

Studies of the Magnetite Nanoparticles by Means of Mössbauer Spectroscopy

B. KALSKA-SZOSTKO^a, M. ZUBOWSKA^a AND D. SATUŁA^b

^aUniversity of Białystok, Institute of Chemistry
Hurtowa 1, 15-399 Białystok, Poland

^bUniversity of Białystok, Institute of Experimental Physics
Lipowa 41, 15-424 Białystok, Poland

The magnetite nanoparticles were prepared by modified Massart's method in water and in alcohol. The influence of the condition of preparation on the properties of magnetite nanoparticles were investigated by Mössbauer spectroscopy. The size of the particles were determined by transmission electron microscopy. It was shown that the particles size in the alcoholic reaction is smaller than in aqueous reaction. Moreover, the increase in the reaction time improves the stoichiometry of magnetite nanoparticles.

PACS numbers: 61.18.Fs, 75.50.Tt, 78.66.Vs

1. Introduction

Magnetite is a mineral crystallized in a cubic inverse spinel structure with two nonequivalent Fe sites assigned as A and B [1]. These positions have tetrahedral and octahedral symmetry, respectively. The iron atoms are in Fe²⁺ (B site) and Fe³⁺ (A and B sites) oxidation states. At room temperature due to electron hopping between Fe²⁺ and Fe³⁺ (in B site) only two sextets are observed. The first one with higher hyperfine magnetic field belongs to A site and the second one with smaller hyperfine field assigned to B site. In stoichiometric bulk magnetite the ratio between intensity of A and B sextets is equal to $\beta = 1.94$ [2] due to different recoil-free factors of Fe in A and B positions. This parameter is sensitive to the stoichiometry of the magnetite and to the diameter of the particle [2, 3]. The excess of oxygen leads to the creations of the vacancies in the B site. The vacancies screen the charge transfer and cause that the Fe³⁺ in A and B positions are indistinguishable. Each vacancy influences five Fe³⁺ atoms.

The wet chemical route to prepare nanoparticles is an alternative to preparation by physical methods like lithography and sputtering among others. In the present study Massart's method [4] of preparation of particles was adapted with some modifications. It is observed that the conditions of the sample preparation

have a significant influence on the properties of the final particles as evidenced, for example, by the difference in Mössbauer spectra [5]. This suggests an influence of the chemical environment and size on the magnetic properties of the particles. In this study, we investigated the relation between the iron oxide particles formation condition and their properties. We focused on the problem of the non-stoichiometry of the magnetite particles.

2. Experimental

The main reactions steps to produce magnetite nanoparticles are followed after Massart [4]. The particles in water solvent are prepared by the hydrolysis of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in NH_3 aqueous solution flashed by Ar in two separated flasks. The condensation takes place after mixing these two solutions. The mixture is stirred and flashed with gas. Tetrabutylammonium hydroxide (TBAOH) was used as a surfactant. In case of alcoholic solution 1-propanol was used as a solvent. Moreover, the influence of various time of reactions (0.5 h, 1 h, 3 h and 1.5 h, 3 h, 6 h in water and alcohol, respectively) the properties of the synthesized nanoparticles were studied. All used liquids are heavily stirred and flashed with Ar for half an hour to reduce O_2 contamination. To prepare samples for Mössbauer spectroscopy the solutions were dried out to obtain powder. The powder was mixed with BN and formed in tablets which contain about 12 mgFe/cm^2 .

The room temperature Mössbauer spectra were measured in a spectrometer working in a constant acceleration mode with ^{57}Co Rh as a source.

3. Results and discussions

To determine the crystal structure of the particles the X-ray diffraction measurements were carried out. The shape and position of main diffraction peaks allowed us to conclude that the obtained material is a crystalline magnetite. The position and relative intensity of all diffraction peaks match well with Fe_3O_4 nanoparticles published in Ref. [6].

The example of transmission electron microscopy (TEM) images of the particles synthesized in water and in alcohol are shown in Fig. 1a and b, respectively. Both pictures were taken with the same magnification.

It can be seen that using different solvents, keeping other conditions the same, a change of the final size of the particles is observed. The aqueous reactions result in bigger particles compared to alcoholic reaction. From the analysis of the images we found that the average size of particles is $12 \pm 2 \text{ nm}$ and $13 \pm 2 \text{ nm}$ for reaction time equal to 0.5 h and 3 h, respectively. In alcohol case we obtained $8 \pm 2 \text{ nm}$ diameter for 1.5 h reaction duration.

In Fig. 2 the room temperature Mössbauer spectra are presented. In panel A spectra from aqueous and in panel B from alcoholic reactions are shown. The spectra measured for nanoparticles prepared in water are well resolved while prepared

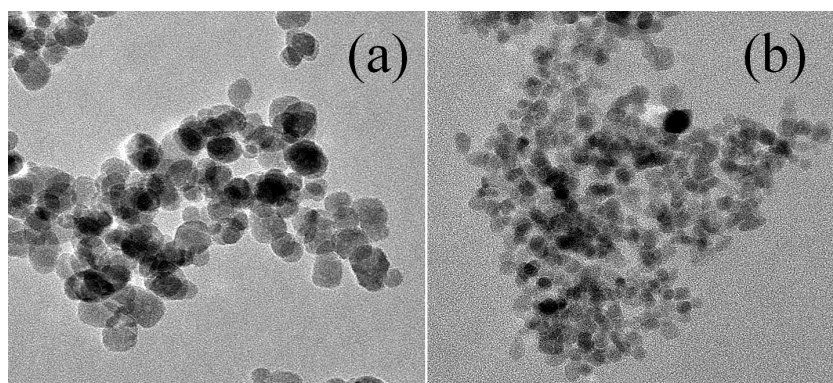


Fig. 1. TEM (230×230 nm) image of the magnetite nanoparticles: (a) synthesis 0.5 h — in water, (b) 1.5 h — in alcohol.

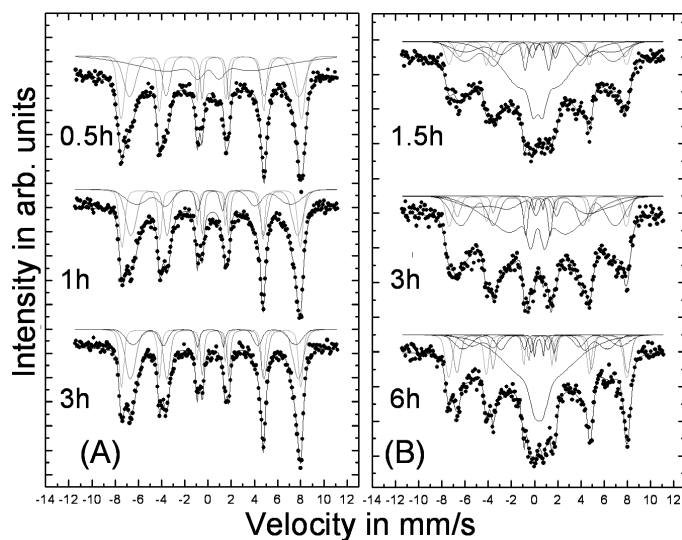


Fig. 2. Room temperature Mössbauer spectra collected for aqueous (A) and alcoholic (B) synthesis with reaction time as marked.

in alcohol are broad with large central part of the spectra. The presence of component with low hyperfine field is due to existence of particles with the size for which the relaxation processes start at room temperature. These results are well correlated with the results obtained from TEM analysis where one can see that in alcohol we have obtained smaller objects.

To evaluate spectra we applied a model with three subspectra to be fitted to the data for aqueous solutions nanoparticles (Fig. 2A). The two outermost components were assigned to A and B site of magnetite. The obtained values of isomer shift and quadrupole splitting are very close to the bulk parameters. The

hyperfine magnetic fields are slightly lower than in bulk [7] which agree with the data published in [5, 2]. The third sextet has hyperfine magnetic field, isomer shift, and quadrupole splitting not belonging to either A or B position. It seems that this sextet may be assigned to the surface part of the particles where the hyperfine parameters are modified [5] and/or the existence of relaxation process [8].

As one can see from Fig. 2A the reaction time influences the shape of the measured spectra. The longer reaction time improves the β ratio. The analysis showed that $\beta = 1.10 \pm 0.05$, 1.41 ± 0.05 , and 1.66 ± 0.05 for 0.5 h, 1 h, and 3 h time of reaction, respectively. All these values are smaller than $\beta = 1.94$ obtained for stoichiometric bulk magnetite [2]. It can be concluded that the longer reaction time improves the stoichiometry of obtained nanoparticles.

In Fig. 2B the Mössbauer spectra for various reaction time of samples prepared with the use of alcohol as a solvent are presented. The model which was proposed for describing those spectra needed two more components in comparison to the aqueous solution case. One can see that the increase in reaction time leads to gradually better resolved spectra particularly in the outermost part. This behavior suggests that with the prolongation of reaction the stoichiometry was improved as observed in the aqueous case. The obtained β parameters are smaller than in the aqueous case (for the longest reaction time is equal to 0.85 ± 0.15).

With the increase in reaction time, the fraction in the middle part of the spectra is changing from 82%, 81%, to 68% for 1.5 h, 3 h, and 6 h, respectively. This result can be explained as a gradual increase in particles size with increasing reaction time. The collapsed part of the spectrum comes from the particles which are close to the transition from superparamagnetic to ferrimagnetic state. It means that for magnetite nanoparticles covered with TBAOH the critical size is slightly below 8 nm. It has been reported that the paramagnetic doublet can be observed for the magnetite particles smaller than 10 nm embedded in a polymer matrix [9]. The difference in the magnetic behavior of the particles can have an origin in strength of dipole interaction between particles in different matrices. Thus the result shows again that the environment influences heavily properties of the nanoscale objects.

4. Conclusions

Three main conclusion one can get from this study:

- (i) The aqueous and alcoholic synthesis lead to the various sizes of the particles.
- (ii) The prolongation of reaction time improves the stoichiometry of the nanoparticles.
- (iii) The transition to superparamagnetic at room temperature occurs for particles below 8 nm of diameter in case of magnetite nanoparticles covered with TBAOH.

Acknowledgment

We would like to thank Prof. Dobrzyński for collaboration, K. Rećko for taking the XRD spectra and also N. Sobal for performing the TEM measurements.

References

- [1] N.N. Greenwood, T.C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall Ltd, London 1971, p. 258.
- [2] J. Korecki, B. Handke, N. Spiridis, T. Ślęzak, I. Flis-Kabulska, J. Haber, *Thin Solid Films* **412**, 14 (2002).
- [3] Yu.F. Krupyanskii, I.P. Suzdalev, *J. Phys. (France)* **35**, C6-407 (1974).
- [4] R. Massart, V. Cabuil, *J. Chim. Phys.* **84**, 967 (1987).
- [5] S. Morup, H. Topsoe, J. Lipka, *J. Phys. (France)* **37**, C6-287 (1976).
- [6] S. Sun, H. Zeng, D.B. Robinson, S. Raoux, P.M. Rice, S.X. Wang, G. Li, *J. Am. Chem. Soc.* **126**, 732 (2004).
- [7] S.R. Hargrove, W. Kündig, *Solid. State Commun.* **8**, 303 (1970).
- [8] W. Winkler, *Phys. Status. Solidi A* **84**, 193 (1984).
- [9] A.A. Novakova, V.Yu. Lanchinskaya, A.V. Volkov, T.S. Gendler, T.Yu. Kiseleva, M.A. Moskvina, S.B. Zezin, *J. Magn. Magn. Mater.* **258-259**, 354 (2003).