Abstract

Perovskite iridates have emerged as a new paradigm for studying the strongly correlated electron physics with strong spin-orbit coupling. The “113” alkaline-earth iridates AIrO$_3$ (A = Ca, Sr, Ba) display a rich variety of crystallographic and electronic states and are now attracting growing research interest. This chapter aims to provide an overview for these “113” iridates, including the materials’ synthesis, crystal structure, major physical properties, and other interesting results such as the effects of pressure and chemical substitutions, as well as theoretical perspectives.

Keywords: Perovskite iridates, Spin-orbit coupling, Post-perovskite, Polytype, Semimetal

1. Introduction

The discoveries of high-transition-temperature superconductivity in cuprates and the colossal magnetoresistance in manganites made the first-row (3d) transition-metal oxides (TMOs) with perovskite-related structures the central topics of condensed matter physics over the past four decades. The strong electron–electron correlations intrinsic for these narrow-band 3d-electron systems are believed to be at the heart of rich physics. Following the general wisdom based on the 3d TMOs, the third-row (5d) counterparts having a spatially much extended 5d orbitals were expected to have much reduced electron–electron correlations, $U$, and broaden bandwidth, $W$, i.e. $U \ll W$, leading to a Pauli paramagnetic metallic ground state, Figure 1(a). Such an expectation, however, was recently found to be violated in many 5d-electron iridium oxides (iridates), such as Sr$_2$IrO$_4$ [1], in which an antiferromagnetic insulating ground state was instead observed. Recent studies have revealed that such discrepancy originates from the inherently strong spin-orbit coupling (SOC) for these heavy 5d elements, which have a typical...
value of SOC, $\zeta_{SO} \approx 0.3$–$0.5$ eV, comparable with the magnitude of $U$ and $W$, and thus cannot be treated as a negligible perturbation as in the 3d TMOs.

Since an unrealistically large $U$ is required to open a Mott gap in $\text{Sr}_2\text{IrO}_4$, Figure 1(b), Kim et al. [2] proposed that the strong SOC splits the otherwise broad $t_{2g}$ band of the octahedral-site, low-spin $\text{Ir}^{4+}$($5d^5$) array into a filled, low-energy $J_{\text{eff}} = 3/2$ quartet band and a half-filled, high-energy $J_{\text{eff}} = 1/2$ doublet band, Figure 1(c, e). A moderate Hubbard $U$ can then open a Mott gap, leading to the SOC-driven $J_{\text{eff}} = 1/2$ Mott insulating state, Figure 1(d). Subsequent experimental [3] and theoretical [4] investigations have confirmed such a novel $J_{\text{eff}} = 1/2$ state in the strong SOC limit. Since then, the 5d TMOs have emerged as a new paradigm for studying the strongly correlated electron physics with strong SOC. In particular, the iridates have attracted special attention in that the combination of relativistic SOC and electron–electron correlations has been proposed to generate more exotic, unprecedented quantum states of matters, such as the strong topological insulators, Weyl semimetal, quantum spin liquids, and even unconventional superconductors [5].

**Figure 1.** Schematic energy diagrams for the 5$d^5$ ($t_{2g}^5$) configuration: (a) without SOC and $U$, (b) with an unrealistically large $U$ but no SOC, (c) with SOC but no $U$, and (d) with SOC and $U$, (e) 5d level splitting by the crystal field and SOC. Adapted from Reference [2].
Since the importance of SOC was first recognized in Sr$_2$IrO$_4$, which is the $n = 1$ member of the Ruddlesden–Popper series Sr$_n$Ir$_n$O$_{3n+1}$ ($n = 1, 2, \infty$), these perovskite (Pv) iridates are currently archetypal systems for studying the interplay of SOC and electron–electron correlations. During the past few years, numerous studies have been performed on the single-layer Sr$_2$IrO$_4$ ($n = 1$) and bilayer Sr$_3$Ir$_2$O$_7$ ($n = 2$); for a review, see Reference [6]. With increasing the number of Pv layers $n$, the bandwidth of the $J_{\text{eff}} = 1/2$ band is expected to increase, and a dimensionality controlled insulator-to-metal transition is eventually realized in the orthorhombic Pv SrIrO$_3$ ($n = \infty$) [7]. Recent advances in this emergent field have turned much attention to the “113” alkaline-earth iridates AlIrO$_3$ (A = Ca, Sr, Ba) with the Pv-related structures. However, in-depth investigations on these compounds are hindered to a great extent by the harsh synthesis conditions as well as their complex structural variations. For example, the above-mentioned orthorhombic Pv SrIrO$_3$ can only be stabilized in the bulk form under high-pressure and high-temperature (HPHT) conditions [8], or in the form of thin films by applying epitaxial strain [9]. Recent theoretical investigations proposed an intriguing topological semimetal state for the orthorhombic Pv phase [10]. When synthesized at ambient pressure, on the other hand, SrIrO$_3$ adopts a so-called six-layer (6H) polytype [8], which has been characterized as a non-Fermi-liquid metal approaching a ferromagnetic quantum critical point [11]. As the sister compounds of SrIrO$_3$, both CaIrO$_3$ and BaIrO$_3$ also display multiple structural polymorphs with interesting structural–property relationships. Depending on the synthesis conditions, CaIrO$_3$ can be stabilized in either the Pv or the post-perovskite (pPv) structure, which displays, respectively, a paramagnetic metal and an antiferromagnetic insulator ground states [12, 13]. Although the pPv CaIrO$_3$ was regarded as the $J_{\text{eff}} = 1/2$ Mott insulator [14], recent studies revealed a clear deviation from the ideal $J_{\text{eff}} = 1/2$ state due to the pronounced structural distortions [15]. In addition, in the field of geosciences, CaIrO$_3$ has been studied extensively as an analog of MgSiO$_3$ to elucidate the mechanism of Pv to pPv transition at the boundary of Earth’s lowermost mantle, or the D” layer [16]. In the case of BaIrO$_3$, it also exhibits multiple structural polytypes with interesting structural–property relationship. At ambient pressure, BaIrO$_3$ adopts a nine-layer structure (9R). It is the first known ferromagnetic insulator among the 5d TMOs and exhibits intriguing charge-density-wave formation accompanying the ferromagnetic order [17, 18]. When treating the 9R phase under different pressures, three more polytypes, i.e. 5H, 6H, and 3C, have been identified [19]. Following the sequence of 9R $\rightarrow$ 5H $\rightarrow$ 6H $\rightarrow$ 3C, their ground states change progressively from a weak ferromagnetic insulator with $T_c = 180$ K for 9R, through a ferromagnetic metal with $T_c = 50$ K for 5H, and an exchange enhanced non-Fermi-liquid metal for 6H approaching a ferromagnetic quantum critical point, finally to a Pauli paramagnetic Fermi-liquid metal for 3C [20, 21]. These results demonstrate an intimate structure–property relationship that has been well documented in the 3d TMOs. A brief summary of the structural types and interesting physical properties for these “113” alkaline-earth iridates AlIrO$_3$ (A = Ca, Sr, Ba) is given in Table 1.

Although there are many publications dealing with an individual compound, a monograph that provides a comprehensive overview for these “113” alkaline-earth iridates is still lacking to our knowledge. Taking into account the growing research interests on these iridates, it is imminent to summarize the currently available knowledge in a single chapter. Thus, this chapter aims to bring together the available information in literature for these “113” iridates.
In the following, we will give a comprehensive literature survey for each AlrO$_3$ covering the materials’ synthesis, crystal structure, and major physical properties, as well as other interesting results such as the effects of chemical substitutions and theoretical investigations. Finally, we will give a brief concluding remark on the current research status and provide an outlook on the future research directions on these iridates.

| Compound | Structure type | Interesting physical properties |
|----------|---------------|---------------------------------|
| CaIrO$_3$ | pPv | AF insulator with $T_N = 110$ K, stripe-type AF order with spin canting; |
| | Pv | PM semimetal with possible Dirac node protected by reflection symmetry |
| SrIrO$_3$ | 6H | Exchange enhanced PM metal with nFL behaviors due to proximity to a FM QCP |
| | Pv | PM semimetal with possible Dirac node protected by reflection symmetry |
| BaIrO$_3$ | 9R | Weak FM insulator with a simultaneous CDW formation below $T_c \approx 180$ K |
| | 5H | Weak FM metal with $T_c \approx 50$ K |
| | 6H | Exchange enhanced PM metal with nFL behaviors due to proximity to a FM QCP |
| | 3C | FL PM metal |

AF: Antiferromagnetic; PM: Paramagnetic; FM: Ferromagnetic; FL: Fermi liquid; nFL: non Fermi liquid; CDW: Charge density wave; QCP: Quantum critical point

Table 1. A summary of the “113” Alkaline-earth iridates AlrO$_3$ (A=Ca, Sr, Ba)

2. CaIrO$_3$

CaIrO$_3$ has two different orthorhombic polymorphs, i.e. the layered pPv structure with space group Cmcm and the GdFeO$_3$-type Pv structure with space group Pbnm. These two compounds have been known since 1960s [22, 23] and received significant attention from geologists since 2004 as an analogy of MgSiO$_3$, the main constituent mineral of the Earth’s lower mantle [16, 24]. More recently, they have emerged as important correlated 5d-electron systems with strong SOC [14, 25]; the strong local distortion in pPv CaIrO$_3$ makes it a model system to investigate the interplay of non-cubic crystal field splitting and SOC [15], while the orthorhombic Pv CaIrO$_3$ might be considered as an intriguing semimetal with symmetry-protected Dirac points [26].

2.1. Synthesis

There are some discrepancies in literature regarding the synthesis of pPv CaIrO$_3$ at ambient pressure. In the earlier studies [12, 22], it was reported that single-phase pPv phase cannot be obtained at ambient pressure through a solid-state reaction from CaCO$_3$ and IrO$_2$ in air. Recently, Harai et al. [27] reported that pure pPv CaIrO$_3$ can be prepared by heating the stoichiometric mixture of CaO and IrO$_2$ powders sealed in an evacuated silica tube at 1000°C.
over 20 h. On the other hand, since the pPv structure is a high-pressure phase, pPv CaIrO$_3$ can be readily obtained by utilizing HPHT synthesis. For example, Ohgushi et al. [25] reported the synthesis of single-phase pPv CaIrO$_3$ at 4 GPa and 1150°C.

Needle-shaped pPv CaIrO$_3$ single crystals have been reported to grow out of the CaCl$_2$ flux. By adopting a tenfold flux and a relatively low soaking temperature of 836 and 950°C, respectively, Sugahara et al. [28] and Hirai et al. [29] obtained tiny single crystals for the purpose of crystal-structure refinements. On the other hand, Ohgushi et al. [14] seems to grow sizable pPv CaIrO$_3$ single crystals for anisotropic magnetic property measurements by employing a higher flux molar ratio (16:1) and a higher soaking temperature of 1200°C. However, our attempts by using the latter approach ended up with Ca$_2$IrO$_4$ rather than the pPv CaIrO$_3$.

Because Pv CaIrO$_3$ is a metastable phase, it cannot be synthesized via a solid-state reaction route at ambient pressure. Alternatively, Sarkozy et al. [12] reported the preparation of pure Pv phase by thermal decomposition at 650–700°C in air of the hydroxide intermediate CaIr(OH)$_6$, which can be obtained according to the following wet-chemical reaction scheme:

$$K_2IrCl_6 \xrightarrow{H_2O} IrCl_6^{2-} \xrightarrow{KOH, pH=10-12} Ir(OH)_6^{2-} \xrightarrow{Ca^{2+}} CaIr(OH)_6.$$ 

By following this approach, we obtained nearly single-phase Pv CaIrO$_3$ with a trace amount of IrO$_2$ (0.2 wt.%) and Ca$_2$IrO$_4$ (1.3 wt.%) [30]. Recently, Kojitani et al. [31] determined a large positive Clapeyron slope for the pPv/Pv transition of CaIrO$_6$, i.e. Pv structure is the high-temperature phase of pPv. Thus, Pv CaIrO$_3$ can be obtained by transforming pPv phase at higher temperature under given pressures. For example, Ohgushi et al. [13] have reported the synthesis of single-phase Pv CaIrO$_3$ at 1 GPa and 1450°C. In addition, thin films of Pv CaIrO$_3$ have recently been epitaxially stabilized on various substrates [26, 32].

### 2.2. Crystal structure

**pPv CaIrO$_3$** As shown in Fig. 2(a), the crystal structure of pPv CaIrO$_3$ can be described as a pseudo-2D layered structure having IrO$_6$ octahedral sheets stacked alternatively with the Ca$^{2+}$ ions along the crystallographic b axis. Within the octahedral sheets, IrO$_6$ octahedra share edges along the a axis to form rutile-type chains; these chains are then interconnected with each other via apical oxygen atoms along the c axis. Because of the significant interest in geosciences, the crystal structure of pPv CaIrO$_3$ have been thoroughly studied by several groups [28, 29]. To illustrate the peculiar features of pPv CaIrO$_3$, here we adopted the results given by Sugahara et al. [28] who refined the crystal structure based on the single-crystal X-ray diffraction (XRD) technique. The crystal structure was refined in an orthorhombic space group *Cmcm* (No. 63) with Ca at 4c (0, y, 1/4), Ir at 4a (0, 0, 0), O1 at 4c (0, y, 1/4), and O2 at 8f (0, y, z) sites, respectively. The obtained unit cell parameters are $a = 3.147$ Å, $b = 9.866$ Å, $c = 7.302$ Å, and $V = 226.7$ Å$^3$ at room temperature. The refined positional parameters and selected bond lengths and bond angles after Reference [28] are listed in Table 2. Within the buckled octahedral layer, the IrO$_6$ octahedral chains display an alternative rotation about the a axis,
resulting in Ir-O1-Ir bond angles of 134.3°. As a result, for a given octahedron the local $z$ axis that is along the Ir-O1 bond deviates from the crystallographic $c$ axis by about 23°. In addition, IrO$_6$ octahedra show a significant tetragonal compression, with two short Ir-O1 (1.978 Å) and four long Ir-O2 (2.066 Å) bonds. Octahedral-site distortions can be generally described by the orthorhombic vibrational modes $Q_2 = l_x - l_y$ and $Q_3 = (2l_z - l_x - l_y)/\sqrt{3}$, where $l_x$, $l_y$, $l_z$ are the bond lengths for bonding along local $x$, $y$, $z$ directions. In pPv CaIrO$_3$, the octahedral-site distortion corresponds to a negative mode of $Q_3 = -0.102$. For comparison, the PtO$_6$ octahedra in the pPv CaPtO$_3$ with a filled t$_{2g}^6$ manifold show a negligible $Q_3 = -0.001$. Such a comparison highlights a strong orbital-lattice coupling in pPv CaIrO$_3$ with low-spin t$_{2g}^5$ configuration for Ir$^{4+}$ ions, for which the single hole would be expected to have a dominant $yz \pm izx$ orbital character [30], which has been confirmed recently by the resonant inelastic X-ray spectroscopy [15].

Figure 2. Crystal structure of CaIrO$_3$ polymorphs: (a) pPv and (b) Pv.

Pv CaIrO$_3$ As shown in Fig. 2(b), the crystal structure of Pv CaIrO$_3$ is built up from corner-shared IrO$_6$ octahedra in three dimensions with Ca cations in the interstitial positions. It has been known over 40 years that Pv CaIrO$_3$ adopts the GdFeO$_3$-type structure; however, structural refinements have not been performed until recently. We present here our Rietveld refinement results [30] based on the high-resolution synchrotron XRD on polycrystalline Pv CaIrO$_3$ prepared with the wet-chemical method mentioned above. The crystal structure was refined in space group $Pbnm$ (No. 62) with Ca at 4c ($x$, $y$, 1/4), Ir at 4b (0.5, 0, 0), O1 at 4c ($x$, $y$, 1/4) and O2 at 8d ($x$, $y$, $z$) sites, respectively. The lattice parameters at room temperature are determined as $a = 5.35046$ Å, $b = 5.59291$ Å, $c = 7.67694$ Å, and $V = 229.73$ Å$^3$. The obtained positional parameters and selected bond lengths and bond angles after Reference [30] are listed in Table 3. In comparison with the pPv phase, the IrO$_6$ octahedra are less distorted with three sets of Ir-O distances of 2.006 Å, 2.020 Å, and 2.038 Å; the average Ir-O distance of 2.021 Å is
consistent with the ionic radii sum for Ir$^{4+}$ (0.625 Å) and O$^{2-}$ (1.40 Å). The averaged Ir-O-Ir bond angle is about 145.5° in the Pv phase.

| Atom | Site | x   | y        | z | B$_{iso}$ (Å$^2$) |
|------|------|-----|----------|---|-------------------|
| Ca   | 4c   | 0   | 0.7492   | 1/4 | 0.40              |
| Ir   | 4a   | 0   | 0        | 0  | 0.32              |
| O1   | 4c   | 0   | 0.0779   | 1/4 | 0.70              |
| O2   | 8f   | 0   | 0.3658   | 0.4452 | 0.79          |

Ir-O1 (×2) 1.978 Ir-O1-Ir 134.3
Ir-O2 (×4) 2.066 O1-Ir-O2 86.3
<Ir-O> 2.037 O1-Ir-O2 93.7
Ir-Ir (×2) 3.1472
Ir-Ir (×2) 3.651

Table 2. Refined positional parameters and selected bond lengths (Å) and bond angles (°) for pPv CaIrO$_3$ from single-crystal XRD [28]: space group Cmcm (No. 63), a = 3.1472 Å, b = 9.8655 Å, c = 7.3018 Å, V = 226.71 Å$^3$, Z = 4.

| Atom | Site | x         | y         | z   | B$_{iso}$ (Å$^2$) |
|------|------|-----------|-----------|-----|-------------------|
| Ca   | 4c   | -0.01403  | 0.05962   | 1/4 | 0.71              |
| Ir   | 4b   | 0.5       | 0         | 0   | 0.27              |
| O1   | 4c   | 0.10487   | 0.47110   | 1/4 | 0.92              |
| O2   | 8d   | 0.69257   | 0.30488   | 0.05602 | 1.07          |

Ir-O1 (×2) 2.006 Ir-O1-Ir 146.15
Ir-O2 (×2) 2.020 Ir-O2-Ir 144.95
Ir-O2 (×2) 2.038
<Ir-O> 2.021

Table 3. Refined positional parameters and selected bond lengths (Å) and bond angles (°) for Pv CaIrO$_3$ from powder XRD[30]: space group Pbnm (No. 62), a = 5.35046 Å, b = 5.59291 Å, c = 7.67694 Å, V = 229.73 Å$^3$, Z = 4.

2.3. Physical properties

pPv CaIrO$_3$. It is an antiferromagnetic insulator with $T_N \approx 110$ K. Due to the difficulty in obtaining single-phase samples, the physical properties of pPv CaIrO$_3$ were not characterized until 2006 by Ohgushi et al. [25], who first reported its electrical transport and magnetic properties on polycrystalline samples synthesized under HPHT conditions. As shown in Figure 3, its resistivity $\rho(T)$ increases quickly upon cooling, following the Arrhenius-type behaviour, i.e. $\rho(T) = \rho_0 \exp(\Delta/T)$, with the activation energy $\Delta = 0.17$ eV; magnetic susceptibility $\chi = M/H$ exhibits a sharp transition at $T_N = 115$ K, below which a weak ferromagnetic moment of $\sim 0.04 \mu_B$/Ir was observed from the isothermal magnetization curve. In addition, a huge coercive field
Hc ≈ 4 T was evidenced at low temperatures. Density functional calculations by Subedi [33] demonstrated that the inclusion of SOC can split the t2g bands into fully filled Jeff = 3/2 bands and half-filled Jeff = 1/2 bands, as shown schematic in Figure 1(c), and that both SOC and moderate U are required to reconcile the experimentally observed Mott insulating behaviour. By performing the resonant X-ray diffraction at the L absorption edges of pPv CaIrO3 single crystals, Ohgushi et al. [14] determined its magnetic structure as a stripe-type antiferromagnetic order, i.e. the Ir moments are aligned parallel along the a axis and antiparallel along the c axis with a canted ferromagnetic component along the b axis. Bogdanov et al. [34] carried out ab initio quantum chemical calculations and reproduced such a striped antiferromagnetic structure. Moreover, their calculations predicted a strong antiferromagnetic exchange interaction of Jz = 121 meV through the corner-shared path along the c axis, and a weak nearest-neighbour ferromagnetic coupling of Jc ≈ -7.3 meV within the edge-shared chains along the a axis. In this regard, pPv CaIrO3 can be regarded as a Jeff = 1/2 quasi-1D antiferromagnet. Although the above results suggested that a Jeff = 1/2 ground state is realized in pPv CaIrO3, first-principles calculations [33, 34] evidenced significant deviations from the ideal Jeff = 1/2 state with highly uneven admixture of the t2g components due to the pronounced tetragonal distortion. In agreement with these calculations, a very recent resonant inelastic X-ray scattering (RIXS) study by Sala et al. [15] confirmed the departure from the Jeff = 1/2 state. By analyzing the RIXS spectrum, they estimated the effective tetragonal crystal field splitting Δ = -0.71 eV and the SOC ζSO = 0.52 eV, from which a ground state wave function |0, ±⟩ = ±0.32|xy⟩, ±0.67(yz, ±)∓0.67|xz, ±⟩) with a dominant yz±ixx orbital character was derived.

The Mott insulating nature of quasi-2D pPv CaIrO3 have motivated Ohgushi et al. [25] to metallize it via the carrier doping. They successfully prepared a series of hole-doped Ca1-xNa2xIrO3 (0 ≤ x ≤ 0.37) with pPv structure under HPHT conditions and realized a filling-control antiferromagnetic insulator to paramagnetic metal transition around x = 0.3, near which, however, no superconductivity was observed. Nevertheless, anomalous properties such as the non-Fermi-liquid behaviour and positive magnetoresistance violating Kohler’s rule were observed for the metallic samples. In the same report, attempt of electron doping via Y3+ substitutions for Ca2+ was unsuccessful due to the formation of pyrochlore phase. In a recent work by Gunasekera et al. [35], however, Y-substituted Ca1-xYxIrO3 (0 ≤ x ≤ 0.5) samples with pPv structure were successfully fabricated via a conventional solid-state reaction route at ambient pressure. Similar with the Na+-doped case, about 30%-Y3+ doping can also drive an insulator-to-metal transition; superconductivity was not observed either in this case. In striking contrast with the gradual suppression of TN by Na doping, surprisingly, TN remains unchanged upon Y substitutions up to 50%, except that the magnitude of ac susceptibility peak decreases about one order. Further experiments are needed to exclude the possibility that the magnetic order arises from the minor CaIrO3 phase. Anyhow, metallization of the quasi-2D pPv CaIrO3 represents an interesting direction to pursue exotic electronic state in the vicinity of metal–insulator transition.

Pv CaIrO3, In sharp contrast with the antiferromagnetic insulating ground state of pPv CaIrO3, the Pv phase has been reported as a Pauli paramagnetic metal by Sarkozy et al. [12] in 1974.
Recent characterizations by Ohgushi et al. [13] on the dense pellets obtained via HPHT synthesis confirmed the paramagnetic nature, but the temperature dependence of resistivity shows bad metal behaviour with a non-diverge upturn at low temperatures, Figure 3. Such a bad metallic behaviour was reproduced on the epitaxially stabilized thin films grown on various substrates [26, 32], and has been ascribed to a semimetallic ground state with the conduction and valence band touching at Fermi level. The observations of a sign change and a nonlinear magnetic-field dependence of the Hall resistance are consistent with the coexistence of electron and hole charge carriers [26]. As discussed below for Pv SrIrO$_3$, the semimetallic state might originate from the symmetry-protected Dirac nodes around the Fermi level due to a combined effect of SOC and reflection symmetry of the $Pbnm$ orthorhombic lattice. In light of the recent theoretical proposals for the orthorhombic Pv iridates discussed below, further experimental studies on the semimetallic Pv CaIrO$_3$ are highly desirable.

$p$Pv versus Pv CaMO$_3$ ($M = Ir, Rh, Ru$) The distinct ground states of pPv and Pv CaIrO$_3$ reflect the intimate structural–property relationships. In addition to CaIrO$_3$, both CaRuO$_3$ [36] and CaRhO$_3$ [37] have also been reported to possess quenchable Pv and pPv polymorphs. Besides the importance in geosciences as analogy materials of MgSiO$_3$, these compounds with partially filled d-electron shells are important correlated electron systems with intriguing physical properties [37, 38]. In a similar manner as CaIrO$_3$, their ground states differ sharply as the

Figure 3. Temperature dependence of (a) resistivity $\rho(T)$ and (b) magnetic susceptibility $M/H$ for the two polymorphs of CaIrO$_3$, pPv for post-perovskite and Pv for perovskite. Adapted from Reference [13].
structure changes: Pv CaRuO$_3$ is a well-known exchanged-enhanced paramagnetic metal on the verge of a ferromagnetic instability, whereas the pPv phase is an antiferromagnetic insulator with $T_N = 270$ K \[38\]; Pv CaRhO$_3$ is a Pauli paramagnetic metal while the pPv phase is insulating and undergoes a canted antiferromagnetic transition below $T_N = 90$ K \[37\]. Current first-principles calculations for the pPv compounds failed to capture the correct ground state; it seems that in addition to electron–electron correlations, SOC also plays an essential role in producing the insulating ground state for these 4d and 5d-electron systems \[39\].

In addition to the interest in fundamental physics, the CaIrO$_3$ ceramics have also been investigated by Keawprak et al. \[40\] for the potential thermoelectric applications. They prepared both phases of CaIrO$_3$ with spark plasma sintering technique and evaluated their thermoelectric properties from room temperature up to 1023 K. The highest dimensionless figure of merit (ZT) reaches 0.02 and 0.003 for Pv and pPv phase, respectively.

3. SrIrO$_3$

Depending on the synthesis conditions, SrIrO$_3$ can form in two different structures, i.e. the monoclinically distorted 6H polytype and the orthorhombic GdFeO$_3$-type Pv structure \[8\]. The
former is a rare stoichiometric oxide exhibiting non-Fermi-liquid behaviours near a ferromagnetic quantum critical point [11]. The latter was recently found to be an exotic narrow-band semimetal that may harvest many topological and magnetic insulating phases [10, 41, 42].

3.1. Synthesis

The 6H phase can be readily prepared in the polycrystalline form at ambient pressure by sintering the stoichiometric mixture of SrCO$_3$ and IrO$_2$ (or Ir) at 900–1,100°C in air [8]. Single crystals of 6H phase with dimensions ~0.4 × 0.4 × 0.6 mm$^3$ have been grown in Pt crucibles with the SrCl$_2$ self-flux techniques [11]. The Pv phase is a HP form of SrIrO$_3$. Longo et al. [8] performed the first HPHT syntheses and established the temperature–pressure phase diagram for the 6H-Pv transformation of SrIrO$_3$. It was found that the 6H phase transforms to the Pv structure above 1,650°C at 2 GPa and above 700°C at 5 GPa. Recent HPHT syntheses of Pv SrIrO$_3$ were usually performed at 1,000–1,100°C and 5–6 GPa [43, 44]. For these samples, Rietveld refinements on the powder XRD patterns evidenced the presence of ~3–4 wt.% IrO$_2$ impurity. Since the Pv phase is metastable, it remains a challenge to obtain sizable bulk single crystals under HP conditions. However, Pv SrIrO$_3$ films and superlattices have been stabilized at ambient pressure via applying the epitaxial strain with various techniques, including the metalorganic chemical vapour deposition [9], pulsed laser deposition [45], and reactive oxide molecular-beam epitaxy [42]. As discussed below, given the tolerance factor $t < 1$, it is unusual for SrIrO$_3$ to adopt the 6H structure at ambient pressure. It was recently reported [46, 47] that the 6H structure of SrIrO$_3$ can be destabilized by partial substitution of M = Li, Fe, Co, Ni, Zn for Ir in SrIr$_{1-x}$M$_x$O$_3$ and converted to the Pv structure within a narrow composition range around $x = 0.2$. In these cases, it was suggested that the presence of e$_g$ type orbitals on the M ions contributes to the breakdown of face-sharing octahedral dimmers in the 6H structure.

3.2. Crystal structure

6H SrIrO$_3$ The crystal structure of 6H SrIrO$_3$ was first determined by Longo et al. [8] as a monoclinic distortion of the hexagonal BaTiO$_3$ structure. The 6H hexagonal structure can be described as close-packed SrO$_3$ layers stacked perpendicular to the c axis in the sequence hcchcc, where h and c refer to hexagonal (ABAB...) and cubic (ABCABC...) close packing, respectively. The Ir atoms occupy the oxygen octahedra formed by the SrO$_3$ layers, and the IrO$_6$ octahedra share common faces across an h layer and common corners across a c layer. As a result, the above hcchcc stacking sequence results in two independent positions for the Ir atoms. As shown in Figure 5(a), two IrO$_6$ octahedra form pairs of face-shared octahedra that are joined by common corners to a plane of corner-sharing IrO$_6$ octahedra. Therefore, the 6H structure can be alternatively depicted as a stacking of layers of corner- (C) and face (F)-sharing IrO$_6$ octahedra in the sequence FCCFCC along the c axis.

In the original work by Longo et al., the oxygen positional parameters were not refined due to the low scattering of oxygen relative to Ir and Sr. Based on the neutron diffraction data, Qasim et al. [46] recently provided a full refinement on the crystal structure of 6H SrIrO$_3$ with $a = 5.6040$ Å, $b = 9.6256$ Å, $c = 14.1834$ Å, and $\beta = 93.202^\circ$ in space group C2/c (No. 15). The refined positional parameters and selected bond lengths and bond angles after Reference [46] are listed
in Table 4. In this structure, the Ir1O₆ octahedron has an average Ir-O distance of 2.006 Å typical of Ir⁴⁺ with the individual distances in a narrow range 1.987–2.038 Å. In contrast, the Ir2O₆ octahedra in the Ir₂O₉ dimers are not regular with a longer average Ir-O distance of 2.030 Å. The Ir2–Ir2 distance, 2.770 Å, is relatively short and close to the separation of 2.72 Å found in Ir metal, suggesting a strong Ir–Ir bonding across the common faces. Variable temperature XRD measurements on the 6H phase confirmed that the monoclinic structure is stable without any structural transition up to 1,000°C in air.

![Figure 5](image)

**Figure 5.** Crystal structure of SrIrO₃ polytypes: (a) 6H and (b) Pv.

**Pv SrIrO₃** Similar as Pv CaIrO₃, it consists of a 3D network of corner-sharing IrO₆ octahedra that are cooperatively rotated and tilted about the pseudocubic [110] and [001] axes, Figure 5(b). Blanchard et al. [44] recently performed a thorough study on the crystal structure of Pv SrIrO₃ based on the synchrotron and neutron diffraction data. The crystal structure was refined in space group *Pbnm* (No. 62) with Sr at 4c (x, y, 1/4), Ir at 4a (0, 0, 0), O1 at 4c (x, y, 1/4), and O2 at 8d (x, y, z) sites, respectively. The lattice parameters at room temperature are determined as a = 5.60075 Å, b = 5.57115 Å, and c = 7.89601 Å. The obtained positional parameters and selected bond lengths and bond angles after Reference [44] are listed in Table 5. As can be seen, the individual IrO₆ octahedron is relatively rigid with three Ir–O distances being approximately equal. The average Ir–O distance at 300 K of 2.016 Å is consistent with the ionic radii sum for Ir⁴⁺ and O²⁻. From the refined atomic coordinates, Blanchard et al. also estimated the two independent octahedral tilt angles, i.e. ψ = 11.5° for out-of-phase tilt about the pseudocubic [110] axis, and φ = 8.7° for in-phase tilt about the pseudocubic [001] axis, respectively. These tilting angles were found to be nearly temperature-independent below room temperature. The orthorhombic *Pbnm* structure was shown to persist over the temperature range 3–1,070 K.

**6H-Pv transformation** As pointed out by Longo et al. [8], SrIrO₃ and SrMnO₃ are the only SrBO₃ (B = Ti, Zr, Hf, Cr, Mo, Tc, Fe, Ru, Sn, Pb, Ce, Th) compounds that do not adopt the Pv structure at ambient pressure. Given the tolerance factor t ≤ 1, the Pv structure would be stabilized for these compounds. However, SrMnO₃ has the 4H polytype structure with a
stacking sequence of hchc along the c axis, while SrIrO$_3$ crystallizes in the 6H polytype as mentioned above. It would appear that the hexagonal polytypes with their face-shared octahedra and trigonal crystal fields are stabilized by the outer electron configurations that allow for metal–metal bonding along the c axis. For example, in the case of low-spin Ir$^{4+}$, the trigonal crystal field of the hexagonal polytype should split the $t_{2g}^5$ orbitals to e$_g^0$e$_g^4$a$_{1g}^1$ which allow for metal–metal bonding along the c axis via the half-filled a$_{1g}$ orbitals. Thus, the 6H SrIrO$_3$ and 4H SrMnO$_3$ can be regarded as a compromise between the continuous face-shared chains of the 2H polytype and the geometrically favoured Pv structure. Since high pressure prefers the cubic close packing with a higher density than the hexagonal close packing, 6H SrIrO$_3$ transforms to the Pv structure under high-pressure conditions with a ~3% volume reduction.

| Atom | Site | x   | y   | z   | B$_{iso}$ (Å$^2$) |
|------|------|-----|-----|-----|------------------|
| Sr1  | 4e   | 0   | 0.0092 | 1/4 | 0.0285  |
| Sr2  | 8f   | 0.0122 | 0.6667 | 0.0957 | 0.0482  |
| Ir1  | 4a   | 0   | 0   | 0   | 0.0478  |
| Ir2  | 8f   | 0.9820 | 0.6660 | 0.84698 | 0.0459  |
| O1   | 4e   | 0   | 0.4981 | 1/4 | 0.0584  |
| O2   | 8f   | 0.2411 | 0.2649 | 0.2603 | 0.0287  |
| O3   | 8f   | 0.8112 | 0.4077 | 0.0474 | 0.0572  |
| O4   | 8f   | 0.9407 | 0.1544 | 0.4087 | 0.0535  |
| O5   | 8f   | 0.3238 | 0.4204 | 0.1058 | 0.0586  |

Ir1-O3 (×2) 2.038  Ir1-O3-Ir2 149.6
Ir1-O4 (×2) 1.987  Ir1-O4-Ir2 158.8
Ir1-O5 (×2) 1.994  Ir1-O5-Ir2 149.3
<Ir1-O> 2.006
Ir2-O1 2.100  Ir2-O1-Ir2 82.5
Ir2-O2 2.055  Ir2-O1-Ir2 85.1
Ir2-O2 2.040
Ir2-O3 1.974
Ir2-O4 1.957
Ir2-O5 2.051
<Ir2-O> 2.030
Ir2-Ir2 2.770

Table 4. Refined positional parameters and selected bond lengths (Å) and bond angles (°) for 6H SrIrO$_3$ from neutron diffraction [46]: space group C2/c (No. 15), $a = 5.60401$ Å, $b = 9.6256$ Å, $c = 14.1834$ Å, $\beta = 93.202^\circ$, $V = 763.89$ Å$^3$, $Z = 12$. 

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### Table 5. Refined positional parameters and selected bond lengths (Å) and bond angles (°) for \( PV \) \( SrIrO_3 \) from neutron diffraction [44]: space group \( Pbnm \) (No. 62), \( a = 5.60075 \ \text{Å}, \ b = 5.57115 \ \text{Å}, \ c = 7.89601 \ \text{Å}, \ V = 246.376 \ \text{Å}^3, \ Z = 4. \)

| Atom | Site | \( x \) | \( y \) | \( z \) | \( B_{iso} \) (Å²) |
|------|-----|--------|--------|------|----------------|
| Sr   | 4c  | -0.0068 | 0.4687 | 1/4  | 0.019         |
| Ir   | 4a  | 0      | 0      | 0    | 0.017         |
| O1   | 4c  | 0.0718  | 0.0049 | 1/4  | 0.019         |
| O2   | 8d  | 0.2126  | 0.2877 |      | -0.0369      |

\[ \text{Ir-O1} (\times 2) \quad 2.015 \quad \text{Ir-O1-Ir} \quad 156.92 \]
\[ \text{Ir-O2} (\times 2) \quad 2.018 \quad \text{Ir-O2-Ir} \quad 156.22 \]
\[ <\text{Ir-O}> \quad 2.017 \]

3.3. Physical properties

\( 6H \) \( SrIrO_3 \). Although the \( 6H \) \( SrIrO_3 \) has been synthesized more than 50 years ago, its physical properties were not characterized in detail until 2007 by Cao et al. [11], who reported the magnetic, electrical transport, and calorimetric properties of \( 6H \) \( SrIrO_3 \) single crystals grown out of the \( SrCl_2 \) flux. The primary results are summarized in Figure 6. Magnetic susceptibility \( \chi(T) \) measurements evidenced no long-range magnetic order down to 1.7 K, but exhibited at low temperatures strong enhancements that diverge as \( \chi \propto T^\gamma \) with \( 1/2 < \gamma < 1 \), suggesting the proximity to a ferromagnetic instability. The isothermal magnetization \( M(H) \) at 1.7 K indeed displays a saturation behaviour at \( H \sim 3 \ T \), yet the saturation moment is very small, being less than 0.03 \( \mu_B/Ir \). The low-temperature specific heat \( C(T) \) exhibits a pronounced \(-T\log T\) dependence, which is characteristic of non-Fermi-liquid systems. Such a \( C/T \sim -\log T \) behaviour can be readily enhanced in low applied fields up to 1.1 T, vanishes for \( H > 2 \ T \), and eventually changes to a \( T^{3/2} \) power law expected for a ferromagnetically ordered state at \( H = 8 \ T \). In accordance with the \( C(T) \) results, both the \( c \)-axis resistivity, \( \rho_c \), and the \( ab \)-plane resistivity, \( \rho_{ab}(T) \), follow a non-Fermi-liquid \( T^{3/2} \) dependence over a wide temperature range up to 120 K under zero field, while a Fermi-liquid \( T^2 \) behaviour is restored upon applying an external field \( H \geq 5 \ T \). Taking into account all these observations, \( 6H \) \( SrIrO_3 \) can be regarded a rare example of stoichiometric oxide that exhibits non-Fermi-liquid behaviours near a ferromagnetic quantum critical point. As will be shown explicitly in \( BaIrO_3 \) such a quantum critical point can be realized via subtle structural variations.

\( PV \) \( SrIrO_3 \). In the original work by Longo et al. [8], \( PV \) \( SrIrO_3 \) has been described as a Pauli paramagnetic metal. In 2008, Zhao et al. [43] reinvestigated the physical properties of \( PV \) \( SrIrO_3 \) bulk sample prepared under 5 GPa and 1,000°C. They observed two characteristic temperatures \( T \approx 170 \ \text{K} \) and \( T_{MI} \approx 44 \ \text{K} \): at \( T \), the paramagnetic susceptibility \( \chi(T) \) starts to increase with temperature, and the resistivity \( \rho(T) \) exhibits a slope change, followed below \( T \) by the presence of unusual linear field dependence positive magnetoresistance (MR) that reaches about 12% at 5 K and 7 T; a broad metal–insulator transition was observed at \( T_{MI} \). However, these observations are largely disapproved by the very recent work of Blanchard et
al. [44], who studied the bulk samples prepared under 6 GPa and 1,100°C. As shown in Figure 7, it was found in the latter work that \( \rho(\text{T}) \) exhibits metallic conductivity down to 2 K, following Fermi-liquid \( T^2 \) dependence between 2 and 30 K, without showing an upturn at low temperature. In addition, they observed a smaller positive MR up to 2% at 7 T and 2–50 K. These discrepancies might originate from the polycrystalline nature of the studied samples, in which the extrinsic effects such as the grain boundary and impurities can largely influence the transport properties. As mentioned above, \( \text{Pv SrIrO}_3 \) films of single-crystal quality can be stabilized via applying epitaxial strain. The resistivity upturn at low temperatures have been frequently observed in these thin films [9, 48], but the upturn temperature displays a broad distribution, in support of an extrinsic property due to weak Anderson localization. Nevertheless, such sensitivity to defects reflects the bad metal character of semimetallic \( \text{Pv SrIrO}_3 \) approaching the boundary of metal–insulator transition.

As the end member of the Ruddlesden–Popper series \( \text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1} \) (\( n = 1, 2, \infty \)), \( \text{Pv SrIrO}_3 \) has recently attracted much attention due to the presence of nontrivial features within the \( J_{\text{eff}} = 1/2 \) bands. Density-functional theory first-principles calculations by Carter et al. [10] found that in the strong SOC limit the bands near the Fermi energy are mostly composed of \( J_{\text{eff}} = 1/2 \) states. Interestingly, they found a node near the U point, Figure 8(a), thus revealing the semimetallic
nature of Pv SrIrO$_3$. By constructing a tight-binding model, they confirmed the presence of a line node near the U point in the Brillouin zone, and further shown that the line node originates from the reflection symmetry of the crystal structure at the $z = 1/4$ and $3/4$ planes presented in the orthorhombic $Pbnm$ space group. Since the line node is protected by the underlying lattice symmetry, it has been further proposed that perturbations breaking the sublayer reflection symmetry can lift the line node and convert the system into an insulating phase; the system may become a strong topological insulator at a certain point. In addition, as shown in Figure 8(b), magnetically ordered metallic and insulating phases have also been proposed to arise in the U versus SOC phase diagram of Pv SrIrO$_3$ [41]. Moreover, Chen et al. [49] further proposed that the presence of reflection symmetry in orthorhombic Pv iridates may realize a novel class of topological crystalline metals with zero-energy surface states at certain planes.

Recent angle-resolved photoemission spectroscopy on Pv SrIrO$_3$ films by Nie et al. [42] has uncovered such an exotic semimetallic state with very narrow bands near the Fermi surface consisting of heavy hole-like pockets around $(\pm \pi, 0)$ and $(0, 0)$ and light electron-like pockets at $(\pm \pi/2, \pm \pi/2)$. Surprisingly, the bandwidth of Pv SrIrO$_3$ is found to be narrower than that of Sr$_2$IrO$_4$, in contrary to the general expectations of broaden bandwidth with increasing dimensionality [7]. Since the semimetallic ground state has been confirmed experimentally, it is of particular interest to achieve the proposed topological and/or magnetic states via tuning the SOC, U, and/or lattice symmetry. In this regard, Matsuno et al. [45] have made an important step towards these exotic phases; they tailored a spin-orbit magnetic insulator out of the semimetallic state via controlling the dimensionality of $[(SrIrO_3)_m SrTiO_3]$ superlattices. By utilizing HPHT synthesis, we prepared a series of Sn-doped SrIr$_{1-x}$Sn$_x$O$_3$ orthorhombic perovskites. We found that substitutions of isovalent, nonmagnetic Sn$^{4+}$ for Ir$^{4+}$ ions lead to a breakdown of the semimetallic state, and convert the paramagnetic, semimetallic ground state

![Figure 7. Temperature dependence of (a) magnetic susceptibility and (b) resistivity of Pv SrIrO$_3$. Adapted from Reference [44].](image-url)
of \( \text{Pv SrIrO}_3 \) to an antiferromagnetic insulator with a concomitant metal–insulator transition at \( T_N \) [50]. These recent experimental efforts demonstrated that semimetallic \( \text{Pv SrIrO}_3 \) is a promising candidate for realizing distinct topological and magnetic insulating states that deserve further investigations in the near future. On the other hand, the \( \text{Pv SrIrO}_3 \) film has also been regarded as potential electrode material for microelectronic devices [9].

4. \( \text{BaIrO}_3 \)

At ambient pressure, \( \text{BaIrO}_3 \) crystallizes in the nine-layer (9R) polytype. It is the first known ferromagnetic insulator with \( T_c \approx 180 \text{ K} \) among the 5d TMOs [17]. Detailed studies on single
crystals revealed a charge-density-wave (CDW) formation below the ferromagnetic order [18, 51]. Recent experimental [52] and theoretical [53] investigations further revealed it as an exotic spin-orbit Mott insulator that is of great current research interest. Following the general trend of perovskite hexagonal polytypes, we have explored the high-pressure sequences of BaIrO$_3$ and found three more polytypes, i.e. 5H, 6H, and 3C [19, 20, 21]. Their ground states exhibit an interesting evolution from a ferromagnetic insulator to a Pauli paramagnetic metal passing through a ferromagnetic quantum critical point tuned by the gradual structural changes as detailed below.

4.1. Synthesis

The ambient-pressure 9R phase can be readily obtained by sintering the stoichiometric mixtures of BaCO$_3$ and Ir at 1,000°C in air. The sample should be cooled down slowly for the last sintering in order to ensure an oxygen stoichiometry [54]. Single crystals have been reported to grow out of the BaCl$_2$ flux at a relatively low temperature of 1,000 K [18]. HPHT synthesis is needed for all the other polytypes [19, 21, 55, 56]. For the HP syntheses around 1,000°C, the 9R polytype is stable up to 3 GPa, the 5H phase exists only in a narrow pressure range around 4 GPa, the 6H phase is stabilized in a wide pressure range from 5 to ~20 GPa, and the 3C phase was finally obtained at 25 GPa. We have employed the two-stage (Walker- or Kawai-type) multianvil systems for the HPHT syntheses. During the HPHT experiments, the sample was first compressed to the desired pressure by eight truncated tungsten carbide anvils, and then the temperature was increased to ~1,000°C and kept for 30 min before quenching to room temperature. The resultant samples were recovered after releasing pressure and then subjected to various characterizations at ambient pressure.

4.2. Crystal structure

9R BaIrO$_3$. As shown in Figure 9(a), the crystal structure of the 9R phase consists of Ir$_3$O$_{12}$ trimers of face-sharing octahedra that are linked by their vertices to form columns parallel to the c-axis, with a stacking of layers of corner-sharing (C) and face-sharing (F) IrO$_6$ octahedra in the order FFCFFCFFC along the c axis. Except for the monoclinic distortion, it is isostructural with the 9R BaRuO$_3$. The monoclinic distortion generates twisting and buckling of the Ir$_3$O$_{12}$ trimers that are tilted ~12° relative to each other. Here, we adopted the crystal structure of 9R BaIrO$_{2.94}$ obtained by Powell et al. [54] from the NPD data, which were refined in a structural model defined in the C2/m space group, with three kinds of Ba atoms at 4i ($x$, 0, $z$) positions, four types of unequivalent Ir atoms at 4i, 2a (0, 0, 0) and 2d (0.5, 0, 0.5) sites, and six types of oxygen atoms at 4i and 8j ($x$, $y$, $z$) positions. The obtained unit-cell parameters are $a = 9.9992$ Å, $b = 5.7490$ Å, $c = 15.1707$ Å, and $\beta = 103.27^\circ$. The final positional parameters and the selected bond lengths and bond angles after Reference [54] are listed in Table 6. Ir1–Ir2 and Ir3–Ir4 distances, of 2.618 Å and 2.627 Å respectively, are even smaller than the separation of 2.72 Å found in Ir metal, which indicates significant interactions between iridium cations at the centre of face-shared pairs of octahedra. It is important to note that, although this polytype has been compared to the ambient 9R BaRuO$_3$, with rhombohedral (R-3m) symmetry and a stacking
sequence \((FFC)_3\), the monoclinic distortion described for ambient 9R BaIrO\(_3\) actually involves a shorter periodicity, with a stacking sequence \((FFC)_2\) along the \(c\) axis, as shown in Figure 9(a).

**Figure 9.** Crystal structure of the BaIrO\(_3\) polytypes: (a) 9R, (b) 5H, (c) 6H, and (d) 3C.

| Atom   | Site | \(x\)     | \(y\)     | \(z\)     | \(B_{\text{iso}}\) (\(\text{Å}^2\)) |
|--------|------|-----------|-----------|-----------|-----------------------------------|
| Ba1    | 4i   | 0.7779    | 0         | 0.2501    | 0.42                              |
| Ba2    | 4i   | 0.3686    | 0         | 0.0720    | 0.42                              |
| Ba3    | 4i   | 0.1515    | 0         | 0.4224    | 0.42                              |
| Ir1    | 4i   | 0.0845    | 0         | 0.1766    | 0.16                              |
| Ir2    | 2a   | 0         | 0         | 0         | 0.16                              |
| Ir3    | 4i   | 0.4657    | 0         | 0.3230    | 0.16                              |
| Ir4    | 2d   | 0.5       | 0         | 0.5       | 0.33                              |
| O1     | 4i   | 0.2926    | 0         | 0.2287    | 0.33                              |
| O2     | 8j   | 0.0507    | 0.2421    | 0.2617    | 0.33                              |
| O3     | 4i   | 0.8931    | 0         | 0.0994    | 0.33                              |
| O4     | 8j   | 0.1164    | 0.2362    | 0.0839    | 0.33                              |
| O5     | 8j   | 0.4036    | 0.2291    | 0.4040    | 0.33                              |
| O6     | 4i   | 0.6427    | 0         | 0.4240    | 0.33                              |

| Bond   | Length (\(\text{Å}\)) | Bond   | Length (\(\text{Å}\)) |
|--------|------------------------|--------|------------------------|
| Ir1-O1 | 2.049                  | Ir1-Ir2| 2.618                  |
| Ir1-O2 (\(\times 2\)) | 1.979                | Ir3-Ir4| 2.627                  |
| Ir1-O3 | 2.001                  | Ir1-O4 (\(\times 2\)) | 2.032            | Ir1-O1-Ir3 | 157.3 |
| <Ir1-O> | 2.01                       | Ir1-O2-Ir3| 164.0                  |
| Ir2-O3 (\(\times 2\)) | 2.038                  | Ir1-O3-Ir2| 80.8                  |
Table 6. Refined positional parameters and selected bond lengths (Å) and bond angles (°) for 9R BaIrO$_3$ from neutron diffraction [54]: space group C2/m (No. 12), a = 9.9592 Å, b = 5.7490 Å, c = 15.1707 Å, β = 103.27°, V = 848.81 Å$^3$, Z = 12.

5H BaIrO$_3$. The 5H phase was discovered as a new perovskite polytype [19]. As shown in Figure 9(b), its crystal structure contains chains of double dimer units that are corner-connected via oxygen atoms. These clusters of four octahedra are interleaved with single layers of vertex-sharing IrO$_6$ octahedra, forming infinite chains along the c axis. Adjacent chains are interlinked along the a and b directions via Ir–O–Ir vertex-sharing bridges. Alternatively, the structure can be described as stacking of layers of corner-sharing (C) and face-sharing (F) IrO$_6$ octahedra along the sequence FCCFC. The crystal structure was refined in the monoclinic C2/m (No. 12) space group, with three kinds of Ba atoms at 2c (0.5, 0.5, 0.5) and 4i sites, three types of Ir atoms at 2a (0, 0, 0) and 4i sites, and six unequivalent oxygen atoms at 8j (x, y, z), 4i, 2d (0.5, 0, 0.5), and 4f (0.75, 0.75, 0) positions. The lattice parameters at room temperature are determined as a = 9.9554 Å, b = 5.7434 Å, c = 13.8049 Å, and β = 119.23°. The final positional parameters and the selected bond lengths and bond angles after Reference [19] are listed in Table 7. As can be seen, Ir–O distances vary in the range 1.90 Å for Ir1–O4 to 2.23 Å for Ir2–O3. The average value, of 2.03 Å, is consistent with the ionic radii sum for Ir$^{4+}$ and O$^{2-}$. It is noteworthy that the structure contains three kinds of octahedra with rather distinct average sizes: <Ir–O> are 1.985 Å, 2.072 Å, and 2.017 Å for Ir1, Ir2, and Ir3 octahedra. The two largest octahedra, Ir2 and Ir3, are those forming dimers, where the Ir–O bonds are weakened by the Ir–Ir bonds. According to these bond distances, the bond valences for the three types of octahedra are 4.26(8)+, 3.35(8)+, and 4.06(9)+, indicating that Ir1 and Ir2 are under certain compressive and tensile stresses, respectively.

6H BaIrO$_3$. Same as the 6H SrIrO$_3$, the crystal structure of 6H BaIrO$_3$ consists of dimers of face-sharing octahedra separated by single corner-sharing octahedron, showing the sequence FCCFCC along the c axis. Based on the XRD data, we have refined its crystal structure in the monoclinic C2/c space group with two kinds of Ba atoms at 4e (0, y, ¼) and 8f (x, y, z) positions, Ir1 at 4a (0, 0, 0) and Ir2 at 8f sites, and four independent oxygen atoms, O1 at 4e, O2, O3, and O4 at 8f positions. The obtained unit-cell parameters are a = 5.7483 Å, b = 9.9390 Å, c = 14.3582
Å, and $\beta = 91.319^\circ$. The final positional parameters and selected bond lengths and bond angles after Reference [19] are listed in Table 8. As can be seen, the Ir$_2$O$_6$ octahedra within the face-sharing dimmers are considerably more expanded than the Ir$_1$O$_6$ octahedra, with average Ir–O distances of 2.16 and 1.99 Å, respectively. This is probably a consequence of the metal–metal bond linking the couples of Ir$_2$ atoms in the dimmers, with Ir$_2$–Ir$_2$ distances of 2.710 Å.

| Atom    | Site | $x$  | $y$  | $z$  | $B_{iso}$ (Å$^2$) |
|---------|------|------|------|------|------------------|
| Ba1     | 2c   | 0.5  | 0.5  | 0.5  | 1.2              |
| Ba2     | 4i   | -0.191 | 0   | 0.7139 | 0.1              |
| Ba3     | 4i   | -0.247 | 0   | 0.8886 | 0.9              |
| Ir1     | 2a   | 0    | 0    | 0    | 3.2              |
| Ir2     | 4i   | -0.4529 | 0   | 0.8215 | 1.0              |
| Ir3     | 4i   | -0.6046 | 0   | 0.5920 | 2.4              |
| O1      | 8j   | 0.053 | 0.72 | 0.7002 | 2.3              |
| O2      | 8j   | -0.0093 | -0.770 | 0.1085 | 1.2              |
| O3      | 4i   | 0.703 | 0    | 0.303 | 4.0              |
| O4      | 4i   | 0.217 | 0    | 0.0607 | 0.6              |
| O5      | 2d   | 0.5  | 0    | 0.5  | 1.5              |
| O6      | 4f   | 0.75 | 0.75 | 0.5  | 3.9              |

Ir1-O2 (×4) 2.029 Ir2-Ir3 2.735
Ir1-O4 (×2) 1.898
$<$Ir1-O$>$ 1.985 Ir2-O1-Ir3 84.0
Ir2-O1 (×2) 2.12 Ir1-O2-Ir2 165.1
Ir2-O2 (×2) 2.23 Ir2-O3-Ir3 79.1
Ir2-O3 2.038 Ir1-O4-Ir2 160.3
Ir2-O4 2.105 Ir3-O5-Ir3 180
$<$Ir2-O$>$ 2.072 Ir3-O6-Ir3 180
Ir3-O1 (×2) 2.004
Ir3-O3 2.11
Ir3-O5 1.994
$<$Ir3-O$>$ 2.017

Table 7. Refined positional parameters and selected bond lengths (Å) and bond angles (°) for 5H BaIrO$_3$ from neutron diffraction [19]: space group C2/m (No. 12), $a = 9.9554$ Å, $b = 3.7434$ Å, $c = 13.8049$ Å, $\beta = 119.231^\circ$, $V = 688.8$ Å$^3$, $Z = 10$.

3C BaIrO$_3$ A single-phase Pv BaIrO$_3$ was finally obtained at 25 GPa [21]. Instead of the simple cubic phase with space group $Pm-3m$, it was found that the XRD pattern of the Pv phase can
be refined excellently in the tetragonal \( I4/mcm \) (No. 140) space group with the Ba atom at \( 4b \) (0, \( \frac{1}{2} \), \( \frac{1}{4} \)), the Ir atom at \( 4c \) (0, 0, 0), and two kinds of O atoms at \( 4a \) (0, 0, \( \frac{1}{4} \)) and \( 8h \) (\( x \), \( x+\frac{1}{2} \), 0) sites. The obtained unit-cell parameters are \( a = b = 5.7044 \) Å and \( c = 8.0926 \) Å. The final positional parameters and the main bond distances and bond angles after Reference [21] are listed in Table 9. It should be noted that we denoted this phase as “3C” in order to follow the conventional notations.

| Atom | Site | \( x \) | \( y \) | \( z \) | \( B_{iso} (\text{Å}^2) \) |
|------|------|------|------|------|-----------------|
| Ba1  | 4e   | 0    | -0.0052 | \( \frac{1}{4} \) | 0.3             |
| Ba2  | 8f   | 0.0078 | 0.3349 | 0.0912 | 0.25           |
| Ir1  | 4a   | 0    | 0     | 0     | 0.4             |
| Ir2  | 8f   | 0.9936 | 0.3323 | 0.8442 | 0.27           |
| O1   | 4e   | 0    | 0.499 | \( \frac{1}{4} \) | -0.2           |
| O2   | 8f   | 0.2180 | 0.2390 | 0.2427 | -0.2           |
| O3   | 8f   | 0.036 | 0.846 | 0.0852 | -0.2           |
| O4   | 8f   | 0.286 | 0.087 | 0.049  | -0.2           |
| O5   | 8f   | 0.809 | 0.090 | 0.103  | -0.2           |
| Ir1-O3 (\( \times 2 \)) | 1.93 | Ir1-O3-Ir2 | 164.4 |
| Ir1-O4 (\( \times 2 \)) | 2.02 | Ir1-O4-Ir2 | 151.4 |
| Ir1-O5 (\( \times 2 \)) | 2.01 | Ir1-O5-Ir2 | 153.6 |
| \( <\text{Ir1-O} \rangle \) | 1.99 | | | |
| Ir2-O1 | 2.19 | Ir2-O1-Ir2 | 76.4 |
| Ir2-O2 | 2.22 | Ir2-O2-Ir2 | 75.1 |
| Ir2-O3 | 2.23 | | | |
| Ir2-O4 | 2.09 | | | |
| Ir2-O5 | 2.11 | | | |
| \( <\text{Ir2-O} \rangle \) | 2.16 | | | |
| Ir2-Ir2 | 2.710 | | | |

Table 8. Refined positional parameters and selected bond lengths (Å) and bond angles (°) for 6H \( \text{BaIrO}_3 \) from powder XRD [19]: space group \( C2/c \) (No. 15), \( a = 5.7483 \) Å, \( b = 9.9390 \) Å, \( c = 14.3582 \) Å, \( \beta = 91.319° \), \( V = 820.12 \text{ Å}^3 \), \( Z = 12 \).

The small tetragonal distortion of the 3C \( \text{BaIrO}_3 \) phase is unexpected; we should have a cubic phase as found for \( \text{BaRuO}_3 \) formed under high pressure. Such a distortion to tetragonal symmetry by cooperative rotations of the \( \text{IrO}_6 \) octahedra about the \( c \) axis is typical of an \( \text{A}^{2+} \text{B}^{4+} \text{O}_3 \) perovskite with a tolerance factor \( t = (\text{A} – \text{O}) / [\sqrt{2} (\text{B} – \text{O})] \) a little smaller than unity. However, stabilization of \( \text{BaIrO}_3 \) in the 9R polytype at ambient pressure is consistent with \( t > 1 \) obtained from tabulated equilibrium ionic radii. The larger compressibility of the \( \text{Ba–O} \) bond
makes it possible to stabilize the 3C phase of BaIrO$_3$ under 25 GPa pressure, but compression of the Ba–O bond by cubic symmetry should not reduce the tolerance factor below $t = 1$. Retention of the cubic symmetry of the IrO$_6$ octahedra shows that the threefold degeneracy of the 5d $\pi^*$ bands is not a factor. In fact, the tolerance factor calculated from the measured <Ba–O> and <Ir–O> bond lengths in Table 9 gives a $t = 0.998$ consistent with the tetragonal structure observed. Therefore, we conclude that at 25 GPa there has been a first-order transition of the Ba–O equilibrium bond length to give a $t < 1$, which indicates that the 5d $\pi^*$ bands of the IrO$_6$ array may also have transitioned for $J_{\text{eff}} = 1/2$ and 3/2 bands as a result of a reduction of the orbital angular momentum where the bandwidth is broadened. The high-pressure equilibrium (Ba–O) bond length is retained as a metastable bond length on removal of the pressure, and the Ir–O bonds are not under a tensile stress.

| Atom  | Site | $x$  | $y$  | $z$  | $B_{\text{iso}}$ (Å$^2$) |
|-------|------|------|------|------|--------------------------|
| Ba    | 4b   | 0    | 0.5  | 1/4  | 0.72                     |
| Ir    | 4c   | 0    | 0    | 0    | 0.49                     |
| O1    | 4a   | 0    | 0    | 1/4  | 0.8                      |
| O2    | 8h   | 0.2313 | 0.7313 | 0    | 0.8                      |

Table 9. Refined positional parameters and selected bond lengths (Å) and bond angles (°) for 3C BaIrO$_3$ from powder XRD [21]: space group $I4/mcm$ (No. 140), $a = b = 5.7044$ Å, $c = 8.0916$ Å, $V = 263.30$ Å$^3$, $Z = 4$.

**Polytype structures** The polytype structures of the ABO$_3$ oxides and the phase transformation under high pressure were established during the 1960–1970s, see the Review [57]. As a general trend, the number of the hexagonal close packing along the $c$ axis in a unit cell is reduced as the synthesis pressure increases, which led to a decrease (increase) of face(corner)-sharing octahedra. This is consistent with that fact that pressure stabilizes preferentially the denser phase. The observed crystallographic densities of the 9R, 5H, 6H and 3C phases of BaIrO$_3$ are 8.84, 9.08, 9.17, and 9.36 g/cm$^3$, respectively. They progressively increase as expected, since these phases have been stabilized at increasing pressures. This sequence corresponds, therefore, to more dense packing of the BaO$_2$ layers along the $c$ axis, showing an evolution to structures with more corner (C) sharing and fewer face (F) sharing octahedra, i.e. C:F ratios increase in the order 1:2 (9R), 3:2 (5H), 2:1 (6H), and $\infty$ (3C). As detailed below, the physical properties exhibit interesting evolution in response to these systematic structural variations.

### 4.3. Physical properties

**9R BaIrO$_3$** As mentioned above, 9R BaIrO$_3$ is the first known ferromagnet among the 5d TMOs [17]. Cao et al. [18] performed the first detailed experimental study on the single-crystal samples and uncovered a CDW formation accompanying the ferromagnetic order at $T_c \approx 180$
K. The experimental evidences in support of the CDW formation included [18]: (1) a sudden increase of resistivity at $T_c$, (2) the presence of non-linear conductivity with negative differential resistivity below $T_c$, (3) an optical gap formation at $\sim 1,200\ \text{cm}^{-1} \approx 9\kappa_B T_c$ in the electron excitation spectrum and a splitting of a phonon mode at $350\ \text{cm}^{-1}$ for $T < T_c$, and (4) the emergent X-ray satellite structure below $T_c$. Besides the transitions at $T_c = 180\ \text{K}$, two additional anomalies have also been observed [18] upon cooling on the c-axis resistivity $\rho_c$, which first changes to a metallic behaviour below $T_1 = 80\ \text{K}$ and then suddenly enters a Mott-like insulating state below $T_2 = 26\ \text{K}$, Figure 10. These two additional transitions are absent for the resistivity within the ab plane. The simultaneous occurrence of ferromagnetic order and CDW formation is quite unusual, and 9R BaIrO$_3$ has thus been the subject of extensive investigations since then. Later on, Nakano and Terasaki [51] carried out similar current-voltage (I-V) measurements on their single crystals by using a pulsed current in order to exclude the self-heating effects. Their observations of the giant nonlinear conduction only appearing below 30 K, well below $T_c \approx 180\ \text{K}$, questioned the above scenario of a simultaneous onset of a CDW and a ferromagnetic transition. Instead of the sliding motion of CDW, they proposed an interplay between two different bands is likely the origin of the nonlinear conduction observed in BaIrO$_3$ [51]. Such discrepancy might arise from the different sample quality. Nevertheless, a clear gap opening is unambiguously evidenced at $T_c$ by other experimental probes, such as the Seebeck coefficient [51, 58] and the high-resolution photoemission spectroscopy [59]. Currently, it remains elusive whether the gap opening is driven by the magnetic order or the Fermi surface nesting.

The observation of weak ferromagnetism and insulating ground state in the 9R BaIrO$_3$ has attracted renewed interest in recent years in light of the SOC-driven Mott insulating state for iridates. As for the nature of the weak ferromagnetism, there also exist long-standing discrepancies. Experimentally, a tiny Ir moment of $\sim 0.03\ \mu_B$/Ir was observed below $T_c$. In addition, a modified Curie-Weiss fitting to the inverse susceptibility also evidenced a small effective moment of $\sim 0.13\ \mu_B$ [18]. Originally, a spin canting from a localized full-moment antiferromagnetic configuration had been invoked to explain the tiny ordered moment [17]. In contrast, Cao et al. [18] proposed a model of band magnetism with intrinsically small Ir moment due to d–p hybridization and small exchange splitting. Indeed, the muon-spin relaxation measurements by Brooks et al. [60] provided direct experimental evidences in support of a small Ir moment, i.e. they observed clear oscillations below $T_c$ and found an extremely small internal field at the muon site. Such an itinerant picture of band magnetism, however, is incompatible with the observation of high coercive force and anisotropy in magnetization measurements. By employing the X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) techniques, Laguna-Marco et al. [52] recently elucidated an atomic-like nature of the Ir moment with the orbital moment being $\sim 1.5$ times larger than the spin moment, thus highlighting the importance of SOC in addressing the magnetic order of 9R BaIrO$_3$. After taking into account both SOC and moderate on-site coulomb interactions, first-principles calculations by Ju et al. [53] identified 9R BaIrO$_3$ as an exotic spin-orbit Mott insulator with multiple $J_{\text{eff}} = 1/2$ states associated with the unique face-sharing Ir$_3$O$_{12}$ octahedral units within the structure.

Although the atomic-like nature of Ir local moment in 9R BaIrO$_3$ was found to be extremely stable against temperature, pressure, and chemical substitutions [52, 61], these external stimuli
can easily lead to a breakdown of the weak ferromagnetism and nonmetallic ground state. For example, Cao et al. [62] grown a series of Sr-doped Ba\(_{1-x}\)Sr\(_x\)IrO\(_3\) single crystals and found that the chemical pressure applied via Sr doping drastically suppresses \(T_c\) and immediately leads to a non-metal to metal transition at high temperatures. On the other hand, although the application of external pressure of ~4.5 GPa can also quench the weak ferromagnetism as Sr doping, BaIrO\(_3\) becomes more insulating under pressure [61]. Such a disparate response of transport and magnetic properties to the chemical and physical pressure has been ascribed to the different compression rates of the lattice parameters \(a\) and \(c\) upon Sr doping and external pressure. Interestingly, Korneta et al. [63] found that a dilute rare-earth R\(^{3+}\) doping (~4%) of BaIrO\(_3\) can also suppress the weak ferromagnetism and lead to a metallic state, whereas the application of modest external pressure readily restores the insulating state. Further studies are needed to clarify whether the weak ferromagnetism is also recovered in the pressure-induced insulating state. All these above results demonstrate a delicate interplay between structural and electronic degrees of freedom in 9R BaIrO\(_3\).
5H BaIrO₃: The 5H phase is a weak ferromagnetic metal with $T_c \approx 50$ K, Figure 11. Cheng et al. [20] and Zhao et al. [56] have characterized this compound through measurements of magnetic susceptibility $\chi(T)$, resistivity $\rho(T)$, thermoelectric power $S(T)$, and specific heat $C(T)$. A weak ferromagnetic transition at $T_c \approx 50$ K was clearly observed in $\chi(T)$, and well reflected as a kink in the plots of $\rho$ vs $T$, $S/T$ vs $\ln T$, and $C/T$ vs $T$. In situ high-pressure resistivity measurements show that $T_c$ decreases gradually with pressure, and reaches about 40 K under 1.5 GPa.

6H BaIrO₃: The 6H phase has been independently identified and characterized by Zhao et al. [55] and Cheng et al. [20]. Similar with the 6H SrIrO₃, it is an exchange-enhanced paramagnetic metal with non-Fermi-liquid behaviours. Zhao et al. [55] reported that its resistivity $\rho(T)$ follows a linear $T$ dependence below 20 K, whereas a $T^{5/3}$ dependence was observed for $T < 60$ K by Cheng et al. [20]. Such a discrepancy should arise from the polycrystalline nature of the studied samples. As mentioned above, a non-Fermi-liquid $\rho \sim T^{5/2}$ behaviour has also been found in the 6H SrIrO₃ single crystals due to the proximity to a ferromagnetic quantum critical point. In order to verify similar situation taking place in 6H BaIrO₃, we measured the thermopower $S(T)$ that is insensitive to grain boundaries. We indeed found a linear relationship in the plot of $S/T$ versus $-\ln T$ over a wide temperature range, in strong support of the realization of ferromagnetic quantum critical point [20]. Based on the low-temperature specific heat and
magnetic susceptibility, the obtained Sommerfeld–Wilson ratio $R_w = \frac{\pi^2}{3} \left( \frac{k_B}{\mu_B} \right)^2 \frac{x_0}{\gamma} = 2.14(3)$ provides further evidence for strong electron-electron correlations.

$3C\, BaIrO_3$ is characterized as a Pauli paramagnetic metal with a Fermi-liquid behaviour [21]. Its resistivity $\rho(T)$ displays a metallic behaviour down to at least 1.8 K and follows the Fermi-liquid behaviour, i.e. $\rho(T) = \rho_0 + AT^2$ below 6 K with $\rho_0 = 0.0584(1)\, \Omega\, cm$ and $A = 8.1(1)\, \mu\Omega\, cm\, K^{-2}$, respectively. The magnetic susceptibility $\chi(T)$ exhibits a nearly temperature-independent Pauli paramagnetism with a shallow minimum around 85 K as observed around $T^* \approx 170\, K$ in $Pv\, SrIrO_3$. Such an upturn with temperature has been ascribed to the higher-order temperature-dependent term in the Pauli paramagnetism. Low-temperature specific heat $C(T)$ analysis yields an electronic specific-heat coefficient $\gamma = 6.84(6)\, mJ/mol\, K^2$ and a Debye temperature $\Theta_D = 335\, K$.

![Figure 12. A schematic phase diagram of the BaIrO$_3$ polytypes showing the evolution of magnetic transition temperature $T_c$ (left) and the electronic specific-heat coefficient $\gamma$ (right) as a function of the corner-to-face sharing octahedral C:F ratio. Adapted from Reference [21].](image-url)

**Figure 12.** A schematic phase diagram of the BaIrO$_3$ polytypes showing the evolution of magnetic transition temperature $T_c$ (left) and the electronic specific-heat coefficient $\gamma$ (right) as a function of the corner-to-face sharing octahedral C:F ratio. Adapted from Reference [21].

**Structure–property evolutions in the BaIrO$_3$ polytypes** As shown in Figure 9, the major change of the crystal structures for these polytypes can be described by the stacking sequence of IrO$_6$ octahedra that evolves from $9R(CFFCFFCFF) \rightarrow 5H(CFCFF) \rightarrow 6H(CFCFCFF) \rightarrow 3C(CCC)$, where C and F stands for corner- and face-sharing, respectively. Figure 11 displays the temperature dependence of magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$ for the BaIrO$_3$ polytypes, illustrating the evolution of the magnetic ground state. Figure 12 shows a schematic phase diagram of the BaIrO$_3$ polytypes. With increasing C:F ratio in the sequence $9R(1:2) \rightarrow 5H(3:2) \rightarrow 6H(2:1) \rightarrow 3C(\infty)$, the ground states of BaIrO$_3$ evolve from a ferromagnetic insulator with $T_c = 180\, K$ in the $9R$ phase to a ferromagnetic metal with $T_c = 50\, K$ in the $5H$ phase, then to an exchange-enhanced paramagnetic metal with non-Fermi-liquid behaviour near a
ferromagnetic quantum critical point in the 6H phase, and finally to a Fermi-liquid metal in the 3C phase. Such a structure–physical property evolution has been ascribed to a progressive bandwidth broadening in the sense that the corner-shared arrangement of IrO$_6$ octahedron can facilitate the Ir overlap integral mediated via O-2p orbitals. Since the electronic specific-heat coefficient $\gamma$ is proportional to the density of states at the Fermi energy, the gradual enhancement of $\gamma$ from 9R to 6H phase shown in Figure 12 is in agreement with the bandwidth argument. Both the 6H and 3C phases are metallic. Since the 6H phase is close to a ferromagnetic quantum critical point, the $\gamma$ is much enhanced due to critical fluctuations relative to that in the 3C phase with an even broader bandwidth. From this systematic study on BaIrO$_3$ polytypes, we can understand why the 6H SrIrO$_3$ is a non-Fermi-liquid metal near a ferromagnetic quantum critical point [11]. Moreover, the study on BaIrO$_3$ demonstrated that HPHT synthesis of structurally closely related perovskite polytypes represents an effective approach to fine tune the physical properties of interest via modifying the octahedral arrangement.

5. Conclusions

We have summarized in this chapter the current knowledge on the materials’ synthesis, crystal structure, and physical properties of the “113” alkaline-earth iridates AIrO$_3$ (A = Ca, Sr, Ba), which display a rich variety of crystallographic and electronic states that are of great current research interest. For CaIrO$_3$, it can form in either the layered pPv or the orthorhombic P\textsuperscript{\text{2}} structure, and thus serves as an important analogue of MgSiO$_3$ to investigate the P\textsuperscript{\text{2}}/pPv transformation in the Earth’s lowermost mantle in geosciences. Corresponding to different crystal structures, their electronic ground states differ sharply: the pPv phase is an antiferromagnetic Mott insulator with $T_N = 110$ K while the P\textsuperscript{\text{2}} phase is a paramagnetic semimetal with possible Dirac nodes protected by the lattice symmetry. The presence of strong structural distortion in pPv CaIrO$_3$ makes it a model system to investigate the interplay of non-cubic crystal field and SOC in iridates. On the other hand, metallization of the pPv phase via electron or hole doping represents an important approach to realize the exotic electronic states on the verge of insulator–metal transition. For SrIrO$_3$, it crystallizes in the 6H polytype at ambient pressure and transforms to the orthorhombic P\textsuperscript{\text{2}} structure under high-pressure conditions. The 6H phase is an exchange enhanced paramagnetic metal with non-Fermi-liquid behaviour due to the proximity of ferromagnetic quantum critical point, while the P\textsuperscript{\text{2}} phase is revealed as an exotic narrow-band semimetal with symmetry-protected Dirac nodes within the $J_{\text{eff}} = 1/2$ band near the Fermi level. The presence of nontrivial features in the low energy electronic states makes these “113” orthorhombic P\textsuperscript{\text{2}} iridates AlIrO$_3$ (A = Ca, Sr) promising candidates for realizing various topological and magnetic insulating phases via tuning the SOC, Hubbard interactions, and/or lattice symmetry. In this regard, epitaxial growth of superlattices and high-pressure synthesis of bulk materials with proper chemical design are currently important approaches to tailor the proposed quantum phases out of the semimetallic state. For BaIrO$_3$, it adopts a nine-layer 9R polytype at ambient pressure, and can be transformed to 5H, 6H, and 3C phases under different high pressure conditions. The 9R phase is a weak ferromagnetic insulator with $T_C = 180$ K, and can be regarded as an exotic SOC Mott insulator with multiple $J_{\text{eff}} = 1/2$ states associated with the unique Ir$_3$O$_{12}$ structural units. An atomic-like nature of the
Ir moment driven by strong SOC is rather stable against external perturbations, but the weak ferromagnetism can be easily suppressed by applying chemical and physical pressures or dilute rare-earth substitutions for Ba$^{2+}$. In contrast, the nonmetallic ground state displays distinct response to the chemical and physical pressure, highlighting the delicate interplay of crystal structure and electronic degrees of freedom for this quasi-1D compound. With increasing the ratio of corner-to-face sharing octahedra in the sequence 9R(1:2) → 5H(3:2) → 6H(2:1) → 3C(∞), the ground states of BaIrO$_3$ evolve from a ferromagnetic insulator with $T_c = 180$ K in the 9R phase to a ferromagnetic metal with $T_c = 50$ K in the 5H phase, then to an exchange-enhanced paramagnetic metal with non-Fermi-liquid behaviour near a ferromagnetic quantum critical point in the 6H phase, and finally to a Fermi-liquid metal in the 3C phase. Such a structure–physical property evolution demonstrated that HPHT synthesis of structurally closely related perovskite polytypes represents an effective approach to fine tune the physical properties of interest via modifying the octahedral arrangement.

Acknowledgements

We are grateful to J.-Z. Zhou, J. B. Goodenough, José Alonso, Y. Uwatoko, and M. Akaogi for collaborations on work related to this review. This work is supported by the National Basic Research Program of China (Grant No. 2014CB921500), the National Science Foundation of China (Grant Nos. 11304371, 51402019), and the strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB07020100).

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