Unoccupied electronic structure of Y_{1-x}Ca_{x}TiO_{3} investigated by inverse photoemission spectroscopy


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We have studied the unoccupied electronic structure of the band insulator CaTiO_{3}, the Mott insulator YTiO_{3}, and Y_{0.61}Ca_{0.39}TiO_{3} with a metal-insulator transition (MIT) around 150 K by means of Ti 3p-3d resonant inverse photoemission spectroscopy (RIPES). The Ti 3d partial density of states of CaTiO_{3} deduced from the on- and off-resonance RIPES spectra is in good agreement with results of a band-structure calculation, while that of YTiO_{3} is explained based on a calculation with the dynamical mean-field theory taking into account an electron correlation. In the case of Y_{0.61}Ca_{0.39}TiO_{3}, we have successfully observed the temperature dependence of RIPES spectra across MIT; the intensity of the incoherent part (a remnant of the upper Hubbard bands) relative to the coherent part (quasiparticle bands) is reduced with decreasing temperature from the insulator to metal phases.

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I. INTRODUCTION

The 3d transition-metal (TM) oxides with a perovskite-type structure have attracted much interest because of their unusual electronic and magnetic properties which originate from strong electron correlation, such as a colossal negative magnetoresistance.1 Among them, it is well known that carrier doping to the TM 3d bands and control of the 3d bandwidth give rise to a metal-insulator transition (MIT). According to the Mott-Hubbard picture, MIT is caused by a change in the relative magnitude between the on-site 3d-3d Coulomb interaction U_{d-d} and 3d bandwidth W (U_{d-d}/W). If the number of the 3d electrons for one Ti site is an integer, an energy splitting between the lower and upper Hubbard bands increases with increasing U_{d-d}/W, and MIT takes place at U_{d-d}/W = 1.

There has been a considerable amount of work on occupied electronic states of the perovskite TM oxides investigated by means of photoemission spectroscopy (PES).1–12 According to the results, as a system in the metal phase approaches the insulator phase, the spectral weight transfers from quasiparticle bands near the Fermi level (E_F) (that is, the coherent part) to a remnant of the lower Hubbard bands (that is, the incoherent part). For these Mott-Hubbard systems, the dynamical mean-field theory (DMFT) has been applied to explain the PES and optical spectra.12–16 The PES spectra of SrVO_{3} and CaVO_{3}, categorized into the typical Mott-Hubbard system, are well reproduced by band-structure calculations with the local-density approximation (LDA) taking into account electron correlation using DMFT. On the other hand, there has been only little experimental information on unoccupied electronic structure of the Mott-Hubbard systems, so far.6,7,17 Since DMFT gives electronic structure for conduction bands as well as valence bands, information on the unoccupied parts is crucial to understand the physical properties of the Mott-Hubbard systems.

Y_{1-x}Ca_{x}TiO_{3} with a distorted perovskite structure (GdFeO_{3} type) is a system varying from the d^{1} insulator YTiO_{3} (x=0) to d^{1} insulator CaTiO_{3} (x=1). The system is metallic for the Ca composition x from ~0.4 to ~0.9. YTiO_{3} is well known as the d^{1} Mott insulator with a ferromagnetism below the Curie temperature of T_{c} = 30 K, while CaTiO_{3} is classified as a d^{1} band insulator. The physical properties and electronic structures of Y_{1-x}Ca_{x}TiO_{3} have been studied using polycrystals.7,18,19 PES and inverse photoemission spectroscopy (IPES) experiments have been performed for polycrystals, and the spectral changes occurring on Ca doping have been reported.7

Single-crystal Y_{0.61}Ca_{0.39}TiO_{3} is an insulator at room temperature and exhibits a clearer temperature-induced MIT around 150 K than when polycrystalline. With decreasing temperature, the electrical resistivity along the c axis decreases from ~1 to ~10^{-3} Ω cm steeply at MIT temperature. Hysteresis of the resistivity suggests a strong coupling between electronic states and lattice distortion.20,21 Previously, we have measured temperature-dependent PES spectra of Y_{0.61}Ca_{0.39}TiO_{3} single crystals. MIT is clearly observed as the spectral weight transfers from the incoherent to coherent parts with decreasing temperature.22,23

In this paper, we report the unoccupied overall and Ti 3d electronic structure of single-crystal CaTiO_{3}, YTiO_{3}, and Y_{0.61}Ca_{0.39}TiO_{3} investigated by means of IPES with bremsstrahlung-isochromat-spectroscopy (BIS-IPES) and Ti 3p-3d resonant IPES (RIPES) with tunable-photon-energy mode.

The experimental results of CaTiO_{3} and YTiO_{3} are discussed based on the band-structure calculation and that using DMFT, respectively. It is shown that the MIT of Y_{0.61}Ca_{0.39}TiO_{3} is observed in the temperature-dependent Ti 3d partial density of states (DOS) deduced from the RIPES spectra.

II. EXPERIMENTS

Y_{1-x}Ca_{x}TiO_{3} single crystals were grown by a floating-zone method.20,21 The grown samples were characterized by

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FIG. 1. BIS-IPES spectra of CaTiO₃, YTiO₃, and Y₀.₆₁Ca₀.₃₉TiO₃ measured at 300 K. Emitted photon energy of \( h\nu = 9.4 \text{ eV} \) is detected.

their Laue images, powder x-ray diffraction, and electron-probe microanalysis. As for Y₀.₆₁Ca₀.₃₉TiO₃, MIT was found to take place at around 150 K in the electrical resistivity measurement.

BIS-IPES measurements were done at 300 and 110 K using an IPES spectrometer equipped with an Erdman-Zipt-type low-energy electron gun using a BaO cathode and a bandpass-type photon detector centered at \( h\nu = 9.4 \text{ eV} \). The incidence angle of the electrons was normal to the sample surface. The total energy resolution was 0.56 eV and the working pressure of the analysis chamber was \( 1 \times 10^{-10} \text{ Torr} \). The temperature of the samples was maintained with a liquid N₂ refrigerator.

The Ti 3p-3d RIPES spectra were measured using the same type of electron gun as used in BIS-IPES. Emitted photons from the samples were monochromatized by a varied line-spacing spherical grating with averaged line density of 1200 lines/mm and detected using a CsI-coated multichannel plate. The total energy resolution was estimated to be 0.55 eV at \( E_k = 46 \text{ eV} \), where \( E_k \) denotes the kinetic energy of the incident electrons, and working pressure of the analysis chamber was \( 3 \times 10^{-10} \text{ Torr} \). The angle between the axes of the e-gun and the monochromator was 45° and the incidence angle of the electrons was set to about 20° from the surface normal. The temperature of samples was controlled between 17 and 300 K by a combination of the closed-cycle He refrigerator and heater. For BIS-IPES and RIPES measurements, \( E_F \) was determined from the Fermi edge of the spectra for a fresh Au film, and clean surfaces were obtained by fracturing in situ.

III. RESULTS AND DISCUSSION

Figure 1 shows the BIS-IPES spectra of CaTiO₃, YTiO₃, and Y₀.₆₁Ca₀.₃₉TiO₃ measured at 300 K. The abscissa represents energy above \( E_F \). The spectra have been normalized using the intensity around 12 eV. All spectra exhibit two structures near \( E_F \) and between 4 and 10 eV. The energy position of the structure between 4 and 10 eV depends on the compounds, and shifts from \( \sim 7.3 \text{ eV} \) for CaTiO₃ to \( \sim 5 \text{ eV} \) for YTiO₃. In the spectrum of Y₀.₆₁Ca₀.₃₉TiO₃, the structure around 6 eV is assumed to be composed of the two components from structures of CaTiO₃ and YTiO₃, and attributed to the unoccupied Ca 3d and Y 4d states. On the other hand, the spectral feature near \( E_F \) does not change appreciably for compounds, and these structures are ascribed to the unoccupied Ti 3d states. We have found almost no temperature dependence in the BIS-IPES spectrum of Y₀.₆₁Ca₀.₃₉TiO₃ between 300 and 110 K across MIT.

Figure 2(a) displays the \( E_k \) dependence of RIPES spectra of CaTiO₃ measured at 280 K including the Ti 3p-3d absorption region. Structures indicated by dots and arrows are the Ca 3d → 3p and Ti 3d → 3p fluorescence peaks, respectively. (b) CFS spectra of CaTiO₃ for the structures labeled A–F in (a). In the spectrum of A, intensity exhibits the maximum and minimum at \( E_k = 46 \) and 39 eV, corresponding to the Ti 3p-3d on- and off-resonances, respectively.
Ca 3\textit{d}–3\textit{p} resonance, and the structures C–E in Fig. 2(a) are attributed to the Ca 3\textit{d} states. The largest enhancement of D indicates that the Ca 3\textit{d} states contribute dominantly to the energy region around D, which is clearly observed also in the BIS-IPES spectrum in Fig. 1. Since the CFS spectrum for F exhibits no resonance, the structure F is due to the Ti 4\textit{p} states. Two small humps at \( E_k = 46 \) and \( \sim 58 \) eV arise from overlaps of the Ca 3\textit{d}–3\textit{p} and Ti 3\textit{d}–3\textit{p} fluorescence peaks, respectively.

Figure 3(a) shows \( E_k \) dependence of RIPES spectra of YTiO\textsubscript{3} measured at 280 K. We find that two structures around (A) 2.2 and (C) 4.8 eV are mainly enhanced at \( E_k = 39 \) and 46 eV, respectively. The two broad structures indicated by dots and arrows are the Y 4\textit{d}–4\textit{p} and Ti 3\textit{d}
$\rightarrow 3p$ fluorescence peaks. The CFS spectra for the structures at (A) 2.2, (B) 3.8, (C) 4.8, (D) 5.2, and (E) 14.3 eV are presented in Fig. 3(b). The enhancement of structure A around $E_F=46$ eV is attributed to the Ti $3p$-3d resonance as the spectra of CaTiO$_3$, and the structures B–D around $E_F=37$ eV, stem from the Y $4p$-4d resonance. Using the same line of argument for CaTiO$_3$, structures A, B–D, and E are attributed to the Ti 3$d_{t_2g}$, Y 4$d$ together with the Ti 3$d$ e$_{g}$, and Ti 4$p$ states, respectively.

Unoccupied Ti 3$d$ partial DOS’s of CaTiO$_3$ and YTiO$_3$ have been deduced by subtracting off-resonance spectrum from the on-resonance spectrum. These results are shown in the upper parts of Figs. 4(a) and 4(b) as difference spectra (thick lines) together with the on- and off-resonance spectra (thin lines). One notices that the difference spectra have no intensity at $E_F$ and that the Ti 3$d$ states contribute dominantly to $\sim 2.2$ eV for both compounds. In addition, the off-resonance spectra for both compounds are similar to the BIS-IPES spectra in Fig. 1 with respect to the two structures near $E_F$ and between 4 and 10 eV, because of the small cross section of the Ti 3$d$ states for the BIS-IPES spectra measured with $h\nu=9.4$ eV.

Here we compare the difference spectra with the theoretical Ti 3$d$ partial DOS’s of CaTiO$_3$ and YTiO$_3$ in the lower parts of Figs. 4(a) and 4(b), respectively. The theoretical Ti 3$d$ partial DOS of CaTiO$_3$ in Fig. 4(a) is calculated by means of the tight-binding linear muffin-tin orbital method within the atomic sphere approximation for a cubic perovskite-type structure, assuming that $E_F$ is located at conduction-band minimum. The narrow structure below 3 eV is derived from the Ti 3$d_{t_2g}$ states, and the broad structure between 3 and 8 eV is due to the Ti 3$d$ e$_{g}$ states hybridized with the O 2$p$ and Ca 3$d$ states. It should be noticed that the difference spectrum of the theoretical DOS is in fairly good agreement with the off-resonance spectrum. The structures around 3.7 eV, which are buried by the strong tail from the main peak around 2.2 eV toward the higher-energy side in the difference spectrum, are also clearly observed in the off-resonance spectrum. These results show that CaTiO$_3$ is a typical band insulator, well explained in terms of the one-electron band theory.33

![FIG. 4. On- and off-resonance RIPES spectra (thin lines) and the difference spectra (thick lines) of (a) CaTiO$_3$ and (b) YTiO$_3$ in comparison with the theoretical partial DOS’s of Ti 3$d$ states (Refs. 32 and 34).](image)

![FIG. 5. Comparison of the experimental Ti 3$d$ partial DOS deduced from resonant PES (open circles) and RIPES (closed circles) with the calculated DMFT-DOS (line) (Ref. 36).](image)
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FIG. 6. (a) $E_k$ dependence of RIPES spectra for $Y_{0.61}Ca_{0.39}TiO_3$ measured at 17 K around the Ti $3p$-$3d$ absorption region. The structures indicated by dots are due to the Ti $3d \rightarrow 3p$ fluorescence peaks. (b) CFS spectra for the structures labeled A–F in (a). In the spectrum of A, the intensity exhibits the maximum and minimum at $E_k = 46$ and 38 eV, corresponding to the Ti $3p$-$3d$ on- and off-resonances, respectively.

Figure 6(a) shows $E_k$ dependence of the spectra measured at 17 K. These spectra have been normalized using the intensity around 10.5 eV. The spectral features are quite similar to those of CaTiO$_3$ and YTiO$_3$. The structures indicated by dots are due to the Ti $3d \rightarrow 3p$ fluorescence. The CFS spectra for A–E specified in Fig. 6(a) are shown in Fig. 6(b). One can recognize that the spectra are similar to those of CaTiO$_3$ and YTiO$_3$. Structure A is due to the Ti $3d$ $t_{2g}$ states and B–E to the Ti $3d$ $e_g$ states. Weak enhancements around $E_k \approx 36$ eV for D and E are derived from the Ca $3d$ and/or Y $4d$ components.

In order to reveal the change of the Ti $3d$ states in $Y_{0.61}Ca_{0.39}TiO_3$ across MIT, we have measured the temperature dependence of the on-resonance RIPES spectra at $E_k = 46$ eV. Figure 7(a) shows the on-resonance spectra measured at 17, 70, 120, 180, and 250 K. The spectrum at 250 K is presented by broken lines on each spectrum for comparison. Spectra near $E_F$ are shown in the inset. (b) Difference spectra obtained by subtracting the spectrum at 250 K from that at respective temperatures. (c) Variation of the integrated intensities in the difference spectra for each part of $\sim E_F$ and $\sim 2.2$ eV (coherent and incoherent parts, respectively) as a function of temperature. The integrated ranges are indicated by horizontal arrows in (b).

FIG. 7. (a) On-resonance RIPES spectra of $Y_{0.61}Ca_{0.39}TiO_3$ measured at 17, 70, 120, 180, and 250 K. The spectrum at 250 K is presented by broken lines on each spectrum for comparison. Spectra near $E_F$ are shown in the inset. (b) Difference spectra obtained by subtracting the spectrum at 250 K from that at respective temperatures. (c) Variation of the integrated intensities in the difference spectra for each part of $\sim E_F$ and $\sim 2.2$ eV (coherent and incoherent parts, respectively) as a function of temperature. The integrated ranges are indicated by horizontal arrows in (b).
FIG. 8. (a) $E_k$ dependence of difference spectra of $Y_{0.61}Ca_{0.39}TiO_3$ between 17 and 250 K. In all the spectra, the coherent part (gray) is positive and the incoherent part (black) is negative. (b) Integrated intensities of the coherent (gray) and incoherent (black) parts as a function of $E_k$.

The integrated ranges are indicated by horizontal arrows in Fig. 7(b). The variations are relative to the intensity of the RIPES spectrum at 250 K integrated for each range; that is, the ordinate represents the ratio of the intensities of the difference spectra to that of the RIPES spectrum at 250 K integrated in each energy range. With decreasing temperature, both intensities near $E_F$ and around 2.2 eV start to change below the MIT temperature of 150 K (Ref. 21) and the spectral weight transfers from the region around 2.2 eV to the region near $E_F$. We find in Figs. 7(b) and 7(c) that the temperature dependence of the RIPES spectra is symmetrical to that of the PES spectra with respect to $E_F$; the spectral weight in the PES spectrum transfers from the region around 1.4 eV to the region near $E_F$.23 Accordingly, we can reasonably assume that the 2.2 eV peak corresponds to the incoherent part (that is, a remnant of the upper Hubbard bands), while the structure near $E_F$ corresponds to the coherent part (that is, the quasiparticle bands). Although the energy position of the incoherent part relative to $E_F$ (≈2.2 eV) in the RIPES spectra is higher than that of PES (≈1.4 eV), MIT is observed as the spectral weight transfers from the incoherent to coherent parts for both occupied and unoccupied states.

Figure 8(a) shows the $E_k$ dependence of difference spectra between 17 and 250 K, which are derived from the RIPES spectra normalized using the intensity integrated between −3 and 11 eV, and Fig. 8(b) shows the integrated intensities of the coherent (gray) and incoherent (black) parts relative to the intensity of RIPES spectra integrated between −3 and 11 eV. In all the spectra in Fig. 8(a), one sees positive and negative intensities in the coherent and incoherent parts, respectively. In addition, the integrated intensity of the incoherent part exhibits remarkable $E_k$ dependence and reaches a maximum at $E_k$=44 eV, close to the Ti 3p-3d on-resonance energy, and a minimum (nearly zero) at $E_k$=36 eV, close to the Ti 3p-3d off-resonance energy. The intensity of the coherent part is, on the other hand, almost unchanged for $E_k$ in contrast to the incoherent part and, in particular, exhibits no remarkable enhancement around $E_k$=46 eV. These results reveal that the incoherent part mainly consists of the localized Ti 3d states due to large $U_{d-d}$, while the coherent part stems from the delocalized Ti 3d bands hybridized with the other conduction electronic states such as O 2p states. The spectral weight transfer from the incoherent to coherent parts with decreasing temperature implies that the localized Ti 3d states hybridize with the conduction-band states, mainly O 2p states, below the MIT temperature.

As mentioned above, the BIS-IPES spectra with the small cross section of the Ti 3d states exhibit no temperature-dependent features between 280 and 110 K. The off-resonance RIPES spectra at $E_k$=36 eV also show no remarkable temperature-dependent features. These results indicate that the change of the electronic structure of $Y_{0.61}Ca_{0.39}TiO_3$ across MIT takes place mainly in the Ti 3d states.

IV. CONCLUSION

We have studied the unoccupied electronic structure of the band insulator CaTiO$_3$, the Mott insulator YTiO$_3$, and $Y_{0.61}Ca_{0.39}TiO_3$ with MIT by means of BIS-IPES and RIPES. The unoccupied Ti 3d partial DOS’s of these compounds have been deduced from the on- and off-resonance spectra. The Ti 3d DOS feature of CaTiO$_3$ is well reproduced with the band-structure calculation,22 while overall features of YTiO$_3$ are in good agreement with the Ti 3d $t_{2g}$ DOS calculated with DMFT taking into account the electron correlation. These results reveal that CaTiO$_3$ is a typical band insulator and YTiO$_3$ can be regarded as a Mott insulator, where the whole Ti 3d $t_{2g}$ bands are modified by $U_{d-d}$.

For $Y_{0.61}Ca_{0.39}TiO_3$, the RIPES spectral weight transfers from the region of $\sim$2.2 eV to the region near $E_F$ with decreasing temperature across MIT. From the temperature dependence of the spectra, we conclude that the coherent and incoherent parts exist near $E_F$ and around 2.2 eV, respectively. In addition, from the $E_k$ dependences of intensity change of the incoherent and coherent parts between 17 and 250 K, the incoherent part is derived from the localized Ti 3d states and the coherent part from the delocalized Ti 3d states hybridized mainly with the O 2p states below the MIT temperature.

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We have tentatively attempted various normalization procedures using the intensities around some energy positions between 7 and 15 eV, and the intensities integrated between 10 and 17 eV and between −3 and 5 eV. The results shown below were independent of the procedures.

The fluorescence spectra are weaker and broader than the main structures. Hence the peaks do not affect the results of the CFS spectra even if the peaks cross the energy position used for the normalization.


The structure in the Ca 3d partial DOS calculated for cubic perovskite-type structure appears around 3.5 eV, while the Ti 3d states hybridized with the O 2p states observed as the broad structure between 3 and 8 eV in the off-resonance spectrum of CaTiO₃ with GaFeO₃-type distortion. The discrepancy could be attributed to an increase in Ca-O covalency due to GaFeO₃-type distortion in CaTiO₃.


M. Arita (unpublished).