature (°C)* | *$TiO_2$ Phase* | *crystallite size (nm)* | *Lattice Parameter (Å)* | | |
|---|---|---|---|---|---|
| | | | *A* | *b* | *c* |
| 300 | Brookite | 15.978 | 5.4534 | 9.2198 | 5.1085 |
| 500 | Anatase | 9.53 | 3.7781 | 3.7781 | 9.1414 |
| | Rutile | 8.924 | 4.5580 | 4.5580 | 2.9412 |
| 700 | Rutile | 40.79 | 4.5742 | 4.5742 | 2.9683 |

## 4. Conclusion

$TiO_2$ nanopowder with different crystalline phase composition amorphous, brookite, anatase and rutile and crystallite size have been prepared by controlling the heat treatment temperature. The calcination of amorphous $TiO_2$ powder showed that brookite phase transform to anatase (with small proportion of rutile) which was finally transformed to chemically stable structure of rutile phase with increasing of annealing temperature.

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## Author Profile

Assist. Professor **Majida Ali Ameen,** born in Baghdad in 21/3/1974, received a Physics B.Sc. degree from Baghdad University / College of Educational for women in 1995, Master Degree from Baghdad University in 2001 in thin films. And a Ph.D. degree in laser (also, Sol-Gel technique, nanotechnology) from Baghdad University / College of Science for Women in 2008. She interested with research about the laser, Sol-Gel technique and uses it to prepare the laser active medium, nanotechnology and thin films.

**Asmaa J. Kadhim** born in Baghdad in 1979 received a Physics B.Sc. degree from Baghdad University College of Educational for Women in 2001, Master Degree from Baghdad University / College of Science for Women in 2006 in Random laser. And a Ph.D. degree in laser from Baghdad University / College of Science for Women in 2014. She interested with research about the laser, holography, Sol-Gel technique and uses it to prepare the laser active medium, and nanotechnology.