Searching for a route to synthesize in situ epitaxial Pr$_2$Ir$_2$O$_7$ thin films with thermodynamic methods

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In situ growth of pyrochlore iridate thin films has been a long-standing challenge due to the low reactivity of Ir at low temperatures and the vaporization of volatile gas species such as IrO$_3$(g) and IrO$_2$(g) at high temperatures and high $P_{O_2}$. To address this challenge, we combine thermodynamic analysis of the Pr-Ir-O$_2$ system with experimental results from the conventional physical vapor deposition (PVD) technique of co-sputtering. Our results indicate that only high growth temperatures yield films with crystallinity sufficient for utilizing and tailoring the desired topological electronic properties and the in situ synthesis of Pr$_2$Ir$_2$O$_7$ thin films is frustrated by the inability to grow with $P_{O_2}$ on the order of 10 Torr at high temperatures, a limitation inherent to the PVD process. Thus, we suggest techniques capable of supplying high partial pressure of key species during deposition, in particular chemical vapor deposition (CVD), as a route to synthesis of Pr$_2$Ir$_2$O$_7$.

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INTRODUCTION

Complex 5d oxide systems, such as pyrochlore iridates ($RE_2$Ir$_2$O$_7$ with $RE =$ Rare Earth), have an unusual combination of magnetic and structural features that makes them ideal systems for the formation of non-trivial topological phases arising from geometric frustration combined with strong spin–orbit coupling. The spin–orbit-coupled Ir states in $RE_2$Ir$_2$O$_7$ dominate conduction as the iridium-oxygen network is much more covalent than the praseodymium-oxygen network$^{1-9}$. The high entanglement among crystal lattice, strong spin–orbital coupling, and electronic correlation makes the system enticing for thin-film engineering, but this requires high-quality films both in terms of crystallinity and stoichiometry. Synthesis of requisite films has long been impeded due to the volatility of Iridium-Oxygen compounds at high temperatures suitable for crystalline growth.

Attempts at in situ growth via physical vapor deposition (PVD) such as magnetron sputtering, pulsed laser deposition (PLD), and molecular beam epitaxy have failed to yield phase-pure epitaxial thin films, leaving most experimental studies limited to bulk systems. In situ synthesis via PVD techniques, such as PLD, shows that this difficulty comes from the low reactivity between Ir and RE oxides combined with the high volatility of the gas phase of Ir oxides such as IrO$_3$(g)$^{10,11}$. To overcome this difficulty, solid-phase epitaxy has been successfully used to synthesize $RE_2$Ir$_2$O$_7$ epitaxial thin films$^{10,12-19}$. This method circumvents the IrO$_3$(g) volatility dilemma through first depositing amorphous phase at conditions suitable for a stoichiometric balance of elements, then post-annealing at high temperatures in air to induce crystallization. The high temperatures necessary for ex situ crystallization inherently induce surface roughening$^{16}$ and intermixing between adjacent heterostructure layers$^{17}$, limiting the study of $RE_2$Ir$_2$O$_7$ based on heterostructure design. Advancing the study of electronic properties is thus contingent upon success of in situ synthesis to obtain simultaneous stoichiometric growth with near-perfect crystallinity.

The most common methods for synthesizing high-quality ceramic oxide films all employ PVD. PVD requires that the constituents of the film be physically moved from a source material to the substrate, upon which they deposit. The substrate temperature and chamber partial pressures are controlled to create thermodynamic conditions for the formation of gas species involved in film deposition when the source materials propagate towards the substrate surface. Governed by thermodynamic properties and growth conditions, the gas species near the substrate surface for deposition can be different from the species in the flux from the source materials$^{13}$, illustrated in Fig. 1a.

Although many materials have been synthesized successfully via the PVD methods, including some iridates with oxygen pressures close to the upper limit for PVD$^{18,19}$, we show that Pr$_2$Ir$_2$O$_7$ synthesis is thwarted due to the surprising stability of a similar Pr$_2$IrO$_7$ phase, as shown in Fig. 1b. Our experimental sampling of the thermodynamic space yielded only the Pr$_2$IrO$_7$ phase and other species of the constituents, but not Pr$_2$Ir$_2$O$_7$. Seeking to circumvent the formation of this pernicious Pr$_2$IrO$_7$ phase, we calculate the phase diagram for the Pr-Ir-O$_2$ ternary system using the Calculation of Phase Diagrams (CALPHAD) approach$^{20-22}$ for insight into the thermodynamics of Pr$_2$Ir$_2$O$_7$ synthesis. Our results indicate that the presence of volatile IrO$_3$(g) is vital to the formation of the desired Pr$_2$Ir$_2$O$_7$ phase and thus indicate that future attempts for in situ growth should be performed under high deposition pressure, utilizing high-pressure sputtering or chemical vapor deposition (CVD).

RESULTS

As the volatilization of the iridium-oxygen compounds, specifically IrO$_3$, is the prime suspect for Ir deficiency in the synthesis of Pr$_2$Ir$_2$O$_7$, we use computational thermodynamics to predict the vapor pressures of the Ir-O and Pr-O species at conditions relevant to PVD. There are nine relevant gas species in the Pr-Ir-O system based on the Scientific Group Thermodata Europe (SGTE) substance database (SSUBS)$^{23}$: Ir, IrO, IrO$_2$, IrO$_3$, O, O$_2$, O$_3$, PrO, and Pr. The results reveal that IrO$_3$(g) is the dominant gas species,
which has a partial pressure up to 1000 times greater than all other gas species in the system, except for molecular oxygen (O$_2$(g)). We then compute the isothermal phase diagram to elucidate how the relative proportion of supplied constituents from the source materials will impact the compounds that crystallize on the substrate. In the isothermal ternary phase diagram, we identify the Pr$_3$IrO$_7$ compound, which is Ir deficient relative to the desired Pr$_2$Ir$_2$O$_7$, yet structurally similar. As our primary growth control is via the selection of the gas partial pressures, and almost all iridium in the system oxidizes into IrO$_3$(g), we plot potential phase diagrams of partial pressures of gas species O$_2$(g) and IrO$_3$(g) for various stable compounds from the ternary phase diagram. The relationship between O$_2$(g), IrO$_3$(g), and the solid-phase compounds serves as a guide to changing growth conditions for Pr$_2$Ir$_2$O$_7$ synthesis. The computational calculations are confirmed by thin-film deposition using a range of conditions throughout the relevant thermodynamic windows. Overall, we find that Pr$_3$Ir$_2$O$_7$ can only form when both O$_2$(g) and IrO$_3$(g) partial pressures are high, indicating that IrO$_3$(g) appears to be the principal species by which hybridized Ir becomes incorporated into the film crystal. In particular, the IrO$_3$(g) partial pressure, the dynamic equilibrium value in the gas phase, must be at or above the equilibrium value at the substrate growth temperature, indicated in Fig. 2, and shown over a wider range in Supplementary Fig. 1. We note that the O : Ir ratio of 3.5 in Pr$_2$Ir$_2$O$_7$ is very close to the ratio in IrO$_3$(g), and that solid-phase Ir (s) forms in films deposited under conditions of high Ir and low-oxygen partial pressures. These results point to deposition techniques that can support high deposition pressure up to 9 Torr as promising routes toward successful in situ synthesis.

Vapor pressures of the binary systems IrO$_2$ and Pr$_2$O$_3$

As the final film composition is determined by the equilibrium between solid and vapor phases at the substrate temperature, we start by considering the partial pressure vs. temperature relationship for the binary Ir-O and Pr-O systems. As shown in Fig. 2, IrO$_3$(g) has the highest partial pressure by at least three orders of magnitude of the species, except Oxygen, throughout the range of temperatures considered. At our growth temperature of 1163 K, the partial pressure of IrO$_3$(g) is $2 \times 10^{-3}$ Torr. With O$_2$(g) in the growth chamber, regardless of the Ir flux type (Ir metal vapor or Ir-O binary compounds, or Ir precursor) provided from the source materials, the dominant Ir flux to the substrate surface is gaseous IrO$_3$(g). The partial pressure of IrO$_3$(g) depends on the equilibrium of species in gas phase such as O$_2$(g) and Ir(g), and is not an independent thermodynamic variable nor an independent experimental growth parameter. This high vapor pressure of IrO$_3$(g) explains the common Ir deficiency of thin films$^{24}$. 

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**Fig. 1** Schematic in situ co-sputtering thin-film deposition. In the actual experiment, Pr$_2$Ir$_2$O$_7$ and IrO$_2$ targets are simultaneously sputtered, (a). The details are included in Supplementary Fig. 2. The condensation of the vapor species is key to the thin-film synthesis, (b). By synthesizing epitaxial Pr$_2$Ir$_2$O$_7$ thin films, we can tailor the properties based on breaking the cubic symmetry. The strong spin–orbital coupling, originating from the Ir, opens paths toward a new generation of spintronics based on frustrated antiferromagnetic (AFM) conductors.

**Fig. 2** Partial pressures of gas species in the Ir-O$_2$ and the Pr-O$_2$ binary systems. In thermodynamic calculations, the ratios of the components of Ir : O$_2$ and Pr : O$_2$ were fixed at 1 : 1 and 2 : 1.5, to represent the compositions of IrO$_2$ and Pr$_2$O$_3$, respectively. The vertical dot-dashed black line indicates the growth temperature (1163 K) and the dot-dashed horizontal lines refer to the partial pressure of IrO$_3$(g), IrO$_2$(g), and Pr(g) gas species, respectively. More information is shown in Supplementary Fig. 1.
By comparison, the most volatile Pr-O species is Pr(g), followed by PrO(g), both of which have partial pressures more than 10^8 times lower than IrO_3(g) at our growth temperature. As such a low partial pressure is easily satisfied by the available O_2(g) and has minimal contribution to total pressure, the Pr-containing compounds condense on the substrate at a much higher rate than the Ir-containing compounds. Our attempt to compensate for this effect, adding a separate IrO_2(s) target as shown in Supplementary Fig. 2, proved insufficient on its own to synthesize in situ Pr_2Ir_2O_7.

Isothermal phase diagram of the Pr-Ir-O_2 system at 1163 K

Having determined the main factors controlling element proportions of gaseous species above the substrate, we utilize a ternary isothermal phase diagram to study which compounds form when different stoichiometries are present on the substrate. We base our calculations on the SSUBS database for the binary oxides and the formation energies of Pr_2IrO_5 (227) and Pr_3IrO_7 (317) from first-principles calculations, which were further refined by experimental partial pressure of oxygen. The calculated isothermal Pr-Ir-O_2 phase diagram at our deposition temperature of 1163 K and 760 Torr is plotted in Fig. 3 with the stoichiometric phases shown by points, and the two- and three-phase regions shown by lines and areas, respectively. Although the gas phase is dominated by O_2, many other species are present as shown in Fig. 2. We think of the gas phase as necessary to transport constituents to the substrate surface, making the presence of oxygen important in addition to the higher-pressure oxygen iridates. First, the calculations do not consider any stable phases along the Ir-Pr binary system axis, because this binary system has not yet been modeled by the CALPHAD method. Possible Ir-Pr phases are not critical for the present work due to the current interest in oxides with much higher stability than the compounds between Ir and Pr under experimental conditions. It can be seen in Fig. 3 that, in addition to the desired Pr_2IrO_5 phase, Pr_3IrO_7 becomes stable at lower Ir concentrations. As a result, we expect that iridium deficiency will lead to some amount of Pr_3IrO_7 in our films. The Pr_2IrO_5 (227) and Pr_3IrO_7 (317) phases are in equilibrium with the gas phase, forming a three-phase invariant equilibrium region of “317 + 227 + gas.” Figure 3 also shows that Pr_2IrO_5(s) is in equilibrium with the solid Ir(s) and oxides IrO_3(s), whereas Pr_3IrO_7(s) is additionally in equilibrium with Pr_3IrO_7(s). These results indicate that Ir(s) and oxides IrO_3(s), Pr_3IrO_7(s), and Pr_2IrO_5(s) are possible secondary phases during the synthesis of Pr_2IrO_5(s).

Potential phase diagram of the Pr-Ir-O_2 system at 1163 K

Figure 4 illustrates the calculated isothermal Gibbs-potential-derived phase diagram of the Pr-Ir-O_2 system at 1163 K and 760 Torr as a function of the partial pressures of O_2(g) and IrO_3(g)—the two dominant gas species (Fig. 2). The phase diagram shows the species, which minimize the Gibbs thermodynamic potential at each condition. In this potential phase diagram, the cross-points indicate three-phase invariant equilibria, the lines show the two-phase equilibria, and the areas are the single-phase regions. It is understood that when the partial pressure of O_2(g) equals to the total pressure of 760 Torr, the region is a single gas phase. When analyzing the potential phase diagram for growth considerations, we consider the plotted partial pressures as representative of the conditions immediately above the substrate during growth.
The most striking aspect of the potential phase diagram is that the compounds with more Ir become stable with lower $P_{O_2}$ for a given $P_{IrO_3}$, even ones with lower oxygen-to-cation ratios. Although this is apparent for pure-phase Ir(s), it is less so for the sequence of IrO$_2$ to Pr$_2$IrO$_2$ to Pr$_7$IrO$_2$ at high $P_{IrO_3}$ with increasing $P_{O_2}$. We attribute this trend to the volatilization of Ir in the presence of O$_2$(g) as a higher $P_{O_2}$ requires a lower $P_{Ir}$ to maintain the same $P_{IrO_3}$, stabilizing the phases with lower Ir concentration. At low $P_{IrO_3}$, $P_{O_2}$ increases with the amount of oxygen towards Pr$_7$O$_2$(s). Furthermore, pure Ir(s) corresponds to exceedingly large $P_{IrO_3}$ partial pressure at any $P_{O_2}$ within the total pressure constraint. These phase relationships highlight the delicate balance of needing enough oxygen for Ir(s) to hybridize into the film crystal but not too much that it forms a high vapor pressure in equilibrium with the desired phase. Furthermore, as $P_{IrO_3}$ decreases at the same $P_{O_2}$ value, the proportion of Pr present in the solid increases, as seen in the “227” stability adjacent to the IrO$_2$ region, which has the same Ir oxidation state. When the O$_2$(g) partial pressure reaches the total pressure of 760 Torr, only the gas phase, dominated by $O_2$, is stable, as everything oxidizes to volatile compounds.

Experimentally, we grew thin films via PVD co-sputtering and compared the stabilized phases to the potential phase diagram. We determined which phases we stabilized using X-ray diffraction, compared the stabilized phases to the potential phase diagram. In the calculated phase diagrams, the points represent three-phase equilibria, the lines two-phase equilibria, and the areas one-phase equilibria. The dashed red arrows indicate the minimum requirement of $IrO_3$ and $O_2$ partial pressures for the 227 phase.

Effect of the growth temperature on the phase relationships

We sought to enlarge the Pr$_2$IrO$_2$ stabilization window by changing the temperature, as in accordance with Fig. 2, a lower temperature allows for much lower IrO$_3$ partial pressure. The previously discussed growth temperature of 1163 K was chosen to optimize the kinetic aspects of film growth to ensure single-crystalline films for heterostructure engineering. Thermodynamic calculations, however, indicate that lower growth temperatures could reduce the impact of the requirements for high Ir-component pressures. In addition, thermostability experiments, shown in Supplementary Fig. 4, show Pr$_2$IrO$_2$ is more stable at 1273 K than at 1373 K. The vapor pressure calculations in Fig. 2 indicate that the equilibrium partial pressure of IrO$_3$ drops off by orders of magnitude if the growth temperature is lowered to 1000 K. Figure 5 illustrates the effects of the temperature on the phase relationships in the Pr-Ir-O$_2$ system. Calculations at 1000 K indicate that the Pr$_2$IrO$_2$ phase forms with $P_{IrO_3}$ as low as $9 \times 10^{-7}$ Torr, which is almost 1000 times lower than that at 1163 K, and that the minimum $P_{O_2}$ value decreased by 70 times from 9.2 Torr at 1163 K to 0.13 Torr at 1000 K. The same relationship between $P_{IrO_3}$ and $P_{O_2}$ to maintain Pr$_2$IrO$_2$ phase stability occurs at 1000 K; notably, the interplay of increasing $P_{IrO_3}$ coinciding with increasing $P_{O_2}$. These results also indicate that phase stability at fixed partial pressures is very sensitive to temperature, resulting in a narrow growth window for Pr$_2$IrO$_2$.

Unfortunately, our experimental films grown below 1073 K showed poor crystallinity, negating the benefits of the Pr$_2$IrO$_2$ phase for heterostructuring applications that demand high-quality films, forcing us to pursue high-pressure in situ growth such as CVD in the future.

**DISCUSSION**

In summary, we utilized the CALPHAD modeling technique to explore thermodynamic properties of the Pr-Ir-O$_2$ system and find that Pr$_2$IrO$_2$ can only form high-quality crystals above 1073 K and under oxygen partial pressures much higher ($P_{O_2} > 9$ Torr). These conditions cannot be achieved with conventional PVD methods and provide insights into why PVD is an inadequate synthesis pathway. However, these conditions can be accessed in CVD growth. Our study, therefore, suggests exploring CVD growth for high-quality Pr$_2$IrO$_2$ films.

**METHODS**

**Details of thermodynamic calculations**

Thermodynamic calculations of the Pr-Ir-O$_2$ system were performed by the Thermo-Calc software in terms of the SSUB5 database. Structural space groups from the Materials project, used for phonon calculations, are shown.

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Fig. 5 Calculated potential phase diagrams of the Pr-IrO$_3$-O$_2$ system at 1000, 1100, and 1163 K. In the calculated phase diagrams, the points represent three-phase equilibria, the lines two-phase equilibria, and the areas one-phase equilibria. The dashed red arrows indicate the minimum requirement of $IrO_3$ and $O_2$ partial pressures for the 227 phase.
in Supplementary Table 1. The thermodynamic properties of ternary compounds of interest, i.e., \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) and \( \text{Pr}_3\text{Ir}_3\text{O}_7 \), absent in the SSUBS database, can be estimated with respect to binary oxides as follows:

\[
\begin{align*}
\text{Pr}_2\text{O}_3 + 2 \text{Ir}_2\text{O}_3 & = 2 \text{Pr}_2\text{Ir}_2\text{O}_7 \\
\text{Pr}_2\text{O}_3 + \text{Pr}_2\text{O}_3 + 2 \text{Ir}_2\text{O}_3 & = 3 \text{Pr}_3\text{Ir}_3\text{O}_7
\end{align*}
\]

(1)

In the present work, the reaction entropies for Eqs. (1) and (2) are assumed to be zero, because there is no net change of gas species involved. The controllability of these parameters guarantees a direct comparison of the conditions between experiments and thermodynamic predictions. The thermodynamic calculations thus work well in most cases. Thermo-chemical source materials: a comprehensive thermodynamic analysis. 

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AUTHOR CONTRIBUTIONS

L.G. and C.B.E. conceived the project. C.B.E., M.S.R., and P.G.E. supervised experimental work and Z.K.L. supervised thermodynamic calculations. L.G. performed the films growth and structural characterizations. S.L.S. performed thermodynamic calculations. L.G., N.G.C., and S.L.S. wrote the manuscript. C.B.E. directed the research.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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