

## STUDY OF $\text{Fe}_x\text{O}_y\text{-SiO}_2$ NANOPARTICLES OBTAINED BY SOL-GEL SYNTHESIS

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Nanocomposites  $\text{Fe}_x\text{O}_y\text{-SiO}_2$ , with an iron content of 3wt. % has been prepared by the sol-gel method starting from tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) precursors as the  $\text{SiO}_2$  sources. This original method produces large quantities of amorphous gels that are thermally treated at 550 °C and 1000 °C as the final step of the synthesis. The average diameter of iron particles in the nano-composite materials can be controlled by the iron concentration and thermally treatment. The dried gel was treated at increasing temperatures, and the samples were characterized by transmission electron microscopy (TEM), IR-spectroscopy and magnetic measurements. The result indicates that the formation and the stability of the iron oxide phases are strongly affected by the precursors used as the  $\text{SiO}_2$  sources.

*Keywords:* Nanocomposites, Iron oxide in silica matrix, Sol-gel, magnetic properties

### 1. Introduction

$\text{Fe}_x\text{O}_y\text{-SiO}_2$  nano-composite materials can be prepared by a variety of methods. The problem is that the traditional methods of synthesis from material science are not able to produce uniform and reproducible particles of nanometer size. On the other hand the magnetic particles having nanometer dimensions have the tendency to agglomerate [1]. The sol-gel method has revealed the formation of the  $\text{Fe}_x\text{O}_y$  nanoparticles in organic polymers or in silica matrixes [2-4]. The porous nature of the silica matrix provides the sites for nucleation of the iron oxide particles and minimizes their aggregation [5-6]. It is well known that the structure and composition of nano-oxides formed by sol-gel method depend on the preparation condition, the nature of the precursors, the ion source and pH. All the previous studies have shown that the final product of the decomposition is  $\alpha\text{-Fe}_2\text{O}_3$ , whose properties depend of the temperature of annealing [7], treatment condition [8-9] and the crystallinity of the initial material [10].

The present paper presents the preparation of some  $\text{Fe}_x\text{O}_y\text{-SiO}_2$  nano-composites obtained by the sol-gel method, recently proposed for the synthesis of Me-SiO<sub>2</sub> systems [11-15]. The size and morphology of the particles were observed by transmission electron microscopy (TEM). The interaction of iron oxide with the silica matrix in  $\text{Fe}_x\text{O}_y\text{-SiO}_2$  nanocomposites has been investigated by IR-spectroscopy. The magnetic properties were monitored by susceptibility measurements.

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## 2. Experimental

The  $\text{Fe}_x\text{O}_y\text{-SiO}_2$  nanomaterials have been obtained using the alkoxide route of the sol-gel method, varying the silica precursors, in order to evidence its role on the properties of the obtained nanocomposites. The tetraethoxysilan (TEOS) from Merck, methyltriethoxysilan and (MTEOS) from Fluka, have been used as  $\text{SiO}_2$  sources. The absolute ethyl alcohol from Riedel de Haen was used as solvent, in all cases. The iron source was also a common one, respectively the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  salt, from Romanian “Reactivul” company, which was introduced in the reaction mixtures as aqueous solution. All the sol-gel reactions were accomplished using a 25 wt. % ammonia solution from Reactivil as catalyst and deionized water for the hydrolysis. The final iron content for all the prepared nanocomposites was calculated to be of 3 wt. %, related to  $\text{SiO}_2$ . Table 1 presents the chemical compositions and the experimental conditions of preparation for the synthesized nanomaterials.

Table 1. The chemical composition and the experimental condition of preparation for the  $\text{Fe}_x\text{O}_y\text{-SiO}_2$  nanocomposites. All the synthesis was carried out on magnetic stirrers with controlled temperature.

Sample	Silica precursor	Molar ratios		Gelation	
		EtOH/ $\text{SiO}_2$	$\text{H}_2\text{O}/\text{SiO}_2$	T, ( $^\circ\text{C}$ )	t, (h)
T	TEOS	4	13.37	65	1
M	MTEOS	8	13.37	65	3

Nano-particles in the silica matrices were observed in electron micrographs obtained by transmission electron microscopy (TEM) with a JEOL 200-CX microscope. FT-IR spectra from 2000 to  $350\text{ cm}^{-1}$  were obtained using a BX spectrometer on KBr pellets of the samples. The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. Measurements were performed on finely ground samples. The magnetic data were corrected for the sample holder.

## 3. Results and discussions

The influence of the silica source on the properties of the prepared nanocomposites is also evidenced in Figs. 1 and 2, which presents the TEM micrographs of the samples T and M. The dark field micrographs indicate the amorphous character of the majority of nanoparticles in the samples treated at temperatures lower than  $600\text{ }^\circ\text{C}$ . An illustration is given by the TEM observations of the samples T treated at  $550\text{ }^\circ\text{C}$  (Fig. 1a) that presents only an amorphous character. In the case of sample treated at  $1000\text{ }^\circ\text{C}$  (Fig. 1b) it was possible to observe nanoparticles with dimensions ranging from 7-14 nm.

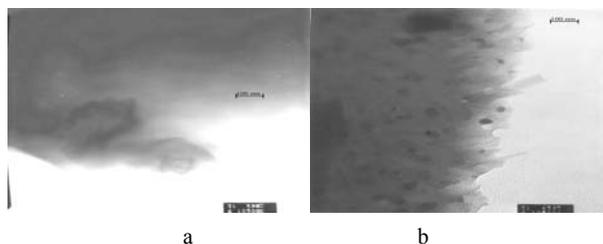


Fig. 1. TEM micrographs of system  $\text{Fe}_2\text{O}_3\text{-SiO}_2$  started with TEOS at  $550\text{ }^\circ\text{C}$  (a) and  $1000\text{ }^\circ\text{C}$  (b).

TEM micrographs of the samples M obtained with MTEOS show particles embedded into the SiO<sub>2</sub> matrix in all the prepared samples. In those samples it could be observed that iron oxide “nanoclusters” appear already at 550 °C (Fig. 2a). These “clusters” appear probably due to the hydrophobic nature of the matrix. It could be observed in the micrographs in Fig. 2a that this sample presented a dark field, which can be attributed to the amorphous part of the sample. The dimension of nanoparticles that was possible to observe is between 38-45 nm. In the case of sample treated at 1000 °C (Fig. 2b), it could be observed that Fe<sub>2</sub>O<sub>3</sub> nanoclusters crystallized. In this case it was possible to observe particles with dimensions between 35-50 nm. The dimensions of particles in the system Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> obtained with MTEOS did not increase significantly after treatment up to 1000°C. The results are in agreement with XRD data. In the sample T, at 550 °C, no iron oxide nanoparticles were noticed, probably because the iron(II) ions are embedded and dispersed in the Si-O-Si network, by -Si-O-Fe-O-Si- type bonds [16, 17].

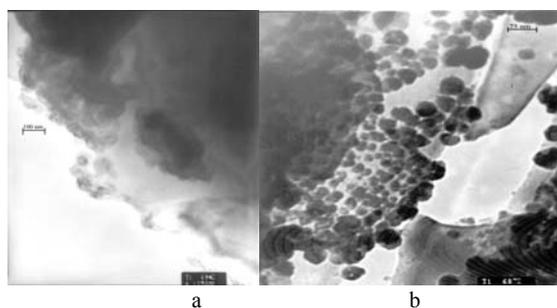


Fig. 2. TEM micrographs of system Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> started with MTEOS at 550 °C (a) and 1000 °C (b).

Figs. 3 and 4 shows respectively the IR spectra between 2000 and 400 cm<sup>-1</sup> of the T and M samples, after thermal treatment at 550 °C and 1000 °C. All spectra presented in Figs. 3 and 4 shows the main features attributed to Si-OH, Si-O-Si, Fe-O, as it was reported by other authors [18-21]. The band at 1640 cm<sup>-1</sup> is due to bending of the adsorbed H<sub>2</sub>O molecules which can interact through hydrogen bonds with silanol groups. S. Bruni in [22] suggests that this band is at higher wave number in the case of nanocomposites. In all cases the characteristic vibration bands of a SiO<sub>2</sub> gel, mainly: ν<sub>as</sub>(Si-O-Si) at 1200 cm<sup>-1</sup> and 1075 cm<sup>-1</sup>; ν<sub>as</sub>(Si-OH) at 970 cm<sup>-1</sup>; ν<sub>s</sub>(Si-O-Si) at 795 cm<sup>-1</sup>; ν(Si-O-Si) from cyclic tetramers at 540 cm<sup>-1</sup> and δ(Si-O-Si) at 460 cm<sup>-1</sup> were identified in accord with literature data [22]. The band at 950 cm<sup>-1</sup> disappears for sample S indicating the polycondensation process [20-25]. The ν(Fe-O) vibration band (530 cm<sup>-1</sup>) appears distinctly only for sample T. For sample S it is hidden by the overlapping with the vibration band characteristic to the silica matrix (540 cm<sup>-1</sup>, Si-O-Si from cyclic tetramers).

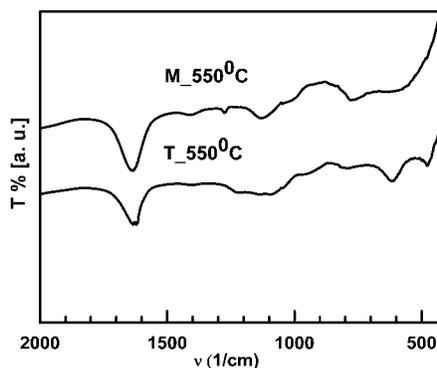


Fig. 3. FT-IR spectra of KBr pellets of samples T and M treated at 550 °C.

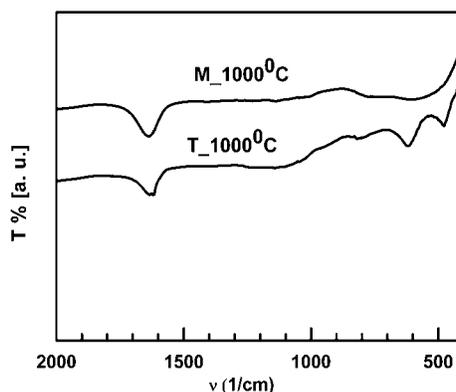


Fig. 4. FT-IR spectra of KBr pellets of samples T and M treated at 1000 °C.

The magnetic susceptibility (defined as  $\chi = M/H$ ) for samples T heated at 1000 °C was measured. At room temperature, the magnetic susceptibility is about  $\sim 3.5 \times 10^{-6}$  emu/g of both compounds. Decreasing the temperature, the magnetic susceptibility for the sample (with an iron content of 3 wt. %, related to SiO<sub>2</sub>) continuously increased as observed on Fig. 5a. Significant negative deviation is apparent in the  $1/\chi$  plot (Fig. 5b) for these samples at  $T < 100$  K. The magnetic susceptibility follows a Curie-Weiss behavior with  $C \approx 0.0007$  emu·K/g·Oe and  $\theta \approx -0.4$  K. Similar deviations from Curie-Weiss behaviour are observed in the related class of ferrite materials above their Curie points [26]. It is reasonable to postulate that the iron ions may be bonded to each other through the oxygen atoms in hydroxyl bridges (e.g., Fe-OH-Fe). In the related class of materials, ferrites, the magnetic interaction between Fe atoms is also via an oxygen atom. In this case, this interaction is known to be antiferromagnetic [27]. The small but negative Weiss constant indicates that the Fe is present in nanometer-sized regions and exists in ionic form (Fe<sup>3+</sup>). The compartment of magnetic susceptibility  $\chi$  and  $1/\chi$  vs. temperature T confirm the iron ions in the matrix. It is reasonable to suppose that the iron ions may be bonded to each other through the oxygen atoms in SiOH groups.

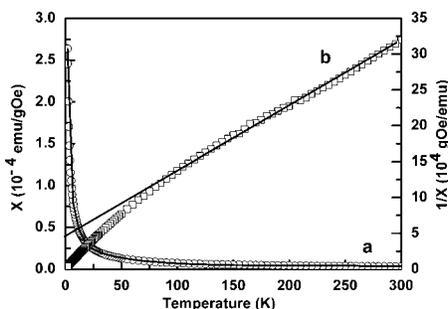


Fig. 5. Magnetic susceptibility  $\chi$ , and  $1/\chi$  vs. T data for sample T treated at 1000 °C measured at 1000 Oe. The solid line represents the best least-square fitting of the data using a Curie Weiss law.

Further information concerning the magnetic behavior of our samples will be reported in future studies.

#### 4. Conclusions

Fe<sub>x</sub>O<sub>y</sub>-SiO<sub>2</sub> nanocomposites were prepared by sol-gel method which used tetraethoxysilane (TEOS), methylethoxysilane (MTEOS) and FeSO<sub>4</sub>·7H<sub>2</sub>O as starting materials. The influence of the matrix obtained from the TEOS and MTEOS precursors plays a major role in the evolution of the processes. The presence of the dark-field micrographs indicates the amorphous character of the nanoparticles in the samples. The tendency of crystallization of iron oxides increases in the case of the material obtained using methylethoxysilane (samples M). In the samples M the same nano-clusters were visible already in the materials thermally treated at 550 °C. For samples T (obtained by thermal treatment using tetraethoxysilane) the same iron oxide nanoparticles were observed at 1000 °C. The tendency of crystallization did not appear up to 550 °C because the iron ions might be bonded the silicate skeleton: O-Si-O-Fe-O-Si-O.

#### References

- [1] R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrotra, M. W. Russel, D. R. Huffman, *Science* **257**, 219 (1992).
- [2] S. Onodera, H. Kondo, T. Hawana, *MRS Bull* **21**, 35 (1996).
- [3] C. R. F. Lund, J. A. Dumesic, *J. Phys. Chem.* **86**, 130, (1982).
- [4] L. Nixon, C. A. Koval, R. D. Nobl, G. S. Staff, *Chem. Mater.* **4**, 117 (1992).
- [5] C. Cannas, D. Gatteschi, A. Musinu, G. Piccaluga, C. Sangregorio, *J. Phys. Chem. B* **102**, 7721 (1998).
- [6] G. Ennas, A. Musinu, G. Piccaluga, D. Zedda, D. Gatteschi, C. Sangregorio, J. L. Stanger, G. Concas G. Spano, *Chem. Mater.* **10**, 495 (1998).
- [7] A. Y. Vlasov, G. V. Loseva, G. S. Sakash, L. S. Solntseva, *Zh. Prikl. Spektrosk. Russ.* **12**, 1130 (1970).
- [8] R. Derie, M. Ghodsi, C. Calvo-Roche, *J. Termal Anal.* **9**, 435 (1976).
- [9] D. G. Klissurski, V. N. Bluskov, *Mater. Chem.* **5**, 67 (1980).
- [10] S. Goni-Elizalde, M. E. Garcia-Clavel, *Thermochim. Acta* **124**, 359 (1899).
- [11] R. D. Shull, J. J. Ritter, A. J. Shapiro, L. Swartzendruber, L. H. Bennet, *J. appl. Phys.* **67**, 4490 (1990).
- [12] S. Roy, A. Chatterjee, D. Chakravorty, *J. Mater. Res.*, **8**, 689 (1993).
- [13] J. P. Wang, H. L. Luo, *J. Appl. Phys.* **75**, 7425 (1994).
- [14] P. Tartaj, T. G. Carreno, C. J. Serna, *J. Phys. Chem. B*, **107**, 20 (2003).
- [15] M. Fernandez-Garcia, A. Martinez-Arias, J. C. Hanson, J. A. Rodriguez, *Chem. Rev.* **104**, 4063 (2004).
- [16] M. R. Ayers, X. Y. Song, A. J. Hunt, *J. Mater. Sci.* **31**, 6251 (1996).
- [17] T. Lopèz, J. Mendèz, T. Zamudio, M. Villa, *Mater. Chem. Phys.* **30**, 161 (1992).
- [18] A. Jitianu, M. Crişan, A. Meghea, I. Rău, M. Zaharescu, *Mater. Chem.* **12**, 1401 (2002).
- [19] M. Nogami, N. Asuha, *J. Mater. Sci. Lett.* **12**, 1705 (1993).
- [20] C. Chaneac, E. Tronc, J. P. Jolivet, *J. Mater. Chem.* **6**(12), 1905 (1996).
- [21] J. Y. Ying, J. B. Benziger, A. Navrotsky, *J. Am. Ceram. Soc.* **76**(10), 2571 (1993).
- [22] S. Bruni, F. Cariati, M. Casu, A. Lai, A. Musinu, G. Piccaluga, S. Solinbas, *NanoStructured Materials*, **5**(11), 573 (1999).
- [23] C. A. Capozzi, L. D. Pye, R. A. Condrate – Vibrational spectral/structural changes from the hidrolisis/polycondensation of methyl – modified silicates. Comparisons for single monomer condensates – *Mat. Lett.* **15**, 130 (1992).
- [24] R. A. Nyquist, R. O. Kagel, *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, 99 (1971).
- [25] N. T. Mc.Devitt, W. L. Baun, *Spectrochim. Acta* **20**, 799 (1964).
- [26] A. Serres, *Ann. Phys.* **17**, 5 (1932).
- [27] C. G. Shull. E. O. Wollan, W. C. Koehler, *Phys. Rev.* **84**, 912 (1951).