Magnetic ordering in amorphous films of $BiFeO_3$-$ZnFe_2O_4$

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We report the observation of a ferromagnetic behavior with a uniaxial anisotropy through magnetization and ferromagnetic resonance measurements on rf sputtered amorphous compounds of $(1-2x)BiFeO_3$-$xZnFe_2O_4$ for $x=0$ to 0.5. The as-deposited amorphous films are paramagnets for all x values. The samples develop a ferromagnetic moment and a uniaxial anisotropy on annealing in air at temperatures $T_a=400-775$ °C. The room-temperature magnetization increases with T_a and shows a maximum for $T_a=500-700$ °C, depending on the x value. Further increase in T_a results in the crystallization of phases such as $24Bi_2O_3\cdot ZnO$, $BiFeO_3$, and α-Fe_2O_3 in the sample and is accompanied by a decrease in the magnetization. The Curie temperature for the films is about 600 K and is lower than the crystallization temperature. We propose that the observed magnetic moment in the system is due to the formation of ferrimagnetic clusters.

In crystalline $BiFeO_3$, the negative superexchange interaction between trivalent iron ions leads to an antiferromagnetic ordering of spins with a Néel temperature of 645 K. In the presence of crystalline disorder, one expects a random antiferromagnetic ordering in $BiFeO_3$ and the compound is reported to show a paramagnetic behavior at room temperature.[1] However, several investigators have reported a ferromagnetic or a ferromagnet-like character in rapidly quenched amorphous (a-)$BiFeO_3$ substituted with Fe_2O_3 and one of the following oxides: ZnO, CuO, CaO, and Li_2O.[2–5] The key results of these investigations are (i) the samples prepared by rapid quenching techniques are amorphous for a relatively narrow range of substitutions, (ii) the room-temperature magnetization varies from a maximum of 17 emu/g for samples with ZnO to a minimum of about 5 emu/g for samples containing Li_2O, (iii) room-temperature Mössbauer studies indicate the coexistence of paramagnetic and ferromagnetic phases,[3] and (iv) it is suggested that the ferromagnetic phase exists as less disordered clusters or microcrystals.

This study is concerned with the observation of a ferromagnet-like behavior in a-$[(1-2x)BiFeO_3$-$xZnFe_2O_4]$ prepared by rf sputtering techniques. The report also constitutes an observation of ferromagnetic resonance (FMR) absorption in such amorphous insulators. The FMR measurements reveal the presence of an uniaxial anisotropy field perpendicular to the sample plane. One also observes a strong temperature dependence of the gyromagnetic ratio. It is proposed that ferrimagnetic clusters in the samples give rise to the observed ferromagnetic character.

The as-sputtered films obtained in the present work are paramagnetic at room temperature and our studies do not show any evidence for magnetically ordered phases that are suggested to exist in samples prepared by rapid quenching techniques. However, the samples develop a large magnetic moment when annealed in air at temperature $T_a=400-775$ °C. For annealed samples, the room-temperature saturation induction $4\pi M$ increases with T_a and shows a maximum for a specific T_a value which depends on x. With further increase in T_a, crystalline phases are precipitated in the film and one observes a decrease in $4\pi M$. The crystallization temperatures are found to be higher than the Curie temperatures. The results of these studies are presented below.

Films of a-$[(1-2x)BiFeO_3$-$xZnFe_2O_4]$ for $x=0-0.5$ were prepared by the rf sputtering technique. With this technique it is rather easy to prepare amorphous films over a wide substitution range, from $x=0$ to 0.5, whereas a partial crystallization is reported for $x>0.2$ in samples prepared by rapid quenching.[2] Polycrystalline sintered sputtering targets for each composition were made from powders of α-Fe_2O_3, Bi_2O_3, and ZnO. Further details on target preparations are provided elsewhere.[6] The targets were attached to a sputtering gun (Kurt Lesker, Torus 2C) and the system was evacuated to a base pressure of 10^{-5} Torr. Samples were deposited onto unheated Corning 7059 glass substrates in 50% oxygen and 50% argon atmospheres at a pressure of 1 or 25 mTorr. The rf power was 150 W and the deposition was carried out for 30–120 min. The film thickness measured with a stylus profilometer varied from 0.4 to 1 μm depending on the target composition and sputtering pressure. The sputtering rate was about 100 Å/min. For the analysis of film composition, energy dispersive x-ray spectroscopy techniques were used. The films were rich in Fe (2%) and Bi (10–15 %), but deficient in Zn. A maximum deficiency of 25% in Zn concentration was estimated for films with low x values. In the discussion to follow, the films are designated by the target composition. The amorphous nature of the as-deposited films were verified with x-ray-diffraction measurements.

Magnetization measurements were performed with a Faraday balance with Lewis gradient coils. As-deposited films show a room-temperature paramagnetic susceptibility of about 2×10^{-5} emu/g. There was no systematic compositional dependence of the susceptibility. The sam-

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ples were then annealed in air for 60 min at temperatures T_a ranging from 100 to 775 °C. The annealed sample with $x=0$, $BiFeO_3$, remained paramagnetic at room temperature for all T_a values. Samples with $x>0$ develop a spontaneous magnetic moment when annealed at temperatures above 400 °C. Figure 1 shows the T_a dependence of the room-temperature saturation induction $4\pi M$ for a representative sample. The data are for a sample with $x=0.125$. A static magnetic field of 5 kOe was applied parallel to the film plane. The important features of the data are (i) there is no noticeable change in $4\pi M$ for $T_a<450$ °C, (ii) the magnetization increases for higher annealing temperatures and shows a maximum for $T_a=500$ °C, (iii) one observes a decrease in $4\pi M$ when T_a is increased further, and (iv) a sharp increase in the magnetization is evident for the film annealed at 775 °C.

The effects of annealing on the crystal structure of the samples were monitored with x-ray-diffraction measurements. Figure 2 shows such data for a series of annealing temperatures for the sample with $x=0.125$. The diffraction pattern are for (i) the unannealed sample, (ii) films annealed at temperatures just below and above the T_a value of 500 °C corresponding to the maximum in the magnetization in Fig. 1, and (iii) the sample annealed at 775 °C at which $4\pi M$ shows an abrupt increase. It is clear from the data that as-deposited samples are amorphous. One begins to see peaks corresponding to the crystalline $24Bi_2O_3\cdot ZnO$ phase for $T_a=475$ °C. A substantial increase in the intensity of such peaks is observed for $T_a=525$ °C. At higher T_a values, additional phases such as $Bi_2Fe_4O_9$ and α-Fe_2O_3 are precipitated in the sample. For $T_a=775$ °C, one observes peaks corresponding to 24 $Bi_2O_3\cdot ZnO$, $BiFeO_3$, and γ-Fe_2O_3 in the film.

Now we discuss the origin of the observed ferromagnetic character in annealed samples. The behavior can-

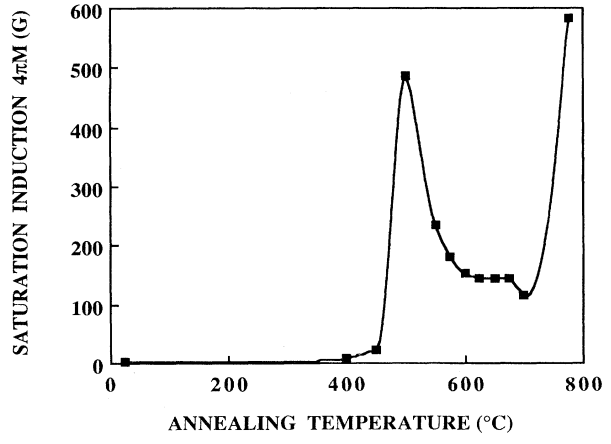

FIG. 1. Room-temperature saturation induction $4\pi M$ vs annealing temperature T_a data for a sample of rf-sputtered amorphous $(1-2x)BiFeO_3$-$xZnFe_2O_4$ with $x=0.125$ for an in-plane static field of 5 kOe. The sample was sputtered in 50% oxygen and 50% argon atmosphere and the annealing was performed at T_a in air for 60 min.

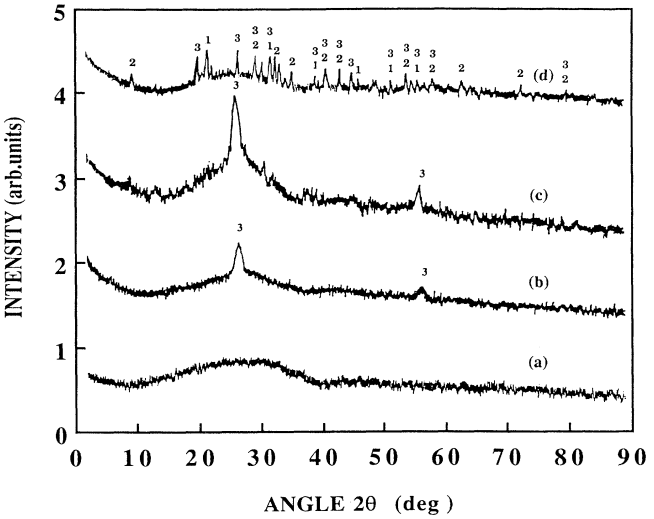

FIG. 2. X-ray-diffraction pattern at room temperature for (a) as-sputtered films of $0.75BiFeO_3$-$0.125ZnFe_2O_4$ and for samples annealed at (b) 475 °C, (c) 525 °C, and (d) 775 °C. The high-temperature annealing leads to the precipitation of crystalline (1) $BiFeO_3$, (2) γ-Fe_2O_3, and (3) 24 $Bi_2O_3\cdot ZnO$ phases.

not be attributed to crystalline magnetic phases since the data in Fig. 2 do not show the presence of such phases for T_a values corresponding to the region of a relatively large magnetic moment in Fig. 1. Next we consider the possible presence of magnetically ordered clusters or microcrystals in the sample. Several unsuccessful attempts were made in recent years to probe the existence, nature, and composition of such clusters in a-$BiFeO_3$ containing nonmagnetic ABO_3-type compounds or $CuFe_2O_4$ using a variety of techniques including reflection high-energy electron diffraction and transmission electron microscopy (TEM).[1,3] The failure was attributed to difficulties such as the crystallization of amorphous insulators when subjected to an intense electron beam in TEM techniques. However, small-angle x-ray scattering measurements showed the presence of inhomogeneous regions in a-($BiFeO_3$-$CuFe_2O_4$) compounds and these regions were suggested to be clusters of the ferrimagnetic compound $CuFe_2O_4$.[3] We propose that similar ferrimagnetic clusters result in a ferromagnetic behavior in the present system and their presence is evident from results of magnetization measurements which are described later.

The data in Figs. 1 and 2 do provide some indirect evidence for the role of zinc in the formation of magnetically ordered clusters in the sample. First, as-sputtered and annealed samples that do not contain any zinc, i.e., pure $BiFeO_3$, are paramagnetic. Second, the loss of Zn from the amorphous lattice in the form of crystalline 24 $Bi_2O_3\cdot ZnO$, seen as an increase in the intensity of the crystalline peak for $T_a=525$ °C in Fig. 2, is accompanied by a decrease in the magnetization as shown in Fig. 1. One also notices a further decrease in the magnetization at higher T_a values due to the loss of Fe from the amorphous lattice when crystalline antiferromagnetic phases

α-Fe_2O_3 and $BiFeO_3$ are formed. Finally, the increase in $4\pi M$ for $T_a = 775\,^\circ C$ is due to the formation of γ-Fe_2O_3 which is a ferrimagnet with a Curie temperature of 675 °C.

The effects of Zn substitution on the magnetic properties of a-$BiFeO_3$ was further investigated by measuring the T_a dependence of $4\pi M$ for a series of samples with $x = 0.125$–0.5. Such data at room temperature for $H = 5$ kOe applied parallel to the film plane are shown in Fig. 3. Since the amount of iron present in the samples is independent of x, the figure essentially shows the dependence of the sample magnetization on the concentration of nonmagnetic Zn. Consider first the variation of $4\pi M$ with T_a. With the exception of the sample with $x = 0.5$, which do not show noticeable variation in the magnetization, one observes an initial increase in $4\pi M$ with T_a and is followed by a sharp or broad maximum. In general, the annealing temperature corresponding to the maximum in saturation induction, $4\pi M_{max}$, shows an increase with x. The increase in $4\pi M$ at $T_a = 750$–$775\,^\circ C$ is due to the formation of γ-Fe_2O_3 in the films. Consider now the variation of $4\pi M$ with x. As the concentration of Zn is increased, an overall increase in $4\pi M_{max}$ is observed in Fig. 3 for $x \leq 0.3$. The largest $4\pi M$ value of 1.8 kG is obtained for $x = 0.3$. A drastic reduction in the magnetization occurs for higher x values.

The Curie temperature T_c for the films were determined from the temperature dependence of $4\pi M$. Such data for samples with various x values and annealed at 650–700 °C are shown in Fig. 4. The measured T_c is about 600 ± 10 K. The absence of any systematic variation in T_c with x indicates that high-temperature annealing results essentially in the formation of a specific type of magnetically ordered clusters in all Zn-substituted samples. It is obvious from the T_c value that the observed moment cannot be due to microcrystalline $Bi_3Fe_5O_{12}$, γ-Fe_2O_3, or Fe_3O_4. Such phases have T_c values either higher or lower than the Curie temperature for the amorphous films. Figure 5 shows the magnetization per formula unit, n, at 80 K versus the concentration of zinc x. The n values, expressed in Bohr magneton, were estimated from data as in Fig. 4. One notices an increase in n with x for $x \leq 0.3$ in Fig. 5 and the magnetization decreases for higher x values. A somewhat similar dependence of n on the amount of zinc substitution is observed in crystalline ferrimagnets such as $MnFe_2O_4$, $NiFe_2O_4$, and $MgFe_2O_4$ and is due to a canted spin structure for high Zn concentrations.[7] The expected magnetic moment per formula unit in a-$[(1-2x)BiFeO_3$-$xZnFe_2O_4]$ for a parallel alignment of Fe^{3+} ions is $5\mu_B$ at 0 K, independent of the x values, and is a factor 5–10 larger than the measured n values. Therefore, the relatively small magnetization can be attributed to clusters consisting of ferrimagnetically coupled iron ions. For example, since n also corresponds to the

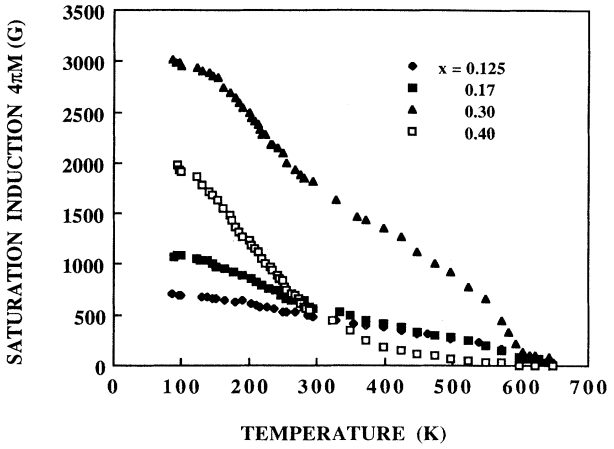

FIG. 4. Saturation induction vs temperature data for samples of $(1-2x)BiFeO_3$-$xZnFe_2O_4$ annealed at 650–700 °C.

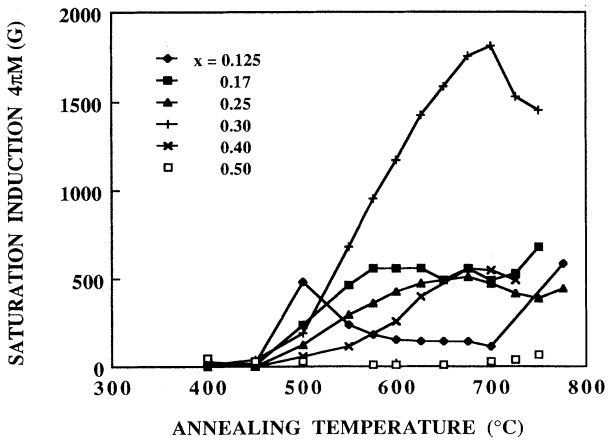

FIG. 3. Data as in Fig. 1 for samples of $(1-2x)BiFeO_3$-$xZnFe_2O_4$.

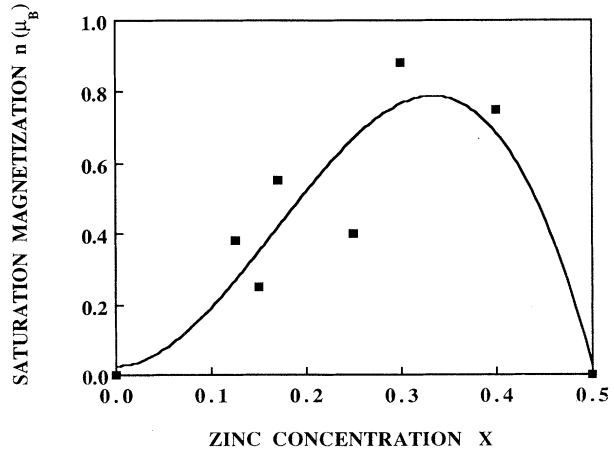

FIG. 5. Saturation magnetization n per formula unit at 80 K as a function of zinc concentration x for rf-sputtered films of $(1-2x)BiFeO_3$-$xZnFe_2O_4$.

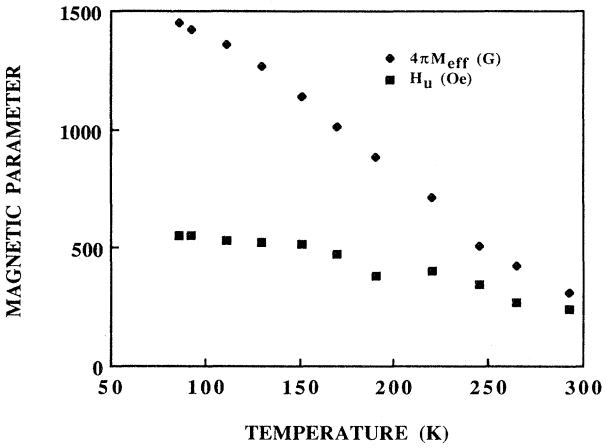

FIG. 6. Variation of the effective magnetization $4\pi M_{\text{eff}}$ with temperature obtained from ferromagnetic resonance measurements at 9.2 GHz on an annealed sample of $0.2BiFeO_3$-$0.4ZnFe_2O_4$. The perpendicular anisotropy field H_u was determined from $4\pi M_{\text{eff}}$ values and data on $4\pi M$ in Fig. 4.

average magnetic moment per iron ion, a cluster with a 2:3 spin structure will have an n value of $1\mu_B$ which is approximately equal to the moment for the sample with $x=0.3$. The fact that the Curie temperature is independent of x indicates that the dominant superexchange between magnetic ions within clusters are not significantly altered by the amount of Zn.

The presence of an uniaxial anisotropy in the amorphous samples was clearly evident from ferromagnetic resonance studies. The measurements were performed at 9.2 GHz for applied static fields parallel and perpendicular to the sample plane. Data on the resonance fields for these two configurations were used to estimate the effective saturation induction $4\pi M_{\text{eff}}=4\pi M-H_u$, where H_u is the uniaxial anisotropy field. One can then determine H_u values from FMR data on $4\pi M_{\text{eff}}$ and static magnetization results on $4\pi M$. Results of such studies for a representative sample are shown in Fig. 6. The figure shows the variation of $4\pi M_{\text{eff}}$ and H_u with temperature T for a sample with $x=0.4$. The perpendicular anisotropy fields are small so that the easy axis of magnetization is parallel to the sample plane. The data show an overall decrease in H_u with T. We also noticed a pronounced dependence of the gyromagnetic ratio γ on T. The γ value increased from 2.75 GHz/kOe at 293 K to 3.02 GHz/kOe at 80 K.

In conclusion, amorphous films of $BiFeO_3$-$ZnFe_2O_4$ show a ferromagnetic character when annealed at high temperatures. The films prepared by rf sputtering have a much higher magnetization and Curie temperature than for samples prepared by rapid quenching. The ferromagnetic behavior is attributed to ferrimagnetically ordered clusters in the material.

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