Magnetic and FMR study on CoFe2O4/ ZnFe2O4bilayers

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Magnetic and FMR study on $CoFe_2O_4$/ $ZnFe_2O_4$bilayers

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$CoFe_2O_4$/$ZnFe_2O_4$ bilayers were deposited by the pulsed laser deposition technique on amorphous fused quartz substrate at substrate temperatures of 350 °C and in oxygen pressure of 0.16 mbar. The films were studied after ex-situ annealing for 2 hrs in air at various temperatures up to 650 °C. The magnetic properties of the bilayer were studied at 300 K and at 10 K. Ferromagnetic resonance was carried out at x-band frequencies at room temperature. It was found that as a result of annealing, the diffusion between Co-ferrite and Zn ferrite starts around 350 °C and leads to a large line width system having magnetization, which remains undetected by FMR.

***Keywords*: Ferrite Thin Films, Bilayer, Ferromagnetic Resonance.**

I. Introduction

Zinc ferrite (ZnF) is a normal ferrite in bulk but is known to get partially inverted when prepared in nanocrystalline form. The magnetism thus changes between anti ferromagnetism and ferrimagnetism depending on the grain size [1-3]. One of the special advantages of ZnF films is that it is possible to obtain good magnetic properties even while maintaining relatively low deposition and processing temperatures [3-4]. This is unlike most other ferrite systems which need temperatures at least of the order of 700 °C for obtaining even reasonable magnetic properties.[6] ZnF can also show low ferromagnetic resonance (FMR) line width, if prepared appropriately [7]. Cobalt ferrite (CoF), an inverse ferrite, is a well-known hard spinel ferrite, which has been studied in detail due to its high coercivity (H_C) and moderate saturation magnetization [8].

It is known that cation distribution and hence magnetic properties of both Co and Zn ferrite depend sensitively on deposition parameters. With an aim of achieving interesting properties while maintaining low processing temperatures, a preliminary study on CoF/ZnF bilayers was recently reported. It was found that the best magnetic properties were obtained in a bilayer that was deposited at a substrate temperature 350 °C [9]. In order to further understand and tune the magnetic properties of such a bilayer, we carried out annealing study on CoF/ZnF bilayers deposited at 350 °C. This study is being reported in this paper.

II. Experimental Details

The bilayer of Co ferrite (CoF) and Zn ferrite (ZnF) were deposited on fused quartz substrate by the Pulsed Laser Deposition (PLD) using third harmonic (355 nm) of Nd: YAG laser with 10 Hz repetition rate and 5–6 ns pulse width. The CoF and ZnF target used for ablation were prepared by standard ceramic route. A typical fluence of the focused laser beam on the target was 1.6 watt at the time of deposition. The chamber was first evacuated to a base pressure of 2.5×10^{-5} mbar. The films were deposited in oxygen atmosphere with oxygen partial pressure of 0.16 mbar. The substrate to target distance was kept at 45 mm. Initially CoF thin film was deposited for 15 minutes on the fused quartz substrate at a substrate temperature (T_S) of 350 °C. After the deposition of CoF, the film was kept in the chamber in oxygen atmosphere without laser beam. After 15 minutes, ZnF thin film was deposited on the top of the earlier deposited CoF thin film. The thickness was measured by using Stylus profilometer. The nominal thickness of CoF and ZnF layer was 160 nm and 230 nm respectively and the thickness of the bilayer was found to be 390 nm. These films were further annealed in air for two hours at temperatures ranging from 350-650 °C. Every time a fresh film was inserted in the furnace for annealing.

X-ray diffraction (XRD) of all these bilayers was taken by a PANalytical X'Pert PRO X-ray diffractometer using CuK_α radiation. Magnetic properties of the CoF/ZnF bilayer were measured using vibrating sample magnetometer (VSM) of Quantum Design Physical Property Measurement System (PPMS). The M-H loop was measured at room temperature (300 K) and 10 K by applying dc magnetic field upto 80 KOe in plane of the film. The diamagnetic contribution of the fused quartz substrate was subtracted for obtaining the magnetization (M) vs. applied magnetic field (H) hysteresis (M–H) loops. Ferromagnetic resonance (FMR) spectra were measured using a cavity measurement by using a home-made spectrometer at a frequency of 9.524 GHz. The measurements were made both with applied field parallel and perpendicular (normal) to the film plane. The FMR linewidths (ΔH) were taken as the field difference between maximum and minimum of the derivative absorption curve, whenever the mode was symmetric. In case of asymmetric modes, ΔH values were estimated by doubling the half width from the portion where line shapes were good [7].

III. Result and Discussion

X-ray diffraction measurements show that the as deposited bilayer as well as the ones annealed at different temperatures contain only ferrite phase. However, the X-ray lines were broad due to nano-crystalline nature of the films and it was not possible to resolve the Zn and Co-ferrite phases even in the as deposited bilayer. It is to be remarked here that the lattice constants of Zn and Co ferrites are 0.844 and 0.839 nm respectively, which are quite close to each other [9].

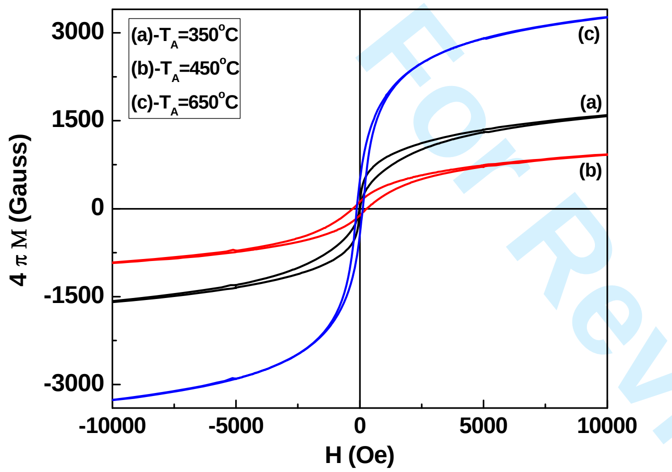

Fig.1 M-H loop at 300 K of CoF/ZnF bilayer annealed at different temperature

The *M–H* loops at 300 K of our samples are shown in Fig. 1 in the range of plus minus 10 kOe. The loop of the as deposited sample was similar to the one annealed at 350 ºC and hence has not been shown in the figure. It is seen from Fig. 1 that the loops do not saturate properly. They did not saturate even at the highest applied field of 80 KOe. The non-saturation of M–H loops is commonly observed in nanocrystalline ferrite thin films [5]. We obtained the spontaneous magnetization ($4\pi M_S$) of all the bilayers by extrapolating the highest field part to zero applied fields [9]. These values are shown in Table 1 along with H_C values. It is seen from Table 1 that the $4\pi M_S$ is highest for the bilayer annealed at 650 ºC, while it is smallest for the one annealed at 450 ºC. This result is interesting because generally an increase in the annealing temperature causes the magnetization to go up [6]. In our case, on the other hand, the magnetization of 450 ºC annealed bilayer is smaller than the one annealed at 350 ºC and then it further goes up for higher T_A. We also note that the H_C values of as deposited and the sample annealed at T_A= 350 ºC are similar. There is a sharp increase in its value for T_A= 450 ºC. The value of H_C is again found to decrease when T_A=650 ºC. Thus the magnetic properties show a non-monotonic behavior with the T_A.

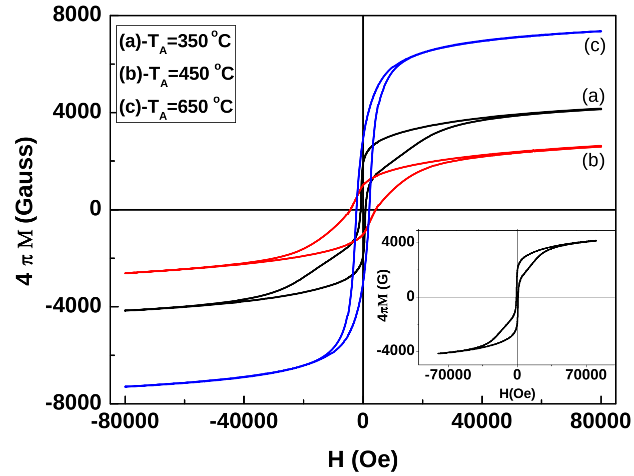

Fig.2 M-H loop at 10 K of CoF/ZnF bilayer annealed at different temperature. Inset: M-H loop at 10 K of CoF/ZnF bilayer annealed at 350 °C.

Fig.2 shows 10 K hysteresis loop of the CoF/ZnF bilayer annealed at different temperatures. It is seen from this figure that the M-H loop of CoF/ZnF bilayer annealed at T_A= 350 °C shows two-step hysteresis loop. Such types of two stepped M–H loops were also observed in other ferrite bilayers. We also saw a similar loop in our as deposited bilayer [9-11]. The two step loop indicates the superposition of two loops of different H_C corresponding to the soft ZnF and hard CoF layers [9]. For the bilayer annealed at 450 ºC, we see a loop in which the two steps are not seen clearly. For the bilayer annealed at 650 ºC, the M-H loop indicates a clear one step hysteresis loop with highest $4\pi M_S$. This gives an indication that the two individual layers have a tendency of getting mixed up when annealing temperature exceeds 350 ºC [12].

Table.1 Spontaneous magnetization and H_C of CoF/ZnF bilayer at 300 K and 10 K

Sample	$4\pi M_S$ at 300K (G)	$4\pi M_S$ at 10K (G)	H_C at 300K (Oe)	H_C at 10K (Oe)
T_A=350 °C	1900	3345	15	795
T_A=450 °C	1145	1845	260	4210
T_A=650 °C	3620	6585	115	2090

Another interesting feature seen from Fig.2 pertains to the closing of the M-H loops of the samples. We note that the M-H loop of sample annealed at 350 ºC closes at a field around ~ 50 KOe. This is the approximate field at which the upper and lower portions of the loop meet. The M-H loop of as deposited sample (not shown in the figure) closes even at larger field ~53 KOe. For the sample annealed at 450 ºC, the closing occurs close to 40 KOe. The M-H loop of the film annealed at 650 ºC, on the other hand, closes at a moderately low field of around ~18 KOe. These results indicate that the as deposited films have some sort of large anisotropy at low temperatures, which is preventing them from saturation. This anisotropy decreases monotonically upon annealing.

The $4\pi M_S$ and the H_C values of the bilayer at 10 K are also listed in Table 1. From the Table it is seen that similar to 300 K, even at10 K the $4\pi M_S$ and H_C values of the samples do not show a monotonic change with annealing temperature. We note that the $4\pi M_S$ at 300 K of the bilayer annealed at 650ºC is about twice that of the sample annealed at 350 ºC and thrice that of the sample annealed at 450 ºC. At 10 K, similar trend continues and the $4\pi M_S$ of the bilayer annealed at 650 ºC is about twice that of the sample annealed at 350 ºC and about 3.5 times that of the sample annealed at 450 ºC. We also note that even the H_C values at 10 K show a similar behavior with annealing temperature as was observed at 300 K, even though their values are considerably higher at low temperature.

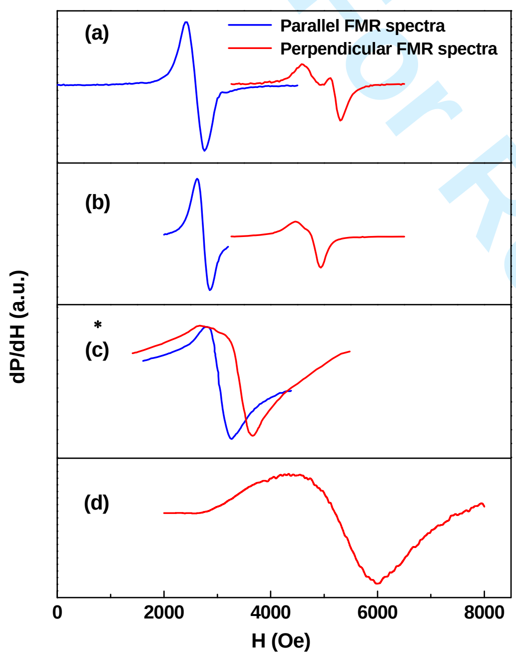

Fig.3 Room temperature FMR spectra of CoF/ZnF bilayer (a) deposited at 350 ºC measured at 9.524 GHz (b) annealed at 350 ºC measured at 9.524 GHz (c)*annealed at 450 ºC measured at 9.1 GHz (d) annealed at 650 ºC measured at 9.524 GHz.

To get a clear idea regarding the behavior of magnetization as a function of annealing temperature, we carried out FMR measurement at room temperature. Fig.3 shows the parallel and perpendicular FMR spectra of CoF/ZnF bilayers annealed at various temperatures. For the sample annealed at 650 °C, the parallel FMR could not be observed due to large ΔH and has not been shown. For all other samples the parallel FMR showed a single line. The perpendicular FMR spectra of the as deposited film, on the other hand, showed two clear modes. For the sample annealed at 350 and 450 ºC we see a small shoulder on the left hand side of the main peak in perpendicular. For 650 ºC annealed sample, a very broad resonance is seen in perpendicular. We also note that the perpendicular and parallel modes come close to each other with increasing annealing temperature except for the 650 ºC annealed sample. The values of the resonance fields (H_R) and the ΔH for all the films have been shown in Table 2.

We calculated the $4\pi M_{eff}$ and the spectroscopic splitting factors factor, '*g*' for both low and high field modes of the as deposited film using Kittel's equations assuming them to be uniform precession [5]. For this, we took the same observed parallel mode field. For the films annealed at 350 and 450 ºC, we calculated $4\pi M_{eff}$ and 'g' values using main perpendicular and the only parallel FMR mode. For 650 ºC annealed sample, we assumed g=2 and calculated the $4\pi M_{eff}$ without using any parallel mode position. The values thus obtained have also been shown in Table 2. From the Table we find that the value of 'g' is close to 2 for all the samples. However, $4\pi M_{eff}$ decreases with annealing temperature up to 450 °C and then again goes up for 650 °C annealed sample.

The earlier studies carried out on CoF and ZnF single layer thin films indicate that the room temperature $4\pi M_S$ of the ZnF is of the order of 4000 G, while the same of CoF is smaller and is of the order of 2400 G [9]. The ferrimagnetism in ZnF films arises from the changed cation distribution which makes them partially inverted for low grain sizes. As the grain sizes increase, ZnF returns to normalcy, which makes it antiferromagnetic and the magnetization drops. The magnetization thus is a very sensitive function of the grain size in ZnF and is smaller both for larger and smaller grain sizes, peaking somewhere in between [3]. The Co ferrite, on the other hand, has smaller magnetization due to its smaller grain size caused because of lower substrate temperature deposition. An increase in its grain size, for example by annealing, would cause an increase in its magnetization.

It has also been shown earlier that ZnF can have small ΔH if deposited appropriately [6]. Recent work done by Bohra *et al.* [6] showed that the ΔH of ZnF thin films gradually increases with the increase in annealing temperature. They also observed that the ΔH of ZnF films deposited by PLD at 350 ºC is 360 Oe, which matches well with the ΔH value of the main peak of as deposited sample. This along with the higher effective magnetization ($4\pi M_{eff}$) corresponding to this peak; lead us to believe that the high field peak corresponds to ZnF, even though the $4\pi M_{eff}$ of this film is smaller than the single layer value. The lower field peak may thus correspond to CoF. The weighted value of $4\pi M_{eff}$ as obtained from FMR by using nominal thicknesses comes out to be 1683 G and is close to the measured film magnetization of 1785 G.

Even though for the as deposited sample the observed $4\pi M_{eff}$ matches well with $4\pi M_s$measured from VSM, one of the most surprising results of this study is that for all other samples the two values are quite different from each other.

For the samples annealed at 350 and 450 ºC, we note that $4\pi M_{eff}$shows a decrease with T_A, reaching a very small value for the higher temperature. The same trend of $4\pi M_s$ was seen in the single layer values of ZnF, where it reached a value close to zero after annealing at 450 ^oC. [13] Thus the resonance that we see for these bilayers clearly belongs to ZnF layer. The question then arises as to what has happened to the CoF layer and where has the excess magnetization measured by VSM gone? These questions can be answered if we assume that this layer has got mixed up with part of ZnF layer, leading to a defective system. This system carries a magnetic moment but its ΔH is too large for its FMR mode to get resolved.

For the sample annealed at 650 ºC, even if there is some un-diffused ZnF single layer remaining in the bilayer, it would be nonmagnetic. Hence the broad mode that we see in FMR has to be from an intermixed CoF layer. The ΔH of this mode is very large and it is not easy to comment on the value of magnetization that we obtained from this assuming a value of g equal to 2.

Table.2 Detail values of FMR.

Sample	$\boldsymbol{H_R^{\parallel}}$ (Oe)	$\boldsymbol{H_R^{\perp}}$(Oe)	ΔH‖ (Oe)	$\Delta H_\perp$ (Oe)	g	$4\pi M_{eff}$ (G)
As Depo. Mode-1	2595	4800	330	---	2.08	1529
As Depo. Mode-1	2595	5175	330	300	2.02	1789
T_A=350^{o}C	2748	4760	240	---	2.00	1388
*T_A=450ºC	3010	3390	460	---	2.07	255
T_A=650ºC	---	5054	---	1470	2.00	1650

*FMR measured at 9.1GHz

IV. Conclusion

The as deposited CoF/ZnF bilayers show a two-step M-H loop at 10 K coming out from individual layers. The two layers show a tendency of mixing up when the annealing temperature exceeds 350 ^oC. For the partially mixed samples, a non-agreement is found between the $4\pi M_{eff}$ obtained from FMR and $4\pi M_s$ obtained from VSM. This can be understood if we assume that during mixing a high line width system is getting formed, which though carries significant magnetization, but is not detected from FMR.

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References

1. C.N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, H. Guérault, and J. M. Greneche," Magnetic properties of nanostructured ferrimagnetic zinc ferrite," *J. Phys.: Condens. Matter,* vol. 12, pp. 7795-7805, 2000.
2. M. Arias, V. M. Pantojas, O. Perales, W. Otaño, "Synthesis and characterization of magnetic diphase $ZnFe_2O_4/\gamma\text{-}Fe_2O_3$ electro spun fibers," *J Magn.Magn Mater.,* vol. 323, pp. 2109–2114, 2011
3. Murtaza Bohra, Shiva Prasad, Naresh Kumar, D. S. Misra, S. C. Sahoo, N. Venkataramani, and R. Krishnan," Large room temperature magnetization in nanocrystalline zinc ferrite thin films," *Appl. Phys. Lett.*, Vol. 88, pp. 262506, 2006
4. Seisuke Nakashima, Koji Fujita, Katsuhisa Tanaka, Kazuyuki Hirao,Tomoyuki Yamamoto, and Isao Tanaka," Thermal annealing effect on magnetism and cation distribution in disordered $ZnFe_2O_4$ thin films deposited on glass substrates," *J Magn.Magn Mater.,* vol. 310, pp. 2543–2545, 2007
5. J. Dash, S. Prasad, N. Venkataramani, R. Krishanan, P. Kishan, N. Kumar, S. K. Date, and S. D. Kulkarni, "Study of magnetization and crystallization in sputter-deposited LiZn ferrite thin films," *J. Appl. Phys.,* vol. 86, pp. 3303–3311, 1999.
6. Subasa Chandra Sahoo, Narayanan Venkataramani, Shiva Prasad, Murtaza Bohra, and Ramanathan Krishnan," Substrate Temperature Dependent Anomalous Magnetic Behavior in $CoFe_2O_4$ Thin Film," *IEEE Trans. Magn.*, vol. 47, pp. 337–3340, 2011.
7. Murtaza Bohra, Shiva Prasad, N. Venkataramani, Naresh Kumar, S. C. Sahoo, and R. Krishnan," Narrow Ferromagnetic Resonance Linewidth Polycrystalline Zn-Ferrite Thin Films," *IEEE Trans. Magn.*, vol. 47, pp. 345-348, 2011
8. Jae-Gwang Lee, Jae Yun Park, Young-Jei Oh, and Chul Sung Kim ," Magnetic properties of $CoFe_2O_4$ thin films prepared by a sol-gel method," *J. Appl. Phys.,* Vol. 84, pp. 2801-2804, 1998
9. S.C. Sahoo, N. Venkataramani, Shiva Prasad, Murtaza Bohra and R. Krishnan," Magnetic Properties of Nanocrystalline $CoFe_2O_4/ZnFe_2O_4$ Bilayers," *J. Supercond. Nov. Magn.,* DOI 10.1007/s10948-011-1237-y
10. Y. Suzuki, R. B. van Dover, E. M. Gyorgy,Julia M. Phillips, and R. J. Felder," Exchange coupling in single-crystalline spinel-structure. $Mn,Zn.Fe_2O_4/CoFe_2O_4$ bilayers," *Phys. Rev. B,* vol. 53, pp. 14016, 1996
11. Ana V. Ramos, Sylvia Matzen, Jean-Baptiste Moussy, Frédéric Ott, and Michel Viret," Artificial antiphase boundary at the interface of ferrimagnetic spinel bilayers," *Phys. Rev. B,* vol. 79, pp. 014401, 2009
12. D.C. Crew, J. Kim, L.H. Lewis and K. Barmak, "Interdiffusion in bilayer CoPt/Co films: potential for tailoring the magnetic exchange spring," *J. Magn. Magn. Mater,* vol. 233, pp. 257–273, 2001.
13. B.N. Sahu, S.C. Sahoo, N. Venkataramani, Shiva Prasad, and R. Krishnan, Unpublished result.