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High-temperature cluster glass state and photomagnetism in Zn- and Ti-substituted NiFe₂O₄ films

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We report on the cluster glass nature and photoinduced magnetization (PIM) of (Ni, Zn, Fe, Ti)₃O₄ thin films prepared using a pulsed-laser deposition (PLD) technique. The films exhibit cluster glass behaviors with a spin-freezing temperature T_f of approximately 230 K. It was found that the magnetization increases following light irradiation below T_f. The experimental results suggest that the electronic transitions induced by photons are intrinsic to the observed PIM rather than the thermal heating effects resulting from light irradiation. The change in the magnetization from the original dark value at 10 K was approximately 40% for the Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O₄ film, and it was approximately 5% for the Ni_{0.4}Zn_{0.6}Fe₂O₄ film when the excitation intensity is 1.48 mW/mm². The analysis of the excitation energy dependence of PIM suggests that an intervalence charge transfer Ti⁴⁺+Fe²⁺→Ti³⁺+Fe³⁺ contributes to the observed enhancement in the PIM of the Ti-substituted films. © 2005 American Institute of Physics. [DOI: 10.1063/1.1863422]

I. INTRODUCTION

The investigations concerning photoinduced magnetization (PIM) are of great importance, not only from the viewpoint of delineating the fundamental mechanism involved, but also in relation to the problems involving practical applications, such as in the photon-mode magneto-optical memories that could replace the conventional thermodriven magneto-optical (MO) memories. The PIM has been reported in several kinds of materials such as the diluted magnetic semiconductors, ¹ spin-crossover complexes, ² and Prussian blue analogs.³ Most of these, however, exhibit PIM only at lower-temperature ranges below 50 K and required a high external magnetic field of greater than 1 T, causing a serious impediment to the practical application of these materials.

Recently, we reported that the cluster glass behavior was observed near room temperature (RT) in (Mg, Ti, Fe)₃O₄ (Ref. 4) and (Co, Zn)Fe₂O₄ (Ref. 5) spinel ferrite films prepared using a pulsed-layer deposition (PLD) technique, and these films exhibited a PIM below the spin-freezing temperature T_f . In these films, nonmagnetic ions such as Ti^{4+} and Zn²⁺, are considered to break the long-range ferromagnetic order in spinel ferrites into magnetic clusters of various sizes. The spin-freezing states near RT are expected to result from the frustration and randomness of the cluster-cluster interactions. Light irradiation causes the reorientation of freezing spins (i.e., melting of the cluster glass state) and as a result, the magnetization increases. It was found that there was little change in the magnetization following light irradiation in Zn-substituted films⁵ while Ti-substituted films exhibited a large PIM.⁴ This suggests that the Ti⁴⁺ ions are responsible for the large PIM. However, several problems remain unsolved, especially those concerning the fundamental mechanism of the PIM observed in these films. To elucidate the mechanism of PIM, further systematic investigations concerning the role of Ti⁴⁺ ions in PIM are strongly desired. In this work, we have focused on the Ti-substituted Ni-Zn ferrite system (Ni,Zn,Fe,Ti)₃O₄. Ni-Zn ferrites are one of the most versatile magnetic materials for general use. They present a wide choice in the coercive force, permeability, and magnetic and electronic losses.⁶ Moreover, in our previous study, the colossal magnetoresistance (CMR) was found in Ni-Zn ferrites. Thus, Ni-Zn ferrites are promising materials in the magnetic applications. As reported in other works, 8-10 the iron ions in Ni-Zn ferrites could be substituted by the with various contents. Therefore, the (Ni, Zn, Fe, Ti)₃O₄ system is suitable for investigating the dependence of PIM on Ti⁴⁺ content.

II. EXPERIMENTAL PROCEDURES

The target samples (Ni, Zn, Fe, Ti)₃O₄ were prepared by a conventional solid-state reaction. Powdered NiO (99.9%), ZnO (99.999%), Fe₂O₃ (99.99%), and TiO₂ (99.9%) were mixed in an approximate mole ratio and sintered at 1200 °C for 20 h in air and then cooled to room temperature at a rate of 5 °C/min. Thin films were prepared on the α -Al₂O₃(0001) substrates by employing a PLD technique using an ArF excimer laser (wavelength: 193 nm). The substrate temperature and ambient oxygen pressure were maintained at 500 °C and 1.0×10^{-5} Torr, respectively. The typical thickness of the films was 2000 Å and the film growth rate was 30 Å/min. The structural properties were examined by a standard x-ray diffraction (XRD) system using a monochromated $Cu K\alpha$ radiation. All magnetic measurements were performed using a superconducting quantum interference device (SQUID) (Quantum Design MPMS-5S) in the temperature range from 10 to 400 K. Magnetic field H was applied parallel to the substrate surface. For the PIM measurements, a Xe lamp was used for the excitation light source and the light was introduced to the SQUID system through an optical fiber. The typical excitation intensity was 1.48 mW/mm².

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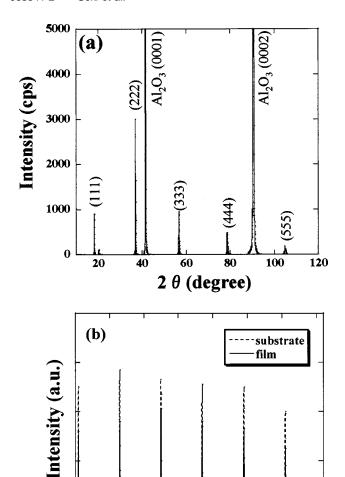


FIG. 1. (a) X-ray diffraction pattern of the Ni_{0.7}Zn_{0.3}Fe₂Ti_{0.3}O₄ film on the α -Al₂O₃(0001) substrate. (b) X-ray φ scan of the Al₂O₃(0001) substrate and the $Ni_{0.7}Zn_{0.3}Fe_2Ti_{0.3}O_4$ film.

150 200 250

 φ (degree)

300

III. RESULTS AND DISCUSSION

50

100

Figure 1(a) shows the XRD $(\theta-2\theta)$ pattern of the $Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O_4$ film grown on the α -Al₂O₃(0001) substrate. The film is clearly shown to be (111)-oriented single phase. An XRD φ scan was also performed for the film and substrate and the result is shown in Fig. 1(b). This figure shows normals of the {111} planes Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O₄ film. The position of the peak is consistent between the film and the substrate, indicating that the film is in good epitaxy with the substrate. The structure of the film is cubic and the symmetry of the {100} planes is threefold for the [111] axis of the film. In Fig. 1(b), there are six peaks for the film and the rotation angle are 60°, suggesting that the film consists of twins or domains. Since twins were also observed in the sapphire substrates of the (0001) plane (sixfold), the prepared film with twins has been grown epitaxially on the substrate.

Figure 2 shows the temperature dependence of the ac

susceptibility for the Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O₄ film, measured under an ac field of 4 Oe in the frequency range of 120-2000 Hz and with a superimposed dc field of 50 Oe. This measurement was performed in the zero-field-cooling (ZFC) mode at a temperature sweep rate of 1 K/min. The dependence of the ac susceptibility on the frequency near the cusp temperature is shown in Fig. 2(b). The cusp shifted to a higher temperature as the frequency increased. This feature is one of the criteria that are used to determine the spin-(cluster) glass nature of a material, and the cusp temperature can be defined as the T_f of the system. 11 Furthermore, as shown in Fig. 2(c), the dependence of T_f on frequency displays a good fit with the Vogel-Fulcher law $f=f_0$ $\times \exp[-E_a/(T_f-T_0)]$ with the fitted parameters of $f_0=2.4$ $\times 10^4$ Hz, E_a =50 K, and T_0 =218 K. This fact suggests the existence of the spin- (cluster) glass phase below T_f . Similar features of ac magnetization were also observed in the films with other compositions.

The temperature dependence of dc magnetization for the $Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O_4$ and $Ni_{0.4}Zn_{0.6}Fe_2O_4$ films are shown in Figs. 3(a) and 3(b), respectively. The hysteresis between the ZFC and field-cooling (FC) modes was observed, which is one of the characteristics of spin- (cluster) glass systems. The cusp temperature in the ZFC curve is consistent with that for the ac susceptibility, i.e., T_f . We observed no steep decrease or sharp cusp in ZFC curves which is a characteristic feature of the spin-glass system, suggesting that the films are in cluster glass state rather than in spin-glass state. The M(T) measured under light irradiation at intensity of 1.48 mW/mm² is also shown in Fig. 3 (open circle). In both films, M(T) increases following light irradiation below T_f in the ZFC states while there is no change in M(T) in the FC states. This behavior indicates the melting of the cluster glass state following light irradiation. As shown in Fig. 3, the PIM was found to be more prominent in the Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O₄ film (approximately 40% change in M from the original dark value at 10 K) than in the Ni_{0.4}Zn_{0.6}Fe₂O₄ film (approximately 5%). These data are consistent with the results in our previous studies, where PIM was significantly enhanced in the Ti-substituted (Mg,Fe)₃O₄ films, while little change in PIM was observed in Zn-substituted CoFe₂O₄ films.⁵ An important question is whether the thermal heating effect on the film following light irradiation or the photoexcitation of electronic states is intrinsic to the observed PIM. Figure 4 shows the excitation intensity dependence of the change ratio of the ZFC magnetization following light irradiation, R_M , for films with various compositions. The R_M is calculated as $R_M(\%)$ = $100 \times (\Delta M/M_0)$, where ΔM is the increase in the ZFC magnetization following light irradiation, and M_0 is the magnetization before light irradiation. The R_M is proportional to the excitation intensity, i.e., the photon number. This suggests that the observed PIM is mainly due to the effect of the photons. As shown in Fig. 4, PIM increases with increasing Ti⁴⁺ content, indicating that Ti⁴⁺ ions play a crucial role in the enhancement of PIM.

In Fig. 5, the absorption spectrum for Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O₄ film measured at 300 K is presented. Several broad absorption bands at 0.81, 2.19, and 2.51 eV are basically assigned as the $3d^n \rightarrow 3d^{n-1}4s$ process for Fe

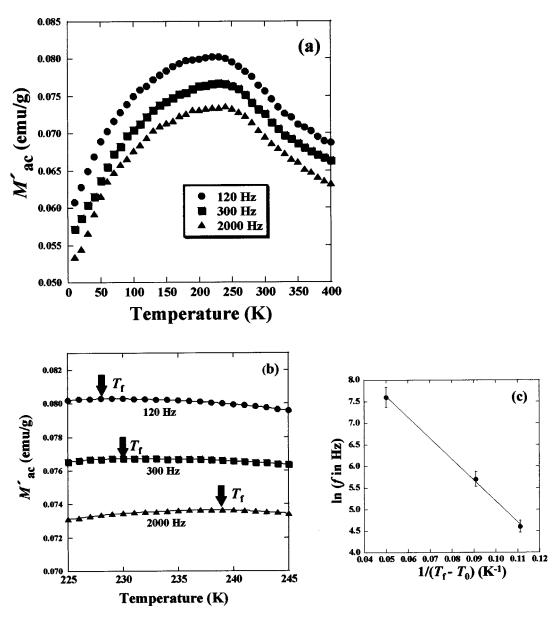
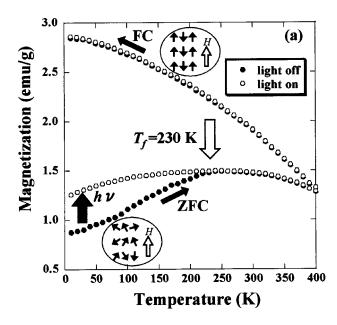


FIG. 2. (a) Dependence of ac susceptibility on temperature for the $Ni_{0.7}Zn_{0.3}Fe_2Ti_{0.3}O_4$ film on the α -Al₂O₃(0001) substrate as a function of frequency and temperature between 10 and 400 K. (b) Magnified (a) for T=225-245 K. (c) Experimental data fitted with Vogel–Fulcher law.

ions in both the tetrahedral site (A site) and octahedral site (B site). 12 In order to identify the optical transition responsible for the enhancement of PIM in the Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O₄ film, the excitation energy dependence was measured by filtering the broadband light of a Xe lamp using the optical bandpass filters. The efficiency of PIM, E can be calculated as $E=(1/I)(\Delta M/M_0)$, where I is the intensity of filtered light. 13 The calculated efficiency E for various energy regions is also presented in Fig. 5. It is clearly shown that the visible-light energy region of the Xe lamp (1.7-2.5 eV) contributes to PIM. One of the possible electronic transitions induced by visible-light excitation in ferrite materials is a charge transfer among cations. The change in magnetic properties due to a photoinduced charge transfer has been reported for several kinds of materials. 3,13–16 For example, in bulk CoFe₂O₄, it was reported that the coercive force decreased due to the charge transfer between Co2+ and Fe3+ ions. 14 As shown in Fig. 5, the efficiency E has a maximum

value at approximately 2.2 eV. This value is consistent with that of the excitation energy for the photoinduced charge transfer between Ti⁴⁺ and Fe²⁺ ions at B sites in the spinel structure: Ti⁴⁺+Fe²⁺ \rightarrow Ti³⁺+Fe³⁺ [generally called intervalence charge transfer (IVCT)], as previously reported in the experimental¹⁷ and theoretical¹⁸ studies. The IVCT explains the mechanism of the observed PIM. If the Fe²⁺ ions, which are well known to have a large magnetic anisotropy, 19,20 are excited to Fe³⁺ ions with no magnetic anisotropy then their magnetic moments will easily rotate and align along H. Consequently, it will become easier for freezing spins to align along H through magnetic interaction with aligned spins, resulting in the melting of the cluster glass state. Furthermore, the IVCT between Fe²⁺ and Fe³⁺ should be taken into account in the Ti⁴⁺-substituted film. Fontijn et al. 21,22 reported that the IVCT between B-site iron ions, $Fe^{2+}+Fe^{3+} \rightarrow Fe^{3+}$ +Fe²⁺, occurs at 1.94 eV. The PIM at approximately 1.9 eV shown in Fig. 5 may be attributed to this IVCT. The change



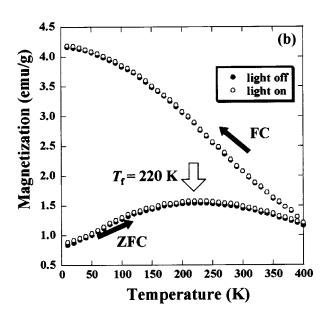


FIG. 3. Dependence of dc magnetization on temperature with or without light irradiation at intensity of 1.48 mW/mm^2 for the (a) $Ni_{0.7}Zn_{0.3}Fe_2Ti_{0.3}O_4$ and (b) $Ni_{0.4}Zn_{0.6}Fe_2O_4$ films on the $\alpha\text{-Al}_2O_3(0001)$ substrates under 100 Oe.

in magnetic properties via this type of IVCT was extensively studied in the Si^{4+} -doped yttrium iron garnet (YIG). 13,15,16 In Si^{4+} -doped YIG, the rearrangement of Fe^{2+} ions via the IVCT causes the appearance of a uniaxial magnetic anisotropy in the sample, which is called a photomagnetic effect. The scenario involving the rearrangement of the Fe^{2+} ions following light irradiation can be applied to the observed PIM in the present study. The arrangement of the Fe^{2+} ions may result in the appearance of the uniaxial anisotropy with a magnetic easy axis parallel to H, as in the case of a Si^{4+} -doped YIG, and consequently, the freezing spins will easily align along H. On the other hand, in the $Ni_{0.4}Zn_{0.6}Fe_2O_4$ film, since most of the Fe ions are trivalent, the IVCT is not expected to occur. However, to a certain

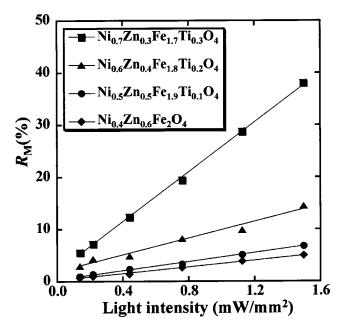


FIG. 4. Excitation intensity dependence of the change ratio of ZFC magnetization R_M for films with various compositions measured at 10 K under H=100 Oe.

extent, Fe²⁺ ions are considered to exist because the film was prepared under low oxygen pressure (10⁻⁵ Torr). These may also induce the IVCT and contribute to the small PIM observed at 10 K, as shown in Fig. 3(b).

The photocontrol of magnetization achieved in the films are expected to pave the way for the development of MO devices. The time-dependent change in ZFC magnetization M(t) at 10 K for the Ni_{0.7}Zn_{0.3}Fe_{1.7}Ti_{0.3}O₄ film is shown in Fig. 6. At the initial stage, M(t) increases by applying a field of 100 Oe. Upon light irradiation, M(t) shows a 40% increase from the original dark value, indicating the melting of the cluster glass, as depicted in Fig. 3(a). A further slight increase in M was observed after switching off the light, and then M decreased after switching on the light again. This

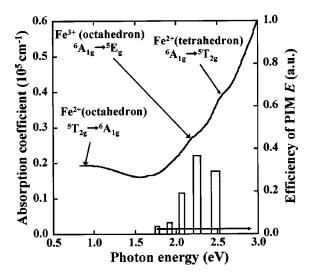
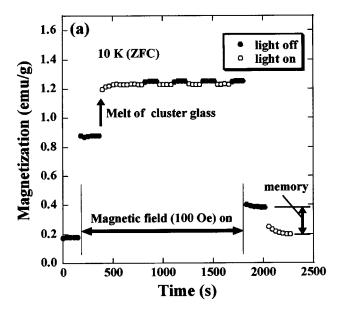


FIG. 5. Optical absorption spectrum at 300 K and an efficiency of PIM E at 10 K for the Ni_{0.7}Zn_{0.3}Fe₂Ti_{0.3}O₄ film on the α -Al₂O₃(0001) substrate. The intensity of filtered light in the various energy regions is equally 0.92 mW/mm².



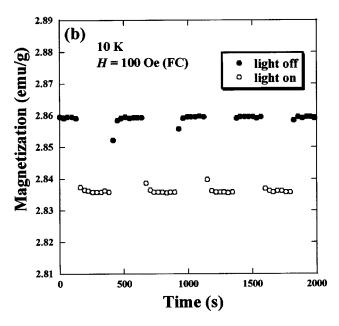


FIG. 6. Time variation of (a) ZFC and (b) FC magnetizations for the $Ni_{0.7}Zn_{0.3}Fe_2Ti_{0.3}O_4$ film on the α -Al $_2O_3(0001)$ substrate with or without light irradiation at intensity of 1.48 mW/mm² measured at 10 K.

increase/decrease in M by light off/on after melting of the glassy phase was also observed in the single-crystalline Cd_{0.63}Mn_{0.37}Te which exhibits a spin-glass behavior below T_f (~9 K), as reported by Kawai and Sato.²³ They concluded that this behavior was due to the magnetic response of the intrinsic paramagnetic components in the spin-glass samples. The coexistence of paramagnetic spins and freezing spins were also observed in the ZnFe₂O₄ spinel ferrite films.²⁴ It should be noted that the small magnetic clusters isolated with the surrounding nonmagnetic Ti⁴⁺ and Zn²⁺ ions do not belong to the spin-freezing states, but mainly contribute to the paramagnetic behavior in the film. In the FC states, a similar pattern (increase/decrease in M) was observed, as shown in Fig. 6(b). In the FC states, no cluster glass phase exists and the magnetization decreases as the temperature increases, as shown in Fig. 3. Therefore, this pattern can be attributed to the thermal heating effect following light irradiation. The increase in the temperature ΔT following light irradiation was estimated to be approximately 3 K using the simple expression $\Delta T \sim \Delta M_{FC} / [\delta M_{FC}(T) / \delta T]_{10 \text{ K}}$, where ΔM_{FC} is a change in the FC magnetization following light irradiation and $[\delta M_{FC}(T)/\delta T]_{10 \text{ K}}$ denotes a slope of the FC curve in Fig. 3(a) at 10 K. This indicates that the excitation intensity (1.48 mW/mm²) is low enough to exclude the heating effects of the light irradiation. As shown in Fig. 6(a), the magnetization decreases significantly after removing the field. The remnant magnetization is still greater than the initial magnetization at the first stage before applying the field, indicating that the film can "remember" the effects of light irradiation even after the light is switched off and the field is removed. This remnant magnetization slowly relaxes and approaches the initial state value. This relaxation is accelerated by the light irradiation. Thus, the information can be written and altered by photons via a change in the magnetization. This phenomenon could be utilized in the development of the photon-mode magneto-optical memories.

IV. CONCLUSIONS

The high-temperature cluster glass state and the photocontrol of magnetization were achieved in Zn- and Tisubstituted NiFe₂O₄ spinel ferrite thin films. The PIM was much larger in Ti-substituted films. It is suggested that the photoinduced charge transfer between the Ti⁴⁺ and Fe²⁺ ions is mainly responsible for the PIM in Ti-substituted films. The optical memory effect observed in the Ti-substituted film can be utilized in the development of magneto-optical memories.

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¹H. Munekata, A. Oiwa, and T. Slupinski, Physica E (Amsterdam) **13**, 516 (2002).

²P. Gütlich, A. Hauser, and H. Spiering, Angew. Chem. **33**, 2024 (1994). ³O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Science **272**, 704 (1996).

Muraoka, H. Tabata, and T. Kawai, Appl. Phys. Lett. 76, 1179 (2000).
Muraoka, H. Tabata, and T. Kawai, Solid State Commun. 120, 225 (2001).

⁶R. Valenzuela, *Magnetic Ceramics* (Cambridge University Press, Cambridge, 1994).

⁷A. K. M. A. Hossain, M. Seki, T. Kawai, and H. Tabata, J. Appl. Phys. **96**, 1273 (2004).

⁸R. C. Srivastava, D. C. Khan, and A. R. Das, Phys. Rev. B 41, 12514 (1990).

⁹D. C. Khan, M. Misra, and A. R. Das, J. Appl. Phys. **53**, 2722 (1982).

¹⁰C. Prakash and J. S. Baijal, Solid State Commun. **50**, 557 (1984).

¹¹J. A. Mydosh, Spin Glass: An Experimental Introduction (Taylor & Francis, London, 1993).

¹²X.-X. Zhang, J. Schoenes, W. Reim, and P. Wachter, J. Phys. C **16**, 6055 (1983)

¹³U. Enz and H. van der Heide, Solid State Commun. **6**, 347 (1968).

¹⁴A. K. Giri, E. M. Kirkpatrick, P. Moongkhamklang, S. A. Majetich, and V. G. Harris, Appl. Phys. Lett. 80, 2341 (2002).

¹⁵R. W. Teale and D. W. Temple, Phys. Rev. Lett. **19**, 904 (1967).

¹⁶R. Albern, J. F. Dillon, E. M. Gyory, and J. P. Remeika, J. Appl. Phys. 42, 1447 (1971).

¹⁷D. M. Sherman, Phys. Chem. Miner. **14**, 364 (1987).

R. G. J. Strens and B. J. Wood, Miner. Mag. **43**, 347 (1979).
J. Kanamori, Prog. Theor. Phys. **17**, 177 (1957).
J. Kanamori, Prog. Theor. Phys. **17**, 197 (1957).
W. F. J. Fontijn, P. J. van der Zaag, M. A. C. Devillers, V. A. M. Brabers, and R. Metselaar, Phys. Rev. B **56**, 5432 (1997).

²²W. F. J. Fontijn, P. J. van der Zaag, and L. F. Feiner, J. Appl. Phys. 85,

²³H. Kawai and T. Sato, J. Appl. Phys. **85**, 7310 (1999).

²⁴Y. Yamamoto, H. Tanaka, and T. Kawai, Jpn. J. Appl. Phys., Part 2 40, L545 (2001).