

## Effect of deposition time on structural and magnetic properties of pulse laser deposited hard-soft composite films

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**Abstract.** Hard-soft composite ( $\text{BaFe}_{12}\text{O}_{19}:\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  (2:1) films, were deposited by 'Pulsed Laser Deposition' (PLD) technique on Si (100) substrate using different deposition time – 30, 60, 90 and 120 minutes. Influence of deposition time on structural and magnetic properties were studied via X-ray diffraction (XRD) and vibrating sample magnetometer (VSM). XRD confirms the presence of soft and hard phases in all the prepared thin films. Small amount of secondary phase -  $\text{Fe}_2\text{O}_3$  is also detected in all the thin films except for the deposition time - 90 mins. With deposition time average grain diameter of both hard ( $\text{BaFe}_{12}\text{O}_{19}$ ) and soft ( $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ ) phase increases. Increase in the distance between the magnetic ions ( $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$ ) at tetrahedral (A) and octahedral [B] site leads to increase in the hopping length at A and B site except for the the deposition time of 60 minutes. Magnetic measurements shows that the coercivity and magnetization of the prepared thin films respectively ranges between 112.07 – 213.03 Oe and  $1.4 \times 10^{-7}$  –  $3.15 \times 10^{-7} \text{ Am}^2$ .

### 1. Introduction

Recently, there has been immense attention on the materials having good exchange spring coupling behavior. According to the exchange spring theory proposed by Kneller and Hawig [1], nanocomposite magnets consist of soft and hard phases, having sufficiently exchanged coupling between both the phases which are known as exchange spring magnets. Exchange spring magnets possess large energy product value and are potential candidates for next generation permanent magnet [2]. The technological realization of such materials shows that they should be crystallographically coherent and consequently they are magnetically exchange coupled [1]. The hard magnetic grains provide the high anisotropy and coercive fields while the soft-magnetic grains enhance the magnetic moment. The soft grains are pinned to the hard-magnet grains at the interfaces by the exchange interaction while the center of the soft magnet grains can rotate in a reversed magnetic field. Such magnets are characterized by enhanced remanent magnetization and reversible demagnetization curves since the soft grains will rotate back into alignment with the hard grains when the applied field is removed [3]. Exchange spring behavior is becoming important and it has been predicted that a single hard-phase magnetic behavior is expected for a nano-composite consisting of both soft- and hard-magnetic phases due to high exchange coupling between the two different phases. This, in turn combines high magnetization of the soft phase with high coercivity of the hard phase. Thus, with an aim to enhance the coercivity and magnetization values, the paper focusses on the effect of deposition



time on structural and magnetic properties of hard-soft composite films prepared via 'Pulsed Laser Deposition' (PLD) technique.

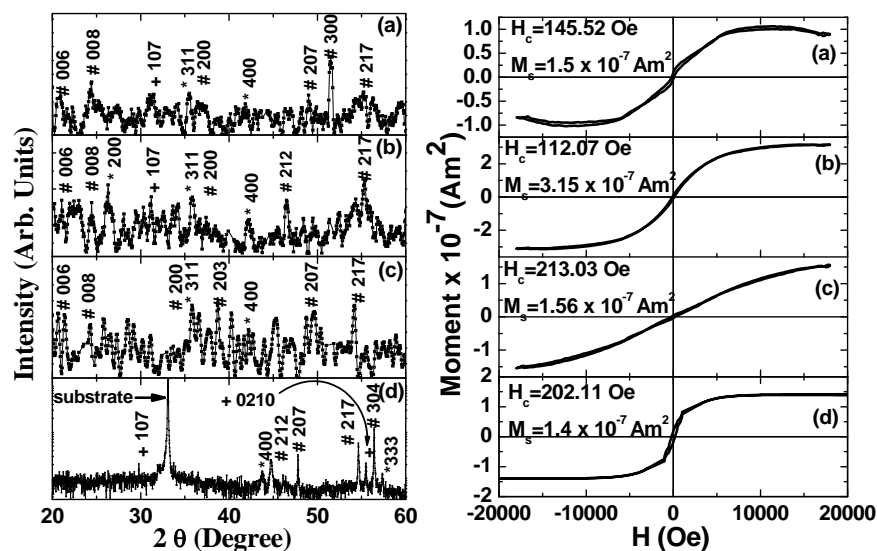
## 2. Experimental details

For depositing hard-soft composite films on Si (100) soft ( $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ ) and hard ( $\text{BaFe}_{12}\text{O}_{19}$  or BaM) ferrite powders were prepared by sol gel auto-combustion method [4]. Composite of hard and soft ferrite was prepared by thoroughly mixing of the individual ferrite components in the ratio 2:1, with an aim to obtain better structural homogeneity and to be able to observe exchange spring behaviour. The composite powder was pressed in the form of a pallet by applying pressure  $\sim 90$  K Newton and, was annealed at  $800^\circ\text{C}$  for 24 hrs. Thin films were deposited using the following composite pallet:  $\text{BaFe}_{12}\text{O}_{19}:\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  (2:1) mounted on a rotating axel, on (100) Si substrate at different deposition time:- 30, 60, 90 and 120 minutes. PLD set-up (Lambda Physik model COMPEX-201) uses a KrF excimer laser of wavelength 248 nm and pulse duration of 20 ns. During deposition the laser energy was kept 200 mJ/pulse, with pulse repetition rate of 10 Hz. The substrate temperature and oxygen pressure were maintained respectively at  $750^\circ\text{C}$  and  $\sim 1$  mTorr (base pressure  $\sim 5 \times 10^{-6}$  Torr). Focussed laser beam was made incident on the target surface at an angle of  $45^\circ$ . The substrate was mounted opposite to the target (on a heater plate) at a distance of 4 cm. After deposition, the sample was cooled slowly to room temperature, in absence of oxygen pressure.

X-ray diffraction (XRD) of the prepared  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  ferrite shows single phase behaviour of both the hard and soft phases [5]. XRD ( $\theta$ - $2\theta$  configuration) measurements of composite hard - soft composite films were done using a Bruker D8 Advance diffractometer, with  $\text{Cu-K}_\alpha$  radiation ( $\lambda = 0.1540562$  nm). Magnetization measurements on deposited thin films were done using LakeShore Model 7410 vibrating sample magnetometer (VSM) with a maximum applied field of  $\pm 1.7$  Tesla.

## 3. Results and discussions

Figure 1 depicts the XRD pattern (Left panel) of the composite  $\text{BaFe}_{12}\text{O}_{19}:\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  (2:1) thin film grown by PLD on silicon (100) substrate for (a) 30 minutes, (b) 60 minutes, (c) 90 minutes



**Figure 1** XRD pattern (Left panel) and hysteresis loop (Right panel) of the composite  $\text{BaFe}_{12}\text{O}_{19}:\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  (2:1) thin film deposited on Si (100) substrate for (a) 30 minutes, (b) 60 minutes, (c) 90 minutes and (d) 120 minutes. (\* Soft phase -  $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ , # Hard phase -  $\text{BaFe}_{12}\text{O}_{19}$ , +  $\text{Fe}_2\text{O}_3$ )

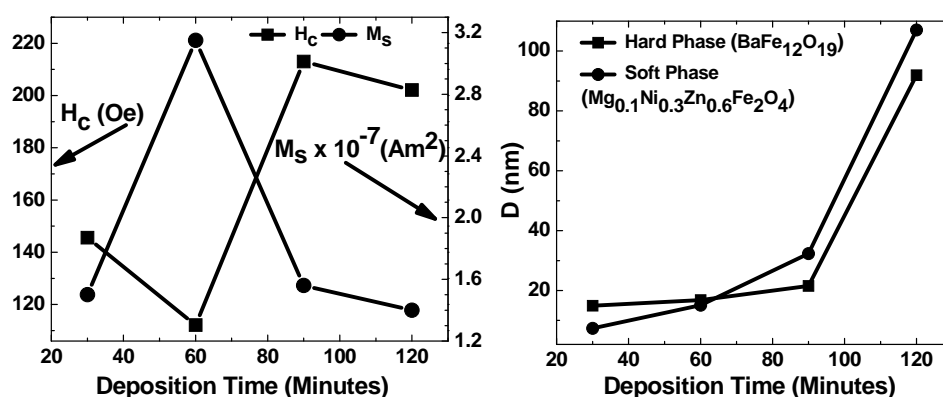
and (d) 120 minutes. The planes shown in the XRD pattern of the composite films were matched with the Joint Committee on powder Diffraction Standard (JCPDS) card of  $\text{BaFe}_{12}\text{O}_{19}$ , which shows the formation of  $\text{BaFe}_{12}\text{O}_{19}$  (hard) phase. XRD pattern of the grown thin film was also compared with the available data in the literature, suggesting the formation of  $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  (soft) phase. A small amount of secondary  $\text{Fe}_2\text{O}_3$  phase is also identified in all the deposited thin films except for the deposition time of 90 minutes. No impurity phase is detected in the XRD patterns of the preliminary powders of  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  ferrite [5], which were used for the preparation of composite films. The presence of secondary phase in the prepared composite films can be ascribed to the oxygen deficiency during the sample preparation. Figure 1 (Right panel) represents the hysteresis loops of the composite  $\text{BaFe}_{12}\text{O}_{19}:\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  (2:1) thin film grown by PLD on silicon (100) substrate for (a) 30 minutes, (b) 60 minutes, (c) 90 minutes and (d) 120 minutes. Coercivity ( $H_c$ ) and magnetization ( $M_s$ ) obtained from the hysteresis loops is represented in figure 1 right panel. Low values of  $H_c$  and  $M_s$  shows the major contribution of the soft phase in the prepared composite films.

Table 1 shows the structural parameters of the phases formed in the prepared composite films deposited for different time. Perusal of  $a$  and  $c$  values reveal the formation of  $\text{BaFe}_{12}\text{O}_{19}$  phase. For soft ferrite value of  $a$ , confirms the formation of cubic spinel structure. Average grain diameter ( $D$ ) of the prepared thin films for different deposition time are also given in table 1. Higher grain size for the hard and soft phase is obtained for the thin film deposited for 120 minutes. The hopping length for tetrahedral - A ( $L_A$ ) and octahedral - B ( $L_B$ ) site for the soft spinel ferrite phase is also shown in table 1. The hopping length/jump length ' $L$ ' (the distance between the magnetic ions) of electrons influences the physical properties of the soft phase. Electrons those are hopping between B- and A sites are less probable compared to that between B- and B sites, because the distance between the two metal ions placed in B-sites is smaller than if they were placed one in B-sites and the other in A-sites.  $L_A$  and  $L_B$  for the soft spinel ferrite phase -  $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  respectively ranges between 0.3589 - 0.3639 nm and 0.2930 - 0.2972 nm.  $L_A$  and  $L_B$  decreases for 60 minutes and then constantly increases up to 120 minutes. The variation in the hopping length at A and B site can be attributed to the increase in the distance between the magnetic ions ( $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$ ) at A and B site for all the values of the deposition time except for 60 minutes.

Figure 2 (left panel) shows the variation of  $H_c$  and  $M_s$  with deposition time. Highest value of  $H_c$  and  $M_s$  is obtained for the deposition time - 90 (213.03 Oe) and 60 ( $3.15 \times 10^{-7} \text{ Am}^2$ ) minutes respectively. Higher values of  $H_c$  and  $M_s$  can be ascribed to the two phase coexistence. It is known that in the PLD process the oxides become more oxygen vacant as the  $\text{O}_2$  partial pressure decreases. The magnetization values increases as the oxygen pressure increases inside the chamber, due to the filling of more vacancies. The substrate temperature was same for all the deposited hard - soft composite films but the deposition time was different. This can be considered as in-situ annealing of the films at different time. For higher deposition time (120 minutes) decrease in magnetization is due to the

**Table 1:-** XRD Parameters: lattice constant ( $a$ ), Grain Size ( $D$ ), hopping length for A ( $L_A$ ) and B ( $L_B$ ) site for the prepared soft ( $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ ) - hard ( $\text{BaFe}_{12}\text{O}_{19}$ ) composite thin film on Si (100) substrate for different deposition time.

Deposition time (minutes)	Phase	$a$ (nm)	$L_A$ (nm)	$L_B$ (nm)	$D$ (nm)
30	$\text{BaFe}_{12}\text{O}_{19}$	$a = 0.5648, c = 2.7347$	-	-	14.92
	$\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	$a = 0.8347$	0.3614	0.2951	7.38
60	$\text{BaFe}_{12}\text{O}_{19}$	$a = 0.5370, c = 2.4182$	-	-	16.84
	$\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	$a = 0.8288$	0.3589	0.2930	15.10
90	$\text{BaFe}_{12}\text{O}_{19}$	$a = 0.5680, c = 2.6132$	-	-	21.56
	$\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	$a = 0.8309$	0.3598	0.2938	32.31
120	$\text{BaFe}_{12}\text{O}_{19}$	$a = 0.5885, c = 2.3462$	-	-	91.97
	$\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	$a = 0.8405$	0.3639	0.2972	107.05



**Figure 2** (Left Panel) Variation of coercivity ( $H_c$ ) and magnetization ( $M_s$ ) with deposition time. (Right Panel) Variation of average grain diameter ( $D$ ) with deposition time.

creation of more oxygen vacancies. Considerable increase in  $M_s$  is obtained for the prepared films but expected increase in  $H_c$  is not observed, ascribable to lower anisotropy and weak exchange coupling strength between the hard and soft phase. Variation of  $D$  for the hard and soft phase with different deposition time is depicted in figure 2 (right panel). As the deposition time increases  $D$  of both hard and soft phases increases, attributed to crystal growth and morphological evolution. Highest grain size for soft and hard phase is obtained for 120 minutes deposition time. Deposition of the thin film at a particular temperature but for higher time can lead to increase in  $D$ .

#### 4. Summary

( $\text{BaFe}_{12}\text{O}_{19}:\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  (2:1)) composite films were deposited by PLD on Si (100) substrate at different deposition time – 30, 60, 90 and 120 minutes. Effect of deposition time on structural and magnetic properties were studied. Formation of hard and soft phases in all the prepared thin films for different deposition time was confirmed by XRD. Presence of  $\text{Fe}_2\text{O}_3$  as secondary phase was also detected in all the composite films except for the deposition time - 90 minutes. With deposition time increase in average grain diameter of both the phases  $\text{BaFe}_{12}\text{O}_{19}$  (hard) and  $\text{Mg}_{0.1}\text{Ni}_{0.3}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$  (soft) were observed, attributed to crystal growth and morphological evolution. Highest value of  $H_c$  (213.03 Oe) and  $M_s$  ( $3.15 \times 10^{-7} \text{ Am}^2$ ) is obtained for the deposition time - 90 and 60 minutes respectively, ascribed to the coexistence of two phases. Objective to get better magnetic parameters -  $M_s$  is somewhat attained but, substantial increase in  $H_c$  is not observed, ascribed to low anisotropy and weak exchange coupling strength between the hard and soft phase.

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