1. Introduction

Lepidocrocite-like titanates have the general chemical formula $A_xTi_{2-y}M_yO_4$, and consist of two-dimensional layers of edge and corner-shared TiO$_4$ octahedra with interlayer alkali ions (A), usually with some interlayer water. Due to the substitution of lower-valence metal atoms or vacancies (M) in Ti sites, the layers have a negative charge compensated by the interlayer cations. The synthesis and characterization of several isomorphous lepidocrocite-like titanates have been reported with different combinations of M and A, where M can be Li, Mg, Zn, Cu, Co, Ni, Fe or a vacancy and A can be Cs, Rb, K, Na or Li [1-7]. Some examples are $H_xTi_{2-x/4}FexO_4 \cdot nH_2O$ (where $\square$ = vacancy) [1], $K_{x}Ti_{2-x/3}Li_{x/3}O_4$ [2] and $H_{x}Ti_{2-x}FeO_4 \cdot nH_2O$ [3].

This material can exfoliate layers into colloidal single sheets with subnanometer thickness by intercalation of bulky species such as tetrabutylammonium [8]. These nanosheets can be used as building blocks in the assembly of nanarchitectures with controllable functionalities [9]. Titania nanosheets have attracted special attention because of their potential photocatalysis [10,11], photoconductivity [12] and photoluminescence [13-15]. Possible application in spin-electronic devices has motivated investigation of TiO$_2$ nanosheet-based ferromagnets (Ti$_{1-x}Co_xO_2$, Ti$_{1-x}Fe_xO_2$, Ti$_{1-x}Mn_xO_2$, Ti$_{0.5-x}Fe_{x/2}Co_{0.2-x/4}O_2$) [16-19].

All reported syntheses of lepidocrocite-like titanates used solid state reactions. Here we present a new method to produce $Na_{x-y}H_yTi_{2-x}Fe_xO_4 \cdot nH_2O$ lepidocrocite-like layered nanosheets by hydrothermal treatment of ilmenite sand. This synthesis is simple and energetically advantageous compared to solid state reactions as it requires very little heat (130°C). Moreover, the use of ilmenite sand, a very low cost precursor, makes it even more cost effective.
by acid exchange. Thus, \( \text{Na}_{x-y}\text{H}_y\text{Ti}_{2-x}\text{Fe}_x\text{O}_4\cdot n\text{H}_2\text{O} \) with a lepidocrocite-like layered structure might be modified to match its physical properties to an application.

In the present work the crystal structure, morphology and optical properties of \( \text{Na}_{x-y}\text{H}_y\text{Ti}_{2-x}\text{Fe}_x\text{O}_4\cdot n\text{H}_2\text{O} \) nanosheets with lepidocrocite-like layered structure hydrothermally synthesized from ilmenite sand were investigated by X-Ray diffraction, transmission electron microscopy and UV-Vis spectroscopy.

### 2. Experimental Procedure

Untreated ilmenite sand from a Brazilian mine was used as a new low cost precursor (~$80 US ton\(^{-1}\)). It was ball milled for 90 min in a SPEX 8000-115 Mixer Mill with a 20:1 ball to ilmenite mass ratio, resulting in a mean particle size of 0.25 µm. In a typical synthesis 0.5 g of ball milled natural ilmenite sand was mixed with 25 mL of 10 M NaOH, transferred to a 30 mL Teflon-lined autoclave (83.3% filling factor) and held at 130°C for 70 h with continuous stirring. The resulting brown powder was dispersed in 200 mL of distilled water, mixed, and filtered. The powder was water washed (up to pH~7) and dried at 80°C for 5 h.

X-ray powder diffraction (XRPD) of precursor and product were performed on a RigakuXRD-6000 powder diffractometer with CuKα radiation at 40 kV and 35 mA. LeBail analyses of XRPD patterns were carried out using Topas Academic software. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) patterns and X-ray energy dispersive Spectrometry (EDS) were carried out in a JEOL-2010 microscope operating at 200 kV and in a Titan 80-300 microscope at 300 kV. TEM specimens were prepared by ultrasonic dispersion of the powder in alcohol, then dropping onto a holey carbon film supported by a copper grid. Product compositions were determined by TEM/EDS. Scanning electron microscopy and EDS (SEM/EDS) were performed using a Zeiss DSM 960. Semi-quantitative X-Ray fluorescence (XRF) analysis (Software SemiQ PW2452) was performed in a Philips/Analytical PW2400 with a Rh-based ceramic tube at 3 kV. UV–Vis absorption spectra, analyzed in transmission mode, of the product suspension in water were obtained on an Agilent 8453 UV-vis spectrophotometer after 30 min of ultrasonication.

### 3. Results and Discussion

X-ray diffraction (XRD) of the ilmenite sand precursor, Fig. 1, shows that it consists of ilmenite as the principal crystal phase; however, pseudorutile, rutile and quartz are also present. X-Ray fluorescence (Table 1) and SEM/EDS (Fig. 2) also show that natural ilmenite sand is not homogeneous, having different impurity elements and phases. However, Fig. 2b (EDS) is consistent with Fig. 1, showing that ilmenite (gray phase in the backscatter image, Fig. 2a) is the principal phase in the sand.

LeBail refinement of the product XRD pattern (Fig. 3) clearly identified three Lepidocrocite-like titanates (space group: Imm2) with similar \( a \) and \( c \) lattice parameters but different interlayer distances (\( b/2 \)), as well as a small amount of hematite nanoparticles (Table 2). The values obtained for \( a \) (~3.8 Å) and \( c \) (~3.0 Å) are similar to those reported by Reid et al. [4]: \( a = 3.805 \) Å and \( c = 2.972 \) Å, for \( \text{Cs}_x\text{Ti}_{2-x}\text{Fe}_x\text{O}_4 \). EDS analysis (Fig. 4a) demonstrated the presence of Na, Fe, Ti and O. Because the samples were prepared in an aqueous environment and subsequently washed, partial ionic exchange of the interlayer cations (Na\(^+\) by H\(^+\)) is plausible, suggesting that the product should be \( \text{Na}_{x-y}\text{H}_y\text{Ti}_{2-x}\text{Fe}_x\text{O}_4\cdot n\text{H}_2\text{O} \). Therefore, the \( a \) and \( c \) lattice parameters (mostly dependent on the layer composition) should be similar to \( a \) and \( c \) for \( \text{Cs}_x\text{Ti}_{2-x}\text{Fe}_x\text{O}_4 \). However, the interlayer distance (\( b/2 \)) depends on the interlayer cation size and proportion (\( x \)) as well as the amount of interlayer water (\( n \)). Sasaki et al. [1] reported that interlayer distances in \( \text{Na}_x\text{Ti}_{2-x/4}\text{O}_4\cdot n\text{H}_2\text{O} \) depend on

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**Table 1.** Semi-quantitative chemical analysis of natural Brasilian ilmenite sand.

| Element     | wt%  |
|-------------|------|
| \( \text{SiO}_2 \) | 1.74 |
| \( \text{TiO}_2 \) | 55.7 |
| \( \text{Fe}_2\text{O}_3 \) | 38.7 |
| \( \text{ZrO}_2 \) | 0.20 |
| \( \text{Nb}_2\text{O}_5 \) | 0.13 |
| MnO         | 1.53 |
| \( \text{Al}_2\text{O}_3 \) | 1.80 |
Na proportion (8.9 Å for x = 0.7 and 11.5 Å for x > 0.7). These values agree with two of the interlayer distances obtained for Nax-yHyTi2-xFexO4•nH2O reported here (Table 2). The three interlayer distances obtained are due to inhomogeneous cation exchange (Na⁺ for H⁺) during washing resulting in particles with different proportions (x) of Na. Sasaki et al. [1] suggested that the phases with lower Na content and interlayer distance of ~9 Å are due to monolayers of cations and H₂O molecules in the galleries, while phases with higher Na content are likely to have a bilayer water/cation cluster, increasing the interlayer distance (b/2).

TEM analyses (Figs. 4-6) show leaf-like nanosheet morphology with thickness less than 30 nm and lengths below 1 µm. The TEM image in Fig. 4b shows both top views (beam perpendicular to the layers, parallel to [010]) and cross section views (beam parallel to the layers, perpendicular to [010]) of the nanosheets allowing thickness and length measurements. From Fig. 4c (HREM image of a nanosheet cross section) it was possible to measure the interlayer distance (b/2).

The measured value, 7 Å, is well below the three values obtained from the XRD measurements. This can be explained by dehydration inside the TEM from the vacuum and heating by the beam. Sasaki et al. [1] reported interlayer contraction from 9.37 Å to 6.6 Å for HxTi2-x/4O4•nH2O after dehydration, supporting our explanation. In agreement with the XRD results, hematite nanoparticles were also present, identified by the increased EDS Fe peak (Fig. 5a) and HREM lattice fringes spaced at 2.7 Å corresponding to hematite (104) planes (Fig. 5b).

Table 2. LeBail refinement results.

| phase | Lepidocrocite-like titanate - 1 | Lepidocrocite-like titanate - 2 | Lepidocrocite-like titanate - 3 | Hematite Fe₂O₃ |
|-------|---------------------------------|---------------------------------|---------------------------------|---------------|
| Space group | Imm2                           | Imm2                           | Imm2                           | R-3cH         |
| a (Å)  | 3.751                          | 3.779                          | 3.847                          | 5.057         |
| b (Å)  | 17.8                           | 19.8                           | 22.274                         | -             |
| c (Å)  | 2.983                          | 3.054                          | 3.079                          | 13.943        |
| Interlayer distance (b/2) | 8.9                            | 9.9                            | 11.37                          | -             |

r_exp = 7.036, r_exp_dash = 12.044, r_wp = 9.163, r_wp_dash = 15.686, r_p = 7.031, r_p_dash = 13.517, weighted_Durbin_Watson = 1.287, gof = 1.302.
As most of the nanosheets fell on the grid with [010] parallel to the beam the selected area diffractions patterns show a crystallographic texture, where the rings correspond to \((h0l)\) or \((h1l)\) planes. From the \(a\) and \(c\) parameters and the \(b\) value of \(\sim 14\ \text{Å}\), the interplanar distances between different crystallographic planes \((hkl)\) were calculated to index the SADP (Fig. 6) acquired on the lepidocrocite-like product. The results agree with those reported by Sasaki et al. [20] for \(\text{H}_x\text{Ti}_{2-x/4}\text{O}_4\cdot n\text{H}_2\text{O}\) exfoliated nanosheets.

It is well established that hydrothermal synthesis of layered titanates proceed by dissolution-precipitation [21]. The first step is ilmenite dissolution:

\[
\text{FeTiO}_3 + \text{NaOH} \rightarrow \text{Fe}^{2+} + \text{TiO}_3^{2-} + \text{Na}^+ + \text{OH}^-
\]

The oxidation state of Fe was assumed to be \(2^+\), however, \(\text{Fe}^{3+}\) was present in the product as \(\text{Fe}_2\text{O}_3\) (hematite) nanoparticles. There are two possible explanations. One is the oxidation of \(\text{Fe}^{2+}\) to \(\text{Fe}^{3+}\) during synthesis, while the other recognizes that natural ilmenite may also containing some \(\text{Fe}^{3+}\) accompanied by \(\text{Ti}^{3+}\) [22]. For partial substitution of \(\text{Ti}^{4+}\) by \(\text{Fe}^{3+}\) the formula will be \(\text{Na}_x\text{Ti}_{2-x}\text{Fe}_x\text{O}_4\), and if \(\text{Ti}^{4+}\) is partially substituted by \(\text{Ti}^{3+}\) and \(\text{Fe}^{3+}\) it will be \(\text{Na}_x\text{Ti}_{2-x/2}\text{Fe}_{x/2}\text{O}_4\). On the other hand, if \(\text{Ti}^{4+}\) is substituted by \(\text{Fe}^{3+}\) the formula will be \(\text{Na}_x\text{Ti}_{2-x/2}\text{Fe}_{x/2}\text{O}_4\). As we have no data on the Fe and Ti oxidation states we will assume the formula containing \(\text{Fe}^{3+}\) and \(\text{Ti}^{4+}\), i.e., \(\text{Na}_x\text{Ti}_{2-x/2}\text{Fe}_x\text{O}_4\). Therefore, the second step, crystallization of lepidocrocite-like nanosheets, can be represented by:

\[
x \text{Na}^+ + x \text{Fe}^{3+} + (2-x) \text{TiO}_3^{2-} + z \text{OH}^- \rightarrow \text{Na}_x\text{Ti}_{2-x}\text{Fe}_x\text{O}_4 + w \text{H}_2\text{O} \quad (\text{where } w = 2 + z - 3x)
\]
The third step is the washing with H₂O, where interlayer cation exchange (Na⁺ by H⁺) takes place:

\[
\text{Na}_x\text{Ti}_{2-x}\text{Fe}_x\text{O}_4 + y \text{H}_2\text{O} \rightarrow \text{Na}_{x-y}\text{H}_y\text{Ti}_{2-x}\text{Fe}_x\text{O}_4 + y \text{NaOH}
\]

It is well known that H₂O molecules can be incorporated between TiO₂-based layers [1] resulting in a formula \(\text{Na}_{x-y}\text{H}_y\text{Ti}_{2-x}\text{Fe}_x\text{O}_4 \cdot n\text{H}_2\text{O}\). A feature observed in our previous work [23,24] on nanostructured layered titanates and also by Sasaki et al. [1] for \(\text{Na}_x\text{Ti}_{2/4}\text{O}_4 \cdot n\text{H}_2\text{O}\) is that the amount of interlayer water is proportional to the Na content. As this cation exchange was probably not homogeneous, resulting in three phases with different Na contents, different H₂O contents and interlayer distances resulted. To obtain a single phase (one interlayer distance) we plan longer washing times with aqueous HCl to completely displace Na⁺ from the interlayer galleries by H⁺.

**Figure 5.** (a) EDS spectrum and (b) HREM image of hematite nanoparticles.

**Figure 6.** (a) TEM image of the \(\text{Na}_{x-y}\text{H}_y\text{Ti}_{2-x}\text{Fe}_x\text{O}_4 \cdot n\text{H}_2\text{O}\) nanosheets and (b) corresponding SADP.

**Figure 7.** Optical absorption spectra of colloidal suspension of \(\text{Na}_x\text{H}_y\text{Ti}_{2/4}\text{Fe}_x\text{O}_4 \cdot n\text{H}_2\text{O}\) nanosheets.
Nax-yHyTi2-xFexO4 •nH2O nanosheets with lepidocrocite-like layered structure synthesized by hydrothermal treatment of ilmenite sand

Higher synthesis temperatures yield different products. Between 150°C and 170°C the product contains a mixture of Nax-yHyTi2-xFexO4 •nH2O leaf-like nanosheets, titanate nanobelts of the family A2TixO2x+1 •nH2O (where A is the alkali metal cation often partially or fully exchanged for a proton) free of Fe and hematite nanoparticles. Further temperature increase yields NaxFexTi2-xO4 with the CaFe2O4 crystal structure and arrow-like crystal morphology, as reported elsewhere [25].

To evaluate the optical properties and potential photocatalyst application an aqueous suspension of Nax-yHyFexTi2-xO4 •nH2O nanosheets was analyzed by transmission UV-Vis absorption spectrophotometry (Fig. 7). The 5.11 eV peak is assigned the band gap energy. Sasaki et al. [26] analyzed Ti1-xxO24x- nanosheet crystallites by UV-Vis absorption and obtained a peak at 4.67 eV. They also estimated a band gap energy of 3.24 eV for the parent bulk layered compound H0.7Ti1.8250.175O4•H2O from a diffuse reflectance spectrum using the Kubelka-Munk method. Comparing these two values they attributed the blue shift to size quantization. The band gap (5.11 eV) obtained for NayHx-yFexTi2-xO4 •nH2O nanosheets in the present work is close to the 4.67 eV obtained for Ti1-xxO24x- nanosheet crystallites by Sasaki et al. [26]. This indicates that lepidocrocite-like titanate nanosheets with thickness up to 30 nm (present work) show a significant band gap blue shift compared to bulk layered titanates or anatase (3.18 eV) and rutile (3.03 eV). Fig. 7 also shows a tail out to 600 nm (corresponding to ~2 eV) due to hematite, which has a 2.2 eV band gap [27].

4. Conclusions

Na2xHxFeTi3-xO4•nH2O nanosheets with lepidocrocite-like layered structure were synthesized from ilmenite sand for the first time by alkaline hydrothermal treatment at low temperatures (130°C). This process is energetically advantageous and cost effective compared to a solid state reaction, the most common process used to produce this type of material. TEM showed that the product has a leaf-like nanosheet morphology with thickness below 30 nm and lengths below 1 µm. Three Lepidocrocite-like titanates (Imm2 space group) with similar a and c lattice parameters and different interlayer distance (b/2), as well as a small amount of hematite were identified through LeBail refinement of the product XRPD. The three interlayer distances obtained were attributed to inhomogeneous cation exchange (Na+ for H+) during washing resulting in particles with different proportions (x) of Na. The band gap (5.11 eV) obtained for Na2xHxFeTi3-xO4•nH2O nanosheets in the present work is close to the 4.67 eV obtained for Ti1-xxO24x- nanosheet crystallites by Sasaki et al. [26].

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