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# Preparation of $CuFe_2O_4/SiO_2$ nanocomposite by the sol-gel method

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This work aims at characterizing the phase relations in the $CuFe_2O_4/SiO_2$ system. Samples were prepared by the sol-gel method. Final heat treatment of the samples was carried out at temperatures in the range of 800–1100 °C. Final products were characterized by HR TEM, X-ray diffraction, magnetic measurements, and Mössbauer spectroscopy. HR TEM revealed nanocrystals with sizes of 7–130 nm, depending on the heat treatment temperature. The spinel structure of $CuFe_2O_4$ in the amorphous silica matrix proved to be stable up to 1100 °C without decomposition to copper silicate and iron (III) oxide. At the same time, the amorphous silica matrix recrystallized to cristobalite at 1100 °C.

Key words: *sol-gel; spinel ferrite; silica matrix; nanocomposite; Mössbauer spectroscopy; transmission electron microscopy; magnetic measurements*

## 1. Introduction

Nanocomposites have been the subject of many studies in recent years due to the new properties they are expected to exhibit [1]. One of the interesting groups consists of metal oxide compounds in a silica matrix. These materials can have interesting magnetic and magnetooptical properties [2]. One of the ways to prepare nanocomposites with the required properties is the sol-gel method. The advantages of this method are better homogeneity of materials and lower temperatures of treatment. In the case of nanocomposites in a silica matrix, samples with an arbitrary cation to silica ratio can be prepared and the particle size can be controlled by the parameters of heat treatment.

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This method was, for example, successful in the preparation of a metastable phase in the $Fe_2O_3/SiO_2$ system [3–5]. Studies have revealed that the metastable $\gamma$-$Fe_2O_3$ could be present in this nanocomposite up to 800 °C and that the intermediate phase $\varepsilon$-$Fe_2O_3$ also appears [6]. In the case of ternary oxides with a spinel structure, the situation is more complicated due to the possible formation of silicate. The $MFe_2O_4/SiO_2$ system is metastable from the theoretical point of view ($M^{2+}$ silicates are formed). Previous studies have revealed, however, that the spinel phase was formed in the silica matrix and that the formation of $MFe_2O_4$ nanoparticles strongly depends on the type of $M^{2+}$. Spinel nanocrystals in the silica matrix are stable up to 1100 °C in the case of M = Co, Ni, and Zn [7, 8] and mainly cadmium silicate and iron(III) oxide were found in the final heat treated product in the case of Cd [8].

This work presents the preparation of another $MFe_2O_4/SiO_2$ system (here M = Cu) and the characterization of the phase relations in this system. It also concerns the ferrite/silica-nanocomposite system prepared by the sol-gel method, which has not yet been studied. This work aims to show the suitability of this method for preparing copper ferrite nanoparticles in the silica matrix. $CuFe_2O_4/SiO_2$ nanocomposites were prepared by the sol-gel method and were heat treated in the temperature range of 800–1100 °C. The final products were studied by X-ray diffraction, HR TEM, magnetic measurements, and Mössbauer spectroscopy.

## 2. Experimental

*Sample preparation.* Samples were prepared using the conventional sol-gel method. Copper and iron nitrates were used as spinel precursors. TEOS, $HNO_3$ as an acid catalyst, formamide as a modifier, and methanol as a solvent were employed for silica matrix preparation. $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were first dissolved in methanol. The Si/Fe molar ratio was 100/20, which corresponds to a $SiO_2/CuFe_2O_4$ molar ratio of 100/10 (28.5 wt. % of $CuFe_2O_4$). The gelation time was approximately 18 hours at 45 °C and the samples (pellet shape, 5 mm thick and 15 mm in diameter) were left for two days to age. Then they were dried at 40 °C for three days in flowing $N_2$-atmosphere. After drying, they were first preheated at 300 °C in vacuum for two hours and then heated for four hours at various temperatures (800, 900, 1000, and 1100 °C) in air. The resulting samples were then characterized using powder X-ray diffraction, Mössbauer spectroscopy, HR TEM, and magnetic measurements.

*Experimental techniques.* A high-resolution transmission electron microscope (Topcon) was used for the direct observation of particle appearance. Particle sizes determination was carried out using Scion Images software. X-ray patterns were measured at ambient temperature using a Siemens D5000 diffractometer. Mössbauer spectra measurements were done in transmission mode with $^{57}Co$ diffused into a Cr matrix as the source moving with constant acceleration. The spectrometer was calibrated by means of a standard $\alpha$-Fe foil and the isomer shift was expressed with re-

spect to this standard at 300 K. The fitting of spectra was performed with the help of the NORMOS program. Magnetic measurements were carried out in a vibrating sample magnetometer (VSM) at 298 K.

## 3. Results

The samples of $CuFe_2O_4/SiO_2$ nanocomposites were obtained by the sol-gel method. Previous studies indicated that vacuum treatment restrains $\alpha$-$Fe_2O_3$ (hematite) formation and leads to ferrite formation [7]. For this reason, the samples were first treated at temperatures up to 300 °C under vacuum and then the final heat treatment at 800–1100 took place. Samples annealed at 800 and 900 °C were amorphous, but for those annealed at 1000 °C the crystallization of the silica matrix began. This fact was confirmed by X-ray diffraction, where diffraction peaks of cristobalite appeared at 1000 and 1100 °C. All of the $CuFe_2O_4/SiO_2$ samples heated in the above-mentioned temperature range were dark brown.

### 3.1. X-ray diffraction measurements and HR TEM observations

All samples were characterized by X-ray diffraction measurements (step 0.1°, time 50 s/step), and the results are shown in Fig. 1. X-ray diffraction patterns of samples

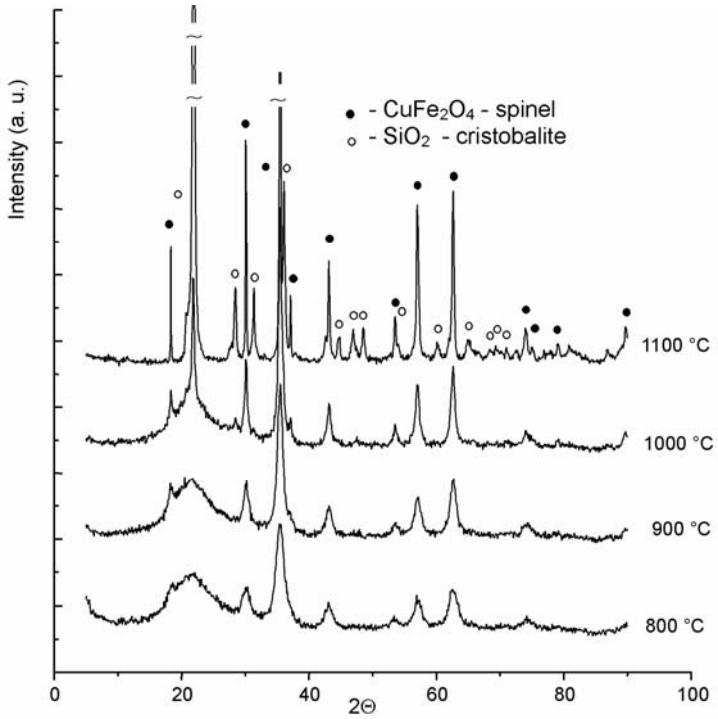


Fig. 1. X-ray diffraction patterns of the $CuFe_2O_4/SiO_2$ samples

heated at 800 °C indicate the presence of amorphous $SiO_2$, manifested by the characteristic very broad diffraction at 20° ($2\theta$). The recrystallization of the silica matrix into cristobalite starts at 1000 °C and there is no evidence of an amorphous phase (the broad diffraction at 20° is absent) in the sample treated at 1100 °C. The diffraction patterns of phases other than $SiO_2$ exhibit broad peaks that become sharper with increasing temperature of heat treatment. This corresponds well to the crystal growth. These diffractions were found in all the studied samples annealed at the above-mentioned temperatures and can be well attributed to the ferrite spinel structure. Bulk copper ferrite spinel is slightly distorted due to the Jahn-Teller (JT) effect, therefore it has a tetragonal symmetry.

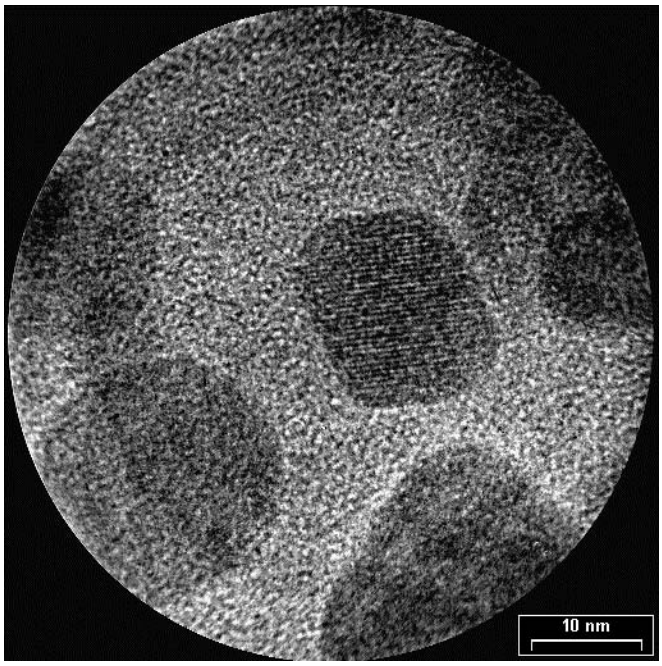


Fig. 2. HRTEM of the $CuFe_2O_4/SiO_2$ sample heated at 1000 °C

Table 1. Average particle size of the $CuFe_2O_4/SiO_2$ composite depending on the annealing temperature

| Temperature | 800 °C | 900 °C | 1000 °C | 1100 °C |
|---|---|---|---|---|
| Particle size (nm) | 7±2 | 9±3 | 15±3 | 130±17 |

Direct particle size observation by means of HR TEM confirms the tendency shown by the X-ray diffraction. The mean particle size of the $CuFe_2O_4$ in $SiO_2$ nanocomposite heated at 800 °C is 7 nm. Particle size rapidly increases with increasing temperature. The sample heated at 1000 °C show a mean particle size of 15 nm

(Fig. 2, Table 1) and the mean particle size of the spinel ferrite particles in the sample heated at 1100 °C is 127 nm. Particles were very well defined and did not exhibit a diffused appearance.

### 3.2. Mössbauer spectra

X-ray diffraction cannot distinguish between $CuFe_2O_4$ and $\gamma$-$Fe_2O_3$ spinel structures, especially in the case of very small particles, due to very close lattice parameters of both structures. For this reason, the measurements of Mössbauer spectra were carried out. Mössbauer spectra also yield information about the site occupation of the spinel structure and about the number of non-equivalent iron atoms.

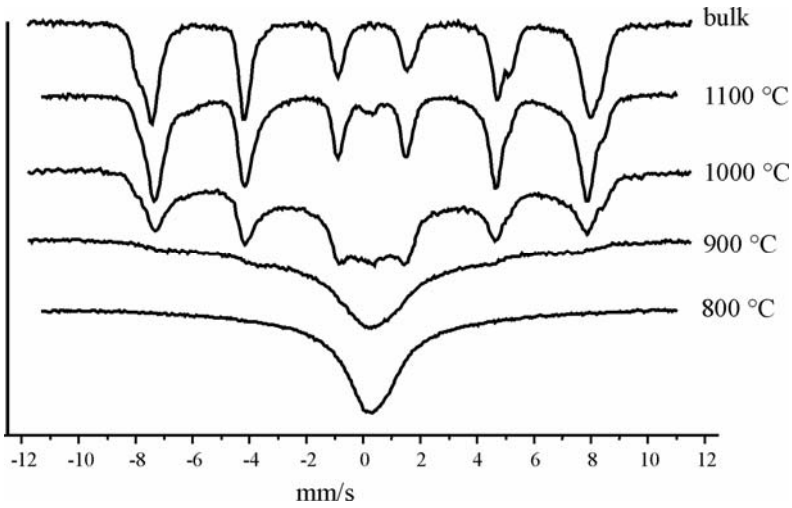


Fig. 3. Room temperature Mössbauer spectra of $CuFe_2O_4/SiO_2$ samples treated at various temperatures in the range of 800–1100 °C, compared to bulk $CuFe_2O_4$

Figure 3 represents spectra obtained at room temperature for samples annealed at 800, 900, 1000, and 1100 °C. The sample treated at 800 °C exhibits a very large

Table 2. Interpretation of the room-temperature Mössbauer spectra of the $CuFe_2O_4/SiO_2$ composite heated at 1100 °C

| Subspectrum | Isomer shift $\delta$ (mm/s) | Quadrupole splitting $E_Q$ (mm/s) | Hyperfine field $B_{hf}$ (T) | Full line width at half height (mm/s) | Relative area (%) |
|---|---|---|---|---|---|
| 1 | 0.361±0.001 | –0.065±0.004 | 50.296±0.012 | 0.416±0.008 | 15.6±0.318 |
| 2 | 0.275±0.001 | 0.014±0.002 | 47.597±0.012 | 0.406±0.005 | 40.0±0.899 |
| 3 | 0.310±0.002 | –0.043±0.003 | 45.779±0.022 | 0.455±0.007 | 26.7±0.859 |
| 4 | 0.391±0.006 | –0.036±0.013 | 40.881±0.023 | 0.813±0.022 | 14.2±0.395 |
| 5 | 0.225±0.014 | 0.000±0.825 | | 0.950±0.033 | 3.4±0.094 |

singlet, which is characteristic of the superparamagnetic state. In the following spectra (increasing heat treatment temperature) we can see that this band becomes broader and transforms into a sextet, which is well defined for the 1000 °C annealed sample. The 1100 °C heat-treated sample shows a Mössbauer spectrum that can be decomposed into four sextets and one singlet (Fig. 4). The parameters of this fit are given in Table 2. The doublet represents nanoparticles (smaller than the critical size) that are still in the superparamagetic state, but a relative area of 3.4 % suggests that almost all particles are in the ferromagnetic state. For confirming the $CuFe_2O_4$ phase in our nanocomposite, we compared the Mössbauer spectrum of pure bulk $CuFe_2O_4$ (Figure 3, top trace) with the other nanocomposites. The sextet of $\alpha$-$Fe_2O_3$ (hematite), which is the most stable phase at these conditions, was not found.

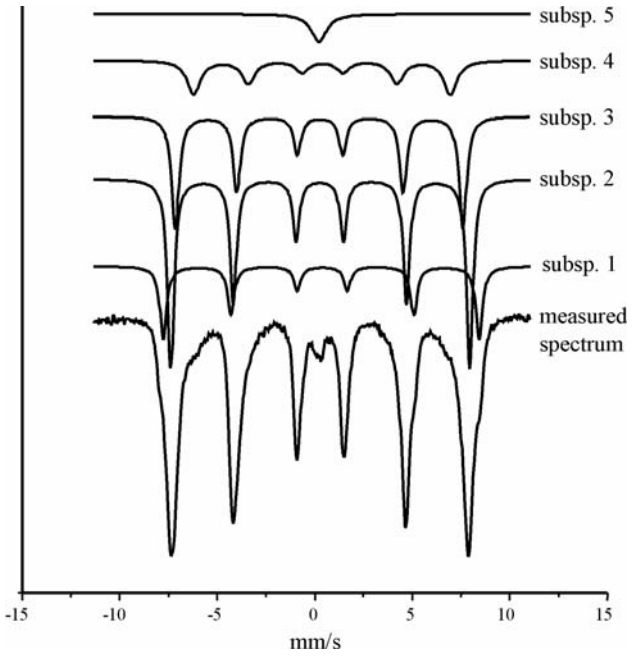


Fig. 4. Room temperature Mössbauer spectrum of $CuFe_2O_4/SiO_2$ samples treated at 1100 °C

### 3.3. Magnetic measurements

Figure 5 shows a plot of the magnetic moment of our nanocomposites as a function of the applied field (hysteresis curves), measured at room temperature, for all the heat treatment temperatures. We can see from this figure that the saturation magnetization values increase as particle size increases with annealing temperature. The values of saturation magnetization for the prepared samples are listed in Table 3. This Table gives both the values related to the entire nanocomposites and to the ones recalculated for their pure copper ferrite components.

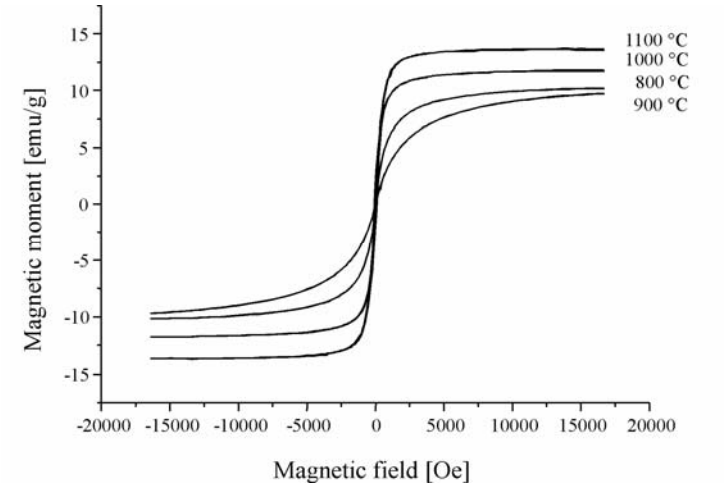


Fig. 5. Magnetic moments of samples heated at 800, 900, 1000, and 1100 °C, measured at 298 K. (Magnetic moments of the entire samples including the $SiO_2$ matrix)

Table 3. The saturation magnetic moments measured at 298 K of the $CuFe_2O_4/SiO_2$ composite heated at 800, 900, 1000, and 1100 °C

| Temperature of treating (°C) | Saturation magnetic moment (emu/g) | |
|---|---|---|
| | Composite | Pure $CuFe_2O_4$ |
| 800 | 7.9 | 27.7 |
| 900 | 9.2 | 32.3 |
| 1000 | 11.2 | 39.4 |
| 1100 | 13.4 | 46.9 |

## 4. Discussion

It can be seen from the powder X-ray diffraction data that the spinel phase of $CuFe_2O_4$ is formed in the silica matrix and that it is still stable in the sample annealed at 1100 °C. The presence of iron (III) oxide phases was not proved. There is a theoretical possibility for the presence of $\gamma$-$Fe_2O_3$, because it has the same spinel structure with lattice parameters very close to those of $CuFe_2O_4$. The presence of iron oxide, however, should be accompanied by copper ferrite decomposition and the probable formation of copper silicates. On the other hand, there are no other copper compounds present in the XRD patterns, which can be considered to be indirect evidence supporting our interpretation. In addition, Mössbauer spectroscopy results clearly show that only $CuFe_2O_4$ spinel phase is present. Another finding from XRD is that the spinel phase in the composite has cubic symmetry, while pure stoichiometric $CuFe_2O_4$ is reported to be tetragonal due to the JT effect. This could be caused by the fact that the

diffractions of the spinel phase are broad and therefore we cannot observe the splitting of the diffraction lines due to the JT effect. Nevertheless, there are copper ferrites reported to have cubic symmetry, e.g. cuprospinel, which can be found in the mineral database of powder diffraction files [9]. It is expected that this mineral has neither the stoichiometry of pure copper ferrite nor regular occupation of the cation sites. We probably have a similar situation in our nanocomposite, which means that the structure of our copper ferrite in the silica matrix is not exactly the same same as the structure of inverse spinel. The occupation of tetrahedral and octahedral sites is rather statistical, resulting in a cubic symmetry of spinel structure.

Pure $CuFe_2O_4$ is reported to have a saturation magnetization of about 25 emu/g at room temperature [10]. The ideal inverse spinel structure of $(Fe\downarrow)[Cu\uparrow Fe\uparrow]O_4$ (parenthesis means tetrahedral positions, bracket means octahedral ones) corresponds to the saturation magnetic moment of 1 $\mu_B$. The values of 1.3–2.5 $\mu_B$, however, have been reported in literature [11] corresponding to mixed state of spinel. These various values of $\mu$ and thus of saturation magnetization are supposed to be due to different cooling rates during spinel preparation. $CuFe_2O_4$ is known to have cation vacancies, whose amount varies with preparation conditions. This fact must be taken into account for the detailed interpretation of magnetic measurements. In our case, namely the study of the phase relations in the $SiO_2/CuFe_2O_4$ system, we do not take these vacancies into account in the first approach to our interpretation of measurements.

The calculated value of the saturation magnetization of the pure spinel ferrite phase for the 1100 °C heated sample amounts to 46,9 emu/g, which is much higher than the reported value for purely inverse spinel [10]. This can be explained by the mixed character of the spinel structure; some of the copper atoms are located in tetrahedral sites. The formula of our copper ferrite can be written as: $(Fe_{(1-x)}Cu_x)[Fe_{(1+x)}Cu_{(1-x)}]O_4$. From this formula, we can write the equation for the theoretical value of $\mu$ as a function of the stoichiometric coefficient $x$.

$$\mu = 1 + 8x \quad [\mu_B]$$

From our experimental value of $M_S$ (46,9 emu/g), we can calculate the experimental value of 2,01 $\mu_B$ per formula unit, which corresponds to $x = 0.13$. Therefore, the formula of our copper ferrite can be written as $(Fe_{0,87}Cu_{0,13})[Fe_{1,13}Cu_{0,87}]O_4$.

The temperature of the Curie point for $CuFe_2O_4$ is 728 K [10], but the coercive field is very low due to a low value of magnetocrystalline anisotropy of copper ferrite. The loops are very compact. Thus, the question whether the corresponding particles in the sample are in the superparamagnetic or ferromagnetic state cannot be answered by magnetization measurements alone. Mössbauer spectra measurements must also be taken into account. From these spectra, we can see that the samples annealed at 800 and 900 °C (with corresponding mean particle size of 7 and 9 nm) are superparamagnetic at room temperature, while the ones annealed at 1000 and 1100 °C (with corresponding mean particle size of 15 and 130 nm, respectively) are predominantly ferrimagnetic.

From HRTEM observations, the sample annealed at 1100 °C contains particles with a mean size of 130 nm, which is a very high value compared to other spinel ferrites in the silica matrix that were prepared in the past [7, 8]. The characteristic values of the particle size for this annealing temperature in the case of Zn, Co, and Ni ferrites are about 10–15 nm. They are probably due to higher diffusion of the $Cu^{2+}$ cation in the silica matrix.

## 5. Conclusions

$CuFe_2O_4/SiO_2$ nanocomposites were prepared by the sol-gel method and investigated using powder X-ray diffraction, HR TEM, magnetic measurements, and Mössbauer spectroscopy. The $CuFe_2O_4$ spinel phase, which is formed in the studied nanocomposite, is stable up to 1100 °C. The presence of $Cu^{2+}$ cations significantly affects the crystallization of the amorphous silica matrix. Crystallization starts at 1000 °C and leads to a cristobalite phase without any amorphous phase at 1100 °C. Magnetic measurements revealed that the spinel structure of copper ferrite has a mixed-state character. The calculated saturation magnetic moment is consistent with an approximate distribution of Cu and Fe in the tetrahedral and octahedral positions corresponding to the formula $(Fe_{0,87}Cu_{0,13})[Fe_{1,13}Cu_{0,87}]O_4$.

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