

## Composite thin films of nanosized $\text{CoFe}_2\text{O}_4$ in polymer matrix

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Nanosized cobalt ferrite was prepared by a solution combustion method. Metal nitrates in a stoichiometric ratio and sucrose were used as starting reagents. The “as prepared” cobalt ferrite powder has a mean crystallite size up to 10 nm. By further thermal treatment at 600°C a nanosized material with average crystallite size of about 30–40 nm is obtained. The composite was prepared by adding cobalt ferrite to an aqueous solution of carboxymethylcellulose with a subsequent 5 minute sonication. Thin layers were deposited on a glass substrate by spin coating technique in a laboratory centrifuge at 6000 rpm. Drying was carried out at room temperature. Thin composite layers were characterized as to the crystal structure, crystallite size, magnetic phase, and oxidation state, by X-ray powder diffraction, transmission electron microscopy, scanning electron microscopy and Mössbauer spectroscopy.

**Key words:** polymer- $\text{CoFe}_2\text{O}_4$  composite, X-ray diffraction, electron microscopy, Mössbauer spectroscopy

### INTRODUCTION

Spinel cobalt ferrite represents a type of magnetic material with a high magnetic stability, good magnetization properties, large magneto-optic rotation ability, and high coercivity. Cobalt ferrites are usually prepared by a solid state reaction procedure: the reactants have to be grounded, mixed, and calcinated, and the reactions take place at high temperatures, lasting for a long period of time [1–3]. However, by this method, it is very difficult to obtain the pure spinel phase products; also the resultant particles are always obtained in a large size of the order of “ $\mu\text{m}$ ”. For many applications it is very important to develop different protection techniques to stabilize the magnetic nanoparticles against degradation. Various types of coating layers, both organic and inorganic were used for this purpose [4]. In the last several years many “soft chemistry” methods for preparing nanosized materials have been developed. One of them is the so-called solution combustion method, which is based on a combustion reaction of metal nitrates (oxidizers) and some organic reductors (such as glycine, urea, citric acid, etc.) acting as a fuel [5, 6]. The method provides simple operation procedures and short processing times, thus it is time and energy-saving. What is more important for the method is that the reactants are in highly homogeneous form during

the whole reaction process. An additional advantage of the short time and low temperature of decomposition of the precursors and formation of the oxide materials is that the as obtained products are amorphous or have small crystallite size of the order of a few tens of “nm” and the particle size can be adjusted within a range by variation of the reaction parameters. For these reasons the method is very suitable for preparation of nanosized materials with controlled particle size. In the present work a composite material comprising cobalt ferrite nanoparticles (obtained by a solution combustion method) and carboxymethylcellulose (CMC) polymer (as a protector) is prepared. The composite material was deposited as a thin layer of a few “ $\mu\text{m}$ ” thickness on a glass substrate. The composite layer was characterized as to the, crystal structure, crystallite size, magnetic phase, and oxidation state, by means of a X-ray powder diffraction, transmission electron microscopy, scanning electron microscopy, and Mössbauer spectroscopy.

### EXPERIMENTAL

Magnetic nanoparticles of cobalt ferrite were synthesized by a solution combustion synthesis technique. The method is based on a combustion reaction of metal nitrates (oxidizers) and some organic reductors (glycine, urea, citric acid, etc.) acting as a fuel. As starting reagents  $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) were used. The molar ratio between the nitrates and sucrose was calcu-

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lated according to the principles of combustion reaction on the basis of the total oxidising and reducing power of the metal nitrates (O) and the sucrose (F) ensuring that the oxidation power of nitrates is equal to the reducing power of sucrose i.e.  $F:O=1$ . The intense evolution of gaseous products of decomposition of initial reagents during the reaction causes the formation of a voluminous product consisting of loosely packed particles. The as-prepared materials consist of crystallites with mean size of about 3-5 nm. A heat treatment for 1h at  $400^\circ\text{C}$  is usually performed to ensure the burning of the residual organic components. The final thermal treatment for 1 hour at  $600^\circ\text{C}$  was applied to obtain cobalt ferrite nanoparticles with mean size in the range 30 nm. The composite CMC -  $\text{CoFe}_2\text{O}_4$  was prepared by adding powder of cobalt ferrite to an aqueous solution of carboxymethylcellulose with a subsequent 5 minutes treatment with ultrasonic processor SONIX, USA (20 KHz, 750 W). Thin layers were deposited on a glass substrate by spin coating technique in a laboratory centrifuge at 6000 rpm. Drying was carried out at room temperature 10 min.

Powder X-ray diffraction patterns were collected within the range from  $5.3$  to  $80^\circ 2\theta$  with a constant step  $0.02^\circ 2\theta$  on Bruker D8 Advance diffractometer with  $\text{Cu K}\alpha$  radiation and LynxEye detector. Phase identification was performed with the Diffracplus EVA using ICDD-PDF2 Database. Mean crystallite size were determined with the Topas-4.2 software package using the fundamental parameters peak shape description including appropriate corrections for the instrumental broadening and diffractometer geometry.

Transmission electron microscopy (TEM) investigations were performed by TEM JEOL 2100 with 200 kV accelerating voltage. The specimens were grinded and dispersed in ethanol by ultrasonic treatment for 6 min. The suspensions were dripped on standard holey carbon/Cu grids. SEM analyses were made in a JEOL-JSM-6390 scanning electron microscope.

$^{57}\text{Fe}$  Mössbauer measurements were performed using a constant acceleration spectrometer. A source of  $^{57}\text{Co}(\text{Rh})$  with activity of 10 mCi was used. The Mössbauer absorber with a thickness of  $40 \text{ mg}\cdot\text{cm}^{-2}$  Fe was made as follows. Small flakes of deposited thin film material were scraped from the glass substrate. They were mixed with powder of polyvinyl alcohol (glue material) and then pressed into a disk pellet. The  $\text{CoFe}_2\text{O}_4$  spectrum was taken in transmission

mode at room temperature (RT). The experimental Mössbauer spectrum was decomposed through the so-called "thin sample approximation" when the spectrum is represented as a sum of few simple spectra (sextets). The parameters of the fitted Mössbauer spectra corresponding to isomer shift (IS), quadrupole shift (QS), magnetic field at the site of the Fe nucleus (H) and relative spectral area are summarized in Table 1. The geometric effect is taken into account as well.

## RESULTS AND DISCUSSION

Figure 1(a-c) shows the XRD patterns of the  $\text{CoFe}_2\text{O}_4$  material-as prepared and thermally treated subsequently, at  $400^\circ\text{C}$  and  $600^\circ\text{C}$  for 1 hour. All patterns were indexed within the cubic  $\text{Fd-}3\text{m}$  space group.

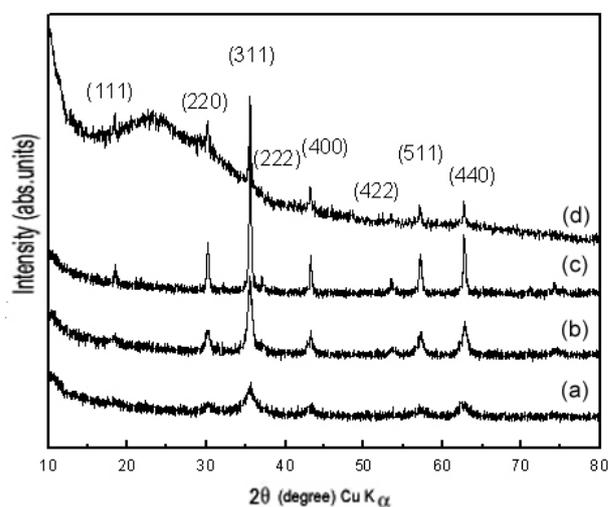


Fig. 1. XRD patterns of samples of  $\text{CoFe}_2\text{O}_4$ : (a) as prepared; (b) heated 1 hour at  $400^\circ\text{C}$ ; (c) heated 1 hour at  $600^\circ\text{C}$ ; (d)  $\text{CoFe}_2\text{O}_4$  in CMC-film.

The unit cell parameter slightly increases with heating temperature due to the slight variation of the oxidation state of Co and Fe cations. The dependence of the mean crystallite size on the temperature is much more pronounced. It is seen that the mean crystallite size of the material increases with increasing the temperature of the thermal treatment. Fig. 1d represents the powder diffraction pattern of material heated at  $600^\circ\text{C}$  for 1h in carboxymethylcellulose matrix. The hump of amorphous CMC - matrix of the composite films is clearly seen as well as the peaks of the nanosized  $\text{CoFe}_2\text{O}_4$  material. No reaction between the material and the matrix is observed.

In Fig. 2 a TEM photograph is shown of  $\text{CoFe}_2\text{O}_4$  nanosized particles obtained by solution combustion

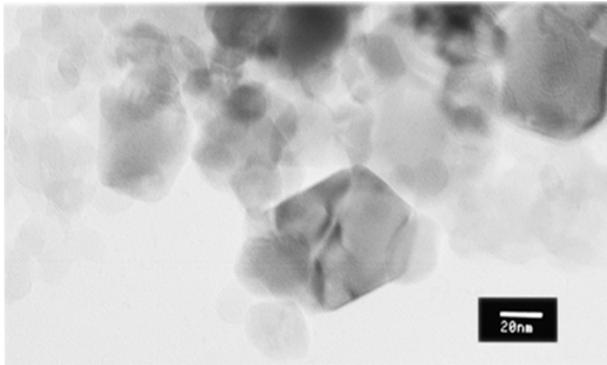


Fig. 2. A TEM photograph of  $\text{CoFe}_2\text{O}_4$  nanosized particles obtained by a solution combustion method.

method and heated 1h at  $600^\circ\text{C}$ . Individual well defined particles with hexagonal form and mean size about 30-40 nm can be observed.

Some smaller particles still have oval form. The distribution of the  $\text{CoFe}_2\text{O}_4$  nanoparticles in CMC-matrix was studied by SEM imaging. Fig. 3 (a,b) shows the secondary electrons image (SEI) photographs of CMC- $\text{CoFe}_2\text{O}_4$  composite layer at different magnifications. The magnetic particle aggregates are uniformly distributed within the polymer CMC-layer. As can be seen, the  $\text{CoFe}_2\text{O}_4$  nanoparticles tend to stick together and form relatively big aggregates from 500 nm to 3  $\mu\text{m}$  in size.

In Fig. 4 the Mössbauer spectrum of  $\text{CoFe}_2\text{O}_4$  at room temperature is shown. The experimental Mössbauer spectrum was decomposed as a sum of three sextets, which is an evidence of complete fer-

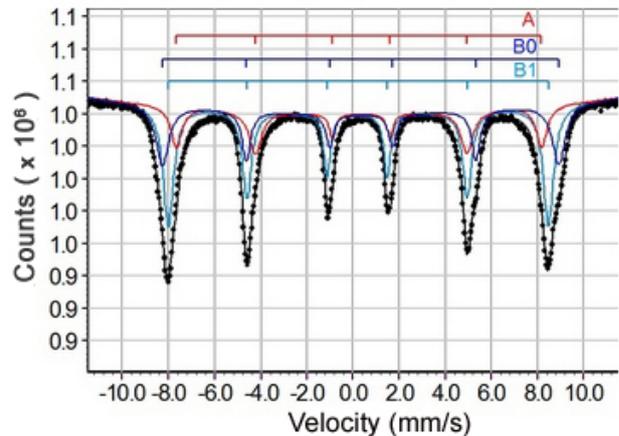
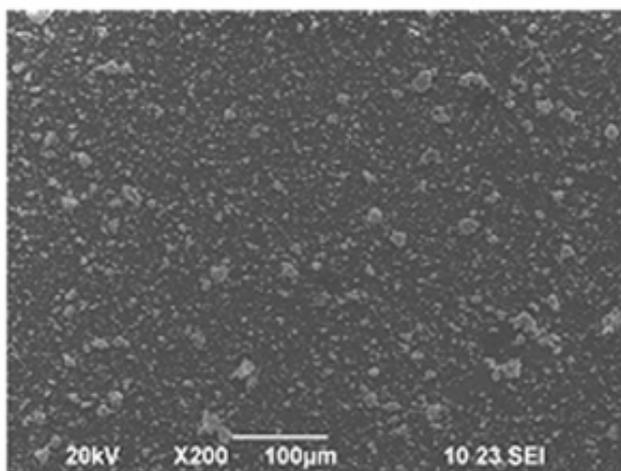


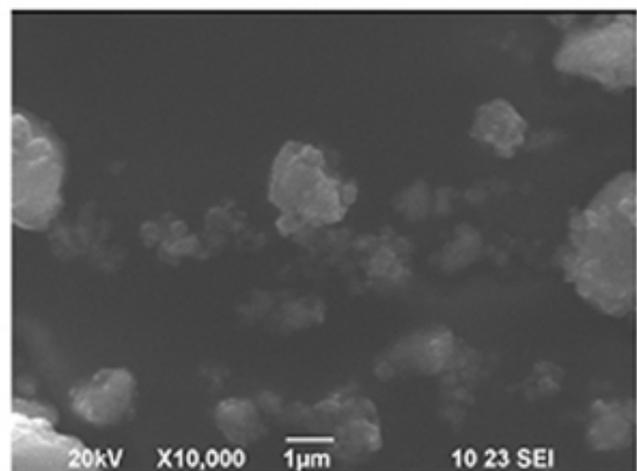
Fig. 4. Mössbauer spectrum of nanosized  $\text{CoFe}_2\text{O}_4$  in polymer thin films.

rimagnetic behavior of the sample. Indeed, within the experimental error, there is no any superparamagnetic components in the Mössbauer spectrum. The general formula of spinel ferrites is  $\text{MO} \cdot \text{Fe}_2\text{O}_3$ , where M is usually divalent transition metal ion.

The Spinel ferrite structure consists of a cubic close-packed oxygen arrangement, in which the cations occupy tetrahedral and octahedral sites within the unit cell. Occupation of tetrahedral sites with divalent metal ions yields a normal spinel structure typical for  $\text{M}^{2+}$ :  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ , while occupation of octahedral sites with the divalent metal ions  $\text{M}^{2+}$ :  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  results in an inverse spinel structure.



(a)



(b)

Fig. 3. SEI photographs of CMC- $\text{CoFe}_2\text{O}_4$  composite layers at different magnifications.

Table 1. The parameters of a Mössbauer spectrum of a nanocomposite CoFe<sub>2</sub>O<sub>4</sub> layer.

Glassed CoFe <sub>2</sub> O <sub>4</sub>	T, K	Component	IS, mm/s	FWHM, mm/s	QS, mm/s	H, kOe	Spectr. area, %
	Room temperature (RT)	A	0.31	0.22	-0.0451	492.5	22.1
		B0	0.34	0.32	-0.0119	534.5	28.95
		B1	0.2	0.24	0.028	512.6	48.95

The cobalt ferrite, depending on the different ways of synthesising, could be completely inverse spinel or partially inverse spinel. In a partial inverse spinel system a fraction of the cobalt ions enters at the tetrahedral sites. In a complete inverse spinel system, concerning CoFe<sub>2</sub>O<sub>4</sub> each Fe<sup>3+</sup> ion in the octahedral B-site is surrounded by six Fe<sup>3+</sup> ions in tetrahedral A-sites as the second nearest neighbors.

According to [7] the super-exchange interaction via oxygen anion between Fe<sup>3+</sup> ions at A-B sites is strongest. The interaction at the A-A sites or at the B-B sites is much weaker. Entering of cobalt ions into tetrahedral sites will reduce A-B interaction and hence will reduce hyperfine magnetic field on Fe<sup>3+</sup> ions in B-site. On the other hand each Fe<sup>3+</sup> ion in a tetrahedral site is surrounded by twelve Fe<sup>3+</sup> ions in a B-site. A replacement of Fe<sup>3+</sup> ions by Co<sup>2+</sup> ions in a B-site does not produce a large change in the total super-exchange interaction which would lead to negligible change of the hyperfine magnetic field on the Fe<sup>3+</sup> in A-site. The presence of three sextets for each Mössbauer spectrum in Fig. 4 shows unambiguously that we are dealing with a partial inverse spinel system. The sextet A with the smallest magnetic field should be assigned to the Fe<sup>3+</sup> cations in a tetrahedral A-site. The sextet B0 with the largest magnetic field should be assigned to the Fe<sup>3+</sup> ions in B-site at a sixfold Fe<sup>3+</sup> surrounding from the A-site i.e. without any Co<sup>2+</sup> in the A-site. The sextet B1 corresponds to Fe<sup>3+</sup> in a B-site where one or more Fe<sup>3+</sup> ions in a tetrahedral site were being replaced by Co<sup>2+</sup>. From the measured relative spectral areas of the sextets A, B0, and B1, we can derive the formula for the cation distribution in the sample. In our case the formula reads (Co<sub>0.56</sub>Fe<sub>0.44</sub>)[Co<sub>0.44</sub>Fe<sub>1.56</sub>]O<sub>4</sub>.

#### CONCLUSIONS

Nanosized CoFe<sub>2</sub>O<sub>4</sub> has been obtained by solution combustion method. The method allows

producing oxide materials with a predefined particle size within the nanoscale range by simple control of heating temperature. A composite material comprising CoFe<sub>2</sub>O<sub>4</sub> nanoparticles in amorphous CMC-film was prepared. Thin composite layers were characterized by X-ray powder diffraction, high resolution transmission electron microscopy, scanning electron microscopy and Mössbauer spectroscopy. The Mössbauer spectroscopy measurements of the nanosized CoFe<sub>2</sub>O<sub>4</sub> revealed partially inverse spinel structure where the cation distribution (of the Co and Fe cations) is presented by the formula (Co<sub>0.56</sub>Fe<sub>0.44</sub>)[Co<sub>0.44</sub>Fe<sub>1.56</sub>]O<sub>4</sub>.

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#### REFERENCES

- [1] S. R. Ahmed, S. B. Ogale, G. C. Papaefthymiou, R. Ramesh, P. Kofinas, *Applied Physics Letters* **80**, 1616-1618 (2002).
- [2] J. G. Lee, J. Y. Park, C. S. Kim, *Journal of Materials science* **33**, 3965-3968 (1998).
- [3] P. Chandramohan, M. P. Srinivasan, S. Velmurugan, S. V. Narasimhan, *Journal of Solid State Chemistry* **184**, 89-96 (2011).
- [4] D. Kovacheva, T. Ruskov, P. Krystev, S. Asenov, N. Tanev, I. Mönch, R. Koseva, U. Wolff, T. Gemming, M. Markova-Velichkova, D. Nihtianova, K.F. Arndt, *Bulgarian Chemical communications* **44**, 90-97 (2012).
- [5] S.R.Jain, K.C.Adiga, V.R.Pai Verneker, *Combust. Flame* **40**, 71-79 (1981).
- [6] M.M.A.Sekar, K.C.Patil, *J.Mater.Chem.* **2**, 739-743 (1992).
- [7] G.A.Sawatzky, F. Van Der Woude and A.H. Morrish, *J.Appl.Phys* **39**, 1204 -1206 (1968).

КОМПОЗИТНИ ТЪНКИ СЛОЕВЕ ОТ НАНОРАЗМЕРЕН CoFe<sub>2</sub>O<sub>4</sub>  
В ПОЛИМЕРНА МАТРИЦА

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(Резюме)

Прахообразен материал от наноразмерен кобалтов ферит беше синтезиран по метода на горене от разтвор (комбустивен синтез). Като изходни реагенти са използвани съответни кобалтов нитрат и железен нитрат в стехиометрично съотношение, както и захароза. Така полученият кобалтов ферит има среден размер на кристалитите около 10 nm. Чрез допълнително термично третиране при 600°C е получен материал със среден размер на кристалитите 30–40 nm. Композитът бе получен чрез добавяне на кобалтов ферит към воден разтвор на карбоксиметил целулоза с последваща ултразвукова обработка. Нанасянето на тънките слоеве върху стъклена подложка е извършено по метода на спинеруването в лабораторна центрофуга при 6000 грм. Изсушаването е извършено при стайна температура. Тънките композитни слоеве бяха характеризирани с методите на праховата рентгенова дифракция, сканираща електронна микроскопия и Мьосбауерова спектроскопия.