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Junyi Yang, Lin Hao, Peyton Nanney, Kyle Noordhoek, Derek Meyers, Lukas Horak, Joshua Sanchez, Jiu-Haw Chu, Christie Nelson, Mark. P. M. Dean, and Jian Liu

AFFILIATIONS
1Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA
2Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York 11973 USA
3Department of Condensed Matter Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czech Republic
4Department of Physics, University of Washington, Seattle, Washington 98105, USA
5National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, USA

Authors to whom correspondence should be addressed: jyang43@vols.utk.edu; lhao3@utk.edu; and jianliu@utk.edu

ABSTRACT

Ruddlesden-Popper type Sr$_{n+1}$Ir$_n$O$_{3n+1}$ compounds are a major focus of condensed matter physics, where the subtle balance between electron-electron correlation, spin–orbit interaction, and crystal field effect brings a host of emergent phenomena. While it is understandable that a canted antiferromagnetic insulating state with an easy-plane anisotropy is developed in Sr$_2$IrO$_4$ as the two-dimensional limit of the series, it is intriguing that bilayer Sr$_3$Ir$_2$O$_7$, with slightly higher effective dimensionality, stabilizes c-axis collinear antiferromagnetism. This also renders Sr$_3$Ir$_2$O$_7$ a unique playground to study exotic physics near a critical spin transition point. However, the epitaxial growth of Sr$_3$Ir$_2$O$_7$ is still a challenging task because of the narrow growth window. In our research, we have studied the thermodynamic process during the synthesis of Sr$_3$Ir$_2$O$_7$ thin films. We expanded the synthesis window by mapping out the relationship between the thin film crystal structure and the gas pressure. Our work thus provides a more accessible avenue to stabilize metastable materials.

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Layered compounds of Ruddlesden-Popper (RP) oxides $A_{n+1}B_nO_{3n+1}$ are a fertile playground to study and engineer the interplay of electronic and magnetic properties with crystal lattice dimensionality. The crystal structure of the RP series can be viewed as $n$ consecutive $ABO_3$ perovskite layers sandwiched by rock-salt $AO$ layers along the $c$-axis. When $n$ varies from 1 to infinity, the lattice undergoes an evolution from the quasi-two-dimensional (2D) limit to the threedimensional (3D) limit, leading to a dimensional crossover of electronic and magnetic interactions. For example, the 2D limit of the iridate RP family, Sr$_2$IrO$_4$ [Fig. 1(a)], represents a spin–orbit coupled Mott insulator. The subtle balance between spin–orbit coupling, onsite Coulomb repulsion, and crystal field effect leads to a pseudospin $S = 1/2$ moment on each Ir site that orders antiferromagnetically within the 2D perovskite layer with an easy ab-plane anisotropy and spin canting. The magnetic structure is extremely sensitive to the dimensionality, as a slight increase in $n$ to 2 stabilizes the $c$-axis collinear antiferromagnetic (AFM) insulating state in Sr$_2$IrO$_4$ [Fig. 1(a)], rendering a dimensionality-controlled spin flop transition. When further moving toward the 3D limit, the insulating ground state melts into a topological semimetallic state in paramagnetic SrIrO$_3$ [Fig. 1(a)].

To study and control the emergent phenomena within the dimensional crossover, epitaxial growth of the RP series is a particularly appealing route due to additional tunability of the lattice structure, such as imposing epitaxial strain. However, while epitaxial thin films of Sr$_3$Ir$_2$O$_7$ and SrIrO$_3$ can be readily obtained and have been characterized by many techniques, epitaxial growth of Sr$_3$Ir$_2$O$_7$ is much more challenging. It was reported that by using a single SrIrO$_3$ target, the Sr$_3$Ir$_2$O$_7$ phase can be obtained through careful control of the oxygen pressure and the temperature within a small region of the parameter space. The low thermodynamic stability and the narrow growth window of the Sr$_3$Ir$_2$O$_7$ phase were later confirmed by using a target of the Sr$_2$IrO$_4$ phase.

In this work, we performed a systematic investigation of the thermodynamic stability of the iridate RP series in relation to the growth atmosphere. By using a target of the Sr$_2$IrO$_4$ phase, we were able to obtain high-quality thin films of single phase Sr$_3$Ir$_2$O$_7$, Sr$_2$IrO$_4$, and SrIrO$_3$ by varying the pure oxygen pressure. Magnetometry and magnetic resonant scattering experiments demonstrate that the obtained Sr$_3$Ir$_2$O$_7$ film retains the same antiferromagnetic ground state as the single crystal counterpart. The obtained growth window of the
Sr$_3$Ir$_2$O$_7$ phase in a pure oxygen atmosphere is narrow and similar to the previous reports on SrIrO$_3$ and Sr$_3$Ir$_2$O$_7$ targets. By introducing argon into the growth atmosphere, we found a significant expansion of the growth window as a function of oxygen partial pressure.

Sr$_{n+1}$Ir$_x$O$_{3n+1}$ thin films with thickness around 100 nm were deposited on SrTiO$_3$ (001) (STO, $a_{pc} = 3.905$ Å) single crystal substrates by using a pulsed laser deposition system (KrF excimer laser). During deposition, the laser fluence was kept at 3 J/cm$^2$. The growth pressure was chosen to be 850 mTorr. By introducing argon into the growth atmosphere, we found a significant expansion of the growth window as a function of oxygen partial pressure.

Sr$_{3}$Ir$_2$O$_7$ thin films were grown in a pure oxygen atmosphere but with different pressures. At the lowest pressure value used in this study (1 mTorr), only a set of (0 0 L) Bragg reflections that corresponds to the Sr$_3$IrO$_4$ phase can be seen. This observation indicates the epitaxial growth of Sr$_3$IrO$_4$ on the SrTiO$_3$ substrate along the [001] direction without observable impurity phases. The single Sr$_3$IrO$_4$ phase is also observed at 10 mTorr and 20 mTorr, which is consistent with previous reports. At 80 mTorr and 100 mTorr, a different phase appears with all the film peaks that can be indexed as the (0 0 L) Bragg reflections of the Sr$_3$Ir$_2$O$_7$ phase. A further increase of the growth pressure to 120 mTorr suppresses the Sr$_3$Ir$_2$O$_7$ phase and leaves only a set of film peaks near the substrate (0 0 L) peaks, characteristic of a single SrIrO$_3$ perovskite phase. These results indicate that not only the $n = 1$ and $n = \infty$ structures of the RP series can be epitaxially grown by using a Sr$_3$IrO$_4$ target, the $n = 2$ structure can also be stabilized by carefully varying the atmosphere pressure.

To further elucidate on this point, we performed detailed physical property measurements. Figure 2(a) displays the temperature dependent resistivity of the Sr$_3$Ir$_2$O$_7$ and Sr$_3$IrO$_3$ films. The monotonic increase in resistivity with decreasing temperature reveals the insulating state of both thin films. The Sr$_3$IrO$_3$ film is evidently less insulating than the Sr$_3$Ir$_2$O$_7$ film considering the smaller room-temperature resistivity and the relatively weaker insulating temperature dependence, consistent with the reports on the bulk counterparts. The observation indicates that the dimensionality evolution of the electronic ground state of the iridate RP phases was preserved in thin films. A resistivity anomaly was also observed for the Sr$_3$Ir$_2$O$_7$ thin film at $T \sim 250$ K. From the relationship between $d(\ln\rho)/d(1/T)$ and $T$ [inset of Fig. 2(a)], a $b$-like cusp can be clearly seen, suggesting a...
significant change in the electronic properties. Figure 2(b) shows the film magnetization as a function of temperature measured under an in-plane magnetic field. The Sr$_2$IrO$_4$ film displays a weak but nonzero magnetization when temperature cools below 210 K. Note that the net magnetization of Sr$_2$IrO$_4$ is due to spin-canting of the antiferromagnetically coupled $I_{Ir}=1/2$ moments. The magnetic measurement thus implies an antiferromagnetic transition of the Sr$_2$IrO$_4$ film with the Neel transition temperature $T_N=210$ K. In contrast, there is no comparable jump in magnetization in the Sr$_3$Ir$_2$O$_7$ film even down to the base temperature of 10 K.

While the absence of net magnetization along with the resistivity kink observed in the thin film is compatible with a collinear antiferromagnetic configuration as reported for Sr$_3$Ir$_2$O$_7$ single crystals, direct verification of the antiferromagnetic ordering is usually highly challenging for thin film samples. To this end, we exploited x-ray magnetic resonant scattering, which has been proven to be a powerful probe of the magnetic structure of iridates due to element selectivity and resonant enhancement. By tuning the x-ray photon energy to the Ir $L_3$-edge, we performed magnetic resonant scattering measurements on the Sr$_3$Ir$_2$O$_7$ film at 10 K. The ($-0.5$ 0.5 24) AFM Bragg peak was clearly identified by the $L$-scan, as shown in Fig. 2(c), directly demonstrating that the Ir moments are antiferromagnetically ordered within each IrO$_2$ plane. Figure 2(d) shows the energy profile at the representative magnetic reflection across the Ir $L_3$-edge. A clear resonant effect can be seen, at energies slightly lower than the Ir $L_3$ white line similar to other iridium compounds, confirming the dominant role of Ir ions in developing the long-range magnetic ordering. This observation agrees well with the G-type AFM structure as reported in Sr$_3$Ir$_2$O$_7$ single crystals, along with the structural analysis, we conclude that the as-obtained film under intermediate pressure indeed has a single Sr$_3$Ir$_2$O$_7$ phase.

The growth evolution of the RP phases as a function of oxygen atmosphere pressure is summarized in the left panel of Fig. 3(a). As the oxygen pressure increases from 1 mTorr to 100 mTorr, the obtained thin film evolves from a single Sr$_3$Ir$_2$O$_7$ phase to a single Sr$_2$IrO$_4$ phase. Between these two single phases, there is an intermediate region where a mixed phase is observed. The growth window of the pure Sr$_3$Ir$_2$O$_7$ phase is relatively narrow and spans a range of ~20 mTorr only. It is important to note that this growth window, the changes in the thermodynamic phase stability are strongly influenced by the oxygen partial pressure range of interest, from 10 to 80 mTorr. The right panel shows the results obtained under an argon-mixed oxygen atmosphere. The black, red, and blue regions denote, respectively, where a single phase of Sr$_3$Ir$_2$O$_7$, Sr$_2$IrO$_4$, and SrIrO$_3$ is observed. The Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ phases-mixed region is drawn as pink. Batwing markers label synthesized thin films. X-Ray diffraction $0$ $2\theta$ plots of thin film samples synthesized under $P_O=80$ mTorr (b), 50 mTorr (c), 20 mTorr (d), and 10 mTorr (e) in pure oxygen and argon-mixed oxygen atmospheres. Plots of samples grown in a mixed atmosphere are vertically shifted for clarity.

![FIG. 3. (a) Growth phase diagram of Sr$_{n\pm1}$Ir$_{3n\pm1}$O$_{3n\pm1}$ thin films. The left panel summarizes the results obtained under a pure oxygen atmosphere and the dashed rectangle highlights the oxygen partial pressure range of interest, from 10 to 80 mTorr. The right panel shows the results obtained under an argon-mixed oxygen atmosphere. The black, red, and blue regions denote, respectively, where a single phase of Sr$_3$Ir$_2$O$_7$, Sr$_2$IrO$_4$, and SrIrO$_3$ is observed. The Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ phases-mixed region is drawn as pink. Batwing markers label synthesized thin films. X-Ray diffraction $0$ $2\theta$ plots of thin film samples synthesized under $P_O=80$ mTorr (b), 50 mTorr (c), 20 mTorr (d), and 10 mTorr (e) in pure oxygen and argon-mixed oxygen atmospheres. Plots of samples grown in a mixed atmosphere are vertically shifted for clarity.](Image 322x535 to 552x709)

A mixed atmosphere is sketched in the right panel of Fig. 3(a). As compared to that obtained in a pure oxygen atmosphere, it is clear that the growth window of the Sr$_3$Ir$_2$O$_7$ phase has been greatly expanded after the introduction of argon.

From the chemical formula $A_{n\pm1}$Ir$_{B3n\pm1}$O$_{3n\pm1}$ of the RP oxides, it can be seen that the $B/A$ cation ratio increases from 0.5 for $n=1$ to 1 for $n=\infty$. The Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ phases can be considered as variants of SrIrO$_3$ with different degrees of Ir-deficiency. It is indeed possible for SrIrO$_3$ to decompose into various RP members with the by-product of Ir and O$_2$, or vice versa. As shown by previous studies, such controllability of the thermodynamic stability of the three RP phases can be achieved during the growth by varying the ambient pressure of pure oxygen, which is also observed in our study. On the other hand, the background pressure of pulsed laser deposition is also known to strongly influence the plasma plume dynamics, including the ratio and the energetics of different ions. This effect may also have significant impact on the growth kinetics, such as the sticking coefficients of different ions and species, especially when the pressure is tuned by more than two orders of magnitude. Such an impact is confirmed by the observed expansion of the growth window of the Sr$_3$Ir$_2$O$_7$ phase when the overall pressure is maintained by introducing argon. In other words, when reducing the pressure under a pure oxygen atmosphere, the changes in the thermodynamic phase stability and the plume dynamics both favor the conversion from Ir-rich to Ir-deficient phases. This combination results in a sharp evolution between the two end members, the Sr$_2$IrO$_4$ and SrIrO$_3$ phases with a narrow window of the Sr$_3$Ir$_2$O$_7$ phase in-between. Indeed, previous studies and ours all found a remarkably similar phase dependence on...
the oxygen pressure from the level of 1 mTorr to 100 mTorr regardless of the target stoichiometry. Such a phase evolution is significantly slowed down when the plume dynamics is stabilized by introducing argon to maintain the total pressure, extending the growth window of the Sr$_3$Ir$_2$O$_7$ phase.

In conclusion, we systematically investigated the effect of growth atmosphere on the epitaxial growth of Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series. The magnetic scattering measurements in combination with structural analysis and physical property measurements enable us to draw the growth phase diagram as a function of oxygen pressure, upon which the narrow growth window of the Sr$_3$Ir$_2$O$_7$ phase is highlighted. We demonstrated that this growth window can be greatly expanded by introducing argon into the growth chamber. Although it is well known that pure oxygen is widely used during the oxide synthesis process, the present study affords an efficient route to synthesize a metastable phase during epitaxial growth.

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REFERENCES

1) G. Rau, E. K. H. Lee, and H. Y. Kee, Annu. Rev. Condens. Matter Phys. 7, 195 (2016).
2) G. Cao and P. Schlottmann, Rep. Prog. Phys. 81, 042502 (2018).
3) S. J. Moon, H. Jin, K. W. Kim, W. S. Choi, Y. S. Lee, J. Yu, G. Cao, A. Sumi, H. Funakubo, C. Bernhardt, and T. W. Noh, Phys. Rev. Lett. 101, 226402 (2008).
4) Q. Wang, Y. Cao, J. A. Waugh, S. R. Park, T. F. Qi, O. B. Korneta, G. Cao, and D. S. Dessau, Phys. Rev. B 87, 245109 (2013).
5) L. Pallecchi, M. T. Ruscaglia, V. Buscaglia, E. Gillioli, G. Lamura, F. Telesio, M. R. Cimberle, and D. Marre, J. Phys.: Condens. Matter 28, 065601 (2016).
6) G. Cao, I. Bolivar, S. McCall, J. E. Crow, and R. P. Guertin, Phys. Rev. B 57, R11039(R) (1998).
7) S. Chikara, O. Korneta, W. P. Crummett, L. E. DeLong, P. Schlottmann, and G. Cao, Phys. Rev. B 80, 10407(R) (2009).
8) S. Fujiioka, H. Ohsumi, T. Komese, J. Matsujo, B. J. Kim, M. Takata, T. Arima, and H. Takagi, Phys. Rev. Lett. 105, 246405 (2010).
9) S. J. Moon, H. Jin, W. S. Choi, J. S. Lee, S. S. A. Seo, J. Yu, G. Cao, T. W. Noh, and Y. S. Lee, Phys. Rev. B 86, 195110 (2009).
10) G. Cao, V. Durairaj, S. Chikara, L. E. DeLong, S. Parkin, and P. Schlottmann, Phys. Rev. B 76, 100402(R) (2007).
11) Y. F. Nie, P. D. C. King, C. H. Kim, M. Uchida, H. I. Wei, B. D. Faeth, J. P. Ruf, L. Xie, X. Pan, C. J. Fennie, D. G. Schlom, and K. M. Shen, Phys. Rev. Lett. 114, 016401 (2015).
S. Boseggia, R. Springell, H. C. Walker, A. T. Boothroyd, D. Prabhakaran, D. Wermeille, L. Bouchenoire, S. P. Collins, and D. F. McMorrow, Phys. Rev. B 85, 184432 (2012).

C. Dhital, S. Khadka, Z. Yamani, C. de la Cruz, T. C. Hogan, S. M. Disseler, M. Pokharel, K. C. Lukas, W. Tian, C. P. Opeil, Z. Wang, and S. Wilson, Phys. Rev. B 86, 100401(R) (2012).

R. Eason, Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Function Materials (John Wiley & Sons, Inc, HoboKen, New Jersey, 2007).

J. C. Miller and R. F. Haglund, Jr., Experimental Methods in the Physical Sciences, Volume 30, Laser Ablation and Deposition (Academic Press, San Diego, 1998).