

Artikel 1_2

by Ariswan Ariswan

Submission date: 29-Apr-2019 09:07PM (UTC+0700)

Submission ID: 1121334259

File name: Artikel_1_2.pdf (536.55K)

Word count: 5459

Character count: 27623

Qualitative and Quantitative Phase-Analysis of Undoped Titanium Dioxide and Chromium Doped Titanium Dioxide from Powder X-Ray Diffraction Data

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Received October 11, 2017; Accepted February 2, 2018

ABSTRACT

Undoped titanium dioxide (TiO_2) and a series of chromium(III) doped TiO_2 (Cr-doped TiO_2) with various %wt Cr atom were prepared by a reflux technique. The undoped TiO_2 and Cr-doped TiO_2 of 1.1, 3.9, 4.4 %wt Cr atom have been successfully analyzed both qualitative and quantitative analysis of powder X-ray diffraction (XRD) data. The qualitative analysis was carried out with the identification of phases in all samples by comparison with Crystallography Open Database (COD) and International Centre for Diffraction Data (ICDD), while the quantitative phase analysis was calculated by reference intensity ratio (RIR) and whole-pattern fitting (Rietveld analysis) methods. The undoped TiO_2 consist of three phases: anatase, rutile, and brookite. In the 1.1 %wt Cr-doped TiO_2 are detected presenting two phases: anatase (major) and rutile (minor). In the 3.9 %wt Cr-doped TiO_2 and in the 4.4 %wt Cr-doped TiO_2 consist of anatase as major phase, while CrO_2 and TiO_2 -II phases can be detected as minor phases. The undoped TiO_2 was refined in the phase, crystal system and space group of anatase (tetragonal, $I4_1/amd$), rutile (tetragonal, $P4_2/mnm$) and brookite (orthorhombic, $Pbca$), while the 1.1 %wt Cr-doped TiO_2 was refined based on anatase (tetragonal, $I4_1/amd$), rutile (tetragonal, $P4_2/mnm$). Finally, in the 3.9 %wt Cr-doped TiO_2 and 4.4 %wt Cr-doped TiO_2 , respectively were refined in the crystal system and space group of anatase (tetragonal, $I4_1/amd$).

Keywords: titanium dioxide; Rietveld analysis; X-ray powder diffraction

ABSTRAK

Titanium dioksida (TiO_2) dan TiO_2 terdada variasi % berat Cr(III) berhasil dipreparasi dengan teknik refluks. Titanium dioksida dan TiO_2 terdada 1,1; 3,9; dan 4,4% berat atom Cr dianalisis secara kualitatif dan kuantitatif dari data difraksi sinar-X (XRD) serbuk. Analisis kualitatif dilakukan dengan cara mencocokkan data pola XRD sampel dengan data pola XRD standard dari Crystallography Open Database (COD) dan International Centre for Diffraction Data (ICDD). Analisis kuantitatif dihitung berdasarkan metode "reference intensity ratio" (RIR) and "whole-pattern fitting" (metode Rietveld). Sampel TiO_2 berisi tiga fasa kristal: anatas, rutil, dan brookit, sedangkan TiO_2 terdada 1,1% berat atom Cr mengandung dua fasa: anatas (utama) dan rutil (minor). Masing-masing, pada TiO_2 terdada 3,9% berat atom Cr dan TiO_2 terdada 4,4% berat atom Cr terkandung anatas sebagai fasa utama, sedangkan fasa CrO_2 dan TiO_2 -II hadir dalam jumlah sangat sedikit. Penghalusan Rietveld pada TiO_2 dilakukan dengan berdasarkan atas fasa, sistem kristal dan kelompok ruang: anatas (tetragonal, $I4_1/amd$), rutil (tetragonal, $P4_2/mnm$) dan brookit (ortorombik, $Pbca$), sedangkan pada TiO_2 terdada 1,1% berat atom Cr dilakukan penghalusan berdasar atas sistem kristal dan kelompok ruang: anatas (tetragonal, $I4_1/amd$) and rutil (tetragonal, $P4_2/mnm$). Akhirnya, penghalusan struktur pada TiO_2 terdada 3,9% berat atom Cr dan pada TiO_2 terdada 4,4% berat atom Cr dilaksanakan berdasar atas sistem kristal dan kelompok ruang: anatas (tetragonal, $I4_1/amd$).

Kata Kunci: titanium dioksida; analisis Rietveld; difraksi sinar-X serbuk

INTRODUCTION

Titanium dioxide (titania, TiO_2) is the most commonly employed of the n-type semiconductors due to its high photoactivity and stability, relatively low cost,

and non-toxicity. TiO_2 is widely employed in various applications, especially in photocatalyst [1-3], antibacterial [4-6] and photovoltaic devices [7-9], super-hydrophilic and light-induced amphiphilic surfaces [10-12].

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Titanium dioxide has eleven different structure phases (allotropes): anatase, rutile, brookite, $\text{TiO}_2(\text{B})$, $\text{TiO}_2(\text{H})$ -hollandite, $\text{TiO}_2(\text{R})$ -ramsdellite, TiO_2 -columbite (α - PbO_2 type, TiO_2 -II), TiO_2 -baddeleyite (TiO_2 -MI), TiO_2 -orthorhombic (TiO_2 -OI), TiO_2 -fluorite (CaF_2 type), and TiO_2 -cotunnite. Three of these crystalline forms of TiO_2 occur in nature as mineral: anatase (tetragonal, $I4_1/amd$) [13], rutile (tetragonal, $P4_2/mnm$) [13], and brookite (orthorhombic, $Pbca$) [14], but only rutile and anatase have been able to be synthesized in pure form at low temperature until recent days.

A semiconductor is characterized by the presence of band energetic structure, with a band gap between the lower, valence band (VB) and the higher energetic, conduction band (CB). Electrons present in the occupied band (VB) are photoexcited and move to the CB, leaving a positive charged hole (h^+), when the semiconductor is photo-irradiated by light with photon energy ($h\nu$) at least equal to the band gap. Once formed, the electron (e^-) and hole (h^+) pair may undergo either fast recombination. A photocatalytic reaction will occur that leads to the development of useful processes. Anatase shows a band gap of 3.2 eV, corresponding to a UV wavelength adsorption of 387 nm [15]. In contrast, rutile has a smaller band gap (3.0 eV), with excitation wavelengths that extend into the visible light range (410 nm) [16] and the band gap of the metastable brookite is 3.54 eV [17]. Many metal ions are used as dopant to increase the λ radiation adsorption, such as niobium [18], argentum [19-20], vanadium [21], ferrum [22], zinc [23], and chromium [24-26].

X-ray diffraction is the most useful technique for qualitative and quantitative phase analysis in multi-phase. Qualitative analysis identifies phases in a specimen compared to "standard" patterns such as American Society for Testing and Materials (ASTM), Joint Committee on Powder Diffraction Standards (JCPDS), Crystallography Open Database (COD), Inorganic Crystal Structure Database (ICSD) and International Centre for Diffraction Data (ICDD). X-ray diffraction pattern gives information about peak positions, intensity, and shape. Qualitative analysis of powder diffraction data is the identification of crystal phase, peak position and intensity related to unique crystal structure. Quantitative analysis of powder diffraction data refers to the determination of amounts of different phases in multi-phase samples. Quantification can be carried out because the intensity of the diffraction pattern of a phase or phases in a mixture depends on its concentration. There are several methods of X-ray diffraction to quantify phases such as direct comparison, internal standard, external standard, absorption-diffraction, reference intensity ratio (RIR) and whole-pattern fitting (Rietveld analysis) [27-30].

The objectives of this research are (1) qualitative phase analysis in undoped titanium dioxide and a series of chromium doped TiO_2 compared to "standard" patterns: COD and ICDD, (2) analysis of quantitative phase in the samples by comparing two methods: RIR and whole-pattern fitting (Rietveld analysis). This research is important to know the precise and accurate method of qualitative and quantitative analysis in determining the crystalline phases contained in a sample of Cr doped TiO_2 solid solutions.

EXPERIMENTAL SECTION

Materials

Ammonium hydroxide (NH_4OH , 28-30% NH_3) solution, hydrogen peroxide (H_2O_2 , 10 %wt in H_2O), ammonium chromate ($(\text{NH}_4)_2\text{CrO}_4$, 99%), titanium (IV) chloride (TiCl_4 , 99%) were purchased from Sigma-Aldrich. All the reagents were used without further purification. Titanium dioxide hydrate ($\text{Ti}(\text{O}_2)\text{O}\cdot 2\text{H}_2\text{O}$) was obtained from the reaction of TiCl_4 and H_2O_2 [31]. A series of chromium(III) doped TiO_2 with various %wt Cr atom were prepared by the reflux technique. In a typical synthesis, 10 g $\text{Ti}(\text{O}_2)\text{O}\cdot 2\text{H}_2\text{O}$ is dissolved in 50 mL of distilled water under vigorous stirring. The solution was kept stirring for 4 h to obtain colloid A. In order to investigate the effect of the $(\text{NH}_4)_2\text{CrO}_4$ concentration, in a separated beaker 0, 3, 6, and 9 %wt Cr-doped TiO_2 respectively were adopted. It was dissolved in 20 mL of distilled water thoroughly under vigorous stirring to obtain solution B1, B2, B3, and B4, respectively. Each solution B1, B2, B3 and B4 was then slowly added to each solution A. The final solution mixture was sealed and further stirred for 2 h, then added dropwise NH_4OH until pH \approx 8-10. Finally the solution is heated with a magnetic stirrer in equipment reflux at 150 °C for 6 h. Precipitate is filtered, washed with distilled water and dried at 70 °C for 3 h. Furthermore, the precipitate was calcined at 600 °C for 2 h.

Instrumentation

In order to obtain XRD powder data, a Rigaku Miniflex 600-Benchtop diffractometer with a copper tube and $\text{K}\alpha$ radiation of $\lambda = 1.5406 \text{ \AA}$, operating at 40 kV and 15 mA, was used. The samples were mounted in a silica glass sample holder. The powder XRD data were collected in the 2θ interval ranging from 2° to 90° with a step width of 0.02° and a counting time of 5 sec/step.

Scanning electron microscope (Phenom ProX Desktop SEM) equipped with energy dispersive X-ray spectroscopy (EDS) was used to analyze the presence

of Ti and O elements in the TiO₂ and the presence of Ti, Cr, and O elements in the Cr-doped TiO₂.

Procedure

Qualitative phase analysis

Diffraction patterns are unique "fingerprints" of the crystal structure of materials that can be used to determine phase composition of a polycrystalline material. Phase identification is essentially an exercise of pattern comparison between the unknown and a database of single-phase reference patterns. The qualitative analysis was carried out with the identification of a phase or phases in the samples by comparison with "standard" patterns: COD and ICDD.

Quantitative phase analysis

Quantitative analysis of diffraction data usually refers to the determination of amounts of different phases in multi-phase samples. The quantitative phase analysis was calculated by comparing two methods: reference intensity ratio (RIR) and whole-pattern fitting (Rietveld analysis).

Reference Intensity Ratio (RIR) method. The RIR is a method used for quantitative analysis by powder diffraction and is based upon scaling all diffraction data to the diffraction of standard reference materials. The RIR method can be used to determine concentrations by using ratios and measuring peak areas. Klug and Alexander were first to describe a technique for quantification using intensities of the crystalline phases in a mixture as in equation 1 [27]:

$$\frac{I_{(hkl)A}}{I_{(hkl)B}} = k \frac{X_A}{X_B} \quad (1)$$

where, ratio of peak intensity from unknown phase 'A' ($I_{(hkl)}$) to a standard 'B' ($I_{(hkl)}$) is a linear function of the mass fraction of 'A' in the original sample and the amount of minerals in known internal standards (eg, rutile, silica) is used to calibrate unknown phase intensities.

ICDD PDF-2 uses corundum (Al₂O₃) as reference B and gives k for 50:50 mixtures of phase A and corundum. RIR is I/I_{cor} using intensity of the strongest peak (100%), If I_1/I_{cor} is k_1 and I_2/I_{cor} is k_2 , then I_1/I_2 is k_1/k_2 . The RIR values or intensity ratio of the more intense peak of each phase respect to the (113) peak of corundum reported in the PDF of the ICDD is expressed as (2) [32]:

$$w_1 = \frac{I_1^k w_{corundum}}{I_{corundum}^{113} RIR_{1,corundum}} \quad (2)$$

where, w_1 = weight fraction of phase 1 and $w_{corundum}$ = weight fraction of corundum.

Whole-pattern fitting method (Rietveld analysis).

Rietveld (1969) developed a method to refine crystal structure information using neutron powder diffraction [32]. The Rietveld method is based on a least-squares fit between step-scan data of a measured diffraction pattern and a simulated X-ray diffraction pattern. The simulated XRD pattern is calculated from a large number of parameters, including crystal-structure parameters of each component phase, a scale factor for each constituent phase to adjust the relative intensities of the reflections, parameters describing the peak profile and the background, and parameters simulating the instrumental aberrations as well as effects resulting from size-related strain, preferred orientation, and particle size. A key feature of the quantitative analysis of phase proportions by the Rietveld method is that the phase abundances of the constituent phases can be directly calculated from the refined scale-factors. To refine each XRD spectrum in the research, The Rietveld analysis was applied by using Fullprof software by Roisnel and Rodriguez Carbajal on the package WinPlotr [33]. In the refinement procedure, a calculated pattern is fitted to an observed diffraction pattern by the least-squares method, until the best fit is obtained. The least-squares refinement leads to a minimal residual quantity (χ^2) in the Rietveld Method [34] is,

$$\chi^2 = \sum_{i=1}^n w_i \{y_i - y_{c,i}(\alpha)\}^2 \quad (3)$$

with $w_i = 1/\sigma_i^2$, being σ_i^2 the variance of the "observation" y_i , y_i = observed intensity at the i^{th} step, and $y_{c,i}$ = calculated intensity at the i^{th} step. The calculated profile of X-ray powder pattern can be well described by the equation:

$$y_{c,i} = \sum_{\phi} S_{\phi} \sum_h I_{\phi,h} \Omega(T_i - T_{\phi,h}) + b_i \quad (4)$$

In Fullprof, the term phase is synonymous of a same procedure for calculating the integrated intensities ($I_{\phi,h}$). Rietveld phase quantification (sometimes called also standardless phase analysis, multiphase Rietveld quantitative analysis or Rietveld XRD quantification) is a powerful method for determining the quantities of crystalline and amorphous components in multiphase mixtures. The weight fraction (W_i) for each phase was obtained from the refinement relation [34]:

$$W_i = \frac{S_i (ZMV)_i}{\sum_j S_j (ZMV)_j} \quad (5)$$

where i is the value of j for a particular phase among the N phases present. The S , Z , M , and V are, respectively, the Rietveld scale factor, the number of

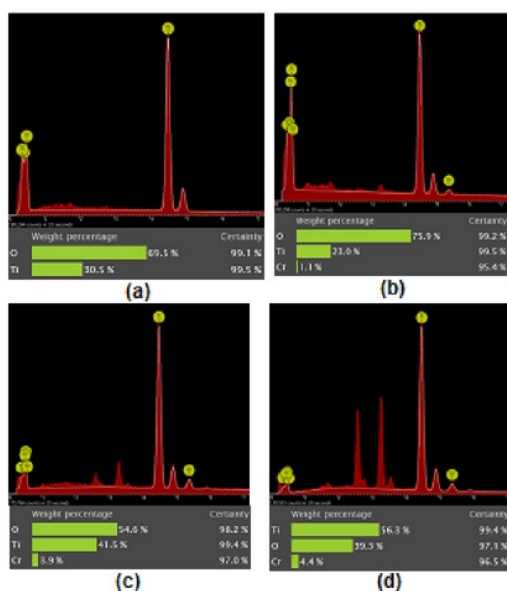


Fig 1. EDS analysis and weight percentage of Ti, O and Cr of (a). undoped TiO₂, (b). 1.1 %wt Cr-doped TiO₂, (c). 3.9 %wt Cr-doped TiO₂, and (d). 4.4 %wt Cr-doped TiO₂

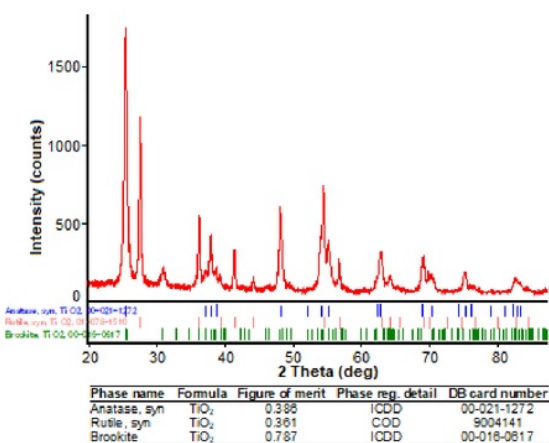


Fig 2. XRD diagram and the result of qualitative analysis of undoped TiO₂

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formula units per cell, the mass of the formula unit (in atomic mass units) and the unit cell volume (in Å³). The fit must be evaluated by visual comparison between the observed and calculated pattern. The quality of the agreement between observed and calculated profiles is measured by a set of nowadays-conventional factors (profile factor (R_p), weighted profile factor (R_{wp}), expected

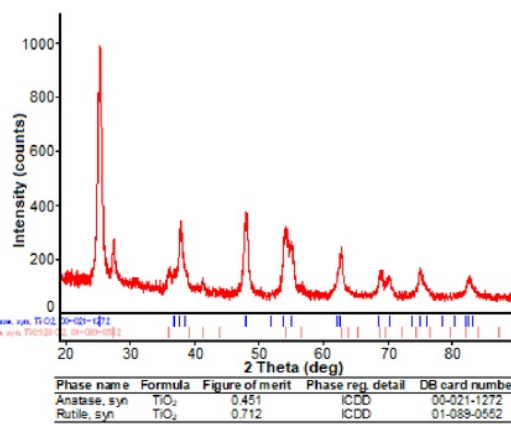


Fig 3. XRD diagram and the result of qualitative analysis of 1.1 %wt Cr-doped TiO₂

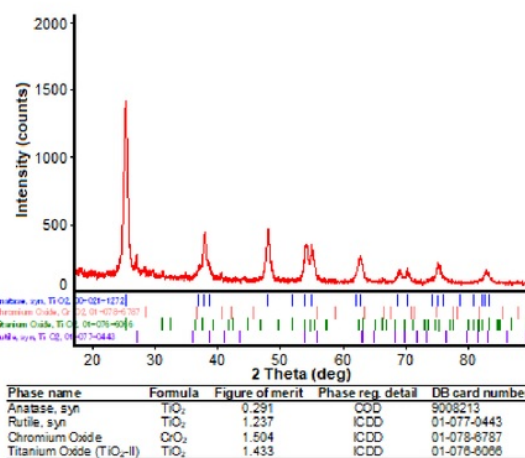


Fig 4. XRD diagram and the result of qualitative analysis of 3.9 %wt Cr-doped TiO₂

weighted profile Factor (R_{exp}), and goodness of fit indicator (GoF).

RESULT AND DISCUSSION

EDS Analysis

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The scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis reveals the presence of Ti and O elements in undoped TiO₂ and of Ti, Cr, O elements in various %wt Cr-doped TiO₂. On the theoretical, addition of each: 3, 6 and 9 %wt Cr-doped TiO₂ produced experimentally only 1.1, 3.9 and 4.4 %wt Cr-doped TiO₂ respectively (Fig. 1).

Based on the composition of the atoms, the molecular formula of solid solutions ($Ti_{1-x}Cr_xO_2$) for 1.1, 3.9 and 4.4 %wt Cr-doped TiO_2 are $Ti_{0.983}Cr_{0.017}O_2$, $Ti_{0.940}Cr_{0.060}O_2$, and $Ti_{0.932}Cr_{0.068}O_2$, respectively.

Qualitative Phase Analysis

Fig. 2, 3, 4 and 5 show XRD patterns of undoped TiO_2 and Cr-doped TiO_2 at various %wt Cr atom. All XRD patterns exhibit strong diffraction peaks at 2θ : 25.36, 37.84, 48.11, 54.38, 55.07, and 62.88° indicating TiO_2 of anatase phase and at 2θ : 27.53, 36.14, 41.32, and 54.38 indicating TiO_2 of rutile phase. The main diffraction peaks are indexed as the (101), (103), (200), (105), (211), (213) reflections of crystalline anatase phase, corresponding to those shown in the ICDD card No. 00-021-1272 and the main diffraction peaks are indexed as the (110), (101), (200), (111), (211) reflections of crystalline rutile phase, corresponding to those shown in the COD card No. 9004141. In the undoped TiO_2 , there are three phases: anatase, rutile, and brookite (Fig. 2). Fig. 3 shows that the 1.1 %wt Cr-doped TiO_2 sample is detected presenting two phases of TiO_2 : anatase (major) and rutile (minor). In the 3.9 %wt Cr-doped TiO_2 (Fig. 4)

and the 4.4 %wt Cr-doped TiO_2 (Fig. 5) show the presence of anatase (major), rutile (minor), chromium

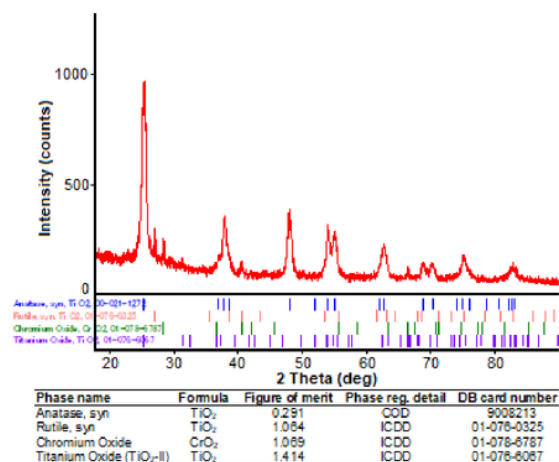


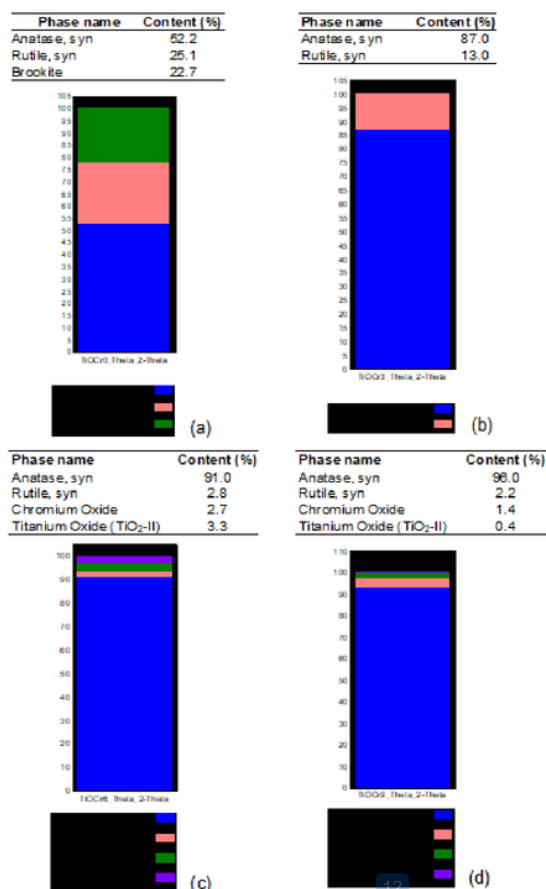
Fig 5. XRD diagram and the result of qualitative analysis of 4.4 %wt Cr-doped TiO_2

Table 1. Phase content of TiO_2 and (hkl) in undoped TiO_2 and various %wt Cr-doped TiO_2

| Samples | | | | (hkl) planes | | | | |
|-----------------|--------------------------|--------------------------|--------------------------|--------------|--------|----------|---------|-------------|
| Undoped TiO_2 | 1.1 %wt Cr-doped TiO_2 | 3.9 %wt Cr-doped TiO_2 | 4.4 %wt Cr-doped TiO_2 | Anatase | Rutile | Brookite | CrO_2 | TiO_2 -II |
| 25.36 | 25.29 | 25.31 | 25.33 | (101) | | (210) | | (110) |
| | | 27.10 | 27.06 | | | | (011) | |
| 27.53 | 27.39 | | | | (110) | | (110) | |
| 30.95 | | 28.39 | 28.39 | | | (211) | | (111) |
| 36.14 | 36.04 | 31.24 | 31.29 | | (101) | | | |
| 37.05 | | 36.90 | 36.94 | (103) | | | | |
| 37.84 | 37.76 | | | (004) | | | | |
| 38.04 | 37.80 | 37.82 | 37.93 | (112) | | (311) | | |
| 38.67 | | | | | | (220) | | |
| 39.24 | | | | | (200) | (400) | | |
| | | 40.54 | 40.43 | | | | (020) | |
| 41.32 | 41.34 | | | | (111) | | | |
| 44.13 | | | | | (210) | | | |
| 48.11 | 48.00 | 48.01 | 48.01 | (200) | | (402) | | |
| | 53.98 | 53.99 | 53.96 | | | | | |
| 54.38 | | | | (105) | (211) | | | |
| 55.07 | 55.10 | 55.04 | 55.02 | (211) | | | | |
| 56.63 | | | | | (220) | | | |
| 62.88 | 62.79 | 62.75 | 62.72 | (213) | (002) | | | |
| 64.13 | | | | | (310) | (023) | | |
| | | | 66.38 | | | | | (023) |
| 68.96 | 68.87 | 68.95 | 68.77 | (116) | (301) | | | |
| 69.85 | | | | | (112) | | | |
| 70.34 | 70.19 | 70.20 | 70.08 | (220) | | | | |
| 75.06 | 74.94 | 75.04 | 75.02 | (215) | | | | |
| 75.98 | | | | (301) | | | | |
| 82.54 | 82.57 | 82.78 | 82.63 | (224) | (321) | (440) | | |

Table 2. Phase content of TiO₂ in undoped TiO₂ and various %wt Cr-doped TiO₂ calculated using RIR method

| Samples | Phase (%) | | | | |
|-----------------------------------|-----------|--------|----------|------------------|----------------------|
| | Anatase | Rutile | Brookite | CrO ₂ | TiO ₂ -II |
| UndopedTiO ₂ | 52.2 | 25.1 | 22.7 | - | - |
| 1.1 %wt Cr-doped TiO ₂ | 87.0 | 13.0 | - | - | - |
| 3.9 %wt Cr-doped TiO ₂ | 91.0 | 2.8 | - | 2.7 | 3.3 |
| 4.4 %wt Cr-doped TiO ₂ | 96.0 | 2.2 | - | 1.4 | 0.4 |

**Fig 6.** Composition XRD diagram of (a). undoped TiO₂, (b). 1.1 %wt Cr-doped TiO₂, (c). 3.9 %wt Cr-doped TiO₂, and (d). 4.4 %wt Cr-doped TiO₂

oxide (minor) and TiO₂-II (minor). The results of identification of a phase or phases and (hkl) in the samples are showed in Table 1.

Quantitative Phase Analysis

RIR method

Fig. 6 shows the weight fraction of TiO₂ phases calculated using the RIR method. The phase content of

all samples calculated by RIR method are showed in Table 2. In the undoped TiO₂ shows the following phase compositions: anatase (52.2%), rutile (25.1%) and brookite (22.7%), while in the 1.1 %wt Cr-doped TiO₂, its phase composition are anatase (87.0%) and rutile (13.0%). The chromium oxide, rutile and TiO₂-II present in the 3.9 %wt Cr-doped TiO₂ and the 4.4 %wt Cr-doped TiO₂, respectively. In the 3.9 %wt Cr-doped TiO₂ are detected 91.0% of anatase, 2.8% of rutile, 2.7% of CrO₂, and 3.3% of TiO₂-II, while in the 4.4 %wt Cr-doped TiO₂ consist of 96.0% of anatase, 2.2% of rutile, 1.4% of CrO₂, and 0.4% of TiO₂-II.

Whole-pattern fitting method (Rietveld analysis)

X-ray diffraction-Rietveld refinement was carried out with the method supplied by the Fullprof software to undoped TiO₂ and various %wt Cr-doped TiO₂. The results of Rietveld refinement are shown in Fig. 7, 8, 9 and 10. The experimental points are given as dot (.) and theoretical data (calculated by eq. (3)) are shown as solid line. Difference between experimental data and theoretical is shown as bottom line. The vertical lines represent the Bragg's allowed peaks. In the undoped TiO₂ were refined in the crystal system and space group of anatase (tetragonal, *I*₄/amd), rutile (tetragonal, *P*₄₂/mnm) and brookite (orthorhombic, *P*bca) (Fig. 7). No reflections of anatase (major) and rutile (minor) phases are observed in the 1.1 %wt Cr-doped TiO₂ (fig. 8) and it's were refined in the crystal system and space group of anatase (tetragonal, *I*₄/amd), and rutile (tetragonal, *P*₄₂/mnm). In the 3.9 %wt Cr-doped TiO₂ and 4.4 %wt Cr-doped TiO₂ respectively consist of anatase phase, while rutile, chromium dioxide and TiO₂-II phases can't be detected by Rietveld refinements. Fig. 9 and 10 depict Fullprof Pattern Matching of anatase phase in the 3.9 %wt Cr-doped TiO₂ and 4.4 %wt Cr-doped TiO₂ respectively. The results of crystal system, cell parameters (a, b, c) and atomic position (x, y, z) are presented in Table 3.

Fig. 11 shows the relationship between cell volumes of anatase at various %wt Cr atom of Cr-doped TiO₂. The cell volume of anatase crystals have increased with increasing %wt Cr atoms of Cr doped TiO₂. This is due to the replacement of Ti(IV) ions which have crystal radii of 0.746 Å replaced by Cr(III) ions having larger crystal radii that is 0.755 Å [35].

Table 3. The crystal system, cell parameters (a, b, c) and atomic position (x, y, z) of TiO₂ phases in undoped TiO₂ and various %wt Cr-doped TiO₂ calculated by Rietveld method

| Samples | Phase | a (Å) | b (Å) | c (Å) | V (Å ³) | Atom | x | y | z |
|---|--|--------|--------|--------|---------------------|------------------|---------|--------|--------|
| Undoped TiO ₂ | Anatase (Tetragonal, <i>I4₁/amd</i>) | 3.7819 | 3.7819 | 9.5008 | 135.89 | Ti ⁴⁺ | 0.0000 | 0.0000 | 0.5000 |
| | O ²⁻ | | | | | 0.0000 | -0.5000 | 0.5447 | |
| | Rutile (Tetragonal, <i>P4₂/mnm</i>) | 4.5901 | 4.5901 | 2.9553 | 62.26 | Ti ⁴⁺ | 0.0000 | 0.0000 | 0.0000 |
| | O ²⁻ | | | | | 0.3064 | 0.3064 | 0.0000 | |
| Brookite (Orthorhombic, <i>Pbca</i>) | Ti ⁴⁺ | 9.1601 | 5.4291 | 5.1476 | 255.99 | Ti ⁴⁺ | 0.1292 | 0.0912 | 0.8658 |
| | O ₁ ²⁻ | | | | | 0.0331 | 0.1830 | 0.1427 | |
| | O ₂ ²⁻ | | | | | 0.2136 | 0.0949 | 0.5469 | |
| 1.1 %wt Cr-doped TiO ₂ | Anatase (Tetragonal, <i>I4₁/amd</i>) | 3.7930 | 3.7930 | 9.5075 | 136.78 | Ti ⁴⁺ | 0.0000 | 0.0000 | 0.5000 |
| | O ²⁻ | | | | | 0.0000 | -0.5000 | 0.5447 | |
| | Rutile (Tetragonal, <i>P4₂/mnm</i>) | 4.5925 | 4.5925 | 2.9574 | 62.37 | Ti ⁴⁺ | 0.0000 | 0.0000 | 0.0000 |
| O ²⁻ | 0.3041 | | | | | 0.3041 | 0.0000 | | |
| 3.9 %wt Cr-doped TiO ₂ | Anatase (Tetragonal, <i>I4₁/amd</i>) | 3.7978 | 3.7978 | 9.5205 | 137.32 | Ti ⁴⁺ | 0.0000 | 0.0000 | 0.5000 |
| | O ²⁻ | | | | | 0.0000 | -0.5000 | 0.5405 | |
| 4.4 %wt Cr-doped TiO ₂ | Anatase (Tetragonal, <i>I4₁/amd</i>) | 3.7972 | 3.7972 | 9.5159 | 137.21 | Ti ⁴⁺ | 0.0000 | 0.0000 | 0.5000 |
| | O ²⁻ | | | | | 0.0000 | -0.5000 | 0.5347 | |

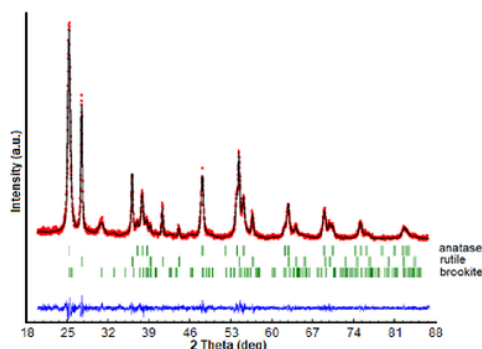


Fig 7. X-ray diffraction Fullprof Pattern Matching of undoped TiO₂

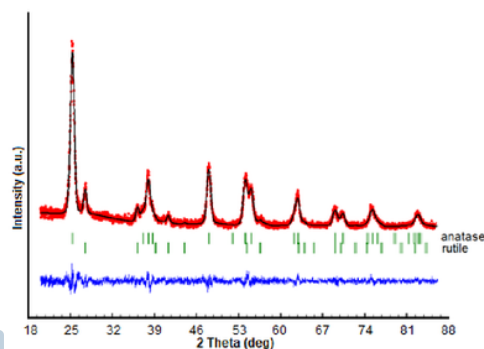


Fig 8. X-ray diffraction Fullprof Pattern Matching of 1.1 %wt chromium doped TiO₂

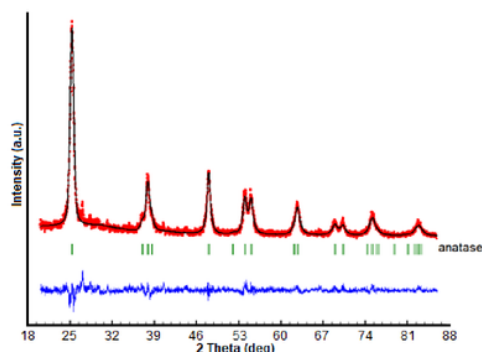


Fig 9. X-ray diffraction Fullprof Pattern Matching of 3.9 %wt chromium doped TiO₂

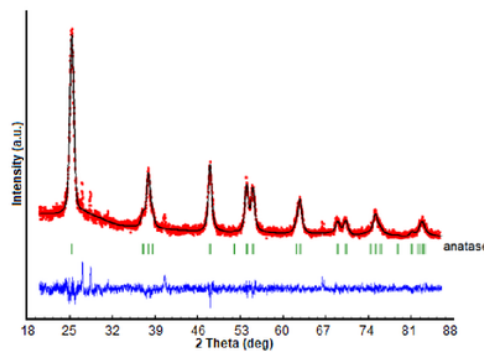
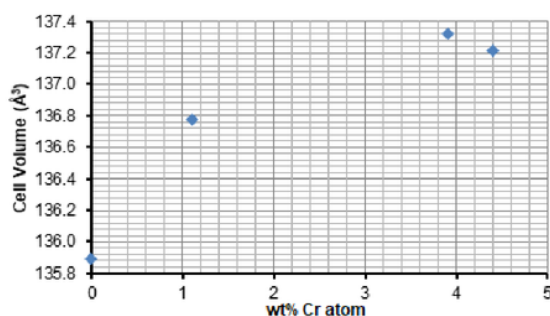


Fig 10. X-ray diffraction Fullprof Pattern Matching of 4.4 %wt chromium doped TiO₂

Table 4. Phase content of TiO₂ in undoped TiO₂ and various %wt Cr-doped TiO₂ calculated using Rietveld method

| Samples | Phase (%) | | | | | R_p (%) | R_{wp} (%) | R_{exp} (%) | GoF |
|-----------------------------------|-----------|--------|----------|------------------|----------------------|--------------|-----------------|------------------|------|
| | Anatase | Rutile | Brookite | CrO ₂ | TiO ₂ -II | | | | |
| Undoped TiO ₂ | 49.58 | 38.39 | 12.03 | - | - | 7.02 | 9.06 | 8.37 | 1.08 |
| 1.1 %wt Cr-doped TiO ₂ | 88.45 | 11.50 | - | - | - | 7.53 | 9.72 | 9.43 | 1.03 |
| 3.9 %wt Cr-doped TiO ₂ | 100.00 | - | - | - | - | 7.84 | 10.30 | 8.69 | 1.18 |
| 4.4 %wt Cr-doped TiO ₂ | 100.00 | - | - | - | - | 8.20 | 11.10 | 8.88 | 1.25 |

**Fig 11.** Cell volume of anatase at various %wt Cr atom of Cr-doped TiO₂

The weight percentages of the phases were calculated by using the Rietveld method with the Fullprof software. Quantitative phase analysis obtained by Rietveld analysis by eq. (5). By the Rietveld refinement, the undoped TiO₂ shows the following phase compositions: anatase (49.58%), rutile (38.39%) and brookite (12.03%), while in the 1.1.%wt Cr-doped TiO₂, its phase composition are anatase (88.45%) and rutile (11.50%). In the 3.9 %wt Cr-doped TiO₂ and 4.4 %wt Cr-doped TiO₂ respectively consist of 100% of anatase phase, while rutile, chromium dioxide and TiO₂-II phases can't be refined by Rietveld analysis. According to these results and the quality of the agreement between observed and calculated profiles, it can be saw that the handling of Table 4.

CONCLUSION

Undoped TiO₂ and 1.1, 3.9, 4.4 %wt Cr-doped TiO₂ have been successfully analyzed from powder x-ray diffraction data by qualitative and quantitative analysis using various method. Qualitative analysis was carried out with the identification of a phase or phases in the samples by comparison with "standard" patterns: COD and ICDD. In the undoped TiO₂, three titania phases: anatase, rutile, and brookite were obtained. In the 1.1 %wt Cr-doped TiO₂ is detected presenting two phases of TiO₂: anatase (major) and rutile (minor), while anatase (major), rutile (minor), chromium oxide (minor) and TiO₂-II (minor) present in the 3.9 %wt Cr-doped TiO₂ and the

4.4 %wt Cr-doped TiO₂. The quantitative phase analysis was calculated by comparing two methods: reference intensity ratio (RIR) and whole-pattern fitting (Rietveld analysis). The phase content of all samples calculated by RIR method are showed that the undoped TiO₂ consist of anatase (52.2%), rutile (25.1%) and brookite (22.7%) phases, while in the 1.1.%wt Cr-doped TiO₂ present anatase (87.0%) and rutile (13.0%). In the 3.9 %wt Cr-doped TiO₂ are detected anatase (91.0%), rutile (2.8%), CrO₂ (2.7%), and TiO₂-II (3.3%), while in the 4.4 %wt Cr-doped TiO₂ have contents anatase (96.0%), rutile (2.2%), CrO₂ (1.4%), and TiO₂-II (0.4%). The Rietveld refinement method was applied to extract structural parameters of undoped TiO₂ and a series of various %wt Cr-doped TiO₂ using the Fullprof program. The undoped TiO₂ consist of anatase (49.58%), rutile (38.39%) and brookite (12.03%), while in the 1.1 %wt Cr-doped TiO₂ present anatase (88.45%) and rutile (11.50%) phases. In the 3.9 %wt Cr-doped TiO₂ and in the 4.4 %wt Cr-doped TiO₂ respectively consist of 100% of anatase phase, while chromium dioxide and TiO₂-II phases can't be detected by Rietveld refinements. The undoped TiO₂ was refined in the crystal system and space group of anatase (tetragonal, $I4_1/amd$), rutile (tetragonal, $P4_2/mnm$) and brookite (orthorhombic, $Pbca$), while the 1.1.%wt Cr-doped TiO₂ was refined in the crystal system and space group of anatase (tetragonal, $I4_1/amd$), rutile (tetragonal, $P4_2/mnm$).

ACKNOWLEDGEMENT

This research was financially supported by a PUPPT₃₀(Penelitian Unggulan Perguruan Tinggi) Grant from Directorate General of Higher Education - Ministry of Education and Culture of the Republic of Indonesia No. 230/UPT-BOPTN/UN34.21/2014.

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