

## Synthesis and properties of nanoscale films of the $Y_2O_3$ – $Fe_2O_3$ system on silicon

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Thin films of the  $Y_2O_3$ – $Fe_2O_3$ /Si system with nanometer-scale thicknesses were synthesized by centrifugation with application of sol and gel of  $YFeO_3$ . It was found that the samples formed from the gel are characterized by the following composition:  $Fe_2O_3$ ,  $Fe_3O_4$ , and  $Y_2O_3$ ,  $YFeO_3$ , which is not consistent with the data, obtained for powder products, and can indicate that the thermal annealing conditions were insufficient for the formation of a single-phase product. For the first time, the magnetic properties of thin ferrite films of yttrium on the surface of the silicon formed from the gel were measured. The nature of the hysteresis loop of nanofilms of yttrium ferrite with different parameters of time and speed of centrifugation suggests that the samples exhibit soft magnetic properties of a ferromagnet. The correlation between the value of specific magnetization and thickness of nanofilms was established.

**Keywords:** sol-gel synthesis, nanofilms, centrifugation, yttrium orthoferrite, magnetic properties.

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### 1. Introduction

The wide application of multiferroics is due to the fact that these materials have two kinds of orderings – ferromagnetic and ferroelectric – which have utility in microelectronics, recording devices, and the storage and reading of information [1–7]. According to the study [8], yttrium orthoferrite also shows multiferroic properties.

There are various methods of producing films of semiconducting metal oxides. The sol-gel method is most promising for the formation of nanofilms of ferrites involving the deposition of metal hydroxides, their conversion into a colloidal state, the colloidal solution applied on the substrate and crystallization of oxide phases during thermal dehydration [9].

The popularity of this technology is associated, primarily, with high chemical homogeneity of the products, which in turn reduces the temperature and duration of final thermal treatment. Despite the large number of studies devoted to the sol-gel technology, the synthesis of specific samples requires an individual approach, providing the precipitation of highly dispersed, easily translatable in a colloidal state [10–12].

The goal of this study was the formation and investigation of magnetic properties of nanodimensional  $Y_2O_3$ – $Fe_2O_3$  films, synthesized by the sol-gel method on a surface of Si.

### 2. Materials and methods

#### 2.1. Initial substances

For the formation of thin films, the sol-gel synthesis of  $YFeO_3$  technique was used [13]. The following reagents were used as original reactants: nitrate iron (III) 9-water,  $Fe(NO_3)_3 \cdot 9H_2O$  (h), yttrium nitrate 6-aqueous  $Y(NO_3)_3 \cdot 6H_2O$  (H. h), distilled water.

#### 2.2. The synthesis of $Y_2O_3$ – $Fe_2O_3$ films

The substances were taken in stoichiometric ratio, concentration of the solutions was 0.008 M, the total volume of solution was 100 ml. Solutions of nitrates of iron (III) and yttrium in distilled water was boiled prior to gel formation, and then applied on the silicon substrate by centrifugation, at a speed of 2000 – 5000 rpm within 1 – 15 min. The films were annealed in a muffle furnace for one hour at 750 °C. Such thermal annealing parameters were chosen based on the results of [13] for the synthesis of  $YFeO_3$  nanopowders.

### 2.3. Methods of investigation

The thickness of the synthesized films was determined by spectroscopic ellipsometry (Ellipse 1891).

Determination of sample compositions was conducted by x-ray diffraction (XRD, x-ray diffractometer Thermo ARL X'tra) and infrared spectroscopy (X-ray, ft-IR spectrometer Vertex 70).

The surface morphology of the formed films was investigated by atomic force microscopy (AFM, Solver P47 Pro Corporation NT-MDT).

The study of the magnetic characteristics (magnetization  $J$ , the coercive force  $H_C$ ) of films on silicon synthesized from the gel was performed at room temperature using vibrating magnetometer sample (VSM, "Lakeshore", model 7404).

### 3. Results and discussion

The results of determination of film thickness, confirming the nanometer range, are presented in Table 1.

TABLE 1. The thickness of the films synthesized from the gel on the Si surface after annealing at 750 °C, defined by spectral ellipsometry

No.	$\tau$ rotation speed, min.	$\nu$ rotation speed, rpm	thickness, nm
1	5	2000	17
2	15	2000	19
3	5	4000	20
4	5	5000	15
5	15	5000	15
6	1	5000	49
7	15	5000	38

The qualitative picture of the concentration of components in the film was established by x-ray diffraction analysis conducted by x-ray diffractometer Thermo ARL X'tra in a small angle range. This was necessary to ensure that the high-intensity peaks of the substrate do not overlap the peaks of the film. The data obtained (Figs. 1, 2 and Tables 2, 3) demonstrated that samples no. 6 and no. 7 showed in Table 1 contain following phases:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{YFeO}_3$ .

TABLE 2. The results of digital processing of diffraction pattern of sample No. 6

The angle of incidence of the x-ray beam	$D_{hkl}$ (Å)	Phase
25.47	3.32	$\text{Fe}_2\text{O}_3$
49.38	1.84	$\text{Fe}_2\text{O}_3$
37.47	2.40	$\text{Fe}_3\text{O}_4$
57.98	1.59	$\text{Fe}_3\text{O}_4$
40.80	2.21	$\text{Y}_2\text{O}_3$
49.38	1.84	$\text{Y}_2\text{O}_3$
51.91	1.76	$\text{Y}_2\text{O}_3$
23.37	3.80	$\text{YFeO}_3$
51.91	1.76	$\text{YFeO}_3$

It should be noted that the most intensive peaks were peaks corresponding to the substrate at all diffractograms. This fact suggests that the thickness of the film grown on the surface did not exceed a few hundred nanometers and it was confirmed by the studies of thickness using spectroscopic ellipsometry.

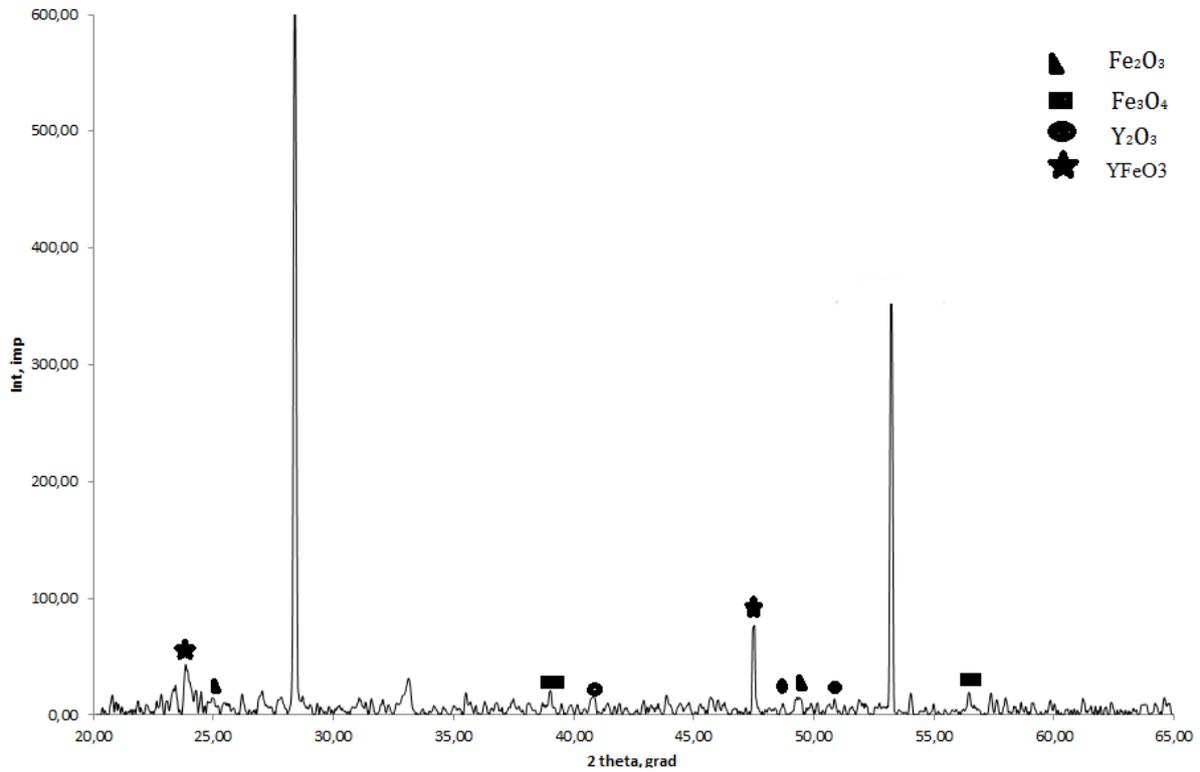


FIG. 1. X-ray powder diffraction patterns of sample No. 6 ( $\tau = 1$  min,  $\nu = 5000$  rev./min.), synthesized from the gel on the surface of Si

TABLE 3. The results of digital processing of diffraction pattern of sample No. 7

The angle of incidence of the x-ray beam	$D_{hkl}$ (Å)	Phase
40.23	2.24	$Fe_2O_3$
60.18	1.53	$Fe_2O_3$
59.20	1.56	$Fe_3O_4$
33.15	2.70	$Y_2O_3$
34.91	2.57	$Y_2O_3$
56.92	1.61	$Y_2O_3$
26.13	3.41	$YFeO_3$
53.22	1.72	$YFeO_3$
56.92	1.61	$YFeO_3$

IR absorption spectra of the samples were recorded for establishing the correlation with XRD data.

According to IR spectroscopy data (Fig. 3), the composition of the films included:  $Y_2O_3$  ( $\nu = 480\text{ cm}^{-1}$ ),  $Fe_2O_3$  ( $\nu = 620\text{ cm}^{-1}$ ),  $Fe_3O_4$  ( $\nu = 1160\text{ cm}^{-1}$ ),  $YFeO_3$  ( $\nu = 1300\text{ cm}^{-1}$ ) and these data correlated with the results of XRD.

The surfaces of the synthesized samples had a developed structure with a pronounced wavy nature (the AFM data). Comparison of the images detected the decrease of the grain surface with increasing size of the individual nanocrystallites.

The observed result indicates the significant effect of centrifugation parameters on the nature and structure of the resulting films. Increasing the speed and time of rotation contributed to the smoothing of film topography. For

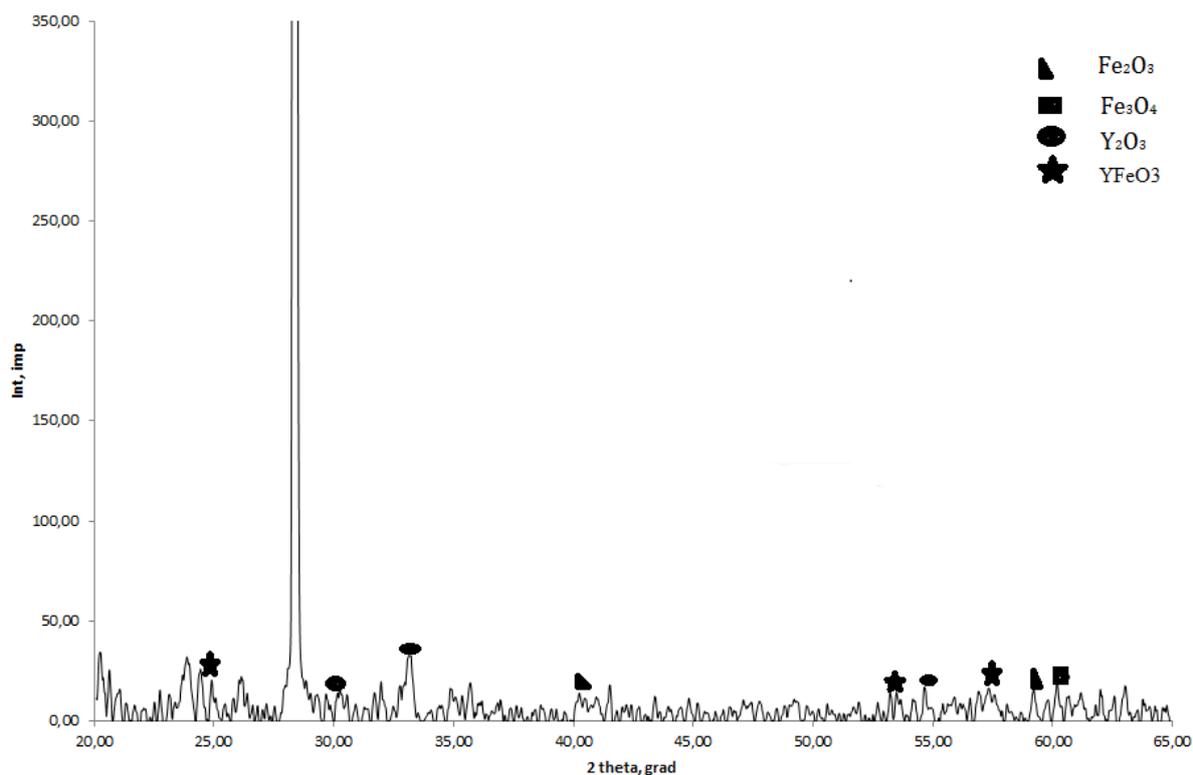


FIG. 2. X-ray diffraction pattern of sample No. 7 ( $\tau = 15$  min.,  $y = 5000$  ob./min). Synthesized from the gel on the surface of Si

example, by increasing the centrifugation time (Figs. 4 and 5) during film formation from the gel decreased the difference in height of the terrain from 8 to 6 nm.

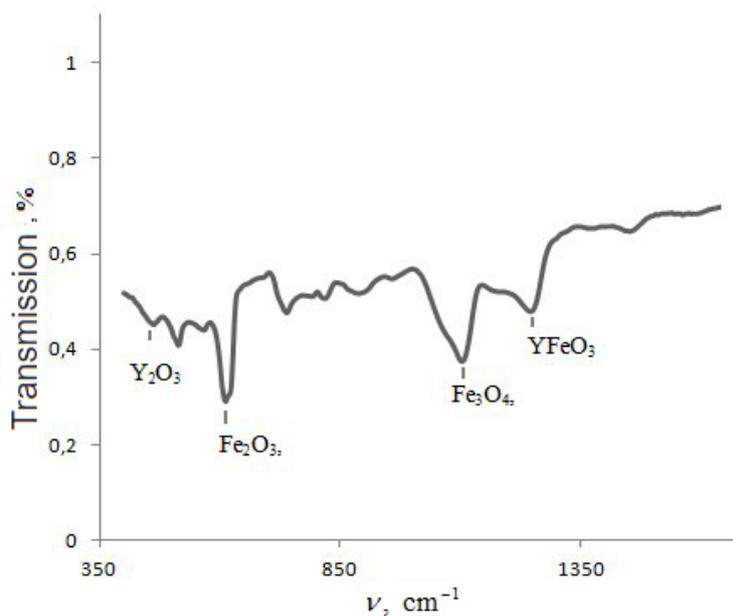


FIG. 3. The IR absorption spectrum of the sample No. 6, synthesized from the gel on the surface of Si

Increasing the centrifugation speed from 4000 rpm to 5000 rpm also caused surface smoothing, the height of the terrain decreased from 12 nm to 10 nm.

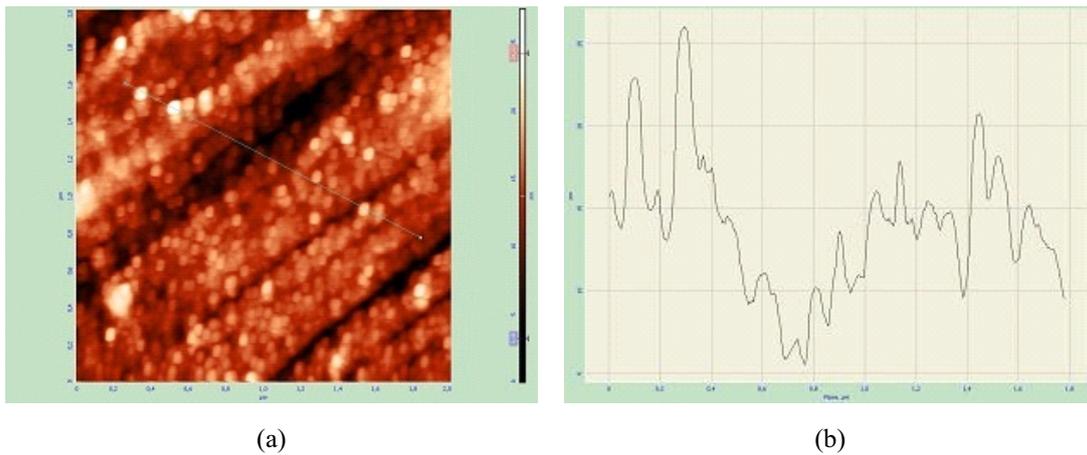


FIG. 4. AFM image (a) and surface profile (b) of sample No. 1 ( $\tau = 5$  min,  $v = 2000$  rpm), synthesized from the gel on the surface of Si

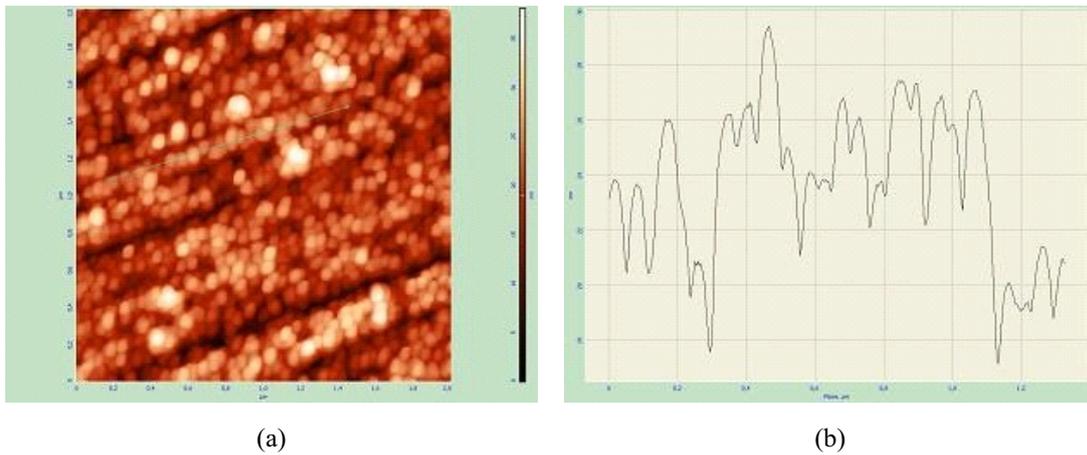


FIG. 5. AFM image (a) and surface profile (b) of sample No. 2 ( $\tau = 15$  min,  $v = 2000$  rpm), synthesized from the gel on the surface of Si

Thus, by varying the process parameters, it is possible to achieve the formation of films with a given structure and morphology.

Determination of the magnetic characteristics (magnetization  $J$ , the coercive force  $H_C$ ) of the synthesized gel film was carried out using a VSM ("Lakeshore", model 7404) at room temperature. The magnetic field was directed in the film plane.

The field dependence of the magnetic moment of the sample with nanofilm on Si (smooth curve obtained by interpolation of the original data of Langevin curve by least square method) deposited by centrifugation of the gel for 1 min at a speed of 5000 rpm./min (sample no. 6 of Table 1) is shown in Fig. 6. The specific magnetization in a field of 1250 kA/m was 47 A·m<sup>2</sup>/kg. The determination of coercive force of the sample was not possible due to the low magnetic moment and high noise signal. According to estimates, the coercive force of yttrium ferrite nanofilms was not more than 100 Oe, which indicates magnetically soft ferromagnet. On the other hand, the magnitude of the saturation field exceeded 500 kA/m, which shows high magnetic anisotropy. We can assume that the axis of easy magnetization of magnetic anisotropy is oriented perpendicular to the film's plane.

Figure 7 shows the dependence of the magnetic moment of the thin film sample on the Si surface, deposited by centrifugation of the gel for 15 min. at a speed 5000 rev./min (sample no. 7) from the intensity of the applied field. The sample reached magnetic saturation in a field of 450 kA/m,  $J = 37.5$  A·m<sup>2</sup>/kg. The shape of the hysteresis loop was similar to the previous dependence also indicates the ferromagnetic character of the nanoscale films.

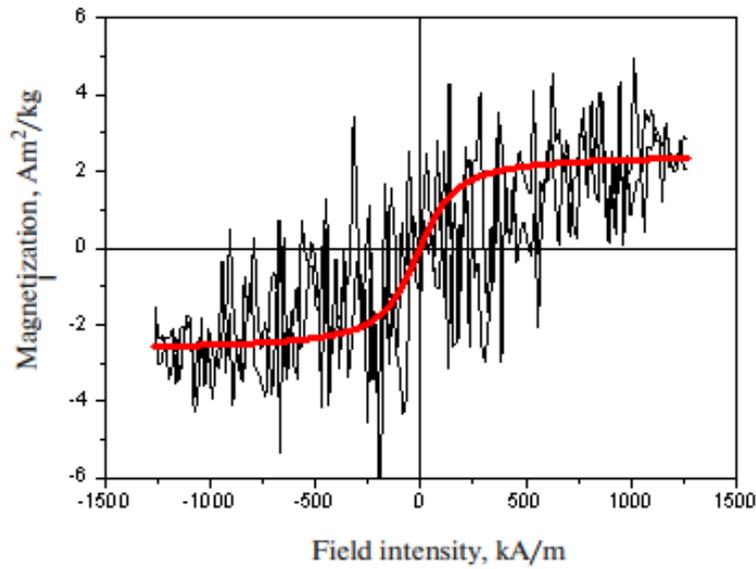


FIG. 6. Field dependence of the magnetization of the sample No. 6  $\text{YFeO}_3/\text{Si}$  ( $\tau = 5$  min,  $\nu = 2000$  rpm), synthesized from the gel after annealing at  $750^\circ\text{C}$ , 60 min. Smooth curve is obtained by interpolation of the original data curve Langevin least squares

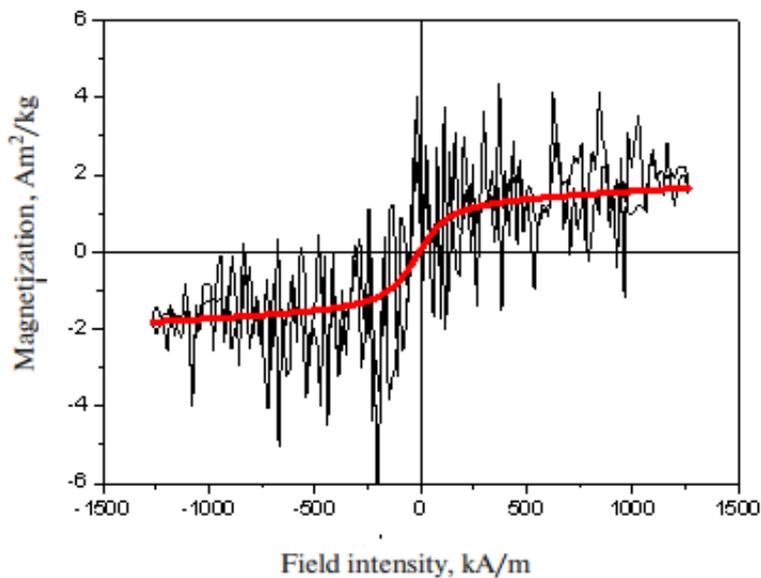


FIG. 7. Field dependence of the magnetization of the sample No. 7  $\text{YFeO}_3/\text{Si}$  ( $\tau = 15$  min,  $\nu = 5000$  rpm), synthesized from the gel after annealing at  $750^\circ\text{C}$ , 60 min. Smooth curve was obtained by interpolation of the original data of the Langevin curve by the least square method

Thus, with the decrease in thickness of the  $\text{YFeO}_3$  films from 49 to 38 nm (Table 1) a decrease of the specific magnetization in a field of 1250 kA/m  $47 \text{ A}\cdot\text{m}^2/\text{kg}$  to  $37.5 \text{ A}\cdot\text{m}^2/\text{kg}$  was observed. The values of the saturation field of both samples were close, indicating the magnetocrystalline nature of the magnetic anisotropy. For yttrium ferrite nanopowders, synthesized by the sol-gel method,  $J = 0.242 \text{ A}\cdot\text{m}^2/\text{kg}$  [13]. The relatively high value of specific magnetization of the synthesized samples was due to the presence of impurity  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  phases with a pronounced ferromagnetism [14, 15].

The results can be used to produce bulk composite materials, as well as for the manufacture of devices requiring a rapid remagnetization using minimal energy, for example, transformer coils [16, 17]. The synthesized films, along with other oxides of transition metals [18, 19] can act as catalysts for the formation of functional layers by thermal oxidation of binary semiconductor compounds  $\text{A}_3\text{B}_5$ .

#### 4. Conclusions

Samples of the  $Y_2O_3$ - $Fe_2O_3$ /Si system with the application of  $YFeO_3$  gel were synthesized by centrifugation. These samples were thin films on silicon with nanometer range thickness. The samples formed from the gel were characterized by the following composition:  $Fe_2O_3$ ,  $Fe_3O_4$ ,  $Y_2O_3$ ,  $YFeO_3$ , which is not consistent with the data obtained for powder products [13], and may indicate that thermal annealing is insufficient for the formation of a single-phase product.

The generated samples had a developed surface morphology with a pronounced wavy structure. The average surface elevation for the samples synthesized from the gel ranged from 8 to 10 nm. Surface morphology of synthesized samples was smoother with increasing time and speed of the centrifugation of the substrate.

Nanofilms of yttrium ferrite are magnetically soft ferromagnets, the specific magnetization increased with increasing film thickness in the range of 38 – 49 nm from 37.5 to 47  $A \cdot m^2/kg$  in field 1250 kA/m. The presence of impurity phases of iron oxides in the samples increases the magnetization value and increases the range of application of the formed heterostructures.

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