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Synthesis of strong-magnetic nanosized black pigment $Zn_xFe_{(3-x)}O_4$

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Abstract

In this paper, $Zn_xFe_{(3-x)}O_4$ ($0 \leq x \leq 0.5$), nanosized magnetic black pigments, were synthesized using phase transformation at 70 °C. It was found that the specific saturation magnetization intensity and color properties of the pigments were improved by the addition of Zn^{2+} in the preparation of Fe_3O_4, especially, when the value of x is 0.1, the properties of pigment prepared are best, with bigger specific saturation magnetization intensity valued 86.92 $A\ m^2\ kg^{-1}$ and more atrous color with Munsell marking N 0.01 /, and the sample particles are of uniform distribution and nearly spherical shape with the mean size of about 10.1 nm.

Keywords: Method of phase transformation; $Zn_xFe_{(3-x)}O_4$; Nanometer; Black pigments; Magnetism

1. Introduction

Fe_3O_4 is a significant spinel ferrite [1] and enjoys a wide range of applications in many fields such as in the manufacture of paints and printing inks thanks to its easy preparation and the low price of the raw materials employed in its synthesis. Nanosized Fe_3O_4 magnetic pigments can disperse fully and suspend readily in liquids due to the extreme fineness of the pigment particles as well as the function of surfactant. The properties of a magnetic printing ink comprising such magnetic particles can be improved greatly. The magnetism of a magnetic pigment is related to the particle size of the pigment grains; the larger the particle size, the stronger is the magnetism of the pigment, even though large particle size may lead to printing ink instability. Although the stability of a magnetic printing ink, formulated using small size magnetic grains, can be improved, its magnetism may be weak. Therefore, the synthesis of Fe_3O_4 magnetic pigment of both strong magnetism and small size is the key to the provision of printing inks with good characteristics. In addition, nanosized Fe_3O_4 can be used in, for example, microwave absorption [2], catalysis [3], biomedical areas [4–6] and manufacturing magnetic records [7]. Many methods for the synthesis of nanosized Fe_3O_4 powder have been reported in the literature[8–12], in the paper the method of phase transformation at low temperature was used to prepare black pigment $Zn_xFe_{(3-x)}O_4$($0 \leq x \leq 0.5$).

2. Experimental

2.1. Preparation of samples

NaOH (3 mol L^{-1}) solution was heated in a water bath and, when its temperature had reached 70 °C, a mixture of $FeSO_4$, $FeCl_3$ and $ZnSO_4$ was added with stirring, in the mole ratio of $[n(Zn^{2+}) + n(Fe^{2+})]/n(Fe^{3+}) = 1/2$, so as to make the products meet the general expression AB_2O_4 of spinel compound.

The reaction was allowed to proceed for 1 h at 70 °C with constant stirring after which time, the precipitate was washed with de-ionized water until no other impurity ions such as Cl^- and Na^+ remained. Then the products were treated in the following steps: filtered using filter paper on the condition of pressure reduction, dried by vacuum drier at 60 °C, and finally ground using agate mortar box.

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2.2. Characterization of samples

The crystal phase structure of $Zn_xFe_{(3-x)}O_4$ ($0 \le x \le 0.5$) was investigated using a BDX-3300 X-ray diffractometer (XRD). A transmission electron microscope (TEM), (JEOL 100CX-II) was used to characterize the $Zn_xFe_{(3-x)}O_4$ powders with respect to particle size and shape. Magnetic properties were examined at room temperature using an LDJ Vibrating Sample Magnetometer (VSM). The hydroxy compound was analysed using WTC-1 differential thermal analysis (DTA) and thermogravimetry (TG). The color characteristics were measured using a JFY-PS color analysis apparatus under illuminant D_{65}.

3. Results and discussion

3.1. The synthesis of nanosized $Zn_xFe_{(3-x)}O_4$ magnetic pigments

Fig. 1 shows the X-ray diffraction pattern for sample 1. All the peak positions are consistent with the standard data of Fe_3O_4 structure (JCPDS card file No. 3-863), without other unexpected peaks being present. This shows that the sample prepared using this method was pure. According to Scherrer's formula, using peak width at half-height of the X-ray diffraction, the mean particle size of the sample was 7.8 nm.

At the same time it can also be seen from the TEM photograph of sample 2 (Fig. 2) that the particle size, about 10 nm, was small, which is consistent with the results estimated by Scherrer's formula. The sample grains were of uniform distribution and nearly spherical shape with no obvious aggregation.

At low temperature, with the exception of $Fe(OH)_3$ that is produced by the reaction between Fe^{3+} ion and NaOH, FeOOH will also be partly produced, which can be concluded from the TG curve (Fig. 3) for the hydroxide compound formed between Fe^{3+} and NaOH at 70 °C. Total water loss ratio was 17.4% for the hydroxide compound; moreover, $Fe(OH)_3$ and FeOOH lost water completely and became Fe_2O_3, having water loss ratios of 25.2% and 10.1%, respectively. So it can be concluded that the ratio of FeOOH:-$Fe(OH)_3$ in the hydroxide compound was 1.08:1, that is, the molecule number ratio was 1.3:1, from which it is evident that FeOOH formed a large part of the hydroxide compound.

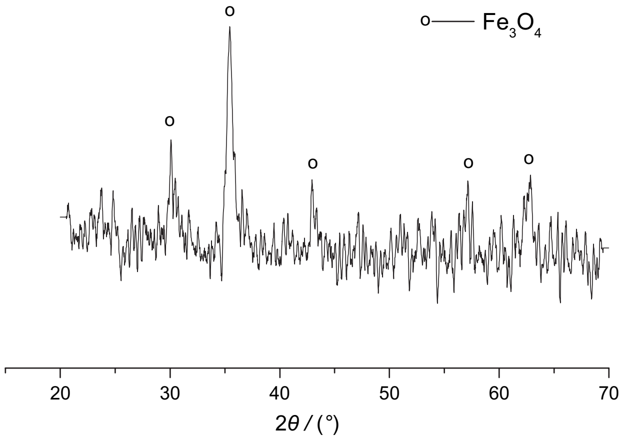

Fig. 1. X-ray diffraction pattern for Fe_3O_4.

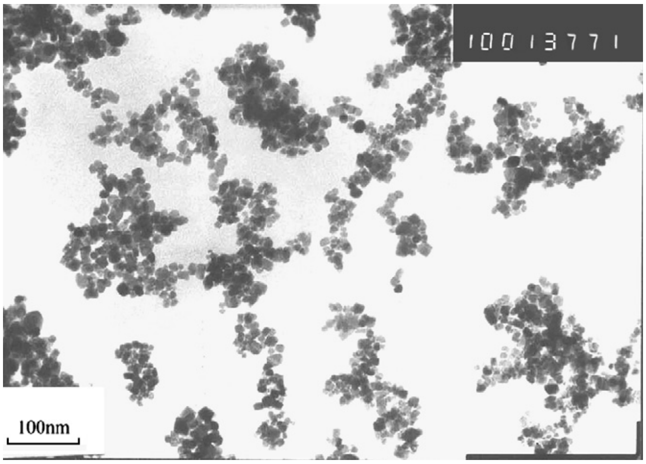

Fig. 2. TEM image for the sample 2.

In the preparation of Fe_3O_4 using phase transformation, the following reactions may take place:

$$2FeOOH + Fe(OH)_2 \longrightarrow Fe_3O_4 + 2H_2O$$

$$2Fe(OH)_3 + Fe(OH)_2 \longrightarrow Fe_3O_4 + 4H_2O$$

In phase transformation, alkaline solution was heated to reaction temperature and to this was then added the solution containing metal ions; the reaction finished soon, which could be seen from the color of the reaction solution turning black. Therefore, the method is suitable for the preparation of super fine powders. When Zn^{2+} were used in pigment production, the reaction of $Zn_xFe_{(3-x)}O_4$ occurred as follows:

$$2FeOOH + xZn(OH)_2 + (1-x)Fe(OH)_2 \longrightarrow Zn_xFe_{(3-x)}O_4 + 2H_2O$$

$$2Fe(OH)_3 + xZn(OH)_2 + (1-x)Fe(OH)_2 \longrightarrow Zn_xFe_{(3-x)}O_4 + 4H_2O$$

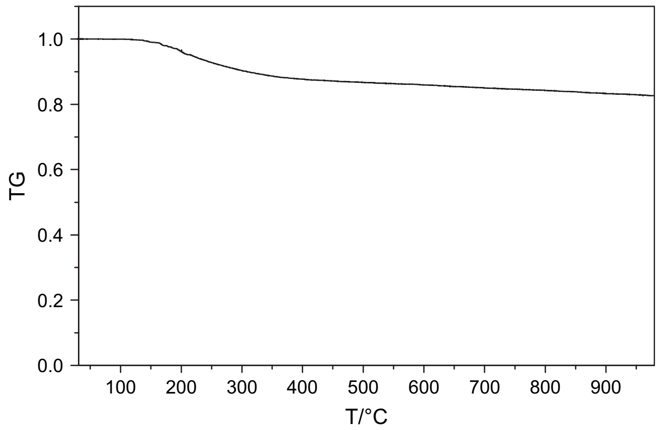

Fig. 3. TG curve of the sample.

3.2. Impact of Zn^{2+} on the magnetism of $Zn_xFe_{(3-x)}O_4$ pigment

As can be seen from Table 1, the specific saturation magnetization intensity σ_s increased with the increase of x (the amount of Zn^{2+}) at first, and then decreased with further increase of x when above 0.2. Based on the crystal lattice structure of the Fe_3O_4 subferromagnet and its mechanism of magnetism [13], $Zn_xFe_{(3-x)}O_4$ was formed during the preparation of Fe_3O_4 in the presence of added Zn^{2+}. The ionic distribution of the compound ferrite was $(Fe^{3+}_{(1-x)}Zn^{2+}{}_x)$ $[Fe^{3+}_{(1+x)}Fe^{2+}_{(1-x)}]O_4$, the parenthesis and square brackets expressing a tetrahedral cavity (site A) and octahedral cavity (site B) of spinel, respectively. Generally, ions occupying the same type of site have the same orientation of magnetic moment, while the orientation of magnetic moment of site A is opposite to that of site B. The net magnetic moment of the $Zn_xFe_{(3-x)}O_4$ molecule is the difference between the total magnetic moment of ions located in sites B and A, and Zn^{2+} is the nonmagnetic ion with zero magnetic moment, so the net magnetic moment can be represented as follows:

$$\mu = [5(1+x) + 4(1-x) - 5(1-x)]\mu_B$$
$$= (4+6x)\mu_B \ (\mu_B \text{ referring to Borel magneton})$$

When x is small, the nonmagnetic Zn^{2+} ion enters site A and leads to an equal amount of Fe^{3+} ion in site B, which will make the net magnetic moment of the $Zn_xFe_{(3-x)}O_4$ molecule increase with increasing value of x. As a result, the specific saturation magnetization intensity of the sample increases with the value of x, also. In contrast, when x is large, the super exchange operation among ions in sites A and B will be weakened due to more Zn^{2+} ion entering site A, resulting in a reverse parallel array of magnetic moment within the ions in sites A and B. Meanwhile, the exchange operation between Fe^{2+} ions (B site) and Fe^{3+} ions (B site) will be boosted up because of an increase in the number of Fe^{3+} ions (B site) resulting from Zn^{2+} replacing Fe^{2+} (B site) as well as the ion exchange between Zn^{2+} (B site) and Fe^{3+} (A site), which results in magnetic moment of part ions in site B, with the enhancement of exchange operation between Fe^{2+} ions (B site) and Fe^{3+} ions (B site), tending to be reverse parallel array from parallel array originally.

Therefore, the net magnetic moment of the $Zn_xFe_{(3-x)}O_4$ molecule will not increase any more, but, instead, will decrease with increasing value of x, and the specific saturation magnetization intensity of the sample also weakens for the increase of Zn^{2+} in the $Zn_xFe_{(3-x)}O_4$. Obviously, when x equals 1, $Zn_xFe_{(3-x)}O_4$ will become the nonferromagnetic $ZnFe_2O_4$, with zero value of net magnetic moment of the $Zn_xFe_{(3-x)}O_4$ molecule. Comparing the values of σ_s in Table 1, it is apparent that σ_s values for samples 2, 3 and 4 were large, which shows that these pigments have a strong magnetic moment, when values of x range from 0.1 to 0.3. Furthermore, the values of coercivity (Hc), compared with 10000 Oe outside magnetic field, and magnetizability (σ_r) for the three samples were very small, which shows that 2, 3 and 4 display superparamagnetism [14].

Table 1
The magnetic characteristics of $Zn_xFe_{(3-x)}O_4$ pigments

Sample no.	x	σ_s ($A\ m^2\ kg^{-1}$)	Hc (Oe)	σ_r ($A\ m^2\ kg^{-1}$)
1	0	59.18	6.491	0.5602
2	0.1	86.92	11.77	1.421
3	0.2	98.72	8.044	1.155
4	0.3	91.54	3.728	0.4676
5	0.4	57.52	3.923	0.3031
6	0.5	55.87	4.041	0.2160

3.3. Impact of ZN^{2+} on color properties of $Zn_xFe_{(3-x)}O_4$ pigment

The X, Y, Z, lightness and Munsell values (Table 2) reveal that sample 2, with a Munsell rating N of 0.01/, was the best black pigment among the samples.

According to the theory of color generation via electric charge transfer [15], the blackness of Fe_3O_4 results from the transferring of electric charges between Fe^{3+} and Fe^{2+} ions in different crystal lattices of the Fe_3O_4 crystal structure. In this process, the energy changes correspond to light absorption; this can be expressed as follows:

$$\left(Fe^{2+}\right)\left[Fe^{3+}Fe^{3+}\right]O_4 \xrightarrow{\text{light}} \left(Fe^{3+}\right)\left[Fe^{2+}Fe^{3+}\right]O_4$$

$$Fe^{2+}_A + Fe^{3+}_B \xrightarrow{\text{light}} Fe^{3+}_A + Fe^{2+}_B \tag{1}$$

With the Zn^{2+} added in the preparation of Fe_3O_4, Table 2 shows that the black color of sample 2 is further enhanced compared to sample 1. This stems from the strong tendency of Zn^{2+} taking up site A, and turns some Fe^{3+} ions in site A of $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$ (namely Fe_3O_4) into Zn^{2+}. This process can be expressed as follows:

$$\left(Fe^{3+}\right)\left[Fe^{2+}Fe^{3+}\right]O_4 \xrightarrow{xZn^{2+}} \left(Zn^{2+}_x Fe^{3+}_{(1-x)}\right)\left[Fe^{2+}_{(1-x)}Fe^{3+}_{(1+x)}\right]O_4$$

In this process, the transfer of electronic charge, imparted by the Zn^{2+} ions, also occurs (Eq. (2)) with the electronic charges transferred (Eq. (1)) at the same time

$$xFe^{3+}_A + xFe^{2+}_B \xrightarrow{\text{light}} xFe^{2+}_A + xFe^{3+}_B \xrightarrow[-xFe^{2+}_A]{+xZn^{2+}} xZn^{2+}_A + xFe^{3+}_B \tag{2}$$

In the same way, the transfer of electronic charge leads to a change in energy and, therefore, light absorption. With increase in the amount of Zn^{2+} ions, the amount of Fe^{2+} ions

Table 2
The color characteristics of $Zn_xFe_{(3-x)}O_4$ pigments

Sample no.	x	D (nm)	Tri-stimulus values			Lightness value	Munsell marking
			X	Y	Z	V_Y	N V/
1	0	7.8	0.060	0.028	0.002	0.02	N0.02/
2	0.1	10.1	0.028	0.014	0.002	0.01	N0.01/
3	0.2	10.4	0.624	0.465	0.018	0.40	N0.40/
4	0.3	8.6	0.457	0.333	0.005	0.28	N0.28/
5	0.4	9.2	0.540	0.404	0.005	0.35	N0.35/
6	0.5	9.8	0.898	0.679	0.004	0.58	N0.58/

participating in the transfer of electronic charges according to Eq. (1) will decrease greatly. Therefore, the color of samples 3, 4, 5 and 6 was not as strong as that of 1. When $x = 1$, $Zn_xFe_{(3-x)}O_4$ will become $ZnFe_2O_4$ $(Zn^{2+})[Fe^{3+}Fe^{3+}]O_4)$, in which no electronic charge transfer can occur between Zn^{2+} ion in site A and Fe^{3+} ion in site B, resulting in the observed brown color. This explains why the blackness of sample 6 ($x = 0.5$) was not as strong as that of the other pigments.

In addition, it is known that the blackness of sample 4 is more atrous than that of sample 3, and sample 5 lies in between, which relates to the particle size of samples prepared. The smaller the particle size of the pigment, the weaker will be the dispersion of light, and the deeper will be the blackness.

In summary, the blackness of the $Zn_xFe_{(3-x)}O_4$ magnetic pigments prepared was related to not only the amount of Zn^{2+} ions added, but also the particle size of the ensuing pigments. From a practical point of view, the magnetism, particle size and color of magnetized pigments can be determined by the amount of Zn^{2+} ion added during the preparation of Fe_3O_4.

4. Conclusions

Nanosized $Zn_xFe_{(3-x)}O_4$ $(0 \leq x \leq 0.5)$ magnetic black pigments were synthesized using phase transformation at 70 °C. The magnetism and color of the pigments were improved by the addition of Zn^{2+} in the synthesis. Pigment 2 ($x = 0.1$) displayed optimum pigment properties, having the largest specific saturation magnetization intensity of $86.92\ \mathrm{A\,m^2\,kg^{-1}}$ and the deepest black color of Munsell rating N 0.01/. The particles obtained were of uniform distribution and almost spherical in shape with a mean size of about 10.1 nm.

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