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Physicochemical properties of pseudobrookite Fe_2TiO_5 synthesized from ilmenite ore by co-precipitation route

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Abstract: Pseudobrookite (Fe_2TiO_5) is a semiconductor with numerous potential applications. Low-grade ilmenite ore has been used as an inexpensive source of Fe and Ti for preparation of Pseudobrookite. Ilmenite was first leached with 20% hydrochloric acid for 3 h at 70°C. Co-precipitation of soluble Fe and Ti from the rich filtrate was carried out at $\text{pH} \geq 9.1$ followed by calcination at different temperatures (900-1300°C) for 2 h. X-ray diffraction patterns (XRD) showed that a single-phase nanocrystalline pseudobrookite powder was produced. The pH was a critical parameter for the evolution of formation the different sizes, structural morphology, and the magnetic properties of the product. Scanning electron microscope (SEM) images showed that particles synthesized at pH 11.2 contained more agglomerations and were more porous than those synthesized at pH 9.1. As the calcination temperature increases, the Fe_2TiO_5 changes from a small rod-like structure to an elongated rod-like structure, and finally to interconnected aggregated crystals. The magnetization of the synthesized Fe_2TiO_5 was measured using a vibrating sample magnetometer (VSM) and was found steadily increase with increasing calcination temperature from 1000 (≈ 9 emu/g) to 1300°C (16 emu/g). Such a large saturation of magnetization might be due to the high phase purity and well-defined crystallinity of Fe_2TiO_5 .

Keywords: ilmenite ore, pseudobrookite, Co-precipitation, nanocrystalline, magnetic properties

1. Introduction

Titanium-substituted iron oxides are widespread and represent an important mineral resource for the commercial extraction of both iron and titanium. Pseudobrookite is an iron titanium oxide mineral with the formula Fe_2TiO_5 , occurring in small brown or black orthorhombic crystals. While it is not a commonly occurring mineral, pseudobrookite is of both commercial and scientific interests. Pseudobrookite is produced in substantial quantities during the processing of ilmenite ores as a by-product of iron and titanium extraction (Borowiec et al., 2003).

Synthesized Fe_2TiO_5 is a semiconductor material and has many potential applications. It has a narrow band gap of ~ 2.18 eV, so it was studied as a photo catalyst for utilizing visible light (Ginley and Butler, 1977; Kozuka and Kajimura, 2001) and it has been widely studied for its interesting catalytic properties (Li et al., 2015; Tasdemir et al., 2015). Fe_2TiO_5 had also drawn attention because of its unique magnetic properties, anisotropic spin glass behavior at low temperature, electrical properties (Atzmony et al., 1979; Singh et al., 1995; Min et al., 2012), electronics and gas sensing applications (Yu et al., 2010; Djuric et al., 2014), and its usefulness in fuel cells (Hooshyari et al., 2014; Shabanikia et al., 2015) and proton exchange membranes (Beydaghi et al., 2016), among many other applications. Fe_2TiO_5 has been used in ceramic pigments due to its thermal stability and nice dispersity in glazes (Mesíková et al., 2006; Dondi et al., 2007). Fe_2TiO_5 is a prototype of a series of materials, which have similar crystal structures, such as Al_2TiO_5 , FeTi_2O_5 , MgTi_2O_5 , Ti_3O_5 and $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Ti}_2\text{O}_5$ (Tilloca, 1991). Although most researchers

consider Fe_2TiO_5 has an orthorhombic structure (Guo et al., 1999), others have argued that they have synthesized Fe_2TiO_5 as monoclinic (Drofenik et al., 1981; Shiojiri et al., 1984; Gennari et al., 1998). The crystal structure of Fe_2TiO_5 significantly affects its properties (Hanžel et al., 1981; Gao et al., 2015).

Ilmenite (FeTiO_3) is a major source of titanium minerals and is found in excessive amounts in the Eastern part of Egypt. Ilmenite ore is commonly used as raw material for production of titanium dioxide by the complicated sulfuric acid process. We have previously developed methods for acid leaching of Egyptian ilmenite ore for preparation of titanium dioxide using simple hydrochloric acid process (Mahmoud et al., 2004; Abdel-Aal et al., 2010; Mostafa et al., 2013). Controlled leaching of ilmenite in hydrochloric acid at mild conditions produced a solution rich in iron and titanium, without hydrolysis. This solution can be utilized as an inexpensive source of titanium and iron and is suitable for synthesis of materials containing both metals for advanced applications. Pure Ti solution was successfully separated from ilmenite leachant and used for the preparation of nano TiO_2 in a controlled crystal form. We have investigated loading of the prepared TiO_2 with platinum metals and applied these nanopowders as advanced catalysts for degradation of organic and inorganic pollutants (Mahmoud et al., 2012). Our group also succeeded in precipitation of zero-valent iron on the synthesized TiO_2 , which could be used to remove nitrate from water (Mahmoud et al., 2016). We did not find in literature any research work for preparation of Fe_2TiO_5 based on such kind of cheap and readily available source of titanium and iron such as ilmenite.

At elevated temperatures, a solid-solid reaction between Fe_2O_3 and TiO_2 forms the Fe_2TiO_5 phase, where large grains or aggregates were obtained (Madare and Salvi, 2005). We have successfully prepared pure Fe_2TiO_5 by the oxalate precursor technique after calcination at 1000°C (Aljuraide et al., 2011). This technique depends on mixing pure chemical compounds of TiO_2 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with an oxalic acid solution, followed by drying and subsequent calcination.

The co-precipitation technique is known to be more efficient for producing nano-materials of unique properties, avoiding the high temperature and limited properties of the traditional techniques (Lu et al. 2007). Moreover, the pH of co-precipitation is a controlling factor in physicochemical properties of synthesized nanomaterials. Increasing the pH from 10 to 11.5 increased the formation and magnetic properties of strontium hexaferrite, $\text{SrFe}_{12}\text{O}_{19}$, prepared by the co-precipitation method (Hessien et al., 2008).

This work aims to utilize inexpensive, readily-available materials, such as ilmenite ore, as a source of titanium and iron for preparation of advanced- magnetic pseudobrookite by the co-precipitation technique. The leaching solution of ilmenite will contain iron and titanium in a soluble and homogeneous form. Co-precipitation of Fe and Ti will produce homogenous material that would be suitable for preparation of the targeted Fe_2TiO_5 at an expected low temperature, shorter calcination time, and with unique crystal size, morphology, and magnetic properties. The effect of pH (9.1-11.2) on formation and structure of the formed pseudobrookite was studied. The crystal structure and magnetization were found to be sensitive to the calcination temperature.

2. Materials and methods

2.1. Materials

All chemicals used in this work (hydrochloric acid HCl, 37%, nitric acid HNO_3 , 65%, sodium hydroxide NaOH 99.8%, ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.99%) were of analytical grade. Double distilled water was used throughout. Ilmenite ore was obtained from the Abu Ghalaga region, Red Sea, Egypt. Chemical analysis of Fe ions was carried out in aqueous solutions using an Inductively Coupled Plasma Optically Emission Spectrometer (ICP-OES, Perkin Elmer, Optima 2000DV). Titanium was determined spectrophotometrically by the hydrogen peroxide method at a wavelength of 410 nm (Vogel, and Mendham, 2000). The chemical composition of the ilmenite ore is shown in Table 1.

2.2. Preparation of pseudobrookite by co-precipitation method

Fig. 1 shows a schematic diagram of the applied synthesis method of pseudobrookite. A representative sample of 10 kg ilmenite ore was thoroughly mixed, crushed, ground until 100% particles of the sample was not larger than $75 \mu\text{m}$, and used for the preparation of iron and titanium solutions. Acid leaching of

ilmenite ore was carried out using a 500 cm³ Pyrex three-necked glass reactor, including a reflux condenser, a mechanical agitator, and a thermometer. Hydrochloric acid (200 cm³, 20% v/v) was heated to 70°C in the reactor using a thermostatically controlled glycerol/water bath. Then, 20g of ilmenite ore was added, and the mixture was stirred at 400 rpm for 3 h at 70°C. The slurry was filtered off, and the separated un-dissolved solids were thoroughly washed with 20 cm³ of 3% HCl, and the wash liquor was mixed with the first filtrate. The produced ilmenite leachant was found to contain 21 g/l Ti and 36.4 g/l Fe. The leachant was diluted with 50 cm³ distilled water, then, 20 cm³ of concentrated nitric acid was added, and the solution was boiled for 15 min to enhance the oxidation of Fe²⁺ to Fe³⁺. After determining the iron and titanium contents, the calculated amount of ferric chloride (2.513g) was added to this solution to achieve the Fe:Ti stoichiometric ratio of 2:1, as of the Fe₂TiO₅ form. In subsequent procedures, iron and titanium were simultaneously precipitated from the ilmenite leachant at alkaline pH values to form the targeted composite material of both metals. The residual acid in the leach liquor was first neutralized by adding 5 M NaOH, and the pH was then adjusted to values of 9.1 and of 11.6 for subsequent experiments. These pH values were selected to ensure that all Fe²⁺, Fe³⁺ and Ti⁴⁺ were completely precipitated. The precipitated solids were then separated by filtration under vacuum, washed with distilled water and then with acetone, and dried at 110°C for 36 h. The dried precursors were calcined to the required temperatures (ranging from 900 to 1300°C) in a muffle furnace for 2h in a static air atmosphere and then cooled gradually to room temperature. These calcined solids were crushed gently with a spatula and kept in plastic bags for characterization.

Table 1. The chemical composition of ilmenite ore

Component	Wt%
TiO ₂	41.95
Fe (total)	37.68
FeO	37.71
Fe ₂ O ₃	11.92
SiO ₂	2.18
CaO	0.06
MgO	0.83
Al ₂ O ₃	1.07
MnO	0.27
V ₂ O ₅	0.025

2.3. Characterization of obtained materials

The crystalline phases present in the different calcined samples were identified by X-ray diffraction (XRD) using a Bruker axis D8 diffractometer using Cu-K α ($\lambda = 1.5406$) radiation and a secondary monochromator in the 2 θ range, from 10 to 80°. The morphologies of the synthesized particles were observed using a scanning electron microscope (SEM, JSM-5400). The magnetic properties of the synthesized materials were measured at room temperature using a vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) in a maximum applied field of 7 kOe. From the obtained hysteresis loops, the saturation magnetization (M_s), remanence magnetization (M_r), and coercivity (H_c) were determined.

3. Results and discussion

Ilmenite ore, a cheap, available source of iron and titanium, was used for the preparation of pseudobrookite. Dissolution of ilmenite at mild conditions (70°C, 20% HCl for 3 h) gave a valuable starting mixture of Fe and Ti in solution. The Fe content in this solution is usually less than the required 2:1 stoichiometry of Fe:Ti in the targeted material (Fe₂TiO₅). Thus, a corresponding amount of ferric chloride was calculated and added to the solution to reach the required stoichiometric ratio. Co-precipitation of Fe and Ti was then done raising the pH of the solution to the alkaline region (pH 9.1 and 11.2).

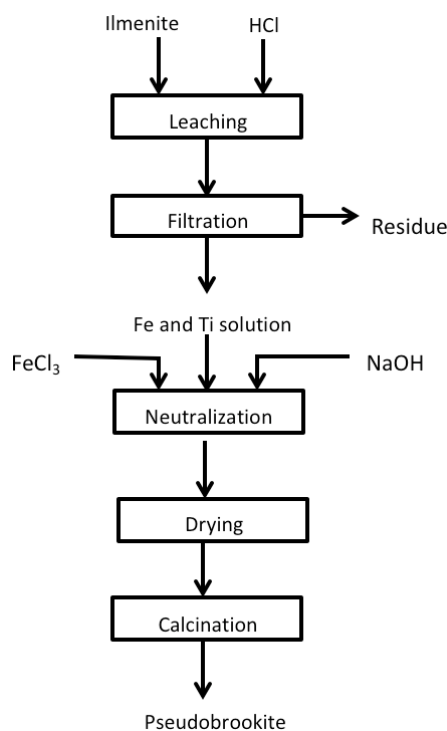


Fig. 1. Schematic diagram of synthesis method of pseudobrookite Fe_2TiO_5

3.1. X-ray diffraction investigation

The XRD patterns of the obtained materials, calcined at temperatures ranging from 900 to 1300°C for 2h, are shown in Figs. 2 and 3. Investigation of these charts shows that the co-precipitation at pH 9.1 and subsequent calcination at 900°C produces an impure material composed of a mixture of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS No. 89-0599) and orthorhombic pseudobrookite Fe_2TiO_5 (JCPDS No. 41-1432) phases. The crystallization of the pseudobrookite phase (* marked peaks) began along with traces of the hematite phase (+ marked peaks). The diffraction peaks at 2θ values of 18.16°, 25.52°, 32.56°, 36.5°, 37.2° and 46.1° corresponded to the strongest diffraction planes (020), (110), (023) (130), (113) and (043). These patterns ascribed to orthorhombic pseudobrookite Fe_2TiO_5 phase. Moreover, the diffraction planes (104), (110), (116), (024) and (012) at 2θ values of 33.17°, 35.66°, 54.06°, 49.46° and 24.14° reflected the presence of $\alpha\text{-Fe}_2\text{O}_3$ phase.

Calcination at temperatures higher than 900°C enhanced the interaction between the iron and titanium phases. This was observed through the decrease in intensity of the hematite phase and increase in the intensity of pseudobrookite phases as the temperature was increased from 900°C to 1000°C. Almost pure peaks of the pseudobrookite phase were obtained after calcination at temperatures higher than 1000°C (1100, 1200, and 1300°C. At these temperatures, the nanocrystalline powder displayed sharp and intense peaks, indicating a fine, crystalline, orthorhombic Fe_2TiO_5 phase. These findings indicate that a single-phase of pure nanocrystalline pseudobrookite powder can be synthesized using the co-precipitation route. Fig. 3 shows that co-precipitation at a higher pH value, such as 11.2, favored the formation of pseudobrookite. This can be easily recognized by comparing the major peaks of Fe_2TiO_5 and minor peaks of Fe_2O_3 at a lower calcination temperature, such as 1000°C, with the corresponding peaks at the lower pH value of 9.1. At pH 11.2, a single phase of Fe_2TiO_5 was obtained at calcination temperatures greater than 1000°C, indicating the formation of an almost pure pseudobrookite structure. The high intensity and sharp peaks of the XRD patterns suggest that calcination at 1100°C is suitable for synthesis of the highly crystalline pseudobrookite Fe_2TiO_5 single phase from the co-precipitated iron and titanium composite material at the studied pH range (9.1–11.2).

The obtained XRD results of this work, utilizing natural inexpensive ilmenite ore, are in agreement with a previous work carried out via oxalate precursor route using pure chemicals. In addition, single

phase Fe_2TiO_5 was obtained at 1100 °C compared with at 1200 °C using the oxalate precursor route (Aljuraide et al., 2011).

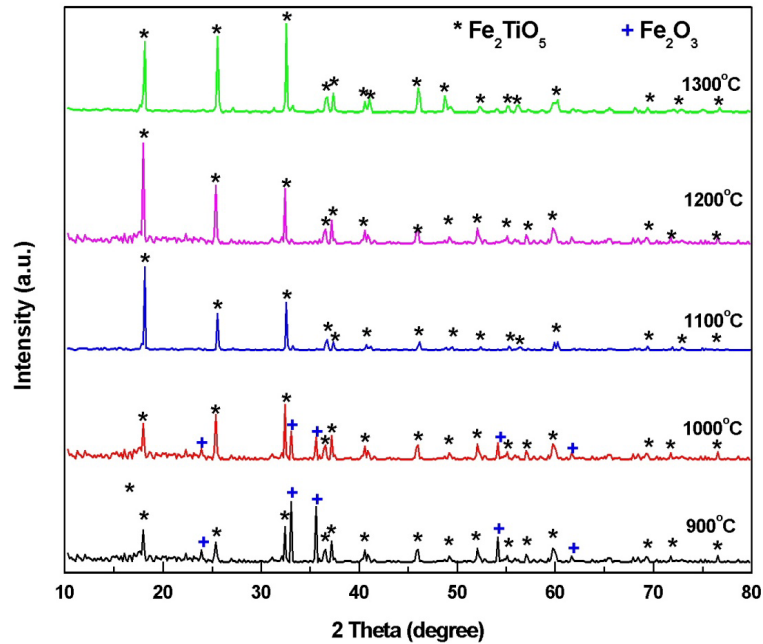


Fig. 2. XRD patterns of the produced Fe_2TiO_5 at pH 9.1

The effect of annealing temperature (1000 – 1300 °C) and co-precipitation pH (9.1 and 11.2) on the crystallite size of the produced Fe_2TiO_5 pseudobrookite phase for the most intense peak (023) was determined from X-ray diffraction data using Debye–Scherrer (Table 2). As expected, the crystallite size of Fe_2TiO_5 increased by increasing annealing temperature. The crystallite size of the sample prepared at pH 9.1 and annealing temperature 1000 °C was about 80.5 nm. This value increased to about 165.6 by increasing the temperature to 1300 °C. The same phenomena was also observed at a higher preparation pH such as at pH 11.2. The average crystallite size varied from about 100.2 to 170.7 nm with the annealing temperature from 1000 to 1300 °C. It can be concluded from these data that both the pH and annealing temperature have increasing effect on the crystallite size.

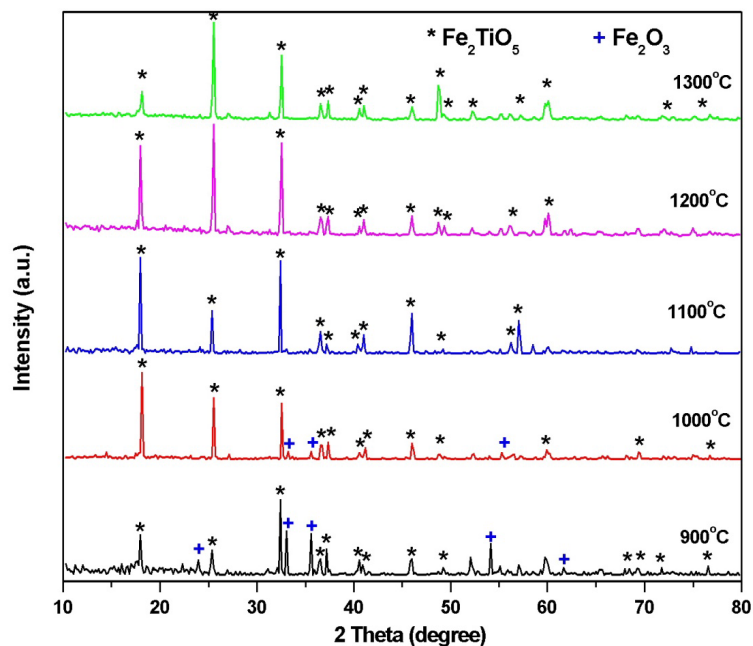


Fig. 3. XRD patterns of the produced Fe_2TiO_5 at pH 11.2

Table 2. Crystallite size of synthesized nanocrystalline Fe₂TiO₅ by co-precipitation technique at different annealing temperatures and pH values

Annealing Temperature, °C	Crystallite Size, nm	
	pH 9.1	pH 11.2
1000	80.5	100.2
1100	105.3	120.8
1200	140.1	150.9
1300	165.6	170.7

3.2. Scanning electron microscope investigation

Morphology of powders obtained by co-precipitated at pH 9.1, and calcined at 1000–1300°C, was examined by SEM (Fig. 4a–h). It can be seen that the calcination temperature has an obvious effect on the morphology of the produced Fe₂TiO₅. We found that, as the calcination temperature increased, the morphology of the produced sample progressively changed from a small rod-like structure to an elongated rod-like structure, and finally to interconnected aggregates crystals. Figs. 4a and 4b display an irregular morphology and non-uniformity formation and agglomerate nature, with diverse morphologies of Fe₂TiO₅ at 1000°C. The particles form rod-like-shaped grains with a single crystalline structure. With further increase in the calcination temperature, the rod-like structures grow rapidly and become much larger than the surrounding grains. A micrograph of powder sample calcined at 1100°C (Fig. 4c and d) exhibits well-structured long rods of Fe₂TiO₅ with various orientations. Moreover, it can be seen that there are few nanoparticles aggregates around the single rods-like crystals. Figs. 4e and 4f show that the Fe₂TiO₅ rod-like structures are shorter and thicker than those at lower calcination temperatures. This might be due to the fusion of particles at the higher temperature (1200°C). We also detected the formation of aggregates of elongated hyperfine structures on the surface of thick rod-like structures at a calcination temperature of 1200°C. It seems that the elongated, hyperfine structures were formed from the aggregation of the nanoparticles that were observed around the single rod-like crystals at 1100°C (Fig. 4c and d). At the calcination temperature of 1300°C (Fig. 4g and h), abnormal grain growth was observed. It seems that some grains are semi-fused into a very large grain, producing grains with a size of several microns. At the calcination temperature of 1300°C, shown in Figs. 4g and 4h, the grain growth rate was high. Pores might be left behind by rapidly moving grain boundaries, resulting in pores that are trapped inside grains (intra-granular pores). The discontinuous growth of grains hindered the migration of pores to the grain boundary.

The SEM morphology of all powders obtained from the precursors precipitated at pH 11.2 and calcined at 1200–1300°C are shown in Figs. 5a–d. These micrographs show that the preparation procedure, at a higher pH of 11.2, has a significant influence on the morphologies of the synthesized products. The particles synthesized at pH 11.2 exhibited more agglomerations and were more porous than the particles synthesized at pH 9.1. We found that Fe₂TiO₅ powder granules were made up of overall crystallite aggregates. Some grains were semi-fused into a very large grain, giving grains of several microns. These abnormal grains resulted in pores that are trapped inside the grains (intra-granular pores).

The present effect of calcination temperature on morphology of Fe₂TiO₅ particles was slightly different when compared with same material synthesised by the oxalate precursor method. In the later, thin strings of joined particles were formed at lower calcination temperature of 900°C and strings became shorter and thicker at higher temperature. The string feature vanishes at 1100°C and a very large increase in the grain size was observed at 1200°C (Aljuraide et al., 2011). In other work, the Fe₂TiO₅ powder prepared through hydrothermal method exhibited a narrow size distribution and sphere-like morphology, with an average diameter of 50– 200 nm (Min et al., 2012).

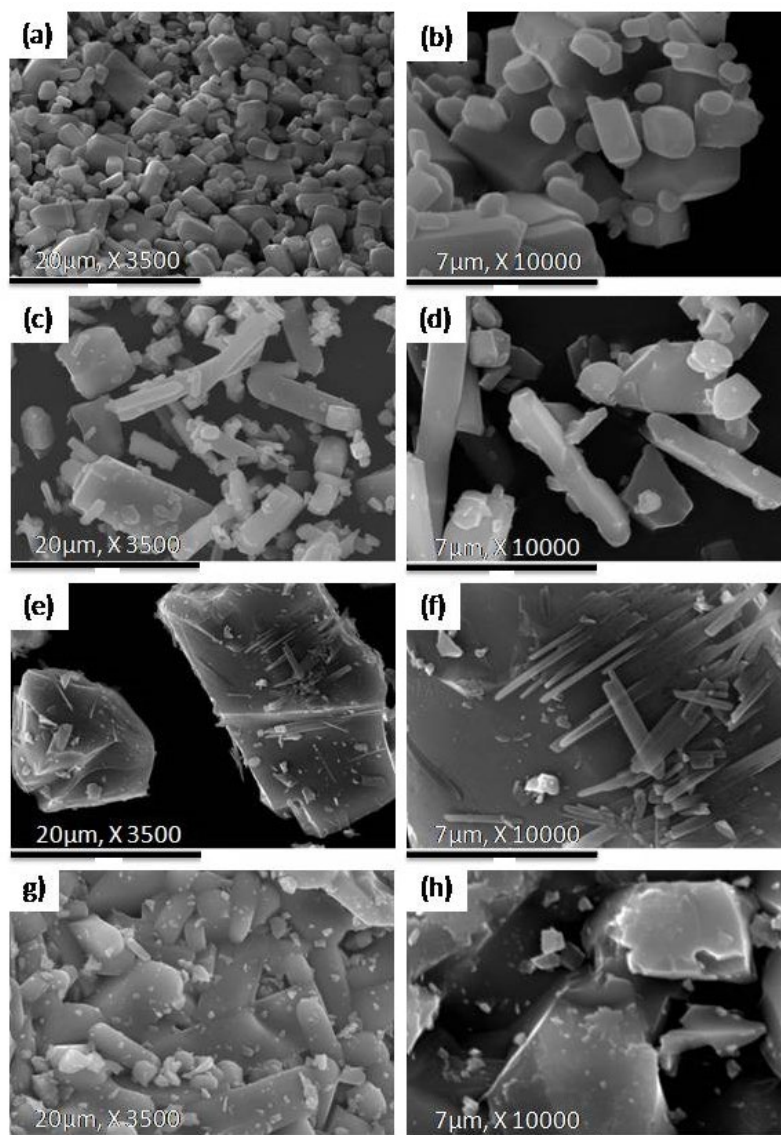


Fig. 4. SEM micrograph of the produced nanocrystalline Fe_2TiO_5 powders from the ilmenite ore at pH 9.1 and calcined at (a, b) 1000 °C, (c, d) 1100 °C, (e, f) 1200 °C, and (g, h) 1300 °C

Crystallite size estimated from XRD analysis (Table 2), were in the nano size range, while, the average particle size observed in the SEM images (Fig. 4,5) were not in the nano size range. It is known that crystallite size is completely different from particle size unless the particle is a single crystal. Particles can be polycrystalline or just one crystallite. In case of only one crystallite, the particle size and crystallite size are the same. During the processing, smaller crystallites come closer and grow to become larger. The agglomeration of particles was related to many factors such as shape factor, surface area, porosity, and density. Therefore, the average particle size was larger than a crystallite size (Hessien, et al., 2015).

3.3. Magnetic properties

Iron titanates are reported as ferrimagnetic materials, but specifically an anti-ferromagnetic ordering with weak ferromagnetism has been predicted for Fe_2TiO_5 (ENHESSARI, et al., 2014). The magnetization of the nanocrystalline Fe_2TiO_5 ferrite powder was performed at room temperature under an applied field of 7000 Oe, and the hysteresis loops of the ferrite powders synthesized by the co-precipitation route were obtained. A plot of magnetization (M) as a function of the applied field (H) for the effect of

calcination temperature (1000–1300°C) for Fe_2TiO_5 ferrite precipitated at pH 9.1 and 11.2 are shown in Fig. 6 and 7, respectively. The hysteresis loops measured at room temperature demonstrate the ferromagnetic-paramagnetic behavior of the Fe_2TiO_5 powders. Iron titanates are reported as ferrimagnetic materials, but specifically, an anti-ferromagnetic ordering with weak ferromagnetism has been predicted for Fe_2TiO_5 . The small magnitude of saturation magnetization (M_s) shows that Fe_2TiO_5 is a weak magnetic system. It is clear that the increase in calcination temperature has a pronounced effect on the magnetic properties for both the two pH values. The magnetization of the Fe_2TiO_5 ferrite was steadily increased with increasing treatment temperature from 1000 (≈ 6 and 9 emu/g) to 1300°C (≈ 15 and 16 emu/g) at pH 9.1 and 11.2, respectively. These values were much higher than those obtained for Fe_2TiO_5 prepared by sol-gel technique and calcined at 900 °C (≈ 0.8 emu/g) (ENHESSARI, et al., 2014). Such a large saturation magnetization for the synthesized ferrite calcined at $\leq 1300^\circ\text{C}$ can be attributed to the high phase purity and well-defined crystallinity of Fe_2TiO_5 , as clearly evidenced from XRD (Fig.2) and SEM (Fig.4). Figs. 8 and 9 show the effect of precipitation pH on the magnetic properties of the co-precipitated specimens at 1200 and 1300°C, respectively. We found that the magnetization decreases with the increase of pH, which might be due to the change in size and shapes of the particles.

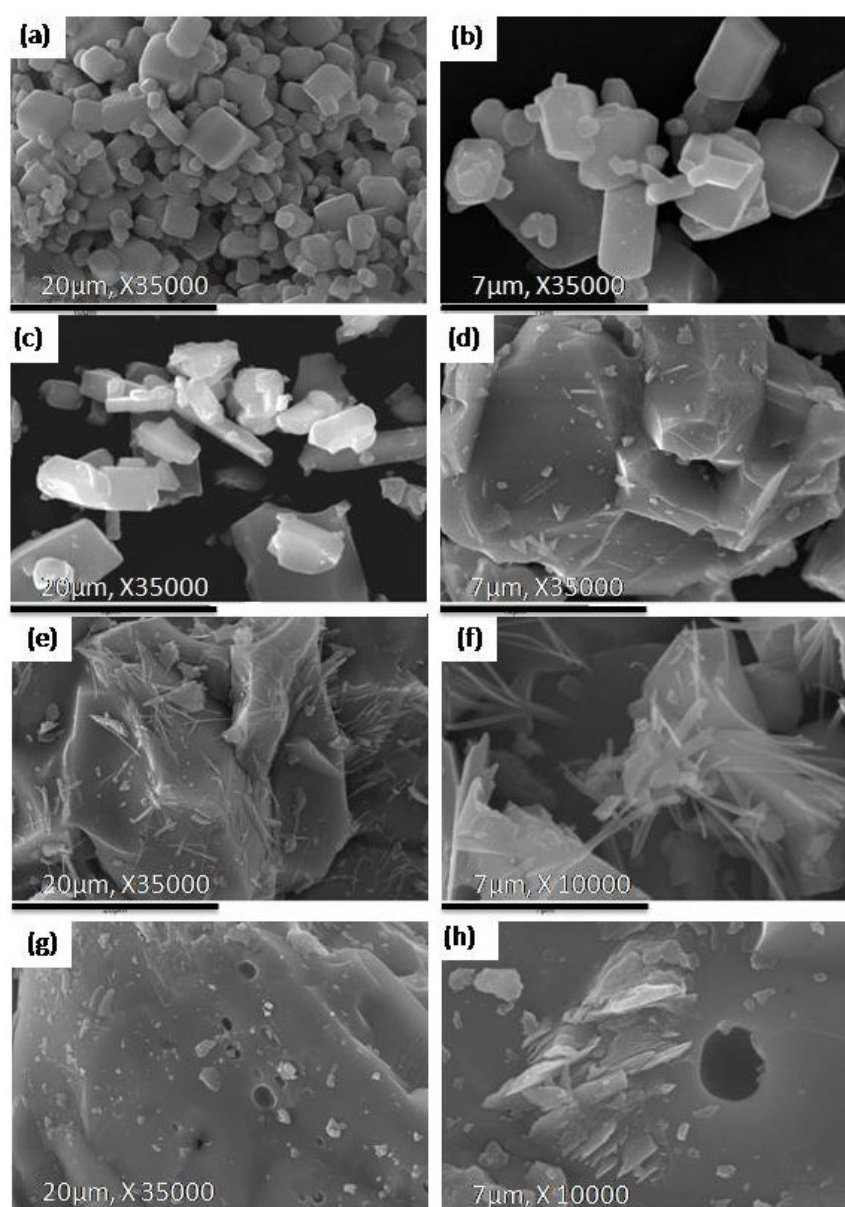


Fig. 5. SEM micrograph of the produced nanocrystalline Fe_2TiO_5 powders from the ilmenite ore at pH 11.2 and calcined at; (a, b) 1000 °C, (c, d) 1100 °C, (e, f) 1200 °C, and (g, h) 1300 °C

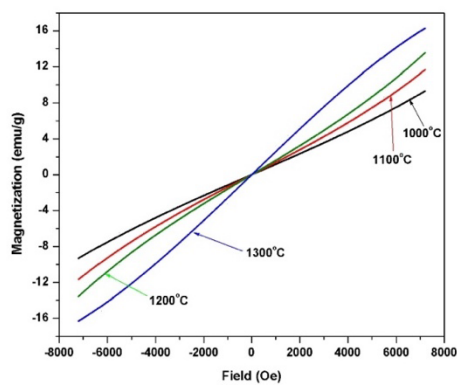


Fig. 6. Effect of calcination temperature on the M-F hysteresis loop of Fe_2TiO_5 synthesized at pH 9.1

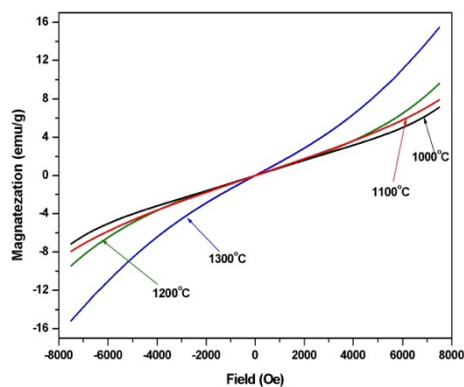


Fig. 7. Effect of calcination temperature on the M-F hysteresis loop of Fe_2TiO_5 synthesized at pH 11.2

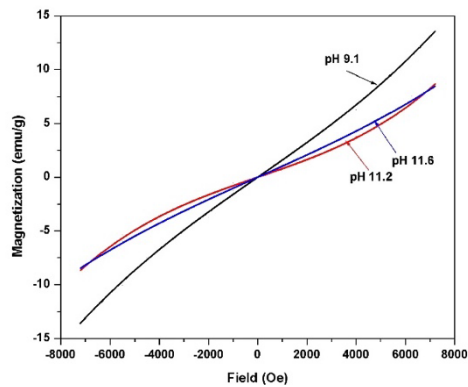


Fig. 8. Effect of precipitation pH on the M-H hysteresis loop of Fe_2TiO_5 synthesized at 1200°C

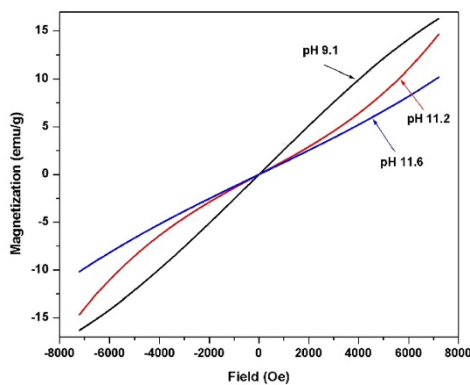


Fig. 9. Effect of precipitation pH on the M-H hysteresis loop of Fe_2TiO_5 synthesized at 1300°C

4. Conclusions

Nanocrystalline pseudobrookite Fe_2TiO_5 powders were synthesized from ilmenite ore, as a cheap natural source of iron and titanium, via a co-precipitation route. The effects of pH and calcination temperature on the physicochemical properties were investigated. A single phase nanocrystalline pseudobrookite Fe_2TiO_5 phase was obtained at a calcination temperature of 1100°C for pH 9.1 and at 1000°C for pH 11.2. Crystallite size ranged from 80 to 165 nm at pH 9.1 and from 100 to 170 nm at pH 11.2. The Fe_2TiO_5 changed from a small to an elongated rod-like structure, and finally to interconnected aggregates as the calcination temperature increased. At 1300°C , an abnormal grain growth with inter-granular pores was observed. Particles synthesized at pH 11.2 exhibit more agglomerations and have a more porous morphology. Magnetization was found to steadily increase with increasing calcination temperature from 1000 (≈ 9 emu/g) to 1300°C (16 emu/g).

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