

Obtaining of Nanostructured Powders of Barium and Strontium Hexaferrite by the Polymer Precursor Method

V.G. Kostishyn*, A.V. Timofeev, D.N. Chitanov

National University of Science and Technology "MISiS", 4, Leninsky Prosp., 119049 Moscow, Russia

(Received 01 October 2015; published online 24 December 2015)

Studied the possibility of obtaining by precursors in the polymer nanostructured powders of barium hexaferrite $\text{BaFe}_{12}\text{O}_{19}$ and strontium hexaferrite $\text{SrFe}_{12}\text{O}_{19}$. The reagents were used as starting barium nitrate, strontium nitrate and ferric nitrate nonahydrate (III), and polyethylene glycol-400 used this technology as a polymer.

Keywords: Barium hexaferrite, Strontium hexaferrite, Nanoparticles, Grain, Polymer, Microstructure.

PACS numbers: 75.50.Gg, 75.75.+a

1. INTRODUCTION

At present a special interest of researchers around the world is getting nanoparticles hexaferrites M-type, endowed with interesting set of complex magnetic properties [1, 2]. High chemical and thermal resistance hexaferrites particularly important for their use in the development of advanced devices, media, electrically switchable permanent magnets, high-frequency devices, etc.; as well as for applications in the medical field [3, 4].

The purpose of this work was to obtain nanosized powders of barium hexaferrite $\text{BaFe}_{12}\text{O}_{19}$ and strontium hexaferrite $\text{SrFe}_{12}\text{O}_{19}$ by coprecipitation precursors [5, 6] as well as the study of the effect of annealing on the morphology and microstructure of the powders.

2. THE METHOD OF OBTAINING THE OBJECTS OF RESEARCH

Experimental samples were prepared by the following technology. Sample starting reagents barium nitrate $\text{Ba}(\text{NO}_3)_2$, strontium nitrate $\text{Sr}(\text{NO}_3)_2$ and nitrate nonahydrate iron (III) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in distilled water and glycerin solution $\text{C}_3\text{H}_5(\text{OH})_3$ and distilled water, respectively. The prepared solution was mixed at an atomic ratio of Ba to Fe and Sr to Fe, 1 : 10. Then the mixture was continuously heated and stirred at 55 °C for 1 hour. Then added aqueous ammonia $\text{NH}_3 \cdot \text{H}_2\text{O}$ and polyethylene glycol-400. The formed colloidal solution is continuously heated and stirred at 85 °C for 7 hours. The next operation of a colloidal dispersion by centrifugation at 11,000 rpm to remove water and organic solvents. The resulting precipitate was calcined in an oven at 450 °C for 1.5 hours to remove residual organic impurities. Next powders pulverized in a mortar and calcined in air: the powder with Ba at 1000 °C for 3 hours, and the powder with Sr at 1100 °C for 3 hours. Upon completion of the annealing process carried out natural cooling to room temperature.

This technology was made five samples of each composition.

3. METHODS OF EXPERIMENTAL RESEARCH

X-ray diffraction analysis was performed on the X-ray powder diffractometer ARL X'Tra company Thermo Fisher Scientific (Switzerland) with a copper anode.

Scan angles of 15 and 75°, with a step scanning 0,02°. Primary data processing was carried out under the program WinXRD, qualitative analysis on the program Crystallographica Search-Match, a quantitative analysis by the Rietveld method on the program Siroquant. A research also was performed on diffractometer Bruker D8 Advance (Germany) with CuK_α radiation and diffractometer Discover D8 (Bruker-AXS, Germany) in the parallel beam geometry. The latest X-ray source was an X-ray tube with a copper anode (radiation CuK_α). Focus – a line. The beam width of 0.2 mm. Shooting Mode – 40 kV, 40 mA. To increase the intensity of the primary beam and the partial collimation and monochromatic plane diffraction mirror was used Hebel. The horizontal beam divergence (in the plane of diffraction) is 0.03°. Secondary monochromator was used. Measurement mode: circuit 2θ - θ -scan. Qualitative phase analysis was performed using the program EVA (Bruker-AXS) and the database format ICDD PDF-2.

The morphology, microstructure and chemical composition of the powders were investigated by the scanning electron microscope (SEM) JEOL JSM-7800F microanalysis system of Oxford Instruments Nano Analysis (OINA) on the basis of X-ray energy dispersive spectroscopy (EDS). For the electron beam used accelerating voltage of 3-30 kV.

4. RESULTS AND DISCUSSION

Method of X-ray diffraction found that the samples with Ba after annealing at 1000 °C were polycrystalline and biphasic, composed of barium hexaferrite $\text{BaFe}_{12}\text{O}_{19}$ with lattice parameters $a = 5,89 \text{ \AA}$, $c = 23,18 \text{ \AA}$ and spinel BaFe_2O_4 ; and the samples with Sr were polycrystalline and represented strontium hexaferrite with lattice parameters $a = 5,88 \text{ \AA}$, $c = 23,05 \text{ \AA}$. Characteristic X-ray diffraction patterns are presented in Fig. 1 and in Fig. 2. Also in the works are carried out X-ray analysis of the powders with Ba before annealing with the purpose of identifying the intermediates involved directly in the synthesis reaction of barium hexaferrite. Detailed analysis of the diffraction pattern shown in Fig. 3, showed the presence of magnetite Fe_3O_4 and witherite BaCO_3 phases. The presence of compounds with carbon can be explained by lack of time of calcination.

* drvgkostishyn@mail.ru

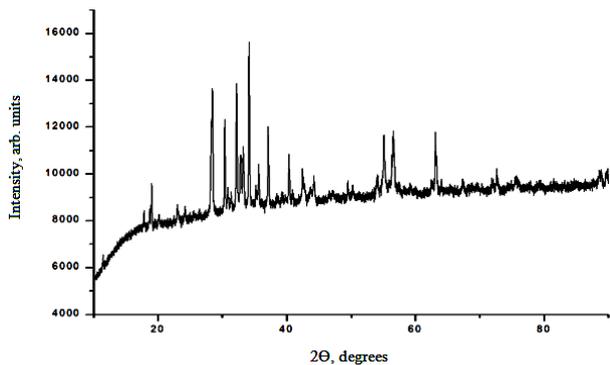


Fig. 1 – The characteristic X-ray diffraction phases of barium hexaferrite BaFe₁₂O₁₉ and spinel BaFe₂O₄

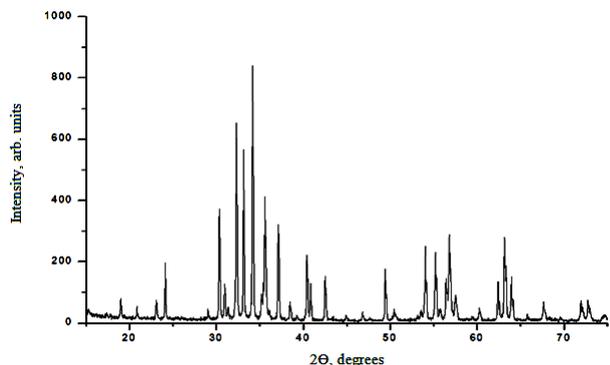


Fig. 2 – The characteristic X-ray diffraction of strontium hexaferrite SrFe₁₂O₁₉

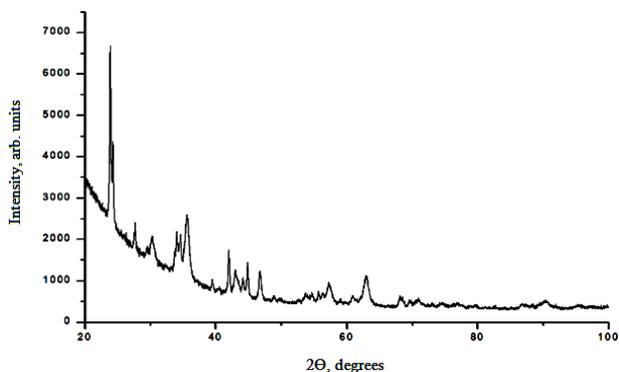


Fig. 3 – The XRD pattern of samples with Ba before annealing

In the work by SEM was to study the effect of annealing on microstructure, morphology and chemical composition of nanoparticles. From Fig. 4 shows the structure of the obtained powder with Ba – uniform, spectral analysis of the selected area aside from the basic elements also shown by the presence of carbon, which indicates the presence of carbon compounds. Spectrogram itself is shown in Fig. 5. In Fig. 6 shows an image of powder with Sr to annealing at a magnification of 3000 times, which shows that the structure is inhomogeneous, and spectral analysis of the highlighted area in Fig. 7 does not contain any element of Sr, indicating a lack of connections with strontium. The spectrogram is shown in Fig. 8.

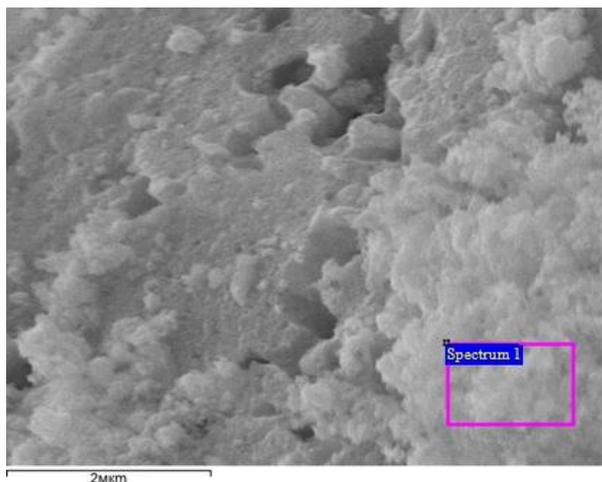


Fig. 4 – Picture powder with Ba before annealing. The increase of 20,000 times, the accelerating voltage of 20 kV. Rectangle highlighted area to be scanned EDS

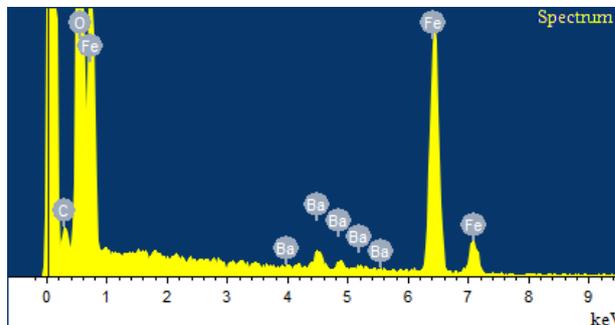


Fig. 5 – The spectrogram of the elemental composition of the powder with Ba before annealing

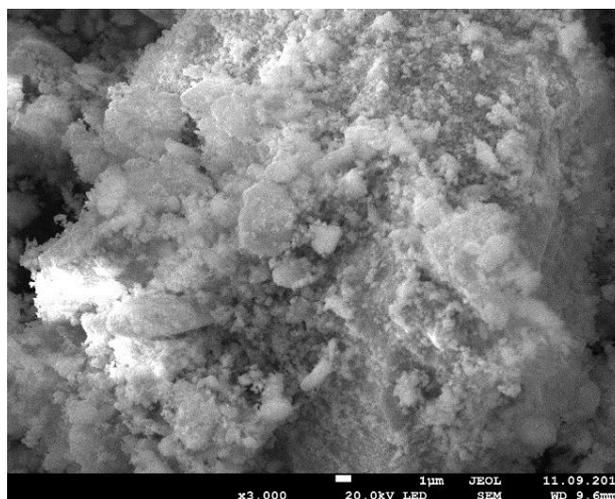


Fig. 6 – The powder with Sr before annealing, shot with a magnification of 3,000 times

Images of samples with Ba after sintering is shown in Fig. 9, which shows that the formation of randomly oriented lamellar grains. Grains have typical dimensions of 90 to 250 nm. In addition to nano-sized particles visible non-structural formations that are likely to be spinel phases BaFe₂O₄, because study by EDS of these areas showed the presence of all the major elements. The reason for the presence of another

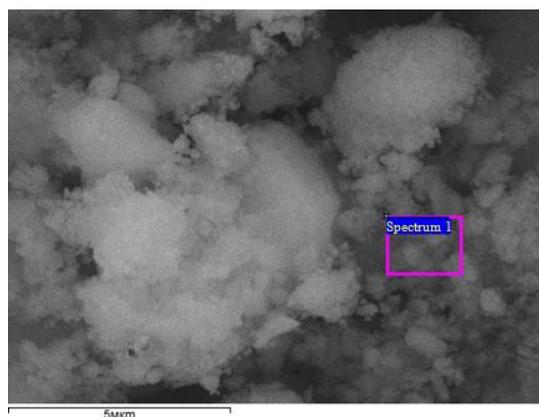


Fig. 7 – Picture powder with Sr before annealing. The increase of 10,000 times, the accelerating voltage of 20 kV. Rectangle highlighted area to be scanned EDS

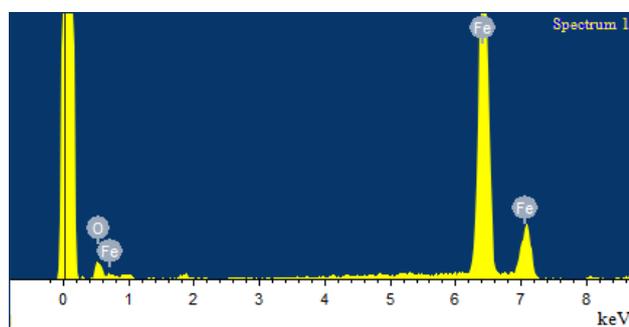


Fig. 8 – The spectrogram of the elemental composition of the powder with Sr before annealing

phase in the powder may be explained by insufficient annealing temperature and time. SEM image of the sintered samples with Sr shown in Fig. 10, which shows that there was a formation of granules in the whole volume of the powder with a characteristic size of a few microns. In turn, these pellets are composed of randomly oriented nanoparticles. The grains have a characteristic size of 90 to 250 nm, which can be seen from Fig. 11. Study of EDS different areas and points showed that the atomic ratio of Sr to Fe ranges from 1 : 11.2 to 1 : 12.6, which almost corresponds to an atomic ratio in a real molecule strontium hexaferrite $\text{SrFe}_{12}\text{O}_{19}$.

5. CONCLUSION

Method precursors in the polymer using barium nitrate $\text{Ba}(\text{NO}_3)_2$, strontium nitrate $\text{Sr}(\text{NO}_3)_2$ and nitrate nonahydrate iron (III) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as starting materials and polyethylene glycol-400 as the polymer obtained nanostructured powders barium hexaferrite $\text{BaFe}_{12}\text{O}_{19}$, containing spinel phase BaFe_2O_4 , and strontium hexaferrite $\text{SrFe}_{12}\text{O}_{19}$. After sintering in air samples with Ba at 1000 °C for 3 hours began to form grains, which ranged from 100 to 250 nm. In addition to the grains present nonstructural education, suggesting the need for improvements of this technology, namely: either increase the temperature or sintering time in order to obtain a single-phase material in the form of nanoparticles of

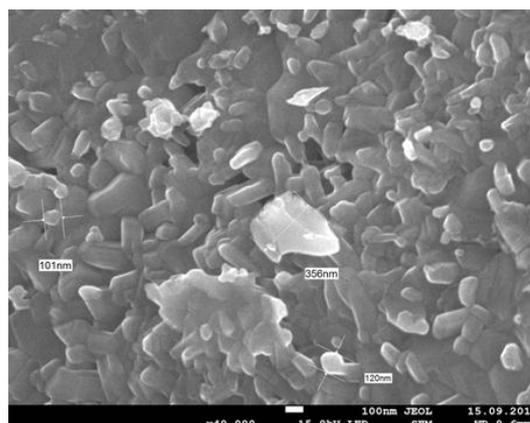


Fig. 9 – Sintered powder with Ba, taken with a magnification of 40,000 times

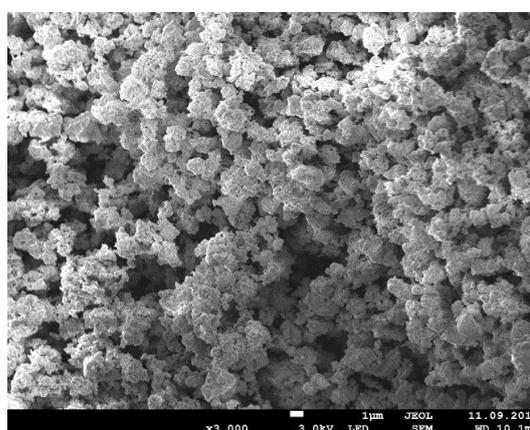


Fig. 10 – Sintered powder $\text{SrFe}_{12}\text{O}_{19}$, taken at a magnification of 3,000 times

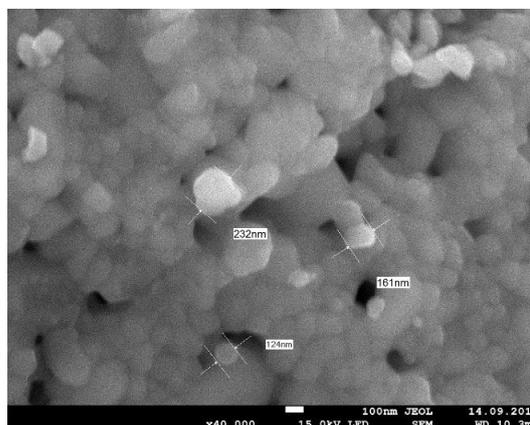


Fig. 11 – Sintered powder $\text{SrFe}_{12}\text{O}_{19}$, taken at a magnification of 40,000 times

barium hexaferrite. After annealing the samples with Sr in air at 1100 °C for 3 h formed grain size varied from 90 to 250 nm, which allows the use of this technology for producing nanoparticles strontium hexaferrite.

Work performed under the task № 11.2502.2014 / K by 07/17/2014, on the execution of the research work in the framework of the project of the state task in the field of scientific activity (topic № 3219022).

REFERENCES

1. N. Yang, H. Yang, J. Jia, X. Pang, *J. Alloy. Compd.* **438**, 263 (2007).
2. V.G. Kostishin, L.V. Panina, L.V. Kozhitov, *Techn. Phys.* **60**, 1189 (2015).
3. L.M. Letyuk, V.G. Kostishin, A.V. Gonchar, *Technologymagneto-electronic ferrite materials* (M.: MiSiS: 2005).
4. D.D. Zaitsev, S.E. Kushnir, P.E. Kazin, *J. Magn. Magn. Mater.* **301**, 489 (2006).
5. G. Tan, X. Chen, *J. Electron. Mater.* **42** No 5, 906 (2013).
6. G. Tan, X. Chen, *J. Magn. Magn. Mater.* **327**, 87 (2013).