Microstructure Ti–Fe Phase Separation Mechanism in the Direct Reduction Process of Titanomagnetite with Coal by Microwave Heating

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Synopsis: Although microwave heating has been used in the field of metallurgy since the 1980s, there are few reports on using microwave heating to strengthen Ti–Fe phase separation in the reduction process of titanomagnetite. Microstructure Ti–Fe phase separation by microwave heating was found to be beneficial to the reduction process of titanomagnetite through the investigation of formation enthalpy and reduction difficulties. The dielectric properties and energy band structure of Fe$_3$O$_4$, Fe$_2$O$_3$, and TiO$_2$ were determined, the dielectric constant ($\epsilon'_r$: 20.00) and dielectric loss ($\epsilon''_r$: 2.82) of Fe$_3$O$_4$ were significantly superior to those of TiO$_2$ ($\epsilon'_r$: 3.42, $\epsilon''_r$: 0.04), and the physical thermal stress between Fe$_3$O$_4$ and TiO$_2$ phases in the reduction process was conducive to the microstructure Ti–Fe phase separation process. Besides thermal stress, microstructure Ti–Fe phase separation was mainly due to the ampere traction force generated between local isotropic ring current in adjacent iron atoms. This study revealed the microstructure Ti–Fe phase separation mechanism in the reduction process of titanomagnetite by microwave heating.

Keywords: Titanomagnetite; Formation enthalpy; Reduction; Microwave; Ti–Fe phase separation
1 Introduction

Titanomagnetite is a polymetallic co-associated mineral with iron and titanium as the main metal elements, followed by other elements (vanadium, cobalt, nickel, chromium, copper, scandium, selenium, and gallium) \(^1\)-\(^5\). Titanomagnetite is widely distributed in the world, mainly in Russia, South Africa, New Zealand, China, the United States, Canada, Norway, Finland, India, and Sweden \(^6\)-\(^8\). Fe, V, Ti, and other associated metal elements in titanomagnetite have played a vital role in developing human society. Therefore, titanomagnetite is widely recognized as a strategic mineral resource \(^4\),\(^9\)-\(^13\). However, realizing the large-scale and comprehensive clean recovery of Fe, V, and Ti in titanomagnetite remains a challenge due to a technical bottleneck caused by the poor phase separation effect of the associated Ti–Fe \(^14\),\(^15\). The blast furnace process, which is the mainstream process for treating titanomagnetite concentrate (TC), can recover Fe and V, but the grade of the Ti-bearing blast furnace slag produced using this process is too low (TiO\(_2\): 25 wt.\%) to be further used, and the resultant large amount of stockpiled slag does not only pollute the environment but also wastes titanium resources \(^6\),\(^11\),\(^15\),\(^16\); however, researchers are trying to comprehensively recover Fe, V, and Ti from TC through the development of nonblast-furnace smelting methods \(^2\),\(^8\),\(^11\),\(^17\)-\(^21\). TC is treated by direct reduction and electric furnace melting in a typical nonblast-furnace smelting process. Two major problems must be addressed in the development of this process: 1. The associated Ti makes the TC more stable and increases the difficulty of reduction; 2. Titanium oxide (TiO\(_2\)) migration occurs simultaneously in the reduction process of iron oxides, and the flux materials (CaO/CaCO\(_3\)) added to improve the TiO\(_2\) migration dilute the slag phase and reduce the slag’s TiO\(_2\) grade, making further recovery difficult \(^11\),\(^18\). Researchers change the lattice structure of TC through conventional heating preoxidation treatment (Fe\(_3\)O\(_4\)→Fe\(_2\)O\(_3\)) \(^14\),\(^16\),\(^19\),\(^22\), which reduces the reduction difficulties to some extent. However, TiO\(_2\) reacts with Fe\(_2\)O\(_3\) to form Fe\(_2\)TiO\(_5\) (Fe\(_2\)O\(_3\) + TiO\(_2\) = Fe\(_2\)TiO\(_5\)), which is more stable and difficult to reduce \(^14\),\(^23\). Microwave heating could also enhance the reduction process of TC for the rapid heating rate of iron oxides as an extension of conventional heating preoxidation treatment \(^24\).

Xuewei Lv \(^25\) investigated the carbothermal reduction process of TC by microwave heating. The results showed that the heating rate of TC in the microwave field could be divided into three stages: very fast, slow, and fast. Microwave carbothermal reduction was suggested as a treatment
for TC because it could reduce the use of coal and CO\textsubscript{2} emissions. Research results of microwave carbothermal reduction of hematite by Ying Lei \textsuperscript{26} showed that the rapid microwave heating of iron oxides could not only improve the reduction rate but also facilitate the phase separation and removal of impurity elements. Nagata \textsuperscript{27} designed a magnetite-continuous-microwave carbothermal reduction reactor, which confirmed that this conclusion (microwave heating facilitates the phase separation and removal of impurity elements) was also applicable to magnetite. N. Standish \textsuperscript{28} investigated the microwave carbothermal reduction process of hematite and magnetite, and the results showed that coal could obtain a better iron oxide reduction effect than coke, and Mourao \textsuperscript{29} reported a similar conclusion on the microwave carbothermal reduction process of iron ore composite pellets. Malmberg \textsuperscript{30} discovered that the selective microwave heating of the iron ore could reduce the heat loss caused by fly dust, smoke, and atmosphere flow in the reduction process. Ishizaki \textsuperscript{31-34} systematically investigated the microwave carbothermal reduction process of magnetite. The magnetite with the main Fe\textsubscript{3}O\textsubscript{4} phase could be quickly heated to 1200°C within 500 s in a 2450 MHz time-varying electromagnetic field and reduced according to the step-by-step reduction mode of Fe\textsubscript{3}O\textsubscript{4} \rightarrow FeO \rightarrow Fe; these results have reference significance for the study of microwave carbothermal reduction of TC. Hayashi \textsuperscript{35} compared the microwave carbothermal reduction process of hematite and magnetite, investigated the ratio change of CO and CO + CO\textsubscript{2} \{p_{CO}/(p_{CO} + p_{CO_2})\} in the reduction process using a mass spectrometer, and analyzed the reduction process of iron oxides with Fe–C–O phase diagram. At around 900°C, Fe\textsubscript{3}O\textsubscript{4} began to reduce to wustite (FeO) as the CO content increased \{p_{CO}/(p_{CO} + p_{CO_2}) \approx 0.3\}, and wustite (FeO) began to reduce to Fe with the further increase in CO content \{p_{CO}/(p_{CO} + p_{CO_2}) \approx 0.7\}; this conclusion was consistent with the step-by-step reduction mode of Fe\textsubscript{3}O\textsubscript{4} \rightarrow FeO \rightarrow Fe confirmed in Ishizaki's research. In addition, Hayashi \textsuperscript{35} also discovered that magnetite (Fe\textsubscript{3}O\textsubscript{4}) had a faster microwave carbothermal reduction rate than hematite (Fe\textsubscript{2}O\textsubscript{3}) and that when it reached a certain temperature, it began to reduce to Fe\textsubscript{3}O\textsubscript{4}, and then the reduction process was quickened. Zhiwei Peng \textsuperscript{36,37} investigated the dielectric properties of iron oxides (Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3}) using a cylindrical cavity perturbation method and discovered that Fe\textsubscript{3}O\textsubscript{4} was a good microwave absorbing material, and the dielectric parameters of Fe\textsubscript{3}O\textsubscript{4} increased rapidly as the temperature increased from 500°C; similarly, the dielectric parameters of Fe\textsubscript{2}O\textsubscript{3} increased rapidly from 700°C. In addition, Zhiwei Peng
discovered that Fe$_2$O$_3$ changes from a wave transmitting state to a wave absorbing state during heating, indicating that temperature had a crucial effect on the dielectric parameters of iron oxides. Hotta ³⁸) investigated the variation of dielectric parameters of Fe$_3$O$_4$ with frequency using the coaxial transmission line method. The results showed that the most suitable microwave frequency for Fe$_3$O$_4$ heating was 2450 MHz. Sano ³⁹) measured the microwave absorptivity using a vector network analyzer and discovered that 72% of the heat generated in microwave-heated iron powder (<45μm) was from magnetic losses and 28% from dielectric losses. Fujisaki ⁴⁰) simulated the eddy and displacement currents of five 2-mm conductive particles in a microwave field using $j\omega$-based finite element method. An electric field cannot pass through the particles due to their good uniform conductivity, whereas a magnetic field would produce an induced eddy current inside the particles, which was a significant reference for understanding the interaction mode between metal particles and microwave. Fujisaki ⁴¹) also simulated the current microstructure of iron oxide without uniform conductivity, and its anisotropic current microstructure was significantly lower than the wavelength. The key to understanding the microwave heating process of iron oxides is to figure out how to construct the current microstructure of iron oxides.

In summary, scholars have extensively investigated the process parameters and heating mechanism of microwave carbothermal reduction of iron oxides, paving the way for the use of microwave heating technology in the smelting of iron ore. The future development direction for microwave carbothermal reduction of TC is to achieve comprehensive recovery of Fe, V, and Ti. This study investigates microwave functional heating (Table 1) to analyze the microwave response behavior of iron oxides and TiO$_2$ in the reduction process using dielectric parameters and energy band structure and to reveal the microstructure Ti–Fe phase separation mechanism. This study could provide a theoretical basis for developing the carbothermal reduction process of TC by microwave heating.

**2 Materials and Methods**

**2.1 Materials and reduction difficulties**

Table 2 shows the composition of TC (from Panzhihua, Sichuan, China); because the molar ratio of Fe:Ti = 2.524:0.476, the main phase in TC could be expressed as Fe$_{3-x}$Ti$_x$O$_4$ ($x = 0.476$). X-ray diffraction analysis (XRD) (Figure 1a) patterns confirmed that Fe$_3$O$_4$ and FeTiO$_3$ were the
two main phases in TC; SEM (Figure 1b) surface scan results of TC show that the strong positions of Fe, O, and Ti were consistent, indicating that Ti–Fe was closely coassociated. X-ray photoelectron spectroscopy (XPS) analysis (Figure 1c) showed that the iron oxides on the surface of TC mainly existed in the approximate structure of Fe$_3$O$_4$. Table 3 shows the industrial analysis of coal used for the reduction of TC. The particle sizes of the TC and coal powders were ground to less than 100 μm. These two powders were fully mixed according to the mass ratio of 5:1 to obtain a mixture of titanomagnetite concentrate and coal (MTC) for comparative reduction experiments. Besides TC mixed with different amounts of pulverized coal (accounting for 0–20 wt.% of TC), analytically pure Fe$_3$O$_4$, Fe$_2$O$_3$, and TiO$_2$ powder were also used to measure dielectric parameters.

Metal elements for FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_{3-x}$Ti$_x$O$_4$($x = 0.476$), Fe$_2$TiO$_5$, Fe$_2$TiO$_4$, FeTiO$_3$, and FeTi$_2$O$_5$ are all bonded with oxygen; Fe element is +2 or +3 valence and Ti element is +4 valence, and they have different bond energies, which would change the stability of related oxides, forming a reduction difficulty order. According to the discussion above, the formation enthalpy per unit of oxygen of FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_{3-x}$Ti$_x$O$_4$($x = 0.476$), Fe$_2$TiO$_5$, Fe$_2$TiO$_4$, FeTiO$_3$, and FeTi$_2$O$_5$ describes the stability of the O element to characterize the reduction difficulty of the oxides.

The formation enthalpy of FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_2$TiO$_5$, Fe$_2$TiO$_4$, FeTiO$_3$, FeTi$_2$O$_5$, and TiO$_2$ was calculated using HSC thermodynamic calculation software according to Equations 1–8. However, because there are no relevant data on Fe$_{3-x}$Ti$_x$O$_4$($x = 0.476$) in the HSC database, the formation enthalpy of Fe$_{3-x}$Ti$_x$O$_4$($x = 0.476$) cannot be calculated directly. In this study, a ternary two-parameter method was used to calculate the formation enthalpy of Fe$_{3-x}$Ti$_x$O$_4$($x = 0.476$), and the error was within 2%.

\[
\begin{align*}
\text{Fe}(s) + 0.5\text{O}_2(g) &= \text{FeO}(s) \\
2\text{Fe}(s) + 1.5\text{O}_2(g) &= \text{Fe}_2\text{O}_3(s) \\
3\text{Fe}(s) + 2\text{O}_2(g) &= \text{Fe}_3\text{O}_4(s) \\
2\text{Fe}(s) + \text{Ti}(s) + 2.5\text{O}_2(g) &= \text{Fe}_2\text{TiO}_5(s) \\
2\text{Fe}(s) + 2\text{O}_2(g) + \text{Ti}(s) &= \text{Fe}_2\text{TiO}_4(s) \\
\text{Fe}(s) + \text{Ti}(s) + 1.5\text{O}_2(g) &= \text{FeTiO}_3(s) \\
\text{Fe}(s) + 2.5\text{O}_2(g) + 2\text{Ti}(s) &= \text{FeTi}_2\text{O}_5(s)
\end{align*}
\]
\[ \text{Fe}_3\text{O}_4 + \text{CO}(g) = 3\text{FeO} + \text{CO}_2(g) \] (9)

\[ \text{FeO} + \text{CO}(g) = \text{Fe} + \text{CO}_2(g) \] (10)

\[ \text{CO}_2(g) + \text{C}(s) = \text{CO}(g) \] (11)

The ternary two-parameter method is commonly used to calculate the thermodynamic parameters of complex minerals. First, disassemble \( \text{Fe}_{3-x}\text{Ti}_x\text{O}_4(x = 0.476) \) into a combination of three oxides: 0.476\( \text{TiO}_2 \), 0.524\( \text{Fe}_2\text{O}_3 \), and 1.476\( \text{FeO} \); Secondly, search the double parameters of \( \text{TiO}_2 \), \( \text{Fe}_2\text{O}_3 \), and \( \text{FeO} \) (Table 4) \(^{47,48}\). Finally, calculate the formation enthalpy of \( \text{Fe}_{3-x}\text{Ti}_x\text{O}_4(x = 0.476) \) according to Formulas 1 and 2 in Table 4; Table 5 shows the calculation results of average molar formation enthalpy \((\Delta\text{H})\) per unit oxygen of the oxides and corresponding reduction difficulty coefficient \((H)\). If TC was treated by preoxidation before the reduction process, the lattice structure in \( \text{Fe}_{3-x}\text{Ti}_x\text{O}_4(x = 0.476) \) is transformed from \( \text{Fe}_3\text{O}_4 \) to \( \text{Fe}_2\text{O}_3 \), which is conducive to the reduction process \(^{14,49}\) according to the decrease in \( H \) from 89.52\% \( \text{(Fe}_3\text{O}_4 \) to 88.00\% \( \text{(Fe}_2\text{O}_3 \).

2.2 Reduction description and comparative reduction experiments

The reduction process of MTC mainly involves two group reactions: 1. The reduction process of iron oxides (Equations 9 and 10); 2. The gasification process of carbon (Equation 11).

\[ \text{Fe}_3\text{O}_4 + \text{CO}(g) = 3\text{FeO} + \text{CO}_2(g) \] (9)

\[ \text{FeO} + \text{CO}(g) = \text{Fe} + \text{CO}_2(g) \] (10)

\[ \text{CO}_2(g) + \text{C}(s) = \text{CO}(g) \] (11)

The CO\(_2\) gas product from the first group reactions was the reactant of the second group reactions, and the CO gas product of the second group reactions was the reactant of the first group reactions, so the two groups of reactions were coupled in this way, and formed a reaction system. We used the Dmol\(^3\) module \(^{50}\) to calculate the activation energy of the step reduction process of iron oxides, and the generalized gradient approximation (GGA) in density functional theory (DFT) was used, Perdew, Burke, and Ernzerhof (PBE) were selected for exchange gradient correction \(^{51-53}\), ultra-soft pseudopotential was adopted, the energy cutoff was set to 381 eV, and a linear synchronous transition was used to calculate the transition state search iterative calculation of the reduction process of simplified nonlattice iron oxides. The convergence accuracy of energy was better than \( 10^{-5} \) eV/atom, and all calculations were completed under a medium grid. The step reduction process of simplified nonlattice iron oxides was further analyzed using the frontier molecular orbital theory \(^{54}\). Comparative reduction experiments by microwave and conventional heating methods were conducted to verify the microwave-enhanced Ti–Fe phase separation effect.
in the reduction process. Figure 2 shows the heating equipment used in the comparative reduction experiments, and the specific experimental steps are as follows:

First, a 48-g MTC sample (40 g ore and 8 g coal) was placed in a 100-ml ceramic crucible and loaded in the heating cavity, which was wrapped with thermal insulation materials (wave transmitting). The microwave heating equipment’s power was 2 kW to maintain rapid sample heating, and the power was automatically adjusted to stay after reaching target temperatures. The conventional heating rate was set to 10°C/min for equipment protection, and the temperature was automatically controlled to stay after reaching the target temperatures. The temperature was measured through a WRP series S-type thermocouple, and the thermocouple was inserted into the samples during microwave and conventional heating to control the measurement error within ±4°C.

Second, set the reduction time to 30 min (heating time at the target temperatures), with the reaction cavity airtight at that period. Third, set the heating target temperature as 600°C, 800°C, 1000°C, and 1050°C, and conduct a group of comparative reduction experiments every 50°C from 1050°C by microwave and conventional heating methods until the Ti–Fe phase separation effect in the reduction process of the two heating methods is confirmed by SEM analysis. Finally, XRD analysis was conducted on the samples in the reduction process of microwave heating at different temperatures.

2.3 Measurement of dielectric parameters and calculation of the energy-band structure

Equation 12 defines the dielectric parameters and the relative complex dielectric constant ($\varepsilon_r$) 

$$\varepsilon_r = \varepsilon'_r - i\varepsilon''_r$$  \hspace{1cm} (12)

The dielectric constant ($\varepsilon'_r$), which is the real part of $\varepsilon_r$, reflects the ability of a substance to store microwave energy through polarization, and dielectric loss ($\varepsilon''_r$), which is the imaginary part of $\varepsilon_r$, reflects the ability of a substance to convert microwave energy into heat through dipole high-frequency damping motion or conductive loss. In addition, the loss tangent ($\tan\delta$) and penetration depth ($D_p$) were also important parameters. The loss tangent was the ratio of $\varepsilon''_r$ to $\varepsilon'_r$ (Equation 13). The fluctuation in the temperature of $\tan\delta$ indicates a reaction or phase transition \(^{56}\). Equation 14 was used to calculate the penetration depth into materials, which describes how microwave energy decays from the material surface to 1/e of the energy before incident \(^{56}\).

$$\tan\delta = \frac{\varepsilon''_r}{\varepsilon'_r}$$ \hspace{1cm} (13)

$$D_p = \frac{\varepsilon_0 c}{2\pi f \varepsilon'_r}$$ \hspace{1cm} (14)
\[ D_p = \frac{c}{2 \sqrt{2} \pi f \varepsilon'_r \left( 1 + \left( \frac{\varepsilon'_r}{\varepsilon''_r} \right)^2 \right) - 1} \]  

(14)

Here, \( i \) denotes the imaginary unit, \( c \) denotes the speed of light in free space \((3 \times 10^8 \text{ m/s})\), and \( f \) denotes the frequency of the microwave \((2450 \text{ MHz})\).

The dielectric parameters of TC, Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), and TiO\(_2\) were tested based on the cylindrical cavity perturbation method using the equipment as shown in Figure 3 \(^{57}\). In the MTC reduction process, the valence of Fe in iron oxides \((\text{Fe}_3\text{O}_4, \text{Fe}_2\text{O}_3)\) gradually decreased, whereas the valence of Ti remained unchanged \((\text{TiO}_2)\). The resonant frequency of the cylindrical cavity was 2450 MHz.

The sample was filled in a small bottom-end sealed quartz and the top-end was sealed with thermal insulation material to keep the sample airtight, and the sample quartz could slide in the quartz pipe through an air pump switch. The sample rose to the cylindrical resonator during the test. After a test at room temperature \((25^\circ \text{C})\), the sample was dropped to the heating area, where it was heated and held at the target temperature \((\text{every 50}^\circ \text{C from 50}^\circ \text{C to 1000}^\circ \text{C})\) for 5 min, and then slide up for high-temperature measurement. The temperature was measured by an S-type thermocouple in an eddy current heating carbon rod. Calibration experiments with air and water as reference materials were conducted to ensure test accuracy. Table 6 shows that the air is a low loss material, the measured data of \( \varepsilon'_r \text{(air)} \) is close to the reference data and nearly equals 1, and \( \varepsilon''_r \text{(air)} \) nearly equals 0; alternatively, water is a high loss material, the measurement data of \( \varepsilon'_r \text{(water)} \) is close to the reference data, and \( \varepsilon''_r \text{(water)} \) is between the reference data. The accuracy of the data could be ensured based on the calibration experiments.

The energy band and electron density of states (DOS) of different phases \((\text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4, \text{and TiO}_2)\) were calculated based on the Cambridge Series total energy package module \(^{61}\), the GGA in DFT was applied, PBE was selected to exchange the gradient correction, ultra-soft pseudopotential was adopted, the energy cutoff was set to 381 eV, the energy convergence accuracy was better than \(10^{-5} \text{ eV/atom}\), and all calculations were completed under the dispersion of a medium grid. The crystal structures of \(\text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4, \text{and TiO}_2\) used in the calculation, as shown in Table 7, were from the Inorganic Crystal Structure Database.
2.4 Characterizations

The speciation of Fe on the surface of TC was evaluated by the XPS (Thermo K-Alpha+, Thermal Fisher) with Al Kα radiation. Chemical analysis was used to detect the chemical compositions of TC. SEM (Phenom ProX; Phenom) was used to detect the phase separation of Fe⁰ and slag in MTC. XRD (Rigaku D/MXA-3B with Cu Kα radiation at 40 kV and 40 mA) was used to confirm and detect the main phase composition of TC in the reduction process.

3 Results and discussion

3.1 Activation energy of stepwise reduction and frontier molecular orbital theory

Although the reducing agent was solid-phase pulverized coal, while the solid-phase reduction was limited by the contact area between coal and TC particles, the actual dominant reaction was the indirect gas-phase reduction. The indirect gas-phase reduction reaction system comprised two groups of coupled chemical reactions, and this process is described in Figures 4a, 4b, 4c, and 4d. We divided this process into three steps \( \text{Fe}^{3+} \xrightarrow{\text{Step 1}} \text{Fe}^{2+} \xrightarrow{\text{Step 2}} \text{Fe}_2\text{O}^{2+} \xrightarrow{\text{Step 3}} \text{Fe}^0 \) and calculated the activation energy of each step through the simplified nonlattice iron oxide models. The results showed that the activation energy increased as the valence of Fe decreased, \( E_a - \text{Step 1}(157.0 \text{ kJ/mol}) < E_a - \text{Step 2}(170.2 \text{ kJ/mol}) < E_a - \text{Step 3}(185.5 \text{ kJ/mol}) \); thus, the activation energy calculation results indicated the preferential reduction of high valence Fe and the occurrence of the Fe⁰ phase.

Alternatively, the electrons in the highest occupied molecular orbital (HOMO) of iron oxides would form a transition state (TS) with CO in the reduction process (Figures 5a–c) according to the frontier molecular orbital theory (Figure 5), and the energy level of iron oxides and corresponding TS were so close that the electrons from CO could transfer to iron oxides through TS, resulting in the breakage of Fe–O bond and the formation of C–O bond. The reaction process involved the interaction between the HOMO electrons in iron oxides and CO to form TS and the transfer of the HOMO electrons in CO to iron oxides through TS; thus, the closer the HOMO energy level of iron oxides was to that of TS, the easier the reaction would be. Taking the reduction of \( \text{Fe}_2\text{O}_3 / \text{Fe}_2\text{O}^{2+} \) as an example because the HUMO energy level of TS (Figure 5a) was 0.429 eV higher than that of \( \text{Fe}_2\text{O}_3 \), the formation of TS was harder while the transfer of electrons through TS was easier. Because the Humo energy level of TS was 0.503 eV lower than that of \( \text{Fe}_2\text{O}^{2+} \), the formation of TS was easier while the transfer of electrons through TS was harder. Because the activation energy
increased as the valence of Fe decreased, the effect on the reduction process of electron transfer through TS was greater than that on the TS formation.

In addition, the indirect gas-phase reductant, CO, was a polar molecule \{CO (gas): 0.125D; H₂O (gas): 1.85D; H₂O (liquid): 3.0D, 1D = 3.33564e-30 C·m\}⁶²,⁶³, which would swing in the time-varying electromagnetic field, so microwave irradiation was conducive to the formation of TS, whereas the gas-phase product, CO₂, of iron oxide reduction reactions was a nonpolar molecule.

### 3.2 Phase transformation determined by XRD in the microwave heating reduction process

Figure 6 shows the XRD patterns of MTC samples treated under different temperatures by microwave heating, which are used to describe the phase transformation of MTC in the reduction process. The reduction process was divided into the following four stages: mixing, microstructure Ti–Fe phase separation, reduction, and melting separation. In the first stage, MTC was fully mixed at room temperature (Figures 6a and b); the second stage was the microwave heating microstructure Ti–Fe phase separation process, which started from rapid heating of MTC (600°C) to the end of the reduction stage; in the third stage, the Fe⁰ phase (marked in a blue belt in Figure 6) generation began from 1000°C (Figures 6e–h); In the fourth stage, slag and Fe⁰ phase started to melt and separate (Figures 6i and j). Microstructure Ti–Fe phase separation process was a marked stage of the microwave heating reduction process of MTC due to the dielectric properties difference, iron oxides were rapidly heated by microwave, and physical thermal stress between iron oxides (Fe₂O₃, Fe₃O₄, and many others) and titanium oxide (TiO₂) was conducive to the microstructure Ti–Fe phase separation. As the temperature increased, the disappearance of the titanium oxide (marked in the green ellipse area in Figure 6) phase in the XRD patterns was not caused by the change in titanium valence but by the phase dispersion caused by the relative migration of titanium oxide (TiO₂), and this relative migration was conducive to the Ti–Fe phase separation and the reduction of MTC.

In addition, the microstructure Ti–Fe phase separation in the reduction process was also related to FeTiO₃. Because FeTiO₃ was generated from the first step reduction of high-valent iron oxides in TC, and FeTiO₃ would eventually reduce to Fe⁰ + TiO₂, the corresponding peak of FeTiO₃ would increase first and then disease, whereas the microwave field caused the phase separation of Ti–Fe earlier than the reduction of FeTiO₃, so the 2θ of FeTiO₃ moved to the right side slightly, as shown in Figure 6, indicating that the FeTiO₃ transformed into microstructure-separated FeO and TiO₂.
3.3 Dielectric properties and energy-band structure

3.3.1 Dielectric properties

Figure 7 shows the dielectric parameters (Dielectric constant $\varepsilon'$, dielectric loss $\varepsilon''$, loss tangent $\tan\delta$, and penetration depth $D_p$) of TC mixed with different amounts of pulverized coal (accounting for 0–20 wt.% of TC) from room temperature to 1000°C. The significant increase in $\varepsilon'$ at 850°C was 100°C higher than that of $\varepsilon''$, which increased significantly at 750°C in the initial reduction process of TC (600°C–1050°C); the increasing temperature lag of $\varepsilon'$ behind $\varepsilon''$ and the corresponding fluctuation of $\tan\delta$ could be explained through reaction intermediates generated by electron transfer and the new bond formation. The emergence of intermediates increased the electronic activity of iron atoms at the start of the reaction, causing a significant increase in $\varepsilon''$ by polarization damping and conductivity losses. However, only when the reaction scale was large enough to form a stable number of intermediates did the polarization energy storage (described by $\varepsilon'$) increase significantly, indicating that $\varepsilon''$ was more sensitive to the intermediates in the process of microwave heating chemical reactions; similar results were also observed in microwave synthesis of TiC. $D_p$ decreased as the temperature increased, and the $D_p$ of TC mixed with different amounts of pulverized coal was consistent in the temperature range of 750°C–1000°C, the average $D_p$ was 1.6 cm, implying that the pellet diameter of MTC should be around 1.6 cm to obtain a good microwave heating effect and energy usage rate.

The dielectric properties of Fe$_3$O$_4$, Fe$_2$O$_3$, TiO$_2$, and SiC were measured and compared to analyze the dielectric difference between iron and titanium oxides in the reduction process of MTC by microwave heating. Figure 8 shows that both $\varepsilon'$ and $\varepsilon''$ of Fe$_3$O$_4$ were much higher than those of Fe$_2$O$_3$, TiO$_2$, coal, and even SiC and the dielectric difference was conducive to realizing the aggregation of iron oxides and the microstructure Ti–Fe phase separation in the reduction process. SiC is a good microwave absorbing material; however, MTC had a better microwave heating behavior than SiC, as shown in Figure 9, which was attributed to the excellent dielectric properties of iron oxides in MTC.

3.3.2 Energy-band structure

The local conductivity of the Fe$_3$O$_4$ crystal structure could be further analyzed by energy-band structure analysis. We calculated the energy band structure of Fe$_2$O$_3$, Fe$_3$O$_4$, and TiO$_2$ according to
the Brillouin zone scanning paths of different crystal structures \(65\), and the results (Figure 10) showed that both \(\text{Fe}_3\text{O}_4\) and \(\text{Fe}_2\text{O}_3\) crystals had a conduction band, while the bandgap of \(\text{TiO}_2\) crystals was around 2.142 eV, which is consistent with other published calculations using the GGA method \(66,67\). The experimental band gap value of \(\text{TiO}_2\) was 3.22 eV, and this small computed value is due to the renowned disadvantage of the GGA method; however, trends in the energy band structure calculation and related qualitative features were accurately predicted by this method \(68\).

The differences in conductivity between \(\text{Fe}_2\text{O}_3\), \(\text{Fe}_3\text{O}_4\), and \(\text{TiO}_2\) facilitated the microstructure Ti–Fe phase separation in the reduction process of TC by microwave heating. Combining the energy band structure information with the calculation results of DOS indicated that free electrons contributing to the micro-local conductivity in \(\text{Fe}_3\text{O}_4\) and \(\text{Fe}_2\text{O}_3\) were mainly from the Fe element’s d-orbital. This group of free electrons could move around the adjacent Fe atoms of \(\text{Fe}_3\text{O}_4\) and \(\text{Fe}_2\text{O}_3\) crystal structures, allowing them to respond to the electric and magnetic fields via conductive polarization and eddy current. Few electrons could transition to higher energy levels to contribute to conductivity due to the bandgap of \(\text{TiO}_2\), making it inactive in the microwave field. The difference in response mode and intensity between iron oxides (\(\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3\)) and \(\text{TiO}_2\) was crucial in achieving the microstructure Ti–Fe phase separation in the reduction process of TC using microwave heating.

The above discussion shows that the electromagnetic field gathers the phase of iron oxides through the ring current in adjacent iron atoms for iron oxides with local free electrons in the Fe element’s d-orbit, whereas no local free electrons in the d-orbit of \(\text{TiO}_2\) respond to microwave, thus \(\text{TiO}_2\) had no active phase aggregation. This difference in the response mode was conducive to the microstructure Ti–Fe phase separation. Rajavaram’s research showed that after microwave heating to 1300°C, magnetite’s main XRD peak slightly moved to the right side, indicating that the lattice structure became more compact according to the Debye-Scherrer equation \(69\), and this phenomenon was essentially consistent with the phase aggregation of iron oxides in this study and were all attributed to the isotropic ring current traction effect caused by local free electrons around adjacent Fe atoms in the microwave field.

**3.4 Microstructure Ti–Fe phase separation effect in the reduction process**

Microstructure Ti–Fe phase separation effects of microwave and conventional heating were
1. Because the reduction difficulty order was Fe$_2$O$_3$ < Fe$_3$O$_4$ < Fe$_{3-x}$Ti$_x$O$_4$($x = 0.476$) based on the formation enthalpy, the microstructure Ti–Fe phase separation was conducive to the reduction process of titanomagnetite.

2. The activation energy order in the step reduction process of titanomagnetite ($\text{Fe}^{3+}$, $\text{Fe}^{2+}$) calculated using the simplified iron oxide models was $E_a$ – $\text{Step 1}$ ($157.0 \text{ kJ/mol}$) < $E_a$ – $\text{Step 2}$ ($170.2 \text{ kJ/mol}$) < $E_a$ – $\text{Step 3}$ ($185.5 \text{ kJ/mol}$), which supports the

Compared using SEM analysis of reduction comparison experiments, as shown in Figures 11 and 12. Conventional heating failed to achieve the microstructure Ti–Fe phase separation even under higher temperatures, whereas microwave heating achieved better Ti–Fe phase separation and reduction effects (Figures 11 and 12). We concluded that TC had good overall dielectric properties, which could enable rapid heating in the microwave field, based on the comparative analysis of stability, dielectric properties, and energy band structure of Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_{3-x}$Ti$_x$O$_4$($x = 0.476$), and TiO$_2$, as shown in Table 8. Moreover, the dielectric properties between the iron oxide phase (Fe$_2$O$_4$) and TiO$_2$ in the reactions were quite different, which resulted in physical thermal stresses in the process of microwave heating. Alternatively, free electrons from the Fe element’s d-orbital in TC iron oxides moved around the adjacent Fe atoms and formed micro-local isotropic ring currents, resulting in active traction and aggregation of iron oxides and Fe$^0$ phases in the reduction process by ampere force (Figure 11c), causing the relative displacement of Ti–Fe (Figure 11b). The Fe$^0$ phase produced in the reduction process would also form a local isotropic ring current under the action of a microwave field, which would have a traction effect on the Fe atoms reduced from iron oxides and form a Ti–Fe relative displacement conducive to the aggregation of the Fe$^0$ phase, ensuring the smooth microstructure Ti–Fe phase separation. The Ti–Fe phase separation effect in the reduction process was enhanced by microwave heating (Figure 13) because of the microstructure based on the reduction difficulty coefficient, $H$.

4 Conclusion

The microstructure Ti–Fe phase separation mechanism in the reduction process of titanomagnetite by microwave heating was revealed by dielectric properties and energy-band structure analysis. The main conclusions are as follows:

1. Because the reduction difficulty order was Fe$_2$O$_3$ < Fe$_3$O$_4$ < Fe$_{3-x}$Ti$_x$O$_4$ ($x = 0.476$) based on the formation enthalpy, the microstructure Ti–Fe phase separation was conducive to the reduction process of titanomagnetite.

2. The activation energy order in the step reduction process of titanomagnetite ($\text{Fe}^{3+} \xrightarrow{\text{Step 1}} \text{Fe}^{2+}$, $\text{Fe}_2\text{O}_3 \xrightarrow{\text{Step 2}} \text{Fe}^{2+}$, $\text{Fe}^{2+} \xrightarrow{\text{Step 3}} \text{Fe}^0$) calculated using the simplified iron oxide models was $E_a$ – $\text{Step 1}$ ($157.0 \text{ kJ/mol}$) < $E_a$ – $\text{Step 2}$ ($170.2 \text{ kJ/mol}$) < $E_a$ – $\text{Step 3}$ ($185.5 \text{ kJ/mol}$), which supports the
preferential reduction of Fe with high valence.

3. Titanomagnetite’s overall dielectric properties were so good that it allowed for quick microwave heating and facilitated the reduction of iron oxides. The dielectric properties of Fe$_3$O$_4$ were much better than those of TiO$_2$, and the Fe$_3$O$_4$ crystal had a conduction band while the bandgap of TiO$_2$ was around 2.142 eV. The difference in dielectric properties and micro-local conductivity between Fe$_3$O$_4$ and TiO$_2$ was crucial for the active aggregation of iron oxides in the reduction process and microstructure Ti–Fe phase separation by microwave heating.

4. The main power source for microstructure Ti–Fe phase separation and Fe$^0$ phase active aggregation in the reduction process of titanomagnetite by microwave heating was physical thermal stress generated in phase interface (Fe$_3$O$_4$, TiO$_2$) and ampere traction force generated in iron oxides and Fe$^0$.

Acknowledgments

This work was supported by National Key R&D Program of China (2018YFC1900500); Yunnan Province Special Key Project of Basic Research (202101AS070014); Science and Technology Major Project of Yunnan Province (202202AG050007); the Key Disciplines of Liupanshui Normal University (LPSSYZDXX202001).
References


58) **Source**: [http://www.vias.org/encyclopedia/phys_dielectric_const.htm](http://www.vias.org/encyclopedia/phys_dielectric_const.htm).


Figure list

Graphical abstract

Figure 1. a-XRD patterns, b-SEM, and c-XPS analysis results of TC

Figure 2. Schematic of a-microwave heating equipment and b-conventional heating equipment (a-1: Console; a-2: Anti-microwave leakage metal shell; a-3: Microwave heating cavity; a-4: Thermocouple temperature measuring hole; a-5: Inlet and outlet holes; a-6: Magnetron; a-7: Wave transmitting insulation material; a-8: Support platform; b-9: Water cooling inlet pipe; b-10: Water cooling outlet pipe; b-11: Atmosphere inlet pipe; b-12: Atmosphere outlet pipe; b-13: Heating cavity; b-14: Temperature control table)

Figure 3. Dielectric parameter test equipment (1: Test area; 2: Vector network analyzer; 3: Data output port; 4: Transformer; 5: Control panel; 6: Water cooler; 7: Air pump; 8: Heating area and pneumatic lifting control system; 9: Cylindrical resonator; 10: Sectional view of the cylindrical resonator)

Figure 4. Schematic of iron oxide reduction reaction and the calculation results of activation energy. (a: TC; b/c: Lattice structure of iron oxide (e.g. Fe₃O₄); d: Reduction system; e: Step reduction of simplified iron oxide models (Fe³⁺→Fe²⁺→Fe₂O³⁺→Fe⁰⁺); TS is the transition state with the relative highest energy level in the reduction process; f/g/h: Calculation results of each step)

Figure 5. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy-level analysis of step-by-step reduction reaction of iron oxide in the reduction process of MTC (a/b/c) and the orbit matching (d) in the reactions

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Figure 7. a: Dielectric constant ε', b: dielectric loss ε'', c: loss tangent tan δ, and d: penetration depth D_p of TC mixed with different amounts of pulverized coal (0–20 wt.%) from room temperature to 1000°C

Figure 8. Dielectric parameters of a: Fe₂O₃, b: Fe₃O₄, c: TiO₂, and d: SiC as functions of temperature, and e: dielectric constant and f: dielectric loss of Fe₂O₃, Fe₃O₄, TiO₂, and SiC at room temperature

Figure 9. Microwave heating behavior of MTC and SiC (2450 MHz)

Figure 10. Scanning path of a: Fe₂O₄ (FCC), c: Fe₂O₃ (RHL1), and e: TiO₂ (BCT2); DOS and energy band structure of b: Fe₃O₄, d: Fe₂O₃, and f: TiO₂

Figure 11. Ti–Fe phase separation effects (a: conventional heating; b: microwave heating) and c: microwave-
enhanced Ti–Fe phase separation mechanism in the reduction process.

**Figure 12.** Comparison of microstructure Ti–Fe phase separation effects in the reduction process under different heating conditions (a: microwave heating: 1200°C; b: conventional heating: 1300°C)

**Figure 13.** Reduction direction of TC by microwave and conventional heating methods based on the reduction difficulty coefficient, $H$ (Table 5)
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Table 3. Industrial analysis of pulverized coal for the reduction

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Table 5. Average molar formation enthalpy per unit oxygen of iron oxides, titanium iron oxides in the temperature range of 25°C–1400°C, and corresponding reduction difficulty coefficient.

Table 6. Calibration results of the dielectric testing system in Figure 3 (2450 MHz/25°C)

Table 7. Crystal structure parameters involved in the energy band and the electron density of states calculation

Table 8. Comparative analysis of the lattice stability, dielectric properties (room temperature), and energy band structure of Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_{3-x}$Ti$_x$O$_4$(x = 0.476), and TiO$_2$
Graphical Abstract

2087x1116mm (72 x 72 DPI)
Figure 1. a-XRD patterns, b-SEM, and c-XPS analysis results of TC

515x597mm (149 x 149 DPI)
Figure 2. Schematic of a-microwave heating equipment and b-conventional heating equipment (a-1: Console; a-2: Anti-microwave leakage metal shell; a-3: Microwave heating cavity; a-4: Thermocouple temperature measuring hole; a-5: Inlet and outlet holes; a-6: Magnetron; a-7: Wave transmitting insulation material; a-8: Support platform; b-9: Water cooling inlet pipe; b-10: Water cooling outlet pipe; b-11: Atmosphere inlet pipe; b-12: Atmosphere outlet pipe; b-13: Heating cavity; b-14: Temperature control table)

$m_{\text{Ore}} : m_{\text{Coal}} = 4:1$
Figure 3. Dielectric parameter test equipment (1: Test area; 2: Vector network analyzer; 3: Data output port; 4: Transformer; 5: Control panel; 6: Water cooler; 7: Air pump; 8: Heating area and pneumatic lifting control system; 9: Cylindrical resonator; 10: Sectional view of the cylindrical resonator)
Figure 4. Schematic of iron oxide reduction reaction and the calculation results of activation energy. (a: TC; b/c: Lattice structure of iron oxide (e.g. Fe3O4); d: Reduction system; e: Step reduction of simplified iron oxide models (Fe3+→ Fe2+→ Fe2O2+→ Fe0); TS is the transition state with the relative highest energy level in the reduction process; f/g/h: Calculation results of each step)
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Figure 7. a: Dielectric constant $\varepsilon_r'$, b: dielectric loss $\varepsilon_r''$, c: loss tangent $\tan\delta$, and d: penetration depth $D_p$ of TC mixed with different amounts of pulverized coal (0–20 wt.%) from room temperature to 1000°C.
Figure 8. Dielectric parameters of a: Fe2O3, b: Fe3O4, c: TiO2, and d: SiC as functions of temperature, and e: dielectric constant and f: dielectric loss of Fe2O3, Fe3O4, TiO2, and SiC at room temperature.
Figure 9. Microwave heating behavior of MTC and SiC (2450 MHz)

MTC (coal: 20%)
(2kW, 48g)

SiC
(2kW, 48g)

Temperature (°C)

Time (s)

Figure 9. Microwave heating behavior of MTC and SiC (2450 MHz)
Figure 10. Scanning path of a: Fe$_3$O$_4$ (FCC), c: Fe$_2$O$_3$ (RHL1), and e: TiO$_2$ (BCT2); DOS and energy band structure of b: Fe$_3$O$_4$, d: Fe$_2$O$_3$, and f: TiO$_2$. 

1972x2271mm (72 x 72 DPI)
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Figure 13. Reduction direction of TC by microwave and conventional heating methods based on the reduction difficulty coefficient, H (Table 5)

237x237mm (72 x 72 DPI)
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<thead>
<tr>
<th>Materials</th>
<th>Heating effect and function</th>
<th>Heating mechanism</th>
<th>Reference</th>
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</thead>
<tbody>
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<td>Waste tobacco stem</td>
<td>Dehydration and expansion to improve the quality of tobacco stems</td>
<td>Dielectric heating of water</td>
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<tr>
<td>Spent activated carbon supported mercuric chloride catalysts</td>
<td>Reduce the surface adsorption energy of activated carbon and strengthen the mercury removal process</td>
<td>Local conductive heating of carbon</td>
<td>43)</td>
</tr>
<tr>
<td>Biomass</td>
<td>Oil and gas extraction, structural carbonization</td>
<td>Dielectric heating of water and organic substance</td>
<td>44)</td>
</tr>
<tr>
<td>Plastic waste</td>
<td>Oil and gas extraction, polymer catalytic decomposition</td>
<td>Dielectric heating of inorganic materials</td>
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<td>Titanomagnetite</td>
<td>Microstructure separation of titanium and iron</td>
<td>Dielectric and local conductive heating of the ore</td>
<td>This work</td>
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Table 2. Chemical composition analysis of TC

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<th>Ore</th>
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<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
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<td>Parameter 1</td>
<td>Parameter 2</td>
<td>Formation enthalpy</td>
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<tr>
<td>TiO₂</td>
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<td>$B' = 175.42$</td>
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<tr>
<td>FeO</td>
<td>$c = 1.476$</td>
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**Formula 1**  
$$\Delta H = a \Delta H_{\text{TiO}_2} + a \Delta H_{\text{Fe}_2\text{O}_3} + a \Delta H_{\text{FeO}} + \Delta \text{H}$$

**Formula 2**  
$$\Delta H = aA + bB + cC + \frac{a(b + c)}{a + b + c}A' + \frac{b(a + c)}{a + b + c}B' + \frac{c(a + b)}{a + b + c}C'$$
Table 5. Average molar formation enthalpy per unit oxygen of iron oxides, titanium iron oxides in the temperature range of 25°C–1400°C, and corresponding reduction difficulty coefficient.

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<tr>
<th></th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Fe₃O₄</th>
<th>Fe₃₋ₓTiₓO₄</th>
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<th>Fe₂TiO₄</th>
<th>FeTiO₃</th>
<th>FeTi₂O₅</th>
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<td>-270.16</td>
<td>-273.58</td>
<td>-305.61</td>
<td>-348.78</td>
<td>-376.02</td>
<td>-444.11</td>
<td>-464.81</td>
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<tr>
<td>H (%)</td>
<td>85.84%</td>
<td>88.00%</td>
<td>89.52%</td>
<td>100.00%</td>
<td>114.13%</td>
<td>123.04%</td>
<td>145.32%</td>
<td>152.09%</td>
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</table>

ΔfH - Average molar formation enthalpy in the temperature range of 25-1400°C; n-Subscript number in chemical formula; H - reduction difficulty coefficient according to ΔfH/n (taking the H of Fe₃₋ₓTiₓO₄ as 100%)
Table 6. Calibration results of the dielectric testing system in Figure 3 (2450 MHz/25°C)

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>$\varepsilon_r^\prime$</th>
<th>$\varepsilon_i^\prime$</th>
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<td>Air</td>
<td>Reference</td>
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<td>Water</td>
<td>Reference</td>
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<td>Reference</td>
<td>76.66</td>
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<td>Measured</td>
<td>78.19</td>
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**Table 7.** Crystal structure parameters involved in the energy band and the electron density of states calculation

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Space group</th>
<th>Coll code</th>
<th>Crystal type</th>
<th>Crystal cell structure diagram</th>
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<td>Fe$_3$O$_4$</td>
<td>FD-3MZ</td>
<td>20596</td>
<td>Magnetite</td>
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<tr>
<td>TiO$_2$</td>
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<td>9852</td>
<td>Anatase</td>
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Table 8. Comparative analysis of the lattice stability, dielectric properties (room temperature), and energy band structure of Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_{3-x}$Ti$_x$O$_4$($x = 0.476$), and TiO$_2$

<table>
<thead>
<tr>
<th></th>
<th>Fe$_2$O$_3$</th>
<th>Fe$_3$O$_4$</th>
<th>Fe$_{3-x}$Ti$_x$O$_4$</th>
<th>TiO$_2$</th>
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<tbody>
<tr>
<td>Lattice stability</td>
<td>Stable</td>
<td>More stable</td>
<td>Most stable</td>
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<tr>
<td>(Bonding energy)</td>
<td>(3662 kJ/mol)</td>
<td>(4936 kJ/mol)</td>
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<td>Oxygen atom stability</td>
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<td>(Bonding energy per O)</td>
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<td>(1234 kJ/mol)</td>
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<td>Reduction difficulty ($H$)</td>
<td>Hard (88%)</td>
<td>Harder (89.52%)</td>
<td>Hardest (100%)</td>
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<tr>
<td>($\varepsilon_r, \varepsilon_r'$)</td>
<td>Small (3.3,0.08)</td>
<td>Largest (20.0,3.4)</td>
<td>Larger (8.5,1.42)</td>
<td>Smallest (2.8,0.04)</td>
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<td>Energy band structure</td>
<td>Conduction band</td>
<td>Conduction band</td>
<td>Conduction band</td>
<td>Band gap: 2.14 eV</td>
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Note: The conduction band indicated the existence of free electrons which from the d orbital of Fe atoms.