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The formation of ilmenite $FeTiO_3$ powders by a novel liquid mix and H_2/H_2O reduction process

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Abstract $FeTiO_3$ powder was prepared via a liquid mix and H_2/H_2O reduction process. First, an intermediate compound was synthesized by a liquid mix process. This precursor compound to $FeTiO_3$ was characterized by thermal analysis (TG/DTA) and Fourier Transform Infrared spectroscopy (FT-IR). Second, the precursor was annealed in the air, $H_2/H_2O(g)$ mixing gas stream, respectively. The obtained powder was characterized by X-ray diffraction (XRD), energy dispersive X-ray analysis spectroscopy (EDAX) and scanning electron microscope (SEM). It was showed that pure and homogenous $FeTiO_3$ was successfully obtained below 600 °C.

Introduction

$FeTiO_3$ is a wideband gap (2.54 eV) anti-ferromagnetic semiconductor, which is of interest due to their potential applications in a large number of novel devices such as radiation immune solar cells, high temperature integrated circuits and high power electronic devices. The appeal in investigating this compound is due to its wide band gap properties. In order to explore the novel magnetic/dielectric properties of this material, some interesting work has been done by Zhou and Fujii [1–4]. The $FeTiO_3$ structure is derived from α-Fe_2O_3 by replacing every other layer of Fe atoms in (001) planes by a layer of Ti atoms, thus producing alternating hexagonally close-packed O layers. The formal valence of metal ions in this structure is given by the formula $Fe^{2+}Ti^{4+}O_3$. Fe^{2+} ($3d^6$) and Ti^{4+} ($3d^0$) cations across the shared face are alternatively located along the *c* axis. FeO_6 and TiO_6 octahedra are respectively located in a plane parallel to (001) and linked with adjacent octahedra with a shared edge. A schematic representation of $FeTiO_3$ structure is showed in Fig. 1.

Natural ilmenite does contain a significant amount of hematite (Fe_2O_3) [5]. It is not easy to prepare ferrous titanate ($FeTiO_3$), one of the major obstacles in the preparation of ferrous titanate is instability of the Fe^{2+} ion. Therefore, there are few reports on synthesis of $FeTiO_3$ powder in the literature. The conventional method of production of pure $FeTiO_3$ is the solid-state reaction under vacuum at temperatures higher than 1200 °C [6–8]. The solid state reaction method is generally based on mixing of fine powders and heating at very high temperature. This method has inherent disadvantages as chemical inhomogeneity, coarse grain size and entrance of impurities during the milling process. In order to get crystalline particles of $FeTiO_3$, wet chemical methods such as hydrothermal synthesis and sol–gel process have been developed [9]. Wet chemical methods are known to be better than the solid state reaction methods for intimate mixing of reactants, high product purity, fine particle size and low processing temperature. In the present study, the feasibility of synthesis of $FeTiO_3$ powder utilizing a liquid mix and H_2/H_2O reduction process was investigated. This route is based on the gelling and subsequent heat treatment the precursor in air, H_2/H_2O atmosphere, and a

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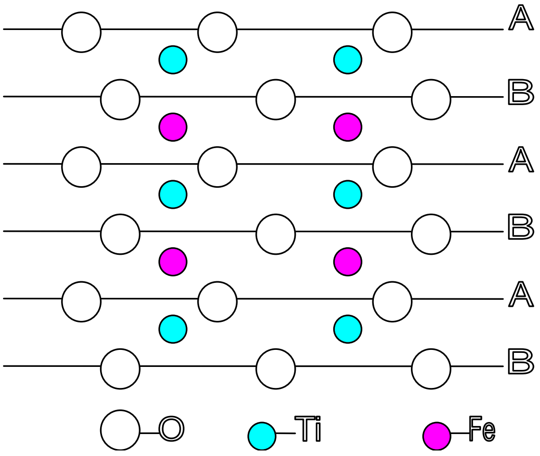

Fig. 1 Simplified model of $FeTiO_3$ structure

detailed experimental process was presented for the preparation of $FeTiO_3$ powder. The main objective was to synthesize ultra-fine $FeTiO_3$ powder. It was expected that the preliminary results could be significantly promoting the development of synthesized ilmenite oxide $FeTiO_3$ materials.

Experimental

In this study, ferrite nitrate, tetrabutyl titanate, anhydrous ethanol, ammonia solution, and acetylacetone were used as the starting chemicals, double distilled water was also used as a solvent. All reagents were of analytical grade, and were used without further purification. In a typical procedure, 0.05 mol of tetrabutyl titanate was first dissolved in 30 mL anhydrous ethanol with acetylacetone under vigorous stir under dry nitrogen for 30 min. Ferrite nitrate (0.05 mol) was dissolved into 15 mL deionized water and 20 mL of anhydrous ethanol. Subsequently, two solutions were mixed under vigorous stir at room temperature (RT) for 3 h to obtain a well dissolved solution. Ammonia solution was slowly added to adjust the pH value of the mixed solution to 6.5. Finally, the solution was evaporated at RT to allow the gel formation and dried at in oven at 100 °C for 24 h. The dried precursor was ground to break up large agglomerates. Based on the thermogravimetric-differential thermal analysis, the dried precursor was calcined in the horizontal quartz tube furnace at 450 °C for 1 h in the flowing air, and subsequently annealed at 600 °C for 1 h in a flow of N_2 (80 mL/min)/H_2 (3 mL/min) passed through a water column kept at RT leading to a H_2/H_2O of 1(mol/mol).

In order to determine the temperature of possible decomposition, the dried precursor was subjected to thermogravimetric-differential thermal analysis. The analysis was carried out in a Dupont Model 950 thermoanalyzer with DTA and TG stages, specimens were annealed in flowing air from 50 to 800 °C at 20 °C/min. The final product obtained was a lustrous black powder. Fourier Transform Infrared spectroscopy (FT-IR) spectra of species in the IR range of 400–4000 cm^{-1} were measured by FT-IR spectrometer (Equinox 55, Bruker Analytische Messtechnik GmbH). The crystal structures of the sample were analyzed at RT by powder X-ray Diffraction (XRD) using a Bruker AXS D8 Advance diffractometer with the wavelength of 1.5418 Å of CuK_α radiation in the range $2\theta = 15–90^o$. The average crystallite size of powders was also measured by the X-ray line broadening technique employing the Scherrer formula using the profiles of the (1 0 4) peak. Particle size and morphology of the obtained particles were observed by scanning electron microscopy (SEM) (Philips SEM XL30, Made in Holland). The element analysis was performed by energy dispersive X-ray analysis spectroscopy (EDAX) (Oxford EDAX, PV9100).

Results and discussion

TG and DTA measurements were performed to study the thermal behavior of the precursor, and the respective curves are shown in Fig. 2. It can be seen that in the temperature region 50–150 °C, an endothermic peak with a weight loss appeared which can be assigned to remove of the solvent and inner water in the precursor. The weight loss corresponding to a stronger exothermic peak at about 184 °C is mostly owing to the burning of the carbon based materials coming from alkoxide, solvent and chelating agent in the precursor together with the evolution of great amounts of gases such as H_2O and CO_2 from the precursor. Another abrupt weight loss occurs near 250 °C, which ends about at 350 °C. The DTA curve indicates that the strongest exothermic peak is at about 258 °C, which is related to the oxidation of residual organics.

To determine the changes in chemical environment of the sample, the FT-IR spectrum taken over a wave number of 4000–400 cm^{-1} for the dried precursor and precursor annealed at 450 °C for 1 h are recorded and shown in Fig. 3. The spectrum of the dried precursor Fig. 3a clearly shows a broad absorption around 3410 cm^{-1}, which is a characteristic stretching vibration of hydroxylate (O–H) [10]. Two small peaks at 2920 and 2849 cm^{-1} are attributed to the stretching vibrations of CH_2 and CH_3. Peaks localized at 1560 and

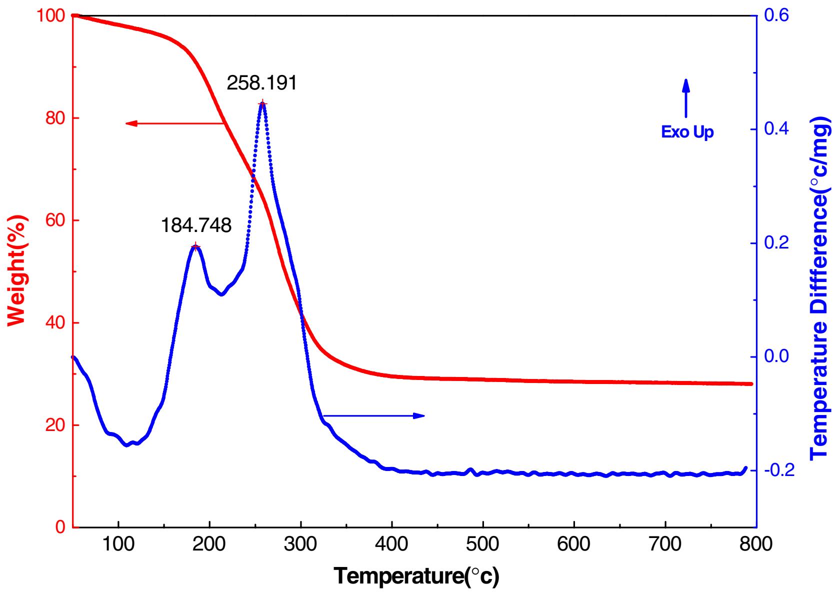

Fig. 2 TG/DTA curves of the dried precursor

1390 cm^{-1} are assigned to asymmetrical and symmetrical stretching vibration of carboxylate (O–C=O), respectively. It was also observed that C–O stretching vibration of C–OH at 1080 cm^{-1} is seen for the dried precursor. The characteristic bands of nitrate ions are not detected, indicating that an oxidation–reduction reaction occurred during drying dried process, in which nitrate ions act as oxidizers and the carboxyl is reducing agent. Peaks localized at 796 and 643 cm^{-1} are assigned to deformation vibration of the C–H group. It could be concluded that Fe^{3+}–Ti^{4+}-organic complex formed in the solution. Obviously, after heating of the precursor Fig. 3b, the functional groups of COO^- have been decomposed. The new band at 518 cm^{-1} should be ascribed to metal-oxygen stretching vibration of heated powders. However, slight absorption bands of hydroxylate and carbonate remain.

The X-ray diffraction pattern of the obtained powders is shown in Fig. 4. The XRD result shows that the product is pure ilmenite oxide $FeTiO_3$, with a rhombohedral structure, all peaks in the XRD pattern of the obtained powders could be indexed based on a rhombohedral structure with a space group of $R\bar{3}$, and the diffraction data are in good agreement with JCPDS card of $FeTiO_3$ (JCPDS no. 75–1206) [11].

The mechanism of $FeTiO_3$ powder generation can be described as following:

$$\text{Organic-metal complex precursor} \rightarrow Fe_2O_3 + TiO_2$$

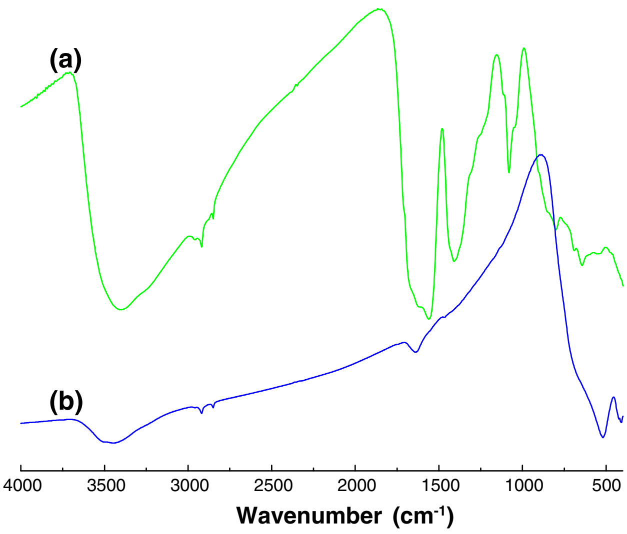

Fig. 3 FT-IR spectra of the (**a**) dried precursor and (**b**) precursor calcinated at 450 °C for 1 h

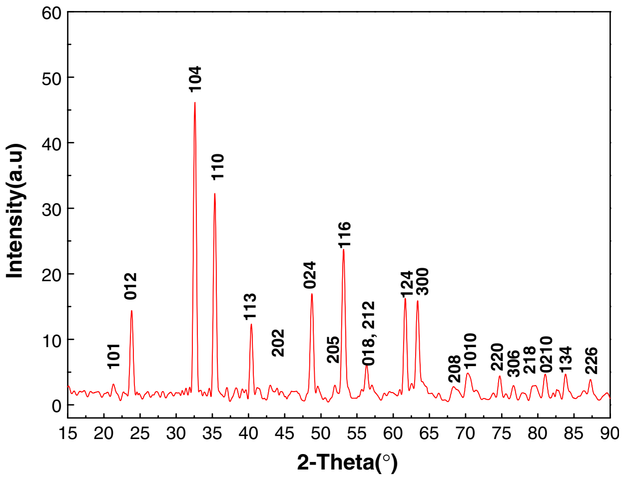

Fig. 4 XRD pattern of the the obtained powder

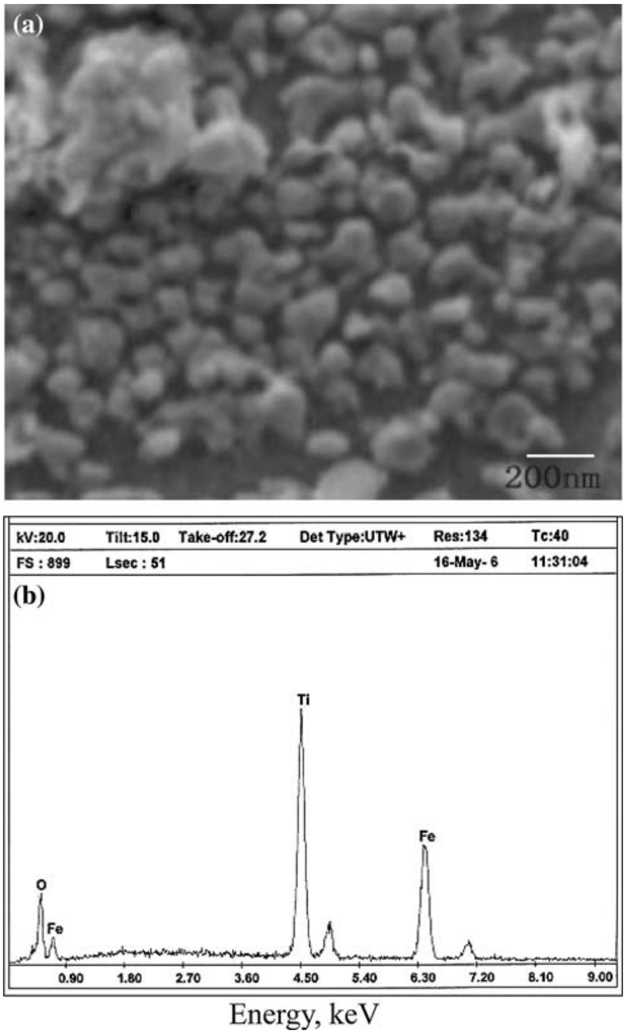

Fig. 5 Scanning electron micrograph (**a**) and EDAX (**b**) of the obtained $FeTiO_3$ powder

$$Fe_2O_3 + H_2/H_2O \rightarrow FeO$$

$$FeO + TiO_2 \rightarrow FeTiO_3.$$

The calculated lattice constants by least squares fit are $a = 5.132$ Å and $c = 14.076$ Å. The particle size calculated using the Debey–Scherrer formula [12]:

$$D = K\lambda/(\beta\cos\theta).$$

where D is the average size of the particles, assuming particles are spherical, $K = 0.9$, λ is the wavelength of X–ray radiation, β is the full width at half maximum of the diffracted peak and θ is the angle of diffraction, is 76 nm. The results indicate that this method is useful to prepare fine and homogeneous $FeTiO_3$ materials.

Table 1 The elementary constituents of the prepared $FeTiO_3$ powder determined by EDAX

Elements	O	Ti	Fe	Total
Mass percentage (%)	33.83	32.19	33.98	100.00
Atomic percentage (%)	62.28	19.80	17.92	100.00

Figure 5 presents the scanning electron micrograph and EDAX for the obtained powders. As shown in Fig. 4a, the powders are irregular in both particle size and shape. EDS was performed to further confirm the composition of obtained products. Figure 4b shows that the products are composed of Fe, Ti and O. The mass and atomic fractions of all elementary constituents in the $FeTiO_3$ phase determined by EDAX are presented in Table 1. It is observed that the mole ratio of Fe, Ti and O atoms is approximately equal to1:1:3, which further confirms that the formed material is of $FeTiO_3$.

Conclusion

In summary, pure ilmenite oxide $FeTiO_3$ with a rhombohedral crystal structure can be synthesized. The overall process of synthesizing ilmenite $FeTiO_3$ powders involves two steps: the formation of the dried precursor; the precursor was annealed in the air, a mixture gas stream of H_2/H_2O, respectively. This process is easy, simple, and low cost because of using cheap reagents.

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