

Mechanochemical Preparation and Magnetic Properties of Fe₃O₄/ZnS Nanocomposite

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Powder nanocomposite of Fe₃O₄/ZnS was prepared by mechanochemical synthesis in a planetary ball mill. In this reaction natural magnetite mineral Fe₃O₄ was used, together with zinc acetate (CH₃COO)₂Zn · 2H₂O and sodium sulfide Na₂S · 9H₂O, as precursors for the zinc sulfide ZnS. X-ray diffraction revealed that the sample is composed of small nanocrystalline particles, containing Fe₃O₄ and ZnS. The non-milled magnetite showed distinctive Verwey transition at around 120 K, this becomes suppressed after milling, as a consequence of structural disorder and presence of defects. Moreover, the reduction of saturation magnetization from 91 A m²/kg to 69.2 A m²/kg was observed, as a consequence of the milling process. The magnetization of the Fe₃O₄/ZnS nanocomposite was the lowest (34.5 A m²/kg), due to the milling and to the decreased weight fraction of the ferrimagnetic component. Nevertheless, the Fe₃O₄/ZnS sample demonstrates ferrimagnetic behavior as well, and its structure is less perturbed by milling, the Verwey transition, although less impressive, but is preserved.

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1. Introduction

Materials with multifunctional properties are in the focus of materials science of the last years [1–3]. Bifunctional nanocomposite materials with the unique combination of magnetic and fluorescent properties are of special interest, they are studied mostly for their potential applications in optoelectronics and in biomedicine [4]. The development of suitable drug delivery vehicles for targeted therapy is also of growing interest, as the efficiency of a drug can be rapidly increased and the reduction of the undesirable side effects can be achieved [5]. In the above aspects the magnetite (Fe₃O₄) based materials have irreplaceable position due to specific properties of magnetite. By using external magnetic field it is possible to control their biodistribution [6]. Magnetite with its cubic inverse spinel structure (Fe³⁺)_A(Fe^{2.5+})_BO₄ has tetrahedrally (A) and octahedrally (B) coordinated iron cations and strong ferrimagnetism.

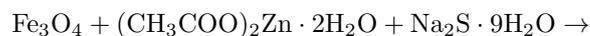
Among the materials having fluorescent properties the II–VI group semiconductors are the most studied inorganic, optically active materials, especially in the form of nanostructures [7–9]. Zinc sulfide (ZnS), one of the most known members of this semiconductor group, with its large band gap energy (3.54 eV and 3.80 eV for cubic and hexagonal structures, respectively), is intensively studied as an attractive material in optoelectronics, where it is applied in lasers, solar cells, photovoltaic devices, or electroluminescent displays [10, 11]. It could be potentially useful for application in biological imaging due to its non-toxicity. The nanocomposite Fe₃O₄/ZnS has been

already prepared [4, 12, 13]. In the mentioned works, magnetite was in the first step prepared by chemical coprecipitation methods. Subsequently, the zinc sulfides were precipitated on the magnetite surface.

In this work we have used natural mineral magnetite and precursors of zinc sulfide (zinc acetate and sodium sulfide). The Fe₃O₄/ZnS nanocomposite was prepared in one step, using mechanochemical synthesis. The obtained material was studied from structural point of view and its magnetic properties were investigated.

2. Materials and methods

The Fe₃O₄/ZnS nanocomposite was prepared by milling in a planetary mill Pulverisette 6 (Fritsch) in argon atmosphere for 30 min. The milling was performed in a 250 ml tungsten carbide milling chamber with 50 tungsten carbide balls, 10 mm in diameter. The rotational speed of the planet carrier was 500 rpm. The overall process of preparation lies in the following reaction:



where Fe₃O₄ is a natural mineral magnetite (Kiruna, Sweden), and zinc acetate (99%, Ites) with sodium sulfide (98%, Acros Organics) are precursors of the ZnS compound. After the reaction the sodium acetate was washed out from the product with pure water and after drying the solid phase of Fe₃O₄/ZnS was obtained. The sample was prepared in molar ratio Fe₃O₄ : ZnS = 1 : 4.

X-ray diffraction (XRD) measurements were carried out using a D8 Advance diffractometer (Bruker) with a θ/θ goniometer, Cu K_α radiation (40 kV, 40 mA), and a scintillation detector. The diffraction data were collected over an angular range of $10^\circ < 2\theta < 80^\circ$, with steps of

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0.03° and a counting time of 20 s/step. The commercial Diffrac^{plus} Eva software was used for phase analysis according to the ICDD-PDF2 database. The average crystallite size was determined using Rietveld refinement, implemented in Diffrac^{plus} Topas.

The temperature dependence of magnetization down to 2 K was measured using the Quantum Design MPMS-XL5 device in magnetic field of 10 mT, both in zero field cooling (ZFC) and field cooling (FC) regimes. The room-temperature hysteresis loops were taken in magnetic fields up to 5 T by the same device.

3. Results and discussion

The XRD pattern of the outgoing natural mineral magnetite is shown in Fig. 1a. It can be seen that the mineral is of very pure quality Fe₃O₄ phase. According to the ICDD, the fcc cubic (*Fd-3m*) phase (71-6336) has been detected. The obtained diffraction peaks are narrow, suggesting that the sample is crystalline. The estimated average crystallite size is 187±17 nm. After milling the observable massive peak broadening is a sign of nanocrystalline formation (Fig. 1b), the mean crystallite size decreased to 8±1.6 nm. In Fig. 1c the pattern of Fe₃O₄/ZnS shows the coexisting Fe₃O₄ and ZnS phases.

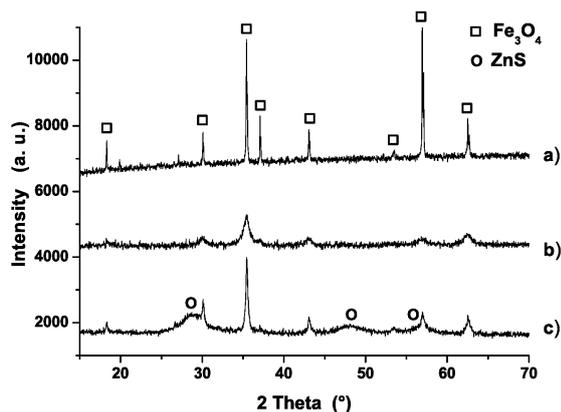


Fig. 1. XRD pattern for (a) natural, (b) milled Fe₃O₄ and (c) mechanochemically prepared Fe₃O₄/ZnS nanocomposite.

The peaks are also broad, reflecting the nanocrystalline character of the sample, however, the diffraction peaks corresponding to magnetite are broadened not to such extent like in case of pure magnetite, despite the same milling time. Average crystallite size of 22±5 nm was obtained. On the other hand, the diffraction peaks corresponding to ZnS are very broad, smeared, suggesting its very fine, almost amorphous structure, with crystallites of 2.5±0.1 nm. The fcc cubic (*F-43m*) phase (65-1691) was identified.

Figure 2 shows the temperature dependence of magnetization of the samples, both in FC and ZFC modes. The natural non-milled magnetite has a transition at temperatures around 120 K, which could be assigned to the so-

called Verwey transition [14]. As found by Verwey, magnetite, the metallic ferrimagnet at room temperature, becomes electrically insulating below 123 K, and also a structural transformation from cubic to monoclinic symmetry occurs. The transition is sensitive to structural peculiarities, such as oxygen stoichiometry, vacancy and cation distribution, etc. After milling, as it can be expected due to the strong size reduction and surface disorder, the magnetization decreases and the Verwey transition vanishes.

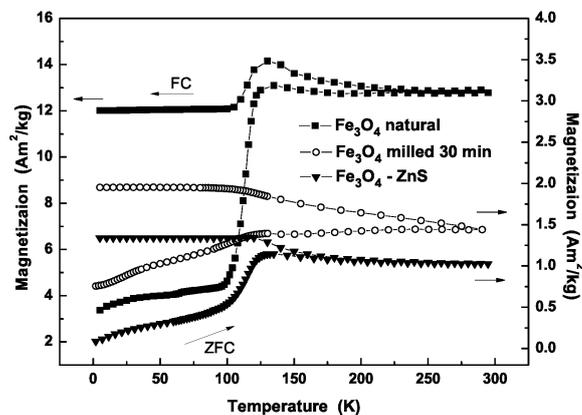


Fig. 2. Temperature dependence of magnetization, measured in external magnetic field of 10 mT in FC and ZFC modes.

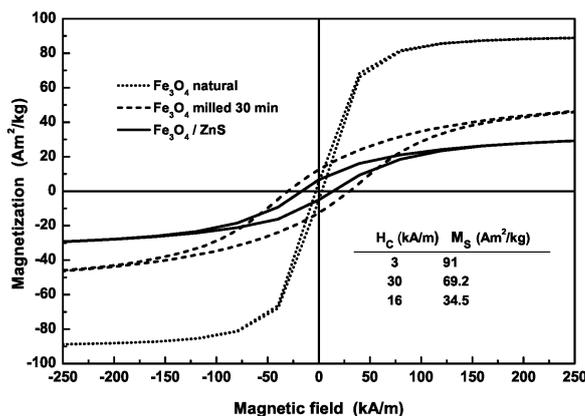


Fig. 3. Room-temperature hysteresis loops.

It has been reported that this transition is also size dependent, and with decreasing nanocrystal size it smears out. This smearing starts in systems with crystal size 20 nm and is completely finished for nanocrystals below 6 nm [15]. Our results are in correspondence with the above findings. In the mixed Fe₃O₄/ZnS system, with magnetite crystallite size around 22 nm the Verwey transition even though smeared, but survived, while in the milled magnetite with crystallite size 8 nm it becomes suppressed.

In Fig. 3 the room-temperature hysteresis loops of the samples are displayed. It is not surprising that the

natural non-milled magnetite has the largest saturation magnetization, 91 A m²/kg. This is almost the theoretical value, the spin moment in the inverse spinel structure magnetite, determined as ≈ 4 Bohr magnetons (92 A m²/kg) [16], indicating high purity and defect-free structure of the mineral. The saturation magnetization decreases with milling to 69.2 A m²/kg. The magnetization of the Fe₃O₄/ZnS nanocomposite is the lowest (34.5 A m²/kg), which is reasonable, since the weight fraction of the ferrimagnetic component is smaller. Nevertheless, the Fe₃O₄/ZnS sample demonstrates ferromagnetic behavior as well. The increased hysteresis after milling is connected with the structural changes — crystalline size reduction, increased specific surface strain and disorder (Fig. 3).

4. Conclusions

Nanocrystalline Fe₃O₄/ZnS with unique combination of magnetic and fluorescent properties was prepared by mechanochemical synthesis in a planetary ball mill, using natural magnetite mineral with zinc acetate and sodium sulfide precursors. X-ray diffraction revealed the nanoscale structure, composed of Fe₃O₄, with average crystalline size of 22 nm, and ZnS, having even finer crystallites of 2.5 nm. Milling of pure Fe₃O₄ leads to stronger reduction of crystallite size (8 nm). From magnetic point of view, the Fe₃O₄/ZnS nanocomposite demonstrates ferrimagnetic behavior, it has reduced saturation magnetization 34.5 A m²/kg in comparison to natural magnetite (91 A m²/kg), but the Verwey transition around 120 K, observed in the natural magnetite, although less impressive, is still preserved. This is not true for the milled pure magnetite, for which the strong crystallite size reduction, structural disorder and introduction of defects suppresses the transition. The presence of precursors and the ZnS formation during the milling due to its energy consumption decreases the mechanical impact of milling on the structure of magnetite, thus, allows the Verwey transition to survive.

Acknowledgments

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