

# Structural and Magnetic Properties of CdFe<sub>2</sub>O<sub>4</sub> Thin Films Fabricated via Sputtering Method

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**CdFe<sub>2</sub>O<sub>4</sub> thin films have been prepared by a sputtering method, and their structural and magnetic properties have been examined. As-deposited film shows magnetic transition like that of cluster-spin glass or superspin glass, and possesses large magnetization even at room temperature. The magnetic behaviors are partly attributed to crystal structure with a random distribution of cations in CdFe<sub>2</sub>O<sub>4</sub> nanocrystals. Annealing of the as-deposited film at 200 °C leads to an increase in magnetization while the magnetization is decreased when the film is annealed at 400 °C. The effect of annealing on the magnetic properties has been discussed in terms of the change of microstructure as well as chemical structure of the thin films.**

**Index Terms**—Ferrite films, magnetic susceptibility.

## I. INTRODUCTION

**C**ADMIUM FERRITE (CdFe<sub>2</sub>O<sub>4</sub>) possesses a normal spinel structure as its stable phase, where Cd<sup>2+</sup> and Fe<sup>3+</sup> ions occupy tetrahedral sites (A sites) and octahedral sites (B sites), respectively, in a face-centered-cubic close packing of oxide ions. Fe<sup>3+</sup> ions in the B sites form a pyrochlore lattice. Hence, strong magnetic frustration based on the geometry is observed for the three-dimensional network of corner-sharing tetrahedra like the pyrochlore lattice when its vertices are occupied by spins with antiferromagnetic interaction among nearest neighbors. Although it is well known that the normal spinel type of CdFe<sub>2</sub>O<sub>4</sub> behaves like an antiferromagnet with a Néel temperature of 13 K, strictly speaking, spin freezing occurs with only short-range correlation at 13 K and no long-range order is observed down to 0.1 K due to the geometrical frustration, as revealed by Kamazawa *et al.* using neutron scattering experiments [1].

The stable phase of zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>) also has a normal spinel structure. Like CdFe<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub> shows the geometrical frustration which prevents magnetic moments of Fe<sup>3+</sup> ions in the B sites from long-range order down to 1.5 K [2]. However, nonzero magnetization and high magnetic transition temperature can be observed for ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles fabricated by co-precipitation method [3] and high energy ball-milling [4] and for ZnFe<sub>2</sub>O<sub>4</sub> thin films derived by gas-phase deposition methods such as sputtering [5], [6] and pulsed laser ablation [7]. These non-equilibrium processes yield a metastable phase of ZnFe<sub>2</sub>O<sub>4</sub>. The large magnetization and high magnetic transition temperature are attributed to such a metastable structure that a site exchange between Zn<sup>2+</sup> in the A site and Fe<sup>3+</sup> in the B site takes place. The strong superexchange interaction between Fe<sup>3+</sup> ions in the A and B sites leads to a ferrimagnetic order even above room temperature, although the magnetic order may be restricted within a localized region due to a random distribution of cations.

Recently, ferromagnetic properties have been observed for ultrafine particles of CdFe<sub>2</sub>O<sub>4</sub> prepared via co-precipitation [8] and ball-milling processes [9]. The ferromagnetic behaviors are thought to stem from the site inversion between Cd<sup>2+</sup> ions in the A sites and Fe<sup>3+</sup> ions in the B sites. In this study, we report on structural and magnetic properties of CdFe<sub>2</sub>O<sub>4</sub> thin films prepared by the sputtering method; we demonstrate that the sputtered CdFe<sub>2</sub>O<sub>4</sub> thin films exhibit large magnetization and high magnetic transition temperature.

## II. EXPERIMENT

CdFe<sub>2</sub>O<sub>4</sub> thin films were prepared by utilizing a radio frequency (rf) sputtering method (ULVAC RFS-200). CdO and Fe<sub>2</sub>O<sub>3</sub> (hematite) powders were weighed so that the molar ratio of Fe<sub>2</sub>O<sub>3</sub> to CdO was 1.25. The powders mixed thoroughly were compacted into a mould made of copper and used as a target. The composition of sputtering target was different from that of stoichiometric CdFe<sub>2</sub>O<sub>4</sub> because resultant sputtered thin films were richer in CdO than the target as described below. Thin films were deposited on a silica glass substrate under conditions that the rf power was 100 W, the atmosphere was O<sub>2</sub> and the gas pressure was 1.5 × 10<sup>-2</sup> Torr. Deposited films were annealed at 200 and 400 °C in air for 3 h. The bulk sample was also fabricated via solid-state reaction. CdO and Fe<sub>2</sub>O<sub>3</sub> powders weighed so that the molar fractions of CdO and Fe<sub>2</sub>O<sub>3</sub> were equivalent to each other were thoroughly mixed and pressed into a pellet. Covered with CdO powder, the pellet was calcined at 800 °C for 3 h in air.

It was confirmed by energy dispersive X-ray spectroscopy and Rutherford backscattering spectroscopy (RBS) that both the as-deposited film and the bulk sample had stoichiometric compositions of CdFe<sub>2</sub>O<sub>4</sub>. X-ray diffraction (XRD) analysis was performed using Cu K<sub>α</sub> radiation (Rigaku RINT2500) to identify the crystal structure of films. Fe-*K* edge X-ray absorption near edge structure (XANES) was obtained to explore the local structure of Fe ions by using X-ray-fluorescence-yield mode at BL01B1 beamline in SPring-8, Harima, Japan. The microstructure of thin films was observed by transmission electron microscopy (TEM) at an accelerating voltage of 200 kV. Magnetic properties of the samples were examined by using

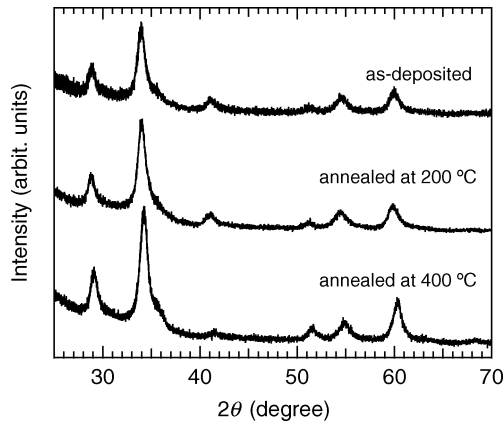


Fig. 1. X-ray diffraction patterns for CdFe<sub>2</sub>O<sub>4</sub> thin films prepared by a sputtering method. The XRD patterns for the as-deposited film and the films annealed at 200 and 400 °C are shown.

a superconducting quantum interference device magnetometer (Quantum Design MPMS-XL).

### III. RESULTS AND DISCUSSION

#### A. Structural Properties of CdFe<sub>2</sub>O<sub>4</sub> Sputtered Thin Films

Fig. 1 illustrates XRD patterns of the as-deposited and annealed thin films. The diffraction lines in the patterns of all the films indicate that a single phase of CdFe<sub>2</sub>O<sub>4</sub> precipitates in the films. It is found that the diffraction lines become sharper and shift to a higher angle side as the annealing temperature is increased. The narrowing of the diffraction lines suggests that the size of crystallite becomes larger. The crystallite size of the as-deposited film is estimated to be about 6 nm from the broadening of the diffraction lines using the following Scherrer's equation:

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where  $d$  is the diameter of crystallite,  $\beta$  is the full width at half maximum of diffraction line,  $\theta$  is the diffraction angle, and  $\lambda$  is the X-ray wavelength, and 1.5405 Å for the present case. The shift of the diffraction lines to a high angle side corresponds to a decrease in the lattice parameter. This fact suggests that annealing the as-deposited film at relatively low temperatures like 200 °C to 400 °C provides the crystals in the film with higher density.

TEM images of the CdFe<sub>2</sub>O<sub>4</sub> thin films with or without annealing are shown in Fig. 2. As shown in Fig. 2(a), it is revealed that the as-deposited film is composed of single crystalline particles possessing a size of about 5 nm dispersed in an amorphous phase. This is consistent with the crystallite size estimated from the broadened line in the XRD pattern. In the film annealed at 200 °C, crystals slightly larger than those in the as-deposited film are observed, while the amorphous phase still remains. On the other hand, the TEM image of the film annealed at 400 °C indicates that grain coarsening occurs. In the film, there are no amorphous regions, but grain boundaries are observed.

Fig. 3 shows Fe- $K$  edge XANES spectra for the films and the bulk sample prepared by solid-state reaction. The intensity of the XANES spectra is normalized by using the intensity at

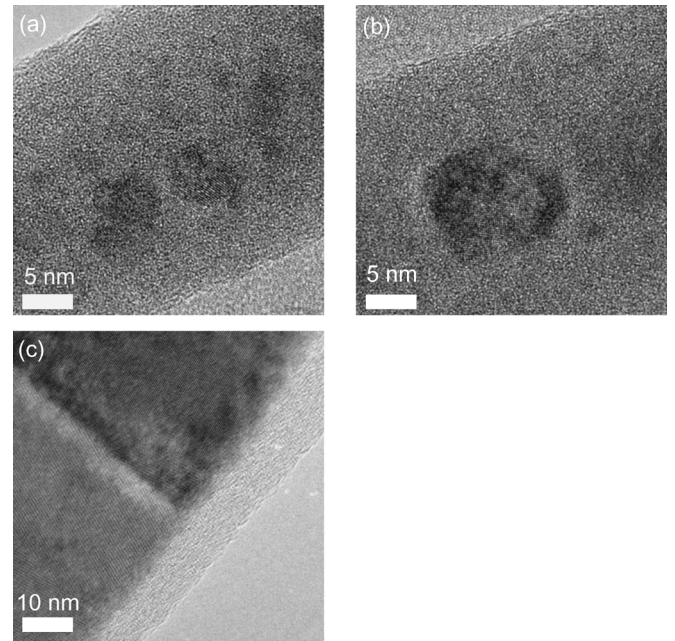


Fig. 2. TEM images of (a) as-deposited film and films annealed at (b) 200 °C and (c) 400 °C.

$E = 7.100$  and  $7.140$  keV, both of which are off-sides of Fe- $K$  edge. As the annealing temperature is increased for the thin films, the main absorption bands centered at  $E = 7.129$  keV become sharper and the profile of the spectra approaches that for the bulk sample. A similar variation was observed for ZnFe<sub>2</sub>O<sub>4</sub> thin films prepared by a sputtering method [10]. Another important point is that the intensity of the pre-edge peak observed at around  $E = 7.111$  keV is reduced by an increase in the annealing temperature. It is well known that the pre-edge peak stems from the Fe<sup>3+</sup> ions in the A sites for spinel-type crystalline materials [11]. The results suggest that the number of Fe<sup>3+</sup> ions coordinated by six oxide ions increases as the annealing temperature increases.

#### B. Magnetic Properties of CdFe<sub>2</sub>O<sub>4</sub> Sputtered Thin Films

Figs. 4(a) and (b) depict magnetic field dependence of magnetization for the CdFe<sub>2</sub>O<sub>4</sub> thin films measured at 5 K and 300 K, respectively. All the films show ferromagnetic behavior even at room temperature. This may be due to the site exchange between Cd<sup>2+</sup> in the A site and Fe<sup>3+</sup> in the B site in the spinel structure. The magnetization of the film annealed at 200 °C is larger than that of the as-deposited film, and the film annealed at 400 °C has smaller magnetization than the as-deposited film.

Temperature dependence of magnetization for the films is shown in Fig. 5. Both field cooling (FC) and zero-field cooling (ZFC) were performed for all the films. A magnetic field of 50 Oe was applied for the measurements. For the as-deposited film, ZFC magnetization exhibits a broad maximum at around 200 K and ZFC and FC magnetization deviates from each other below 300 K. These behaviors resemble those observed in cluster-spin glasses and superspin glasses, suggesting that a ferrimagnetic order occurs only for localized magnetic moments. The film annealed at 200 °C exhibits magnetic behaviors similar to the as-deposited film. On the other hand,

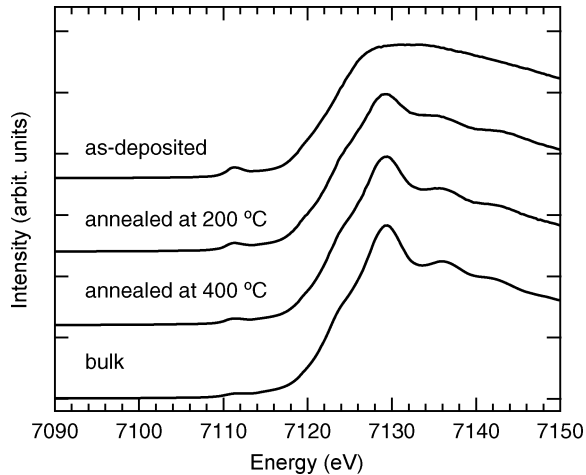


Fig. 3. X-ray absorption near edge structure spectra of  $\text{CdFe}_2\text{O}_4$  thin films and bulk sample in the vicinity of the Fe-K edge.

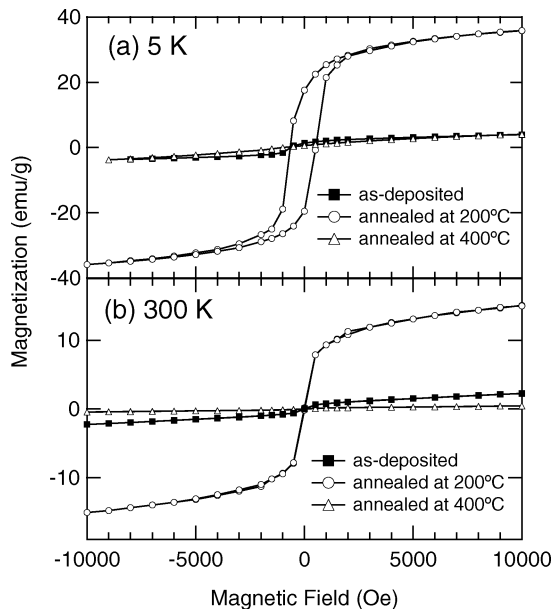


Fig. 4. Magnetic field dependence of magnetization for  $\text{CdFe}_2\text{O}_4$  thin films measured at (a) 5 K and (b) 300 K.

the magnetic behavior of the thin film annealed at 400 °C resembles that of bulk  $\text{CdFe}_2\text{O}_4$ , although the magnitude of magnetization of the film is significantly larger than that of the bulk sample.

Let us consider the effect of annealing on the magnetization of  $\text{CdFe}_2\text{O}_4$  thin film in terms of the structural change of the film induced by the annealing. The annealing at 200 °C causes great enhancement of magnetization up to 36 emu/g at 5 K. This increase is explainable as follows. During the annealing at 200 °C, the crystallization of the amorphous phase and/or the grain growth of the initial crystallites occur, while the random distribution of  $\text{Fe}^{3+}$  ions in the spinel structure is preserved for the most part. Subsequently, the number of magnetic moments contributing to a ferrimagnetic arrangement is increased. A value of 69.2 emu/g is expected at 0 K for  $\text{CdFe}_2\text{O}_4$  with

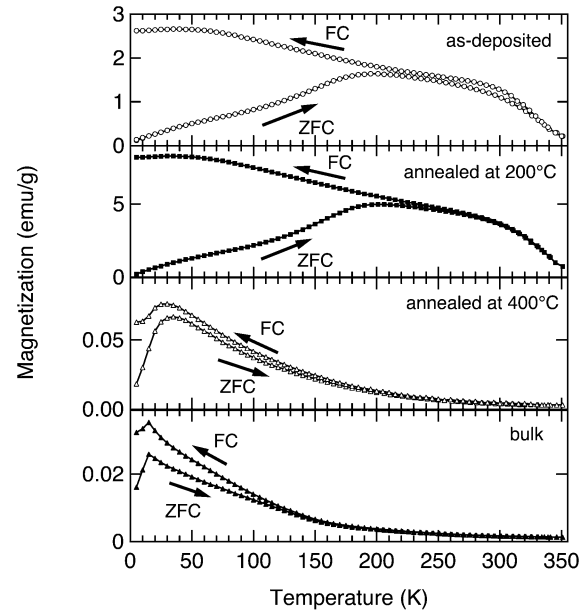


Fig. 5. Temperature dependence of magnetization for  $\text{CdFe}_2\text{O}_4$  thin films and bulk  $\text{CdFe}_2\text{O}_4$ . Both zero-field and field cooling were performed. A magnetic field of 50 Oe was applied for the measurement.

a cation distribution being perfectly random, the composition of which can be denoted as  $[\text{Cd}_{0.33}\text{Fe}_{0.67}]_A[\text{Cd}_{0.67}\text{Fe}_{1.33}]_B\text{O}_4$ . The magnetization of the thin film annealed at 200 °C does not reach such a large value because of the presence of amorphous phase which should possess lower magnetization. On the other hand, the annealing at 400 °C results in a decrease in magnetization. The annealing of the thin films at high temperatures such as 400 °C likely brings about the grain coarsening and the formation of  $\text{CdFe}_2\text{O}_4$  with normal spinel structure, a thermodynamically stable phase, leading to the magnetic behavior similar to that of bulk  $\text{CdFe}_2\text{O}_4$ . It is considered that the thin film annealed at 400 °C shows larger magnetization than the bulk sample because the conversion into the normal spinel structure is not completed even after the annealing for 3 h.

Lastly, it is worth referring to another possible mechanism for the high magnetization of the  $\text{CdFe}_2\text{O}_4$  nanocrystals. According to recent research on nanoparticles of spinel ferrites such as  $\text{MgFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ , the magnetization of nanocrystals larger than those of the corresponding bulk crystals is explained in terms of the competition between the effects of spin canting and site exchange of cations on the surface regions of nanoparticles, while the interior of the nanocrystals has the same structure and magnetic properties as the bulk crystals [12]–[14]. It should be noted that the magnetization decreases monotonously as the annealing temperature becomes higher in those systems. This behavior is clearly inconsistent with the present  $\text{CdFe}_2\text{O}_4$  thin films, where the film annealed at 200 °C has magnetization higher than the as-deposited film, indicating that the mechanism of the spin canting does not rationalize well the case of this study. Nevertheless, more detailed information is required to confirm that a random distribution of cations prevails not only in the surface region but also in the interior region of the nanocrystals [10].

## IV. CONCLUSION

A large magnetization and a high magnetic transition temperature were obtained for as-deposited CdFe<sub>2</sub>O<sub>4</sub> thin film prepared by a sputtering method. It is thought that a random distribution of cations in the structure of CdFe<sub>2</sub>O<sub>4</sub> nanocrystals, where the Fe<sup>3+</sup> ions occupy not only the B sites but also the A sites, causes a cluster-spin or superspin glass like magnetic ordering. The annealing of the film at 200 °C leads to grain growth as well as crystallization of CdFe<sub>2</sub>O<sub>4</sub> with a random distribution of cations from the amorphous phase, resulting in the enhancement of magnetization. The grain coarsening of normal spinel CdFe<sub>2</sub>O<sub>4</sub> crystalline phases takes place when the thin film is annealed at 400 °C. In consequence, the film annealed at 400 °C exhibits magnetic properties similar to those of bulk CdFe<sub>2</sub>O<sub>4</sub>.

## ACKNOWLEDGMENT

The authors would like to thank Dr. H. Tsuchida and Prof. A. Ito of Graduate School of Engineering, Kyoto University, for RBS measurements. Fe-*K* edge XAFS measurements were performed at BL01B1 in SPring-8 with the approval of Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2007B1452). The authors appreciate the support from JASRI. One of authors (H. Akamatsu) thanks the Grant-in-Aid for Fellow (No. 20-6726) from Japan Society of the Promotion Science (JSPS).

## REFERENCES

- [1] K. Kamazawa, S. Park, S. H. Lee, T. J. Sato, and Y. Tsunoda, "Dissociation of spin objects in geometrically frustrated CdFe<sub>2</sub>O<sub>4</sub>," *Phys. Rev. B*, vol. 70, p. 024418, 2004.
- [2] K. Kamazawa, Y. Tsunoda, H. Kadowaki, and K. Kohn, "Magnetic neutron scattering measurements on a single crystal of frustrated ZnFe<sub>2</sub>O<sub>4</sub>," *Phys. Rev. B*, vol. 68, p. 024412, 2003.
- [3] S. J. Stewart, S. J. A. Figueroa, J. M. Ramallo López, S. G. Marchetti, J. F. Bengoa, R. J. Prado, and F. G. Requejo, "Cationic exchange in nanosized ZnFe<sub>2</sub>O<sub>4</sub> spinel revealed by experimental and simulated near-edge absorption structure," *Phys. Rev. B*, vol. 75, p. 073408, 2007.
- [4] G. F. Goya, H. R. Rechenberg, M. Chen, and W. B. Yelon, "Magnetic irreversibility in ultrafine ZnFe<sub>2</sub>O<sub>4</sub> particles," *J. Appl. Phys.*, vol. 87, p. 8005, 2000.
- [5] K. Tanaka, S. Nakashima, K. Fujita, and K. Hirao, "High magnetization and the Faraday effect for ferromagnetic zinc ferrite thin film," *J. Phys.: Condens. Matter*, vol. 15, p. L469, 2003.
- [6] S. Nakashima, K. Fujita, K. Tanaka, and K. Hirao, "High magnetization and the high-temperature superparamagnetic transition with inter-cluster interaction in disordered zinc ferrite thin film," *J. Phys.: Condens. Matter*, vol. 17, p. 137, 2005.
- [7] Y. Yamamoto, H. Tanaka, and T. Kawai, "The control of cluster-glass transition temperature in spinel-type ZnFe<sub>2</sub>O<sub>4-δ</sub> thin film," *Jpn. J. Appl. Phys.*, vol. 40, p. L545, 2001.
- [8] M. Yokoyama, E. Ohta, T. Sato, and T. Sato, "Magnetic properties of ultrafine particles and bulk material of cadmium ferrite," *J. Magn. Magn. Mater.*, vol. 183, p. 173, 1998.
- [9] C. N. Chinnasamy, A. Narayanasamy, N. Ponpandian, R. Justin Joseyphus, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, K. Tohji, K. Nakatsuka, and J.-M. Greneche, "Ferrimagnetic ordering in nanostructured CdFe<sub>2</sub>O<sub>4</sub> spinel," *J. Appl. Phys.*, vol. 90, p. 527, 2001.
- [10] S. Nakashima, K. Fujita, K. Tanaka, K. Hirao, T. Yamamoto, and I. Tanaka, "First-principles XANES simulation of spinel zinc ferrite with a disordered cation distribution," *Phys. Rev. B*, vol. 75, p. 174443, 2007.
- [11] K. Matsumoto, F. Saito, T. Toyoda, K. Ohkubo, K. Yamawaki, T. Mori, K. Hirano, M. Tanaka, and S. Sasaki, "Site-specific studies on X-ray magnetic circular dichroism at Fe *K* edge for transition-metal ferrites," *Jpn. J. Appl. Phys.*, vol. 39, p. 6089, 2000.
- [12] V. Šepelák, I. Bergmann, D. Menzel, A. Feldhoff, P. Heitjans, F. J. Litterst, and K. D. Becker, "Magnetization enhancement in nanosized MgFe<sub>2</sub>O<sub>4</sub> prepared by mechano-synthesis," *J. Magn. Magn. Mater.*, vol. 316, p. e764, 2007.
- [13] V. Šepelák, A. Feldhoff, P. Heitjans, F. Krumeich, D. Menzel, F. J. Litterst, I. Bergmann, and K. D. Becker, "Nonequilibrium cation distribution, canted spin arrangement, and enhanced magnetization in nanosized MgFe<sub>2</sub>O<sub>4</sub> prepared by a one-step mechanochemical route," *Chem. Mater.*, vol. 18, p. 3057, 2006.
- [14] V. Šepelák, I. Bergmann, A. Feldhoff, P. Heitjans, F. Krumeich, D. Menzel, F. J. Litterst, S. J. Campbell, and K. D. Becker, "Nanocrystalline nickel ferrite, NiFe<sub>2</sub>O<sub>4</sub>: Mechano-synthesis, nonequilibrium cation distribution, canted spin arrangement, and magnetic behavior," *J. Phys. Chem. C*, vol. 111, p. 5026, 2007.

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