The electronic structure of epitaxially stabilized 5d perovskite \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) \((x = 0, 0.5, \text{and} 1)\) thin films: the role of strong spin–orbit coupling

**S Y Jang**, **H Kim**, **S J Moon**, **W S Choi**, **B C Jeon**, **J Yu** and **T W Noh**

1 ReCFI, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Republic of Korea
2 CSCMR, Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Republic of Korea

E-mail: twnoh@snu.ac.kr

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Abstract

We have investigated the electronic structure of meta-stable perovskite \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) \((x = 0, 0.5, \text{and} 1)\) thin films using transport measurements, optical spectroscopy, and first-principles calculations. We artificially fabricated the perovskite phase of \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \), which has a hexagonal or post-perovskite crystal structure in bulk form, by growing epitaxial thin films on perovskite GdScO\(_3\) substrates using an epi-stabilization technique. The transport properties of the perovskite \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) films systematically change from nearly insulating (or semi-metallic) for \( x = 0 \) to weakly metallic for \( x = 1 \). Due to the extended wavefunctions, 5d electrons are usually delocalized. However, the strong spin–orbit coupling in \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) results in the formation of effective total angular momentum \( J_{\text{eff}} = \frac{1}{2} \) and \( \frac{3}{2} \) states, which puts \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) in the vicinity of a metal–insulator phase boundary. As a result, the electrical properties of the \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) films are found to be sensitive to \( x \) and strain.

Online supplementary data available from stacks.iop.org/JPhysCM/22/485602/mmedia

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Numerous discoveries of fascinating physical phenomena relating to transition metal oxides (TMOs) have been reported, including a metal–insulator transition (MIT), high-temperature superconductivity, and colossal magneto-resistance [1–5]. Many of these phenomena can be understood in terms of Mott physics, where the on-site Coulomb repulsion, \( U \), and the bandwidth, \( W \), are in competition with one another. Generally, when \( U \ll W \), the system is metallic, but when \( U \gg W \), it becomes insulating [1, 2].

In most 3d or 4d TMOs, \( U \sim 3–5 \text{ eV}, \ W \sim 3–5 \text{ eV} \), and crystal field splitting is typically 2–3 eV. Spin–orbit (SO) coupling is typically of the order of 0.1 eV for most 3d or 4d TMOs, and therefore is usually neglected when describing the physical properties [2]. On the other hand, the situation is quite different for 5d TMOs. It is predicted that \( W \) \((U) \) of 5d TMOs is larger (smaller) than that of 3d and 4d TMOs, as the wavefunctions are more spatially extended. Therefore, according to the Mott physics, we can expect that most 5d TMOs should be metallic [6, 7]. However, some 5d TMOs, such as \( \text{Sr}_2\text{IrO}_4 \), \( \text{Sr}_3\text{Ir}_2\text{O}_7 \), and \( \text{Ba}_2\text{NaOsO}_6 \), are known to...
have insulating ground states [8–11]. To solve this problem, previous researchers pointed out the role of the SO coupling [12–15]. As the strength of the SO coupling is proportional to \( Z^2 \) (where \( Z \) is the atomic number), it can be as large as 0.3–0.5 eV in 5d TMOs [16], making the magnitude of the SO coupling comparable to \( U \) or \( W \).

Recently, we demonstrated that SO coupling should play a significant role in the physical properties of 5d \( \text{SrIrO}_3 \) [17]. It was found that the insulating ground state could be described more accurately by considering an effective total angular momentum \( J_{\text{eff}} = 1/2(J_{\text{eff},1/2}) \) state in the strong SO coupling limit, rather than the well-known spin \( S = 1/2 \) state for conventional Mott insulators. The SO coupling induces the formation of \( J_{\text{eff},1/2} \) and \( J_{\text{eff},3/2} \) bands which are occupied by five electrons. The \( J_{\text{eff},1/2} \) bands can be very narrow due to a reduced hopping integral caused by the isotropic orbital and mixed spin characteristics. Therefore, even when \( J \) is small the \( J_{\text{eff},1/2} \) bands can be split into a lower Hubbard band (LHB) and an upper Hubbard band (UHB), opening a Mott gap. This study was extended to the Ruddlesden–Popper series of \( \text{Sr}_{x+1}\text{IrO}_{3n+1} \) \( (n = 1, 2, \text{ and } \infty) \) [18], and it was found that \( W \) was expected to become larger when the number of neighbouring Ir atoms, \( z \), increases. Experimentally, it was found that the layered perovskites \( \text{Sr}_2\text{IrO}_4 \) \( (z = 4) \) and \( \text{Sr}_4\text{Ir}_2\text{O}_7 \) \( (z = 5) \) are in insulating states, but that the \( \text{SrIrO}_3 \) \( (z = 6) \) is in a metallic state. Moreover, electrodynamic studies of \( \text{SrIrO}_3 \) showed that it should be in a correlated metallic state, indicating that it is quite close to the metal–insulator (MI) phase boundary [18].

Considering the dimensionality-controlled MIT in \( \text{Sr}_{n+1}\text{IrO}_{3n+1} \), perovskite \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) should be a very intriguing material system. As the ionic size of the \( A \)-site ion becomes smaller than that of \( \text{Sr} \) ion, the distortion angle of the \( \text{IrO}_6 \) octahedra should increase. Such a structural change could result in a decrease of \( W \) [19], which would provide us with an opportunity to study the \( W \)-controlled MIT in 5d TMOs. However, the stable form of \( \text{CaIrO}_3 \) is known to be a post-perovskite crystal structure, and \( \text{SrIrO}_3 \) to be a hexagonal crystal structure [20, 21]. Therefore in order to investigate \( W \)-controlled MIT and the role of the SO coupling in the 5d TMOs, it is highly desirable to fabricate perovskite \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) phases.

In this paper, we report growth of perovskite \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) \( (x = 0, 0.5, 1) \) thin films and their electronic and structural properties. We fabricated meta-stable perovskite \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) thin films using epi-stabilization techniques [23] and investigated the electronic structure using transport measurements, optical spectroscopy, and first-principles calculations. We found that perovskite \( \text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3 \) is located very close to an MI phase boundary, so the electronic properties are quite sensitive to external perturbations such as \( x \) and strain. The first-principles calculations indeed showed that the SO coupling should play an important role in putting the iridates close to an MI phase boundary.

3. Results and discussions

Figure 1(a) shows an XRD \( \theta–2\theta \) pattern for the \( \text{CaIrO}_3 \) film on a \( \text{GdScO}_3(110) \) substrate. The strongest sharp peaks are Bragg reflections from the \( \text{GdScO}_3(110) \) substrate. The pattern shows pure (001)-oriented perovskite \( \text{CaIrO}_3 \) reflections, with no trace of impurities or additional phases. For comparison, the peak positions of the post-perovskite \( \text{CaIrO}_3 \) phase is also shown. Figure 1(b) shows an x-ray reciprocal space mapping (X-RSM) to a pseudo-cubic reciprocal lattice unit (r.l.u.) of the \( \text{GdScO}_3 \) substrate. The X-RSM clearly shows that the pseudo-cubic \((–103)\) reflection of the perovskite \( \text{CaIrO}_3 \) phase is on the same pseudo-cubic reciprocal plane of \( \text{GdScO}_3 \). Further details can be found in the supplementary data (available at stacks.iop.org/JPhysCM/22/485602/mmedia). As shown in the inset of figure 1(a), the \( \varphi \)-scans of the \( \text{CaIrO}_3(–103)\) reveal a four-fold symmetry, having the same peak positions as \( \text{GdScO}_3(–103)\). The X-RSM and \( \varphi \)-scans indicate that the perovskite \( \text{CaIrO}_3 \) film was deposited epitaxially. Moreover, the X-RSM data show that the perovskite \( \text{CaIrO}_3 \) film is almost fully strained to the substrate. The measured \( c \)-axis lattice constant of 3.872 Å is quite consistent with the simple elastic calculation result of 3.855 Å with a Poisson ratio \( \nu = 0.35 \) [25]. We also investigated the structural properties of \( \text{Ca}_{0.5}\text{Sr}_{0.5}\text{IrO}_3 \) and \( \text{SrIrO}_3 \) films, and found that they also have similar high-quality perovskite phases (not shown).

Figure 2 shows \( \rho(T) \) for the perovskite \( \text{CaIrO}_3, \text{Ca}_{0.5}\text{Sr}_{0.5}\text{IrO}_3, \) and \( \text{SrIrO}_3 \) thin films grown on \( \text{GdScO}_3(110) \) substrates. Interestingly, the temperature dependence of \( \rho \)}
CaIrO₃ film peaks. The inset of (a) shows the that we have epitaxial growth of the perovskite CaIrO₃ phase. (b) X-ray reciprocal space mapping around the (−103)c Bragg reflection from the GdScO₃ substrate and CaIrO₃ film peaks. The inset of (a) shows the ϕ-scans of the (−103)c peaks for the CaIrO₃ film and GdScO₃ substrate, which demonstrates that we have epitaxial growth of the perovskite CaIrO₃ phase.

is quite weak for all Ca₁₋ₓSrₓIrO₃ compounds, and dρ/dT changes its sign from positive to negative as x decreases. SrIrO₃ (x = 1) shows metallic behaviour (dρ/dT > 0) and has a resistivity of just less than 10⁻³ Ω cm, which corresponds to the Mott minimum metallic conductivity [1]. Note that a previous optical study showed that SrIrO₃ is a correlated metal near the MI phase boundary [18], which is consistent with this transport measurement result. Ca₀.₅Sr₀.₅IrO₃ (x = 0.5) also shows a nearly metallic behaviour (dρ/dT > 0) and has a ρ slightly larger than that of SrIrO₃, lying at the Mott boundary. The value of ρ for CaIrO₃ (x = 0) is somewhat above the Mott boundary and exhibits insulator-like behaviour (dρ/dT < 0). However, ρ(T) does not diverge at very low temperatures, which suggests that it might have semi-metallic behaviour. Considering the highly metallic character of 4d perovskite Ca₁₋ₓSrₓRuO₃ and Ca₁₋ₓSrₓRhO₃ compounds [27–29], the 5d Ca₁₋ₓSrₓIrO₃ films seem to constitute a unique system, which is located near the borderline of the MIT.

Figures 3(a) and (b) show σ(ω) of the perovskite Ca₁₋ₓSrₓIrO₃ films at room temperature. Most d–d transitions between the Ir 5d orbital states were found to be located below 2 eV [18]. Values of σ(ω) below 0.5 eV show clear changes as x decreases, which is consistent with the transport data. For SrIrO₃, a distinct Drude-like response appears due to the free charge carriers. For Ca₀.₅Sr₀.₅IrO₃, the Drude-like feature is slightly suppressed; however, it still dominates the low energy optical response. On the other hand, for CaIrO₃, a peak structure develops as ω approaches ~0.2 eV from the high frequency side. In order to ensure that a sharp peak structure and not a Drude peak is present, we independently measured the reflectance spectra of the far-infrared energy region (6–80 meV) [30] and obtained σ(ω) below 80 meV.⁵ We

⁵ Recently, polycrystalline perovskite CaIrO₃ was reported to have a larger resistivity than our epitaxial film case [26], which might be due to the grain boundary effect.

⁶ In the far-infrared region, the strong phonon signal of the GdScO₃ substrate barely allows the transmission of light. Hence, we tried to extract σ(ω) from the Lorentz oscillator model fit of the reflectance spectrum. However, due to its low symmetry, the phonon modes of GdScO₃ are too complicated to extract the pure optical response of the film. As SrTiO₃ has a rather simple phonon mode, we measured the reflectance of CaIrO₃ film on SrTiO₃ substrate. For the CaIrO₃ film on SrTiO₃, the perovskite CaIrO₃ phase was also confirmed by HRXRD measurements, and an insulator-like temperature-dependent resistivity curve, which has a slightly larger value than that of CaIrO₃/GdScO₃, was obtained from transport measurement.
Figure 3. Optical conductivity spectra, $\sigma(\omega)$, of (a) SrIrO$_3$, Ca$_{0.5}$Sr$_{0.5}$IrO$_3$, and (b) CaIrO$_3$ thin films grown on GdScO$_3$ (110) substrates, except for the blue curve (separate curve near 0 eV) in (b), $\sigma(\omega)$ of CaIrO$_3$ on SrTiO$_3$(001). In (b), $\sigma(\omega)$ of Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ (from [18]) are also shown for comparison. Theoretical dispersion relations of CaIrO$_3$ from (c) LDA + $U$ and (d) LDA + SO + $U$ calculations.

reflect $W$ of the initial and final bands. The width of peak $\alpha$ for CaIrO$_3$ from the Lorentz oscillator model fitting is about 0.42 eV, which is close to that of Sr$_3$Ir$_2$O$_7$ (~0.45 eV) and larger than that of Sr$_2$IrO$_4$ (~0.27 eV) [18]. The results indicate that $W$ of $J_{\text{eff},1/2}$ bands in CaIrO$_3$ is similar to that of $J_{\text{eff},1/2}$ bands in Sr$_3$Ir$_2$O$_7$, which was smaller than that of $J_{\text{eff},1/2}$ bands in SrIrO$_3$ due to the reduced dimensionality.

To gain more insight into the electronic structure of perovskite CaIrO$_3$, we performed local density approximation (LDA) + $U$ calculations with SO coupling included. For the first-principle analysis, we used the linear combination of pseudo-atomic-orbital (LCPAO)-based code OpenMX, in which a fully relativistic $j$-dependent pseudo-potential and LDA + $U$ scheme is implemented. We used double s and p, and single d pseudo-atomic-orbital calculations for all of the atoms, with cut-off radii of 7.0 au for Ca and Ir and 5.0 au for oxygen. For the $k$-grid integration, we used $(10 \times 10 \times 7)$ $k$-space points over the first Brillouin zone and a 400-Ryd energy cut-off for the real-space numerical integration and solution of Poisson’s equation. For the lattice structure, we used the lattice constants given by the XRD analysis as a starting point and carried out full lattice relaxation up to $5.0 \times 10^{-4}$ Hartree Å$^{-1}$ as the force criterion. For the LDA + SO + $U$ calculations, $U = 2.0$ eV was used.

Figures 3(c) and (d) show the calculated band structures of CaIrO$_3$ with the LDA + $U$ and LDA + SO + $U$ calculations, respectively. In the energy region between $-2.5$ and $0.5$ eV, the Ir 5d $t_{2g}$ states were the main contributors. The LDA + $U$ result in figure 3(c) yields a metallic ground state with complex $t_{2g}$ bands crossing the Fermi energy ($E_F$). The band structure changes only slightly from the LDA one (not shown), since $W$ is so large that the small $U$ cannot play a major role. When the SO coupling is included, the band structure changes remarkably: the bands crossing $E_F$ are split off due to formation of the $J_{\text{eff},1/2}$ and $J_{\text{eff},3/2}$ bands. The light and dark lines in figure 3(d) represent the $J_{\text{eff},1/2}$ and $J_{\text{eff},3/2}$ bands, respectively.

We assigned the optical transition peaks shown in figure 3(b) according to calculated data. The transitions from the lower $J_{\text{eff},1/2}$ bands to the upper $J_{\text{eff},1/2}$ bands and from the $J_{\text{eff},3/2}$ bands to the upper $J_{\text{eff},1/2}$ bands result in the peaks $\alpha$ and $\beta$, respectively. Because the narrow $J_{\text{eff},1/2}$ bands are located near $E_F$, the increase in $W$ could easily induce the density of states at the $E_F$. This effect should be reflected as the broadening of peak $\alpha$ and finally results in the coherent Drude response in $\sigma(\omega)$.

It should be noted that, although a gap is opened, the conduction and valence bands still touch $E_F$, resulting in a small hole and electron pocket, as shown in figure 3(d). This phenomenon is similar to semi-metallic behaviour. In the transport data, the overall behaviour of $\rho(T)$ is insulator-like, but does not diverge at low temperatures, which is also
consistent with the semi-metallic character. On the other hand, the optical transition is quite sensitive to the direct transition, so semi-metallic character would be difficult to observe. This semi-metallic behaviour indicates that CaIrO$_3$ is positioned between metallic and insulating phases during the process of the band dispersion lifting by IrO$_6$ distortion.

From the structural optimization by the LDA calculations, we found rotation and tilting angles both of $\sim 17^\circ$ for CaIrO$_3$. These angles were changed to $\sim 11^\circ$ and $\sim 13^\circ$, respectively, for SrIrO$_3$. The $W$ values of the separate upper $J_{eff:1/2}$ bands were estimated to be about 0.52 and 0.58 eV for CaIrO$_3$ and SrIrO$_3$, respectively.

From the experimental and theoretical results, we can conclude that the strong SO coupling pushes the Ca$_{1-x}$Sr$_x$IrO$_3$ system into the vicinity of an MIT by inducing the formation of $J_{eff}$ bands. Due to this Mott instability, it is expected that the electronic properties are sensitive to changes in $x$ and strain. Using optical spectroscopy and first-principles calculations, we demonstrated that strong spin–orbit coupling results in the semi-metallic behaviour indicates that CaIrO$_3$ is positioned between metallic and insulating phases during the process of the band dispersion lifting by IrO$_6$ distortion.

From the experimental and theoretical results, we can conclude that the strong SO coupling pushes the Ca$_{1-x}$Sr$_x$IrO$_3$ system into the vicinity of an MIT by inducing the formation of $J_{eff}$ bands. Due to this Mott instability, it is expected that the electrical ground state could be easily tuned by subtle external perturbations, such as changes in the lattice parameters. To demonstrate such a high sensitivity, we controlled the lattice parameters of Ca$_{0.5}$Sr$_{0.5}$IrO$_3$, which can affect $W$, by epitaxially growing the films on different substrates. That is, we deposited Ca$_{0.5}$Sr$_{0.5}$IrO$_3$ on a SrTiO$_3$ substrate, which has a smaller lattice constant than GdScO$_3$, resulting in compressive strain. Figure 4(a) shows XRD $\theta$–2$\theta$ patterns for the Ca$_{0.5}$Sr$_{0.5}$IrO$_3$ film on GdScO$_3$ (110) and SrTiO$_3$ (001) substrates. Because the lattice parameter of Ca$_{0.5}$Sr$_{0.5}$IrO$_3$ is between GdScO$_3$ and SrTiO$_3$, the Ca$_{0.5}$Sr$_{0.5}$IrO$_3$ film is under a tensile strain when it is grown on GdScO$_3$ and a compressive strain when it is grown on SrTiO$_3$. Figure 4(b) shows $\rho(T)$ for the Ca$_{0.5}$Sr$_{0.5}$IrO$_3$ thin films on GdScO$_3$ and SrTiO$_3$ substrates. The film that was grown on SrTiO$_3$ shows insulator-like behaviour, whereas the film on GdScO$_3$ shows nearly metallic behaviour. This implies that the $W$ of the $J_{eff:1/2}$ bands in the film on SrTiO$_3$ substrate decrease, which might be due to the enhanced distortion of oxygen octahedra. Compressive strain of the SrTiO$_3$ substrate could be a reason for the enhanced distortion, but more detailed study is needed. This result demonstrates that the Ca$_{1-x}$Sr$_x$IrO$_3$ system is indeed very close to the Mott instability due to the strong SO coupling of the 5d Ir ion.

4. Conclusions

We successfully fabricated meta-stable perovskite Ca$_{1-x}$Sr$_x$IrO$_3$ ($x = 0, 0.5, and 1$) thin films and observed that the electronic properties are sensitive to changes in $x$ and strain. Using optical spectroscopy and first-principles calculations, we demonstrated that strong spin–orbit coupling results in the semi-metallic character of the Ca$_{1-x}$Sr$_x$IrO$_3$ being located very close to a metal–insulator phase boundary due to the formation of effective total angular momentum $J_{eff} = 1/2$ and 3/2 states. This work provides further advancement in understanding the underlying physics of the $J_{eff}$ state in 5d transition metal oxides and manipulation of this state by changing the chemical pressure and strain state.

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References

[1] Mott N F 1990 Metal–Insulator Transitions (London: Taylor and Francis)
[2] Imada M, Fujimori A and Tokura Y 1998 Rev. Mod. Phys. 70 1039
[3] Hubbard J 1963 Proc. R. Soc. A 276 238
[4] Bednorz J G and Muller K A 1986 Z. Phys. B 64 189
[5] Tokura Y 2000 Colossal Magnetoresistive Oxides (New York: Gordon and Breach Science)
[6] Mattheiss L F 1969 Phys. Rev. 181 987
[7] Mattheiss L F 1976 Phys. Rev. B 13 2433
[8] Cao G, Bolivar J, McCall S, Crow J E and Guerlin R P 1998 Phys. Rev. B 57 R11039
[9] Cao G, Xin Y, Alexander C S, Crow J E, Schlotmann P, Crawford M K, Harlow R L and Marshall W 2002 Phys. Rev. B 66 214412
[10] Erickson A S, Misra S, Miller G J, Gupta R R, Schlesinger Z, Harrison W A, Kim J M and Fisher I R 2007 Phys. Rev. Lett. 99 016404
[11] Moon S J et al 2006 Phys. Rev. B 74 113104
[12] Haverkort M W, Elfimov I S, Tjeng L H, Sawatzky G A and Damascelli A 2008 Phys. Rev. Lett. 101 026406
[13] Singh D J, Blaha P, Schwarz K and Sofo J O 2002 Phys. Rev. B 65 155109
[14] Xiang H J and Whangbo M H 2007 Phys. Rev. B 75 052407
[15] Liu G-Q, Antonov V N, Jepsen O and Andersen O K 2008 Phys. Rev. Lett. 101 026408
[16] Rossnagel K and Smith N V 2006 Phys. Rev. B 73 073106
[17] Kim B J et al 2008 Phys. Rev. Lett. 101 076402
[18] Moon S J et al 2008 Phys. Rev. Lett. 101 226402
[19] Okimoto Y, Katsufuji T, Okada Y, Arima T and Tokura Y 1995 Phys. Rev. B 51 09581
[20] Ohgushi K, Gotou H, Yagi T, Kiuchi Y, Sakai F and Ueda Y 2006 Phys. Rev. B 74 241104(R)
[21] Cao G, Durairaj V, Chikara S, DeLong L E, Parkin S and Schlottmann P 2007 Phys. Rev. B 76 100402
[22] Chamberland B L and Philpotts A R 1992 J. Alloys Compounds 182 355
[23] Lee J-H et al 2006 Adv. Mater. 18 3125
[24] Noh T W, Song P H, Lee S-I, Harris D C, Gaines J R and Garland J C 1992 Phys. Rev. B 46 4212
[25] Stølen S and Trønnes R G 2007 Phys. Earth Planet. Inter. 164 50
[26] Ohgushi K, Yagi T, Gotou H, Kiuchi Y and Ueda Y 2009 Physica B 404 3261
[27] Yamaura K and Takayama-Muromachi E 2001 Phys. Rev. B 64 224424
[28] Yamaura K and Takayama-Muromachi E 2006 Physica C 445 54
[29] Eom C B, Cava R J, Fleming R M, Phillips J M, van Dover R B, Marshall J H, Hsu J W P, Krajewski J J and Peck W F Jr 1992 Science 258 1766
[30] Kim S I, Seo S S A, Moon S I, Choi W S, Hur N H, Seo Y K and Lee Y S 2007 J. Korean Phys. Soc. 51 S161