Study of hard-soft magnetic ferrite films prepared by pulsed laser deposition

M. Satalkar, S. N. Kane, A. Ghosh, S. Raghuvanshi, P. Tapkir, N. Ghodke, D. M. Phase, R. J. Chaudhary, Alexandre Pasko, M. Lobue, et al.

Study of hard-soft magnetic ferrite films prepared by pulsed laser deposition

M Satalkar[a], S N Kane[a,1], A Ghosh[a,b], S Raghuvanshi[a], P Tapkir[a], N Ghodke[c], , D M Phase[c], R J Chaudhary[c], A Pasko[d], M LoBue[d], and F Mazaleyrat[d]
[a]School of Physics, D. A. University, Khandwa road Campus, Indore – 452001, India
[b] Dronacharya Group of Institutions, Knowledge Park 111, Greater Noida, India
[c]UGC-DAE CSR, University Campus, Khandwa Road, Indore – 452 001, India
[d]SATIE, ENS Cachan, CNRS, UniverSud Paris, 61 av President Wilson, 94235 Cachan, France

[1]Corresponding author, E-mail: kane_sn@yahoo.com (S. N. Kane)

Abstract. Soft magnetic $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ and hard magnetic $BaFe_{12}O_{19}$ bulk nanocrystalline ferrites were synthesized using the sol-gel auto-combustion method, and were used as targets to deposit soft-hard thin films by the pulsed laser deposition (PLD) method. Various soft-hard thin films with different preparation conditions were deposited on Si (100) substrate, which can be effectively utilized to get better magnetic properties. The prepared films were characterized by the X-ray diffraction (XRD), atomic force microscopy (AFM) and magnetic measurements. XRD confirms the presence of soft and hard phases in the thin films. Coercivity of the prepared films ranges from 1.67 to 2.66 kA/m. AFM images show clustering of grains at the film surface with a characteristic columnar growth.

1. Introduction

Exchange spring systems have stimulated intense research activities in the recent years because of the prediction of improvement in the magnetic properties of these systems [1–2]. In the nanocomposite exchange spring media, two magnetically hard layers and a magnetically soft layer are strongly exchange coupled, which can be achieved by their crystallographic coherence [3]. This in turn combines high magnetization of the soft phase with high coercivity of the hard phase, and is determined by the distribution of hard and soft magnetic phases [4]. The objective of the present work is to get the appropriate preparation conditions for depositing soft-hard composite films by the pulsed laser deposition (PLD) and to use them to obtain improved magnetic properties (higher coercivity and magnetization) in the studied composite magnets.

2. Experimental details

The soft magnetic $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ and hard magnetic $BaFe_{12}O_{19}$ (BaM) ferrite powders were prepared using the sol-gel auto-combustion method. For synthesis, citrate-nitrate precursors were mixed in stoichiometric proportion with citric acid as fuel. The salt to fuel mass ratio was taken as 1:1. All the precursors were dissolved in de-ionized water, and pH was maintained at 7 by adding ammonia solution (NH_4OH). The solution was heated at 110 °C in air for about 1 hour to obtain the gel and finally to get loose powder known as dry gel) [5]. The composite of hard and soft ferrites was prepared by mixing of the individual ferrite components in a ratio of 2:1. The composite powder was pressed in the form of a pellet by applying a pressure of 3.6 GPa and subsequently annealed at 800 °C for 24 hours. The pellet was used as a target for the deposition of soft-hard ferrite composite thin film on Si (100) substrate which was mounted on a rotating axel. The deposition time was two hours. The PLD setup uses a KrF excimer laser (Lambda Physik model COMPEX-201) with a wavelength of 248 nm and a pulse duration of 20 ns. During deposition the laser energy was 200 mJ/pulse, the substrate temperature and oxygen pressure were maintained respectively at 750 °C and 0.13 Pa (base pressure 0.67 mPa). The focused laser beam was made incident on the target surface at an angle of 45°. The substrate was mounted opposite to the target at a distance of 4 cm on a heater plate. After deposition the sample was cooled slowly to room temperature. During cooling the effect of oxygen pressure on the deposited soft-hard composite thin film was studied.

X-ray diffraction (XRD) measurements were performed in θ-2θ configuration using a Bruker D8 Advance diffractometer with Cu-K_α radiation ($\lambda = 0.154$ nm). Atomic force microscopy (AFM) image of the sample was taken by Nanoscope-E using a pyramidal silicon nitride tip in contact mode. Magnetization measurements on the deposited soft-hard composite thin film were done using 7 T MPMS SQUID-VSM setup with a maximum applied field of 2 T. Magnetic properties of the bulk hard ferrite powders were measured using a SQUID magnetometer, Quantum Design MPMS-5S. Magnetic characterization of the synthesized bulk soft magnetic ferrite samples was done using a conventional induction technique at 50 Hz by applying a maximum field of 87.5 kA/m.

3. Results and discussion

In Figure 1, the left panel and its inset show the XRD pattern and magnetization loop of $BaFe_{12}O_{19}$ powder, confirming the formation of hard magnetic phase, whereas the right panel and its inset depict the XRD pattern and magnetization loop of $Mg_{0.1}Ni_{0.3}Zn_{0.6}$ powder, prepared by the sol-gel auto combustion method. The $BaFe_{12}O_{19}$ ferrite serves as a hard phase and the $Mg_{0.1}Ni_{0.3}Zn_{0.6}$ ferrite as a soft phase in the hard-soft composite used for depositing the exchange spring magnet on Si (100) substrate. XRD validates the formation of a single-phase cubic spinel structure, magnetic measurements prove the soft magnetic nature of this powder. Table 1 depicts the structural and magnetic data for the bulk samples (hard and soft ferrites). The obtained *a* and *c* values reveal that the synthesized hard ferrite is a single phase $BaFe_{12}O_{19}$ and confirm the formation of a spinel structure in the soft ferrite powder. The structural and magnetization data match well with the values reported in the literature.

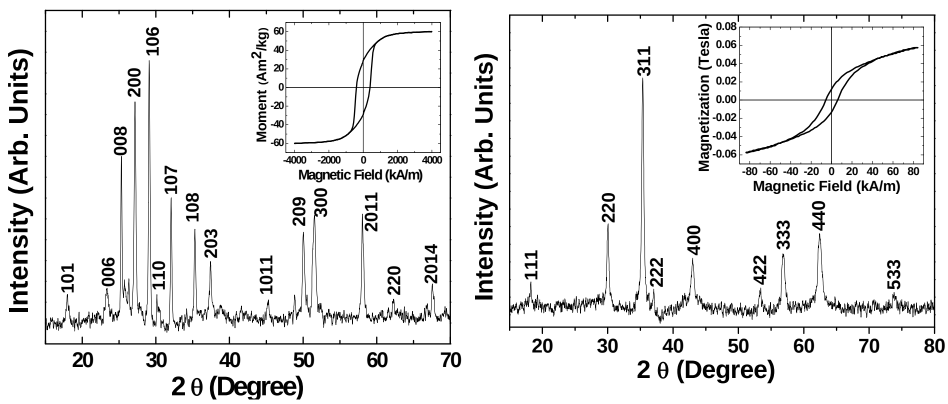

Figure 1. XRD pattern and hysteresis loop for the $BaFe_{12}O_{19}$ powder (left panel and its inset) and the $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ powder (right panel and its inset).

Table 1: Structural and magnetic parameters for the $BaFe_{12}O_{19}$ and $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ powders.

Phase	Lattice parameters (nm)	Grain Size (nm)	Coercivity (kA/m)	Saturation magnetization
$BaFe_{12}O_{19}$	*a* = 0.5589, *c* = 2.3215	78	394	60.1 (Am^2/kg)
$Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$	*a* = 0.8405	24	5.77	57 (mT)

Figure 2 depicts the XRD pattern (left panel) and magnetization loop (right panel) of the composite $BaFe_{12}O_{19}$ + $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ (2:1) thin film deposited on Si (100) substrate, when cooled in the presence of oxygen. The left panel inset shows the surface morphology of the soft-hard composite. AFM image shows clustering of grains on the surface of the film with grain size ~ 130 nm, RMS roughness ~ 0.39 nm, maximum height of the grains ~ 3.46 nm and average height of the grains ~ 1.07 nm. The high vertical resolution of AFM revealed that the film has a characteristic columnar growth with crystallites of height ~ 3.5 nm. Table 2 shows the structural parameters of the phases formed in the prepared thin film. Perusal of *a* and *c* values confirm the presence of hard magnetic phase $BaFe_{12}O_{19}$, soft magnetic phase $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$, and a small amount of secondary Fe_2O_3 phase, which can be ascribed to oxygen deficiency during the sample preparation. The obtained coercivity and magnetic moment values were respectively 26.6 kA/m and 5.89×10^{-7} Am^2.
Figure 3 left panel depicts the XRD pattern of the composite $BaFe_{12}O_{19}$ + $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ (2:1) thin film grown by PLD on Si (100) substrate, when cooled in the absence of oxygen. The XRD pattern was compared with available data in the literature, suggesting the formation of $BaFe_{12}O_{19}$ phase.

Table 2: XRD parameters for the soft-hard composite thin film deposited on Si (100) substrate.

Phase	Lattice parameters (nm)	Grain size (nm)
$BaFe_{12}O_{19}$ (hard magnetic phase)	*a* = 0.5885, *c* = 2.3462	1132
$Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ (soft magnetic phase)	*a* = 0.8405	143
Fe_2O_3 (secondary phase)	*a* = 0.5465, *c* = 2.3136	220

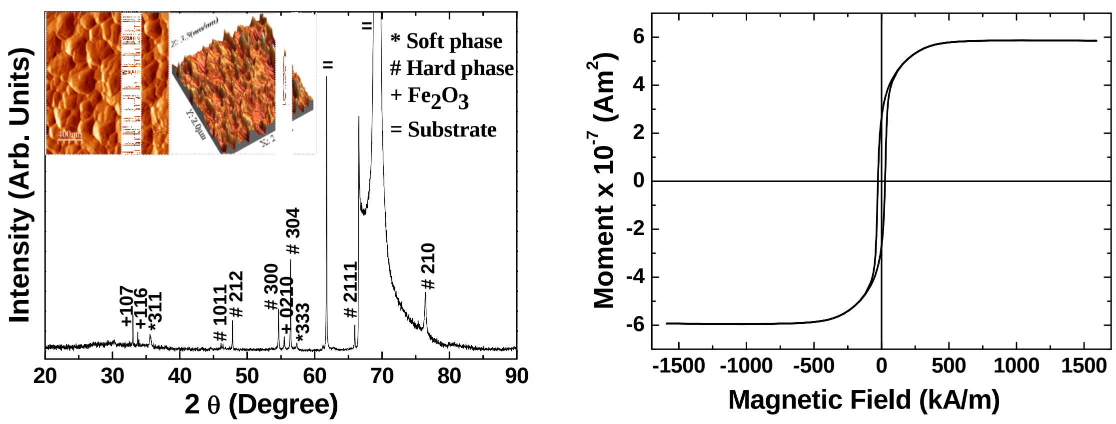

Figure 2. Composite $BaFe_{12}O_{19}$ + $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ thin film deposited on the Si (100) substrate, when cooled in the presence of oxygen pressure: XRD pattern (left panel), AFM 2D and 3D images (inset), and hysteresis loop (right panel).

Journal of Physics: Conference Series **534** (2014) 012043 doi:10.1088/1742-6596/534/1/012043

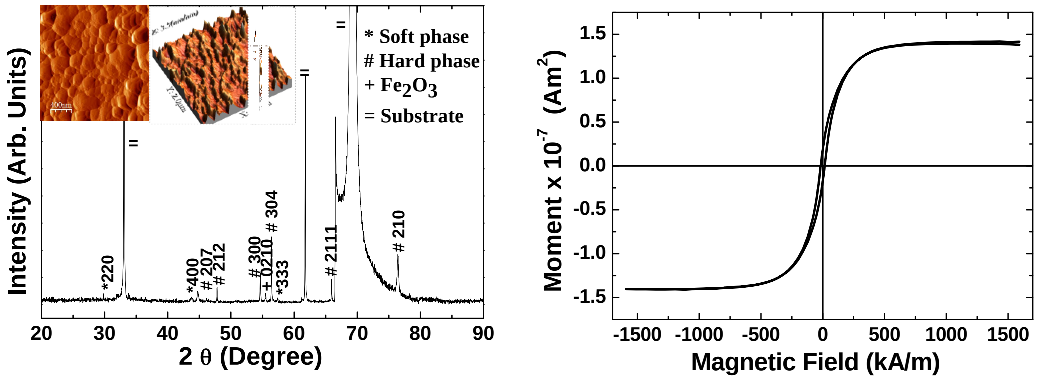

Figure 3. Composite $BaFe_{12}O_{19}$ + $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ thin film deposited on the Si (100) substrate, when cooled in the absence of oxygen pressure: XRD pattern (left panel), AFM 2D and 3D images (inset), and hysteresis loop (right panel).

The left panel inset shows the surface morphology of the soft-hard composite, AFM image shows clustering of grains on the surface of the film. Figure 3 right panel depicts the hysteresis loops of the thin film. The measured coercivity is 16.1 kA/m and magnetic moment is 1.40×10^{-7} Am^2. Table 3 depicts the parameters obtained by analyzing the XRD data.

Table 3: XRD parameters of the soft-hard composite deposited on Si (100) substrate, when cooled in the absence of oxygen.

Phase	Lattice parameters (nm)	Grain size (nm)
$BaFe_{12}O_{19}$ (hard magnetic phase)	a = 0.5885, c = 2.3462	92
$Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ (soft magnetic phase)	a = 0.8405	107
Fe_2O_3 (secondary phase)	a = 0.5465, c = 2.3136	85

Figure 4 depicts the XRD pattern (left panel) and hysteresis loop (right panel) of the composite $BaFe_{12}O_{19}$ + $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ (2:1) deposited on the barium ferrite thin film on Si (100) substrate. Table 5 depicts the parameters obtained by analyzing the structural data. Analysis of the XRD pattern reveals the formation of the following phases: $BaFe_{12}O_{19}$, $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$, Fe_2O_3 and $BaFe_2O_4$. The measured coercivity is 1.75 kA/m and magnetic moment is 11.5×10^{-7} Am^2.

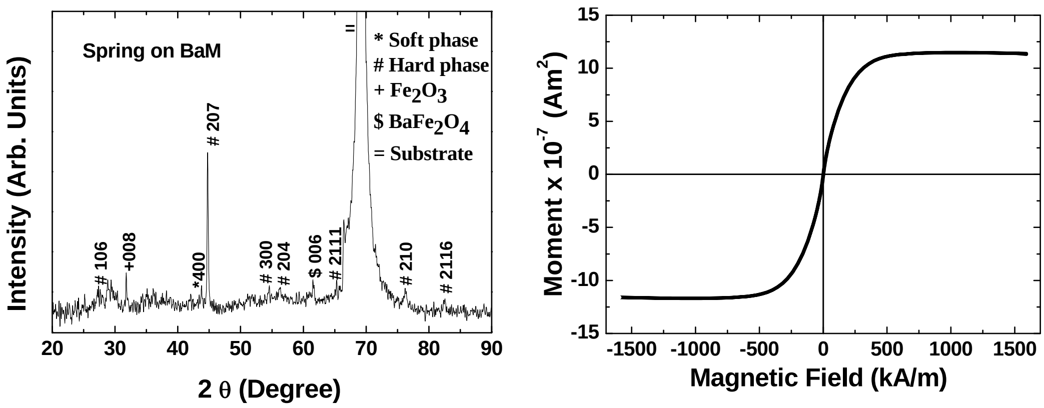

Figure 4. Composite $BaFe_{12}O_{19}$ + $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ thin film deposited on the barium ferrite thin film on the Si (100) substrate, when cooled in the absence of oxygen pressure: XRD pattern (left panel), AFM 2D and 3D images (inset), and hysteresis loop (right panel).

Table 4: XRD parameters of the soft-hard composite deposited on $BaFe_{12}O_{19}$ thin film on Si (100) substrate, when cooled in the absence of oxygen.

Phase	Lattice parameters (nm)	Grain size (nm)
$BaFe_{12}O_{19}$ (hard magnetic phase)	a = 0.5885, c = 2.3462	31
$Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ (soft magnetic phase)	a = 0.8405	66
Fe_2O_3 (secondary phase)	a = 0.5465, c = 2.3136	55
$BaFe_2O_4$ (secondary phase)	a = 0.54, c = 0.91	18

Comparison of the results shown in Figures 2 and 3 yields the following important information on the relation between the preparation conditions and the obtained magnetic properties: XRD pattern of the $BaFe_{12}O_{19}$ + $Mg_{0.1}Ni_{0.3}Zn_{0.6}Fe_2O_4$ composite thin film deposited on Si (100) substrate by PLD reveals that the absence of oxygen ensures more phase purity of the soft-hard composite, whereas the presence of oxygen promotes the formation of Fe_2O_3, indicating that the stoichiometry was not transferred effectively in both conditions. Higher amount of Fe_2O_3 helps in the grain growth of soft, hard and secondary phases. For the hard-soft composite thin film deposited on Si (100) substrate, when the film is cooled in the presence of oxygen, the grain coarsening leads to higher coercivity. Therefore, the presence of oxygen during cooling can be utilized effectively in obtaining improved magnetic properties.

4. Conclusion

To summarize, PLD was used to deposit soft-hard composite thin films on Si (100) substrate using different cooling conditions. It is shown that the presence of oxygen during cooling can be effectively utilized to obtain improved magnetic properties. Formation of soft and hard phases in the prepared thin films was confirmed by XRD. The presence of Fe_2O_3 and $BaFe_2O_4$ as secondary phases was also detected in the films. Magnetic measurements show that the coercivity of the prepared thin films ranges from 1.67 to 2.66 kA/m. AFM images of the composite film show clustering of grains at the film surface exhibiting columnar growth.

Acknowledgments

Support in the form of UGC-DAE CSR project No. CSR-I/CSR51/2011-12 is gratefully acknowledged. Authors are grateful to Dr. M. Gupta and Dr. V. Ganesan, UGC-DAE CSR, Indore respectively for doing XRD and AFM measurements. This work is partly supported by MPCST project No. 1783/CST/R & D/Phy and Engg Sc/2013. AG acknowledges financial support from UGC Dr. D. S. Kothari post-doctoral fellowship.

References

[1] Jiang J S, Pearson J E, Liu Z Y, Kabius B, Trasobares S, Miller D J, and Bader S D, 2005 *J. Appl. Phys.* **97** 10K311
[2] Davies J E, Hellwiga O, and Fullerton E E, 2005 *Appl. Phys. Lett.* **86** 262503
[3] Kneller E F, Hawig R 1991 *IEEE Trans. Magn.* **27** 3588
[4] Roy D, Shivakumara C, and Anil Kumar P S 2009 *J. Magn. Magn. Mater.* **321** L11–L14
[5] Ghosh A, Satalkar M, Rathod S, Nag S P, Vyas P, Kane S N, Ghodke N, Prasad R, and Dwivedi R 2013 *Int. J. Mod. Phys.: Conf. Ser.* ***22*** 28