Room temperature ferromagnetic behavior in the hollandite-type titanium oxide

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A hollandite-type KxTi8O16 polycrystalline sample has been prepared and studied by magnetization, resistivity and x-ray photoelectron spectroscopy (XPS). Room temperature ferromagnetic behavior is observed in the magnetic hysteresis measurement. The sample shows a semiconductive temperature dependence in the resistivity measurement. Analysis of the Ti 2p3/2 core-level XPS spectrum indicates that the titanium ions have a mixed valence of Ti4+ and Ti3+. In addition, the valence band spectrum reveals that the 3d electrons tend to localize on Ti3+ ions in the hollandite-type TiO2 lattice. Also, analysis of the valence band spectrum shows that the prepared sample is a wide-gap oxide with a band gap of 3.6 eV. These results indicate that the present hollandite-type KxTi8O16 sample can be classified as a TiO2-based wide-gap semiconductor with Curie temperature above room temperature. Room temperature ferromagnetism (RTFM) decreases in the sample prepared under a strong reducing gas atmosphere, accompanied with the decrease in the resistivity. The results imply that the localized 3d electrons are responsible for the RTFM of the KxTi8O16 sample. © 2010 American Institute of Physics. [doi:10.1063/1.3369500]

I. INTRODUCTION

Titanium dioxide TiO2 is a well-known material and has technologically important properties such as excellent optical transmittance in visible and near-infrared region, high refractive index and high dielectric constant. Recently, Matsumoto et al.1 discovered room temperature ferromagnetism (RTFM) in Co-doped anatase TiO2 thin film. Since that discovery, many materials with anatase (A) and rutile (R)-type TiO2 structures have been developed in the form of film2-3 and bulk4,5 and their magnetic properties have been studied. So far, RTFM is observed when A and R-type TiO2 are doped with transition metal ions,2,4 and even when pure A and R-type TiO2 are reduced6,7 or implanted by Ar and N ions.8 Now it is believed that TiO2 has an additional physical property of ferromagnetism and is a potential material in an application field of spintronics devices. Concerning the mechanism of RTFM, it is considered that oxygen vacancies play an important role as the origin of RTFM.3,5,9,10 It is also speculated that in some systems11,12 carriers introduced into the lattice are essential for the appearance of RTFM. Although numerous studies have been claimed ferromagnetism above room temperature, the precise mechanism responsible for this behavior is subjected to debate.

It is very interesting and important to develop a new member of TiO2-based RTFM because new material can provide valuable information for understanding the underlying physics of RTFM and also extend the possibility to develop the TiO2-based devices for spintronics applications.

Hollandite-type TiO2 is one of polymorphs in titanium dioxides and consists of a one-dimensional tunnel structure surrounded by interlinking of edge-shared TiO6-octahedral units as shown in Figs. 1(a) and 1(b). The general formula of the hollandite-type titanium oxide is given as A3Ti8O16 (0 ≤ x ≤ 2), where A represents the ions such as Li+, K+, and Cs+. The A cations occupy the tunnel, resulting in a mixed valence of titanium ions as Ti4+ and Ti3+ to preserve charge balance. Since interaction between the cations and hollandite-type TiO2 framework is weak, the cations can be easily intercalated into and deintercalated from the tunnel with keeping intact the overall original structure. Because of the unique microporous feature, hollandite-type TiO2 has been studied from the viewpoint of crystal structure13 and application such as battery characteristics14,15 and immobilization of radioactive elements.16

FIG. 1. (Color online) Crystal structure of hollandite-type A3Ti8O16 (A represents ions such as Li+, K+, and Cs+) projected (a) along a axis and (b) along c axis. Each octahedron corresponds to the TiO6 unit. Crystal structures were illustrated with the program VESTA (Ref. 27).

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The hollandite-type TiO₂ framework is composed of edge and corner-shared TiO₆ octahedron as A and R-type TiO₂ structures are composed. In addition, this material possesses the 3d electron in Ti³⁺ ion (3d⁰) which is an important source of magnetic moment. These characteristics let us have expectation of an appearance of interesting physical properties such as RTFM as seen in A and R-type TiO₂ system. Until now, there are few reports on the physical properties of K₁ₓTi₈O₁₆ and studied the magnetic and electric properties. 

II. EXPERIMENT

Polycrystalline KₓTi₈O₁₆ sample was synthesized by solid-state reaction. Powders of K₂CO₃ and R-type TiO₂ were mixed with the mol ratio of K₂CO₃:TiO₂=1:9 and pressed into a pellet, then calcined at 1050 °C for 10 h under a H₂/Ar (5%/95%) gas atmosphere. After calcination, dark-blue color sample was obtained. The prepared sample was examined by powder x-ray diffraction (XRD) using monochromated Cu Kα radiation (Rigaku RINT-2000/PC). The unit-cell parameters were determined from the observed d-spacing by the least-squares method. Metal ratio of K/Ti in the sample was examined by energy dispersive x-ray (EDX) analysis. Both thermogravimetric and differential thermal analyses (TG-DTA) were done using a Rigaku TG8120. Magnetic measurements were performed using a superconducting quantum interference device magnetometer (Quantum Design MPMS). Resistivity measurements were carried out using a standard four-point probe method in a physical property measurement system (Quantum Design PPMS). XPS measurements were performed at SPring-8 BL27SU. Monochromated x-ray of 1300 eV was used for measurements and the total energy resolution was 370 meV. The KₓTi₈O₁₆ sample was fractured in situ before measurements. The Fermi level position was determined by measuring the total energy resolution was 370 meV . The obtained value is similar to the valence state of Ti³⁺ other than Ti⁴⁺. Figure 3 shows a TG-DTA curve of the prepared sample measured at a heating rate of 5 °C/min in flowing air. A remarkable weight decrease was observed up to 120 °C. This weight loss was due to the desorption of absorbed water from the sample. The weight decreased slightly up to 390 °C, and then a weight increase started. The weight increased up to 580 °C, and then became almost constant. The weight decrease was again observed from 900 °C. On the other hand, an exothermic peak was observed at 600 °C. The obtained results are in good agreement with those in previous report. The weight increase between 390 and 580 °C occurs due to oxidation of the sample. Since the oxidized sample is found from XRD analysis to have a hollandite form, it is plausible that the oxygen is taken into the sample to compensate for the oxygen vacancies in the hollandite lattice. The results of TG-DTA measurements suggest the presence of certain amount of oxygen vacancies in the prepared sample.

III. RESULTS AND DISCUSSION

Figure 2 shows the powder XRD pattern of the prepared sample. By XRD analysis, this sample was found to be a single phase. The XRD pattern was similar to that of K₁.₃₅Ti₈O₁₆ in the Joint Committee for Powder Diffraction Standard files (No. 47–690) and indexed with a tetragonal cell. The a and c parameters of the sample were determined to be a=10.193 Å and c=2.966 Å. These values are in good agreement with those of previous work. Metal ratio in the sample was determined from EDX analysis to be K/Ti = 1.46/8. Assuming that there is no oxygen vacancy in the sample, the chemical formula of the sample can be represented as K₁.₄₆Ti₈O₁₆. The calculated average valence of titanium ions is +3.82, indicating the existence of low valence state of Ti³⁺ other than Ti⁴⁺. Figure 3 shows a TG-DTA curve of the prepared sample measured at a heating rate of 5 °C/min in flowing air. A remarkable weight decrease was observed up to 120 °C. This weight loss was due to the desorption of absorbed water from the sample. The weight decreased slightly up to 390 °C, and then a weight increase started. The weight increased up to 580 °C, and then became almost constant. The weight decrease was again observed from 900 °C. On the other hand, an exothermic peak was observed at 600 °C. The obtained results are in good agreement with those in previous report. The weight increase between 390 and 580 °C occurs due to oxidation of the sample. Since the oxidized sample is found from XRD analysis to have a hollandite form, it is plausible that the oxygen is taken into the sample to compensate for the oxygen vacancies in the hollandite lattice. The results of TG-DTA measurements suggest the presence of certain amount of oxygen vacancies in the prepared sample.
be explained on the hypothesis that a small fraction of Ti$^{3+}$ ions is responsible for the observed ferromagnetism and a large fraction of Ti$^{3+}$ ions is contributed to the paramagnetism. A mixture behavior of multiple magnetic interactions was reported in oxide diluted magnetic semiconductors such as Mn-doped ZnO nanoparticles. The magnetic hysteresis still remains at 350 K, indicating that the Curie temperature of the sample is higher than 350 K. One may think the possibility of the impurity’s contribution to the ferromagnetism. Such possibility can be excluded because no impurity phases are observed by XRD measurements, and also because even though a tiny amount of K–Ti–O related impurity phases are included in the sample such phases do not exhibit ferromagnetism at room temperature. Thus, we conclude that the observed RTFM can be attributed to be intrinsic due to the corporation of Ti$^{3+}$ ions into the hollandite-type TiO$_2$ lattice.

Figure 5 shows the temperature dependence of resistivity $\rho$ for the K$_{1.46}$Ti$_8$O$_{16}$ sample. The sample exhibits the semiconductive temperature dependence with negative $d\rho/dT$. The experimental data was analyzed by using the formula for variable range hopping (VRH) expressed as $\rho(T) = \rho(T_0)\exp(T_0/T^{1/(d+1)})$, where $T_0$ is a characteristic temperature and $d$ is the dimensionality of the system. As shown in the inset of Fig. 5, fit with $d=3$ was successful at the temperature range between 190 and 380 K. This indicates that the dominant conduction mechanism is three-dimensional VRH. However, we should be careful about conclusion because the polycrystalline sample is used for the measurement. For a conclusion of the conduction mechanism, we need to carry out the measurement using single crystal sample.

In order to evaluate the valence state of the Ti ions in the sample, XPS measurements were performed. Figure 6(a) shows the wide scan of XPS spectrum of the sample. The three constituent elements, K, Ti, and O can be readily identified as carbon contamination can. No peak related to the magnetic impurity such as iron was observed within the de-
tection limit (0.1 at. %), supporting that the observed ferromagnetic behavior originates from K$_{1.46}$Ti$_3$O$_{16}$. Figure 6(b) shows the Ti 2$p_{3/2}$ core-level spectrum of the sample. The spectrum showed a peak structure with a shoulder at lower binding energy. The peak was deconvoluted into two symmetric peaks; main peak was at the binding energy of 459.4 eV and the other small peak was at 457.9 eV. The main peak is attributed to the Ti$^{4+}$ state. The small peak separated by 1.5 eV from Ti$^{4+}$ state can be ascribed to the Ti$^{3+}$ state.22 There is no peak from Ti$^{2+}$ state (peak separation from Ti$^{4+}$ is more than 3 eV). This result indicates that the Ti ions take two kinds of valence state of Ti$^{4+}$ and Ti$^{3+}$. The ratio of Ti$^{4+}$/Ti$^{3+}$ is estimated from the peak area of Ti$^{4+}$ and Ti$^{3+}$ state to be 88/12 which corresponds to the average valence of Ti ions of +3.88. The estimated average valence of Ti ions is in good agreement with that from the EDX analysis. Figure 6(c) shows the valence band spectrum for the sample. The valence band spectrum showed a two-peak structure. A peak located at 8 eV is mainly due to the Ti 3d band and the other peak situated at 5.8 eV is mainly due to the O 2p band. The origin of the peak structures is examined by our resonant photoemission spectroscopy measurements (not shown in the paper). A small but distinct peak was observed at around 0.8 eV below the Fermi level. This peak originates from the Ti 3d state.23 The presence of the Ti 3d state is consistent with the result that the Ti$^{3+}$ state is observed in the Ti 2$p_{3/2}$ core-level spectrum. The Ti 3d state had a narrow band width and no intensity at the Fermi level. This means that the 3d electrons tend to localize on the Ti$^{3+}$ ions in the hollandite-type TiO$_2$ lattice. The localized character of the 3d electrons is seen in the result of resistivity measurement where the semiconducting behavior is observed. Such localized unpaired 3d electrons in Ti$^{3+}$ ions can lead to the magnetic moment and a part of them must be contributed to the ferromagnetic behavior as mentioned in Fig. 4. In this sample, assuming that the Fermi level is pinned just below the conduction band,24 this sample is expected to show the magnetic moment at around 0.8 eV below the Fermi level. This peak originates from the Ti 3d state.23 The presence of the Ti 3d state is consistent with the result that the Ti$^{3+}$ state is observed in the Ti 2$p_{3/2}$ core-level spectrum. The Ti 3d state had a narrow band width and no intensity at the Fermi level. This means that the 3d electrons tend to localize on the Ti$^{3+}$ ions in the hollandite-type TiO$_2$ lattice. The localized character of the 3d electrons is seen in the result of resistivity measurement where the semiconducting behavior is observed. Such localized unpaired 3d electrons in Ti$^{3+}$ ions can lead to the magnetic moment and a part of them must be contributed to the ferromagnetic behavior as mentioned in Fig. 4.24 In this sample, assuming that the Fermi level is located at the bottom of the conduction band, the band gap can be estimated from the binding energy of the top of valence band to be 3.6 eV. This band gap is slightly larger compared with values of A and R-TiO$_2$ (3.2 and 3.0, respectively) and thus, K$_{1.46}$Ti$_3$O$_{16}$ is found to be classified in the hollardite-type TiO$_2$ lattice. The sample prepared under a H$_2$/Ar gas atmosphere, larger number of oxygen vacancies can be introduced in the hollandite-type TiO$_2$ lattice for sample-H100. We measured the resistivity and magnetic hysteresis loop for sample-H100 and compared the results with those for sample-H5. Figure 8(a) shows the temperature dependence of resistivity for sample-H100 together with the data of sample-H5 (same as the data of Fig. 5). Sample-H100 shows a semiconducting behavior and is more conductive compared with sample-H5. The smaller resistivity suggests that the introduced oxygen vacancies play a role as n-type doping. An interesting change is observed in the magnetic hysteresis measurement. Figure 8(b) shows the magnetic hysteresis loop at room temperature for sample-H100 together with that for sample-H5 (same as the data of Fig. 4). As seen in the figure, paramagnetism was dominant for sample-H100 although the trace of the ferromagnetism was observed. A saturation magnetization for the ferromagnetic component estimated by subtracting the paramagnetic component was $1.5 \times 10^{-3}$ emu/g. It is obvious that the ferromagnetism decreases compared with sample-H5. The result indicates that partial H$_2$ pressure during sample preparation is one of key parameters for the appearance of the ferromagnetic behavior. It is also found from the results that the ferromagnetism tends to suppress when the sample becomes conductive. This implies that the ferromagnetism stems from the localized 3d electrons in the hollandite-type TiO$_2$ lattice. This picture is different from the case in Co or Fe-doped TiO$_2$ (Refs. 11 and 12) where the 3d electron carriers induce ferromagnetism.

The origin of RTFM of the present hollandite-type K$_{1.46}$Ti$_3$O$_{16}$ is the critical issue to be solved. Our results imply that the localized 3d electrons are responsible for the ferromagnetism of K$_{1.46}$Ti$_3$O$_{16}$. In order to confirm the implication, we intend to study the microstructure of the sample by means of electron spin-resonance spectroscopy. The result will provide information on the origin of the magnetic moment in K$_{1.46}$Ti$_3$O$_{16}$. We also plan to do the measurements of weight increase because of oxidation between 390 and 570 °C, indicating the presence of oxygen vacancies in the sample. The weight increase was found to be 0.50%. The value is larger compared with the case for sample-H5 (0.41%). Since sample-H100 is prepared under a strong reducing gas atmosphere, larger number of oxygen vacancies can be introduced in the hollandite-type TiO$_2$ lattice for sample-H100. We measured the resistivity and magnetic hysteresis loop for sample-H100 and compared the results with those for sample-H5. Figure 8(a) shows the temperature dependence of resistivity for sample-H100 together with the data of sample-H5 (same as the data of Fig. 5). Sample-H100 shows a semiconducting behavior and is more conductive compared with sample-H5. The smaller resistivity suggests that the introduced oxygen vacancies play a role as n-type doping. An interesting change is observed in the magnetic hysteresis measurement. Figure 8(b) shows the magnetic hysteresis loop at room temperature for sample-H100 together with that for sample-H5 (same as the data of Fig. 4). As seen in the figure, paramagnetism was dominant for sample-H100 although the trace of the ferromagnetism was observed. A saturation magnetization for the ferromagnetic component estimated by subtracting the paramagnetic component was $1.5 \times 10^{-3}$ emu/g. It is obvious that the ferromagnetism decreases compared with sample-H5. The result indicates that partial H$_2$ pressure during sample preparation is one of key parameters for the appearance of the ferromagnetic behavior. It is also found from the results that the ferromagnetism tends to suppress when the sample becomes conductive. This implies that the ferromagnetism stems from the localized 3d electrons in the hollandite-type TiO$_2$ lattice. This picture is different from the case in Co or Fe-doped TiO$_2$ (Refs. 11 and 12) where the 3d electron carriers induce ferromagnetism.

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extended x-ray absorption fine structure and Raman scattering to examine the presence of titanium and/or oxygen vacancies in the sample which have been suggested to be critical components of RTFM in A and R-type TiO$_2$. On the other hand, from the viewpoint of applications, it is important to prepare K$_x$Ti$_8$O$_{16}$ thin films and investigate the magnetic properties. In our preliminary work, we succeed in preparing a K$_x$Ti$_8$O$_{16}$ thin film epitaxially grown on a sapphire substrate and find that the film shows ferromagnetic behavior at room temperature. Knowledge from the studies in K$_x$Ti$_8$O$_{16}$ would not only help understand the underlying physics of RTFM in the TiO$_2$-based system but also be useful toward developing the TiO$_2$-based devices for spintronics applications. Finally, we comment on the way to develop new TiO$_2$-based room temperature ferromagnets. There are many polymorphs in TiO$_2$ such as ramsdellite and bronze. The present hollandite-type TiO$_2$ is the only one of them. Our results indicate that the research on polymorphs would be promising for developing new TiO$_2$-based room temperature ferromagnets.

**IV. CONCLUSIONS**

In summary, we have synthesized polycrystalline hollandite-type K$_{1.46}$Ti$_8$O$_{16}$ and studied the magnetic and electric properties and the electronic state of the sample. Ferromagnetic behavior is observed at room temperature in the magnetic hysteresis measurement. The sample shows the semiconducting behavior in the resistivity measurement. XPS measurements indicate that the Ti ions take a mixed valence of Ti$^{4+}$ and Ti$^{3+}$. The valence band spectrum reveals that the unpaired 3$d$ electrons tend to localize on Ti$^{3+}$ ions in the hollandite-type TiO$_2$ lattice. Analysis of the valence band spectrum indicates that K$_{1.46}$Ti$_8$O$_{16}$ is a wide gap oxide with the band gap of 3.6 eV. RTFM decreases in the sample prepared under a strong reducing gas atmosphere, accompanied with the decrease in the resistivity. The results imply that the localized 3$d$ electrons are responsible for the ferromagnetism of K$_{1.46}$Ti$_8$O$_{16}$.

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