Photoexcited spin-glass state in $(Mg,Fe)\{Mg,Fe,Ti\}O_4$ spinel ferrite films

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Spin-glass states above room temperature have been found in $(Mg, Fe)\{Mg,Fe,Ti\}_2O_4$ spinel ferrite thin films formed on Al_2O_3 (0001) and $SrTiO_3$ (111) substrates. The films show a long-time relaxation of the magnetization in zero-field-cooled operation and a frequency dependence of the cusp temperature in ac susceptibility measurement, both of which are typical characteristics of a spin glass. This high-temperature spin-glass state has been achieved by the fine tuning of spin states through the control of composition, random oxygen deficiencies, and the stress induced by the film/substrate lattice mismatch, all of which give rise to effects that enhance the exchange interaction of spins in the ferrite films. We have demonstrated the change of magnetic state by means of light irradiation from spin glass to a ferrimagnet over a wide range of temperatures below 290 K. The direct photoexcitation of spins with photon energy in the visible-light region (1.7–3.2 eV), which corresponds to the spin excitation energy of crystal field for Fe ions located in both tetrahedral and octahedral sites, is effective for realizing photoinduced magnetization. © *2000 American Institute of Physics.* [S0021-8979(00)05601-8]

I. INTRODUCTION

Spinel ferrite oxides, $A^{2+}Fe_2^{3+}O_4$, are one of the typical magnetic materials, and show various magnetic properties depending on the composition. The most advantageous feature of spinel materials is that various ions can be placed at tetrahedral (A^{2+}) and octahedral (Fe^{3+}) sites within the structure [see Fig. 1(a)], which allows us to control the magnetic properties. In addition to ferromagnetism and antiferromagnetism (ferrimagnetism), another unique spin state, the so-called ''spin glass,'' can be assigned in the case of spinel ferrites.

The spin-glass state occurs due to a combination of ''randomness'' and ''frustration'' in spin ordering, caused by the randomly mixed state of the ferromagnetic (spin-parallel) and antiferromagnetic (spin-antiparallel) spin interaction.[1] In order to obtain the spin-glass state for spinel ferrites, Fe ions are substituted by nonmagnetic ions, such as Mg^{2+} or Ti^{4+}, resulting in both the occurrence of dilution of magnetic interactions (randomness) and the competition of exchange interactions (frustration).[2–4] Figure 1(b) shows the model of the spin-glass phenomenon in spinel ferrite AFe_2O_4. The nearest neighbors of metal ions via the O^{2-} anion in the spinel ferrite are shown in Fig. 1(b). A corresponds to the tetrahedral site cation and B stands for the octahedral site cation. Arrows indicate the spin of the Fe ion. The $MgFe_2O_4$ compound, without Ti^{4+} ions, shows the ferrimagnetism with a Curie temperature (T_c) of 715 K. Cations of Mg^{2+} and Fe^{3+} are distributed on A and B sites and the formula is given as $(Mg_{0.33}Fe_{0.67})\{Fe_{1.33}Mg_{0.67}\}O_4$.[5] In this material, all spin interactions are well defined as nearest-neighbor antiferromagnetic, with $|J_{AB}| \gg |J_{BB}| > |J_{AA}|$ [$\bar{J}$ in Fig. 1(b) shows the average value of the spin interactions]. Thus, J_{AB} renders the undiluted spinel ferrimagnetism, with all A-site moments oriented antiparallel to all B-site moments, with BB and AA bonds remaining unsatisfied [left side, Fig. 1(b)]. On dilution of Fe^{3+} ions in the B site by Ti^{4+}-ion substitution, magnetic order is broken and the frustration of certain moments occurs for BB and AA bonds [right side, Fig. 1(b)].

Other than spinel materials, spin-glass behavior has been reported so far in perovskite oxides,[6,7] dilute magnetic alloys,[8–10] and amorphous materials[2,3,11] (spin freezing temperature, $T_f = 3 - 50$ K). In many cases, spin-glass states are observed at temperatures below 50 K ($T_f \leq 50$ K). An exception is spinel cobalt ferrite with a polycrystalline or amorphous form, which is known to exhibit a high T_f near room temperature ($T_f = 284$ or 320 K),[12,13] but such examples are few.

The spin-glass system consists of various metastable states, depending on the degree of ''spin freezing.''[14,15] Accordingly, applying appropriate external fields such as light perturbation to the spin-glass state can cause a ''melt'' of the frozen spins and accelerate the magnetic relaxation, giving rise to an increase in magnetization up to a new steady-state value [Fig. 1(c)]. This type of photoexcited magnetization has been demonstrated for amorphous spin glass in oxides,[16–18] although the operating temperature is low (≤ 2 K), due to the low $T_f (\leq 6$ K) of the materials. If such spin-glass control can be obtained at sufficiently high temperatures, it could be applied to many magneto-optical devices.

According to the three-dimensional Heisenberg theory for anisotropy, D,[19] the spin-freezing temperatures T_f are related as

$$T_f \sim J \cdot (D/J)^{1/4},$$

where J is the exchange interaction, thus T_f depends heavily on the absolute value of J in materials. Hence, the spinel oxides, especially spinel ferrites, are one of the most suitable materials for achieving a higher T_f because of their high T_c,
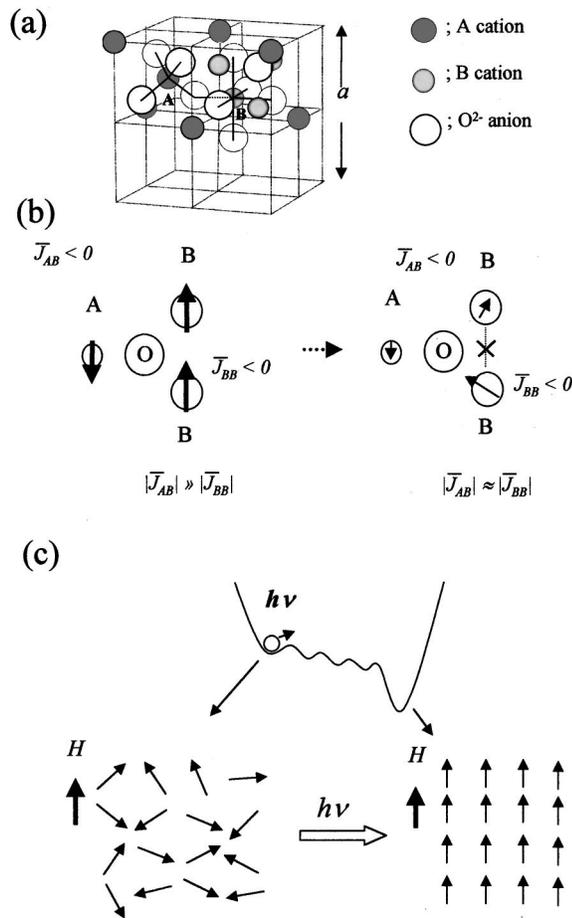
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FIG. 1. (a) Two octants in the unit cell of the spinel structure with lattice parameter a. The general formula of compounds with spinel ferrites is $A\{Fe\}_2O_4$. The O^{2-} anions form a cubic close-packed structure, with A ions occupying the tetrahedral sites (A site), and Fe ions occupy the octahedral sites (B site), of O^{2-} anion packing. (b) Model of the spin-glass phenomenon in spinel ferrite AFe_2O_4. The nearest neighbors of the metal ions via the O^{2-} anion in the spinel ferrite are shown: A: tetrahedral site cation; B: octahedral site cation. Arrows correspond to the spin of Fe ion. (c) Schematic representation of the process of an increase of magnetization in the spin-glass state. Spins are frozen in a low applied magnetic field H (left). The frozen spin glass is irradiated under a magnetic field, and the frozen spins are melted with their direction aligned parallel to the magnetic field H (right).

that is, large J. Furthermore, the value of D in spinel ferrites is controllable by changing their composition.[20]

In this work, we have focused on ferrimagnetic spinel ferrite $(Mg, Fe)\{Fe, Mg, Ti\}_2O_4$ (whose formula is represented as $Mg_{1+t}Fe_{2-2t}Te_tO_4$). The magnetic-phase diagram of this bulk material is shown in Fig. 2.[4] The material shows a spin-glass or a spin-canting state for $0.4 < t < 0.85$, due to the dilution of Fe^{3+} ions by nonmagnetic Mg^{2+} and Ti^{4+} ions, which results in the occurrence of both randomness and frustration of spin ordering in the material. The T_f of this bulk material is $\simeq 22$ K. However, considering the fact that $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ bulk exhibits a high T_c, i.e., has a large J ($|J_{Fe-Fe}|/k_B = 20$ K, where k_B is the Boltzmann constant),[5,20] this material has a significant possibility of exhibiting a higher T_f. In this work, we have prepared this material in the form of a film. In order to obtain a high T_f, even above room temperature, the composition has been tuned to be
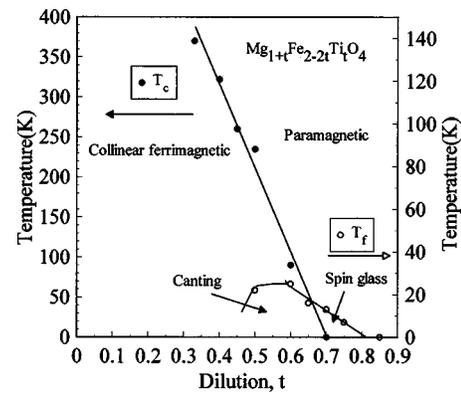

FIG. 2. Magnetic-phase diagram for $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ in bulk material (see Ref. 4).

$Mg_{1+t}Fe_{2-2t}Ti_tO_4$ ($t = 0.5 - 0.4$) which has a high T_c of over 200 K, therefore, a large J, and substrates have been selected that have the effect of enhancing the J value by the strain induced due to lattice mismatch. We have also controlled the spin-glass state of the ferrite film by means of light irradiation.

II. EXPERIMENT

Thin films of (111)-oriented spinel ferrite were prepared by a pulsed-laser deposition technique on sapphire (0001) and $SrTiO_3(111)$ planes. The spinel ferrite targets, $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ ($t = 0.5$, 0.45, and 0.4) were prepared by a normal solid-state reaction. Powders of MgO, Fe_2O_3, and TiO_2 were mixed in approximate molar ratio and sintered at 1200 °C for 4 h under an oxygen atmosphere, and then cooled to room temperature at a rate of 2 °C/min. During the film preparation, the substrate temperature and oxygen pressure was maintained at 500 °C and 1.0×10^{-5} Torr, respectively. The typical deposition rate was about 10 Å/min. The thickness of the films is 3000 Å for films formed on both α-$Al_2O_3(0001)$ and $SrTiO_3(111)$ substrates. All the prepared films were found to be (111)-oriented single-phase by x-ray diffraction (XRD) analysis. X-ray pole figure analysis of these films was also done, which established its epitaxial nature against the substrates. All magnetic measurements were performed using a superconducting quantum interference device (SQUID) (Quantum design MPMS-5S). Magnetic fields were applied parallel to the substrate surface. For photoinduced magnetization measurement, a Xe lamp was used as the light source. From the absorption coefficient measurement, the mean-penetration depth into the film (about 1 μm depth) is larger than the thickness of the film itself (3000 Å), indicating that a bulk photoinduced effect rather than a surface effect can be realized.

III. RESULTS AND DISCUSSION

A. High-temperature spin-glass state in ferrite films

Figure 3(a) shows the XRD pattern of the $Mg_{1.5}FeTi_{0.5}O_4$ film on a $Al_2O_3(0001)$ substrate. By XRD analysis, the film is found to be (111)-oriented single phase. The lattice parameter of the (111) out-of-plane d_{III} was de-
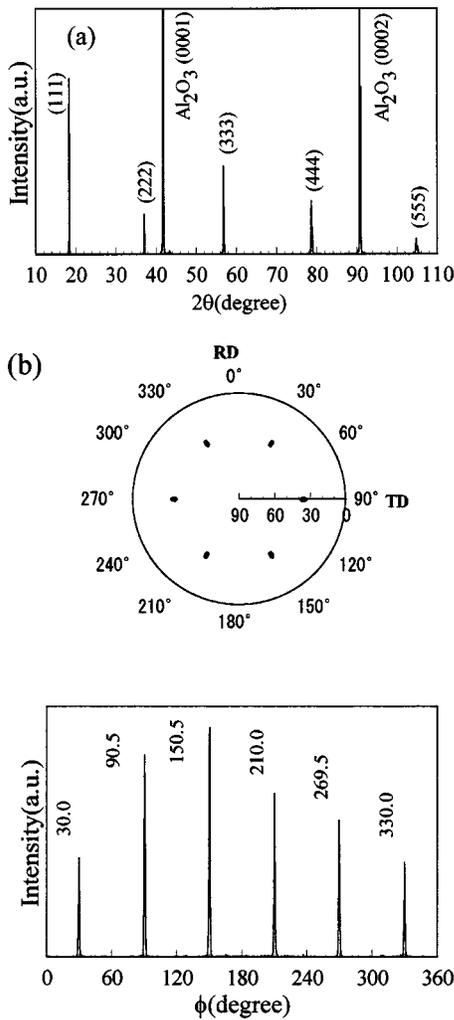
FIG. 3. (a) X-ray diffraction pattern of the (111)-oriented $Mg_{1.5}FeTi_{0.5}O_4$ film on an $Al_2O_3(0001)$ substrate; (b) x-ray pole figure (top graph) and ϕ scan (bottom graph) of the {100} family of planes for the (111)-oriented $Mg_{1.5}FeTi_{0.5}O_4$ film on an $Al_2O_3(0001)$ substrate, obtained around an axis normal to the film surface.
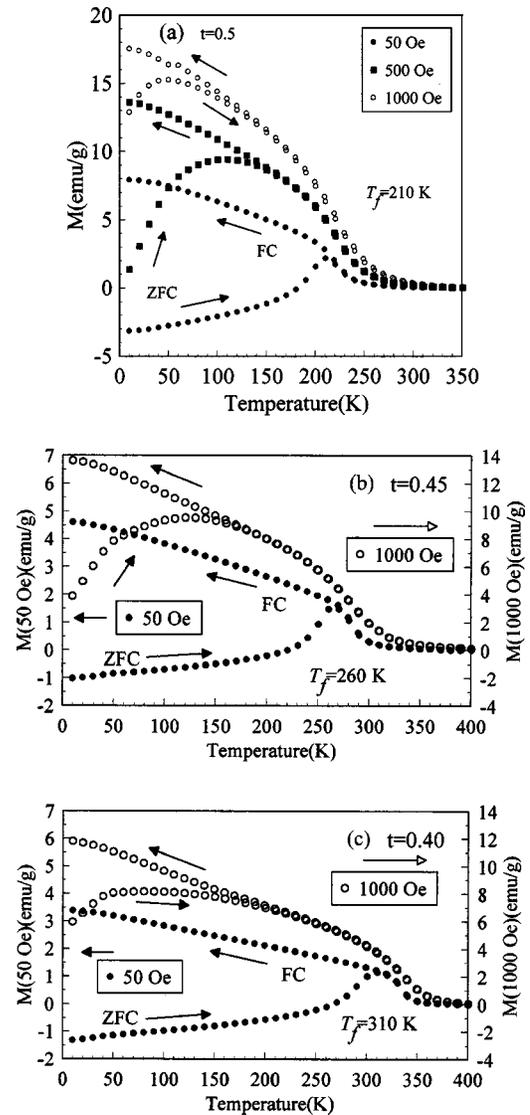

FIG. 4. Temperature dependence of the magnetization for the (a) $Mg_{1.5}FeTi_{0.5}O_4$ film, (b) $Mg_{1.45}Fe_{1.1}Ti_{0.45}O_4$ film, and (c) $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film formed on $Al_2O_3(0001)$ substrates under various applied magnetic fields. The magnetic field was applied parallel to the surface of the substrates.

termined to be 4.864 (1) Å, which is slightly smaller than that of bulk material [4.870 (1) Å] with a cubic symmetry. The x-ray pole figure measurement of the film is also carried out and the result is depicted in Fig. 3(b). Figure 3(b) shows planes of the {100} family of $Mg_{1.5}FeTi_{0.5}O_4$ film, indicating that the film is in well epitaxy with the substrate. The structure of the film is cubic and the symmetry of the {100} planes should be threefold for the [111] axis of the film. In Fig. 3(b), there are six diffraction spots for the film and the rotation angles are 60°, meaning that the film may consist of twins or domains. Since twins are also observed in the sapphire substrates of the (0001) plane (sixfold), the $Mg_{1.5}FeTi_{0.5}O_4$ film with twins has grown epitaxially on the substrate.

Figures 4(a)–4(c) show the temperature dependence of the magnetization for the $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ film ($t=0.5$, 0.45, and 0.4) on the sapphire (0001) substrate under various applied magnetic fields H. In Figs. 4(a)–4(c) the zero-field-cooled (ZFC) and field-cooled (FC) data are shown. In the ZFC operation, the film was cooled in $H=0$ Oe from 350 to

10 K and magnetization measurements were performed at various H during the temperature rise from 10 to 400 K. The temperature sweep rate in the ZFC operation was 2.5 K/min. In the FC operation, various H were applied to the film at 400 K and then the magnetization was measured while cooling the film from 400 to 10 K. In Fig. 4(a), the $Mg_{1.5}FeTi_{0.5}O_4$ film shows a transition from paramagnetism to ferrimagnetism at 270 K, which corresponds to the Curie temperature T_c. Magnetization measurements exhibit a thermal hysteresis. In $H=50$ Oe, the magnetization in the FC curve increases continuously with decreasing temperature, whereas that in ZFC curve shows a cusp shape at 210 K. On increasing applied fields from 50 to 1000 Oe, the cusp in the ZFC curve tends to shift toward lower temperatures, lose its sharpness, and become a broad maximum. These features are one of the typical characteristics of the spin glass. Interestingly, negative magnetization in the ZFC process has been
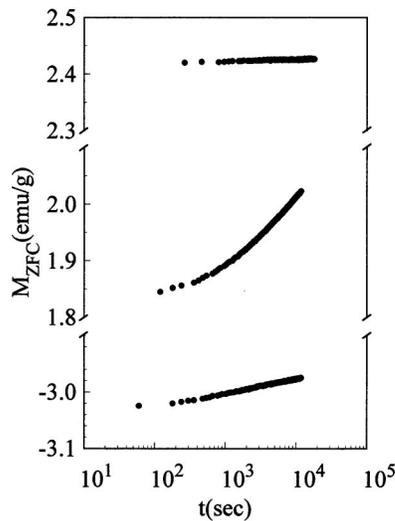
FIG. 5. Time evolution of magnetization M_{ZFC} in the $Mg_{1.5}FeTi_{0.5}O_4$ film on $Al_2O_3(0001)$ at 100 Oe after zero-field cooling from 300 K to 50, 170, and 220 K.

observed below 150 K under $H = 50$ Oe. Similar results have been obtained for the other two films, as is shown in Figs. 4(b) and 4(c). T_c of the $Mg_{1.45}Fe_{1.1}Ti_{0.45}O_4$ and $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film is found to be 300 and 350 K, respectively. The value of T_c increases with decreasing the substituting amount of Ti ions, suggesting the increase of the J value in the films. The cusp is observed in the ZFC curves for both films, and its temperature and shape show the applied magnetic dependence, similar to the case of the $Mg_{1.5}FeTi_{0.5}O_4$ film, showing the character of a spin-glass state. Previously, the spin-glass behavior of $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ ($t = 0.5$, 0.45, and 0.4) has been interpreted as a reentrant spin-glass one.[4] However, we have observed no obvious plateau or steep decrease of the magnetization in the ZFC curves for the ferrite film, which is a characteristic feature of a reentrant spin glass, implying that the film may be in a cluster spin-glass state rather than in the reentrant spin glass, as Muraleedharan *et al.* have mentioned in glassy $Zn_{0.5}Co_{0.5}Fe_2O_4$ ferrite material.[12] For the ferrite film, since the spin-freezing temperature is defined as the cusp temperature in the ZFC curves, T_f in $H = 50$ Oe becomes 210 K for $Mg_{1.5}FeTi_{0.5}O_4$, 260 K for $Mg_{1.45}Fe_{1.1}Ti_{0.45}O_4$, and 310 K for $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film.

The time-dependent isothermal remanent magnetization of the $Mg_{1.5}FeTi_{0.5}O_4$ film was also measured. In this measurement, the film was first cooled from 300 to 50, 170, and 220 K in the ZFC process and then a field of 100 Oe was applied. As soon as the field was applied, measurements were started. Figure 5 shows the plot of magnetization, M_{ZFC} vs $\log(t)$ at 50, 170, and 220 K. A very small change was observed with time at 220 K, but at 170 and 50 K the long-time relaxation characteristic of a spin glass was clearly seen. The temperature of 170 K is below the cusp temperature $T_f(= 210 \text{ K})$ for dc susceptibility [SQUID, see Fig. 4(a)]; hence, the long-time relaxation occurs obviously below T_f.

The spin glass in the ferrite films is also confirmed by the ac susceptibility measurement. Figures 6(a)–6(c) show
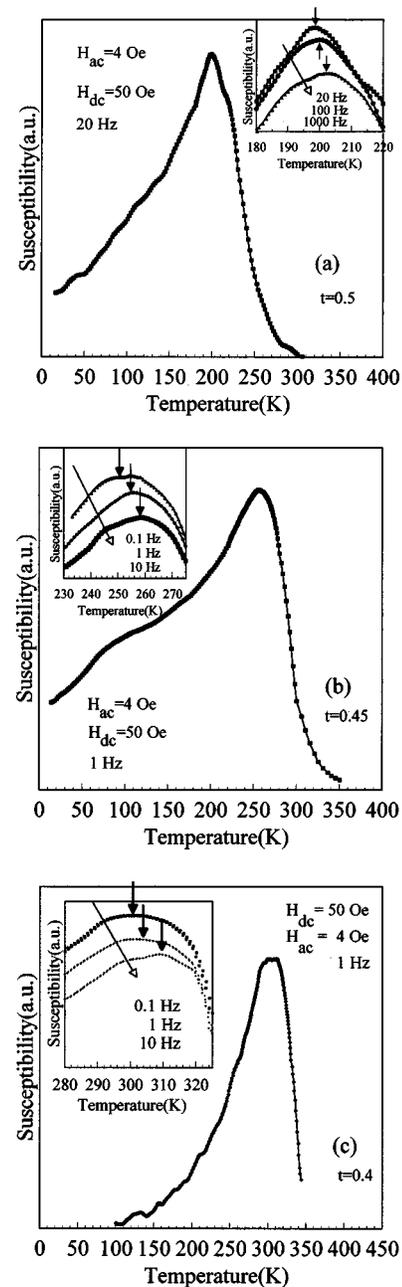

FIG. 6. Temperature dependence of ac susceptibility of the (a) $Mg_{1.5}FeTi_{0.5}O_4$ film, (b) $Mg_{1.45}Fe_{1.1}Ti_{0.45}O_4$ film, and (c) $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film on $Al_2O_3(0001)$ substrates, with an ac field of 4 Oe at a frequency range between 0.1 and 1000 Hz in a superimposed dc field of 50 Oe. The inset displays the ac susceptibility of the films as functions of frequency.

the temperature dependence of ac susceptibility for the $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ film ($t = 0.5$, 0.45, and 0.4) formed on $Al_2O_3(0001)$ substrates, measured under an ac field of 4 Oe at a frequency range between 0.1 and 1000 Hz, with a superimposed dc field of 50 Oe. Measurements were performed in ZFC operation at a temperature sweep rate of 1 K/min. In Fig. 6(a), the susceptibility of the $Mg_{1.5}FeTi_{0.5}O_4$ film increases with increasing temperature, exhibiting a cusp, and then decreases. The cusp temperature is found to be at 200 K, which is consistent with that observed in the dc measurement, as shown in Fig. 4(a). As indicated in the inset of Fig. 6(a), the cusp shows a frequency dependence; it shifts to
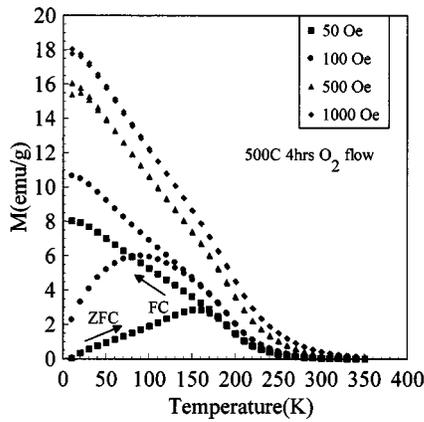
FIG. 7. Temperature dependence of magnetization of the $Mg_{1.5}FeTi_{0.5}O_4$ film on the $Al_2O_3(0001)$ annealed under O_2 atmosphere at 500 °C for 4 h.
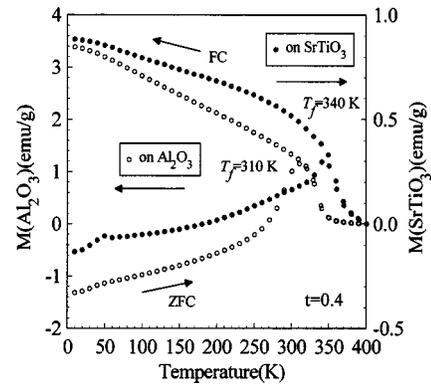

FIG. 8. Temperature dependence of magnetization under $H = 50$ Oe for the $Mg_{1.5}FeTi_{0.5}O_4$ film formed on the $SrTiO_3(111)$ substrate, together with the film on $Al_2O_3(0001)$ substrate.

higher temperatures with increasing frequency. This is another characteristic feature of a spin glass, thus indicating that this film is the spin-glass state below the cusp temperature. The spin-glass behavior is also exhibited in both $Mg_{1.45}Fe_{1.1}Ti_{0.45}O_4$ and $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ films, where the cusp is observed at 258 and 300 K, respectively, as is shown in Figs. 6(b) and 6(c).

B. Oxygen vacancy and strain effects on spin-freezing temperature

T_f of the films is much higher than the reported value for bulk material (22 K).[4] This can be reasonably interpreted as being caused by oxygen deficiencies and stresses in the film. Oxygen vacancies in the film are present because the film is prepared under an ambient oxygen pressure of 1×10^{-5} Torr. Since random oxygen deficiencies in the lattice can change the degree of both randomness and frustration, magnetic spin-glass properties in the films become different from those of the bulk, which are usually prepared under atmospheric oxygen pressure or under air.[21,22] Figure 7 shows the temperature dependence of magnetization of the $Mg_{1.5}FeTi_{0.5}O_4$ film annealed under 1 atom oxygen pressure at 500 °C for 4 h. This film is ferrimagnetic with a T_c of 250 K. Thermal hysteresis is observed between the ZFC and FC curves, and the cusp is found in the ZFC curves under $H = 500$ Oe. The cusp temperature and the shape in the ZFC curves change with increasing applied fields, similar to those observed for the film before oxygen annealing, indicating that the film is still in a spin-glass state. However, the observed cusp temperature in the ZFC curve is 150 K under $H = 50$ Oe and around 10 K under $H = 1000$ Oe, both of which are lower than those obtained in nonoxygen annealing film ($T_f = 210$ K under $H = 50$ Oe). This result indicates that oxygen annealing has the effect of reducing the T_f of the film, in other words, oxygen vacancies in the lattice play an important role in realizing a high T_f of the film. Random distribution of nonmagnetic Ti^{4+} ions in octahedral sites can affect the distribution of Fe ions, which can have a similar effect on T_f to that caused by oxygen deficiencies.

Another possible reason for the difference in the films and the bulk is the lattice mismatch between the substrates

and the thin films. In order to confirm the strain effect, the thin films have been prepared on $SrTiO_3(111)$ substrates, which have a slightly larger lattice mismatch between the substrate and the thin films than those on sapphire. Figure 8 shows the temperature–magnetization curves of the $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film on a $SrTiO_3(111)$ substrate under ap-
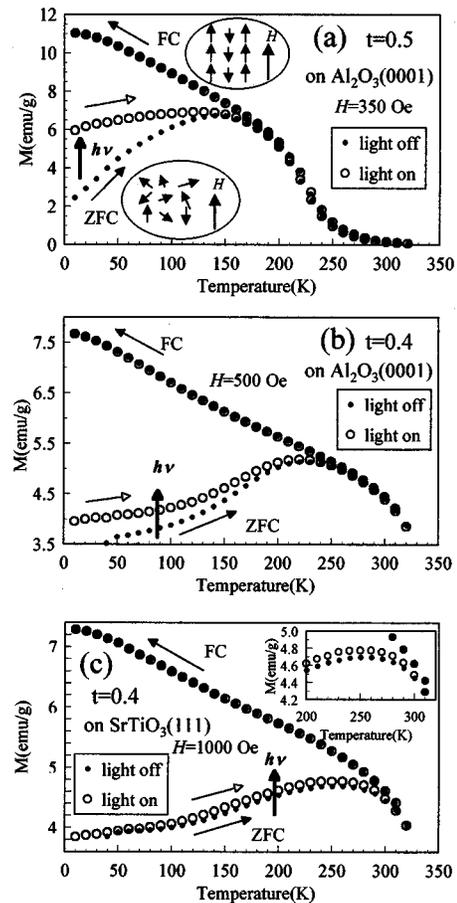

FIG. 9. Temperature dependence of the magnetization without (closed circle) and with (opened circle) light irradiation of (a) the $Mg_{1.5}FeTi_{0.5}O_4$ film on the $Al_2O_3(0001)$ substrate under $H = 350$ Oe, (b) the $Mg_{1.45}Fe_{1.1}Ti_{0.45}O_4$ film on the $Al_2O_3(0001)$ substrate under $H = 500$ Oe, and (c) the $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film on the $SrTiO_3(111)$ substrate under $H = 1000$ Oe.
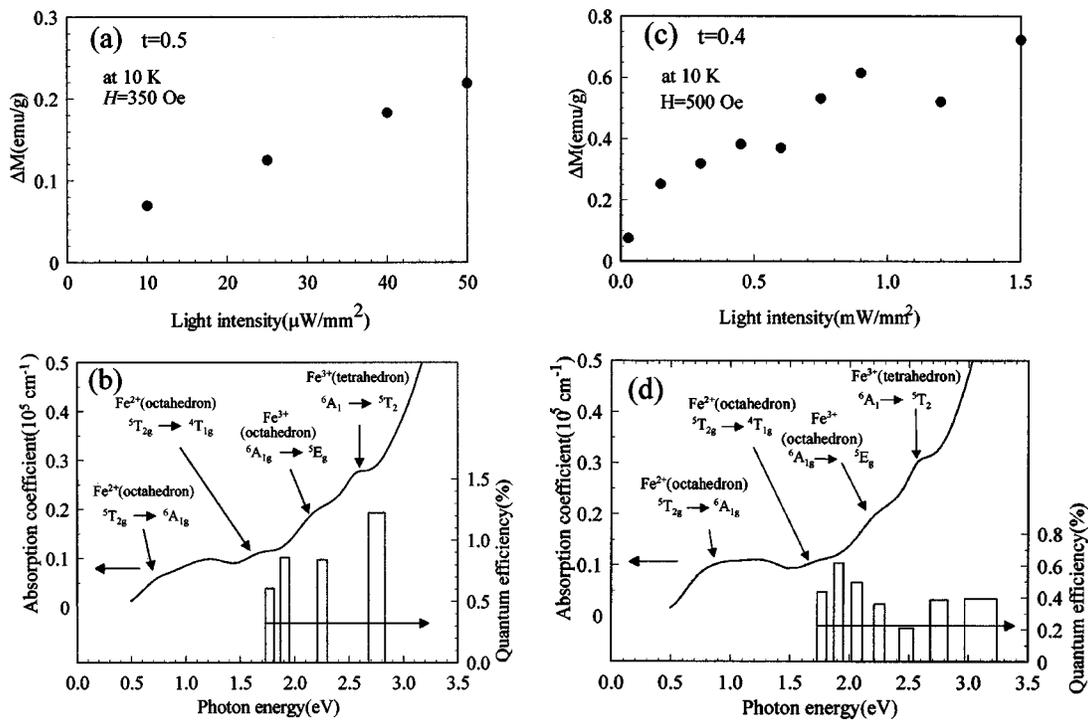
FIG. 10. Light-intensity dependence of the increment of magnetization ΔM for (a) the $Mg_{1.5}FeTi_{0.5}O_4$ film ($H = 350$ Oe) and (c) the $Mg_{1.4}FeTi_{0.4}O_4$ film ($H = 500$ Oe) formed on $Al_2O_3(0001)$ substrates. Measurements were performed at 10 K using a 532 nm double-harmonic YAG laser. ΔM was measured after 50 s of waiting with light irradiation. Optical absorption spectrum at room temperature and quantum efficiency at 10 K for (b) the $Mg_{1.5}FeTi_{0.5}O_4$ film and (d) the $Mg_{1.4}FeTi_{0.4}O_4$ film on $Al_2O_3(0001)$ substrates.

plied fields of $H = 50$, together with the result of the film on an $Al_2O_3(0001)$ substrate. For the film on $SrTiO_3(111)$, T_c is found at around 400 K and the cusp in the ZFC curve is observed at 340 K, which is 30 K higher than that obtained in the film on $Al_2O_3(0001)$. Considering the lattice parameter of the (111) out-of-plane d_{III} of the film on $SrTiO_3(111)$ is determined to be 4.872 (1) Å, which is slightly larger than that of $Al_2O_3(0001)[4.866(1)$ Å], suggesting that more compressive stress is applied to a (111) in-plane film. This compressive stress for a (111) in-plane film makes the bond angle close to 180° between cations on tetrahedral and octahedral sites bridged through an oxygen anion in the spinel lattice, which enhances the exchange interaction J, and therefore, increases T_f of the ferrite film. Another small cusp in the ZFC curves appears around 50 K for the film on $SrTiO_3(111)$, but this cusp temperature does not exhibit a magnetic dependence. The measured T_f is 310 K for the film on the $Al_2O_3(0001)$ substrate, and 340 K for the film on the $SrTiO_3(111)$ substrate, indicating that both films are in the spin-glass state, even at room temperature. T_f of these films is very high. Considering the fact that the energy of the obtained T_f is comparable to that of the phonon frequency region (i.e., a few hundred cm^{-1}), there may be some possibility of using spin-lattice coupling to explain the high T_f of our films.

C. Photoinduced magnetization in spin-glass spinel films

Using light irradiation, we have controlled the spin-glass state of the $Mg_{1+t}Fe_{2-2t}Ti_tO_4$ films ($t = 0.5$, 0.45, and 0.4)

formed on $Al_2O_3(0001)$ and $SrTiO_3(111)$ substrates. White light from a Xe lamp was guided via an optical fiber (200–1060 nm) into a SQUID magnetometer for illumination of the film. The light intensity was 100 $\mu W/mm^2$. The magnetization in the ZFC operation was measured in every step of 10 K from 10 to 320 K at a temperature sweeping rate of 2.5 K/min for both cases, without and with light irradiation. Measurements were started at each appropriate temperature after 10 s of wait for the case without light irradiation and after 30 min of wait for the case with light. By irradiation under a magnetic field, the initial spin-glass state of the ferrite film is expected to change toward the ferrimagnetic state with increasing magnetization, which corresponds to the changes observed between the ZFC and FC curves in Fig. 4. Figure 9(a) shows the temperature dependence of the magnetization of a $Mg_{1.5}FeTi_{0.5}O_4$ film on an $Al_2O_3(0001)$ substrate with and without light irradiation under an applied field of $H = 350$ Oe. Without irradiation, the ZFC curve shows a cusp at 140 K. With light irradiation, the magnetization in the ZFC curve increases with temperature below 160 K, whereas no change is observed in the FC curves. This result suggests that the spin-glass state in this film changes, namely, the melt of the frozen spins in the spin-glass state is accelerated by the irradiation and the glass state approaches the more stable ferrimagnetic state (FC curves). This temperature region is much wider when compared with the previously reported value (up to 2 K).[16–18] Figures 9(b) and 9(c) show the temperature dependence of magnetization with and without light irradiation for the $Mg_{1.45}Fe_{1.1}Ti_{0.45}O_4$ film on $Al_2O_3(0001)$ and the $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film on $SrTiO_3(111)$,

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respectively. In Fig. 9(b), the cusp in the ZFC curve is at 220 K without light irradiation under $H = 500$ Oe. With light irradiation, the increment in magnetization in the ZFC curve is found in a temperature range below 220 K, which becomes 60 K wider than that shown in Fig. 9(a). Interestingly, for the $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film on $SrTiO_3(111)$, such photoinduced magnetization is observed even up to 290 K, as is shown in Fig. 9(c). In other words, the spin-glass state is controlled by the light irradiation up to room temperature.

D. Effect of direct photoexcitation of spins for photoinduced magnetization

The reason for the increase in magnetization, i.e., melting of frozen spins, could be due to the effects of photo- and/or thermal excitation of spins in the lattice. Figure 10(a) shows the amount of a photoinduced magnetization ΔM of a $Mg_{1.5}FeTi_{0.5}O_4$ film on $Al_2O_3(0001)$ as a function of laser light intensity at 532 nm. ΔM increases with increasing light intensity, i.e., photon number. This suggests there is an effect of light-induced spin excitation on the photoinduced magnetization. In the case of film heating due to light irradiation, ΔM should show an exponential light-intensity dependence. However, such a dependence is not observed in Fig. 10(a), meaning that the thermal heating effect is very small or negligible. Actually, the light intensity of 100 μW/mm^2 is weak enough to exclude thermal heating (less than 2 K) as the source of photoinduced magnetization.[17] In order to elucidate the detailed mechanism of photoinduced magnetization, we have measured the optical spectra of the film. Figure 10(b) shows the absorption spectrum at room temperature and the quantum efficiency of the photoinduced magnetization at 10 K of this film. Several broad absorption bands at 0.75, 1.22, 1.70, 2.20, and 2.58 eV are observed in the range between 0.5 and 3.5 eV, which are basically assigned as the $3d^n \rightarrow 3d^{n-1}4s$ process for Fe ions in both the tetrahedral and octahedral sites.[23] The absorption bands at less than 1.0 eV suggest the presence of Fe^{2+} ions in the octahedral site,[24] indicating the existence of oxygen vacancies in the film. The quantum efficiency of this film obtained at 10 K under $H = 350$ Oe is also depicted in Fig. 10(b). It is clearly shown that the photon energy in the visible-light region of the Xe lamp (1.7–3.2 eV) contributes to the photoinduced magnetization, also adding to the evidence that the increase of magnetization under light irradiation occurs due to the photoexcitation of spins. The photoeffect has been checked also for the $Mg_{1.4}Fe_{1.2}Ti_{0.4}O_4$ film on $Al_2O_3(0001)$, and similar results have been obtained, as is shown in Figs. 10(c) and 10(d).

IV. CONCLUSIONS

In conclusion, we have shown the high-spin-freezing temperature T_f, even above room temperature, in $(Mg, Fe) \times \{Mg, Fe, Ti\}_2O_4$ film formed on $Al_2O_3(0001)$ and $SrTiO_3(111)$ substrates. The spin-glass state is confirmed by a long-time relaxation of the magnetization in the zero-field-cooled operation and an ac susceptibility measurement, which shows a frequency dependence of the cusp temperature. The high-spin-glass state has been achieved due to the random oxygen vacancies in the film and the strain effect introduced by the film/substrate lattice mismatch. We have also demonstrated a photocontrol of the spin-glass state even up to room temperature in the ferrite film. The photon energy in the visible-light region has been found to contribute to the increase in magnetization, showing evidence of the effect of direct photoexcitation of spins for photoinduced magnetization.

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