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Preparation and characterization of brown nanometer pigment with spinel structure

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Abstract

Using an alcohol–water co-precipitation method, brown nanometer pigments with spinel structure were prepared. The relationship between crystallizing temperature and grain size was studied and a series of experiments in which the proportion of alcohol to water was changed were performed and the effect of the alcohol to water ratio on the diameter of obtained particles was analyzed. The $ZnFe_2O_4$ nanometer pigments were characterized by XRD and TEM, and the quantum size effect of the pigment particles was investigated and discussed through IR spectra analysis.

Keywords: Alcohol–water system; Co-precipitation; Nanometer; Spinel pigment; Quantum size effect; $ZnFe_2O_4$

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1. Introduction

The particular surface effect, volume effect and quantum size effect [1–2] become apparent because the ratio of the surface atomicity to the bulk atomicity of nanometer particles increases sharply when the diameter of nanometer particles decrease. Therefore, nanometer particles have a series of new physical chemical characteristics, which makes them have considerable application prospects in adsorption, optics, catalysis, electricity and magnetism, etc. Searching for a suitable preparation method of nanometer particles and studying the structure and other properties of nanometer materials are among the important issues involved for nanometer science applications.

Composite oxides with spinel structure (AB_2O_4) are important inorganic metalloid materials and are widely used in different fields. They are used not only as heat-resistant pigments that can be applied to color up porcelain and ceramics [3], but also as gas-sensitive materials [4], catalytic materials [5], magnetic materials [6] and wave absorption materials [7].

The conventional preparation method of spinel pigments is the solid phase synthesis method under high temperature. The shortfall of this method is that it requires a high calcinatory temperature (1200 °C) which consumes a considerable amount of energy. In addition, not only the diameter of pigments obtained is large but also the granularity distribution is nonuniform, and the pigment particle is hard, which influence the performance of pigments. In this paper, brown nanometer pigments with spinel structure were

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Table 1
Preparation conditions of samples 1–6

Sample No.	Solvent (V_{water} : $V_{alcohol}$)	Precipitant ($V_{ammonia}$: V_{water} : $V_{alcohol}$)	Washing by water	Reflowing	Calcinatory	
					Temperature/°C	Times/h
1	1:1	1:1:1	No	No	500	2
2	1:1	1:1:1	No	No	600	2
3	1:1	1:1:1	No	No	900	2
4	1:1	1:1:1	Yes	Yes	800	2
5	1:0	1:1:0	Yes	No	800	2
6	1:0	1:1:0	Yes	No	800 °C 2 h, 900 °C 1 h continuously	

prepared by an alcohol–water co-precipitation method. Proper preparation conditions were investigated via a series of experiments. At the same time, the nanometer particles obtained were characterized by X-ray powder diffraction (XRD), transmission electronic microscopy (TEM) and infrared spectroscopy (IR). The quantum size effect of the particles was discussed through IR spectra analysis.

2. Experimental

2.1. Synthesis of samples

Raw materials ($ZnCl_2$, AR and $FeC1_3{\cdot}6H_2O$, AR) were weighed according to stoichiometric ratio and were dissolved in the solvent. Controlling the temperature of the water bath at 37 °C, an ammonia solution ($V_{ammonia}$:$V_{water}=1{:}1$, ammonia used is 15 mol l^{-1}) as the precipitant or the mixture of the above ammonia solution and alcohol (95%) was added until the pH value was close to 8–9. At this moment, the composite hydroxide depositions formed. Then they were filtered in vacuum, dried and ground. Following this, they were calcined in a high temperature furnace.

The specific experimental conditions such as the solvent used to get the mixture of $ZnCl_2$ and $FeCl_3{\cdot}6H_2O$ solutions, the precipitant to form the composite hydroxide depositions, whether the depositions should be washed or not, whether the filter cake should be reflowed in 95% alcohol or not as well as the temperature and time for calcination are shown in Table 1. The corresponding samples obtained are marked as Nos. 1–6.

2.2. Change of the proportion of alcohol to water

Different solutions containing $ZnC1_2$ and $FeCl_3{\cdot}6H_2O$ were prepared for varying alcohol to water ratios. A 1:1 by volume ammonia solution was added to the prepared solutions at a bath temperature at 37 °C at one time. Composite hydroxide depositions obtained were washed with water to remove Cl^-, then they were calcined at 900 °C for 2 h. Other conditions are shown in Table 2. The corresponding samples are marked as Nos. 7–11.

2.3. Characterization of samples

Samples obtained by crystallizing at high temperature were analyzed using a BDX-3300 automatic X-ray powder diffractometer to determine their crystal phase, with CuK_α radiation, under 36 kV and 20 mA. The scan range was from 10 to 80° and the scan speed was 8°/min. With the aid of a computer, the Scherrer formula was applied to calculate the diameter of particles.

The shape of particles was observed using a Jeol 100CX-II transmission electronic microscope produced in Japan.

IR spectra was obtained and analyzed using a FTS3000 infrared spectroscope, with wave number ranging from 4000 to 400 cm^{-1}.

Table 2
Other preparation conditions

Sample No.	7	8	9	10	11
The proportion of alcohol to water	8:0	6:2	4:4	2:6	0:8
Reflowing	Yes	Yes	Yes	Yes	No

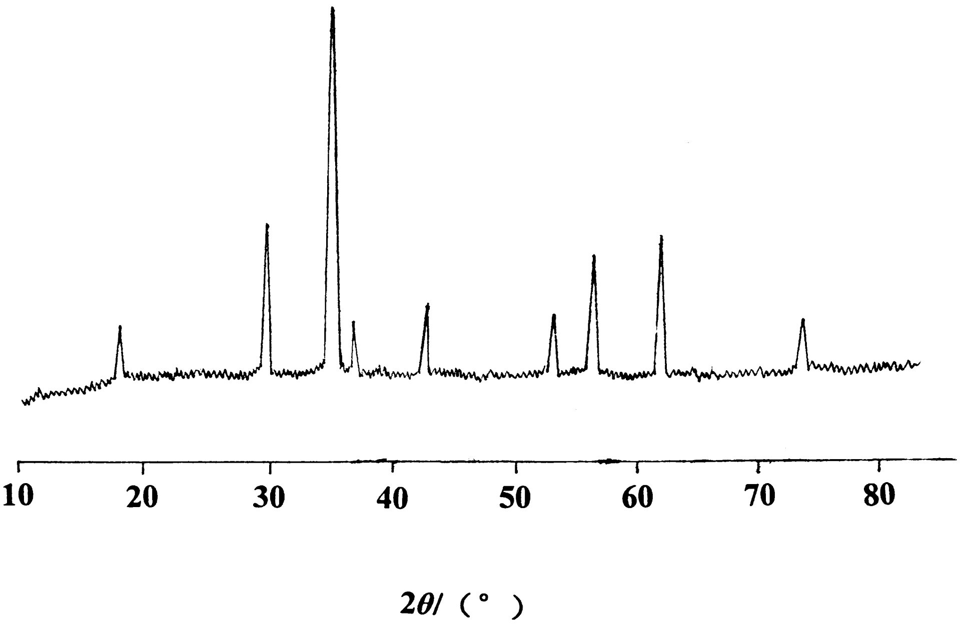


Fig. 1. X-ray diffraction pattern of sample 4.

3. Results and discussion

3.1. *Effect of washing by water on products*

Samples 1 and 2 do not have typical spinel structures by analyzing their X-ray diffraction patterns. Initially, the fact that the calcinatory temperature is not high enough for the spinel structure to be formed is considered as the possible reason. Accordingly, the calcinatory temperature of sample 3 is raised to 900 °C. However, it does not form spinel structure either. Instead, Fe_2O_3 with the trigonal system structure is observed to form by analyzing its X-ray diffraction pattern and comparing the *d* value (interplanar spacing) given by the instrument with that of the Joint Committee on Powder Diffraction Standards (JCPDS) card. One possible reason is that the composite hydroxide depositions are not washed by water, leaving $C1^-$ (the preparation condition in Table 1) that combines with Zn^{2+} to form the compound with the low boiling point —$ZnCl_2$ which volatilizes when the depositions are calcined, resulting in the losing of the component containing Zn. Consequently, samples obtained show a Fe_2O_3 structure rather than the spinel structure. Accordingly, the step of washing the composite hydroxide depositions is added, with other conditions remaining the same. Then the depositions from which NH_4C1 are removed are calcined at 800 °C to prepare sample 4. According to X-ray diffraction pattern (Fig. 1) and the comparison of *d* values with that of JCPDS standard card (22-1012) having the same crystal face index (*hkl*) (Table 3), the

Table 3
Interplanar spacing (*d*) of samples and that from JCPDS card

hkl	111	220	311	222	400	422	511	440	533
d (sample 4)/nm	0.4873	0.2986	0.2546	0.2438	0.2112	0.1724	0.1624	0.1492	0.1287
d (sample 5)/nm		0.3000	0.2554		0.2118	0.1728	0.1627	0.1495	0.1289
d (sample 6)/nm	0.4873	0.2985	0.2545	0.2436	0.2111	0.1723	0.1624	0.1492	0.1289
d (card)/nm	0.4873	0.2984	0.2543	0.2436	0.2109	0.1723	0.1624	0.1491	0.1287

sample obtained is $ZnFe_2O_4$ with a spinel structure. Thus it can be said that the reason for sample 3 having a non-spinel structure is not because the calcination temperature is not high enough, but rather because the composite hydroxide depositions are not washed. The following conclusions can then be drawn: when ammonia is used as the precipitant, impurity (NH_4Cl) will be formed. Although it can be eliminated by calcination, in this experiment, NH_4Cl should be removed by a water washing method before treatment under high temperature. This is in order to avoid the combination of Cl^- and Zn^{2+} and the following volatilization, ensuring the formation of $ZnFe_2O_4$ pigments with a spinel structure.

3.2. Relationship between crystallizing temperature and the grain size

X-ray diffraction patterns of samples 5 and 6 are shown in Fig. 2. Pure water is used as the solvent (from Table 1). As mentioned above, the solvent of sample 4 is a mixture of alcohol and water. Comparison of d values between above samples and JCPDS card (22-1012) with the same crystal face index (hkl) are shown in Table 3. It can be observed that: d values of sample 4 that uses alcohol–water as the solvent and is calcined at 800 °C are consistent with that of standard card, showing that it has a typical spinel structure, while sample 5 that only uses water as the solvent and is calcined at 800 °C does not have a spinel structure. Only when it is further calcined at 900 °C for 1 h can the typical spinel structure be formed (sample 6). It is demonstrated that: using an alcohol–water solvent can lower the crystallizing temperature. Further, by using a peak width at half height, and in the light of the Scherrer formula: $D = k\ \lambda\ / F\cos\theta$ (θ is half angle of difilaction, D is average diameter, k and λ are constants relevant to the instrument, F is the peak width at half height), the diameter of sample 4 is calculated by the computer and it turns out to be 73.4 nm. Analogously, the diameter of sample 6 is 110.8 nm. The following results are obtained: the diameter of sample 4 is small and the crystallizing temperature is low, whereas the diameter of sample 6 is larger and the crystallizing temperature is higher.

3.3. Effect of proportion of alcohol to water on the grain size

The relationship between the diameter and the proportion of alcohol to water from samples 7 to 11 is given in Fig. 3. The following conclusions can be drawn from the figure: the diameter of sample 11 that only uses water as the solvent is large. However, the diameter of samples 7–10 that use alcohol–water as the solvent is smaller compared with that of sample 11. This also yields a particle diameter of 63.1 nm for sample 10, which turns out to be the smallest. TEM photos of samples 10 and 11 are shown in Fig. 4(A) and (B). This demonstrates that the diameter of sample 10, which is prepared by the alcohol–water co-precipitation method is small and the granularity distributes uniformly without apparent aggregation being observed. However, the diameter of sample 11 which is prepared by the water co-precipitation method is large and the granularity distributes nonuniformly, and apparent aggregation is observed. This is because raw materials of the synthesis reaction are inorganic and they dissociate easily in water. When the precipitant is added, a large amount of fine crystal nuclei will be formed. The newly formed nuclei aggregate readily, accounting for the increasing diameter of particles. In contrast, in the alcohol–water mixture solvent, the aggregation of new nuclei can be effectively held back to some extent because of the existence of alcohol molecules, therefore reducing the particle size. However, in the presence of excess alcohol, fine crystal nuclei cannot be formed easily and considerably, which results in large diameters. Only when the proportion of alcohol to water is moderate can enough crystal nuclei be formed. Besides, alcohol molecules can hold back the agglomeration of new nuclei in this case. Specifically, the proportion of alcohol to water in the original solution in this paper is controlled in the range of 1:1–1:3 and the diameter of particles is comparatively small.

3.4. Analysis of IR spectra

IR spectra of samples 4 and 6 are shown in Fig. 5(A) and (B) respectively. There are two apparent absorption peaks for each sample. That of sample 4 appear at around 556, 420 cm^{-1}, and that of sample 6 at around 544, 420 cm^{-1}, which are basically consistent with the literature [8]. The two strong absorption peaks are attributed to the vibration of the chemical bond (Zn^{2+}–O^{2-}) in A location of the tetrahedron and the vibration of the chemical bond (Fe^{3+}–O^{2-}) in B location of the octahedron respectively. From IR spectra of two samples, the following conclusions can be made: when the diameter decreases, comparing sample 4 to 6, one of the strong

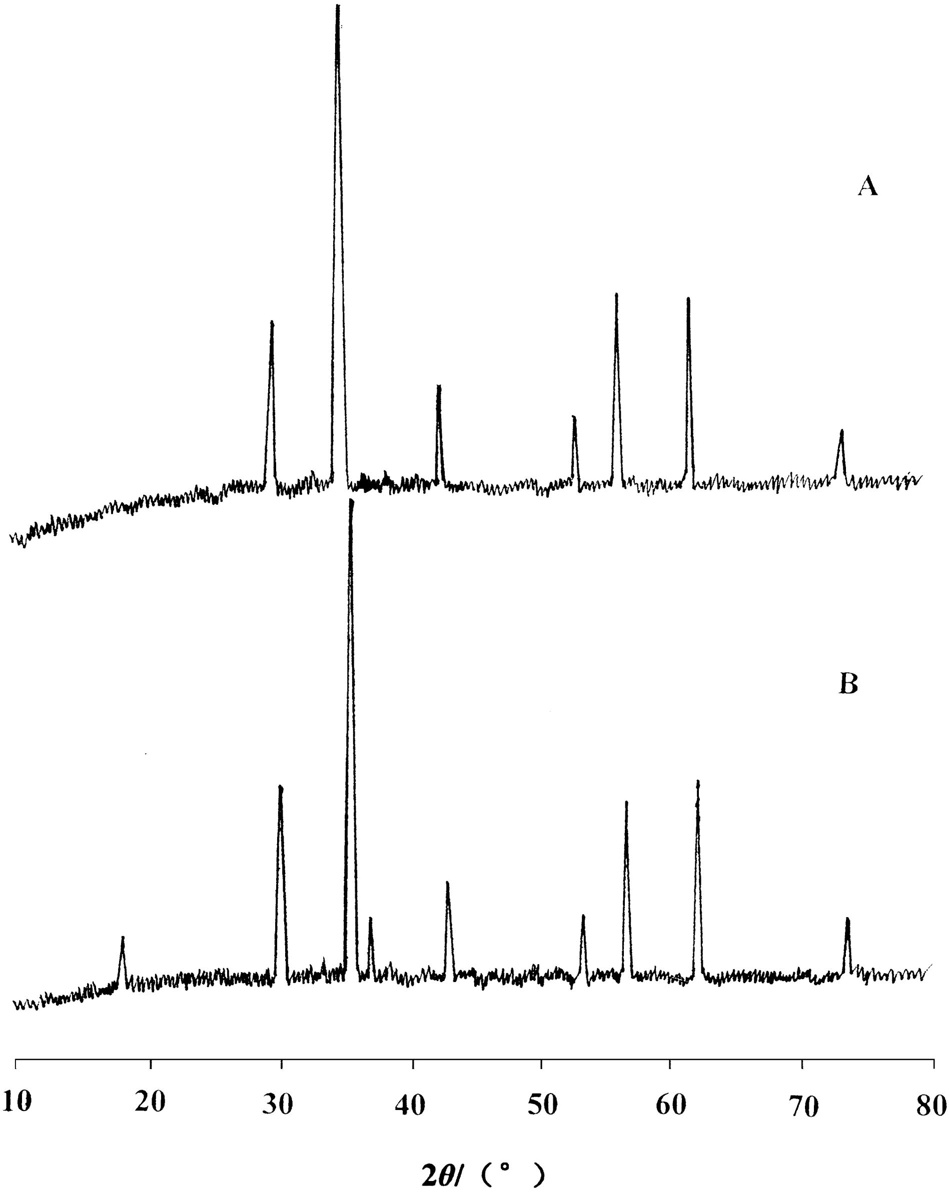


Fig. 2. X-ray diffraction patterns of samples 5 and 6: A = sample 5; B = sample 6.

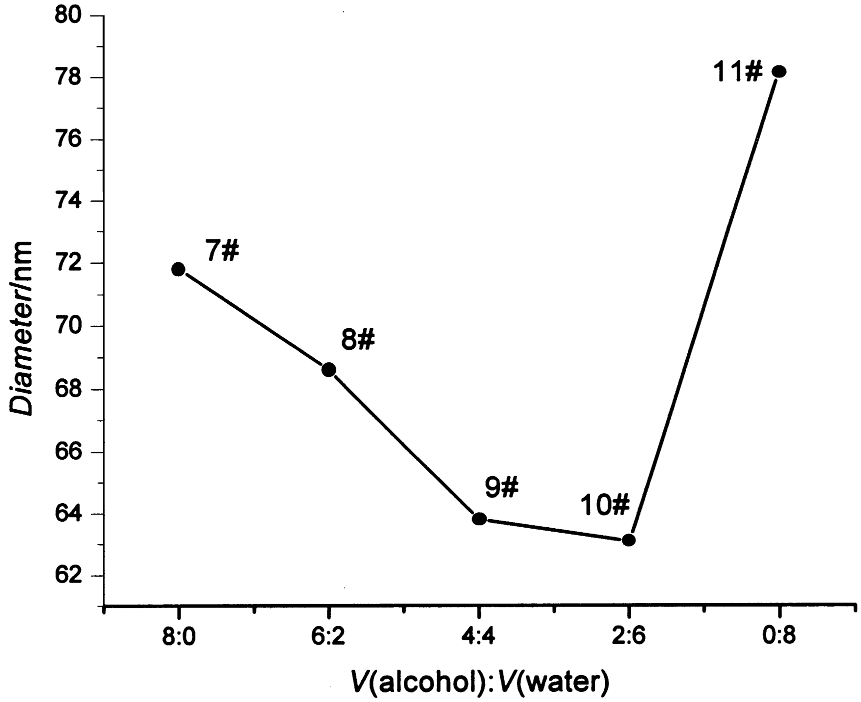
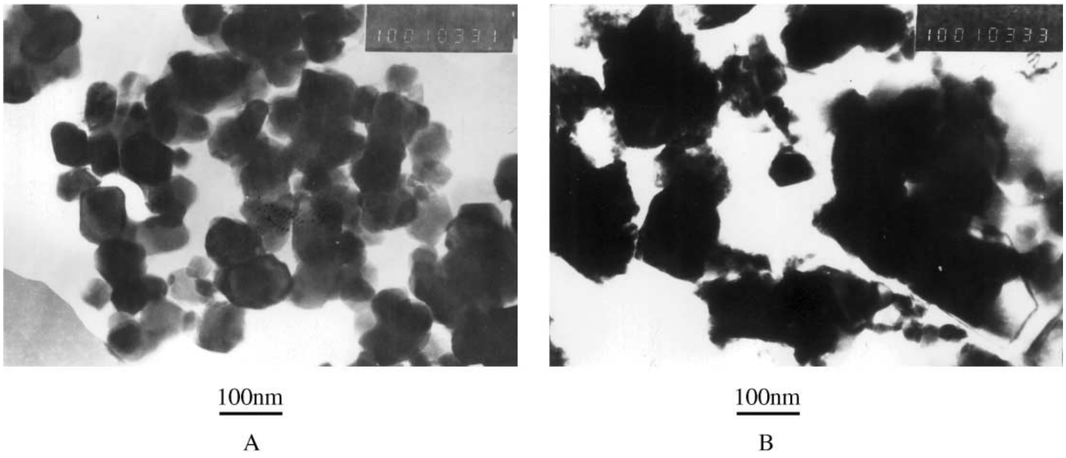


Fig. 3. The relationship between diameter and proportion of alcohol to water.

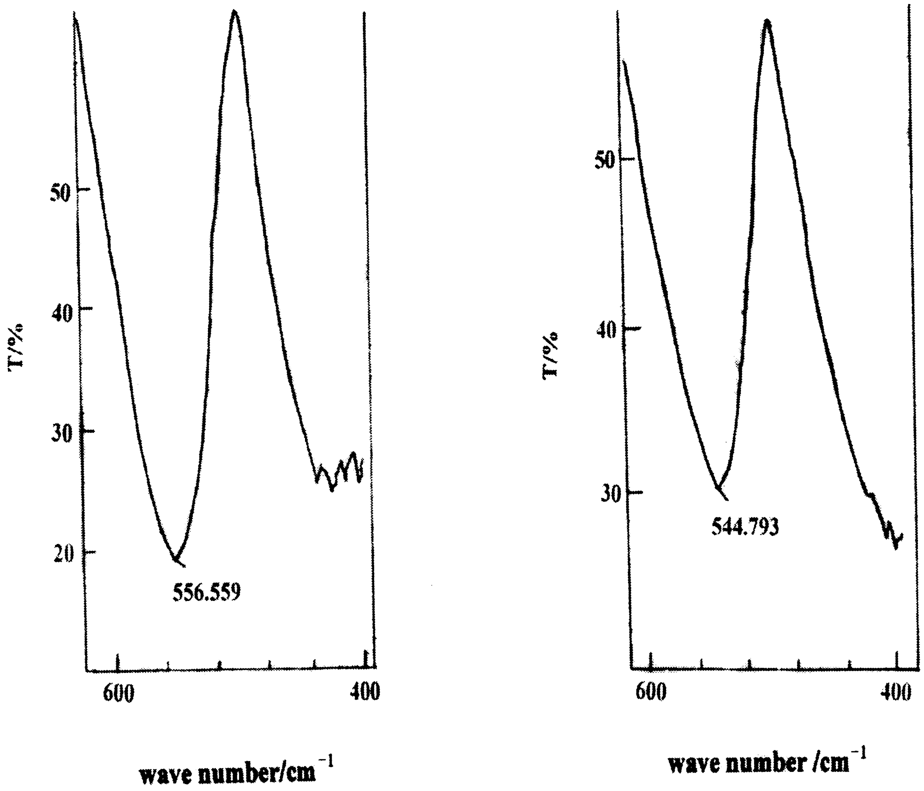


A

B

Fig. 4. TEM photos of the samples: A = sample 10; B = sample 11.

absorption peaks shifts 12 cm^{-1} towards a bigger wave number (i.e., blue shift happens) [9,10], which is caused by the quantum size effect of nanometer particles. The other strong peak broadens and even cleaves. This may be due to the existence of more imperfections in nanometer particles, leading to the wide distribution of vibration frequency of the chemical bond and the dramatically decreased symmetry. Therefore, the band is broadened and cleaved.



A B

Fig. 5. IR spectra of samples 4 and 6: A = sample 4; B = sample 6.

4. Conclusion

In this paper, the alcohol–water co-precipitation method was used to prepare nanometer $ZnFe_2O_4$ pigment with spinel structure. The diameter of samples obtained by using alcohol–water co-precipitation method is smaller compared with that obtained by using water co-precipitation method. When the proportion of alcohol to water is moderate, the diameter of samples is the smallest. At the same time, the relationship between crystallizing temperature and the grain size was studied. It is also found out that the smaller the diameter, the lower the crystallizing temperature. In addition, the analysis of IR spectra reveals the quantum size effect of nanometer pigment particles.

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