Magnetic properties of ilmenite-hematite solid-solution thin films: Direct observation of antiphase boundaries and their correlation with magnetism

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To clarify the relationship between nanostructures and magnetic properties of FeTiO3-Fe2O3 solid-solution thin films, we have carried out dark-field transmission electron microscope (DF-TEM) and high-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) observations. The ordered-phase films show strong ferrimagnetic properties while the films identified as the disordered phase according to x-ray diffraction are weakly ferrimagnetic with high saturation fields, in contrast to completely disordered FeTiO3-Fe2O3 solid solution for which antiferromagnetic properties or rather small magnetizations are expected. The DF-TEM and HAADF-STEM observations revealed that the ordered-phase films typically consist of cation-ordered domains of over 200 nm and that the Fe and Fe-Ti layers stacked alternately along the c axis, which leads to strong ferrimagnetic properties, are clearly distinguishable from each other. On the other hand, the films identified as the disordered phase are found to possess short-range ordered structure with antiphase boundaries distributed in cation-disordered matrix, rather than completely random cation distribution, explaining why the films are weakly ferrimagnetic with high saturation fields. The results demonstrate the significance of atomic-level observation of the cation distribution in this system for understanding the magnetic properties.

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I. INTRODUCTION

A series of solid solutions between ilmenite (FeTiO3) and hematite (α-Fe2O3) occurs as accessory minerals in igneous and metamorphic rocks and are significant bearers of natural remanent magnetization. Also, members of FeTiO3-Fe2O3 solid solutions have received revived interest as novel spintronics materials recently1–7 because of their unique magnetic and electronic properties.8,9 In this system, the magnetic properties are mainly influenced by two processes: (1) cation ordering in the FeTiO3-rich compositions; (2) exsolution or phase separation in intermediate compositions.10 Such peculiar properties are considered to originate from an interesting similarity in crystal structures with different symmetry between FeTiO3 and α-Fe2O3.

FeTiO3 has a corundum-type structure, wherein oxide ions form a distorted hexagonal close packing and Fe ions occupy two thirds of the available octahedral interstices forming Fe layers along the c axis. FeTiO3 adopts a corundum-derivative structure where Fe layers in α-Fe2O3 are alternately replaced by Ti layers. For their solid solutions, two crystalline phases, i.e., ordered and disordered phases, are generally considered depending on the cation distribution. In the ordered phase, Fe+Ti layers and Fe layers are alternately stacked along the c axis. On the other hand, all the cations are randomly distributed in the disordered phase. Ferrimagnetic properties should be observed only in the ordered phase since the negative exchange coupling between adjacent layers usually results in antiferromagnetic properties for the disordered phase.

The ordered phase and disordered phase of FeTiO3-Fe2O3 solid solutions are related to each other via a phase transition in the cation ordering. Upon rapid cooling through the transition temperature, the reduction in symmetry of R3c to R̄3 often leads to the formation of nanoscale antiphase domains (APDs); each domain is composed of the ordered phase with an alternative sequence of Fe+Ti layers and Fe layers, while adjacent domains are separated by cation-disordered antiphase domain boundaries (APBs). The APBs are generally believed to be responsible for the unusual magnetic properties such as the tendency to acquire the self-reversed theromagneticization (SR-TRM).11–13 Namely, the local distribution of Fe and Ti strongly affects the magnetic properties of the solid solutions. Until now, the local cation distribution has been proposed to explain the magnetic anomalies based on conventional transmission electron microscope (TEM) and neutron-diffraction analysis with the aid of computational calculations10–12,14,15; however, spatially selective atomic-level observations are required to clarify the unique cation distribution more definitely, especially at the APBs, and also to understand more comprehensively the magnetic properties of this system.

Recent studies on FeTiO3-Fe2O3 solid-solution thin films have also revealed that the magnetic properties are often inconsistent with those expected from structural analysis using x-ray diffraction (XRD).2,6,10 For example, Droubay et al.2 have fabricated xFeTiO3·(1–x)Fe2O3 (x ≤ 0.15) thin films by a molecular-beam epitaxy method and observed non-negligible magnitude of magnetization for the films characterized as the disordered phase by the XRD pattern. Although the precise atomistic structures are not known, the unusual magnetic properties are presumably associated with the inhomogeneous cation distribution in the crystal. It is not anticipated that detection of the inhomogeneity of cation dis-
tribution utilizing XRD is easy because XRD patterns only
give spatially averaged information of cation distribution and
the difference in x-ray scattering factor between Fe and Ti is
small.

On the other hand, recent development of aberration-
corrected scanning transmission electron microscopy (STEM)
using a high-angle annular dark-field (HAADF) de-
tector achieves a spatial resolution at atomic level for imaging.
In a HAADF image, the intensity of each atomic column,
that is, a series of atoms aligned along the incident
electron-beam direction, is approximately proportional to the
square of atomic number, $Z^2$.17 which generally allows the
qualitative interpretation of the images.

In this study, we report on the dark-field transmission electron microscope (DF-TEM) and HAADF-STEM obser-
vations for two kinds of FeTiO$_3$-Fe$_2$O$_3$ solid-solution thin films, which are identified as the ordered and disordered
phases by XRD analysis, respectively. Despite the rather
small difference in average atomic number between Fe and
Fe-Ti columns, we distinctly identified the atomic struct-
tures of these films by the DF-TEM and HAADF-STEM
images. Through the observations, we can explain why the
films identified as the disordered phase are weakly ferri-
magnetic with high saturation fields.

II. EXPERIMENTAL

Our samples are thin films of solid solutions with com-
positions of $x$FeTiO$_3$-$(1-x)$Fe$_2$O$_3$ ($x=0.6$ and 0.8) epitaxially
grown on c-plane sapphire (0001) substrates by a pulsed la-
sar deposition method. The thin films with the ordered phase
can be obtained by adjusting the oxygen pressure ($P_{O_2}$) and
substrate temperature ($T_S$).18-20 In this study, the ordered-
phase thin films were grown under conditions that $P_{O_2}=2.0$
$\times 10^{-3}$ Pa and $T_S=700$ °C. For comparison, we also pre-
pared thin film at $P_{O_2}=2.0\times 10^{-3}$ Pa and $T_S=600$ °C. After
the deposition, all the samples were rapidly cooled to room
temperature (cooling rate: 70 °C/min) while keeping $P_{O_2}$
constant. XRD analysis with Cu $K\alpha$ radiation was carried out
to identify whether the resultant films were ordered or
disordered. Magnetization data were obtained by a supercon-
ducting quantum interference device. DF-TEM observations
were conducted on a JEOL JEM-2100HC. STEM observations
were carried out at room temperature by using JEOL
JEM-2100F equipped with a CEOS aberration corrector and a
Gatan Enfinia electron-energy-loss spectroscopy (EELS)
spectrometer. The probe-forming semiangle and EELS detec-
tor collection semiangle were around 27 and 23.6 mrad, re-
spectively. Samples for TEM and STEM observations were
prepared by mechanical polishing, dimpling, and Ar ion mill-
ing so that the electron transparency could be obtained. To
minimize the surface damage, the final cleaning was per-
formed by ion milling at 1 kV.

III. RESULTS AND DISCUSSION

Figure 1(a) displays the XRD patterns of $x$FeTiO$_3$-$(1$
$-x)$Fe$_2$O$_3$ ($x=0.6$ and 0.8) solid-solution thin films grown at
$T_S=600$ and 700 °C. It is known that 0003 and 0009 diffra-
ction peaks, as well as 0006 and 00012 peaks, are observed
for the ordered phase, while the 0003 and 0009 diffraction
peaks disappear due to the systematic absence in the disor-
dered phase. For the thin films grown at $T_S=700$ °C, 0003
and 0009 diffraction peaks are present clearly indicative of
the formation of ordered phase. Hereafter we will refer to the
0003 and 0009 diffraction peaks as “order peaks”. For the
thin film grown at $T_S=600$ °C, on the other hand, the ab-
sence of the order peaks suggests the formation of disordered
phase. Obviously, an increased atomic mobility during the
film growth at higher $T_S$ is required to attain the ordered
atomic arrangement. Temperature dependence of magnetiza-
tion of each film is shown in Fig. 1(b). The measurements
were performed under field-cooled condition with an exter-
nal magnetic field of 8500 Oe applied parallel to the film
surface. The films of the ordered phase show strong ferri-
magnetic behavior as reported earlier.19,20 Interestingly, the
thin film identified as a disordered phase by XRD is also
ferromagnetic and possesses high magnetization; it reaches
half of the magnetization of ordered phase with the same
composition. This behavior is inconsistent with the com-
pletely disordered FeTiO$_3$-Fe$_2$O$_3$ solid solution for which an-
tiferromagnetism or rather small magnetizations is expected.
Magnetic field dependence of magnetization measured at 300
K, as shown in Fig. 1(c), gives further insight into the nature
of the magnetism for the film without the order peaks. In
contrast to the magnetization of the film with the order peaks
[closed circles in Fig. 1(c)], the magnetization of the film
without the order peaks [open circles in Fig. 1(c)] is not
saturated up to high magnetic field. It should also be noted
that coercivity at 2 K (not shown) is higher for the film with
the order peaks (~2000 Oe) than for the film without the
order peaks (~1700 Oe). Such features were often observed
in FeTiO$_3$-Fe$_2$O$_3$ solid solution and linked to the presence
of APBs, at which the magnetic domain walls become pinned.21

FIG. 1. (a) XRD patterns of $x$FeTiO$_3$-$(1-x)$Fe$_2$O$_3$ [$x=0.6$ (filled circles) and $0.8$ (gray circles)] solid-solution thin films prepared under the optimized deposition conditions to obtain the ordered phase ($P_{O_2}$ of $2.0\times 10^{-3}$ Pa and $T_S=700$ °C) along with the pat-
tern of $0.6$FeTiO$_3$-0.4Fe$_2$O$_3$ solid-solution thin film prepared at $T_S$ of $600$ °C (open circles). (b) Temperature dependence of magneti-
zation of each film. (c) Magnetic field dependence of magnetization
at 300 K.
Non-saturating behavior of magnetization has also been reported for Fe$_2$O$_3$ films grown on MgO substrates, and the modified superexchange interactions at the APBs are suggested to be the origin of such anomaly. Thus, the effect of APBs on the magnetic properties may be significant for the film without the order peaks; however, there are no reports in which one has directly observed the APBs of solid solution. APBs on the magnetic properties may be significant for the degree of phase separation, as discussed in Ref. 23, because the disordered phase is antiferromagnetic. Moreover, magnetic interactions between the cation-ordered domains need to be considered. When cation-ordered domains are randomly distributed in the cation-disordered matrix, two types of arrangement, in-phase and out-of-phase arrangements, are possible in neighboring domains depending on the relative position of cation layers. In the out-of-phase arrangement, where the position of Fe and Fe-Ti layers are interchanged across the two neighboring domains, negative exchange coupling is expected as in the APBs regardless of the thickness of cation-disordered matrix reducing the magnetization of the sample. Figure 2 clearly demonstrates that the use of only XRD for crystal structural analysis of the solid solutions leads to misunderstanding of the nanostructures. However, the precise atomistic structures of the cation-ordered domains and the interfaces between cation-ordered domains and cation-disordered matrix are hard to determine only by the DF-TEM image. High spatial resolution is necessary to investigate the atomistic structures of the present solid solution.

Thus, in order to identify the cation distribution in the solid solution, atomic-level observations have been performed for the cation-ordered domains using HAADF-STEM. Figure 3(a) shows the HAADF-STEM images of $x$FeTiO$_3$ · $(1-x)$Fe$_2$O$_3$ ($x=0.6$ and $0.8$) solid-solution thin films with the order peaks in the [110] projection. A projected illustration of the atomic arrangement of the ordered FeTiO$_3$·Fe$_2$O$_3$ solid solution is also shown in the left side of Fig. 3(a) for direct comparison. Figure 3(b) depicts the intensity profile extracted from Fig. 3(a). Only pairs of atomic columns of cations are visible, while atomic columns for oxide ion have no contrast at all because of too small Z. Interestingly, the HAADF signal intensities at the pairs of cation columns exhibit clear systematic variation along the c axis for both thin films with compositions of $x=0.6$ and $0.8$. This variation in HAADF signal intensity is ascribable to the presence of the ordered structure, where the positions showing higher and lower intensity correspond to Fe and Fe-Ti columns, respectively. Statistical analysis on several parts of each film has revealed that the average intensity ratios of neighboring brighter and darker columns are 1.11 ~ 1.14 for $x=0.6$ and 1.22 ~ 1.27 for $x=0.8$. This result reflects the fact that the Ti ratio in Fe-Ti layers is higher for $x=0.8$ and, hence, the difference in the average Z between Fe layers and Fe-Ti layers is higher for $x=0.8$. To obtain atomistic information, EELS signals were taken for the film of $x=0.6$ with the STEM probe positioned over each pair of atomic columns [0.2 nm x 0.1 nm in size as shown in Fig. 3(a)]. The regions 1 and 2 correspond to the brighter and darker pairs of atomic columns. As expected, a higher Fe signal and a lower
showed for direct comparison. Black and gray spheres correspond to distribution inside the cation-ordered domains. Figures 4 peaks in XRD pattern to obtain an insight into the cation arrangement of the ordered FeTiO$_3$-Fe$_2$O$_3$ solid solution is also. Intensity profiles extracted from the rectangles of white solid line in 3 Ti signal were observed at brighter spot as shown in Fig. 0.6FeTiO$_3$ ·0.4Fe$_2$O$_3$ solid-solution thin film without the or-tigate cation distribution in the solid solution.

The HAADF-STEM investigation was also performed for 0.6FeTiO$_3$-0.4Fe$_2$O$_3$ solid-solution thin film identified as a disordered phase by XRD. The regions where the reversal of the periodicity in intensity variation occurs. Intensity profiles extracted from long rectangles in (b) are shown in (c) and (d). The regions where the reversal of the periodicity in intensity variation occurs are superimposed on (b) as lines and small rectangles. The boundary is roughly surrounded by thick dotted lines as a guide for the eye.

Our sample is smaller than that estimated from DF-TEM images. Harrison et al. suggested that when the size of APDs is less than approximately 50 nm, the exchange coupling across APBs is negative in the absence of magnetic wall inside the APDs. This situation is the case with our sample and leads to a further decrease in the magnetization. Furthermore, the slightly lower degree of ordering inside the APDs by itself contributes to the decrease in the order peaks in XRD accompanied by the reduction in the magnetization. Consequently, the anomalous magnetic behavior of the film identified as the disordered phase by XRD is attributable to the presence of cation-ordered domains distributed in cation-disordered matrix as well as the presence of APBs. The x-ray takes it as a disordered phase due to the short-range nature of the cation-ordered domains.

Detailed analysis of intensity profile across the APB provides a new insight into the nature of the APB. Although darker columns are located side by side across the boundary at some parts of the APB [Fig. 4(d)], large part of the atomic columns in the APB are relatively bright with small intensity variations [Fig. 4(c)] indicating that the APB is rich in Fe and possess a disordered cation distribution. Moreover, we can also find that the APB is rather diffuse; the positions where the reversal of the periodicity in intensity variation occurs are scattered in the APB. Such features found in the APB are qualitatively consistent with those predicted by Monte Carlo simulations. However, the interpretation of the HAADF image does not seem so straightforward because the boundary is not always located parallel to the thickness direction. For example, when an APB is tilted, it should give relatively bright region with small intensity variation in a HAADF image. Further systematic experiments should be carried out to explore the nature and distribution of the APBs and their relationship with the magnetic properties such as SR-TRM.
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IV. CONCLUSIONS

In conclusion, we have performed DF-TEM and HAADF-STEM observations on the FeTiO$_3$-Fe$_2$O$_3$ solid-solution thin films to clarify the relationship between the atomistic structures and the magnetic properties. Despite the rather small difference in average atomic number between Fe and Fe-Ti columns, we successfully observed the ordered structure in the HAADF image and EELS. Interestingly, such ordered columns, we successfully observed the ordered structure in the HAADF image and EELS. These results demonstrate the significance of atomic-level observation for the cation distribution to interpret the magnetic properties of this system. The present experimental techniques will be useful to clarify further curious magnetic properties of the FeTiO$_3$-Fe$_2$O$_3$ system such as anomalous magnetic properties suggested to stem from unique cation distribution at the interface of nano-scale FeTiO$_3$ and Fe$_2$O$_3$ exsolution lamellae.\textsuperscript{25,26}

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