Epitaxial Ba$_2$IrO$_4$ thin-films grown on SrTiO$_3$ substrates by pulsed laser deposition

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**Abstract**

We have synthesized epitaxial Ba$_2$IrO$_4$ (BIO) thin-films on SrTiO$_3$ (001) substrates by pulsed laser deposition and studied their electronic structure by dc-transport and optical spectroscopic experiments. We have observed that BIO thin-films are insulating but close to the metal-insulator transition boundary with significantly smaller transport and optical gap energies than its sister compound, Sr$_2$IrO$_4$. Moreover, BIO thin-films have both an enhanced electronic bandwidth and electronic-correlation energy. Our results suggest that BIO thin-films have great potential for realizing the interesting physical properties predicted in layered iridates.

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The coexistence of strong spin-orbit coupling and electron-correlation in 5d transition metal oxides has recently attracted lots of attention due to their potential for unprecedented electronic states. For example, a layered iridate compound, Sr$_2$IrO$_4$ (SIO), which is an antiferromagnetic (T$_N$ ~ 240 K) insulator,$^{1,2}$ has been proposed as a $J_{\text{eff}} = 1/2$ Mott insulator.$^{2,3}$ Its electronic as well as structural similarities to La$_2$CuO$_4$, a parent compound to high-$T_c$ superconductors, have led to a theoretical prediction of unconventional high-$T_c$ superconductivity$^{4,5}$ in this layered iridate system. Moreover, due to strong spin-orbit coupling, it is expected to exhibit physical properties that are governed by their topological nature (e.g. Weyl semimetals).$^6$-$^8$ However, the $J_{\text{eff}} = 1/2$ Mott insulator picture has recently been challenged by SIO being proposed to be a Slater insulator.$^9$-$^{11}$ Although there have been some experimental and theoretical efforts on SIO, this remains an open issue. Hence, understanding the true ground state of layered iridate compounds is a very important task since it will direct us to what physical properties should be pursued in future studies.

Ba$_2$IrO$_4$ (BIO) is another layered iridate compound available for us to unveil the physics of coexisting strong spin-orbit coupling and electron-correlation. BIO is also an antiferromagnetic (T$_N$ ~ 240 K) insulator,$^{12}$ and angle resolved photoemission spectroscopy$^{13}$ as well as X-ray resonant magnetic scattering$^{12}$ on BIO show that its electronic and magnetic structure is quite isomorphic to SIO. However, there is a noticeable structural difference between SIO (space group I4$_1$/acd) and BIO (space group I4/mmm) in their Ir-O-Ir bond angles of 157° and 180°, respectively, which means the IrO$_6$ octahedra are not rotated in BIO.$^{14}$ Recently, pressure-dependent experiments on undoped$^{15}$ and doped$^{16}$ BIO samples have revealed a metallic state. Note that the metallic state is not observed in SIO since the insulating nature of SIO is quite robust.$^{17}$-$^{20}$ Hence, investigations of BIO have been thought to be a promising way
of tuning the physical properties of layered iridate compounds in order to ultimately reveal the theoretically predicted properties in the iridates. However, synthesizing BIO crystals is a formidable task due to the fact that it requires a sophisticated high-pressure (P > 6 GPa) synthesis technique. Experimental studies on BIO have been limited to polycrystals or tiny single crystal samples so far. Hence, there is a demand for large area single-crystal and thin-film samples for the wide range of experimental studies and the potential device applications anticipated from this material.

In this letter, we report that epitaxial BIO thin-films can be grown on SrTiO$_3$ (STO) substrates by pulsed laser deposition. The high-pressure conditions required for the synthesis of BIO has been overcome via compressive strain from the substrates. The $dc$-transport and optical spectroscopic data show that the epitaxial BIO thin-films have smaller bandgap energy, wider electronic bandwidths, and more enhanced effective electron-correlation energy than SIO thin-films. Our results provide another technique to fabricate epitaxial thin-films of compounds that require high-pressure-synthesis and to investigate their physical properties.

The epitaxial BIO thin films are deposited on STO (001) single crystalline substrates with a custom built pulsed laser deposition system. The films are approximately 10 nm thick and the preparation of the atomically-flat STO surfaces is described in Ref. 22. The growth conditions are the following: an oxygen partial pressure of 10 mTorr, substrate temperature of 700°C, and laser (KrF excimer, $\lambda = 248$ nm) fluence of 1.2 J/cm$^2$. Bulk BIO has lattice parameters of $a = 4.030$ Å and $c = 13.333$ Å. The lattice mismatch between bulk BIO and STO is $-3.2\%$, resulting in in-plane compressive strain on the BIO thin-film. Assuming the Young’s modulus (Y) of BIO to be about 300 GPa, the in-plane pressure (P) of approximately 9 GPa ($P = Y \cdot \varepsilon_{xx}$) would be exerted on the BIO films by the compressive strain ($\varepsilon_{xx}$), which satisfies the
high pressure conditions required for the synthesis of bulk BIO. Polycrystal targets have been synthesized by conventional solid-state sintering and annealing processes using BaCO$_3$ and IrO$_2$ powders. Since high-pressure synthesis techniques are not used, the poly-crystal target consists of various phases of barium-iridium oxide composites with the appropriate Ba:Ir ratio of 2:1, which is confirmed through energy-dispersive X-ray spectroscopy.

The structural properties of the epitaxial BIO thin-films are measured with X-ray diffraction (XRD) using a Bruker D8 Advance system with Cu-Kα radiation. Figure 1 (a) shows an XRD θ-2θ scan with the (00l) peaks of the BIO thin-film. X-ray reciprocal space mapping (RSM) near the STO (103)-plane (Fig. 1 (b)) shows that the (109)-plane of BIO thin-films with a slight strain relaxation (dashed line), which is common for thin films with such a large lattice mismatch. The green asterisk (*) represents the (109)-plane of bulk BIO. The average lattice parameters of the BIO thin-film estimated from the RSM are $a = 3.91$ Å and $c = 13.45$ Å, which correspond to crystal strains of $\varepsilon_{xx} = -3.0\%$ and $\varepsilon_{zz} = +0.8\%$ and a Poisson ration of $\nu = 0.12$. The small Poisson ration ($\nu < 0.33$) implies that the BIO thin-film does not sufficiently elongate along the c-axis under the in-plane compressive strain. This behavior has also been observed in compressively strained SIO thin-films.\textsuperscript{19} The rocking curve scan of the BIO (006) peak (Fig. 1 (c)), whose full-width half-maximum (FWHM) is 0.07°, confirms the good crystallinity of the BIO thin-films. For comparison, the FWHM of the STO (002) rocking curve peak is 0.06° (data not shown). The four-fold symmetry of the BIO thin-film is also confirmed by pole-figure scans of the BIO (103) reflection (Fig. 1 (d)).

Transport measurements (Fig. 2) show that the samples are insulating with a temperature-dependent energy gap estimated from the activation energy ($\Delta_{res} = 2E_a$). The temperature dependence of the resistivity is shown in Fig. 2 (a) for both BIO (red) and SIO (blue) thin-films.
grown on STO substrates. An Arrhenius plot \((\rho = \rho_0 e^{\Delta_{\text{res}}/2k_B T})\) is presented in Fig. 2 (b), where \(k_B\) is the Boltzmann constant. The magnitude of \(\Delta_{\text{res}}\) is estimated at two temperature regions for both samples and is smaller for BIO thin-films than for SIO thin-films at all temperatures. It is also noteworthy that \(\Delta_{\text{res}}\) for both BIO and SIO thin-films decrease as temperature decreases. This abnormal temperature-dependence of gap energy suggests that they become less insulating at low temperature and has also been observed in iridate bulk-crystals\(^{23}\) and thin-films.\(^{18}\) This indicates that the insulating nature of this system is quite distinct from simple band insulators.

Optical spectroscopic measurements show that BIO thin-films have a similar electronic structure to SIO thin-films with a few different features. The optical absorption coefficient spectra are presented in Fig. 3 for BIO (a) and SIO (b) thin-films. While both spectra have a qualitatively similar shape, the optical transition peaks (\(\alpha\) and \(\beta\)) of BIO thin-films are broader and at higher energies than those of SIO. This means the electronic bandwidth \(W\) is larger for BIO thin-films than for SIO thin-films. Although \(\alpha\) and \(\beta\) occur at higher energies, the significantly larger \(W\) results in the optical gap energy, as estimated from the onset of the optical spectra, of BIO thin-films being smaller than not only SIO thin-films deposited on STO, but for bulk\(^{24}\) and other thin-film\(^{18,19}\) samples of SIO as well.

The gap energies of BIO thin-films estimated through \(dc\)-transport and optical spectroscopic experiments are consistently smaller than SIO thin-films. The increased \(W\), which implies the hopping integral \((t)\) is larger, reduces the gap energies presumably due to the increased Ir-O-Ir bond angle in the BIO thin-films. However, complete gap closing (i.e. a metallic state) does not occur in this system which remains insulating. We can find an important clue about the insulating nature of BIO thin-films from their optical spectra. As mentioned
above, α and β of BIO thin-films occur at higher photon energies than for SIO thin-films. Since the position of these optical transitions is related to $U_{\text{eff}}$,\textsuperscript{24,25} the increased optical-transition peak positions imply that $U_{\text{eff}}$ is also larger in the BIO thin-films. An enhanced $W$ and $U_{\text{eff}}$ has been observed in tensile-strained\textsuperscript{19} and $\alpha$-axis oriented\textsuperscript{18} SIO thin-films as well. At this moment, it is difficult to understand how $U_{\text{eff}}$ can be increased by changes in the lattice of layered iridates, since it requires microscopic studies of local ionic and electronic structure.

It is remarkable that even though $U_{\text{eff}}$ is larger, the electronic structure is dominated by $W$ broadening, which results in BIO thin-films having a significantly reduced optical gap energy. Note that the hydrostatic pressure-induced metal-insulator transition has been observed in bulk BIO,\textsuperscript{15} but not in SIO,\textsuperscript{17} which suggests that the electronic structure of BIO is close to the edge of the metal-insulator phase transition. One of the remarkable theoretical predictions for layered iridate compounds is for superconductivity to be realized with carrier doping.\textsuperscript{4,5} However, superconductivity has not been observed in SIO samples even under various physical tuning parameters such as electrochemical doping,\textsuperscript{23,26,27} hydrostatic pressure,\textsuperscript{17} and lattice strain.\textsuperscript{19} Our experimental observations on BIO thin-films suggest that BIO is a better candidate for intriguing transport properties such as unconventional superconductivity since its electronic structure is closer to the metal-insulator transition due to significantly reduced transport and optical gap energies.

In summary, we have successfully grown epitaxial BIO thin-films on STO substrates by pulsed laser deposition. By transport and optical spectroscopic measurements, we have observed that the BIO thin-films are still insulating but with an appreciably smaller energy gap than SIO. While they have similar electronic structure in character, the BIO thin-films show a larger bandwidth and effective electronic-correlation energy than SIO. We suggest that the BIO thin-
films have great potential for unveiling the intriguing physical properties predicted in the layered iridate compounds due to their electronic structure being close to the metal-insulator transition.

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Figure Captions

**Figure 1**  X-ray diffraction of the BIO films on STO.  a) A $\theta$-2$\theta$ scan where the BIO peaks are clearly labeled and the STO peaks are identified with a ▼ symbol.  b) A reciprocal space map near the STO (103) peak, where the dashed line and the green asterisk (*) represent the position of the substrate peak and bulk lattice parameters, respectively.  c) A rocking curve about the BIO (006) peak ($\omega = 20.33^\circ$).  d) A pole figure about the BIO (103) peak in the range of psi from 0° to 60°.

**Figure 2**  a) Temperature dependence of the normalized resistivity for BIO (red) and SIO (blue) thin-films on STO substrates.  b) Arrhenius plot with gap energy ($\Delta_{res} = 2E_a$) estimated for two temperature regions for BIO (red) and SIO (blue).  Note that SIO curve has a vertical offset for clarity.

**Figure 3**  Optical absorption coefficient spectra for a) BIO and b) SIO.  Inset: Schematic drawing of the electronic structure of the Ir 5$d$ band for a) BIO and b) SIO.
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Figure 1
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Figure 2
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Figure 3