Certain pyrochlore oxides are among the best oxygen catalysts in alkaline media. Hence, exploring epitaxial films of these materials is of great fundamental and technological interest. Unfortunately, direct film growth of one of the most promising pyrochlores, Bi$_2$Pt$_2$O$_7$ [10] has not yet been achieved, owing to the difficulty of oxidizing platinum metal in the precursor material to Pt$^{4+}$. In this work, in order to induce oxidation of the platinum, we annealed pulsed laser deposited films consisting of epitaxial δ–Bi$_2$O$_3$ and co–deposited, comparatively disordered platinum. We present synchrotron x–ray diffraction results that show the annealed films are the first epitaxial crystals of Bi$_2$Pt$_2$O$_7$. We also visualized the pyrochlore structure by scanning transmission electron microscopy, and observed ordered cation vacancies in a bismuth–rich film but not in a platinum–rich film. The similarity between the δ–Bi$_2$O$_3$ and Bi$_2$Pt$_2$O$_7$ structures appears to facilitate the pyrochlore formation. These results constitute a new approach for synthesis of novel pyrochlore thin film oxygen catalysts.

Pyrochlore oxides, A$_2$B$_2$O$_7$ [3] that exhibit catalytic activity are prospective cathode materials for fuel cells. Furthermore, the oxygen ion conductivity of some pyrochlores is comparable to that of oxides with fluorite structure, such as yttria–stabilized zirconia. In this regard, one of the most promising pyrochlores for catalytic applications is bismuth platinum oxide, Bi$_2$Pt$_2$O$_7$. Previous work on powders of Bi$_2$Pt$_2$O$_7$ found its electrochemical activity essentially identical to pure Pt [10]. Furthermore, compared to bulk powders, enhanced catalytic activity has been observed in epitaxially grown perovskite oxides and structural derivatives [3, 14]. These results have contributed to growing interest in epitaxial films of pyrochlore oxides as an oxygen catalyst. However, while nanocrystalline powders of Bi$_2$Pt$_2$O$_7$ by thermal oxidation of Bi–Pt nanoparticles have been reported[13] epitaxial crystals of Bi$_2$Pt$_2$O$_7$ have not yet been achieved.

Here we report the first, successful formation of epitaxial Bi$_2$Pt$_2$O$_7$ (111) on YSZ(111) single–crystal substrates. Our synthesis strategy consists of a deposition step followed by a post-growth anneal. During growth, epitaxial Bi$_2$O$_3$ is formed in its cubic δ phase, while co-deposited platinum forms an as-yet undetermined state, exhibiting only minute amounts of metallic platinum in specular x–ray diffraction (XRD). Annealing in air transforms the δ–Bi$_2$O$_3$ into epitaxial crystals of Bi$_2$Pt$_2$O$_7$ pyrochlore.

Fig.1 displays the side (a), and top (b, c) views of the structural model of Bi$_2$Pt$_2$O$_7$ (111)/YSZ(111). a, View along [101]. The pyrochlore structure consists of corner–linked PtO$_6$ distorted octahedra (the oxygen atoms at their vertices are omitted for clarity) with the Bi atoms filling the interstices. YSZ(111), modeled with a fluorite lattice, is composed of oxygen–metal–oxygen triple layers. b, Kagome arrangements of Bi atoms (Bi, dark yellow; Pt, blue) alternate with kagome patterns of Pt atoms (Bi, purple; Pt, gray) along [111]. (Bi–Bi or Pt–Pt bonds are guides to the eye). c, YSZ(111) surface is oxygen terminated (predicted as the most stable one) [14]. The topmost oxygen ions form an hexagonal array.

Deposition growth of Bi$_2$Pt$_2$O$_7$ pyrochlore

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grown pattern reveals intense peaks that can be assigned to (111), (222) and (333) (not shown) cubic \( \delta \)-Bi\(_2\)O\(_3\). Distinct thickness fringes are observed surrounding the (111) Bragg peak of \( \delta \)-Bi\(_2\)O\(_3\) in the as-grown films (Supplementary Information, Fig. S1) which give evidence of a smooth film surface. Rocking curve measurements for the (111)\( \delta \)-Bi\(_2\)O\(_3\) peak (Supplementary Information, Fig. S2) show a FWHM of \(0.100\pm0.001^\circ\) in omega (rocking curve on YSZ substrates has a nominal FWHM of \(0.014^\circ\) in omega). The measured out-of-plane lattice parameter for \( \delta \)-Bi\(_2\)O\(_3\) is \(5.519\ \text{Å}\), in good agreement with previous reported values\(^{15,19}\).

Although the cubic \( \delta \) phase of Bi\(_2\)O\(_3\) in bulk form is stable only from \(729^\circ\) C up to its melting point at \(825^\circ\) C and transforms to other phases upon cooling, it has previously been stabilized at room temperature on Au substrates by electrodeposition\(^{13}\) on polycrystalline YSZ substrates by atmospheric pressure chemical vapour deposition\(^{23}\) and as \( \delta \)-Bi\(_2\)O\(_3\) nanostructures on perovskite substrates\(^{13}\).

The weak diffraction peak at \(q=2.77\ \text{Å}^{-1}\) in Fig.2 (a, blue pattern) is consistent with that of the (111) plane of a trace amount of platinum metal with an fcc structure. Apart from the small amount of (111)–oriented platinum, these data are in agreement with several possibilities, including either amorphous platinum, \(\sim 1\) nm platinum nanocrystals that diffract similarly weakly to amorphous platinum, or platinum that is somehow incorporated into the \( \delta \)-Bi\(_2\)O\(_3\) lattice.

The phase segregation of the platinum metal and Bi\(_2\)O\(_3\) is a major difficulty of working with this system. Like the as-deposited film, the PLD target exhibits phase separation of the platinum from the bismuth oxide. The precursor material exhibits the pyrochlore phase (Bi\(^{3+}\), Pt\(^{4+}\)) when prepared by solid state reaction at \(650^\circ\)C from stoichiometric mixtures of Bi\(_2\)O\(_3\) and platinum metal (Supplementary Information, Fig. S3). However, as expected, targets sintered at these temperatures are not dense enough for proper ablation. Sintering temperatures higher than \(650^\circ\) C are required to synthesize high-density PLD targets, but at these temperatures Pt\(^{4+}\) reduces to platinum metal. Thus, PLD targets sintered at \(820^\circ\) C (slightly below the melting point of Bi\(_2\)O\(_3\)) contain platinum and Bi\(_2\)O\(_3\) in its monoclinic \( \alpha \) phase (Supplementary Information, Fig. S3). Consequently, platinum metal has to oxidize to Pt\(^{4+}\) so that the pyrochlore phase can form on the substrate. Furthermore, control of the Bi/Pt cation stoichiometry of the film becomes complicated due to the high volatility of the bismuth and the large difference between the melting temperatures of the two components of the target (Bi\(_2\)O\(_3\), \(825^\circ\) C; Pt, \(1770^\circ\) C). Perovskite Bi–based films with the correct stoichiometry have been grown by PLD from bismuth–rich targets\(^{24,25}\) as well as from stoichiometric targets\(^{26,27}\). There is no previous work on epitaxial films of Bi\(_2\)Pt\(_2\)O\(_7\). We used \textit{in situ} x-ray fluorescence (XRF) at grazing incidence to tune the deposition parameters while keeping track of the Bi/Pt ratio of the films. We

FIG. 2: Synthesis of pyrochlore Bi\(_2\)Pt\(_2\)O\(_7\). a, XRD \( \theta \)–2\( \theta \) scans of a film as–grown (blue), and after post–growth anneal (orange), showing the formation of the pyrochlore phase during the anneal. b, Normalized grazing incidence \textit{in situ} XRF. Bi and Pt x–ray emissions in the range 8.5 keV – 12 keV are marked with vertical lines whose heights are proportional to their relative intensity. XRF analysis shows a Bi/Pt ratio of 0.88±0.01. The Hf impurity of the YSZ substrate is also included. c, Pt L\(_{3}\) edge XANES spectra of an annealed film (orange); and, PtO\(_2\) (green) and Pt metal foil (black) used as reference standards. The intense peak confirms the oxidation of platinum in the annealed film. d, AFM image of the annealed film in panels (a) and (b). e, The order of Bi\(^{3+}\) and Pt\(^{4+}\) along (110) and that of vacancies determines two types of fluorite subcells in the pyrochlore structure. Cubic \( \delta \)-Bi\(_2\)O\(_3\) with fluorite structure where each anion site has an average occupancy of \(3/4\).
The smoothness of the surface of the annealed film in Fig. 3(a), (b) was analyzed by atomic force microscopy (AFM). The AFM image shown in Fig. 3(d) reveals a rms roughness of 0.84 nm. It was grown on a YSZ (111) stepped surface with atomically flat terraces (Supplementary Information, Fig. S7).

We investigated the oxidation state of platinum in the annealed films. Fig. 2(c) shows Pt L₃ edge X-ray absorption near edge structure (XANES) spectrum (orange) of a bismuth–rich annealed film (Bi/Pt = 1.62 ± 0.04) with pyrochlore phase (Supplementary Information, Fig. S5 and S6). Fig. 2(c) also displays XANES spectra for a platinum metal foil (black), and PtO₂ (green) used as reference standards. The higher threshold energy (E₀) of the film in relation to that of the platinum reference foil is consistent with a higher oxidation state in the annealed film, most probably Pt⁴⁺. The intense peak, referred to as white line, observed in the spectrum of the film (Fig. 2(c), orange) is indicative of a metal oxide. It is thus clear that platinum oxidized during the post–growth anneal.

The smoothness of the surface of the annealed film in Fig. 3(a), (b) was analyzed by atomic force microscopy (AFM). The AFM image shown in Fig. 3(d) reveals a rms roughness of 0.84 nm. It was grown on a YSZ (111) stepped surface with atomically flat terraces (Supplementary Information, Fig. S7).

The cubic structures shown in Fig. 2(c) reveal striking similarity between the cubic δ-Bi₂O₃ and the pyrochlore structures. Both are based on an ordered oxygen deficient fluorite structure. Bi³⁺ cations in δ-Bi₂O₃, as well as both Bi³⁺ and Pt⁴⁺ in the pyrochlore structure form an fcc lattice. This strongly suggests the stabilization of the δ phase of Bi₂O₃ is essential for the formation of the Bi₂Pt₂O₇ pyrochlore phase during the ex-situ post–growth anneal. In fact, films that contained the monoclinic (α) phase of Bi₂O₃ still exhibit α-Bi₂O₃ as the majority phase after annealing, (Supplementary Information, Fig. S8).

Remarkably, the pyrochlore phase is epitaxial. Along with high intensity peaks characteristic of the parent fluorite structure (h + k, k + l, and l + h are all multiples of four), we observed weak pyrochlore superstructure peaks (their intensity is expected to be two orders of magnitude lower), such as (333) and (331).

The expected positions for the reflections of the epitaxial Bi₂Pt₂O₇/YSZ system are depicted in Fig. S3(a). Peaks from the YSZ substrate with a fluorite lattice are also labeled. Area scans at grazing incidence around asymmetrical reflections of the Bi₂Pt₂O₇ phase were transformed into reciprocal space maps (RSM). They are plotted in Fig. 3(b) and (c) for a bismuth–rich film and for a slightly platinum–rich film, respectively. δ-Bi₂O₃ still present in the bismuth–rich film shows up in the RSM of the Bi₂Pt₂O₇, revealing again the similarity between the fluorite and pyrochlore structures (Supplementary Information, Fig. S9). Superstructure peaks indicative of the pyrochlore phase are highlighted.

In–plane (a||) and out–of–plane (a⊥) lattice constants of the epitaxial Bi₂Pt₂O₇, along [011] and [111] directions, respectively, determined from the RSMs are a|| = 10.46±0.03 Å⁻¹ and a⊥=10.423±0.006 Å⁻¹, for the film in Fig. 3(b); and, a|| = 10.37±0.08 Å⁻¹ and a⊥ = 10.53±0.04 Å⁻¹ (in accordance, within the error, with the value obtained from the θ–2θ scan in Fig. 2(a)) for the film in Fig. 3(c). These figures suggest the pyrochlore is relaxed with respect to the substrate lattice.

Azimuthal φ scans carried out using synchrotron x–ray radiation at grazing incidence on the (200) peak of α–Bi₂O₃ of an as–grown film, Fig. 3(d), and on the (222) peak of Bi₂Pt₂O₇ in an annealed film, Fig. 3(e), confirm the epitaxial nature of the film with an in–plane orientation which gives rise to peaks with threefold symmetry. The FWHM of (200) peaks of α–Bi₂O₃ is 0.5°±0.01, and that of the (222) peaks separated 120° in the φ scan is 0.57°±0.02. In–plane orientation relationships of either [10]YSZ || [10]Bi₂Pt₂O₇ or [10]YSZ || [110]Bi₂Pt₂O₇, rotated 60° respect to each other, can be built with the structural model shown in Fig. 3(b),(c). However, no twin domains were observed in our films.

Fig. 4 shows cross–sectional high–angle annular dark field (HAADF) scanning TEM images for the films whose RSMs are displayed in Fig. 3(b), (c). These studies reveal ~ 100 nm long regions of ordered epitaxial pyrochlore. A wider field of view scanning TEM images showing non–pyrochlore regions are shown in Supplementary Information, Fig.S10. Fig. 4(a) exhibits the expected columns of a pyrochlore structure with cation ordered vacancies (no noticeable contrast in the HAADF is expected between Bi and Pt columns). The presence of vacancies in this case can be due to the deviation from the correct stoichiometry of the film composition, Bi/Pt=1.62±0.04. The platinum–rich film shown in Fig. 4(c) with a Bi/Pt...
The ratio of 0.88±0.01 does not contain cation vacancies in its pyrochlore structure, Fig. 4(c).

In conclusion, these results provide a novel route for the formation of epitaxial Bi$_2$Pt$_2$O$_7$ pyrochlore, thought to be one of the most efficient oxide catalysts. Upcoming work includes the investigation of the oxygen reduction activity of the (111) surface of Bi$_2$Pt$_2$O$_7$, and its comparison with powder pellets. However, the difficulty of controlling Bi/Pt stoichiometry suggests that independent control of volatile bismuth and non-volatile platinum sources may be required for routine growth of pristine films.

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in Fig. 3(b), viewed along [ ¯101] in the NION UltraSTEM. The dark, ordered atomic locations in the image are the result of cation vacancies.

FIG. 4: High–angle annular dark field scanning TEM images. a, HAADF STEM image of the bismuth–rich film shown in Fig.3(c), viewed along [ ¯101] in the Tecnai F20. Cation vacancies are not observed in Black positions mark where the ordered cation vacancies are expected, matching the image in Fig.1(a). c, HAADF STEM image of the platinum–rich film shown in Fig.3(b), viewed along [ ¯101] in the Tecnai F20. Cation vacancies are not observed in this structure.

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Methods

We sintered the PLD target from a mixture of Bi$_2$O$_3$ (99.999%) and Pt powder ($\leq$20 µm, >99.97%) with controlled cation stoichiometry (Bi/Pt=1) in a solid-state reaction. These mixtures were ground in an agate mortar, pressed into pellets, and heated in a box furnace at 800°C for 3 h. Then, the pellets were ground and sintered again at 650°C for 48 h. This annealing at 650°C for 48 h was repeated five times, with intermediate grinding and pressing. In order to get high-density PLD targets, the powders were reground and pressed, and then fired at 820°C for further 24 h. X-ray diffraction patterns (Rigaku SmartLab, Cu source) were taken on the intermediate pellets and on the final targets. Their cation stoichiometry was measured by x-ray fluorescence. Polished cross-sections of the targets were studied by high resolution scanning electron microscopy and energy dispersive X-ray spectroscopy (LEO 1550 Field Emission SEM). Films were grown in the in situ PLD system housed at the G3 hutch of Cornell High Energy Synchrotron Source (CHESS) which utilizes a KrF excimer laser (248 nm) focused onto the target. During the growth, oxygen was supplied in the PLD chamber yielding a background pressure up to 10$^{-1}$ Torr. The substrate temperature, monitored by an optical pyrometer ($\lambda = 4.8–5.5$ µm, $\epsilon = 0.8$) and adjusted to the sample, was fixed in the range of 545°C - 740°C for single crystals 8 mol % Y$_2$O$_3$-stabilized ZrO$_2$ (Zr$_{92}$Y$_8$O$_{192}$) (YSZ) with (111) orientation (MTI Corporation) were used as substrates. Prior to the growth, they were annealed at 1300°C for 3 h in air. Atomic Force Microscopy (AFM, Veeco Dimension 3100 system) on the annealed substrates showed steps of height $\sim$0.3 nm corresponding to the distance of successive (111) planes (oxygen–metal–oxygen triple layer) separated by terraces. The Bi and Pt content of the films were monitored in situ by X-ray fluorescence (XRF) at grazing incidence. The excitation energy was 13.64 keV (synchrotron radiation), above the Bi L$_3$ absorption edge (13.42 keV). L$_{\alpha}$ x-ray emission lines of Bi (L$_{\alpha1}$ at 10.84 KeV) and Pt (L$_{\alpha1}$ at 9.44 KeV) were used to quantify the Bi/Pt ratio. The quantitative analysis of the XRF spectrum was performed by a custom fitting procedure implemented in MATLAB which employs the Elam database. The model provides an estimate of the Bi/Pt ratio by fitting a calculated spectrum to the measured one.

Ex situ XRD /29 scans were performed in a four-circle diffractometer (Rigaku SmartLab, Cu source, Ge(220) 2–bounce incident beam monochromator). X-ray diffraction under grazing incidence experiments were conducted at CHESS G2 hutch with an incident energy of 10.04 keV or 13.64 keV. The incidence angle was set to 0.25° or 0.275°. Area scans around the asymmetrical reflections of the film were transformed to reciprocal space maps (RSM) and combined into a single figure. In-plane and out-of-plane lattice parameters were determined from RSMs. X-ray absorption near edge structure (XANES) measurements at Pt L$_3$ edge (11.564 keV) were carried out at the F3 beamline of CHESS. A silicon (220) double-crystal monochromator with an energy resolution $\Delta E$/E of $\approx$10$^{-4}$ was used. A Pt reference foil standard, used for energy calibration, was measured in transmission mode downstream of the sample between two ion chambers filled with 100% N$_2$. All XANES data were calibrated and normalized using the Demeter Athena XAS software package.

Cross-sectional TEM specimens were investigated in the 5th–order aberration corrected 100 keV NION UltraSTEM with a probe size $\approx$1 Å for a biscrystal-rich sample and the monochromated 200 keV FEI Tecnai F-20 STEM/TEM with a probe size of 1.6 Å for a platinum-rich sample. The specimens were prepared using the FEI Strata 400 focused ion beam, with a final ion milling with 2 keV gallium ions to minimize surface damage. HAADF-STEM imaging was used in both machines, which offers atomic resolution atomic number contrast, going roughly as the square of the atomic number, with heavier atoms appearing brighter.

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**Author contributions**

A.G.L. designed the experiments and led this research project; synthesized and characterized the targets, prepared and characterized the YSZ substrates, and grew the films; performed the *ex situ* XRD \(\theta-2\theta\) scans, the *in situ* XRF, and the AFM measurements; analyzed the XRD (\(\theta-2\theta\)), reciprocal space maps and XRF data; prepared the figures and wrote the manuscript. M.C.S., H.J. and A.G.L. tune the PLD system up. A.W. and A.G.L. performed area scans for asymmetrical reflections at G2 (CHESS). M.E.H. and D.A.M. performed STEM studies. M.C.S. assisted in preliminary growths of films consisting of \(\text{Bi}_2\text{O}_3\) ant Pt phases. M.J.W. prepared the PtO\(_2\) standard for XANES measurements. M.J.W. and H.J. measured XANES at Pt L\(_3\) edge (F3 beamline, CHESS). J.D.B. made available the resources and equipments of his group to develop this research. All the authors discussed the manuscript.

**Additional information**

Supplementary information is available.

**Competing financial interests**

The authors declare no competing financial interests.