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# MICROWAVE HYDROTHERMAL SYNTHESIS OF MAGHEMITE NANOPARTICLES AS A PRECURSOR OF MAGNETIC FLUIDS

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The objective of this study is to explore the microwave hydrothermal (MH) synthesis of $\gamma$-$Fe_2O_3$ powders and to characterize the products obtained by microwave hydrothermal processing. Maghemite particles were prepared by co-precipitation of Fe(III) and Fe(II) in the presence of $NH_4OH$. The suspension was being irradiated for 30 minutes by MW irradiation at the frequency 2.45 GHz (500 W). Finally, the suspension was decantated using deionized water to approximately pH 6.5 and dried. In order to compare the conventional method and the MH method, the same co-precipitation technique was used to prepare a maghemite sample at room temperature. The clear samples were then collected for further analysis. Mössbauer measurements were performed by transmission geometry using a microcomputer-controlled spectrometer in a constant acceleration mode using a $^{57}$Co/Rh $\gamma$-ray source. Surface morphology and particle size were characterized by scanning electron microscopy (SEM). The presence of maghemite particles was confirmed in the spectrum of a sample prepared in a microwave reactor and at room temperature as well.

**1. Introduction.** Magnetite and maghemite nanoparticles have found extensive applications due to their unique magnetic properties. The magnetic fluids can be obtained by dispersing magnetic nanoparticles in water through their surface modification and may be used in mineral processing, biological applications, drug-targeting, diagnostic applications, etc. Microwave hydrothermal reaction is a recent technique, where the advantages of both microwave heating and hydrothermal method are used. The microwave-assisted hydrothermal synthesis of ceramic oxides is another novel method of synthesis. It is a rapidly developing research area. Nowadays, there are several reports, where conventional hydrothermal preparative techniques have been substituted by the microwave hydrothermal method. It offers rapid heating, faster kinetics, homogeneity, higher yield, better reproducibility as well as economical and energy save (Kim *et al.* 2001). In the field of preparation of various oxides, the kinetics of microwave hydrothermal processing has shown significant advantages compared to the conventional hydrothermal processing (Kumada *et al.* 1998, Khollam *et al.* 2001). Maghemite ($\gamma$-$Fe_2O_3$) is useful for high-density recording media because of excellent ferromagnetic properties. The preparation of ultrafine $\gamma$-$Fe_2O_3$ particles has become very interesting due to their potential applications in ferrofluids, magnetic sorbents, bioprocessing, magnetic refrigeration, information storage, gas sensor and color imaging.

**2. Experimental.**

*2.1. Synthesis of* $\gamma$-$Fe_2O_3$. Maghemite particles were prepared by co-precipitation of Fe(III) and Fe(II) in the presence of $NH_4OH$. A solution of mixture of Fe(III) and Fe(II) ions in molar ratio 2:1 was prepared using $FeCl_3 6H_2O$ and $FeSO_4 7H_2O$ in the atmosphere. In order to maintain pH 11.5, an equal volume

of 1 M aqueous ammonia solution was then added dropwise to the iron mixture under vigorous stirring. The suspension was being irradiated for 30 minutes by microwaves. The suspension was finally decantated using deionized water to approximately pH 6.5 and dried. In order to compare the conventional method and the MH method, the same co-precipitation technique was used to prepare a maghemite sample at room temperature. The clear samples were then collected for further analysis.

*2.2. Microwave heating.* All the microwave-assisted hydrothermal reactions were carried out in a microwave oven with 500 W (Panasonics). The system was operated at 2.45 GHz frequency.

*2.3. Powder characterization.* The powder phase was identified using X-ray PHILIPS PW1820 ($CuK_\alpha$ radiation, $\lambda = 0.15418$ nm). The average crystallite size was calculated using the Scherrer equation:

$$D = \frac{Kr\lambda}{b\cos\theta},$$

where $D$ is the average dimension of crystallites, $K$ is the shape factor of the average crystallite (expected shape factor is 0.9), $r$ is the radius of goniometer, $\lambda$ is the wavelength, $b$ is the integral breadth of a reflection located at $2\theta$, and $\theta$ is the peak position. Mössbauer spectroscopy has found an important application in the investigation of Fe–oxides. For this reason, we also applied this technique to investige our samples. Mössbauer measurements have been made in transmission geometry using a microcomputer-controlled spectrometer in a constant acceleration mode using a $^{57}$Co/Rh $\gamma$-ray source. The velocity scale was calibrated relative to $^{57}$Fe in Rh. The transmitted $\gamma$-radiation was detected by a proportional counter. The 'Recoil' spectral analysis software was used for the quantitative evaluation of the Mössbauer spectra. Powder morphology and particle size were characterized by scanning electron microscopy (SEM).

**3. Results and discussion.** X-ray diffractometry was used to analyse the phases of magnetic oxides prepared at room temperature (Fig. 1*a*) and by microwave hydrothermal synthesis (Fig. 1*b*).

The spectrum includes one phase with the spinel structure of the prepared oxide. Although the XRD patterns of $Fe_3O_4$ and $\gamma$-$Fe_2O_3$ show the spinel structure, it is not still a conclusive proof of the structure (very dificult to distinguish from the XRD studies).

The average crystallite size $D$ of the microwave prepared maghemite calculated from the Scherrer equation was 24 nm. Mössbauer spectroscopy offers a

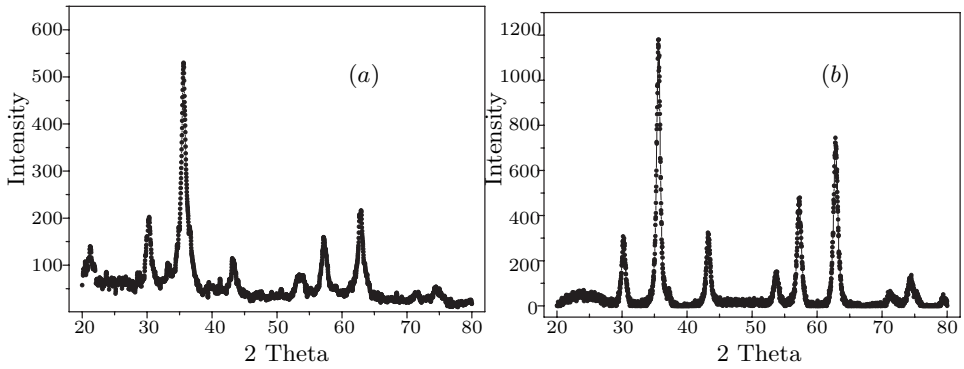


*Fig. 1.* X-ray spectrum of the maghemite prepared (*a*) at room temperature, (*b*) by microwave hydrothermal synthesis.

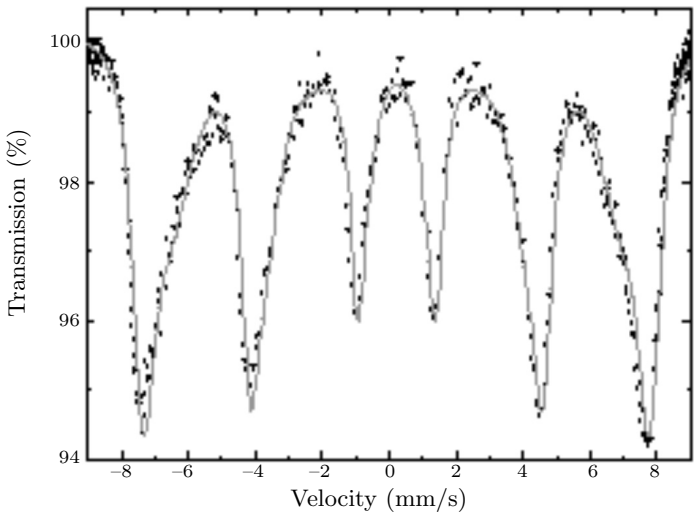


*Fig. 2.* Mössbauer spectra of maghemite (microwave heating).

unique possibility to study different Fe state in iron-containing materials. The presence of maghemite particles was confirmed in the Mössbauer spectrum of the sample prepared in the microwave oven and at room temperature.

The room temperature Mössbauer spectra of maghemite prepared in the microwave reactor (Fig. 2) contains one sextet with a reduced hyperfine field that is characteristic for magnetic splitting of ordered maghemite particles. The isomer shift $\delta = 0.33$ mm/s corresponds to $Fe^{3+}$. The reduction of the hyperfine magnetic field from 46.98 to 32.20 Tesla, Lorentzian HWHM (half width in half maximum) of about 0.26 and the Gauss line from 1.13 to 13.72 correspond to a weak (nano and amorphous) crystal state of maghemite particles. The parameters of the fitted spectrum are in Table 1.

The Mössbauer spectra of the maghemite prepared at room temperature (Fig. 3) well fit two subspectra. The isomer shift 0.33 of super paramagnetic doublet and 0.34 of the ordered state confirm the presence of $Fe^{3+}$. The magnetic

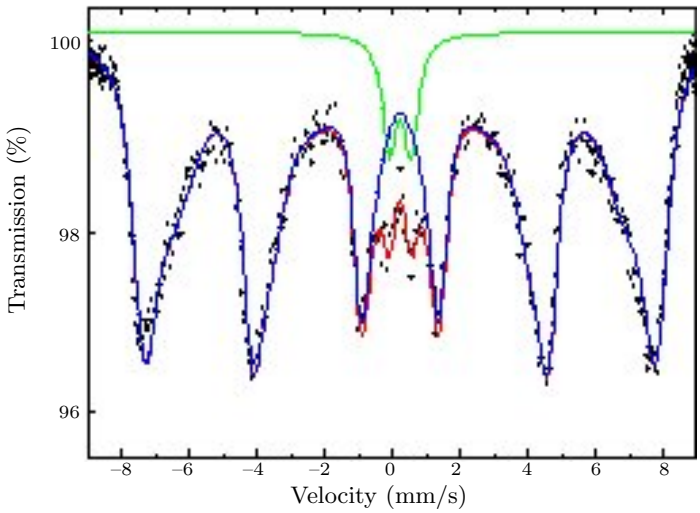


*Fig. 3.* Mössbauer spectra of maghemite (room temperature).

*Table 1.* Mössbauer parameters of maghemite.

| | $\delta$ (mm/s) | $p$ | $H(T)$ | $\sigma_{\mathrm{B}}(T)$ |
|---|---|---|---|---|
| $Fe^{3+}$ | 0.33 | | | |
| Component 1 | | 0.41 | 46.98 | 1.13 |
| Component 2 | | 0.38 | 42.27 | 3.35 |
| Component 3 | | 0.21 | 32.20 | 13.72 |

*Table 2.* Mössbauer parameters of the maghemite spectrum.

| | $IS$ (mm/s) | $I/p$ (%) | $QS/H$ (mm/s)/(T) | $\sigma_{\mathrm{B}}(T)$ |
|---|---|---|---|---|
| $Fe^{3+}$sup. | 0.33 | 5.3 | 0.63 | 0.05 |
| $Fe^{3+}$ | 0.34 | 94.7 | | |
| Component 1 | | (32.7) | 46.9 | 1.29 |
| Component 2 | | (33.9) | 42.1 | 3.46 |
| Component 3 | | (33.4) | 30.1 | 12.84 |

splitting with a reduced hyperfine field and the super paramagnetic doublet are characteristic for relaxation phenomena in maghemite nanoparticles. The shift of the particle-size distribution to lower values confirmed the presence of super paramagnetic state in the spectrum of maghemite prepared at room temperature if compared to the maghemite prepared in the microwave oven. The influence of microwave energy on the synthesis of maghemite was observed. The parameters of the Mössbauer spectrum are in Table 2.

Surface morphology of the synthesized maghemite in the microwave oven is shown in Fig. 4. The formation of aggregates and different particle-size distributions was analyzed by scanning electron microscopy.

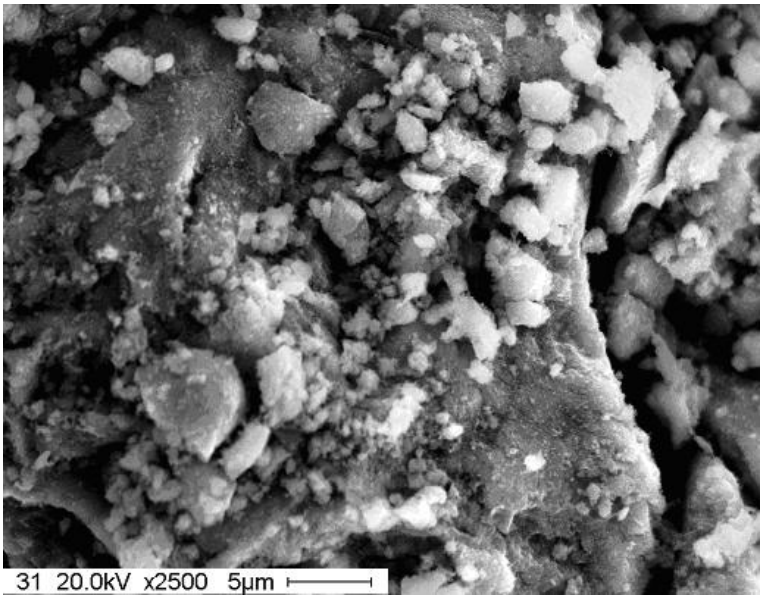


*Fig. 4.* SEM analysis of the maghemite prepared by the microwave hydrothermal method.

**4. Conclusion.** The microwave hydrothermal (MH) processing method has been successfully used to synthesize nanosized spherical particles of maghemite. The influence of microwave energy for the preparation of maghemite is crucial. The particle-size distribution of maghemite prepared in the microwave oven was shifted to lower values in comparison with the maghemite prepared by precipitation at room temperature, which was confirmed by presence of super paramagnetic doublet in the spectrum of the prepared maghemite. The influence of microwave energy at the preparation of magnetic nanoparticles has been revealed. The study of these properties will be continued.

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