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LETTER TO THE EDITOR

High magnetization and the Faraday effect for ferrimagnetic zinc ferrite thin film

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Abstract
The magnetization and Faraday effect in the wavelength range of 350–850 nm have been measured for zinc ferrite thin film prepared by the sputtering method. X-ray diffraction analysis indicates that the thin film is single-phase $ZnFe_2O_4$, whose crystallite size evaluated from Scherrer's equation is 10 nm or so. The thin film is extremely transparent for wavelengths longer than about 600 nm, and exhibits high magnetization, i.e., 32 emu g^{-1}, at 1 T even at room temperature. The absolute value of the Faraday rotation angle is 1.0×10^4 deg cm^{-1} at a wavelength of 470 nm when an external magnetic field of 5 kOe is applied.

1. Introduction

It is well known that the stable phase of zinc ferrite ($ZnFe_2O_4$) possesses the normal spinel structure. The tetrahedral site is occupied by Zn^{2+} because there is a very strong tendency for Zn^{2+} to prefer tetrahedral coordination in oxides with the spinel-type structure. As a result, the superexchange interaction between Fe^{3+} ions at the bond angle of 90° predominantly determines the magnetic properties of $ZnFe_2O_4$. Since this superexchange interaction is negative, and the magnitude of the interaction is small because of the bond angle being 90°, $ZnFe_2O_4$ is antiferromagnetic and the Néel temperature is as low as 10 K or so. In contrast, the occupation of octahedral sites by Zn^{2+} is possible in metastable $ZnFe_2O_4$. Therefore, some of the tetrahedral sites are occupied by Fe^{3+} ions, resulting in the presence of strong superexchange interaction between Fe^{3+} ions in the tetrahedral and octahedral sites. Consequently, ferrimagnetic properties are observed for metastable $ZnFe_2O_4$.

Metastable $ZnFe_2O_4$ which exhibits high magnetization even at room temperature was first reported by Pavljukhin *et al* [1]. They applied mechanical pulverization to bulk $ZnFe_2O_4$ crystal, and revealed that magnetic order is observed at 78 K for $ZnFe_2O_4$ fine particles obtained

after mechanical activation for 20 min, as clearly indicated by sextet absorption lines in the Mössbauer spectrum split due to the hyperfine field. They also clarified that only the surface region of the fine particles of $ZnFe_2O_4$ derived by the mechanical pulverization shows magnetic ordering. By using Mössbauer spectroscopy and magnetization measurements, Chinnasamy *et al* [2] examined the crystallite size dependence of the magnetic properties for nanostructured $ZnFe_2O_4$ prepared by mechanical milling. They revealed that the magnetization at 300 K monotonically increases with decrease in size of the crystal from 90 to 11 nm. Also, fine particles of $ZnFe_2O_4$ crystal prepared by the co-precipitation method, several nanometres in size, show ferrimagnetic properties and high magnetization at room temperature [3, 4]. It was confirmed using extended x-ray absorption fine structure (EXAFS) measurements that some of the Zn^{2+} ions occupy octahedral sites [5]. It is thought that the surface region of nanocrystalline $ZnFe_2O_4$ brings about site exchange between tetrahedral Zn^{2+} and octahedral Fe^{3+} ions, and contributes to the high magnetization at room temperature. Tanaka *et al* reported that similar magnetic structure and properties are realized in rapidly quenched $ZnFe_2O_4$. They demonstrated that Zn^{2+} ions occupy octahedral as well as tetrahedral sites, on the basis of Zn K-edge EXAFS [6–8].

Such magnetic structure can be attained in $ZnFe_2O_4$ thin film deposited from the gas phase, because preparation of solids from the gas phase involves a very rapid cooling process which is preferred for the formation of random arrangements of Zn^{2+} and Fe^{3+} ions in the spinel structure. In addition, the fact that thin film generally has a large surface area is one of the advantages for the formation of metastable $ZnFe_2O_4$. In the present investigation, we utilized a sputtering method to prepare $ZnFe_2O_4$ thin film. The resultant thin film shows large magnetization even at room temperature and is extremely transparent for wavelengths longer than about 600 nm. We report that the $ZnFe_2O_4$ thin film exhibits a large Faraday effect in the visible range as well.

2. Experimental procedure

The $ZnFe_2O_4$ thin film was prepared using an rf sputtering method (ULVAC RFS-200). Reagent-grade ZnO and Fe_2O_3 were heated at 550 °C for 8 h in air to remove water, and mixed thoroughly so that the molar fractions of ZnO and Fe_2O_3 were the same as each other. The powder of the mixture of ZnO and Fe_2O_3 was compacted and used as a target for sputtering. Corning 7059 glass plate was used as a substrate. The sputtering was carried out in an O_2 atmosphere. The gas pressure was 2.7×10^{-2} Torr. The rf output power was 100 W.

X-ray diffraction analysis with Cu Kα radiation (Rigaku RINT2500) was carried out for resultant thin film to identify the crystalline phase. The size of the crystal was evaluated from the linewidth at half-maximum of the diffraction lines using Scherrer's equation. Energy dispersive x-ray fluorescence spectroscopy (EDX; Hitachi EMAX-7000) was performed to analyse the content of Zn and Fe in the resultant thin film. The thickness of the film was evaluated using a surface roughness meter (KLA Tencor, P-15).

Measurements of the magnetization were carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). The external magnetic field was applied up to 1 T. Faraday effect measurements (JASCO, Model K-250) were performed over a wavelength range of 350–850 nm. The applied magnetic field was varied from 1 to 15 kOe. The optical absorption spectrum of the thin film was measured in the visible to near-infrared region at room temperature using a spectrophotometer (Hitachi 330).

3. Results and discussion

Figure 1 shows the x-ray diffraction pattern for the thin film prepared by the sputtering method. All the diffraction lines can be assigned to spinel-type $ZnFe_2O_4$. The size of crystal estimated
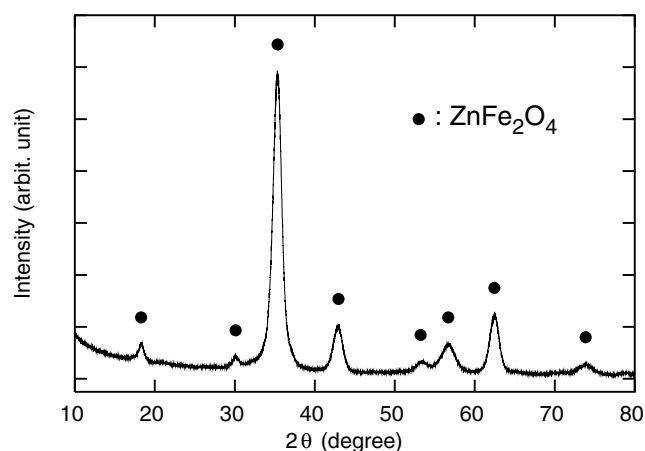
Figure 1. The x-ray diffraction pattern for thin film prepared by the sputtering method. All the diffraction lines are attributable to spinel-type $ZnFe_2O_4$.
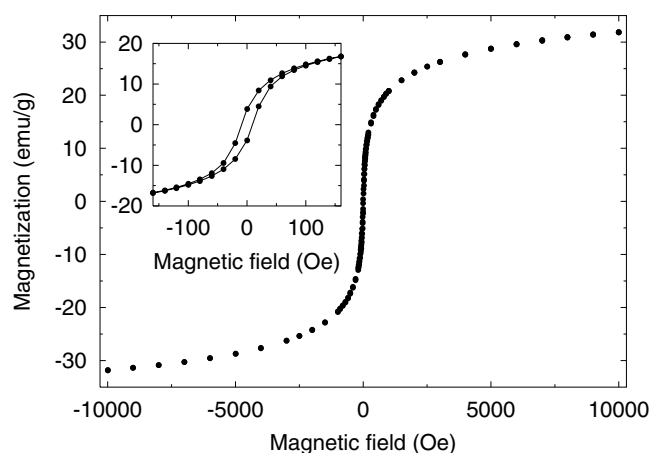

Figure 2. The dependence of the magnetization on the external magnetic field up to 1 T at room temperature for $ZnFe_2O_4$ thin film.

using Scherrer's equation is about 10 nm. The molar ratio of Zn to Fe in the resultant thin film evaluated by EDX is 1.07:2. These values are average ones evaluated on the basis of ten repetitions of the measurements. Although it is suggested that the present thin film is composed of nanocrystalline $ZnFe_2O_4$ whose composition is almost stoichiometric, the experimental value of the Zn to Fe molar ratio may indicate that a small amount of excess Zn is present in the specimen. However, the presence of Fe^{2+} can be ruled out because optical absorption due to Fe^{2+} was not observed, as described below.

Room temperature magnetization as a function of external magnetic field is shown in figure 2. The magnetization tends to be saturated at about 0.1 T and reaches 32 emu g^{-1} at 1 T. The hysteresis loop is clearly observed at around 0 T. These facts indicate that the $ZnFe_2O_4$ thin film exhibits ferrimagnetic behaviour at room temperature. It is thought that the thin film is composed of $ZnFe_2O_4$ possessing the metastable structure; four-coordinated as well as six-coordinated Fe^{3+} ions are present in the crystal structure, leading to strong superexchange interactions between Fe^{3+} ions in the tetrahedral and octahedral sites. As mentioned above,
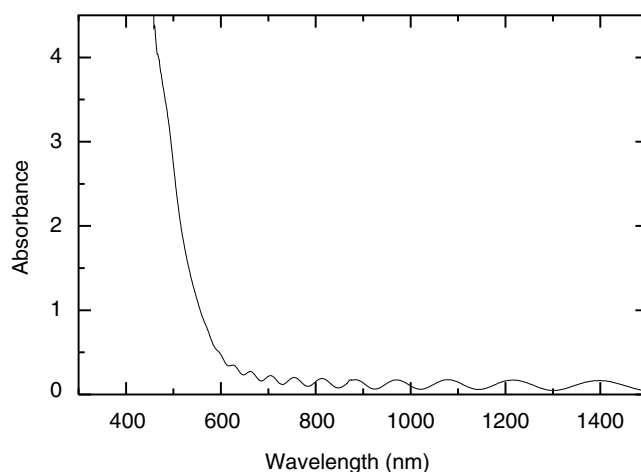
Figure 3. The optical absorption spectrum of $ZnFe_2O_4$ thin film deposited on glass substrate.

only the surface region of the nanocrystalline $ZnFe_2O_4$ derived by mechanical pulverization and the co-precipitation brings about the unusual high magnetization at room temperature [1, 4]. It is unclear whether the magnetic ordering giving rise to the high magnetization is restricted to within the surface region or is spread over the whole of the bulk crystal for the present thin film composed of nanocrystalline $ZnFe_2O_4$. We speculate that the random distribution of Fe^{3+} ions may be attained even inside the nanocrystals, as well as in the surface, since a rapid cooling process such as sputtering was used for the preparation of the thin film.

The magnetic ordering leading to the high magnetization at room temperature is possibly canted ferrimagnetism, but more detailed information is required to confirm this speculation. It should be noted that the spins at B sites are canted at low temperatures in $ZnFe_2O_4$ nanoparticles embedded in ZnO matrix [10]. A similar magnetic structure may be included in the present $ZnFe_2O_4$ thin film. The magnetization at 5 K is about 90 emu g^{-1} [9], indicating that the cation distribution is approximately represented by the formula $(Zn_{0.4}Fe_{0.6})_A(Zn_{0.6}Fe_{1.4})_BO_4$, where A and B denote the A- and B-sites, respectively, if it is assumed that the superexchange interaction between A- and B-sites is dominant. The temperature dependence of the magnetization reveals that the thin film shows a transition from paramagnetism to cluster spin glass at around 325 K when the external field of 20 Oe is applied [9]. The Curie temperature for the ferrimagnetic ordering is thought to be higher than 325 K, although it has not been measured. Details of the magnetic properties of the $ZnFe_2O_4$ thin film, such as the temperature dependence of the magnetization, the difference between the field-cooling and zero-field-cooling behaviours, the frequency dependence of the ac magnetization, will be reported elsewhere [9].

The optical absorption spectrum of the $ZnFe_2O_4$ thin film is illustrated in figure 3. The thin film is extremely transparent for wavelengths longer than about 600 nm, while intense absorption is observed in the shorter-wavelength region. There are no absorption bands in the infrared region (at around 1000 nm), suggesting that Fe^{2+} ions are not present. Figure 4 depicts the dependence of the Faraday rotation angle on wavelength for the $ZnFe_2O_4$ thin film. The variation of the rotation angle obtained at external magnetic fields of 1, 5, and 15 kOe is shown. A minimum of Faraday rotation angle is observed at around 470 and 530 nm. In particular, at the former wavelength, the absolute value of the Faraday rotation angle is rather large. Considering that the thickness of the thin film is estimated to be 1.06 μm, the absolute
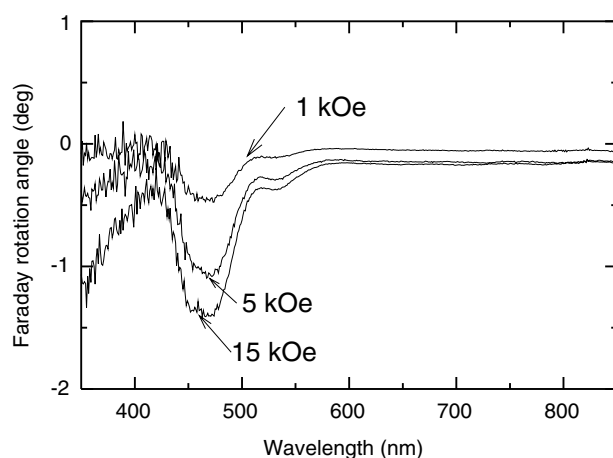
Figure 4. The variation of the Faraday rotation angle with wavelength for $ZnFe_2O_4$ thin film. The spectra obtained at external magnetic fields of 1, 5, and 15 kOe are illustrated.

value of the Faraday rotation angle of the $ZnFe_2O_4$ thin film is 1.0×10^4 deg cm^{-1} at 5 kOe and 1.3×10^4 deg cm^{-1} at 15 kOe, when the wavelength is 470 nm. Thus far, the Faraday effect has been examined for many ferrimagnetic ferrite compounds. For instance, the Faraday rotation angle of Fe_3O_4 thin film was reported to be 3.9×10^4 deg cm^{-1} at 632.8 nm [11]. $NiFe_2O_4$ and $CoFe_2O_4$ films show Faraday rotation angles about two times smaller than that of Fe_3O_4 [11, 12]. For garnet-type $Gd_{3-x}Bi_xFe_5O_{12}$, the absolute value of the Faraday rotation angle at 520 nm changes from about 5×10^3 to 1.2×10^5 deg cm^{-1} as x varies from 0 to 1.4 [13]. The magnetization of the $Gd_{3-x}Bi_xFe_5O_{12}$ was reported to be saturated at an external magnetic field of about 4 kOe. For $BaFe_{10.42}Co_{0.78}Ti_{0.8}O_{19}$ film, the Faraday rotation angle is 7.5×10^3 deg cm^{-1} when the wavelength is 780 nm [14]. The present $ZnFe_2O_4$ thin film exhibits a Faraday rotation angle comparable to those of the above-mentioned ferrites. We speculate that the Faraday rotation at 470 and 530 nm as well as the intense absorption for wavelengths shorter than about 600 nm are ascribed to the $3d^5 \rightarrow 3d^44s$ transitions of Fe^{3+} ions as demonstrated for $LiFe_5O_8$ (lithium ferrite) and $MgFe_2O_4$ (magnesium ferrite) [15]. In this transition, an electron is excited from the localized $3d^5$ state of Fe^{3+} to the conduction band mainly composed of the 4s orbitals of Fe^{3+}. It should be noted that the optical absorption spectrum of the $ZnFe_2O_4$ thin film shown in figure 3 is very similar to those observed for $LiFe_5O_8$ and $MgFe_2O_4$ [15] from the viewpoint that the optical absorption starts to increase when the photon energy is beyond around 2 eV (620 nm). We believe that the electronic structure of the $ZnFe_2O_4$ thin film is almost identical with that of $MgFe_2O_4$ because of the similarity in arrangement of cations between them.

4. Conclusions

We were able to prepare ferrimagnetic $ZnFe_2O_4$ thin film using the rf sputtering method. The resultant film possesses magnetization of 32 emu g^{-1} at 1 T even at room temperature, and is extremely transparent for wavelengths longer than about 600 nm. The absolute value of the Faraday rotation angle is 1.0×10^4 deg cm^{-1} at 470 nm under the external magnetic field of 5 kOe.

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