






Electronic structure and small-hole polarons in YTiO₃

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As a prototypical Mott insulator with ferromagnetic ordering, YTiO₃ (YTO) is of great interest in the study of strong electron correlation effects and orbital ordering. Here we report the first molecular beam epitaxy (MBE) growth of YTO films, combined with theoretical and experimental characterizations of the electronic structure and charge transport properties. The obstacles of YTO MBE growth are discussed and potential routes to overcome them are proposed. DC transport and Seebeck measurements on thin films and bulk single crystals identify *p*-type Arrhenius transport behavior with an activation energy of ~ 0.17 eV in thin films, consistent with the energy barrier for small hole polaron migration from hybrid density functional theory calculations. Hard x-ray photoelectron spectroscopy measurements show the lower Hubbard band at 1.1 eV below the Fermi level, whereas a Mott-Hubbard band gap of ~ 1.5 eV is determined from photoluminescence measurements. These findings provide critical insight into the electronic band structure of YTO and related materials.

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The coupling among charge, orbital, lattice, and spin degrees of freedom in perovskites ABO₃ with partially filled *d* bands can lead to a wide range of fascinating properties, such as colossal magnetoresistance and exotic magnetic behavior [1]. Among the ABO₃ perovskites, the rare-earth titanates RTiO₃ (*R* = rare-earth elements except Eu) are particularly interesting as they are prototypical Mott insulators and provide a perfect playground for the study of strong electron-correlation effects [2]. One of many peculiar features of this isostructural series of compounds is the magnetic ground-state transition from ferromagnetism or ferrimagnetism in RTiO₃ with smaller *R* ions [e.g., YTiO₃, or (YTO)] to antiferromagnetism in those with larger *R* ions (e.g., LaTiO₃) [2–4]. For most RTiO₃, the partially filled 4*f* shell of the rare-earth ions leads to a large total spin angular momentum and, hence, adds complexity to the magnetic properties as the spin degrees of freedom of both Ti³⁺ and rare-earth ions can lead to complex magnetic ordering. However, this complexity can be circumvented in YTO since Y³⁺ does not contain *f* electrons.

Unlike most Mott insulators, YTO shows a ferromagnetic ground state below ~ 30 K [5,6]. The origin of this ferromagnetic state has been the subject of numerous theoretical studies

[7–10] and experimental investigations, including inelastic x-ray scattering [11,12], polarized neutron diffraction [13–15], photoemission spectroscopy [16–18], and Raman scattering [19]. Despite these extensive research efforts, many important questions remain unanswered. For instance, what is the governing transport mechanism in YTO at room temperature? Similarly, the Hubbard band structure of YTO has not been demonstrated experimentally. Early attempts have focused on optical conductivity [$\sigma(\omega)$] measurements to determine E_g [20–24]. The onset in $\sigma(\omega)$ spectrum was attributed to interband transitions. Typical $\sigma(\omega)$ spectra showed two onsets, one at $\lesssim 1$ eV and another at ~ 4 eV, which were attributed to Mott-Hubbard gap transitions from the lower Hubbard band (LHB) to the upper Hubbard band (UHB) ($|d^1d^1\rangle \rightarrow |d^0d^2\rangle$) and charge-transfer gap transitions from occupied O 2*p* states to Ti 3*d* UHB ($|d^1d^6\rangle \rightarrow |d^2p^5\rangle$), respectively [20–24]. More recently, Gösling *et al.* examined ellipsometry data and argued that the lowest electronic transition across E_g occurs at 2.55 eV [25]. Ellipsometry data by Kovaleva *et al.* further support this argument, giving a slightly higher transition energy of 2.85 eV [26]. In contrast, recent density functional theory (DFT) calculations with intrasite Coulomb repulsion *U* predicted $E_g \sim 2$ eV and attributed the low-energy onset in the optical conductivity to excitations of electrons from the LHB to empty (hole) polaronic states [8].

In order to gain deeper insight into the electronic structure of YTO, we synthesized films using hybrid molecular

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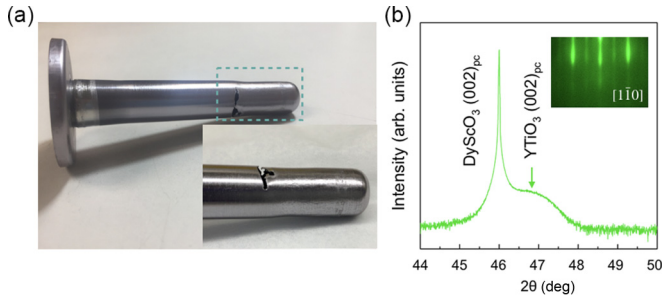


FIG. 1. (a) Image of a cracked Ta crucible. The inset shows a zoomed-in picture around the crack (indicated by the green rectangle) where a clear shrinkage in volume can be observed at the bottom part of the crucible. (b) High-resolution x-ray 2θ - ω couple scan of a 12-nm YTO/ DSO (110) sample. The inset shows a RHEED pattern of the film after growth along the $[1\bar{1}0]$ azimuth of the substrate.

beam epitaxy (MBE) method and investigated the electronic properties of YTO through a combination of hybrid density functional calculations and experimental characterization techniques. We also grow single crystals with the floating-zone technique for some complementary measurements. DC transport and Seebeck measurements reveal that YTO shows p -type Arrhenius transport behavior with an activation energy of 0.17 eV for the film samples. Based on hybrid functional calculations, we attribute this activation energy to a small hole polaron migration barrier. Our hard x-ray photoemission spectroscopy (HAXPES) measurements revealed a LHB at 1.1 eV below the Fermi level, and photoluminescence (PL) measurements indicate a Mott-Hubbard gap of ~ 1.5 eV, which is significantly larger than the onset at ~ 1 eV often observed in optical conductivity spectra. In the following, we describe the experimental and theoretical approaches, paying special attention to the obstacles in the MBE growth of YTO and then report the main results and conclusions of this combined theory-experiment effort.

We emphasize that, to the best of our knowledge, MBE growth of YTO films has not been reported earlier. The main challenge is associated with the evaporation of Y. Since the discovery of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, researchers have been trying to grow yttrium-containing compounds with MBE. However, due to the extremely low vapor pressure of Y (2×10^{-5} mbars at 1540 °C) [27], the majority of the research efforts focused on electron-beam (e-beam) evaporation, which has its own challenges. One of the major challenges of e-beam evaporation is maintaining a stable beam flux, owing to local heating behavior [28]. In the present Rapid Communication, we employed a thermal effusion cell with a tantalum crucible to thermally evaporate/sublimate Y. Ta was chosen owing to its oxygen resistance, high malleability behavior and due to its prior use as a crucible material in e-beam sources [29].

Our initial growth attempts failed—after about 40 thermal cycles, the crucible cracked. We first discuss the lesson learned from this failure. Figure 1(a) shows an image of a cracked Ta crucible for which the bottom part where Y was in contact with the crucible was found shrunk compared to the top part. We can understand this behavior by considering the large linear thermal expansion mismatch between Y ($\alpha_L =$

10.6×10^{-6} K) and Ta ($\alpha_L = 6.3 \times 10^{-6}$ K), which results in thermal stresses during heating/cooling cycles and, eventually, failure. At first, this result was quite surprising given that the effusion cell was operated (between 1400 and 1480 °C) below the melting point of pure Y (~ 1522 °C) and, therefore, Y melting (and, hence, the thermal stresses) was not expected. Looking at the Y-Ta phase diagram, we, however, found a nonzero solid solubility of Ta in Y and a eutectic point at ~ 99.6 at. % Y + ~ 0.4 at. % Ta, which may explain the melting of Y at lower temperatures [30]. An apparent solution of this challenging problem would, thus, be to operate the effusion cell at lower temperatures, which is unfortunately not possible due to the low vapor pressure of Y. Our proposed solution to this issue was, therefore, to avoid thermal cycling by keeping the idle temperature of the cell just below the operating temperature (where vapor pressure is low). The effusion cell can be cooled down slowly to room temperature only after the source material is completely depleted. It may also be possible to avoid thermal stress by using a liner (such as Al_2O_3). Using the former approach, YTO films were successfully grown in the hybrid MBE setup [31–35].

Phase-pure epitaxial 12-nm-thick YTO films were grown on DyScO_3 (DSO) (110) substrates using hybrid MBE approach (details described elsewhere) [31–35]. Stoichiometry optimization and the influence of cation/anion stoichiometry on structural and electronic properties are discussed in Figs. S1–S4 (Supplemental Material) [36]. All films were grown at a fixed substrate temperature of 950 °C (thermocouple temperature). No additional oxygen was used during growth because our source of Ti also supplies oxygen [31–35]. The growth was monitored *in situ* using reflection high-energy electron diffraction (RHEED). High-resolution wide-angle x-ray diffraction scans were used to characterize the samples' structural quality *ex situ*. Bulk YTO crystals were grown using the floating-zone method [20]. Electrical characterization was performed in a Quantum Design, Inc. physical property measurement system (PPMS Dynacool) with Van der Pauw geometry. A 20-nm Ti/100-nm Au was sputtered on the corners of the samples as Ohmic contacts, and indium was soldered on top of the Au to make connections to the PPMS resistivity puck. Seebeck measurements were carried out to characterize charge-carrier type. For Seebeck measurements, a bulk YTO sample was mounted using silver paste and Cu leads in a four-terminal configuration where two leads at the ends of a bar-shaped sample were used to pass current, and the middle two leads were used to measure the temperature difference ΔT and Seebeck voltage ΔV simultaneously. A square wave heat pulse was applied to the sample, and the measured ΔT and ΔV were modeled to extract the Seebeck coefficient using a thermal transport module from Quantum Design.

The valence band (VB) spectra of YTO films were characterized *via* HAXPES, with an excitation energy of 4 keV and using the high-resolution Si (220) channel-cut post monochromator. Slits were closed down to a 0.1-mm gap vertically to minimize beam flux at the sample and reduce sample charging. The analyzer was located at 90° from the incident beam and the sample is at 5° off grazing, giving a take-off angle of 85°. The analyzer was set to 200-eV pass energy. This gives an overall resolution of 250 meV as determined by the

width of the Fermi edge of Au foil. The binding-energy axis was calibrated using both the Fermi edge and the Au 4*f* core lines from the Au foil. The PL measurements were carried out using a 532-nm excitation laser illuminating the sample at a glancing angle to ensure excitation of a region much larger than the PL collection volume. The emitted PL was collected by a lens and analyzed with a grating monochromator and liquid-nitrogen-cooled Si CCD with a resolution limit of approximately 70 μeV .

Our first-principles calculations were based on DFT [37,38] and the screened hybrid functional of Heyd, Scuseria, and Enzerhof [39,40] as implemented in the Vienna *ab initio* simulation code [41,42]. The projector augmented-wave method was used to describe the interaction between the core and the valence electrons [43]. Equilibrium lattice parameters of YTO were obtained by optimizing an orthorhombic primitive cell consisting of 20 atoms, with a $6 \times 6 \times 4$ Γ -centered *k*-point mesh for integrations over the Brillouin zone, and a 500-eV cutoff for the plane-wave basis set. For the calculations of the small hole polaron in YTO, we used a supercell consisting of 160 atoms ($2 \times 2 \times 2$ repetition of the unit cell) and a single *k*-point (1/4,1/4/1/4) for integrations over the Brillouin zone. All the atomic forces were minimized until they reached a maximum threshold of 0.01 eV/Å. For simulating the small polaron, we removed an electron for the 160-atom supercell and broke the symmetry around one of the Ti atoms by slightly displacing the two neighboring O atoms and allowing all the atomic positions to relax. The hole then localizes on this specific Ti atom (i.e., becoming Ti^{4+}) with the resulting Ti-O bond lengths slightly smaller by $\sim 5\%$ of the equilibrium bond length.

First, we present results from the structural characterization of our films. Figure 1 shows the high-resolution 2θ - ω scan of a representative 12-nm YTO/DSO (110) sample, consistent with expectations for an epitaxial and phase-pure film. The film peak is relatively broad due to the small film thickness. The analysis of the film peak yielded an out-of-plane lattice parameter of 3.900 ± 0.002 Å, which is close to the (110)_o interplanar spacing of the bulk YTO crystal, 3.881 Å. This observation is consistent with a nominally stoichiometric (110)_o-oriented YTO films on the (110)_o DSO substrate where subscript “o” refers to the orthorhombic structure of YTO. As shown in Fig. S1 of the Supplemental Material, the film peak, although broad, is far away from the expected coherent-strained peak position, but rather close to the bulk YTO (220)_o peak, indicating a mostly relaxed YTO film [36]. The streaky RHEED pattern of the film after growth is shown in the inset of Fig. 1(b), indicative of a smooth surface morphology. As illustrated in Fig. S2 and S3 of the Supplemental Material, the analysis of x-ray reflectivity of the sample yielded expected electron scattering length density for the film except for the part near the surface, which we attribute to surface oxidation based on XPS analysis (see Fig. S2 of the Supplemental Material) [36].

We now turn to the discussion of charge transport results. The temperature-dependent resistivity of the YTO film shown in Fig. 2(a) indicates insulating transport behavior. Data for a YTO bulk sample is shown for comparison in the inset of Fig. 2(a). An Arrhenius fit to $\rho(T) \sim e^{-E_a/kT}$ yields activation energies of $E_a \sim 0.17$ and ~ 0.31 eV for the film and bulk

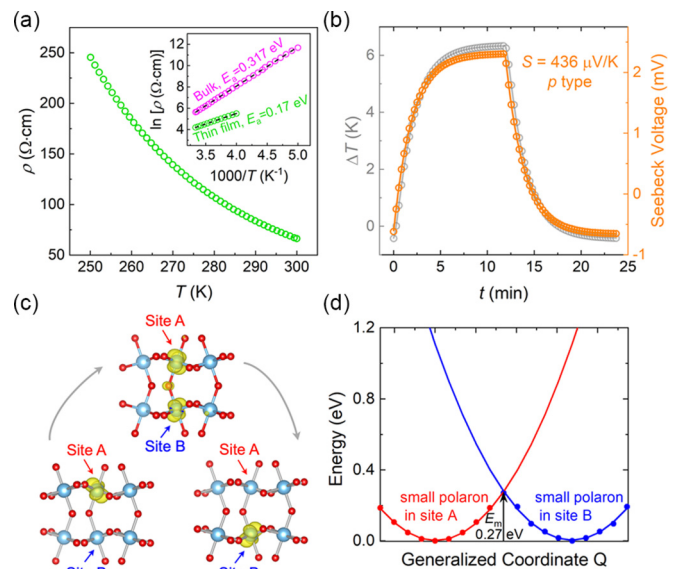


FIG. 2. (a) ρ vs T plot for a 12-nm YTO/DSO (110) sample. The inset: Arrhenius plot for this film and for a bulk YTO single crystal along with the corresponding activation energies. (b) Seebeck measurement of the bulk YTO single crystal. A square-wave heat pulse was applied, then the temperature and voltage difference between the hot and the cold leads were measured. Seebeck voltage (orange) yields the same sign as the temperature differences (gray), confirming *p*-type conduction in YTO. (c) Hopping process schematic of how a small polaron at Ti site A migrates to neighboring Ti site B via an intermediate state. (d) Configuration diagram for the polaron at adjacent Ti sites A and B. The calculated barrier energy for polaron migration is 0.27 eV.

samples, respectively. These values are slightly different from the previously reported bulk value of ~ 0.25 eV [3,21,44], probably due to slight differences in the amount of nonintentional defects in bulk and/or residual strain/nonstoichiometry in films. A careful tuning of the Y/Ti ratio yielded no change in E_a suggesting the important role of residual strain in film or extrinsic point defects in the bulk (Fig. S4 of the Supplemental Material) [36]. Seebeck measurements were performed on the bulk YTO sample to investigate the carrier type. Figure 2(b) shows the same sign for ΔT and ΔV , indicating *p*-type carriers, in agreement with the previous reports [3,44]. Note that the activation energy observed in YTO is significantly smaller than the predicted Mott-Hubbard gap and the observed features in the optical conductivity. In order to understand the origin of this small activation energy, we show in Fig. 2(c) the calculated atomic configuration and charge-density isosurface of a small hole polaron in YTO at a single Ti site (site A or B) as well as the hopping steps between adjacent Ti sites (site A to B). For the small polaron hopping, we generated nine intermediate configurations by interpolating between the two equivalent configurations A and B. The energy barrier was found at the maximum in the small polaron migration path, which corresponds to the intermediate configuration composed of 50% of configuration A and 50% of B. In this particular intermediate configuration, the hole was found to be equally distributed among the two adjacent Ti atoms. The calculated polaron migration barrier energy was 0.27 eV,

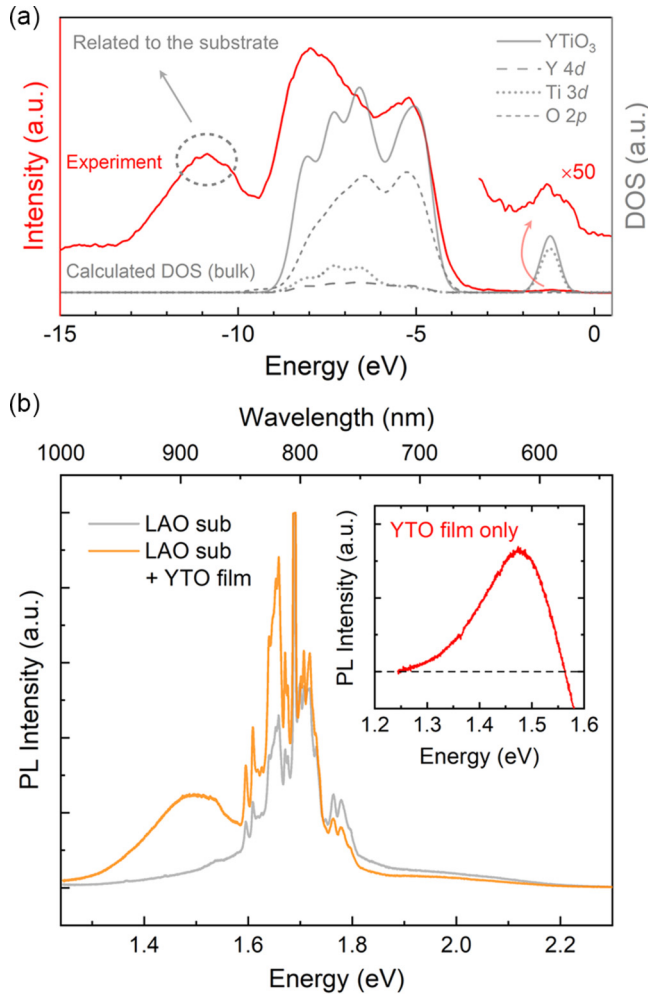


FIG. 3. (a) HAXPES data (red color) from a 12-nm YTO/DSO (110) along with the calculated density of states (gray color) for bulk YTO. The HAXPES data close to the Fermi level are shown on a $\times 50$ scale as an inset for clarity. (b) PL measurement of a YTO/LAO sample and a LAO substrate where a clear signal from the YTO film is observed around 1.2–1.6 eV. The inset shows the PL signal from the YTO film, which is obtained by subtracting the PL signal of the substrate from that of the substrate plus the film.

in reasonably good agreement with the experimentally determined transport activation energy E_a , indicating that the thermally activated behavior in YTO is likely governed by small hole polaron hopping.

Finally, to obtain further insight into the electronic structure, Fig. 3(a) shows the VB spectrum of the same 12-nm YTO/DSO (110) sample using the HAXPES. The data close to Fermi level (E_F) was magnified 50 times to clearly show the LHB. These results show that the LHB is around 1.1 eV below E_F , consistent with previous resonant photoemission spectroscopy data by Arita *et al.* on bulk YTO samples [16]. The calculated density of states (DOS) for YTO is also shown in Fig. 3(a). The HAXPES result matches reasonably well with the hybrid functional calculation, especially with respect to the separation between the O 2p bands and the LHB composed of Ti 3d orbitals. The calculated Mott-Hubbard

gap of YTO is 2.07 eV, in agreement with previous calculations [8]. DFT calculations of the DSO substrate suggest the broad peak at higher binding energies, ~ -11 eV is likely related to the underlying substrate. Other possibilities related to surface impurities/contamination may also be responsible for a measurable DOS in this energy range. Unfortunately, the DSO reference sample was too insulating when trying to measure the VB. Finally, in an attempt to determine this gap experimentally, we carried out PL measurements. The raw data of PL measurements for a LAO substrate and a 10-nm YTO sample on LAO substrate are shown in Fig. 3(b). It is noted that films grown on LAO substrates were used for PL measurements because the DSO substrate yielded a strong background signal in PL, making the interpretation of the data difficult. Figure 3(b) shows a clear PL signal from the YTO film around 1.5 eV. The PL from the pure YTO film obtained by subtracting the substrate signal is shown in the inset of Fig. 3(b). We find a gap of ~ 1.5 eV, which is slightly smaller than the Mott-Hubbard gap from DFT.

To summarize, we have demonstrated the first MBE growth of YTO films. Several challenges associated with the evaporation of Y through effusion cells and plausible ways to overcome these challenges are discussed. The electronic transport and Seebeck measurements of both films and bulk samples revealed a p type with a thermally activated transport behavior. Combined with hybrid functional calculations, we found that the transport in YTO is governed by small-polaron hopping with the calculated polaron migration energy barrier of 0.27 eV consistent with the experimental results. From HAXPES measurements, the LHB of YTO was found to be located 1.1 eV below the Fermi level. Using PL measurements, we determined a Mott-Hubbard band gap of ~ 1.5 eV in the YTO films. This Rapid Communication addresses key MBE growth challenges, and we expect it to facilitate future investigations of electronic and magnetic ground states in strain-engineered heterostructures of MBE-grown YTO films.

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