Journal of Physics: Conference Series

PAPER • OPEN ACCESS

Synthesis of cubic ferrite $CoFe_2O_4$ by spray pyrolysis

To cite this article: R V Minin *et al* 2018 *J. Phys.: Conf. Ser.* **1115** 042011

Synthesis of cubic ferrite $CoFe_2O_4$ by spray pyrolysis

R V Minin[1], V I Itin[1], V A Zhuravlev[2] and V A Svetlichnyi[2]

[1]Tomsk Scientific Center, SB RAS, 10/3 Akademichesky Ave., Tomsk, 634021, Russia
[2]Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russia

E-mail: waserman@yandex.ru

Abstract. The phase composition, morphology, and structural parameters of cobalt ferrospinel powders synthesized by spray pyrolysis combined with drop sol-gel combustion are determined. The obtained data are compared with those of the powders synthesized by sol-gel combustion.

1. Introduction

At present, nanosized and nanocrystalline powders are the basis of new promising materials and methods. There are many methods for the synthesis of such powders, but the main requirements are the obtaining of powders with a narrow granulometric distribution and the absence of agglomeration. It is known that the surface area to volume ratio is very high and the agglomeration process is thermodynamically preferable for nanosized particles.

These requirements are especially important for the production of magnetic nanoparticles, since their characteristics are mainly determined by the size, shape, and the ability to create anisotropic structures [1]. In particular, surface anisotropy plays an important role, since it is proportional to the surface area of the particle rather than to the volume of the particle in contrast to shape and exchange anisotropy. For nanocrystalline magnetic materials, magnetic properties, especially high-frequency ones, are determined not by the displacement of domain boundaries as in large-crystal ferromagnetics, but by the rotation of magnetization vectors of individual nanocrystallites.

It should be noted that the problem of agglomeration can be solved using the synthesis methods in which the formation and separation of particles take place. These methods include the well-known spray pyrolysis methods [2-7] in which liquid solutions of reagents are sprayed and the drops of solution are supplied to a heated reactor or flame. Heat treatment leads to the evaporation of the solvent and the formation of a solid phase in the form of nanosized [6-7] or nanocrystalline [2-5] spherical particles in the absence of agglomeration.

Of particular interest is the synthesis when spray pyrolysis is combined with self-propagating high-temperature synthesis proceeding in the volume of individual liquid drops of sprayed solution (drop sol-gel combustion) [5].

The study showed the formation of an unusual solid phase – large hollow spherical particles that were filled with smaller ones which in turn were filled with smaller spherical particles [5, 6].

2. Method of synthesis and study

To synthesize the powders of cobalt ferrospinels by spray pyrolysis, a chemical reaction is used in the form as follows:

$$Co(NO_3)_2{\cdot}6H_2O + 2Fe(NO_3)_3{\cdot}9H_2O + C_6H_8O_7 + O_2 = CoFe_2O_4 + 6CO_2 + 28H_2O + 5NO_2 + 3NO$$

Aqueous solutions of cobalt nitrates $Co(NO_3)_2{\cdot}6H_2O$ (TU 6-09-02-504-91), iron nitrate 9-hydrate pure $Fe(NO_3)_3{\cdot}9H_2O$ (TU 6-09 -02-553-96) and citric acid $C_6H_8O_7$ (GOST 3652-69) with a concentration of 1M were used as reagents which were mixed in ratio as follows:

$$\{[Co(NO_3)_2 \cdot 6H_2O] : [Fe(NO_3)_3 \cdot 9H_2O]\} : C_6H_8O_7 = \{1 : 2\} : 2$$

Metal nitrates and citric acid were separately dissolved in distilled water. Then, water solutions were mixed. A concentrated solution of ammonium hydroxide NH_4OH (GOST 3760-79) was added dropwise to the obtained mixture, constantly stirring until the solution had a pH of 2. PH of the medium was measured with a portable digital pH meter CheckerHI98103 (HANNA Instruments). Synthesis of cobalt ferrite by spray pyrolysis was conducted using an experimental unit shown in figure 1.

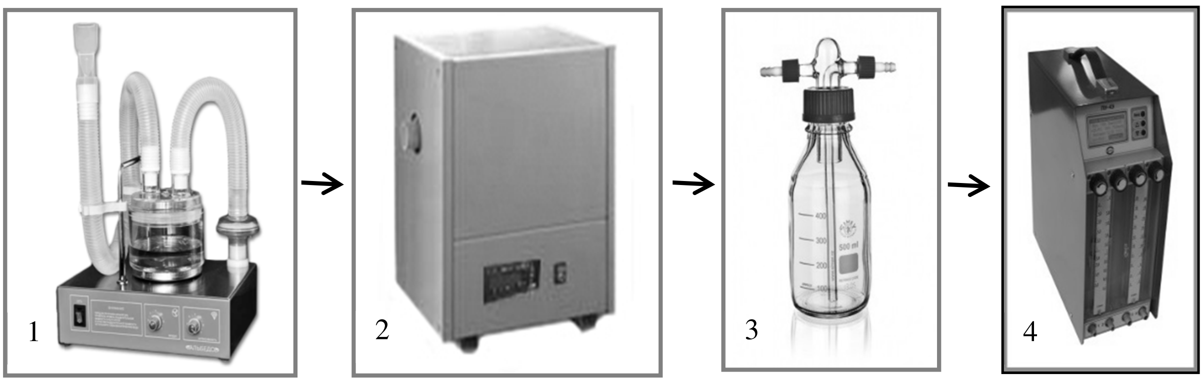

Figure 1. Schematic of the experimental unit. (1) Ultrasonic nebulizer; (2) Tube furnace; (3) Drexel’s flask; (4) Suction pump.

An ultrasonic nebulizer (Albedo IN-7) was used to convert the initial solution into aerosol that through flexible tubes was supplied to the operating zone of a tube furnace heated to a temperature of 1200°C. At this stage, evaporation of water and chemical interaction between the components of the reaction mixture take place, as well as short ferritization. Then the formed ferrite particles, as well as the gaseous combustion products were supplied to the Drexel bottle to trap the solid particles of the synthesized products in distilled water. A PU-4E aspirator was used to control the aerosol flow rate in the operating zone of the furnace and the removal of reaction products.

The obtained suspension was poured from a Drexel bottle into a glass container and placed on a permanent magnet to accelerate the precipitation process. Then, the obtained precipitation was dried.

X-ray diffraction analysis was done using a DRON-UM X-ray diffractometer (CuKα). Recording modes: voltage across the tube is 30kV, anode current is 30mA, and the speed of the goniometer during recording is 2 deg/min. The phase composition of the synthesized product was determined using a PowderCell 2.4 calculation program and the PDF2 database. Morphology of the obtained powders was studied by scanning electron microscopy on the PhillipsSEM515 microscope.

Raman spectra of the final product were recorded with a confocal Raman spectrometer (InVia, Renishaw) equipped with a Leica microscope. The excitation was conducted by a continuous semiconductor laser with a wavelength of 785 nm and a maximum power of up to 100 mW. The

1200 lines/mm diffraction lattice provides a spectral resolution of 1 cm^{-1}, and a microscope with a 50x lens provides excitation up to 2 μm^2.

The phase composition, morphology, and structural parameters of the cobalt ferrospinel powder synthesized by spray pyrolysis combined with drop sol-gel combustion were studied in this work, and the obtained data were compared with those of the powders synthesized by sol-gel combustion [8].

3. Results and discussion

The data of X-ray diffraction and X-ray structural analysis of the synthesized product are shown in figure 2 and in table 1.

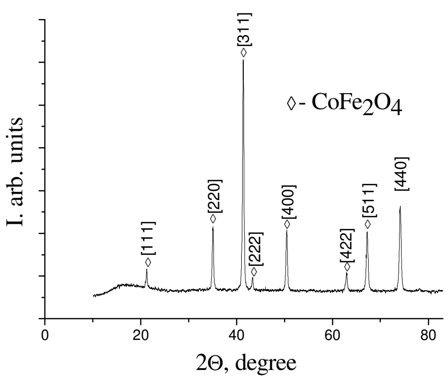

Figure 2. XRDA of the samples after spray pyrolysis.

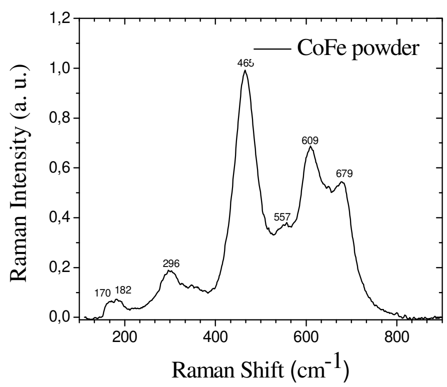

Figure 3. Raman spectra of $CoFe_2O_4$ obtained by spray pyrolysis.

The X-ray diffraction pattern showed that the obtained product consisted of the one phase - cubic cobalt ferrite.

Table 1. Comparison of the phase composition and structural parameters of cobalt ferrospinels synthesized by spray pyrolysis and sol-gel combustion [8].

Method of synthesis	Content $CoFe_2O_4$, vol.%	Lattice parameter, Å	Average size of crystallites, nm	$(\Delta d/d)\cdot 10^3$
Spray pyrolysis	100	8.3989	37	0.4
Sol-gel combustion	91	8.3802	31	0.9

The comparison of the X-ray diffraction and X-ray structural analysis data for the powders synthesized by spray pyrolysis and for the products obtained by sol-gel-combustion given in table 1 shows that the use of spray pyrolysis leads to the complete chemical reaction. The average size of crystallites in both cases is 31-37 nm, which indicates the nanostructured state of the synthesized product. The values of internal elastic microstresses ($\Delta d/d$) differ insignificantly. The difference in the value of the lattice parameter compared to the reference value of $CoFe_2O_4$ is caused, apparently, by the nonequilibrium state of the product synthesized by spray pyrolysis.

Raman spectra of the final product synthesized by spray pyrolysis are shown in figure 3 and in table 2. For their interpretation, the literature data taken from [9-12] were used.

It is known that there are five active Raman modes for the structure of $CoFe_2O_4$ spinel. Comparison of the Raman spectra of the final product synthesized in this study with the spectra presented in papers [9–12] shows that they are identical and, consequently, the final product is cobalt ferrospinel.

IOP Conf. Series: Journal of Physics: Conf. Series **1115** (2018) 042011 doi:10.1088/1742-6596/1115/4/042011

The Raman spectrum of the $CoFe_2O_4$ phase consists of broad bands with a different intensity. The modes at 609 cm^{-1} and 379 cm^{-1} refer to local effects in the tetrahedral sublattice, while other modes reflect local effects in the octahedral sublattice.

Table 2. The main Raman-active modes in $CoFe_2O_4$ obtained by spray pyrolysis.

Wave number, cm^{-1}					Symmetry
[8]	[9]	[10]	[11]	This work	
301	311	300	322	296	E_g
470	470	467	465	465	T_{2g}
	571		560	557	T_{2g}
618	619	608		609	A_{1g}
686	693	686	683	679	A_{1g}

The data of scanning microscopy for the obtained cobalt ferrite are shown in figure 4

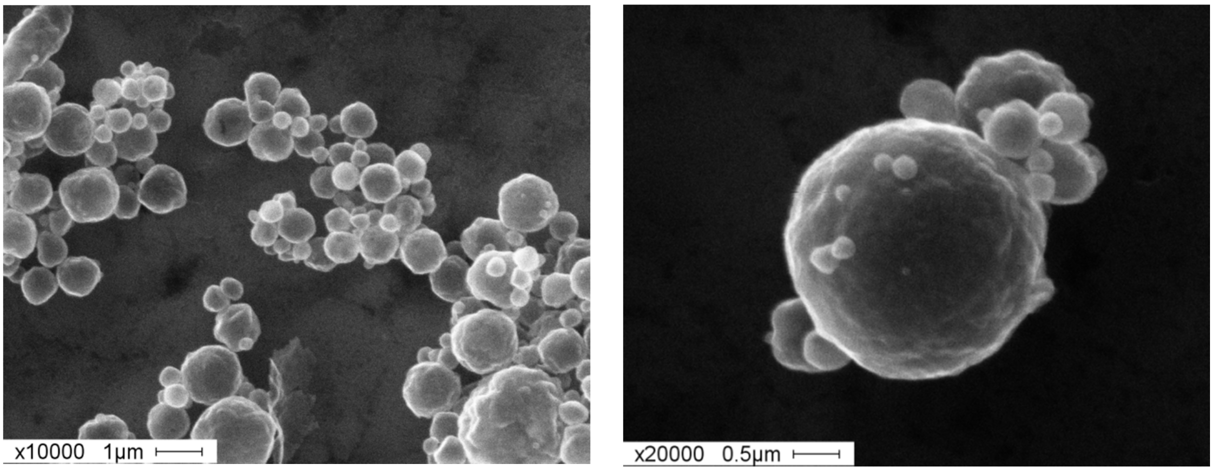

Figure 4. SEM images of synthesized cobalt ferrite particles.

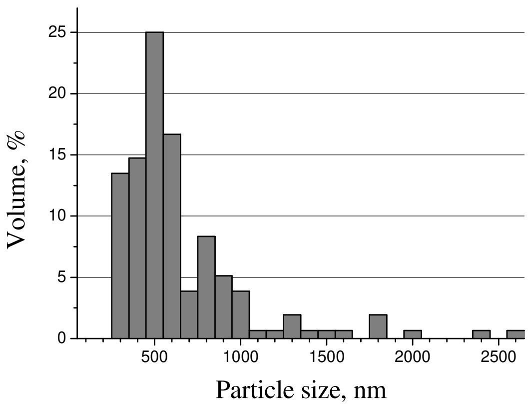

Figure 5. Bar charts with particle size distribution of synthesized products.

It can be seen in the photographs that the synthesized product is slightly agglomerated spherical particles. The particle size varies in a wide range from 200-300 nanometers to 3-5 micrometers.

IOP Conf. Series: Journal of Physics: Conf. Series **1115** (2018) 042011 doi:10.1088/1742-6596/1115/4/042011

The histogram of the particle size distribution is shown in figure 5. The diagram demonstrates that the size of the particles is 300-600 nm and, thus, the synthesized product is a finely dispersed cobalt ferrospinel.

4. Conclusion

The conducted studies have shown that spray pyrolysis combined with drop sol-gel combustion can synthesize a single-phase product in the form of spherical finely dispersed nanosized particles of cobalt ferrospinels.

References

[1] Gubin S P, Koksharov Yu A, Khomutov G B and Yurkov G Yu 2005 *Usp. Khim.* **74** 539
[2] Pankov V V 2007 *Vestnik BGU series 2* **2** 3
[3] Antipov V I, Galahov A V, Vinogradov L V, Kolmakov A G, Baranov E E, Lazarev E M, Aladiev N A and Muhina Yu E 2011 *Inorganic Materials: Applied Research* **1** 53
[4] Galahov A V, Vinogradov L V, Antipov V I and Kolmakov A G 2011 *Nanotechnologies in Russia* **6** 662
[5] Galahov A V and Aladiev N A 2012 *Nanotechnologies in Russia* **7** 434
[6] Suzdalev I P, Maksimov Yu V, Imshennik V K, Novichikhin S V, Matveev V V, Gudilin E A, Petrova O V and Tretyakov Yu L 2007 *Nanotechnologies in Russia* **7** 73
[7] Solero G 2017 *Nanoscience and Nanotechnology* **7** 21
[8] Minin R V, Naiden E P and Itin V I 2013 *Izvestiya VUZov Fizika* **56** 249
[9] Lui Y, Zhang Y, Feng J D, Li C F, Shi J and Xiong R 2009 *J. Experimental nanoscience* 4 159
[10] Sunpo N, Tharajak J, Li Y, Berndt Ch C and Wang J 2014 *J. nanopart res.***16** p 2510
[11] Dascalu G, Pompilian G, Chazallon and Caltun O F, Gurlui S and Focsa C 2013 *Applied Surface Science* **278** pp 38
[12] Naidek K P, Bianconi F, R da Rocha T C, Zanchet D, Bonacin J A, Novak M A, Vaz M G F and Winnischofer H 2011 *J.Colloid and Interface Science* **358** pp 39