ELECTRONIC AND OPTICAL PROPERTIES OF METASTABLE EPITAXIAL THIN FILMS OF LAYERED IRIDATES

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ELECTRONIC AND OPTICAL PROPERTIES OF METASTABLE EPITAXIAL THIN FILMS OF LAYERED IRIDATES

DISSertation

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Arts and Sciences at the University of Kentucky

By
Maryam Souri
Lexington, Kentucky

Director: Dr. Ambrose Seo, Professor of Physics
Lexington, Kentucky

2018

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ELECTRONIC AND OPTICAL PROPERTIES OF METASTABLE EPITAXIAL THIN FILMS OF LAYERED IRIDATES

The layered iridates such as Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$, have attracted substantial attention due to their novel electronic states originating from strong spin-orbit coupling and electron-correlation. Recent studies have revealed the possibilities of novel phases such as topological insulators, Weyl semimetals, and even a potential high-$T_c$ superconducting state with a $d$-wave gap. However, there are still controversial issues regarding the fundamental electronic structure of these systems: the origin of the insulating gap is disputed as arising either from an antiferromagnetic ordering, i.e. Slater scheme or electron-correlation, i.e. Mott scheme. Moreover, it is a formidable task to unveil the physics of layered iridates due to the limited number of available materials for experimental characterizations.

One way to overcome this limit and extend our investigation of the layered iridates is using metastable materials. These materials which are far from their equilibrium state, often have mechanical, electronic, and magnetic properties that different from their thermodynamically stable phases. However, these materials cannot be synthesized using thermodynamic equilibrium processes. One way to synthesize these materials is by using pulsed laser deposition (PLD). PLD is able to generate non-equilibrium material phases through the use of substrate strain and deposition conditions. Using this method, we have synthesized several thermodynamically metastable iridate thin-films and have investigated their electronic and optical properties. Synthesizing and investigating metastable iridates opens a path to expand the tunability further than the ability of the bulk methods.

This thesis consists of four studies on metastable layered iridate thin film systems. In the first study, three-dimensional Mott variable-range hopping transport with decreased characteristic temperatures under lattice strain or isovalent doping has been observed in Sr$_2$IrO$_4$ thin films. Application of lattice strain or isovalent doping exerts metastable chemical pressure in the compounds, which changes both the bandwidth and electronic hopping. The variation of the characteristic temperature under lattice strain or isovalent doping implies that the density of states near the Fermi energy is reconstructed. The increased density of states in the Sr$_2$IrO$_4$ thin films with strain and isovalent doping could facilitate a condition to induce unprecedented electronic
properties, opening a way for electronic device applications. In the second study, the effects of tuning the bandwidth via chemical pressure (i.e., Ca and Ba doping) on the optical properties of Sr$_2$IrO$_4$ epitaxial thin films has been investigated. Substitution of Sr by Ca and Ba ions exerts metastable chemical pressure in the system, which changes both the bandwidth and electronic hopping. The optical conductivity results of these thin films suggest that the two-peak-like optical conductivity spectra of the layered iridates originates from the overlap between the optically-forbidden spin-orbit exciton and the inter-site optical transitions within the $J_{eff} = \frac{1}{2}$ band, which is consistent with the results obtained from a multi-orbital Hubbard model calculation. In the third study, thermodynamically metastable Ca$_2$IrO$_4$ thin-films have been synthesized. Since the perovskite structure of Ca$_2$IrO$_4$ is not thermodynamically stable, its bulk crystals do not exist in nature. We have synthesized the layered perovskite phase Ca$_2$IrO$_4$ thin-films from a polycrystalline hexagonal bulk crystal using an epitaxial stabilization technique. The smaller A-site in this compound compared to Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$, increases the octahedral rotation and tilting, which enhance electron-correlation. The enhanced electron-correlation is consistent with the observation of increased gap energy in this compound. This study suggest that the epitaxial stabilization of metastable-phase thin-films can be used effectively for investigating complex-oxide systems. Finally, structural, transport, and optical properties of tensile strained (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ ($x = 0, 0.025, 0.05$) thin-films have been investigated. While high-$T_c$ superconductivity is predicted in the system, all of the samples are insulating. The insulating behavior of the La-doped Sr$_3$Ir$_2$O$_7$ thin-films is presumably due to disorder-induced localization and ineffective electron-doping of La, which brings to light the intriguing difference between epitaxial thin films and bulk single crystals of the iridates. These studies thoroughly investigate a wide array of novel electronic and optical phenomena via tuning the relative strengths of electron correlation, electronic bandwidth, and spin-orbit coupling using perturbations such as chemical doping, and the stabilization of metastable phases in the layered iridates.

KEYWORDS: complex oxides, iridates, electron-electron correlation, spin-orbit interaction, thin film oxides, pulsed laser deposition.

Author’s signature: Maryam Souri
Date: December 16, 2018
ELECTRONIC AND OPTICAL PROPERTIES OF METASTABLE EPITAXIAL THIN FILMS OF LAYERED IRIDATES

By
Maryam Souri

Director of Dissertation: Ambrose Seo
Director of Graduate Studies: Christopher Crawford
Date: December 16, 2018
To the memory of my father and my brother, who I miss every day.
To my mother for her unconditional love.
To my husband and my beautiful daughter for their endless support and encouragement during the difficulties and challenges of my life.
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Chapter 1 Introduction

1.1 Ruddlesden-Popper series iridates

$5d$ transition metal oxides such as iridium oxide have attracted substantial attention due to their rich variety of electronic states originating from coexisting strong spin-orbit coupling ($SOC$) and electron correlations ($U$). Recent studies have revealed the possibilities of exotic electronic and magnetic states such as topological insulators, Weyl semimetals, spin-orbit Mott insulators, and even a potential high-$T_c$ superconducting state with a $d$-wave gap.

One of the most interesting examples of the $5d$ transition metal oxides are the Ruddlesden-Popper (R-P) series of iridium oxides. This series is described by the formula $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ ($n = 1 - \infty$), where various novel electronic structures are shown as a function of the number of IrO$_2$ layers $n$. The general formula of the R-P phase is $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$, where A and B both represent cations, and O represents an anion (usually oxygen), and $n$ is the number of layers of octahedra in the perovskite-like stack. The perovskite structure is described by the formula $\text{ABO}_3$. Figure 1.1 shows the schematic of the R-P structure, where the A cations are located in the perovskite layer and the B cations are located inside the anionic octahedra.

The competition between comparable energy scales such as crystal field splitting ($CF$), electron correlation ($U$), electronic hoping ($t$), and spin-orbit coupling ($SOC$) in R-P phase iridates determines the ground state of this system. For instance, since the integer $n$ represent the number of SrIrO$_3$ perovskite layers sandwiched between extra SrO layers, an increase in $n$ would increase the coordination number of Ir. An increase in the coordination number of Ir would increase electron hopping across neighboring sites $t$, which determines the bandwidth ($W$) of the system. The competition between $U$, which acts to localize single electrons on each atomic site
Figure 1.1: Schematic of Ruddlesden-Popper (R-P) structure with general formula of $A_{n+1}B_nO_{3n+1}$ ($n = 1 - \infty$). A and B are cations and O is an anion.

and $W$ determines the electronic properties of the system. As it is shown in figure 1.2, by increasing the iridium coordination number ($n$) from Sr$_2$IrO$_4$ to SrIrO$_3$, an insulator-metal transition occurs due to the increased Ir 5$d$ bandwidth. In single-layered Sr$_2$IrO$_4$ ($n = 1$) an insulating gap opens due to reduced Ir 5$d$ bandwidth. In the case of Sr$_2$IrO$_4$ ($W < U$), the Coulomb interaction suppresses the charge hopping and the material is found to be a Mott insulator. [1] This system has been theoretically predicted to show a high-$T_c$ superconducting state [4,13], and $d$-wave gap symmetry has been experimentally observed with electron doping on its surface [5,6,11]. On the other hand, as the dimensionality of the system increases to SrIrO$_3$ ($n = \infty$), the system exhibits strongly correlated metallic behavior due to the increased Ir 5$d$ bandwidth ($W > U$). [14,15]
Moreover, the R-P phases of the irideates are highly susceptible to external perturbations such as lattice strain, chemical doping, pressure, and dimensionality, which can change the magnetic and electronic properties of these systems. For instance, controlling the bandwidth of layered iridate epitaxial thin film of Sr$_2$IrO$_4$ via chemical substitutions of Sr ions by Ca and Ba, (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ ($x = 0 - 0.375$) and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ ($y = 0 - 0.375$), which results in the observation of optical signatures of spin-orbit exciton in these systems. This work will be discussed in further details in chapter 3. [16]. Thus, the R-P phase of layered iridate thin-films under different perturbations such chemical pressure can reveals indispensable information regarding the structural, electronic, and optical properties of layered iridates.
1.1.1 Crystal field effect

As it is shown in the schematic of the R-P structure (Fig. 1.1), in Sr$_2$IrO$_4$ with 5$d^5$, each iridium is surrounded in octahedral oxygen environment (Fig. 1.3 (a)). In order to understand the interaction between Ir and oxygen environment it is necessary to consider the shapes of Ir $d$ atomic orbitals. The orbital shapes describe the regions where electrons occupy orbitals. In other words, the orbitals indicate the regions that have a high probability of finding electrons. There are five different $d$ orbitals: $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{x^2-y^2}$, and $d_{z^2}$. These five orbitals are divided into two categories: 1) The first three ($d_{xy}$, $d_{xz}$, and $d_{yz}$), which lie in the $x-y$, $x-z$ and $y-z$ planes, respectively, with their lobes pointing between the two axes, and 2) The other two orbitals ($d_{x^2-y^2}$, $d_{z^2}$), which their lobes points along the axes. The three degenerate set are called $t_{2g}$ orbitals and the two degenerate set are called $e_g$. In an isolated atom or ion, all of the $d$–orbitals are energetically degenerate. However, as the $d$ orbitals are affected by the oxygens around it, the energy levels of the orbitals are modified.

![Diagram of crystal field effect](image)

Figure 1.3: a) Schematic of Ir and O octahedral molecular geometry. b) Crystal field effect on $d$ orbitals of Ir.
The model that describes how transition metal ions such as Ir are affected by the octahedral arrangement of oxygens around it, is called octahedral crystal field effect (\(CF\)) and the separation between these two sets is called the octahedral CF splitting (\(\Delta_o\) or \(10Dq\)). Based on this model, in case of iridate oxides, the two orbitals (\(e_g\) orbitals) that have maximum overlap with the neighboring \(p\)-orbitals of the oxygen, will feel more repulsion than the other three (\(t_{2g}\) orbitals). Therefore, as it is shown in 1.3 (b), the \(e_g\) orbitals will have a higher energy compared to the \(t_{2g}\) orbitals, which splits the \(d\) orbitals of Ir ions. The \(t_{2g}\) orbitals are stabilized by 0.4 \(\Delta_o\) and \(e_g\) orbitals are destabilized by 0.6 \(\Delta_o\). For an Ir ion with five electrons in the \(d\) orbitals, since the crystal field splitting (\(\Delta_o\) or \(10Dq\)) is larger than the energy required to put two electrons in to the same orbital (Hund’s rule energy, \(J_H \approx 0.5\) eV), all 5 electrons will be in the \(t_{2g}\) orbitals (low spin states) and the \(e_g\) orbitals are empty (Fig.1.3 (b)).

1.1.2 Spin-orbit coupling in 5\(d\) transition metal oxides

The spin-orbit coupling is usually a small interaction in many of the atoms, which dominated by other interaction in the crystalline lattice, such as \(CF\) and \(U\). Spin-orbit coupling (\(SOC\)) originates from a relativistic effect from the coupling between a particle’s spin (\(\mu_e\), electron’s magnetic moment) and the effective magnetic field \(\mathbf{B}\), which an electron experiences while orbiting an atomic nucleus of charge \(Ze\) (\(Z\) is the atomic number of the nucleus and \(e\) is the elementary charge). The Hamiltonian has the following term: \[H_{SO} = -\mu_e \cdot \mathbf{B}\]

where in the rest frame of the electron, \(\mathbf{B}\) is generated by the orbiting nucleus on the
electron and is given by the Biot-Savart law:

\[ \mathbf{B} = -\frac{Ze}{c} \mathbf{V} \times \mathbf{r} / r^3 \]  \hspace{1cm} (1.2)

where \( \mathbf{V} \) is the velocity of the moving atomic nucleus, and \( r \) is the distance between electron and the nucleus.

By substituting \( \mathbf{B} \) in the equation (1.1), we have:

\[ H_{SO} = \frac{Ze \mu_e \cdot (\mathbf{p} \times \mathbf{r})}{mc} \cdot \frac{1}{r^3} \]  \hspace{1cm} (1.3)

where \( \mathbf{p} = m\mathbf{V} \). Considering \( \mu_e = -(e/mc)\mathbf{S} \), and quantized angular momentum \( \mathbf{L} \) for \( l \), we have:

\[ H_{SO} = \frac{Ze^2}{2(mc)^2} \frac{S \cdot L}{r^3} \]  \hspace{1cm} (1.4)

Since the total angular momentum \( \mathbf{J} = \mathbf{L} + \mathbf{S} \), by taking the dot product of this equation with itself, we have: \( \mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2 \mathbf{S} \cdot \mathbf{L} \), therefore:

\[ S \cdot L = \frac{1}{2}(J^2 - L^2 - S^2) \]  \hspace{1cm} (1.5)

Hence, the eigenvalue of the Hamiltonian is:

\[ < H_{SO} > = \frac{Ze^2}{4(mc)^2} < \frac{1}{r^3} > \frac{1}{2}[j(j + 1) - l(l + 1) - \frac{3}{4}] \]  \hspace{1cm} (1.6)
where: \[21\]

\[
\langle \frac{1}{r^3} \rangle = \int \frac{1}{3} r^2 R_{nd}(r) dr = \frac{Z^3}{a_0^3} \frac{1}{n^3l(l+1/2)(l+1)}
\]  

(1.7)

Finally, the correction to the energy due to the spin-orbit coupling is:

\[
< \Delta E_{SO} > = \alpha_{SO} \frac{1}{2} [j(j + 1) - l(l + 1) - \frac{3}{4}] 
\]

(1.8)

where $\alpha_{SO}$ is equal to:

\[
\alpha_{SO} = \frac{Z^4e^2}{4(mc)^2a_0^3} \frac{1}{n^3l(l+1/2)(l+1)}
\]

(1.9)

Because of the spin-orbit coupling, the energy of an electron in the states $j = l + 1$ and $j = l - 1$ is now different. The orbital $d_{x^2}$ has $m = 0$, $d_{xz}$ has $m = \pm 1$, $d_{yz}$ has $m = \pm 1$, $d_{xy}$ has $m = \pm 2$, and $d_{x^2-y^2}$ has $m = \pm 2$. Therefore, for example, the wave function $\varphi_{nd_{yz}}$ is a combination of $Y_1^2$ and $Y_{-1}^2$ functions.

Below is the two different sets of wave functions for the three $t_{2g}$ states and the two $e_{2g}$ states:

— Wave functions for the three $t_{2g}$ states are:

\[
\varphi_{nd_{xy}}(r) = -\frac{i}{\sqrt{2}}[Y_2^2(r) - Y_{-2}^2(r)]R_{nd}(r)
\]

\[
\varphi_{nd_{xz}}(r) = \frac{i}{\sqrt{2}}[Y_1^2(r) + Y_{-1}^2(r)]R_{nd}(r)
\]

(1.10)

\[
\varphi_{nd_{xz}}(r) = -\frac{1}{\sqrt{2}}[Y_1^2(r) - Y_{-1}^2(r)]R_{nd}(r)
\]
—Wave functions for the two $e_{2g}$ states:

$$\varphi_{nd^2}(r) = Y^2_0(r)R_{nd}(r)$$

$$\varphi_{nd^2-y^2}(r) = \frac{1}{\sqrt{2}}[Y^2_2(r) + Y^{-2}_2(r)]R_{nd}(r) \quad (1.11)$$

By using the split forms of the $t_{2g}$ and $e_{2g}$ orbitals, the related wave functions, and the relations below:

$$l_z|\varphi_{lm}\rangle = m\hbar|\varphi_{lm}\rangle$$

$$l_\pm|\varphi_{lm}\rangle = \hbar\sqrt{l(l+1) - m(m \pm 1)}|\varphi_{lm\pm1}\rangle \quad (1.12)$$

$$l_\pm|\varphi_{lm}\rangle = l_x \pm il_y$$

We derive $l_x, l_y, l_z$ as bellow. These matrices are given in the basis $d_{xz}, d_{yz}, d_{xy},$
\( d_{x^2-y^2}, \) and \( d_{z^2} \):

\[
l_x = \begin{pmatrix}
0 & 0 & i & 0 & 0 \\
0 & 0 & 0 & -i\sqrt{3} & -i \\
-i & 0 & 0 & 0 & 0 \\
0 & i\sqrt{3} & 0 & 0 & 0 \\
0 & i & 0 & 0 & 0
\end{pmatrix},
\]

\[
l_y = \begin{pmatrix}
0 & 0 & 0 & i\sqrt{3} & -i \\
0 & 0 & -i & 0 & 0 \\
0 & i & 0 & 0 & 0 \\
-i\sqrt{3} & 0 & 0 & 0 & 0 \\
i & 0 & 0 & 0 & 0
\end{pmatrix},
\]

\[
l_z = \begin{pmatrix}
0 & i & 0 & 0 & 0 \\
-i & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 2i \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & -2i & 0 & 0
\end{pmatrix}
\]

By using the equations above and equation 1.4 we calculate the Hamiltonian of the spin-orbit interaction. Note that the matrix elements of the \( L \) for the \( e_g \) subspace are zero. This means the orbital angular momentum is completely quenched in the \( e_g \) states (\( L.S = 0 \)). The spin-orbit Hamiltonian for the \( t_{2g} \), in the bases of \( (d_{xz} \uparrow, \)


The spin-orbit interaction Hamiltonian \( H_{SO} \), for \( d_{yz} \uparrow, d_{xy} \downarrow, d_{xz} \downarrow, d_{yz} \downarrow, d_{xy} \uparrow \) is as below:

\[
H_{SO} = \begin{pmatrix}
0 & -i & i & 0 & 0 \\
-1 & 0 & 0 & 0 & 0 \\
i & 0 & -1 & 0 & 0 \\
-1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & i & 1 \\
0 & 0 & 0 & -1 & 1 \\
\end{pmatrix} \times \frac{\alpha_{SO}}{2} \tag{1.14}
\]

Using the following \(|d_{xy}\rangle\) and linear combination of \(|d_{xz}\rangle\) and \(|d_{yz}\rangle\):

\[
|\psi_+\rangle = -\frac{1}{\sqrt{2}}(|d_{yz}\rangle + i|d_{xz}\rangle) \\
|\psi_-\rangle = \frac{1}{\sqrt{2}}(|d_{yz}\rangle - i|d_{xz}\rangle) \tag{1.15}
\]

\[
|\psi_0\rangle = |d_{xy}\rangle
\]

The eigenvalues of the Hamiltonian are:

\[
\implies \epsilon_{SO}^{\pm} = +\alpha_{SO}, -\frac{1}{2}\alpha_{SO} \tag{1.16}
\]

The eigenstates associated to the eigenvalue \( \epsilon_{SO}^{\pm} \) are:

\[
|j_{eff} = \frac{1}{2}, m_j = -\frac{1}{2} \rangle = \frac{1}{\sqrt{3}}(|d_{yz},\uparrow\rangle - |d_{xz},\uparrow\rangle - |d_{xy},\downarrow\rangle) \\
|j_{eff} = \frac{1}{2}, m_j = +\frac{1}{2} \rangle = \frac{1}{\sqrt{3}}(|d_{yz},\downarrow\rangle + i|d_{xz},\downarrow\rangle + |d_{xy},\uparrow\rangle) \tag{1.17}
\]
The eigenstates associated to the eigenvalue $\epsilon_{J_{\text{eff}}=\frac{3}{2}}$ are:

\[ |j_{\text{eff}} = \frac{3}{2}, m_j = -\frac{3}{2} \rangle = \frac{1}{\sqrt{2}} (|d_{yz,\downarrow} \rangle - i |d_{xz,\downarrow} \rangle) \]

\[ |j_{\text{eff}} = \frac{3}{2}, m_j = +\frac{3}{2} \rangle = -\frac{1}{\sqrt{2}} (|d_{yz,\uparrow} \rangle + i |d_{xz,\uparrow} \rangle) \]  

\[ |j_{\text{eff}} = \frac{3}{2}, m_j = -\frac{1}{2} \rangle = \frac{1}{\sqrt{6}} |d_{yz,\uparrow} \rangle - \frac{i}{\sqrt{6}} |d_{xz,\uparrow} \rangle + \sqrt{\frac{2}{3}} (|d_{xy,\downarrow} \rangle) \]  

\[ |j_{\text{eff}} = \frac{3}{2}, m_j = +\frac{1}{2} \rangle = -\frac{1}{\sqrt{6}} |d_{yz,\downarrow} \rangle - \frac{i}{\sqrt{6}} |d_{xz,\downarrow} \rangle + \sqrt{\frac{2}{3}} (|d_{xy,\uparrow} \rangle) \]  

Furthermore, the separation between the two multiplets is:

\[ \epsilon_{J_{\text{eff}}=\frac{3}{2}}^{SO} - \epsilon_{J_{\text{eff}}=\frac{1}{2}}^{SO} = -\frac{3}{2} \alpha_{SO} \]  

According to the above equation, the separation between $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = \frac{3}{2}$ is proportional to $\alpha_{SO}$, in which $\alpha_{SO}$ is proportional to the atomic number $Z^4$ ($\alpha_{SO} \propto Z^4$).

In the case of iridates, Ir is an heavy element with atomic number $Z = 77$, which causes to have strong SOC ($\alpha_{SO} \sim 0.4$ eV). Therefore, unlike many transition metals such as $3d$ transition metal oxides, the spin-orbit interaction in $5d$ transition metal oxides such as Ir is quite large. This strong SOC in iridate compounds is comparable to other interactions such as the crystal field effect and electron-electron interaction, in which the energetic competition between these interactions determine the electronic properties of these iridate systems.

### 1.1.3 The effective electron correlation energy

Among transition metal oxides, the $3d$-elements and their compounds have been wildly studied for several decades. Interesting phenomena such as high-$T_c$ superconductivity in cuprates \cite{22,24} and colossal magnetoresistance in manganites \cite{25} have
emerged from 3$d$ transition metal oxides. However, even though the weakly interacting or non-interacting electron model (band picture) can describe the electronic properties of many metallic, semiconducting, and insulating compounds, it can not describe the electronic properties of partially filled 3$d$ transition metal oxides. The electronic structure of this class of materials depend more on electron-electron correlation, which originates from the on-site Coulomb repulsion between the 3$d$–orbitals electrons. The electron-electron correlation energy originates from the Coulomb interaction between electrons at the same orbital. The Coulomb interaction ($\sim e^2/r$) prevents electrons from hopping to the next site.

The Hubbard model is a Hamiltonian model used to explain the correlated electrons, by considering only valence electrons near the Fermi level: \[26\]

\[ H = \sum_{ij,\sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]  

(1.20)

where $i$ and $j$ are the nearest neighbor lattice sites and $\sigma = \uparrow$ or $\downarrow$ indicates the spin direction. The first term is the kinetic energy, explained by electron hopping across neighboring sites $t_{ij}$, this hopping term determines the bandwidth ($W$) of the system. The second term is the Coulomb repulsion that acts to localize single electrons on each atomic site and hence prevent hopping. The competition between $U$ and $W$ determines the electronic properties of the interacting system. In the case of $W < U$, the Coulomb interaction suppresses the charge hopping and the material is found to be a Mott insulator, where as in the case of $W > U$, the system becomes metallic.

While transition metal oxides with 3$d$ elements have strong electron-electron correlation, looking down the periodic table, we notice that the $d$ orbital in the 4$d$ elements is more extended compared to 3$d$ elements, which causes a reduced intra-atomic Coulomb interaction compare to the 3$d$ transition metals. The 5$d$ orbitals are even more extended (smaller $U$) than the 4$d$ orbitals. However, the extended
$d$ orbitals in the $5d$ elements create an environment with comparable fundamental interactions. For instance, the smaller $U$ and larger $SO$ in the $5d$ transition metals such as iridates makes these two fundamental interactions energetically comparable and causes a unique competition between them, which results in physical behaviors different from those of the $3d$ elements and their compounds.

1.2 Spin-orbit coupled Mott insulators

Since the electron bandwidth ($W$) and electron-electron correlation ($U$) are comparable in the $3d$ transition metal oxides, the Mott transition is observed in many of these compounds. As the bandwidth is extended in the $4d$ transition metal oxides, metallic behavior is more common. Therefore, the insulating behavior observed in some of the $5d$ transition metal oxides such as BaIrO$_3$, Sr$_2$IrO$_4$, Sr$_3$Ir$_2$O$_7$ with even more extended $d$ orbitals is unusual. However, in 2008, B. J. Kim et al. [1] pointed out that strong spin orbit coupling in these systems plays an important rule. Because $SOC$ is comparable to the on-site Coulomb repulsion energy in these systems, it is no longer a perturbation parameter. In fact, this additional interaction competes with other energy scales such as the crystal field, and it can modify the electronic structure of these materials.

For instance, as it is shown in figure 1.4 in compounds such as Sr$_2$IrO$_4$ with $5d^5$ Ir$^{4+}$, each iridium is surrounded in an oxygen environment. Therefore, the $d$ orbital of Ir are perturbed by oxygens around it. This effect is called crystal field effect, and causes $5d$ states to split into $t_{2g}$ and $e_g$ states. Due to $SO$ interaction these bands split further to the $J_{eff} = \frac{1}{2}$ and $J_{eff} = \frac{3}{2}$ states. This splitting is proportional to the $SO$ coupling energy of the iridium. Due to the half field $J_{eff} = \frac{1}{2}$ orbital, one could expect iridate to be metallic. However, as is shown in figure 1.4 because $J_{eff} = \frac{1}{2}$ is half filled, it is more susceptible to other atomic correlation interactions in the lattice of the system and undergoes a Mott transition even at a relatively small $U$. 
Figure 1.4: Schematic energy diagrams for the $5d^5$ configuration in compounds such as Sr$_2$IrO$_4$ with $5d^5$ Ir$^{4+}$, considering crystal field effect, spin orbit coupling (SOC) and electron-electron correlation ($U$).

1.3 Metastable thin films

Thin-film (a layer of material with thickness ranging from fractions of a nanometer to several micrometers) materials often exhibit unique properties that are significantly different from the corresponding bulk materials as a result of their physical dimensions, geometry, and non equilibrium microstructure. These characteristic features can modify the physical properties of the material and lead to the discovery of novel phenomena. Moreover, the existence of different thin film deposition techniques creates the possibility of synthesizing a variety of superlattices, heterostructures, and metastable phases of thin films, which are big advantages for fundamental science and device applications.

Each crystal structure of the same material has a distinct energy. The crystal structure with the lowest energy is the thermodynamically stable structure of the material. However, some materials can exist or be made to exist in states which are not the lowest energy state; these are called metastable states.

A metastable state is a stable intermediate state of a system, which has a longer lifetime than the unstable states and usually a shorter lifetime than the lowest stable energy state. Compounds composed of these metastable states are called metastable
metastable thin-films are a class of new materials which can address important questions in science and lead to developments in new materials for device applications. For example, while there are still many questions regarding the fundamental electronic structure of layered iridate systems, these problems are exacerbated by the fact that only a few iridates are available for experimental characterizations. Metastable materials could give us the opportunity to extend our understanding of this system far behind the scope of limited bulk studies.

However, while these metastable materials can not be synthesized using thermodynamic equilibrium processes, thin film deposition techniques such as pulsed laser deposition (PLD) are able to fabricate many of these metastable materials. Note that electronic transport and magnetic properties are strongly affected by the structure, which is a result of the synthesis processes. Therefore, being able to control the deposition and structure of materials will allow the control of their properties.

One example is the metastable growth of $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4$ $(x = 0 - 0.375)$ and $(\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4$ $(y = 0 - 0.375)$ epitaxial thin-films. The tetragonal phase bulk crystals of these compounds are stable only for $(x = 0 - 0.11)$ and $(y = 0 - 0.1)$, respectively. [27,28] The substitution of Sr by Ca and Ba ions systematically tunes both bandwidth and electronic hopping in this system, which changes the electronic and optical properties. The optical conductivity results of these thin films suggest that the two-peak-like spectra of layered iridates originates from the overlap between the optically-forbidden spin-orbit exciton and the inter-site optical transitions within the $J_{\text{eff}} = \frac{1}{2}$ band.

Another example of metastable materials is the R-P phase of $\text{Ca}_2\text{IrO}_4$ which can not be thermodynamically stabilized in the bulk. However, using an epitaxial stabilization technique and proper substrate, the R-P phase of $\text{Ca}_2\text{IrO}_4$ thin-films has been synthesized. The smaller A-site cation in this compound compared to its sisters $\text{Sr}_2\text{IrO}_4$ and $\text{Ba}_2\text{IrO}_4$ compounds, causes an increases in the octahedral rotation and
tilting in this system, which enhances the electron-correlation energy, $U/W$. The details of these two studies will be discussed in chapter 3 and 4. (Fig. 4.1 [29]) Another example is that bulk SrIrO$_3$ is hexagonal, and the perovskite structure of this compound only exist at high temperature and pressure. However, its high pressure phase can be induced via epitaxial stabilization using proper substrates with lattice parameters close to the pseudo-cubic lattice constant of this compound [15] (Fig. 1.5). A metal to insulator transition has been observed in this system. Such studies are entirely unique to thin films, and can not be performed in bulk crystals. The possibility of synthesizing metastable iridate thin-films and also tuning the electronic states of this system can extend our understanding of these compounds further than our knowledge from the bulk crystal studies.
1.3.1 Pulsed laser deposition method

Pulsed laser deposition (PLD) is a widely used method for growth of various thin-films, superlattices, and heterostructures. This technique has gained lots of attention due to advantages such as the capability for stoichiometric transfer of the target materials to the thin film, high deposition rates, possibility of using multiple target for deposition of heterostructure thin films. The purity and stoichiometry of thin-films and heterostructures synthesized by this method are easily comparable to thin film grown by MBE. Using pulsed laser deposition method, artificially layered materials and metastable phases have been synthesized and their properties have been investigated. [15,16,29]

In this growth process, a set of optical components is used to focus a high-power pulsed laser beam over the target’s surface inside a vacuum chamber. The pulsed laser beam strike the target, vaporize the target’s materials and deposits thin films on the substrate (Fig. 1.6 (a)). In our laboratory, we use an ultraviolet (UV) KrF excimer pulsed laser, where the wave length is 248 nm. Therefore the energy of the laser is $\sim 5\,\text{eV}$, which is larger than the band gap of most of oxide materials. Using the pulsed laser deposition method we are able to produce complex oxide thin films. Figure 1.6 (b) shows a photograph of one of our PLD systems in our group.
Figure 1.6: a) Schematic diagram of inside a vacuum chamber, while synthesizing a material using pulsed laser deposition (PLD) method. b) Photograph of the pulsed laser deposition system (PLD) in our group.

During deposition using PLD, many experimental parameters can be changed in order to synthesize a high quality thin film. Some of these parameters are: stoichiom-
etry of the target, lattice mismatch of thin film and substrate, oxygen partial pressure, temperature of the substrate, distance between substrate and target, laser pulse energy, and laser fluence. One example is the effective tuning of electronic structure of \( \text{Sr}_2\text{IrO}_4 \) under lattice-modification that is possible by synthesizing \( \text{Sr}_2\text{IrO}_4 \) thin films on various substrates using PLD. This study help us to better understand physics driven by the coexisting strong spin-orbit coupling and electronic correlation.
Chapter 2  Tunable Mott variable-range hopping in Sr$_2$IrO$_4$ epitaxial thin films by misfit strain and isovalent doping

In this chapter, we have investigated the transport properties of Sr$_2$IrO$_4$ epitaxial thin films under misfit strain and isovalent doping. The three-dimensional Mott variable-range hopping (3D Mott-VRH) transport of Sr$_2$IrO$_4$ epitaxial thin films, analogous to other transition-metal oxide Mott insulators has been observed. However, the characteristic temperature of the 3D Mott-VRH varies under misfit strain or isovalent doping, implying that the density of states near the Fermi energy is reconstructed. Magnetoresistance measurements show that electron-correlations and localization play an important role in the electronic transport of the Sr$_2$IrO$_4$ thin films. These results suggest that the electronic properties of the Sr$_2$IrO$_4$ relativistic Mott insulator can be modulated by subtle external stimuli such as structural modifications, opening an unprecedented way for electronic device applications.

2.1 Introduction

The similar magnetic and structural properties between Sr$_2$IrO$_4$ and layered cuprates, such as La$_2$CuO$_4$, has led to theoretical predictions of new superconducting states \[4,13\] via mapping the $J_{eff} = \frac{1}{2}$ pseudospins of Sr$_2$IrO$_4$ into spin $S = \frac{1}{2}$ using the two-dimensional Heisenberg model. Indeed, $d$-wave gap symmetry has been observed with surface-electron doping, \[5,6,11\] reinforcing the theoretical expectations. However, despite much experimental work using various tuning parameters such as chemical doping, \[16,30,33\] electrical field effect doping, \[34\] pressure, \[35\] and misfit strain, \[29,36,37\] no superconducting transport properties have been observed in this layered iridate system. It is also puzzling that Sr$_2$IrO$_4$ thin films with up to 10-15 % electron-doping \[34,38\] display robust insulating properties although electron-doped Sr$_2$IrO$_4$
bulk crystals are metallic. Moreover, the fundamental electronic structure of this system is still under debate; namely, the insulating gap may open due to antiferromagnetic ordering, i.e. Slater scheme, rather than electron-correlation, i.e. Mott picture. Hence, systematic investigations of layered iridate thin films under external stimuli will give us indispensable information for clarifying these issues in transport properties and the potential for electronic device applications.

In this study, we have investigated the transport properties of Sr$_2$IrO$_4$ thin films under misfit strain and isovalent doping. We have synthesized Sr$_2$IrO$_4$ epitaxial thin films on substrates with various lattice mismatches. All of the Sr$_2$IrO$_4$ thin films exhibit 3D Mott-VRH transport regardless of the misfit strain. However, as we increase the lattice strain (or Ca and Ba-doping), which is not intended to cause carrier doping, the characteristic temperature ($T_M$) decreases, implying that there is a substantial change in the density of states near the Fermi level ($N(E_F)$). Transport experiments under magnetic fields at different temperatures show both positive and negative magnetoresistance, implying that the electronic transport is governed by a disorder induced localization of carriers and electron-electron correlations. These observations indicate that while the electronic properties of Sr$_2$IrO$_4$ thin films are analogous to other Mott insulators such as La$_2$CuO$_4$, $N(E_F)$ can be systematically tuned by subtle structural changes, opening a possibility for unprecedented electronic properties and device applications.

2.2 Method

Epitaxial thin films of Sr$_2$IrO$_4$ with the K$_2$NiF$_4$-type structure have been synthesized by pulsed laser deposition (PLD). We have utilized five different single-crystal substrates, NdGaO$_3$ (110) (NGO), LaAlO$_3$ (110) (LAO), (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (001) (LSAT), SrTiO$_3$ (001) (STO), and GdScO$_3$ (110) (GSO) to induce lattice strain ranging from -1.8% compressive strain (NGO) to +1.6% tensile strain (GSO). These
stoichiometric thin films are 10 unit-cell thick (\(\sim 25 \text{ nm}\)). Details of their structural and optical spectroscopic properties are described in Ref. [36]. We have also synthesized epitaxial thin films of \((\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4\) and \((\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4\) with \(x\) and \(y = 1/8, 1/4, \text{ and } 3/8\) on STO (001) substrates. The thin-films are grown on STO substrates by alternating a \(\text{Sr}_2\text{IrO}_4\) \((I41/acd)\) target, a \(\text{Ca}_2\text{IrO}_4\) \((P62m)\) target, and a ceramic target with \(\text{Ba}:\text{Ir} = 2:1\) stoichiometry comprised mostly of the \(\text{BaIrO}_3\) phase \((C2/m)\) and \(\text{BaO}\) [29, 37]. Atomically flat \(\text{TiO}_2\)-terminated STO substrates are prepared using the method described in Ref. [42]. In order to stabilize the \(\text{K}_2\text{NiF}_4\)-type tetragonal structure, we have used the technique of controlling PLD plume dimensions as reported in Ref. [42]. The thickness of these chemically substituted thin films is approximately 20 nm. We have checked the Ba and Ca concentrations of our samples via energy dispersive x-ray (EDX) spectroscopy. The average concentrations of Ba and Ca ions are found to be within \(\pm 3\%\) of the nominal values of \(x\) and \(y = 0.125, 0.25, 0.375\) in \((\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4\) and \((\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4\) thin-films. All the lattice strained and isovalent doped thin-films are grown with a laser fluence of 1.2 J/cm\(^2\) (KrF excimer, \(\lambda = 248\) nm), a substrate temperature of 700 °C, and 10 mTorr oxygen partial pressure. The epitaxial \(\text{K}_2\text{NiF}_4\)-type structure of the thin-films has been confirmed using x-ray diffraction. We performed a thorough investigation of the transport properties using a four-probe method in a Quantum Design physical property measurement system with a maximum magnetic field of 14 T.
2.3 Results and discussion

Figure 2.1(a) shows the \(\theta-2\theta\) x-ray diffraction scans confirming the c-axis orientation of \((\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4\) and \((\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4\) thin-films. The enlarged scans in figure 2.1(b) clearly show that the \((0012)\) reflections of the thin-films are shifted to lower angles as the out-of-plane lattice parameters become larger from \((\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4\) to \((\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4\).

![X-ray diffraction scans](image)

**Figure 2.1:** (a) X-ray \(\theta-2\theta\) scans of the epitaxial \((\text{Sr}_{1-x}\text{A}_x)_2\text{IrO}_4\) (A: Ca, Ba) thin-films grown on STO substrates, where only the \(00l\)-diffraction peaks of the films \((l = 4, 8, 12, 16, 24)\) are visible. (b) The enlarged scans near \((0012)\) reflections of the films and the \((002)\) reflections of the substrates. The peaks from the substrates are labeled with the filled diamond (\(\odot\)) symbols.

The thickness of the thin films is ca. 20 nm. X-ray reciprocal space mapping
around the (103) reflection of STO (Fig. 2.2 (a)) shows the (1118) reflections of the thin-films.

The vertical alignment of the thin-film peak with that of the substrate indicates that the films are coherently strained in plane. Figure 2.2 (b) summarizes the in-plane (a) and out-of-plane (c) lattice parameters as a function of average A-site ionic radius in (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ thin-films. While the in-plane lattice parameters are constant, the out-of-plane lattice parameters increase systematically as the average A-site ionic radius increases.

The temperature dependence of the resistivity reveals that all the (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ films exhibit insulating behavior (Fig. 2.2 (c)). The room-temperature resistivity of the samples is in the range of 100 - 400 m$\cdot$cm. The decreased $U_{\text{eff}}$ from (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ to (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ would be expected to systematically decrease the resistivity. However, all of the doped samples have lower resistivity than the pure Sr$_2$IrO$_4$ thin-film, which implies that the transport properties of the doped layered iridates are dominated by impurities or defects. Various impurities and defects such as oxygen vacancies may increase the carrier concentrations of the samples by doping electrons while the samples remain insulating. Note also that tetragonal Ca$_2$IrO$_4$ and Ba$_2$IrO$_4$ are thermodynamically metastable phases; hence, we have used a Ca$_2$IrO$_4$ target with a hexagonal structure and a Ba$_2$IrO$_4$ target comprised mostly of the BaIrO$_3$ phase, which may further increase the amount of unidentified impurities or dopants.
Figure 2.2: (a) Reciprocal space map around the (103) reflection of the STO substrates with the (1118) reflection of the $(\text{Sr}_{1-x}\text{Ca}_x)_{2}\text{IrO}_4$ and $(\text{Sr}_{1-y}\text{Ba}_y)_{2}\text{IrO}_4$. (b) The in-plane (left axis) and out of plane (right axis) lattice parameters of the $(\text{Sr}_{1-x}\text{Ca}_x)_{2}\text{IrO}_4$ and $(\text{Sr}_{1-y}\text{Ba}_y)_{2}\text{IrO}_4$ thin-films obtained from the reciprocal space maps and x-ray diffraction scans, respectively, as a function of average A-site ionic radius in the $(\text{Sr}_{1-x}\text{A}_x)_{2}\text{IrO}_4$ thin-films (A: Ca, Ba). The solid red and blue squares represent the in-plane and out of plane lattice parameters, respectively. (c) Normalized resistivity versus temperature of the $(\text{Sr}_{1-x}\text{Ca}_x)_{2}\text{IrO}_4$ and $(\text{Sr}_{1-y}\text{Ba}_y)_{2}\text{IrO}_4$ thin-films on STO substrates which indicates that all the films are insulators.
All Sr$_2$IrO$_4$ epitaxial thin films exhibit a robust 3D Mott-VRH transport behavior regardless of lattice strain. Figure 2.3(a) shows the temperature-dependent resistivity of the Sr$_2$IrO$_4$ thin films deposited on various substrates (NGO, LAO, LSAT, STO, and GSO). All samples show negative $d\rho/dT$, which indicates that they are insulators. To understand the electronic transport mechanism of these samples, we have considered three models: the thermal activation model ($\rho(T) = \rho_0 e^{\Delta/2k_BT}$), where $\rho$ is the resistivity coefficient, $\Delta$ is the activation energy, and $k_B$ is the Boltzmann constant), the Efros-Scklovskii (ES) VRH model ($\rho(T) = \rho_0 e^{(T_{ES}/T)^{1/2}}$), where $T_{ES}$ is the characteristic temperature), and the 3D Mott-VRH model ($\rho(T) = \rho_0 e^{(T_M/T)^{1/4}}$), where $T_M$ is the characteristic temperature). While the thermal activation and ES-VRH models cannot generate good curve fits to the experimental data, the 3D Mott-VRH model works very well over a wide temperature range (50 K - 305 K), as shown in figure 2.3(b). This observation implies that the samples are strongly disordered with localized electron carriers.

It is noteworthy that the characteristic temperature ($T_M$) decreases as lattice strain is applied, presumably due to the increased density of states at the Fermi energy ($N(E_F)$). Figure 2.4 shows $T_M^{1/4}$ obtained from the resistivity fits in figure 2.3(b) versus lattice strain for the Sr$_2$IrO$_4$ thin films deposited on NGO, LAO, LSAT, STO, and GSO substrates (from most compressive to most tensile).

One would expect that lattice strain increases disorder. According to N. F. Mott, $T_M$ is described by:

$$T_M = \frac{18}{k_B N(E_F)a^3}$$

(2.1)

, where $a$ is the localization length, which is decreased by introducing disorder into the system. Since $T_M$ is proportional to the amount of disorder in the system, we can expect that $T_M$ increases as strain increases. However, our experimental data
Figure 2.3: (a) Temperature dependent resistivities of Sr$_2$IrO$_4$ thin-films grown on LSAT, LAO, STO, NGO, and GSO substrates. All samples show negative $d\rho/dT$, which indicates that they are insulators. (b) Linear logarithmic resistivities as a function of $T^{-1/4}$, which are offset along the y-axis for clarity from low to high $T_M$ (bottom to top), show that all the thin-film samples exhibit 3D Mott-VRH conduction. Fits are indicated by thin solid lines.
show the opposite behavior: as lattice strain increases, $T_M$ decreases. This experimental observation can be explained if $N(E_F)$ increases as lattice strain increases or decreases. In general, the change of $N(E_F)$ is due to the doping of carriers into the system. For tensile strained thin films, unintentional oxygen vacancies can change $E_F$ by introducing electron carriers. For example, an increase in $N(E_F)$ has been reported in tensile strained Sm$_{0.5}$Nd$_{0.5}$NiO$_3$ thin films where oxygen vacancies and structural defects coexist. [45] For compressively strained thin films, cation off-stoichiometry can be responsible for the increase in $N(E_F)$. For example, the increase in carrier concentration due to cation off-stoichiometry has been reported in (Ba,La)SnO$_3$ thin films. [46]

Figure 2.4: Characteristic temperature to the power of 1/4 ($T_M^{1/4}$) versus lattice strain for Sr$_2$IrO$_4$ thin-films grown on NGO, LAO, LSAT, STO, and GSO substrates. As lattice strain is increased, $T_M$ decreases. The dashed line is a guide to the eye (Gaussian function).
Magnetoresistance measurements confirm that the transport of Sr$_2$IrO$_4$ thin films is governed by disorder induced localization and electron-electron correlations. The magnetoresistance ($MR$) versus magnetic field for the Sr$_2$IrO$_4$ thin films grown on LSAT, LAO, STO, NGO, and GSO substrates shows both positive and negative contributions as a function of temperature, as shown in figure 2.5. As temperature decreases, $MR$ changes from negative ($T > 100$ K) to positive ($T < 100$ K). This sign change is in contrast to a system with simple electron hopping, where $MR$ would be proportional to $H^2$. However, localization of carriers due to disorder can cause $MR$ to display a sign change. [47,48] Roth et al. demonstrated that negative magnetoresistance at high temperatures is due to the additional term of $aH^c$, as shown in the equation below: [47]

$$\frac{\Delta \rho}{\rho_0} = aH^c + bH^2$$

(2.2)

All of our $MR$ data are well described by this equation. The values of the parameters a, b, and c from curve fits for our samples are listed in Table 2.6. We have found that the value of c is about 1.5, with a less than zero. According to Roth et al., as the temperature increases and the impurity concentration decreases below $10^{18}$ cm$^{-3}$, c increases and falls in the range of 1.0 to 1.5.
Figure 2.5: Magneto-resistance (MR) versus magnetic field for the Sr$_2$IrO$_4$ thin-films grown on LSAT, LAO, STO, NGO, and GSO substrates. Lines represent a least square fit of the data to $\frac{\Delta \rho}{\rho_0} = aH^c + bH^2$
The Sr$_2$IrO$_4$ thin films with isovalent doping (i.e. Ca$^{2+}$ and Ba$^{2+}$ ions) show results consistent with the strain-dependent data. The temperature dependent resistivities of (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ thin films show negative $d\rho/dT$, which indicates that the samples are insulators (Fig. 2.7 (a) and 2.7 (b)). However, the resistivity values decrease with increasing Ca and Ba doping, which is qualitatively consistent with the results of Sr$_2$IrO$_4$ single crystals. Similar to our strain-dependent data, the (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ thin films also show clear 3D Mott-VRH transport behavior, as shown in figure 2.7 (c) and 2.7 (d).
Figure 2.7: (a and b) Temperature dependent resistivities of (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ to (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ thin-films. All samples show negative $d\rho/dT$, which indicates that they are insulators. (c and d) Linear logarithmic resistivities as a function of $T^{-1/4}$, which are offset from low to high $T_M$ along the y-axis for clarity, show that all the thin-film samples exhibit 3D Mott-VRH conduction. Fits are indicated by thin solid lines.

Note that the $T_M$ value of the (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ thin films decreases as Ca or Ba doping increases (Fig. 2.8). These observations imply that applying chemical pressure on Sr$_2$IrO$_4$ thin films through Ca and Ba doping has a qualitatively similar behavior as we observed in stoichiometric Sr$_2$IrO$_4$ under epitaxial strain, that is $N(E_F)$ is enhanced with increasing Ba or Ca concentration.
Figure 2.8: Characteristic temperature to the power of 1/4 ($T_M^{1/4}$) versus doping for ($\text{Sr}_{1-x}\text{Ca}_x$)$_2\text{IrO}_4$ and ($\text{Sr}_{1-y}\text{Ba}_y$)$_2\text{IrO}_4$ thin-films indicate that as Ca or Ba doping increases, $T_M$ decreases. The dashed line is a guide to the eye (Gaussian function). The open circle is from single crystal $\text{Sr}_2\text{IrO}_4$. (Ref. [32])

While 3D Mott-VRH transport is commonly observed in many transition metal oxides, the observed change of $T_M$ in $\text{Sr}_2\text{IrO}_4$ thin films under misfit strain or isovalent doping shows a remarkable difference. For example, the temperature dependent resistivities of $\text{La}_2\text{CuO}_4$, $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$, $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (LCMO), $\text{PrNiO}_3$, and electron doped $\text{SmNiO}_3$ are all explained by 3D Mott-VRH transport. [50–55] However, $T_M$ is observed to increase monotonically as strain varies from compressive to tensile in nickelates and manganates [54,55] such as $\text{PrNiO}_3$ thin films grown on LAO, LSAT, and STO substrates and LCMO thin films grown on SrLaAlO$_4$ (compressive strain) and STO (tensile strain). Note that $T_M$ of $\text{Sr}_2\text{IrO}_4$ thin films decreases for both compressive and tensile strain. It is also noteworthy that the $T_M$ values of $\text{Sr}_2\text{IrO}_4$ thin films vary by two orders of magnitude from the least strained samples (Sr$_2$IrO$_4$ on
LSAT, $T_M \sim 10^8$ K) to the highest strained samples (both compressive and tensile, Sr$_2$IrO$_4$ on NGO and GSO, $T_M \sim 10^6$ K). The order of magnitude of the $T_M \sim 10^6$ K are comparable with that of La$_2$CuO$_4$, [50,51,56,57] a parent compound of High-$T_c$ superconductivity. Hence, we speculate that novel electronic properties such as superconductivity may be achieved in layered iridates by electron- or hole-doping on structurally modified samples.

2.4 Conclusion

In conclusion, Sr$_2$IrO$_4$ epitaxial thin films show 3D Mott-VRH transport with decreased $T_M$ under lattice strain or isovalent doping. The change of $T_M$ can be understood by the increase of $N(E_F)$. A rapid change of $N(E_F)$ is commonly observed when the phase transitions from Mott insulators to correlated metals occur with doping, as reported in cuprates. [58–61] The observed increase of $N(E_F)$ in the Sr$_2$IrO$_4$ epitaxial thin films with strain and isovalent doping could facilitate a condition to induce unprecedented electronic properties.
Chapter 3 Optical signatures of spin-orbit exciton in bandwidth-controlled Sr$_2$IrO$_2$ epitaxial films via high-concentration Ca and Ba doping

In this chapter, the electronic and optical properties of (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ ($x = 0 - 0.375$) and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ ($y = 0 - 0.375$) epitaxial thin-films have been investigated, in which the bandwidth is systematically tuned via chemical substitutions of Sr ions by Ca and Ba. Transport measurements indicate that the thin-film series exhibits insulating behavior, similar to the $J_{eff} = \frac{1}{2}$ spin-orbit Mott insulator Sr$_2$IrO$_4$. As the average A-site ionic radius increases from (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ to (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$, optical conductivity spectra in the near-infrared region shift to lower energies, which cannot be explained by the simple picture of well-separated $J_{eff} = \frac{1}{2}$ and $J_{eff} = \frac{3}{2}$ bands. We suggest that the two-peak-like optical conductivity spectra of the layered iridates originates from the overlap between the optically-forbidden spin-orbit exciton and the inter-site optical transitions within the $J_{eff} = \frac{1}{2}$ band. Our experimental results are consistent with this interpretation as implemented by a multi-orbital Hubbard model calculation: namely, incorporating a strong Fano-like coupling between the spin-orbit exciton and inter-site $d-d$ transitions within the $J_{eff} = \frac{1}{2}$ band.

3.1 Introduction

As we mentioned in chapter 1, the strong spin-orbit interaction in iridium splits the $t_{2g}$ band of 5$d^6$ electrons into the fully occupied $J_{eff} = \frac{3}{2}$ and half-filled $J_{eff} = \frac{1}{2}$ bands. When the bandwidth of the half-filled $J_{eff} = \frac{1}{2}$ band is large enough (e.g., SrIrO$_3$), the system exhibits strongly correlated metallic behavior [14,15]. However, as the dimensionality of the system decreases, a Mott insulating gap is opened due to reduced bandwidth, resulting in a $J_{eff} = \frac{1}{2}$ Mott insulator (e.g., Sr$_2$IrO$_4$), which
has been identified by angle-resolved photoemission spectroscopy, x-ray absorption spectroscopy, optical spectroscopy, and first principle calculations [1, 62, 63]. The $J_{eff} = \frac{1}{2}$ Mott insulator Sr$_2$IrO$_4$ has been theoretically suggested as a prospective compound for new high-$T_c$ superconducting states [4, 13], and $d$-wave gap symmetry has been experimentally observed with electron doping on its surface [5, 6, 11]. While layered iridates are attracting substantial attention, there remain controversial issues regarding the fundamental electronic structure of this system: (1) the origin of the insulating gap is disputed as arising either from an antiferromagnetic ordering (i.e., Slater scheme) [41, 64] or electron correlation (i.e., Mott scheme) [1, 62]. (2) Evidence for the strong hybridization of the $J_{eff} = \frac{1}{2}$ and $J_{eff} = \frac{3}{2}$ states [35, 41, 64] is incompatible with the conventional picture of well-separated $J_{eff} = \frac{1}{2}$ and $J_{eff} = \frac{3}{2}$ bands.

In this study, we report the effects of tuning the bandwidth via chemical pressure (i.e. Ca and Ba doping) on the electronic and optical properties of Sr$_2$IrO$_4$ epitaxial thin-films. Bandwidth control of the $J_{eff} = \frac{1}{2}$ state has been employed to better understand the metal-insulator transition and the electronic structure of R-P series iridates with different dimensionalities [14]. Here, we focus on using different ionic sizes of Ca ($r_{Ca^{2+}} = 1.14$ Å), Ba ($r_{Ba^{2+}} = 1.49$ Å), and Sr ($r_{Sr^{2+}} = 1.32$ Å) ions [35, 41, 64]: substitution of Sr by Ca and Ba ions exerts chemical pressure without changing the 4+ valence state of the Ir ions. Due to the smaller (larger) ionic size of compared to Sr$^{2+}$, Ca (Ba) doping in Sr$_2$IrO$_4$ decreases (increases) the in-plane Ir-O-Ir bond angle ($\theta$). According to the relation between the bandwidth $W$ and $\theta$:

$$W \approx \frac{\cos\left(\frac{\pi-\theta}{2}\right)}{d_{Ir-O}^{3.5}}$$  \hspace{1cm} (3.1)

where $d_{Ir-O}$ is the Ir-O bond length, Ca (Ba) doping decreases (increases) both $W$ and the electronic hopping integral ($t$) [65]. The decreased (increased) $W$ affects the
effective electron-correlation energy, $U_{eff} = U/W$, where $U$ is the on-site Coulomb repulsion.

To explore the effects of the decreased (increased) $W$ on the optical and electronic properties, we have synthesized K$_2$NiF$_4$-type tetragonal (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ epitaxial thin-films with $x$ and $y = 0.125$ (1/8), 0.25 (1/4), and 0.375 (3/8), by epitaxial stabilization. Note that these high doping concentrations of Ca and Ba ions beyond the solubility limit are not readily achievable by conventional solid state chemistry since the tetragonal phase bulk crystals of (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ are stable only for $(x = 0 - 0.11)$ and $(y = 0 - 0.1)$ [27,28]. Epitaxial compressive (tensile) strain can also increase (decrease) the in-plane IrO$_6$ octahedral rotation and decreases (increases) $W$ in the system [36]. However, high-concentration doping with smaller (larger) A-site ions increases (decreases) both the IrO$_6$ octahedral rotation and tilting in the system, which tunes the electronic structure effectively. In order to consider only the effect of A-site doping in the system, we have grown all of the (Sr$_{1-x}$A$_x$)$_2$IrO$_4$ ($A =$ Ca, Ba) thin-films on the same (SrTiO$_3$ (100) (STO)) substrates. From optical spectroscopic characterizations, we have observed an unexpected shift in the optical conductivity spectra to lower energies as $W$ increases from (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ to (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$. This red-shift in $\sigma_1(\omega)$ cannot be explained by the simple picture of well-separated $J_{eff} = \frac{1}{2}$ and $J_{eff} = \frac{3}{2}$ bands [1, 62, 63]. Using multi-orbital Hubbard model calculations, we propose that the overall $\sigma_1(\omega)$ spectral shape of the layered iridates originates from Fano-like coupling between inter-site $d$-$d$ transitions within the $J_{eff} = \frac{1}{2}$ band and the optically-forbidden spin-orbit exciton—which correctly shows the red-shift in $\sigma_1(\omega)$ as $U_{eff}$ decreases in this system.

3.2 Method

Epitaxial thin-films of iridates (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ ($x$ and $y = 0.125, 0.25, 0.375$) with the K$_2$NiF$_4$-type structure have been synthesized on STO.
(001) substrates by pulsed laser deposition (PLD). The thickness of these chemically substituted thin films is approximately 20 nm. Details of their structural and optical properties are described in the chapter 2 and Ref. [16]. The transport properties have been measured by using a conventional four-probe method. The optical transmittance spectra of the thin-films have been taken at normal incidence using a Fourier-transform infrared spectrometer and a grating-type spectrophotometer in the photon energy regions of 0.06 – 0.5 eV and 0.5 – 3.2 eV, respectively. Due to the Reststrahlen band of STO substrates, 0.2 eV is the lowest photon energy limit for the transmittance spectra. We have obtained the in-plane optical conductivity spectra ($\sigma_1(\omega)$) using the Kramers-Kronig transformation. We have numerically calculated the excitation and $\sigma_1(\omega)$ as a function of the electronic hopping integral, which is proportional to the bandwidth ($W$), by solving a multi-orbital Hubbard model [66] including the on-site Coulomb interaction between 5$d$ electrons ($U = 1.86$ eV) and the spin-orbit coupling of iridates ($SO = 0.48$ eV).

### 3.3 Experimental results

Figure 3.1 shows $\sigma_1(\omega)$ of $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4$ and $(\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4$ thin-films with the Lorentz oscillator fits. In order to have the best fit with experimental spectra, we need a minimum of three or four oscillators in the 0.2 – 2 eV photon energy region, which is shown with the fit curves of thin green, red, blue, and orange colors. The thin green oscillator, located at \( \sim 0.25 \text{ eV} \), has been indicated as the inner-gap excitation peak [67]. The high energy tails of the charge-transfer transitions from O 2p band to Ir 5$d$ band above 3 eV and the weak optical transitions from the Ir 5$d$ $t_{2g}$ band to the Ir 5$d$ $e_g$ band above 2 eV are both shown by thin gray curves. The black curves show the total spectra of the fit, which matches well with the experimental spectra.
Figure 3.1: Optical conductivity spectra ($\sigma_1(\omega)$) of the $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4$ and $(\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4$ thin-films at room temperature with the minimal set of Lorentz-oscillators. The experimental spectra are shown by thick olive, cyan, blue, magenta, and orange curves from $(\text{Sr}_{0.75}\text{Ca}_{0.25})_2\text{IrO}_4$ to $(\text{Sr}_{0.75}\text{Ba}_{0.25})_2\text{IrO}_4$, respectively. The fit oscillators are shown by thin green, red, blue, orange and gray curves. The black curves show the total spectra of the fit, which matches with the experimental spectra. Note that the $\beta$ peak position shows a significant red-shift as it goes from $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4$ to $(\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4$. The spectra are shifted vertically for clarity.
Note that, as it is illustrated in the figure 3.1, there are two-peak features (the so-called $\alpha$ peak (thin red curve) at $\sim 0.5$ eV and $\beta$ peak (thin blue curve) at $\sim 0.8$ eV) in $\sigma_1(\omega)$, which have been interpreted as two separate optical transitions from the $J_{eff} = \frac{1}{2}$ lower Hubbard band ($\alpha$) to the $J_{eff} = \frac{1}{2}$ upper Hubbard band and the $J_{eff} = \frac{1}{2}$ band ($\beta$) to the $J_{eff} = \frac{1}{2}$ upper Hubbard band in Sr$_2$IrO$_4$ \cite{1,62,63}.

Figure 3.2: (a) The $\alpha$ and $\beta$ peak positions ($\omega_\alpha$ and $\omega_\beta$) as a function of average A-site ionic radius for the $(\text{Sr}_{1-x}\text{A}_x)_{2}\text{IrO}_4$ thin-films (A: Ca, Ba), obtained from Lorentz oscillator fitting. (b) The ratio of the spectral weight of the $\alpha$ to $\beta$ peaks versus average A-site ionic radius from $(\text{Sr}_{1-x}\text{Ca}_x)_{2}\text{IrO}_4$ to $(\text{Sr}_{1-y}\text{Ba}_y)_{2}\text{IrO}_4$.

Our optical results show that as the A-site radius increases from $(\text{Sr}_{1-x}\text{Ca}_x)_{2}\text{IrO}_4$ to $(\text{Sr}_{1-y}\text{Ba}_y)_{2}\text{IrO}_4$, both $\alpha$ and $\beta$ peak positions shift to lower energies (Fig. 3.2 (b)) and the spectral weight ratio between $\alpha$ and $\beta$ transitions ($SW_\alpha/SW_\beta$) also increases (Fig. 3.2 (b)). According to the simple picture of well-separated $J_{eff} = \frac{1}{2}$ and $J_{eff} = \frac{3}{2}$ bands, the decreased $U_{eff}$ from $(\text{Sr}_{1-x}\text{Ca}_x)_{2}\text{IrO}_4$ to $(\text{Sr}_{1-y}\text{Ba}_y)_{2}\text{IrO}_4$ results in a
decreased separation between the lower Hubbard band (LHB) and upper Hubbard band (UHB). The decrease in the separation causes a shift in the α peak position to lower energy, which is consistent with the red-shift in the α peak position in our optical results (Figs. 3.1 and 3.2 (a)). However, understanding the shift in the β peak position of our optical data using this picture is challenging.

In order to explain the shift in the β peak position based on this picture we consider three different scenarios: 1) As $U_{\text{eff}}$ decreases the separation between the LHB and UHB should decrease. Hence, both LHB and UHB should shift. Since the α peak position is the transition from the $J_{\text{eff}} = \frac{1}{2}$ LHB to the $J_{\text{eff}} = \frac{1}{2}$ UHB, the shift in the α peak position is dependent on the shift in both bands. However, the shift in the β peak position, which is the transition from the $J_{\text{eff}} = \frac{3}{2}$ band to the $J_{\text{eff}} = \frac{1}{2}$ UHB, only depends on the UHB shift. This scenario indicates that the shift in the β peak position should be approximately half of the α peak position shift [14, 68], which is not consistent with the observed shift in the α peak in our optical data (Figs. 3.1 and 3.2 (a)). 2) If we assume the LHB to be fixed and only the UHB to shift to lower energy, the shift in the β peak position should be equal to the shift in the α peak position, which is consistent with our optical data. However, this picture cannot explain the observed changes in the spectral weights between α and β transitions (Fig. 3.2 (b)). 3) Since the peak position is determined by the separation between the $J_{\text{eff}} = \frac{3}{2}$ band and the $J_{\text{eff}} = \frac{1}{2}$ UHB, the β peak energy should be proportional to the spin-orbit coupling energy ($\lambda_{SO}$) [14, 68]. Since $\lambda_{SO}$ is determined by the atomic number of the iridium ($Z$), i.e. $\lambda_{SO} \propto Z^4$, it should remain constant in all (Sr$_{1-x}$A$_x$)$_2$IrO$_4$ thin-films, which does not explain the shift in the β peak in our optical data (Fig. 3.1). Hence, the simple picture of well-separated $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = \frac{3}{2}$ bands cannot explain $\sigma_1(\omega)$ shifting to lower energy region. Moreover, in this picture with well-separated $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = \frac{3}{2}$ bands, the spectral weight ratio ($SW_\alpha/SW_\beta$) should be constant, which does not explain the increased spectral
weight ratio \((SW_\alpha/\beta)\) between \(\alpha\) and \(\beta\) optical transitions (Fig. 3.2 (b)) from \((\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4\) to \((\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4\). Hence, our experimental observations call the current interpretation of \(\sigma_1(\omega)\) for layered iridates based on well-separated \(J_{\text{eff}} = \frac{1}{2}\) and \(J_{\text{eff}} = \frac{3}{2}\) bands into question. Recent theoretical studies also indicate that strong hybridization of the \(J_{\text{eff}} = \frac{1}{2}\) and \(\frac{3}{2}\) states causes a mixing of their energies [35].

### 3.4 Discussion

We suggest that the optically-forbidden spin-orbit exciton overlaps with an electronic continuum originating from the inter-site \(d-d\) transitions within the \(J_{\text{eff}} = \frac{1}{2}\) band, which results in the two-peak-like structures observed in \(\sigma_1(\omega)\) of layered iridates. Resonant inelastic x-ray scattering (RIXS) experiments on \(\text{Sr}_2\text{IrO}_4\) crystals have discovered charge-neutral excitations, which are referred to as the spin-orbit exciton or spin-orbiton [66,69,70]. These neutral particles originate from intra-site electron-hole pairs, i.e. a hole in the \(J_{\text{eff}} = \frac{3}{2}\) band and an electron in \(J_{\text{eff}} = \frac{1}{2}\) band, that move through the lattice and create a tail of flipped spins in the ground state of the system. The energy of this exciton is similar to the energy of spin-orbit coupling as observed by the RIXS measurement [69,70]. By comparing the RIXS spectra with the \(\sigma_1(\omega)\) of our \((\text{Sr}_{1-x}\text{A}_x)_2\text{IrO}_4\) and \((\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4\) thin-films, we have noticed that the energy of the spin-orbit exciton of \(\text{Sr}_2\text{IrO}_4\) lies on top of the dip region in \(\sigma_1(\omega)\), as marked by the red arrows in figure 3.1. As spin-orbit exciton is formed in the ground state of this system, electron-hole pairs partially fill up the \(J_{\text{eff}} = \frac{1}{2}\) band with electrons and the \(J_{\text{eff}} = \frac{1}{2}\) band with holes, respectively. Due to the partial occupation of electrons in the \(J_{\text{eff}} = \frac{1}{2}\) band by the spin-orbit exciton, the spectral weight of inter-site \(d-d\) transitions within the \(J_{\text{eff}} = \frac{1}{2}\) band are reduced with the dip structure appearing around 0.5 – 0.8 eV.

Multi-orbital Hubbard model calculations show consistent results with our proposed model of the spin-orbit exciton overlapping with an electronic continuum orig-
inating from inter-site d-d transitions within the $J_{\text{eff}} = \frac{1}{2}$ band. To calculate the spectral weight of the spin-orbit exciton spectra and $\sigma_1(\omega)$, we adopt the four-site cluster shown in Ref. [66]. For simplicity, we only take into account $t_{2g}$ orbitals and assume that the bond angle is $180^\circ$. The corresponding Hamiltonian is given by:

$$
H = \sum_{i\delta\mu\sigma} t_{\delta\mu\sigma}^\delta c_{i\delta\mu\sigma}^\dagger c_{i\mu\sigma} + \sum_{i\mu\sigma} \Delta_{xy}(\delta_{\mu,xy} - \frac{1}{3}) c_{i\mu\sigma}^\dagger c_{i\mu\sigma} \\
+ \lambda \sum_{i\mu\sigma,\sigma'} (l.s)_{\mu\sigma,\nu\sigma'} c_{i\mu\sigma}^\dagger c_{i\sigma'\nu\sigma} c_{i\sigma\nu\sigma'}
+ \frac{1}{2} \sum_{i\sigma',\mu \neq \nu} U_{\mu\nu} c_{i\mu\sigma} c_{i\sigma'\nu\sigma'} c_{i\nu\sigma} c_{i\mu\sigma}
+ \frac{1}{2} \sum_{i\sigma',\mu \neq \nu} J_{\mu\nu} c_{i\mu\sigma} c_{i\sigma'\nu\sigma'} c_{i\nu\sigma} c_{i\mu\sigma}
$$

where $c_{i\nu\sigma}^\dagger$ is the creation operator of an electron with $\nu$ orbital and $\sigma$ spin at the $i$ site, and $i_\delta$ refers to the neighboring site of the $i$th site whose displacement is $\delta$. When $\delta = \pm dx$, where $d$ is the distance between neighboring sites, $t_{\mu\nu}^\delta$ has nonzero element when $\mu = \nu = xy$ and $\mu = \nu = zx$. The second and third terms describe the local energy splitting due to the tetragonal distortion and spin-orbit coupling, respectively. The last three terms are the Hamiltonian of the local electron-electron correlation. We have parameterized correlation matrices as $U_{\mu\nu} = U, U_{\mu \neq \nu} = U - 2J_H$. We have set $xy = 0.1, \lambda = 0.48, U = 1.86$, and $J_H = 0.5$ eV to be consistent with previous literature [66] and have fitted the experimental optical peak positions. For the $t_{52g}$ configuration, we consider all states in which the total number of holes is four. To solve Eq. 3.2, we employ the exact diagonalization method based on the Lanczos algorithm [71]. We calculate the ground state ($|\psi_0>$) and its energy ($E_0$) with the energy accuracy of 10-10 eV. To explore the distribution of the spin-orbit
exciton, we calculate the following projected excitation spectra

\[ A_2(\omega) = \sum_{nk} <\psi_n|Q_k|\psi_n> \delta(\omega - E_n + E_0) \]

\[ = -\frac{1}{\pi} \text{Im} \sum_k <\psi_k|\frac{1}{\omega - H + E_0 + i\delta}|Q_k> \tag{3.3} \]

where \( n \) and \( |\psi_n> \) are the \( n \)th eigenvalue and state, respectively. \( |Q_k> \) is the \( k \)th orthonormal base state to span the subspace, which consists of the spin-orbit exciton states with one \( J_{eff} = \frac{3}{2} \) hole in one site and one \( J_{eff} = \frac{1}{2} \) hole in other sites. Based on the continued fraction method [71], we solve Eq. 3.3. We have set \( \delta = 0.03 \text{ eV} \) and perform 300 iteration steps. To calculate \( \sigma_1(\omega) \), we use the following Kubo formula,

\[ \sigma_1(\omega) = \frac{\pi \nu}{\omega} \sum_{n \neq 0} |<\psi_n|J_c|\psi_0>|^2 \sigma(\omega - E_n + E_0) \]

\[ = -\nu \text{Im} \sum_{n \neq 0} \frac{|<\psi_n|J_c|\psi_0>|^2}{(E_n - E_0)(\omega - E_n + E_0 + i\sigma)} \]

\[ = -\nu \text{Im} \left[ \frac{1}{\omega + i\delta} <\psi_0|J_c\frac{1}{H - E_0}J_c|\psi_0> \right. \]

\[ + \left. <\psi_0|J_c\frac{1}{\omega - H - E_0 + i\delta}J_c|\psi_0> \right] \tag{3.4} \]

where \( \nu \) is the volume per site and \( J_c \) is the current operator. We also exploit the continued fraction method with 400 iteration steps and \( \delta = 0.1 \text{ eV} \) to solve Eq. 3.4. Note that increased \( t \) from \((\text{Sr}_{1-x}\text{Ca}_x)_{2}\text{IrO}_4\) to \((\text{Sr}_{1-y}\text{Ba}_y)_{2}\text{IrO}_4\) leads to an increase in the bandwidth \( (W) \) of the system. We have used \( t = 0.22 \text{ eV} \) for \( \text{Sr}_2\text{IrO}_4 \), which is a reasonable value for this iridate compound [72]. We have calculated \( \Delta W\% \) as we substitute \( \text{Sr} \) with \( \text{Ca} \) or \( \text{Ba} \) using \( \theta \) from Ref. [29] and Eq. 3.1. By considering the proportionality of \( W \) with \( t \), we have estimated the percentage change of \( t \) \((\Delta t\%)\). This calculation results in \( t = 0.20 \text{ eV} \) and \( 0.23 \text{ eV} \) for \( Ca \) and \( Ba \) substitution, respectively. Figures 3.3 (a) and 3.3 (b) show the calculated spectral weight of the
spin-orbit exciton and calculated $\sigma_1(\omega)$ for three different values of $t$ ($t = 0.20$ eV for $x > 0$, $t = 0.22$ eV for $x = y = 0$, and $t = 0.23$ eV for $y > 0$). Note that the spin-orbit exciton transition [Fig. 3.3 (a)] scales with the dip position in the experimental and calculated $\sigma_1(\omega)$ (Figs. 3.1 and 3.3 (b)).

Using our experimental and theoretical results, we suggest that the overall peak structure is solely from the inter-site $d - d$ transitions within the $J_{eff} = \frac{1}{2}$ band and the dip structure around 0.5 – 0.8 eV in $\sigma_1(\omega)$ of layered iridates is a signature of the optically forbidden spin-orbit exciton. By decreasing $U_{eff}$ (increasing $t$) from $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{IrO}_4$ to $(\text{Sr}_{1-y}\text{Ba}_y)_2\text{IrO}_4$, the overall $\sigma_1(\omega)$ at low energy (below 2 eV) red-shifts while the peak position of the spin orbit exciton does not change. The combination of the inter-site transitions within the $J_{eff} = \frac{1}{2}$ band and the spin-orbit exciton creates a red-shifted two-peak feature in the low energy range of $\sigma_1(\omega)$ (Fig. 5 (b)). These theoretical results are consistent with the observed $\sigma_1(\omega)$, shown in figure 3.1.
Figure 3.3: (a) Calculated spectral weight of spin-orbit exciton and (b) $\sigma_1(\omega)$ at different values of the electronic hopping integral ($t$). The spectra in (b) are shifted vertically for clarity. (c) Schematic diagram representing the Fano-like resonance between the inter-site optical transitions of the $J_{eff} = \frac{3}{2}$ state and the spin-orbit exciton, which creates a two peak-like structure in the final optical spectrum. The red and blue arrows are electrons with up and down spins in the $J_{eff} = \frac{3}{2}$ and $J_{eff} = \frac{1}{2}$ states, indicating the inter-site optical transitions and the on-site spin-orbit exciton.
Since the bandwidth of layered iridates can also change with the variation of temperature, it is worthwhile to compare our experimental results with the temperature-dependent $\sigma_1(\omega)$ from the bulk single crystal Sr$_2$IrO$_4$ [62, 63]. The temperature-dependent data indicate that the spectral weight of the $\alpha$ ($\beta$) peak increases (decreases) as the in-plane Ir-O-Ir bond angle increases. This behavior is consistent with our observation in thin-films in which the ratio of the spectral weight ($SW_\alpha/SW_\beta$) between $\alpha$ and $\beta$ optical transitions increases as it goes from (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ to (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ films (Fig. 3.2 (b) (b)). Further, as the bond angle increases due to thermal expansion, the $\alpha$ peak shifts to lower energy which is consistent with our A-site dependence data as well. However, the red-shift of the $\beta$ peak (by increasing temperature) is less visible in temperature-dependent data [62, 63]. Based on our interpretation of $\sigma_1(\omega)$, as the temperature increases ($U_{\text{eff}} = U/W$ decreases), the overall spectra shifts to lower energy. However, the spin orbit exciton may also be temperature-dependent and move to higher energy, which acts to reduce the resultant red-shift in the $\beta$ peak position. It is necessary to investigate the temperature-dependence of the spin-orbit exciton to fully understand this picture. As shown schematically in figure 3.3 (c), the spin-orbit exciton and the inter-site optical transition of the $J_{\text{eff}} = \frac{1}{2}$ state strongly overlap, which creates a dip structure in $\sigma_1(\omega)$, resulting in the two-peak structure observed in $\sigma_1(\omega)$ of layered iridates system.

The $\sigma_1(\omega)$ of bandwidth controlled (Sr$_{1-x}$Ca$_x$)$_2$IrO$_4$ and (Sr$_{1-y}$Ba$_y$)$_2$IrO$_4$ films provide indirect evidence regarding the nature of the spin-orbit exciton. Hence, we suggest advanced spectroscopic characterizations such as resonant inelastic x-ray scattering experiments on this system to confirm this picture. Moreover, in order to fully understand this (Sr$_{1-x}$A$_x$)$_2$IrO$_4$ thin-film (A: Ca, Ba) system, it is important to obtain the local structural information such as octahedral rotation and tilting as a future study. We have assumed that doping with smaller (larger) A-site ions increases (decreases) rotation and tilting in the system, which is consistent with pre-
vious work \[28\]. However, decrease in the in-plane rotation by the substitution of Ca for Sr has been also suggested recently \[27\].

Our approach of studying bandwidth controlled epitaxial thin-films provides a useful way to unveil controversial issues in strongly correlated materials. By applying chemical pressure beyond the solubility limit, we can control the lattice parameters, Ir-O-Ir bond angle, electronic hopping, and electronic correlation effects in the system. Recently, it has been reported that even a slight increase in the Ir-O-Ir bond angle can create a huge increase in the electronic hopping of compounds like Sr\(_3\)Ir\(_2\)O\(_7\). This can cause a drastic decrease in the resistivity of the system and create a metallic state or possibly even a superconducting state \[32,73\]. Hence, studying iridates under factors like chemical pressure can help us explore these systems and potentially uncover the novel properties that are theoretically predicted.

### 3.5 Summary

We have synthesized and investigated epitaxial thin-films of (Sr\(_{1-x}\)Ca\(_x\))\(_2\)IrO\(_4\) and (Sr\(_{1-y}\)Ba\(_y\))\(_2\)IrO\(_4\) (\(x\) and \(y = 0 - 0.375\)), which effectively act to tune the A-site ionic radius of the layered iridate system and subsequently its bandwidth. Using a systematic study of the A-site dependence on \(\sigma_1(\omega)\) with respect to the change in the bandwidth, we have observed red-shifted optical peak positions in low energies from (Sr\(_{1-x}\)Ca\(_x\))\(_2\)IrO\(_4\) to (Sr\(_{1-y}\)Ba\(_y\))\(_2\)IrO\(_4\). This unexpected observation cannot be explained using the conventional \(J_{eff} = \frac{1}{2}\) and \(J_{eff} = \frac{3}{2}\) band picture. Our experimental observations are consistent with theoretical results using multi-orbital Hubbard model calculations that suggest the spin-orbit exciton and the inter-site optical transition of the \(J_{eff} = \frac{1}{2}\) state strongly overlap due to a Fano-like resonance. This imposes a dip structure in \(\sigma_1(\omega)\) and creates a two peak structure in the spectra. The optical peak positions at low energy red-shift as \(U_{eff}\) decreases from (Sr\(_{1-x}\)Ca\(_x\))\(_2\)IrO\(_4\) to (Sr\(_{1-y}\)Ba\(_y\))\(_2\)IrO\(_4\). Our results confirm that controlling the band-
width of layered iridates can help resolve the controversial issues in understanding the electronic structure of this system. Moreover, the epitaxial growth of thin-films under chemical pressure is a viable technique to expand the scope of materials with competing interactions and provides a platform for investigating the existing arena for novel phenomena in strongly correlated materials.
Chapter 4  Investigations of metastable Ca$_2$IrO$_4$ epitaxial thin-films:  
systematic comparison with Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$

In this chapter, thermodynamically metastable Ca$_2$IrO$_4$ thin-films on YAlO$_3$ (110) substrates have been synthesized by pulsed laser deposition. The epitaxial Ca$_2$IrO$_4$ thin-films are of K$_2$NiF$_4$-type tetragonal structure. Transport and optical spectroscopy measurements indicate that the electronic structure of the Ca$_2$IrO$_4$ thin-films is similar to that of $J_{\text{eff}} = \frac{1}{2}$ spin-orbit-coupled Mott insulator Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$, with the exception of an increased gap energy. The gap increase is to be expected in Ca$_2$IrO$_4$ due to its increased octahedral rotation and tilting, which results in enhanced electron-correlation, $U/W$. Our results suggest that the epitaxial stabilization growth of metastable-phase thin-films can be used effectively for investigating layered iridates and various complex-oxide systems.

4.1 Introduction

While the fundamental electronic structure of the layered iridate is still under debate, it is a formidable task to unveil the physics of layered iridates since only Sr$_2$IrO$_4$ and Sr$_2$IrO$_4$ (Refs [9, 37, 74, 75]) phases are available for experimental characterizations to date. In this chapter, we report the systematic changes of the structural, transport, and optical properties of layered iridates by investigating meta-stable Ca$_2$IrO$_4$ epitaxial thin-films. Since the Ruddlesden-Popper (R-P) phase of Ca$_2$IrO$_4$ is not thermodynamically stable, its bulk crystals do not exist in nature. However, we have successfully synthesized the R-P phase Ca$_2$IrO$_4$ thin-films (Fig. 4.1(b)) from a polycrystalline hexagonal ($P6_2m$) Ca$_2$IrO$_4$ bulk crystal (Fig. 4.1(a)) using an epitaxial stabilization technique. [76] The smaller ionic size of Ca$^{2+}$ compared to Sr$^{2+}$ causes an increased IrO$_6$ octahedral rotation, tilting, or distortion, hence a reduced elec-
tronic band-width ($W$). Thus, investigating Ca$_2$IrO$_4$ in a comparative study with Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ provides a unique opportunity to explore the layered iridate system, as it allows for the enhancement of the electronic correlation effect ($U/W$).

4.2 Method

We have grown metastable Ca$_2$IrO$_4$ epitaxial thin-films with the K$_2$NiF$_4$–type crystal structure on YAlO$_3$ (110) substrates by using a custom-built pulsed laser deposition (PLD) system with in-situ spectroscopic monitoring techniques. The laser ablation is performed on a polycrystalline hexagonal (P6$_2$m) Ca$_2$IrO$_4$ target. The powder x-ray diffraction of the target is presented in figure 4.1 (c). The samples are grown under the growth conditions of 1.2 J/cm$^2$ laser fluence (KrF excimer, $\lambda$ = 248 nm), and 700 °C substrate temperature. In order to avoid defects such as oxygen vacancies during the growth, we have used a laser beam imaging technique with reduced laser beam size in PLD to minimize the kinetic energy of the plume. This technique is essential for the successful growth of Ca$_2$IrO$_4$ thin-films. A relative high oxygen partial pressure of 10 mTorr is also used to minimize oxygen vacancies. Structural quality of the epitaxial Ca$_2$IrO$_4$ thin-films are measured using x-ray diffractometry (Bruker D8 Advance system with Cu-Ka radiation).

Transport properties are measured using a Physical Property Measurement System (Quantum Design) with conventional four-probe and Hall geometries. Optical transmission spectra ($T(\omega)$) are taken at normal incidence using a Fourier-transform infrared spectrometer in the photon energy region of 0.2–0.6 eV and a grating-type spectrophotometer in the range of 0.5–7 eV, where the substrates are transparent. The absorption spectra are calculated using $\alpha(\omega) = -\frac{1}{t} Ln\left(\frac{T(\omega)_{film+sub}}{T(\omega)_{sub}}\right)$, where $t$ is the thin film thickness.
Figure 4.1: Schematic diagram of epitaxial stabilization of tetragonal Ca$_2$IrO$_4$ epitaxial thin-film from (a) the bulk hexagonal phase of Ca$_2$IrO$_4$, which is the source material, i.e. a target of pulsed laser deposition, to (b) Metastable R-P phase of Ca$_2$IrO$_4$ thin-film grown on a single crystal YAIO$_3$ (110) substrate. (c) Powder x-ray diffraction of our target material, which shows x-ray diffraction peaks mainly from hexagonal bulk phase of P62m and some of CaO secondary phase. (d) X-ray $\theta$-2$\theta$ scan of an epitaxial Ca$_2$IrO$_4$ thin-film, where only the (00l)-diffraction peaks of Ca$_2$IrO$_4$ are visible. YAIO$_3$ (110) and (220) peaks are labeled with asterisk (*) symbols.
4.3 Results and discussion

The metastable R-P phase of the Ca$_2$IrO$_4$ thin films is verified by x-ray diffraction and reciprocal space mapping scans, which indicate the films to be stabilized by the epitaxial strain of the substrates and of high crystalline quality. Figure 4.1 (d) shows the $\theta$-2$\theta$ x-ray diffraction scan with the (00l) peaks of a Ca$_2$IrO$_4$ thin film implying the c-axis orientation of the thin films.

The full width at half maximum of the (0012)-reflection rocking curve scan is 0.04$^\circ$, which clearly shows good crystallinity of the thin film (Fig. 4.2 (b)). The thickness of the Ca$_2$IrO$_4$ thin films is about 6 nm. The crystal quality deteriorates considerably as we increase the thickness further, presumably due to its thermodynamically metastable nature. In x-ray reciprocal space mapping (Fig. 4.2 (a)), the (1118) peak of the film is vertically aligned with the YAlO$_3$ substrate (332)-reflection, indicating Ca$_2$IrO$_4$ films are coherently strained to the substrates, i.e. [110]$_{film}$// [001]$_{substrate}$ and [001]$_{film}$ // [110]$_{substrate}$. The lattice parameters obtained from the x-ray diffraction scans show that both in-plane (a) and out-of-plane (c) lattice parameters of Ca$_2$IrO$_4$ films are smaller than those of Sr$_2$IrO$_4$ (Ref. [36]) and Ba$_2$IrO$_4$ (Ref. [37]) (Fig. 4.2 (c)).

At this moment, the local structural information of Ca$_2$IrO$_4$ films such as octahedral rotation and tilting is unknown, which requires substantial microscopic characterizations that we plan to perform as a future study. However, by assuming the rigid Ir-O bond-length to be constant, which is a reasonable assumption, we conjecture the reduced lattice constants (from x-ray diffraction) imply that the Ir-O-Ir bond angle is reduced from 158$^\circ$ (Sr$_2$IrO$_4$) to ca. 140$^\circ$ (Ca$_2$IrO$_4$). According to the relation between the band width ($W$) and the Ir-O-Ir bond angle ($\theta$) which is described by the equation [3.1], we can conclude that $W$ of Ca$_2$IrO$_4$ is decreased due to the reduced $\theta$ and this will result in enhanced electron-correlation, $U/W$, in the Ca$_2$IrO$_4$ compound compared to that of Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ thin films.
Figure 4.2: (a) Reciprocal space map near the YAlO$_3$ (332)-reflection, which shows the Ca$_2$IrO$_4$ (1118)-reflection. The vertical dashed line indicates that the Ca$_2$IrO$_4$ thin-film is coherently strained to the substrate. (b) The rocking curve scan of Ca$_2$IrO$_4$ (0012)-reflection with the full-width half-maximum of 0.04°. (c) The in-plane (left axis) and out of plane (right axis) lattice parameters of Ca$_2$IrO$_4$, Sr$_2$IrO$_4$ (Ref. [36]) and Ba$_2$IrO$_4$ (Ref. [37]) thin films obtained from x-ray diffraction scans, as a function of A-site cation ionic radius. The solid circles and squares present the in-plane and out of plane lattice parameters, respectively. The open symbols indicate
Figure 4.3 (a) shows the temperature-dependent resistivity $\rho(T)$ of a Ca$_2$IrO$_4$ thin film, which shows an insulating behavior. The room-temperature resistivity of the Ca$_2$IrO$_4$ films (ca. 170 mΩcm) is about the same as the room temperature resistivity of Sr$_2$IrO$_4$ (ca. 140 mΩcm) and Ba$_2$IrO$_4$ (ca. 130 mΩcm) thin films on SrTiO$_3$ substrates. We have calculated the energy gap ($\Delta = 2E_a$) of Ca$_2$IrO$_4$ films and compared it with that of Sr$_2$IrO$_4$ (Ref. [37]) and Ba$_2$IrO$_4$ thin films using an Arrhenius plot, $(\rho(T) = \rho_0 e^{\Delta/2k_BT})$, where $k_B$ is the Boltzmann constant. While the Arrhenius plot shows non-linear behaviors in the Sr$_2$IrO$_4$ (Ref. [37]) and Ba$_2$IrO$_4$ thin films, the transport of Ca$_2$IrO$_4$ is quite linear over the entire measured temperature range, and an energy gap of 120 meV is extracted from its Arrhenius plot. Due to the increased $U/W$ in Ca$_2$IrO$_4$, we expect its gap energy to be larger than that of Ba$_2$IrO$_4$ and Sr$_2$IrO$_4$. However, the energy gap of Ca$_2$IrO$_4$ obtained from the room temperature transport is smaller than that of Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ thin films. This puzzling observation implies that the transport properties of layered iridates are mostly dominated by impurities or defects, and intrinsic bandgap energies should be measured using a spectroscopic technique.

Figure 4.3 (b) presents the optical absorption spectra ($\alpha(\omega)$) of Ca$_2$IrO$_4$ compared with Sr$_2$IrO$_4$ (Ref. [36]) and Ba$_2$IrO$_4$ (Ref. [37]) thin films. We have fitted the absorption spectra using a minimal set of Lorentz oscillators in the 0.2 - 2 eV photon energy region. The common features of strong absorption tails due to the charge-transfer transitions from O 2p to Ir 5d bands are above ca. 2 - 3 eV. The black solid curves in Fig. 4.3 (b) are the resultant fit curves using the Lorentz oscillators, which match well with the experimental spectra. The three absorption peaks indicated by $\alpha$, $\beta$, and $\gamma$ are labeled consistently with the previous papers. [62,63]
Figure 4.3: (a) Normalized resistivity ($\rho$) versus temperature data of Ca$_2$IrO$_4$ (red), Sr$_2$IrO$_4$ (blue) and Ba$_2$IrO$_4$ (green) thin-films. The data of Sr$_2$IrO$_4$ is from Ref. [37]. The inset shows the Arrhenius plot of Ca$_2$IrO$_4$, Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$. Solid black lines present the linear fits at room temperature and low temperature. The estimated energy gaps at room temperature are $\Delta_{\text{CIO}} = 120$ meV, $\Delta_{\text{SIO}} = 250$ meV and $\Delta_{\text{BIO}} = 190$ meV. The Arrhenius plots are shifted vertically for clarity. (b) Optical absorption spectra ($\alpha(\omega)$) of Ca$_2$IrO$_4$, Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ thin-films at room temperature. The plots are shifted vertically by $10^5$ cm$^{-1}$ for clarity. The $\alpha$, $\beta$ and $\gamma$ represent the optical transition peak energies obtained from the fit with the minimal set of the Lorentz oscillators. The solid black curves are the fit curves using Lorentz oscillators, which match well with the experimental spectra. (c) Fitted absorption spectra of Ca$_2$IrO$_4$, Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$ at low energy using Wood-Tauc’s method which clearly confirm the increased energy gap from Ba$_2$IrO$_4$ to Ca$_2$IrO$_4$. The estimated optical gap energies using this method are $\Delta_{\text{CIO}} = 230$ meV, $\Delta_{\text{SIO}} = 120$ meV, and $\Delta_{\text{CIO}} = 60$ meV.
Note that as we discussed in chapter 3, the overall low energy spectral shape of the layered iridates originates from Fano-like coupling between inter-site $d$-$d$ transitions within the $J_{eff} = \frac{1}{2}$ band and the optically-forbidden spin-orbit exciton. As it is shown in figure 4.3 (b), the $\alpha$ and $\beta$ peak-positions red shift as it goes from Ba$_2$IrO$_4$ to Ca$_2$IrO$_4$. One possible explanation would be that according to the dip position, the SO exciton peak is shifted to higher energy for Ca$_2$IrO$_4$ and Ba$_2$IrO$_4$ which could be due to increased localization in these systems. The increased localization in Ca$_2$IrO$_4$ originates from smaller Ir-O-Ir bond angle. Moreover, the increased out of plane lattice parameter of the compressive strained Ba$_2$IrO$_4$ thin-film reduces the dimensionality of this system, in which increases the in-plane localization. However, according to the low intensity peak of $\gamma$ in Ca$_2$IrO$_4$, the SO exciton could be wider in Ca$_2$IrO$_4$ thin film which causes to eliminate the inter-site $d$-$d$ transitions within the $J_{eff} = \frac{1}{2}$ band on the right side of the SO exciton. Note that, in case of Ba$_2$IrO$_4$, the SO is not as broad as that of Ca$_2$IrO$_4$, and causes to split the inter-site $d$-$d$ transitions peak and create $\alpha$ and $\beta$ peaks in both sides of SO exciton peak.

We note the increased optical gap energy of Ca$_2$IrO$_4$ thin-films as compared to that of Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$. To calculate the optical energy gap, we have fitted the absorption spectra of our three compounds using the Wood-Tauc’s method [78] (Fig. 4.3 (c)). In this method the strong region of the absorption edge ($\alpha > 10^4$ cm$^{-1}$) can be described by the equation below:

$$\alpha \approx \frac{(E - E_g)\gamma}{E}$$

(4.1)

where $E_g$ is the optical band gap energy, $E$ is the photon energy. The estimated optical gap energies using this method are $\Delta_{CIO} = 230$ meV, $\Delta_{SIO} = 120$ meV, and $\Delta_{BIO} = 60$ meV. For the exponent $\gamma$, we obtained $\gamma = 1.3$ (Ca$_2$IrO$_4$), $\gamma = 3$ (Sr$_2$IrO$_4$), and $\gamma = 1.7$ (Ba$_2$IrO$_4$). While $\gamma = 3$ for Sr$_2$IrO$_4$ is consistent with its indirect bandgap,
the physical origin of the smaller $\gamma$ values in Ca$_2$IrO$_4$ and Ba$_2$IrO$_4$ is not clear at this moment, which requires further theoretical studies for the compounds. Nevertheless, as shown in Fig. 4.3 (c), the optical gap energy is clearly increased for Ca$_2$IrO$_4$ compared to that of Sr$_2$IrO$_4$ and Ba$_2$IrO$_4$. Hence, as we decrease the ionic sizes of A-site cations in layered iridates, the Ir-O-Ir bond angle is reduced, which, in turn, increases $U/W$ and manifests itself as the observed increase in the optical bandgap energy.

Our approach of synthesizing meta-stable phase thin-films of strongly correlated systems offers a new route to understanding the physics of complex oxides. For example, the stabilization of metastable phases can provide compounds with larger effective electronic correlations than presently available by producing increased distortion and tilting in lattice. While simple octahedral distortions usually preserve inversion symmetry in the K$_2$NiF$_4$–type structure, the R-P structure of Ca$_2$IrO$_4$ has been proposed as a candidate material featuring a non-centrosymmetric structure due to its low symmetry. [39] This unique structure, achieved by breaking the inversion symmetry in this system, is expected to induce many interesting phase transitions such as ferroelectricity and multiferroicity. Hence, experimental studies of meta-stable phases allow us to tackle a number of intriguing problems of exotic ground states with novel properties that are theoretically suggested.

4.4 Conclusion

We have successfully stabilized Ca$_2$IrO$_4$ thin-films with the K$_2$NiF$_4$–type crystal structure and determined its higher optical gap energy with respect to its larger A-site cation isosymmetric compounds to originate from its enhanced electron-correlation, $U/W$. The structural study confirms the good crystallinity and coherent strain state of the epitaxial Ca$_2$IrO$_4$ thin-films on YAlO$_3$ (110) substrates. The transport and optical spectroscopic experiments show that Ca$_2$IrO$_4$ thin-films have an insulating
ground state similar to $\text{Sr}_2\text{IrO}_4$ and $\text{Ba}_2\text{IrO}_4$. However, the increased $\text{IrO}_6$ octahedral rotation, tilting, or distortion in $\text{Ca}_2\text{IrO}_4$ increases $U/W$, and thus its optical gap energy is larger than the gap energies of $\text{Sr}_2\text{IrO}_4$ and $\text{Ba}_2\text{IrO}_4$. This approach of metastable thin-film phases can greatly expand the number of available materials and can help to unveil the physics of strongly correlated systems.
Chapter 5  Electronic and optical properties of La-doped Sr$_3$Ir$_2$O$_7$
epitaxial thin-films

In this chapter, the structural, transport, and optical properties of tensile strained
(Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ ($x = 0, 0.025, 0.05$) epitaxial thin-films have been investigated. While high-$T_c$ superconductivity is predicted theoretically in the system, we have observed that all of the samples remain insulating with finite optical gap energies and Mott variable-range hopping characteristics in transport. Cross-sectional scanning transmission electron microscopy indicates that structural defects such as stacking faults appear in this system. The insulating behavior of the La-doped Sr$_3$Ir$_2$O$_7$ thin-films is presumably due to disorder-induced localization and ineffective electrondoping of La, which brings to light the intriguing difference between epitaxial thin films and bulk single crystals of the iridates.

5.1 Introduction

The bilayer ($n = 2$) iridate, Sr$_3$Ir$_2$O$_7$, which is in close proximity to the insulator-to-metal transition with a smaller Mott gap than Sr$_2$IrO$_4$ [73,79,85], is another intriguing iridate material that has not been extensively studied under perturbations such as chemical doping and lattice strain. Sr$_3$Ir$_2$O$_7$ single crystals show antiferromagnetic ordering ($T_N = 285$K [86]) with out-of-plane collinear magnetic moments, in contrast to the in-plane magnetic moments of Sr$_2$IrO$_4$ and high-$T_c$ cuprates [80,87]. Recent theoretical studies suggest that a spinflip transition is expected to occur under biaxial strain since the energy difference between the out-of-plane and the in-plane magnetic moments is only a few meV per iridium atom [88]. Hence, investigating electron-doped Sr$_3$Ir$_2$O$_7$ thin films under epitaxial strain could be a promising direction for revealing new electronic states by altering their magnetic structures.
In this chapter, we report the structural, transport, and optical properties of La-doped Sr$_3$Ir$_2$O$_7$ epitaxial thin-films under coherent tensile-strain. Since the valence state of La is 3+ while that of Sr is 2+, the substitution of La for Sr is widely used for electron doping in many transition metal oxides [89]. However, we have observed that the Sr$_3$Ir$_2$O$_7$ epitaxial thin-films with La doping up to about 5% remain insulating with Mott variable-range hopping characteristics. The La-doped Sr$_3$Ir$_2$O$_7$ epitaxial thin-films show overall higher resistivity and slightly larger optical gap energies than Sr$_3$Ir$_2$O$_7$. We speculate that La doping might reduce the number of inevitable defects in Sr$_3$Ir$_2$O$_7$ epitaxial thin-films such as oxygen vacancies, i.e. two-electron donors. We also have observed structural defects such as stacking faults which commonly appear in RP thin-films through cross-sectional scanning transmission electron microscopy (STEM). Our results imply that, in order to reveal the intrinsic electronic properties of this system, one should look for an effective way of electron doping while reducing chemical and structural disorder.

5.2 Methods

We have synthesized epitaxial thin-films of (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ ($x = 0, 0.025, 0.05$) on atomically flat SrTiO$_3$ (STO) (001) substrates [90] by pulsed laser deposition (PLD). The in-plane lattice parameters of the STO substrate and single crystal Sr$_3$Ir$_2$O$_7$ are 3.905 Å, and 3.896 Å, respectively [79, 91]. Hence, Sr$_3$Ir$_2$O$_7$ epitaxial thin-film coherently grown on STO substrate experiences an in-plane tensile strain ($\varepsilon_{xx} = (a_{film} - a_{bulk})/a_{bulk} \times 100\%$) of +0.23 %. For comparison, Sr$_2$IrO$_4$ and SrIrO$_3$ thin films, which have pseudocubic in-plane lattice parameters of $\sim$3.89 Å [92] and $\sim$3.96 Å [93], experience in-plane +0.38% tensile [36] and -1.0 % compressive [15] strain on a STO substrate, respectively. Sr$_3$Ir$_2$O$_7$ ((Sr$_{0.95}$La$_{0.05}$)$_3$Ir$_2$O$_7$) thin-films are grown using a ceramic Sr$_3$Ir$_2$O$_7$ ((Sr$_{0.95}$La$_{0.05}$)$_3$Ir$_2$O$_7$) target with a stoichiometric Sr:Ir ((Sr,La):Ir) ratio of 3:2 (confirmed by energy dispersive x-ray (EDX) spec-
troscopy) comprised of some additional IrO$_2$ phases (Powder diffraction data not shown.). (Sr$_{0.975}$La$_{0.025}$)$_3$Ir$_2$O$_7$ thin-films are grown by alternating the Sr$_3$Ir$_2$O$_7$ and (Sr$_{0.95}$La$_{0.05}$)$_3$Ir$_2$O$_7$ targets. The thin-films are grown with a laser fluence of 1.2 J/cm$^2$ (KrF excimer, $\lambda = 248$ nm), a substrate temperature of 700 $^\circ$C, and an oxygen partial pressure of 10 mTorr. EDX measurements on the thin-film samples confirms that the average concentration of La ions is consistent with the expected values ($x = 0$, 0.025, and 0.05). The epitaxial tetragonal structure of our thin-films has been confirmed using four-circle x-ray diffraction (XRD). The transport properties have been measured by using a conventional four-probe method. The in-plane optical absorption spectra of the thin-films have been taken at normal incidence using a Fourier-transform infrared spectrometer and a grating-type spectrophotometer in the photon energy regions of 0.06 – 0.5 eV and 0.5 – 3 eV, respectively.

5.3 Results and discussion

Figure 5.1 (a) (left panel) shows the $\theta$-2$\theta$ x-ray diffraction (XRD) scans confirming the c-axis orientation of (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ thin-films. The enlarged scans in Fig. 5.1 (a) (right panel) show that the (0010) reflections of the thin-films are shifted to higher angles as the out-of-plane lattice parameters become smaller by the substitution of La$^{3+}$ on Sr$^{2+}$ sites. The thickness of the thin-films obtained from the XRD interference fringes in the vicinity of the (0010) peak (Fig. 5.1 (a) (right panel)) is approximately 25 nm, which is consistent with the thickness obtained from STEM. X-ray reciprocal space mapping (Fig. 5.1 (b)) shows that the (6)-reflection of the thin-films is vertically aligned with the (103)-reflection of the STO substrates indicating that the thin-films are coherently strained to the substrates. The rocking curves are taken from the (1016)-reflection of the thin-films (Fig. 5.1 (c)) in order to avoid the substrate’s truncation rod and its full-width half-maximum (FWHM) is ca. 0.2° for all the thin-films. These large FWHM of thin-film rocking curves compared
to the substrate (0.04°) imply that the thin-films have structural disorders such as increased mosaicity.

Figure 5.1 (d) summarizes the out-of-plane lattice parameters (c) as a function of La concentration in the (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ thin-films. While the in-plane lattice parameter of the (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ thin-films is constant due to the coherent tensile strain from the STO substrates, La doping decreases the out-of-plane lattice parameter. While c-axis contraction with La doping also has been observed in bulk samples of other transition-metal oxides, including iridates, it has generally been associated with increased unit-cell volumes [28, 94, 95]. However, note that the ionic radius of La$^{3+}$ (1.03 Å) is smaller than that of Sr$^{2+}$ (1.18 Å) [96]. The increased unit-cell volume with La doping is mostly due to the changes in the valence states of transition metal ions (e.g. from Ir$^{4+}$ to Ir$^{3+}$) and/or the creation of oxygen vacancies. Hence, the decreased c-axis lattice parameters of our Sr$_3$Ir$_2$O$_7$ thin-films might imply that La-doping does not dope electron carriers effectively in these samples (See also the following discussions about transport properties).
Figure 5.1: (a) X-ray $\theta$-2$\theta$ scans of the epitaxial $(\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7$ ($x = 0, 0.025, 0.05$) thin-films grown on STO substrates, where only the (00l)-diffraction peaks of the thin-films ($l = 4, 6, 10, 12, 14$) are visible. The enlarged scans near (0010) reflections of the thin-films and the (002) reflections of the substrates are shown on the right. The peaks from the substrates are labeled with asterisk (*) symbols. (b) Reciprocal space map around the (103) reflection of the STO substrates with the (1016) reflection of $(\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7$ ($x = 0, 0.025, 0.05$) thin-films. (c) The rocking curve scan of $(\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7$ thin-films (0010)-reflection which have a full-width half-maximum of 0.2$^\circ$ for all thin-films. (d) The out-of-plane lattice parameters of the $(\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7$ thin-films obtained from the x-ray diffraction are shown as a function of La concentration. The open circle, square, and diamond indicate the out-of-plane lattice parameters of Sr$_3$Ir$_2$O$_7$ single crystals from Refs. [79, 86, 91], respectively.
The temperature-dependent resistivity shows that all of the (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ ($x = 0, 0.025, 0.05$) thin-films exhibit insulating behaviors (Fig. 5.2 (a)). We have compared the resistivity of these compounds with that of Sr$_2$IrO$_4$ (purple) and SrIrO$_3$ (orange) thin-films [15, 29, 37], which shows that the (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ thin-films are more (less) insulating than SrIrO$_3$ (Sr$_2$IrO$_4$) thin-film. The resistivity of the (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ thin-films at room temperature is about $5 \times 10^{-3}$ Ω·cm, which is almost the same as a previously reported Sr$_3$Ir$_2$O$_7$ thin-film [85] but smaller than that of a Sr$_3$Ir$_2$O$_7$ single crystal by approximately two orders of magnitude [73]. While the substitution of La$^{3+}$ on Sr$^{2+}$ sites is expected to dope electrons into the system, the resistivity of our thin-films at low temperatures increases by about three orders of magnitude as the La concentration is increased from 0 to 5 %, which is opposite to the metallic behavior of La-doped Sr$_3$Ir$_2$O$_7$ single crystals [73, 94]. Hence, our experimental data implies that there are differences in electronic structure between these iridate thin-films and single crystals.

To understand the conduction mechanism of these samples, we have considered three transport mechanisms: the thermal activation model, the Efros-Scklovskii (ES) VRH model, and the 3D Mott-VRH model. Both the thermal activation and ES-VRH model do not fit our experimental data, suggesting that these two models cannot describe the conduction mechanism of this system (model fits not shown). However, as shown in Fig. 5.2 (b), the 3D Mott-VRH model fits our experimental data very well over a wide temperature range (2 K – 300 K). This implies that the (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$ thin-films are a strongly disordered system with localized electrons carriers, similar to Sr$_2$IrO$_4$ thin-films [97]. Note that our Sr$_3$Ir$_2$O$_7$ thin-film is less insulating than single crystal Sr$_3$Ir$_2$O$_7$ [73] presumably due to some inevitable oxygen vacancies introduced during the thin-film deposition. However, the La doped Sr$_3$Ir$_2$O$_7$ thin-films show larger low-temperature resistivity and $T_M$ values than the Sr$_3$Ir$_2$O$_7$ thin-films. The estimated $T_M$ using our resistivity results are 100 K (Sr$_3$Ir$_2$O$_7$), 1200
Figure 5.2: (a) Temperature dependent resistivity of the \((\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7\) thin-films, which indicates that all of the thin-films are insulators. The resistivity of \(\text{Sr}_2\text{IrO}_4\) thin-film \cite{ref29} and a \(\text{SrIrO}_3\) thin-film \cite{ref15} on STO substrates is shown for comparison. (b) Logarithmic resistivities versus \(T^{-1/4}\), which are offset along the y-axis for clarity, show that all of the \((\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7\) thin-films display a 3D Mott-VRH conduction mechanism. The dashed lines indicate the linear fit.
K \((\text{Sr}_{0.975}\text{La}_{0.025})_3\text{Ir}_2\text{O}_7\), and 4000 K \((\text{Sr}_{0.95}\text{La}_{0.05})_3\text{Ir}_2\text{O}_7\). Since oxygen stoichiometry can be stabilized near La ions \[98,99\], we speculate that La doping in our \(\text{Sr}_3\text{Ir}_2\text{O}_7\) thin-films might have eliminated some oxygen vacancies reducing electron carriers. Note that a reduction of oxygen vacancies and increased resistivity by La doping has also been reported in some transition-metal oxides such as La-doped \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) single crystals \[98,99\].

Optical absorption spectra confirms the insulating behavior of \((\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7\) thin-films with finite optical gap energies. Figure 5.3 presents \(\alpha(\omega)\) of \((\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7\) thin-films together with \(\text{Sr}_2\text{IrO}_4\) \[36\] and \(\text{SrIrO}_3\) \[15\] thin-films. Due to the Reststrahlen band of the \(\text{STO}\) substrates, \(\sim 0.2\) eV is the lowest photon energy at which optical transmission spectra can be measured. We have performed spectral fits using the minimum set of Lorentz oscillators (black dashed lines), which match well with the experimental spectra. The charge-transfer transitions from O 2p to Ir 5d bands are above \(2\) eV. Similar to \(\text{Sr}_3\text{Ir}_2\text{O}_7\) single crystals \[83\], \(\alpha(\omega)\) of \((\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7\) thin-films show a two-peak feature (indicated by \(\alpha\) and \(\beta\)) at low energies, due to a Fano-like coupling between the spin-orbit exciton and inter-site d-d transitions within the \(J_{\text{eff}} = \frac{1}{2}\) band \[16\]. In order to extract the optical gap energy, we fit the absorption edge of the \(\text{Sr}_3\text{Ir}_2\text{O}_7\) and \((\text{Sr}_{0.975}\text{La}_{0.025})_3\text{Ir}_2\text{O}_7\) thin-films using the Wood-Tauc method, equation \[4.1\] \[78\] (Fig. 5.3 (inset)). The estimated optical gaps are about \(60\) meV and \(80\) meV for \(\text{Sr}_3\text{Ir}_2\text{O}_7\) and \((\text{Sr}_{0.975}\text{La}_{0.025})_3\text{Ir}_2\text{O}_7\), respectively. However, the short tail of the \((\text{Sr}_{0.95}\text{La}_{0.05})_3\text{Ir}_2\text{O}_7\) spectra at low energy makes it difficult to fit using Wood’s method. From our best fit, we obtain \(\gamma = 1.5\) for both \(\text{Sr}_3\text{Ir}_2\text{O}_7\) and \((\text{Sr}_{0.975}\text{La}_{0.025})_3\text{Ir}_2\text{O}_7\), which suggests a direct band gap for the thin-films, in contrast to the indirect band gap \((\gamma = 3.0)\) of \(\text{Sr}_3\text{Ir}_2\text{O}_7\) single crystals \[83\] and \(\text{Sr}_2\text{IrO}_4\) thin films \[29\]. The increase in the optical gap with increasing La concentration is consistent with the systematic increase in the resistivity data of this system.

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Figure 5.3: Optical absorption spectra ($\alpha(\omega)$) of (Sr$_{1-x}$La$_x$)$_3$Ir$_2$O$_7$, Sr$_2$IrO$_4$ (Ref. 29), and SrIrO$_3$ (Ref. 15) thin-films at room temperature. The plots are shifted vertically by $10^5$ cm$^{-1}$ for clarity. The dotted black curves are the fit curves using Lorentz oscillators, which match well with the experimental spectra. The inset shows the fitted absorption spectra at low energy using Wood-Tauc’s method.
Cross-sectional STEM of our samples shows structural defects such as stacking faults, which is consistent with Mott-VRH with strong disorder. Figure 5.4 (a) shows the STEM image of the Sr$_3$Ir$_2$O$_7$ thin-film in which the electron beam is incident along the [100]-direction of the (001) STO substrate. There are three noteworthy regions in the STEM data: 1) The ideal bilayer Sr$_3$Ir$_2$O$_7$ region with no intergrowth (Fig. 5.4 (b) and the orange dashed rectangle in Fig. 5.4 (a)), which is the most widely observed region in large-scale STEM images. 2) the region with a misaligned single SrO layer, i.e. an example of stacking faults, in the Sr$_3$Ir$_2$O$_7$ structure (as shown by the blue arrows in Fig. 5.4 (c) and the yellow dashed rectangle in Fig. 5.4 (a)). This small region may be structurally similar to Sr$_2$IrO$_4$. However, since XRD did not show any sign of Sr$_2$IrO$_4$ phases, the region must be due to structural heterogeneity or defects localized at the nanoscale, and its volume fraction should be negligible. And finally, 3) Figure 5.4 (d) shows an example of three separate atomic layers that are stacked along the b-axis direction (into the page) with vertically shifted SrO layers. The overlap of these three layers is consistent with the region shown by the blue dashed rectangle in the STEM image in Fig. 5.4 (a). Even though x-ray diffraction shows a single phase epitaxial thin-film, STEM images clearly indicate that there are various misaligned Sr$_3$Ir$_2$O$_7$ layers, which affect the transport properties of this system. It is well known that deposition of R-P phase thin-films such as Sr$_2$RuO$_4$ and Sr$_3$Ru$_2$O$_7$ can lead to the formation of unit cell fractions in the crystal $\begin{array}{c} \text{100} \\ \text{103} \end{array}$. The formation of these defects causes translation boundary defects in the compound which result in an out-of-plane shift between regions compared with the ideal crystal structure. Although these extra layered intergrowths are not frequently observed in single crystals, they are common in epitaxial thin-films due to the thermodynamic non-equilibrium process of synthesis $\begin{array}{c} \text{103} \\ \text{105} \end{array}$. 
Figure 5.4: (a) A cross-sectional Z-contrast STEM image of Sr$_3$Ir$_2$O$_7$. The brightest spots are Ir atoms; Sr, Ti, and O atoms are faint due to their small atomic (Z) number. (b) The orange dashed rectangular region of the STEM image in (a) with ideal Sr$_3$Ir$_2$O$_7$ unit cell. The schematic diagram of the unit cell is shown for clarity. Red dots represent Ir atoms in this and following images. (c) The yellow dashed rectangular region of the STEM image and schematic diagram showing the intergrowth of one single layer of SrO, shown by blue arrows, which causes a structural change from Sr$_3$Ir$_2$O$_7$ to Sr$_2$IrO$_4$. (d) The blue dashed rectangular region of the STEM image and schematic diagram that indicates three separate atomic layers sequentially stacked into the page. The foremost layer (red) is the ideal structure, while the second (blue) and third (green) layers contain vertical intergrowth of single SrO layers as shown by the red arrows. These layers show a non-zero overlap as indicated in the rightmost diagram.

5.4 Conclusion

We have investigated epitaxial thin films of tensile-strained, La-doped Sr$_3$Ir$_2$O$_7$, which are in close proximity to the metal-insulator transition. From transport and optical spectroscopic measurements, the thin-film series shows insulating properties with 3D Mott-VRH, where the resistivity increases by increasing the La concentration. The insulating behavior of the La-doped Sr$_3$Ir$_2$O$_7$ thin-films is presumably due to localization of carriers through ineffective electron doping of La and structural defects.
that are observed in STEM. Note that such structural defects strongly affect materials properties in general. For example, stacking faults can alter or even eliminate superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Sr}_2\text{RuO}_4$ $^{102,105,108}$. Attempts to synthesize superconducting $\text{Sr}_2\text{RuO}_4$ thin-films have had mixed results $^{107,109,112}$. The existence of structural defects in this compound limits the in-plane resistivity and quenches the superconductivity $^{102,105,107}$. The transport properties of La-doped $\text{Sr}_3\text{Ir}_2\text{O}_7$ thin-films may have been similarly deteriorated due to the observed stacking faults and disorder-induced localization. Therefore, our results highlight a critical role of characterizing and eliminating these defects in epitaxial thin-films to reveal the intrinsic physical properties of the iridates.

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Appendix A  Vacuum chamber for pulsed laser deposition

A.1 Building a pulsed laser deposition chamber

I recently completed the third vacuum deposition chamber for Prof. Seo’s group. Figure A.1 shows the photograph of the PLD in our laboratory. As shown in the figure A.2, the chamber body uses a simple six-way cross configured from six, 8-inch Conflat flanges.

Figure A.1: Photograph of the pulsed laser deposition system (PLD) in our group
Figure A.2: Photograph and schematic of the chamber body with a six-way cross configured from six, 8-inch Conflat flanges, before installing different parts on the body.
The chamber has been installed on a custom-designed cart (Fig. A.3). For safety reason, it is important that the cart is able to carry the weight of the chamber without breaking. Moreover, the cart should have the proper height. For example, in each growth using our third chamber in our laboratory, the heater on top of the chamber needs to be moved. If the height of the cart is not proper working with chamber would be difficult. Further, the cart should not be too big, since we need to be able to access all four sides quickly.

The chamber includes two reducer flanges that are used to connect the vacuum system as well as the gas ports (O₂ process gas, N₂ vent gas) and gauge ports (Pirani and Ion gauges) to the chamber body. Figure A.4 shows a simple schematic of the chamber design. The vacuum system is a turbo molecular pump that is backed by a dry roughing pump which can bring the small chamber down to a base pressure of about 5×10⁻⁶ Torr. The substrate heater is a custom-designed platinum wire heater with a maximum process temperature of 800 °C. The laser port has been attached by our Department of Physics and Astronomy machine shop and has been optimized to hit the target at the center of the chamber, as shown in the schematic in figure A.2.
Figure A.3: Photograph and schematic of our custom-designed cart.
Figure A.4: Schematic of the chamber design.
A.1.1 Target manipulator

Targets are placed in to the custom-designed and built target manipulator. The target manipulator is a motorized target holder that allows four different targets inside the vacuum chamber at one time. Having more than one target in the chamber gives options for alternating targets during deposition and depositing mixed-phase samples.

The target manipulator operates by using two motors: 1) a Stepper Motor which is connected to the inner rod (see figure A.5). The inner rod connected directly to the top circle plate with four target holders. The stepper motor rotates the whole circle plate on top with the target holders, which allows for target selection and 2) a Rotary Motor that is connected to the thin rod on the left, as it is shown in the figure A.5. By rotating the thin rod using rotary motor, the small gear in the bottom left rotates, which causes the big gear to rotate too. The rotation of the big gear in the bottom causes the rotation of the big gear on top. Finally, the four small gears on top start rotating, which each of them rotates each of the four cups on top (target holder).

Figure A.5 shows a schematic picture of the target manipulator. This design allows us to employ a target “glide mode” as well. During deposition, the target is both rotated by the rotary motor and is moved between two set positions on the stepper motor. Our target manipulator design allows for us to efficiently use nearly the entire target surface during deposition. Our set-up does not generate deep groves in our target, reducing the amount of target surface polishing as well.
Figure A.5: Schematic of the target manipulator. In order for the target manipulator to be operational we use two motors, stepper and rotary motors.
A.1.2 Laser beam path

Figure A.6: Laser beam path from Laser box to one of our chambers. The arrows and numbers are the guide to the eye following the laser beam path from laser box to inside the chamber.

We use UV optics to direct the excimer laser beam to the target inside the vacuum chamber. Figure A.6 shows a picture of the laser beam path from the laser box to one of our chamber. As the laser beam exits the laser box, it hits several UV reflective mirrors that redirect the laser beam to a focusing lens, which is mounted on a sliding
base. After passing the laser through the focal lens, it enters the vacuum chamber through a port that is optimized for the wavelength of the laser ($\lambda = 248$ nm). This focused laser beam hits the target which allows us to deposit our oxide thin-films. The laser beam path is shown by the red arrows and the numbers from the laser box to inside the chamber (Fig. A.6).
References


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