

Influence of the agglomeration in the initial suspension (ferrofluid) on the oriented magnetic structure

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Abstract. The process was studied of preparation of oriented BaFe₁₂O₁₉ films via deposition of BaFe₁₂O₁₉ nanoparticles from a suspension in a magnetic field. The films' structural, microstructural and magnetic properties were investigated by X-ray diffraction, scanning electron microscopy and magnetic measurements. The influence was explored of the particles' agglomeration in the ferrofluid on the films' properties and microstructure. Using time delay deposition, we obtained thick films with a high degree of orientation and good density.

1. Introduction

Barium ferrite (BaFe₁₂O₁₉) is a high-performance material widely used as a permanent magnet because of its large magnetocrystalline anisotropy along the *c*-axis of its hexagonal structure, high Curie temperature and relatively large magnetization, as well as excellent chemical stability and corrosion resistance [1, 2].

Magnetically oriented barium ferrite films have found various uses, such as high-density magnetic recording [3], magneto-optical applications [4] and mm-wave applications [5, 6]. In what concerns the latter of these, barium ferrite-based compounds are without alternative. Due to their high magnetocrystalline anisotropy, they exhibit a ferromagnetic resonance at mm-wavelengths, while, at the same time, being magnetically self-biased. The most suitable form of barium ferrite for mm-wave applications is magnetically oriented thick films. Several techniques have been used to prepare such films, including thermal spraying [7], electrophoretic deposition [8] and screen printing [9].

We report a study on the influence of the aggregation of barium hexaferrite magnetic particles in a ferrofluid on the properties of the thick film formed in a magnetic field. This method consists in dropping a suspension of barium ferrite particles (ferrofluid) on an Al₂O₃ substrate, followed by drying the film in an external magnetic field between two permanent magnets. The technique allows one to grow magnetically oriented thick films while controlling the magnetic properties depending on the agglomeration process in the ferrofluid.

2. Experimental

The BaFe₁₂O₁₉ powder was synthesized using the hydrothermal method [10] in collaboration with the K8 Department, Jozef Stefan Institute, Ljubljana, Slovenia. To prevent the attraction between the particles and their subsequent agglomeration, they were stabilized through adsorption of a surfactant

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on the particles's surface, as described in [11]. The particles were dispersed in an aqueous acid solution with 10 mass % of the surfactant dodecylbenzenesulphonic acid per mass of powder. The ferrofluid consisted of particles with an average size of 10 nm and 80 nm. Such a mixture proved to be the best for obtaining the highest degree of films' density when this stable suspension was subsequently used for deposition of oriented films.

The deposition process was carried out using the experimental setup described below. The barium ferrite suspension prepared was dropped on an Al_2O_3 substrate placed between two permanent magnets. The as-deposited sample was slowly dried between these two permanent magnets for 6 hours. The magnetic attraction force between the particles is too strong even in the presence of a surfactant in the ferrofluid. In order to prevent the particles agglomeration, the suspension was subjected to ultrasound homogenization. Two approaches were employed to investigate the influence of the agglomeration process on the physical properties of the thick films obtained. In the first one (type I), the deposition process was performed immediately after the ultrasound homogenization (without delay). In the second (type II), the deposition process was conducted at a certain time delay after the ultrasound treatment, namely, after 3, 6, 12, 15 and 18 hours. The greatest thickness and homogeneity and the lowest roughness of the films were observed after the 15-hour delay. The film deposited under these optimal conditions was used to study the influence of the particles agglomeration process in a suspension on the thick films' properties. After drying, the samples (from type I and type II depositions) were annealed at $1050\text{ }^\circ\text{C}$ for 10 hours. This annealing temperature was so chosen since below it the degree of crystallization of the ferrite sample is not sufficient, while exceeding it leads to diffusion of Al from the substrate [12].

The barium ferrite thick film samples were characterized by X-ray diffraction (XRD) using an X-ray diffractometer. The microstructures of the samples were observed by a scanning electron microscope and the magnetic properties were measured by a vibrating-sample magnetometer. The magnetic measurements were performed at a maximum magnetic field of 10 kOe applied perpendicular to the sample plane.

3. Results and discussion

Figure 1 shows a typical XRD pattern of barium hexaferrite films annealed at $1050\text{ }^\circ\text{C}$ for 10 hours. Excluding the XRD lines corresponding to Al_2O_3 (the substrate used), all other XRD features observed are assigned to $\text{BaFe}_{12}\text{O}_{19}$.

After the thermal treatment at $1050\text{ }^\circ\text{C}$, the films (both types) were well-crystallized with a high degree of orientation corresponding to the *c*-axis being perpendicular to the film plane, as suggested by the high relative intensities of the 001 peak.

Figure 2a shows a SEM image of the film deposited from the suspension immediately after ultrasound homogenization (type I) and then annealed at $1050\text{ }^\circ\text{C}$. The film has a good density with a thickness around $1\text{ }\mu\text{m}$. The SEM image in figure 2b is of the film deposited from the suspension with a 15-hour delay after ultrasound homogenization and annealed at $1050\text{ }^\circ\text{C}$ (Type II deposition). As can be seen, a type of a sintering process has occurred. The film surface is porous. This film is considerably thicker, with a thickness of $10\text{ }\mu\text{m}$. The barium hexaferrite is a hard magnetic material, so that the magnetic attraction between the $\text{BaFe}_{12}\text{O}_{19}$ particles is very strong even in the presence of the surfactant in the suspension. The ultrasound treatment prevents the agglomeration of the magnetic particles in the suspension.

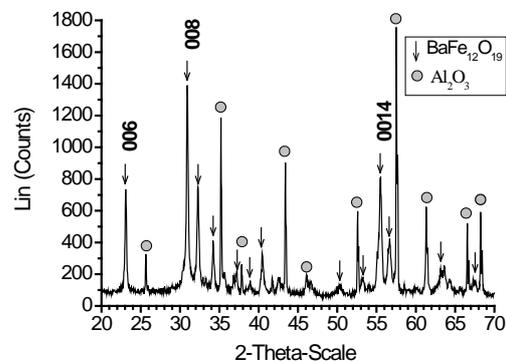


Figure 1. XRD pattern of a type I film annealed at $1050\text{ }^\circ\text{C}$ for 10 hours.

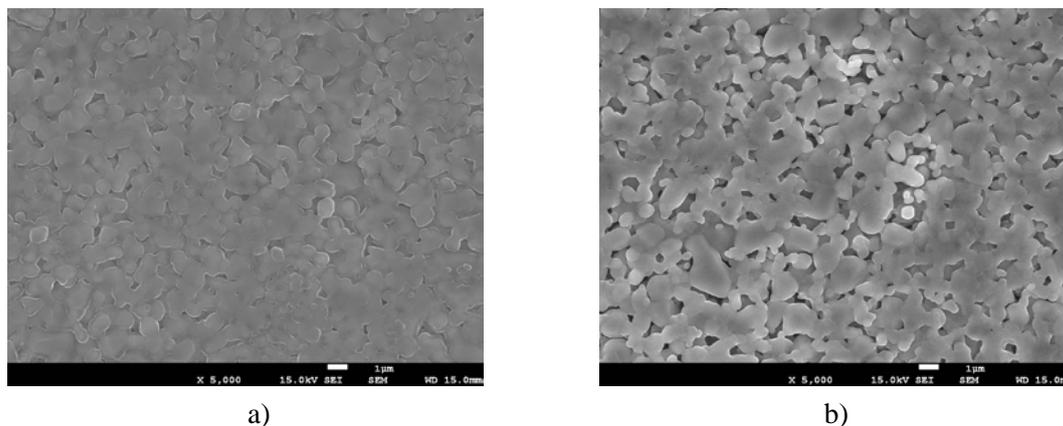


Figure 2. SEM images of the surface of films annealed at 1050°C (a) type I – after ultrasound homogenization without time delay and (b) type II – with a 15-hour time delay after ultrasound homogenization.

In type I deposition, the particles are homogeneously dispersed in the suspension and no agglomeration takes place during the deposition process. Due to the orientation of the deposited particles induced by the external magnetic field applied during the drying process, with the easy magnetic axis (i.e. the crystallographic *c*-axis) perpendicular to the film plane, the grains grow in the film plane, thus improving its density. In the second kind of deposition – type II, the time delay after the ultrasound treatment is sufficient for the particles to agglomerate, which results in preparing thicker films of lower density. This affects the magnetic properties of the films.

The hysteresis loops for a magnetic field applied perpendicularly to the as-deposited BaFe₁₂O₁₉ films prepared by the two deposition types are presented in figure 3. Figure 4 shows the hysteresis loops for a magnetic field applied perpendicularly to the samples annealed at 1050 °C. For the as-deposited type-I sample, the values of the saturation magnetization ($M_s = 4,98$ emu/g) and coercivity ($H_c = 183$ Oe) are considerably lower than those of the corresponding type-II sample, namely, 29,21 emu/g and 2000 Oe, respectively. This can be related to the agglomeration and the greater film thickness. In the first case, the type-I sample consists mainly of small particles (10 nm) with a size on the superparamagnetic limit. The type-II film contains both fractions, 10 nm and 80 nm (stable monodomain particles), so that it exhibits higher coercivity and saturation magnetization.

Figure 4 illustrates the magnetic properties of both type of films, with the external magnetic field applied perpendicularly and in parallel to the film. The annealing dramatically improves the magnetic properties of the type-I BaFe₁₂O₁₉ films, while affecting only slightly the type-II deposited films. The

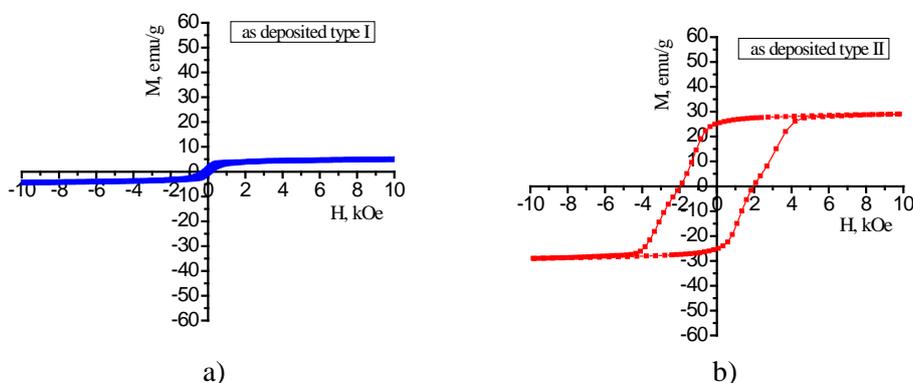


Figure 3. Magnetic properties of as-deposited films prepared by (a) type I – after ultrasound homogenization without time delay and (b) type II – with a 15-hour time delay after ultrasound homogenization.

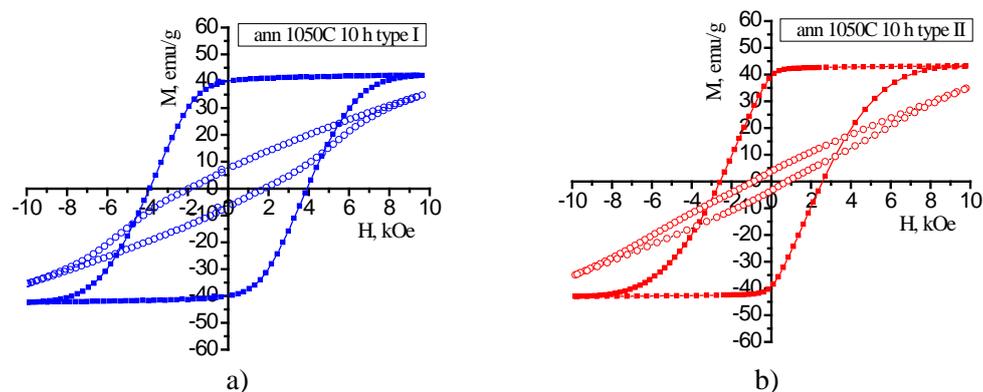


Figure 4. Magnetic properties of films annealed at 1050 °C prepared by (a) type I – after ultrasound homogenization without time delay and (b) type II – with a 15-hour time delay after ultrasound homogenization.

M_s and H_c of the film obtained by the type-I deposition and annealed at 1050 °C are 42,18 emu/g and 3917 Oe, respectively. The M_s and H_c of the film obtained by type-II deposition and annealed at 1050 °C are 43.50 emu/g and 2593 Oe, respectively. i.e., they are higher than those of the as-deposited film. The coercivity does not change significantly after the high-temperature annealing of these films. The possible reason can be the higher porosity in the films obtained by type-II deposition. Both samples show a high degree of orientation, as the squareness ratio $SQR = 0,96$ (the ratio between the remanent and saturation magnetizations).

4. Conclusions

Polycrystalline $BaFe_{12}O_{19}$ films prepared by deposition of $BaFe_{12}O_{19}$ particles in a magnetic field followed by a high-temperature treatment at 1050 °C. The preferential orientation of the crystallites in the film plane resulted in anisotropic magnetic properties. Using a ferrofluid with a different degree of particles' agglomeration (type I and type II depositions), $BaFe_{12}O_{19}$ films of different thickness can be deposited with a very high degree of orientation. The oriented barium ferrite films are promising candidates for perpendicular magnetic recording and for mm-wave application.

Acknowledgments

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