Anomalously large magnetic moment in nanocrystalline Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ thin films

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Abstract

Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ nanocrystalline thin films were deposited by pulsed laser ablation technique on amorphous quartz substrate. These films were as deposited at different substrate temperatures ($T_s$) varying from room temperature (RT) to 750 °C. The RT deposited films were ex situ annealed at annealing temperatures ($T_A$) ranging from 150 °C to 750 °C. The magnetic properties of the films were observed to depend on $T_A$ and $T_s$. A spontaneous magnetization ($4\pi M_S$) value higher than that of the bulk was observed in the as deposited film at $T_s = 750 °C$. This film also showed a higher Curie temperature than bulk. These results were explained based on the grain growth and cation distribution in thin films.

1. Introduction

Existing research carried out on ferrite thin films has yielded notable results at the basic and application level. It is now firmly established that in physical vapor deposited ferrite thin films, the magnetization ‘$M$’ an intrinsic parameter in the bulk, transforms to a processes dependent extrinsic parameter [1–3]. This aspect has led to several basic studies [6–8]. Reproducible deposition of these ferrite thin films with predictable properties has then led to evaluating these thin films for applications in spintronics [9, 10], field controlled devices [11, 12] and composite multiferroic magnetoelectric devices [13–15]. Since ‘$M$’ is a fundamental determining property, specific applications can result through control of it. In the case of high frequency applications, along with $M$, it is the dielectric properties which also determine the usefulness [16, 17].

In the present study we discuss the evaluation of ‘$M$’ in Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ pulsed laser deposited (PLD) thin films resulting from thermal treatment experiments. This system has interesting feature from the stand point of magnetization and is a solid solution of CoFe$_2$O$_4$ and ZnFe$_2$O$_4$. In thin film form, these two binary ferrites attain a magnetization value much higher than its bulk value under vastly different processing conditions [1, 2]. In Co ferrite thin films, higher than bulk spontaneous magnetization ($4\pi M_S$) was observed when films were deposited at RT and ex situ annealed at 750 °C [1]. In this paper we present a study of Zn rich Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ thin films prepared by PLD with an aim to see if higher than the bulk magnetic moment can be obtained even in these films under specific process conditions.

2. Experimental details

Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ thin films were PLD onto fused quartz substrate using the third harmonic (355 nm) of Nd:YAG laser at a 10 Hz repetition rate and 5–6 ns pulse width. Laboratory synthesized single phase Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ target, prepared by solid state reaction, was used for the thin film deposition. A laser beam energy density of 2.5 J cm$^{-2}$ was used to ablate the target, placed at a distance of 4.5 cm from the substrate. The PLD chamber was evacuated to a base pressure of 4.6 × 10$^{-6}$ mbar using turbo molecular pump prior to the deposition. The ferrite thin films were deposited in O$_2$ atmosphere at a pressure of 0.16 mbar at various substrate temperatures.
(T_S) ranging from RT to 750 °C. The RT deposited films were also ex situ annealed in air at a temperature (T_A) ranging from 150 °C to 750 °C for 2 h. All the films were deposited for a duration of 15 min.

Structural properties of the thin films were carried out using a PANalytical X’Pert PRO x-ray diffractometer (XRD) using CuKα radiation and field emission gun transmission electron microscope (300 kV, Tecnai G2, F30). The magnetic properties of the films were studied at 10 and 300 K using a Quantum Design vibrating sample magnetometer attached to a physical property measurement system in a magnetic field up to 50 kOe applied in the plane of the film. The diamagnetic contribution of the substrate was removed for arriving at the magnetization data of the thin film. The spontaneous magnetization (4πM_S) of the films was obtained by fitting the high field part of M–H loops to the zero magnetic fields as the loops do not saturate completely. The thicknesses of the films deposited at various T_S were measured in the cross section mode, using field emission gun scanning electron microscope (JEOL JSM-7600F) and was found to (105 ± 8) nm. The thickness of the films did not change within experimental errors when the films are annealed at temperature up to 750 °C.

3. Results

Figure 1 (a) shows the XRD pattern the Co_{0.3}Zn_{0.7}Fe_{2}O_{4} as deposited thin films at various T_S. Figure 1 (b), on the other hand shows the XRD patterns for the films deposited at RT but ex situ annealed at various temperatures. Well defined XRD peaks are observed in the case of films when T_S and T_A are ≥ 450 °C. For other films, one can see a broad hump in XRD pattern a 2θ value where (311), the highest intensity XRD peak of spinel, would appear. We also note from the figure that all the observed peaks could be indexed to the single spinel phase Co–Zn ferrite (Joint Committee on Powder Diffraction Standards file no: 00-022-1012). The peak widths become narrower with the increase in T_S or T_A indicating an increase in average grain size of the films. We estimated the grain size of the films using Scherrer’s formula [18].

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where D is the grain size, \( \lambda \) is wavelength of the x-ray, \( \beta \) is full width at half maximum of x-ray diffraction peak in radians and \( \theta \) is Bragg angle. The grain size values obtained from XRD were corrected for the instrumental broadening, using a standard Silicon disc [19]. The calculated grain size was found to increase from ~27 to 36 nm for the as deposited films with the increase in T_S from 450 °C to 750 °C. In case of annealed films, it was found to increase from ~23 to ~33 nm with increase in T_A from 550 °C to 750 °C.

The microstructure of the as deposited Co_{0.3}Zn_{0.7}Fe_{2}O_{4} thin films at RT and at T_S = 650 °C was investigated by Transmission electron microscopy (TEM). The TEM images of RT and 650 °C as deposited films are shown in figures 2 (a) and (b) respectively. We observed diffraction rings in TEM image, as seen from figure 2 (a) (top left inset). The observed diffraction rings could be indexed to the spinel phase of ferrite. This film is crystalline but with small grain size. The as deposited film at 650 °C shows discontinuous rings along with spots indicating the presence of larger grains in comparison with as deposited films at RT. The top right inset in the figure 2 shows the corresponding grain size distribution. The grains are observed to be in the range of 4–9 nm size with an average

![Figure 1. XRD pattern of Co_{0.3}Zn_{0.7}Fe_{2}O_{4}. (a) Films deposited at different T_S. (b) RT deposited films annealed at various temperatures.](image-url)
grain size 6 nm for the RT deposited film. But in case of the 650 °C deposited film most of the grains are in the range of 20–50 nm size with the average grain size 33 nm. This average grain size is comparable to the calculated grain size, using Scherrer’s formula (∼34 nm).

Figure 3(a) shows the 10 K M–H loops of the as deposited Co0.3Zn0.7Fe2O4 thick films at RT, 450 °C and 750 °C. As seen from the figure, the RT deposited film does not show any hysteresis loop. For the film deposited at 450 °C and 750 °C, a clear M–H loop is seen. However, these films do not completely saturate and a field dependence of M is seen even at 50 K. Such a non-saturation in M–H loops was also observed in many other nano-crystalline materials and is ascribed to the presence of poorly magnetized grain surface [2, 20, 21]. In our film which have a large Zn concentration, non-saturation is also caused by canting of magnetic moment on B-site. This canting leads to a non-saturation of loop even in bulk materials [22]. Figure 3(b) shows the 10 K M–H loops for RT deposited films annealed at T_A = 450 °C and 750 °C. We note from figure 3(b) that annealed films also show a clear M–H loops.

The 4πM_s values of RT deposited annealed films at 10 K is ∼2.87 kG for T_A = 450 °C and is 5.75 kG for T_A = 750 °C. These 4πM_s values are lower than those of the films deposited at T_S = 450 °C (∼3.75 kG) and T_S = 750 °C (∼7.30 kG).

Figure 4(a) shows the 4πM_s of the films at 10 and 300 K as a function of T_S. The 4πM_s values measured at 10 K increases as the T_S increase and is larger than the bulk value (∼6.24 kG shown by horizontal line in the figure) at T_S = 750 °C. The values of 4πM_s at 300 K show a similar trend, as at 10 K. At 300 K, the 4πM_s value is higher than the bulk value (∼1.8 kG shown by a horizontal line in the figure) above T_S = 450 °C. It is apparent from this data that the magnetic moment and the Curie temperature of the thin film can be significantly higher than the bulk values.
We observed a monotonous increase of $4\pi M_S$ in Co$_0.3$Zn$_{0.7}$Fe$_2$O$_4$ thin films including that of pure Co ferrite [1–3, 5, 23–25]. This increase in $4\pi M_S$ is ascribed to an increase of average grain size with the increase in $T_S$ or $T_A$. In the film with lower grain sizes, the surface to volume ratio is larger [26]. As the material at the surface of the grain is expected to be poorly magnetized, a film with lower average grain size yields a lower value of $4\pi M_S$. The poorly magnetized grain boundary region also results in non-saturation of $M–H$ loops as was discussed earlier. In the case of pure Zn ferrite thin films, on the other hand, the $4\pi M_S$ behaves differently as a function of $T_S$ and $T_A$ [2]. In these films, $4\pi M_S$ is known to increase with increase in either $T_S$ or $T_A$, but only up to ~350 °C, beyond which the $4\pi M_S$ decreases with increase in temperature.

Magnetism in a spinel arises due to the super exchange mechanism [27]. Bulk Zn ferrite is a normal spinel where nonmagnetic Zn$^{2+}$ ions occupy A-site while the magnetic Fe$^{3+}$ ions reside on B-site. This results in the absence of dominant $J_{A-B}$ exchange interaction between A and B sites. Hence the bulk Zn ferrite is paramagnetic at RT [2, 27]. However, ferrimagnetic order has been observed in thin films of Zn ferrite due to the presence of some Fe$^{3+}$ ions on A-site, with an equal number of Zn$^{2+}$ ions on B-site, resulting in the $J_{A-B}$ exchange interaction [2]. This change in cation distribution is believed to be due to the rapid cooling of the plasma while deposition [6, 28].

The initial increase of $4\pi M_S$ observed in Zn ferrite in the range of $T_A = 350$ °C may be attributed to an increase in grain size similar to other ferrite films [1–3, 5, 23–25]. However, the decrease in $4\pi M_S$ at higher $T_S$ or $T_A$ is due to the migration of Zn$^{2+}$ and Fe$^{3+}$ cations back to their original sites [2, 29]. This redistribution of cations also results in a monotonous decrease in the value of exchange stiffness constant with the increase in $T_S$ or $T_A$, causing a decrease in Curie temperature ($T_C$) [29].

The variation of $4\pi M_S$ in our films is similar to the one observed in the case of pure Co ferrite films with increase in $T_S$ or $T_A$ [1] and is different from the one seen in Zn ferrite films [2]. This implies that the cation distribution in our film is quite stable over a range of grain sizes and over higher temperature processing. In order to get an insight to the cation distribution of our thin films, we carried out magnetic measurement on the bulk Co$_0.3$Zn$_{0.7}$Fe$_2$O$_4$ sample. The $M–H$ loop at 300 K is shown in figure 5(a). The value of $4\pi M_S$ for bulk at this temperature found to be ~1.80 kG. The $4\pi M_S$ of the bulk at 10 K (not shown in the figure) was found to be ~6.24 kG. We thus note that there is a 71% drop in the value of $4\pi M_S$ between 10 and 300 K in the bulk. In comparison of this, the $4\pi M_S$ of the film at 10 K with $T_S = 750$ °C (~7.30 kG) was found to drop only by 35% between 10 and 300 K (figure 4(a)). This indicates that for our film, not only the magnetic moment but $T_C$ is also higher than bulk.
In this paper, we present a study of the magnetic properties of PLD Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ nanocrystalline thin films.

### Conclusion

In order to further confirm if $T_C$ of the film is indeed higher than the bulk in the $T_S = 750$ °C film, we measured magnetization of this film and that of bulk as a function of temperature (M–T) in an applied field of 1 kOe [30]. Figure 5(b) shows the $dM/dT$ versus $T$ curves of these materials. As seen from the figure the $T_C$ of the bulk sample is $\sim$265 K. Whereas the absence of minima in thin film until 350 K indicate that the $T_C$ of film is higher than 350 K.

The above results clearly imply that in thin films the cation distribution is different from the bulk. In order to confirm that the changed cation distribution in the films has resulted from the quenching process during deposition, we carried out another experiment. The bulk Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ prepared by us was heated to 1350 °C and then quenched (QN) to liquid N$_2$ temperature. The magnetic properties of such a sample was measured and has also been shown in figures 5(a) and (b). We can see that the 4$\pi$$M_S$ and $T_C$ of the QN bulk sample is $\sim$2.98 kG and $\sim$328 K respectively which is in between that of the bulk and the film deposited at $T_S = 750$ °C. This experiment does show that the quenching causes a change in the cation distribution even in the case of a bulk sample which results in increase of magnetization and the $T_C$.

In bulk Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ ferrite, the expected cation distribution is $(\text{Zn}_{0.7}\text{Fe}_{0.3})\{\text{Co}_{0.3}\text{Fe}_{1.7}\}$, where the cations within small bracket refer to the ions present on A site and the ones within square bracket represent those present on B site [31]. Using the magnetic moments of Zn$^{2+}$ as zero, Co$^{2+}$ as 3 $\mu_B$ and Fe$^{3+}$ as 5 $\mu_B$, the net magnetic moment of Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ using Neel’s collinear model works out to be 7.90 $\mu_B$. On other hand, the measured value of spontaneous moment at 10 K for this sample is only 4.15 $\mu_B$. Even in a field of 70 kOe, the magnetic moment found in bulk is 5.18 $\mu_B$ [31]. These values are significantly lower than the calculated values. This decrease in magnetic moment is known to be due to the failure of linear model in Zn rich Co$_{1-x}$Zn$_x$Fe$_2$O$_4$. As the Zn$^{2+}$ concentration increases on A site, the $J_{A-B}$ interaction weakens and the antiferromagnetic $J_{B-B}$ interaction between the magnetic ions on B site results into a canted structure of magnetic moments. This canting not only reduce the net magnetic moment but also causes non-saturation of loop [22].

As discussed earlier the origin of magnetic moment in pure Zn ferrite is related to the fact that part of the Zn$^{2+}$ ions occupy B-site in addition to A site which results in an overall increase in the $J_{A-B}$ exchange interaction. If we assume that in the as deposited Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ thin films, Zn$^{2+}$ is present on both A- and B-sites, one could get an enhanced $J_{A-B}$ interaction. This would cause not only an increase in the Curie temperature of our samples but would also result in a larger magnetic moment due to reduced canting on B-site. In the light of this we could understand our experimental data.

### Figure 5

(a) The $M-H$ loops at 300 K of bulk and QN bulk Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ along with the thin film deposited at $T_S = 750$ °C. (b) $dM/dT$ versus $T$ curves for bulk, QN bulk Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ and film with $T_S = 750$ °C.

5. Conclusion

In this paper, we present a study of the magnetic properties of PLD Co$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ nanocrystalline thin films deposited at various $T_S$ and on the RT deposited films annealed at various $T_A$. It was found that the spontaneous magnetization of the films increases with $T_S$ and $T_A$. The magnetization higher than bulk was observed in the as deposited films at a $T_S = 750$ °C. We also found that the Curie temperature of this film is higher than the bulk. These results could be understood if we assume that like pure Zn ferrite films, Zn$^{2+}$ ion is present both on A site and B sites, resulting in an overall decrease in the canting of magnetic ions on B site.
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