研究简报

γ-Fe_2O_3 纳米粉的低热固相制备及其电磁损耗特性

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γ-Fe_2O_3 Nanoparticle Prepared by Solid-State Reaction at Low Heating and Its Electromagnetic Characters

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The $Fe(OH)_3$ precursor was prepared by solid -state reaction with $Fe(NO_3)_3 \cdot 9H_2O$, NaOH and dispersed polyethylene glycol at low heating temperature(25 ℃). Synthesis of iron oxide (γ-Fe_2O_3) nanoparticle was achieved by thermal decomposition of $Fe(OH)_3 \cdot xH_2O$ precursor. The nanoparticle was characterized by TG-DTA, X-ray diffraction, TEM *etc*. The results showed that the nanoparticle was composed of γ-Fe_2O_3 and was a better absorber for electromagnetic wave within the low frequency band.

Keywords: **nanoparticle** **γ-Fe_2O_3** **solid-state reaction** **dielectric constant** **magnetic permeabilit**

Nanoparticle refers to the particulate, whose diameter is between 1nm and 100 nm. It is widely applied to the chemical industry, environmental protection, public hygiene, electronic product and catalyzer *etc*. because of its unusual physical and chemical characters that are different from the macroscopic material[1]. Fe_2O_3 is one of the general materials, in that it can be used as pigment, magnetic material, gas-sensing material and nonlinearized optic material[2,3]. Fe_2O_3 nanoparticle Langmuir-Blodgett film can detect ethanol vapor down to 15 ppm[2]. The sol-gel method is primarily used to prepare the ferric oxide, although this method can prepare chemically homogeneous products, it also takes several hours, even ten hours, to form the sol and gel[4]. Compared with the sol-gel method, the solid-state reaction at low heating has many advantages, such as great efficiency, high productivity and high selectivity, and can synthesize the material that cannot be synthesized in the liquid phase or stably existed in liquid phase. The solid-state

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reaction with low heating has become one of the most important methods for preparing nanoparticles.

1 Experiment

1.1 Materials and Synthesis

Starting materials are $Fe(NO_3)_3 \cdot 9H_2O$, polyethylene glycol and NaOH. They are of analytical purity. 8.08 g of $Fe(NO_3)_3 \cdot 9H_2O$ and 2.40 g of NaOH according to 1:3 molar rate were mixed with 5 mL polyethylene glycol (molecular weight: 1 000~2 500) in a mortar, for 30 minutes. Then, the red brown precursor can be obtained. In order to remove unreacted reactants, polyethylene glycol and by-products, the precursor was washed several times with distilled water and absolute alcohol, and then dried in freeze dryer for 8~12 hours. The obtained precursor was decomposed at 300 ℃ for 2 hours according to the result of TG-DTA, with a Germanic Netzsch STA 449C thermal analyzer.

The reactions are as follows:

$$Fe(NO_3)_3 \cdot 9H_2O + 3NaOH = Fe(OH)_3 \cdot xH_2O + 3NaNO_3 + (9-x)H_2O \quad (1)$$

$$2Fe(OH)_3 \cdot xH_2O = Fe_2O_3 + (3+2x)H_2O \quad (2)$$

During the reaction (**1**), we can observe the phenomenon that the interfaces of the reactants change their colors when they touch each other and release some white fog. This is because that the reactants react with each other and emit the crystal water contained in reactants. At the same time, the water is evaporated by the thermal emitted during the reaction and forms the fog.

1.2 Characterization

The as-prepared product was identified by X-ray powder diffraction (XRD) employing a scanning rate of 4.00°·min^{-1} in a 2θ range from 3° to 70°, using a Japanese Rigaku D/max-Ⅲ A X-ray diffractometer equipped with graphite monochromatize Cu$K\alpha$ radiation. The morphology and dimension of the product were observed by Japanese transmission electron microscopy (TEM), which was taken on a H-800 transmission electron microscopy and laser granularity analyzer (MasterSizer 2000), form Malvern Instruments Ltd. The dielectric constant and magnetic permeability of the as-made product was also characterized by Agilent-HP429 1B.

2 Results and Discussion

Fig.1 presents some results from TG-DTA, at temperature from 30 ℃ to 1000℃ at ramp of 10.0 ℃·min^{-1}. The precursor lost its adsorbed ethanol and adsorbed water at 30 ℃ to 77.5 ℃, and the residual polyethylene glycol also decomposed at the same range, so there was an exothermic peak. At the range of 77.5 ℃ to 146.3 ℃, the precursor lost its crystal water, and then the precursor was broken down into γ-Fe_2O_3 at the range of 146.3 ℃ to 495.8 ℃. There is an exothermic peak at 281.2 ℃ in Fig.1 and just at this point, the precursor is decomposed. Within the range of 495.8℃ to 679.8 ℃, γ-Fe_2O_3 changes into α-Fe_2O_3. Macroscopic γ-Fe_2O_3 can directly change into α-Fe_2O_3 at about 400 ℃[5], but if the diameter of γ-Fe_2O_3 was very small, the temperature at which γ-Fe_2O_3 changes into α-Fe_2O_3 would notablely went up because of the intermediate structure ε-Fe_2O_3 [6]. According to the result of TG-DTA, we select 300 ℃ as the decomposed temperature of the precursor.

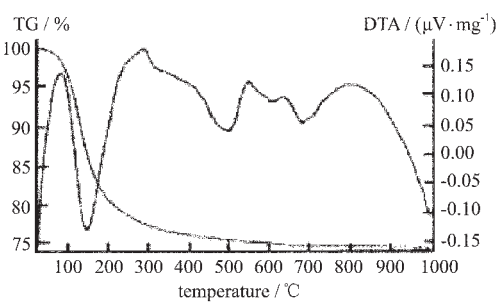

Fig.1 TG-DTA curve of precursor

Fig.2 shows the XRD of the prepared product by thermal decomposition of the precursor of ferric hydroxide $Fe(OH)_3$. Its diffraction peak is quite consistent with the standard JCPDS card of γ-Fe_2O_3. In addition, no characteristic peaks of impurities such as $NaNO_3$, $Fe(OH)_3$ and other precursor compounds were found, this demonstrates that the prepared product is pure phase maghemite γ-Fe_2O_3.

The particle size distribute of γ-Fe_2O_3 is showed in Fig.3. About 85 percent of γ-Fe_2O_3 particle is un-

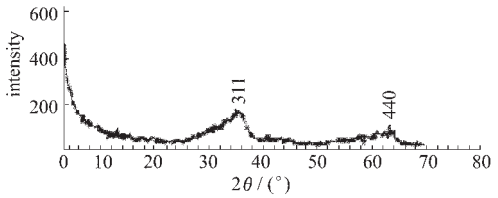

Fig.2　XRD pattern of precursor

der 100 nm and the average dimension is around 70nm in diameter. The particle is so small that the X-ray diffraction peak is widened, as shown in Fig.2.

The TEM morphology of the prepared product is illustrated in Fig.4. Bar length is 125 nm. It can be seen that the product mainly consists of solid ball-like structures. The diameter of the particle, as shown in Fig.4, is within a range from 60 nm to 80 nm. That result is consistent with the one shown in Fig.3.

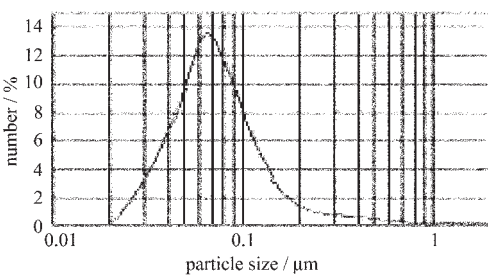

Fig.3　Size distribute of γ-Fe_2O_3

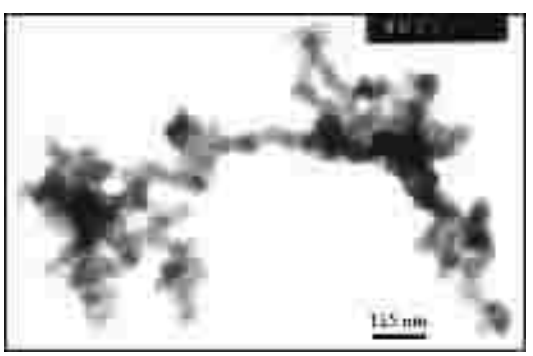

Fig.4　TEM image of γ-Fe_2O_3

Maghemite is one kind of ferrites, with plural dielectric constant and plural magnetic permeability. The primary principle of ferrites′ absorbing electromagnetic wave is that they can convert the energy of electromagnetic wave to some other forms, such as heat energy. The wastage mainly includes dielectric wastage and magnetic wastage. The loss of energy can be characterized by loss tangent[7], which is given by:

$$\mathrm{tg}\delta = \mathrm{tg}\delta_e + \mathrm{tg}\delta_m = \frac{\varepsilon_r''}{\varepsilon_r'} + \frac{\mu_r''}{\mu_r'} \quad (3)$$

where

$\mathrm{tg}\delta_e$ = dielectric loss tangent,

$\mathrm{tg}\delta_m$ = magnetic loss tangent,

ε_r', ε_r'' = real part and imaginary part of relative dielectric constant,

μ_r', μ_r'' = real part and imaginary part of relative magnetic permeability.

Hence, the loss of energy increases with increasing ε_r'' and μ_r''.

To measure the dielectric constant and magnetic principle of the prepared product, we must shape the prepared powder into tablet and cirque. Fig.5 shows the dielectric loss tangent and the magnetic loss tangent of γ-Fe_2O_3 at different frequency. According to the figures, it is obvious that the dielectric loss tangent decreases with increasing frequency, while the magnetic loss tangent increases. It demonstrates that the dielectric loss decreases with increasing frequency and the magnetic loss increases with increasing frequency. Fig.6 shows the loss tangent of prepared

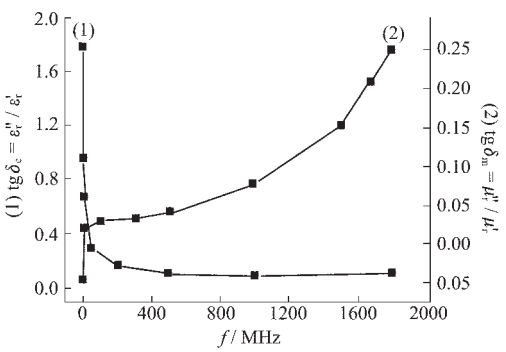

Fig.5　$\mathrm{tg}\delta_e$ and $\mathrm{tg}\delta_m$ of γ-Fe_2O_3

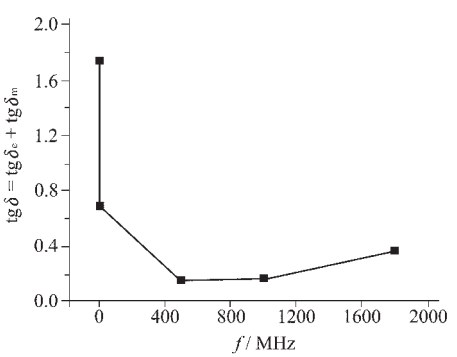

Fig.6　$\mathrm{tg}\delta$ of γ-Fe_2O_3

product at different frequencys. The loss tangent decreases with the increasing frequency. It gets the maximum 1.72 at lower frequency band and decreases to the minimum 0.16 at around 500 MHz and then increases slowly. That is, the γ-Fe_2O_3 can be used as a electromagnetic wave absorber at lower frequency band.

3 Conclusions

In summary, nanoparticle with diameter of 60~70 nm has been successful synthesized by solid-state reaction with low heating method. The morphology of as-prepared γ-Fe_2O_3 is ball-like. The loss tangent of maghemite γ-Fe_2O_3 at the lower frequency band is bilarger and can be applied to electromagnetic wave absorber.

References

[1] Zhang Zhikun, Cui Zuolin *Nanometer Technology and Nanometer Material*, 1st ed. The National Defense Industry Publishing House: Beijing, **2000**,Chap.4,p160.

[2] Lihua Huo, Wei Li, Lehui Lu *Chem. Mater.*, **2000**,**12**,790.

[3] KurikkaV. P., Shafi M., Abraham U., Ansil D. et al. *Chem. Mater.*, **2002**,**14**,1778.

[4] Niu Xinshu, Xu Hong *Chinese J. of Applied Chemistry*, **2000**,**17**(6),611.

[5] Cornel R. M., Schwertman U. *The Iron Oxides. Structure, Properties, Reactions and Uses*, VCH: Weinheim, **1996**.

[6] Tronc E., Chaneac C., Jolivet J. P. *J. Solid State Chem.*, **1998**,**139**,93.

[7] Kvnsrt U. K. et al., Translated by Cai Delu et al. *Material for Microwave Absorbing*, Science Publish House, **1985**.