

Rapid synthesis of dual-element isotope-enriched α -MoO₃ crystals by reactive vapor transport

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In this work, we develop a rapid reactive vapor transport technique to efficiently utilize limited isotopically pure precursors, particularly gaseous ¹⁸O₂, and synthesize mm-scale, high-quality isotope-enriched crystals within few-minute growth durations. We unlock this capability by using metallic molybdenum precursors with high source temperatures (900 °C) and total pressures (~1 atm) to maximize precursor efficiency and yield. Subsequently, we grow α -MoO₃ single crystals with high and uniform enrichment levels of ⁹⁸Mo and ¹⁸O isotopes in several different permutations. As probed by Raman spectroscopy, modest and significant phonon energy redshifts occur following ⁹⁸Mo and ¹⁸O enrichment, respectively. By demonstrating control over both molybdenum and oxygen isotopic enrichments, we establish a powerful tool to advance nanophotonics and thermal management goals using α -MoO₃. This work is motivated by the possibility to enhance and engineer lattice vibrational mode phenomena including thermal conduction and hyperbolic phonon polariton dispersion—with particular interest in comparing the effects of light and heavy element enrichment.

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Introduction. Isotope engineering can tune and optimize phonon-derived phenomena, including thermal conductivity and electron-phonon interactions, by altering elemental atomic masses and nuclear spins [1–4]. For instance, exchanging one isotope for another shifts phonon frequencies, while mixing multiple isotopic species increases phonon scattering events [5–8]. We can exploit these basic modifications to tailor more exotic phenomena as well. In certain strongly anisotropic single crystals with polar bonding, pairs of transverse optical (TO) and longitudinal optical (LO) phonon modes split into hyperbolic spectral regions wherein two principal components of the permittivity tensor have opposite signs [9–11]. These regions, termed hyperbolic Reststrahlen bands, host numerous exotic light-matter behaviors unique to hyperbolic media including low-loss, propagating hyperbolic phonon polaritons (HPhPs)—infrared photons coupled with optical phonons [12–18]. Hyperbolicity was first realized using plasmon polaritons in nanostructured metallic-dielectric metamaterials [19–21]; recently, interest has expanded to include layered van der Waals (vdW) materials like hexagonal boron nitride (h-BN) and orthorhombic molybdenum trioxide (α -MoO₃), which naturally exhibit hyperbolic Reststrahlen bands without nanostructuring demands [16–18,22,23]. Compared to h-BN, α -MoO₃, a biaxially anisotropic material,

commands additional in-plane directional control over polariton propagation and could advance mid-infrared (mid-IR) nanophotonics technologies including chemical sensing, planar focusing, and thermal management [24–29]. However, whereas the flexibility and spectrum of metamaterial design provides high tunability [19,30], alternative frameworks are required to tailor naturally hyperbolic materials. For phonon-derived hyperbolic media like h-BN and α -MoO₃, isotope engineering is uniquely well suited for tuning HPhP modes to individual purposes.

Recent research, primarily using h-BN, has potentially tailored HPhP modes through isotope engineering. Boron is naturally abundant as ~80% ¹¹B and ~20% ¹⁰B; by synthesizing isotopically pure h-¹¹BN and h-¹⁰BN, the HPhP lifetime can be improved manifold by reducing phonon scattering losses [31–33]. Additionally, the Reststrahlen band frequencies can be considerably red-shifted by increasing the ¹⁰B / ¹¹B ratio [31,34], enabling HPhP dispersion engineering and even hetero-isotope nanostructure design [35]. The naturally abundant ¹⁴N can also be replaced with ¹⁵N (0.4% abundance) to further control HPhP modes [34,36]. In the case of α -MoO₃, molybdenum (Mo) exists in seven abundant isotopes ranging from ⁹²Mo to ¹⁰⁰Mo, which introduce significant mass differences that increase phonon scattering losses. Previous studies on isotopically pure α -⁹²MoO₃ and α -¹⁰⁰MoO₃ indicate improved HPhP lifetimes, an over two-fold increase in propagation length, and modest Reststrahlen band shifts compared to naturally abundant crystals [37,38].

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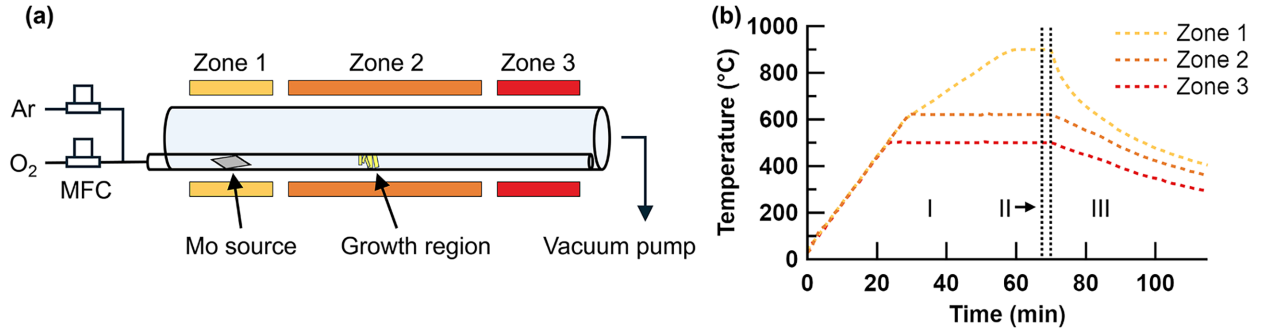


FIG. 1. Reactive vapor transport growth method. (a) Schematic of the growth chamber used for crystal growth. (b) Temperature profile of the three-zone furnace during a typical growth run comprised of the ramp-up (I), growth (II), and cool-down (III) stages.

The oxygen (O) isotope fraction, however, is an unexplored avenue for α -MoO₃; compared to ¹⁶O, which makes up 99.8% of naturally occurring oxygen, ¹⁸O is accompanied by a 12.5% mass increase. Due to the strong mass dependence of optical phonon frequencies [39,40], replacing ¹⁶O with the heavier ¹⁸O could significantly alter the α -MoO₃ phonon modes and associated Reststrahlen bands. First, however, a process must be developed to synthesize α -MoO₃ crystals with control over both Mo and O isotopic enrichments.

Large-area α -MoO₃ single crystals are readily synthesized using physical vapor transport techniques wherein a MoO₃ powder source, which has a high vapor pressure above $\sim 700^\circ\text{C}$ [41,42], is sublimated and subsequently deposited within a temperature gradient [43–47]. This technique can produce mm- to cm-scale single-crystal flakes which are several micrometers in thickness and are easily exfoliated. The Mo isotope fraction can be controlled by using commercially available Mo-isotope-enriched MoO₃ as the evaporation source; however, the reported processes require at least 8 hr for crystal growth [37,38]. Moreover, ¹⁸O enrichment has not yet been demonstrated due to the unavailability of ¹⁸O-enriched MoO₃ sources, the prohibitive expense of ¹⁸O₂ gas cylinders, and the practical challenges of working with very small quantities in an atmospheric-pressure process.

In this work, we use reactive sublimation to synthesize α -MoO₃ single crystals with controlled Mo and O isotopic fractions by using a metallic Mo source, which has a much lower vapor pressure than α -MoO₃ [48–50]. We then rapidly commence the sublimation–deposition process by oxidizing the Mo source with O₂ flow of select isotopic enrichment. Our method efficiently utilizes precursors, enabling high-yield crystal growth using less than 1 standard L of O₂ and 40 mg of Mo. We first develop the reactive vapor transport method using naturally abundant Mo and O₂ precursors and confirm the α -MoO₃ high crystallinity and proper stoichiometry using x-ray diffraction (XRD), Raman spectroscopy, energy-dispersive x-ray spectroscopy (EDS), and atomic force microscopy (AFM). We also control the α -MoO₃ flake size and morphology by modifying the total deposition pressure. We then synthesize single- and dual-element isotopically enriched α -MoO₃ flakes using pure ⁹⁸Mo and ¹⁸O₂ sources and confirm the high attained isotopic enrichments using time-of-flight secondary ion mass spectrometry (ToF-SIMS), unlocking practical ¹⁸O-isotope engineering in α -MoO₃. Finally, using Raman spectroscopy, we investigate

the effects of different isotopes on the vibrational properties of α -MoO₃ with implications for Reststrahlen band and HPhP engineering.

Methods.

Reactive vapor transport synthesis. We perform the reactive vapor transport growths in a three-zone horizontal tube furnace (Thermcraft XST-3-0-24-3V2-F02) shown schematically in Fig. 1(a), where a Mo source is reactively sublimated in a hot zone (Zone 1) and transported to a cooler region (zones 2–3) for deposition. The furnace is equipped with a 14-mm-outer-diameter (OD) quartz tube positioned coaxially within a 50-mm-OD outer tube; the smaller tube serves as the growth chamber to maximize vapor concentrations *via* volume confinement to increase reaction and growth efficiencies. A rotary vane pump and mass flow controllers (MFCs) for Ar and O₂ gas flow are used to manage pressure and enable the controlled oxidation of the Mo metal source; we note that our reported pressures are approximate due to the dependence of the Convectron pressure gauge on gas composition. Prior to growth, 40 mg of Mo foil (Thermo Scientific, 99.95% purity) or ⁹⁸Mo powder (IsoFlex, 99.998% purity, 98.65% enrichment) in a platinum boat is positioned in the smaller tube at Zone 1. For ¹⁸O-enriched growths, the chamber and gas lines are evacuated overnight to 12 mTorr to remove ¹⁶O₂ and adsorbed water. We show a typical experimental temporal temperature profile in Fig. 1(b) and summarize the different growth stages in Table I. During the heating stage (Stage I), we sustain a low-pressure Ar environment to protect the source Mo from oxidizing environments while ramping the furnace zones at 20 °C/min below 600 °C and at 10 °C/min above. Zone 1 is heated to 900 °C for rapid oxidation and vaporization of the Mo source, and Zone 2 to 620 °C for deposition. After allowing 10 min for temperature equilibration, we increase the argon flow to 500 sccm and meter the vacuum pumping speed to increase the total pressure to nearly

TABLE I. Parameters for each heating stage in the reactive vapor transport process.

Stage	Ar flow (sccm)	O ₂ flow (sccm)	Pressure (Torr)
I–Ramp-up	50	0	0.1
II–Growth	0	500	150–740
III–Cool down	500	0	740

1 atm. In Stage II, to oxidize the Mo source and initiate MoO₃ evaporation and transport, we supplant the argon flow with 500 sccm of ¹⁶O₂ or ¹⁸O₂ (Millipore Sigma, 99% purity, 97–99% enrichment) for 2 min. For growth using ¹⁸O₂, due to the limited quantity and low pressure (2.3 atm) of the oxygen supply, the flow rate will decrease after approximately 75 s; at this point, we supplement the gas flow with 500 sccm of argon to transport the remaining MoO₃ vapor (from the rapidly oxidized Mo metal) to the deposition zone. In Stage III, we continue argon flow and cool the furnace naturally before venting to atmosphere, whereupon numerous large flakes are found on the interior walls of the inner quartz tube. We report four α -MoO₃ isotopic permutations: naturally abundant (^{nat}Mo ^{nat}O₃), ⁹⁸Mo-enriched (⁹⁸Mo ^{nat}O₃), ¹⁸O-enriched (^{nat}Mo ¹⁸O₃), and dual-element isotope-enriched (⁹⁸Mo ¹⁸O₃). For the ⁹⁸Mo ^{nat}O₃ sample, 50 mg of ⁹⁸Mo-enriched MoO₃ (IsoFlex, 99.9% purity, 98.42% enrichment) is the source powder. Since no reactive sublimation is necessary for this oxide source, we heat Zone 1 to 800 °C and flow 50 sccm N₂ flow at atmospheric pressure for a 50 min growth duration. After each growth, the furnace zones are heated to high temperatures (950 °C) to remove volatile deposition products.

Characterization. An Olympus BX60M bright-field optical microscope is used to image the α -MoO₃ crystals. Energy-dispersive x-ray spectrometry (EDS) is performed using a Tescan Mira scanning electron microscope (SEM) and EDS detector with an accelerating voltage of 15 keV and beam current of 1 nA. The reported Mo:O ratio is averaged from five EDS point measurements with carbon excluded. The surface morphology is characterized by using an Asylum MFP-3D AFM in tapping mode. XRD is performed using a Panalytical Empyrean diffractometer with a Cu source and Bragg-Brentano^{HD} incident beam optics. For thickness measurements, a reflective W film is sputter deposited onto α -MoO₃ crystals mounted on Si substrates before measuring using a Zygo NexView 3D optical profilometer. A sample size of at least 20 flakes is used for statistical analyses. Raman spectroscopy is performed using a Horiba LabRAM HR Evolution microscope without a polarization analyzer equipped with a 532 nm excitation laser and an 1800 gr/mm grating. To account for the anisotropic Raman response of α -MoO₃ [51,52], the crystal *a* axis is oriented parallel to the linear polarization of the incident laser.

ToF-SIMS measurements were performed using a TOF.SIMS⁵-NSC instrument (ION-TOF GmbH, Germany) operated in positive and negative ion detection modes to measure the Mo and O isotopic fractions, respectively. The Bi₃⁺ ion beam was used as a primary ion source and operated at 30 keV energy and 0.5 nA current in DC mode with a focused ion beam spot size of approximately 120 nm. Imaging was performed over a 100 × 100 μ m area of 256 × 256 pixels with an acquisition time of 19.16 s. Depth profiling was performed with a Cs⁺ ion-sputtering source for both positive and negative ion detection modes operated at 500 eV energy with DC currents ranging from 35–45 nA. The ion-sputtering source was rastered across a 500 × 500 μ m area with 10 sputter frames per analysis scan. A low-energy electron flood gun was used during SIMS measurements to compensate for surface charging effects of the primary ion gun.

Results and discussion.

Growth using naturally abundant isotopes. We first use naturally abundant Mo and O₂ precursors to develop the high-efficiency reactive vapor deposition process. We visually monitor the growth process *in situ* through a viewport on one end of the tube furnace. The high source temperature of 900 °C maximizes growth rates by vaporizing the Mo as quickly as it oxidizes: approximately 10 s after commencing O₂ flow, the metal source begins oxidizing and glows a bright yellow-orange color for 10 s before vanishing as the newly formed MoO₃ fully vaporizes into a whitish cloud. Soon afterwards, small crystals first become visible on the smaller tube interior and continue to grow for several minutes as the remaining MoO₃ vapor is transported to the deposition zone, with growth briefly continuing during cooling in flowing Ar. Afterwards, approximately 10–20 large flakes (>3 mm in at least one lateral dimension) and dozens of smaller flakes (>100 μ m) can be harvested from the smaller tube interior as shown in Fig. 2(a).

The flake morphologies range from needles to plates and are typical of α -MoO₃ grown using PVT techniques, with frequent faceting along the *c* and *a* axes as in the optical micrograph in Fig. 2(b) [47]. The flake thickness varies from several hundreds of nanometers to a few micrometers, and isolating, transferring, and exfoliating thin, smooth samples is facile. We confirmed the α -MoO₃ stoichiometry in Fig. 2(c), which shows a representative EDS spectrum with an approximately 3:1 O:Mo ratio.

The α -MoO₃ crystal structure, sourced from the Materials Project database (ID: mp-20589) [53,54], is shown in Fig. 3(a) and is described by an orthorhombic unit cell (space group *Pbnm*) with the lattice parameters *a* = 3.962 Å, *b* = 13.860 Å, and *c* = 3.697 Å [55,56]. The unit cell is composed of distorted Mo-O₆ octahedra, which are strongly bonded in the *a* – *c* plane and ordered into vdW bilayers along the *b*-axis. In Fig. 3(b), we show a representative XRD scan of a flake transferred onto a sapphire substrate. Only sharp, intense α -MoO₃ (0*k*0) reflections are observed, indicating phase purity and high crystallinity and confirming that the *b*-axis is oriented parallel to the flake thickness. The Raman spectrum shown in Fig. 3(c) displays narrow, intense peaks that are also characteristic of α -MoO₃ [51,57], further indicating the high structural quality. Dieterle *et al.* [57] found that the intensity ratio of the Raman bands at 295 and 285 cm^{−1} can be used to indicate oxygen substoichiometry, which can be common in α -MoO₃ [58]. We do not observe the 295 cm^{−1} peak in our results, agreeing with the EDS analysis in Fig. 3(c) that our α -MoO₃ are close to stoichiometric. The AFM image shown in Fig. 3(d) shows broad terraces with clean, linear steps. The step height is approximately 0.70–0.75 nm, in agreement or slightly larger than the expected *b*/2 interlayer spacing of 0.693 nm [55,56]. Here, the terrace widths alternate between wide (~3.4 μ m) and narrow (~0.35 μ m), although the absolute widths vary at different positions along the crystal. The alternating terrace widths may indicate different step migration or re-evaporation rates of the (010) and (020) planes, although further research is necessary to fully examine the surface dynamics during growth.

We also studied the influence of the total growth pressure on the flake morphology by growing in oxygen-rich

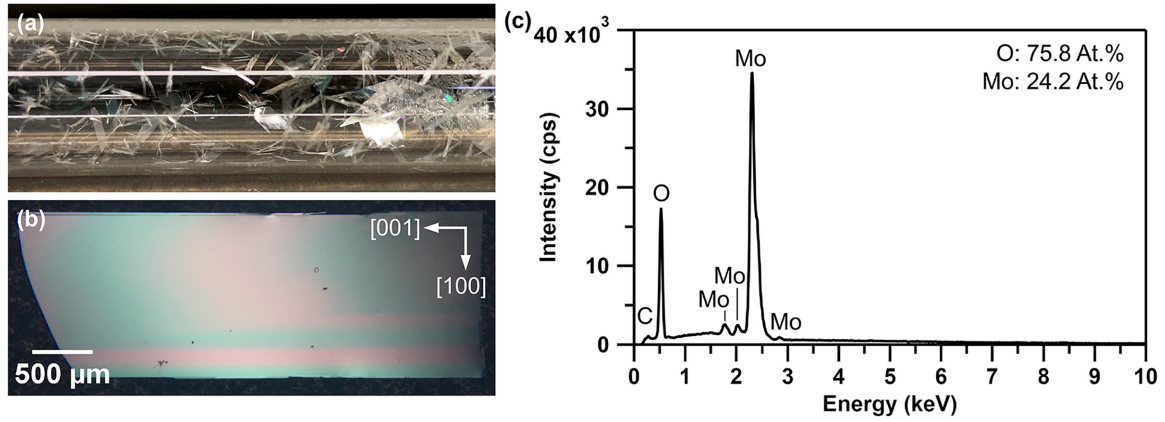


FIG. 2. α - MoO_3 flakes. (a) Photograph of numerous large crystals grown within the small quartz tube. (b) Optical micrograph and (c) EDS spectrum and stoichiometry of the α - MoO_3 crystals.

environments at 150, 360, 490, and 740 Torr, where the resulting flake yields are photographed in Figs. 4(a)–4(d), respectively. At 150 Torr, the reaction rate is low, causing only a modest (~ 10 mg) Mo source mass loss and a relatively low yield of small (< 500 μm) crystals. As we increase the growth pressure, the Mo source is fully consumed, and the flake sizes

and thicknesses increase significantly. Average dimensions of the crystal lengths, widths, and thicknesses are summarized in Table II. At 740 Torr, crystals may exceed several millimeters in length and tens of micrometers in thickness. Additionally, the growth region shifts to the left by ~ 3 cm as the pressure is increased from 150–740 Torr as nucleation and

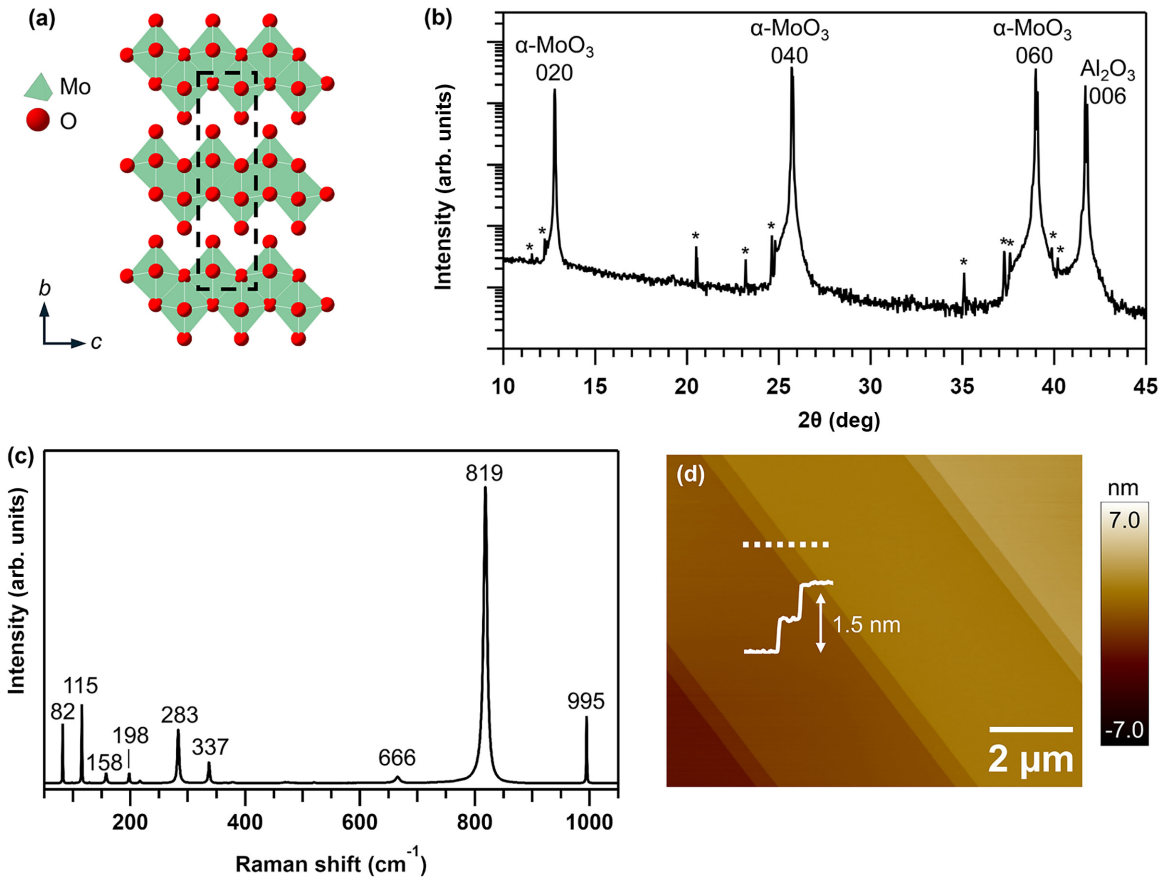


FIG. 3. Physical properties of α - MoO_3 flakes. (a) α - MoO_3 crystal structure viewed along the a axis with the unit cell outlined. (b) XRD θ - 2θ scan of a α - MoO_3 flake transferred onto a c -axis-oriented Al_2O_3 substrate. (*) = reflections arising from secondary and $\lambda/2$ wavelengths. (c) Raman spectrum of a flake transferred onto a Si substrate with the major α - MoO_3 vibration frequencies labeled, and (d) AFM height image and (inset) line profile.

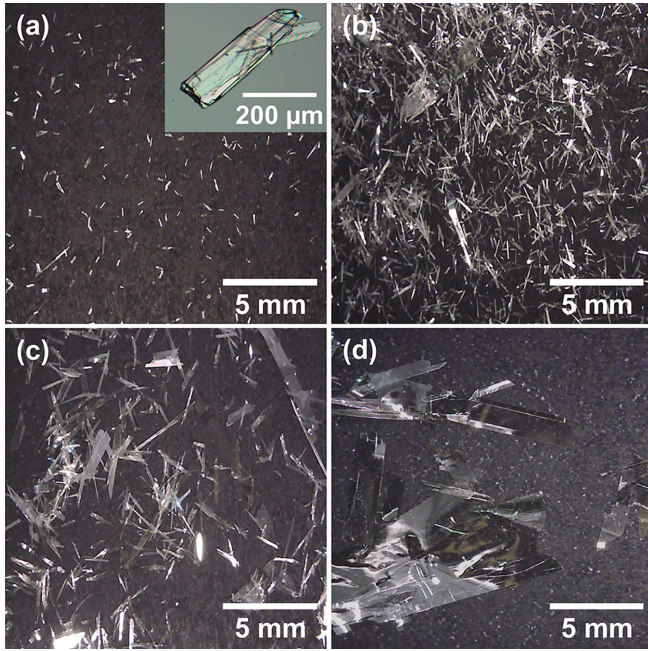


FIG. 4. Pressure dependence of reactive vapor transport growth. Photographs and (inset) optical micrograph of α - MoO_3 flakes grown at different O_2 pressures: (a) 150, (b) 360, (c) 490, and (d) 740 Torr.

growth stabilize at higher temperatures. Although high precursor supersaturations typically result in small crystal sizes by favoring nucleation over growth [59], our results agree with other reported α - MoO_3 vapor transport growths where high vapor concentrations promote larger flakes [47]. The various complexities of the growth process may collectively trigger this counterintuitive relation. In particular, the axial flow velocity decreases at higher total pressures, leading to longer residence times, which increases the duration of the growth stage. We directly observe this effect by visually monitoring the crystal growth onset and termination times, which diverge to allow prolonged growth at higher total pressures.

Growth using enriched ^{98}Mo and ^{18}O precursors. With a sound understanding of and control over the process for large-area, high-quality α - MoO_3 crystal growth from a metal source, we can implement isotope-enriched ^{98}Mo and $^{18}\text{O}_2$ precursors to engineer different isotopic combinations. In addition to the naturally abundant sample ($^{\text{nat}}\text{Mo}^{\text{nat}}\text{O}_3$), we produced ^{98}Mo -enriched ($^{98}\text{Mo}^{\text{nat}}\text{O}_3$), ^{18}O -enriched ($^{\text{nat}}\text{Mo}^{18}\text{O}_3$), and dual-element isotope-enriched ($^{98}\text{Mo}^{18}\text{O}_3$) flakes. The isotopic fractions of metal and oxygen are quantified by ToF-SIMS depth profiles. In Fig. 5(a), we show the ^{98}Mo content of the Mo -enriched and unen-

riched samples as a function of sputter time. We observe a high, uniform, and identical ^{98}Mo fraction of 98.7% for both $^{98}\text{MoO}_3$ and $^{98}\text{Mo}^{18}\text{O}_3$, while the $^{\text{nat}}\text{Mo}^{18}\text{O}_3$ matches the expected $\sim 25\%$ naturally abundant fraction of ^{98}Mo . The incorporation of ^{98}Mo into the α - MoO_3 flakes is limited only by the enrichment level of the Mo precursor. The O-isotope measurements are more challenging to interpret as we observe occasional quantitative disagreement in measurements taken from different locations. To improve our confidence in the quantifications obtained, we measured three areas on different flakes of each isotopic permutation. In some of these scans, unexpected features including high C content near the top surface and anomalous $^{16}/^{18}\text{O}$ profile shapes cause uncertainty in the measurements. To investigate these inconsistencies, we performed Raman spectroscopy on numerous flakes and observed identical spectra—without peak shifting or broadening—across all measured flakes of each batch, confirming that the flakes are uniform and alike. Therefore, we believe that artifacts resulting from variable flake topography and tilt, for instance, result in artificially high ^{16}O signals in some ToF-SIMS measurements [60,61]. In Fig. 5(b), we show the most self-consistent depth profiles of the ^{18}O fractions taken from each sample batch. The near-identical shape and magnitude of the two ^{18}O -enriched profiles give us confidence that the true isotopic fraction is likely $\sim 87\%$ ^{18}O . We note that of the six measurements, the lowest enrichment level is $\sim 64\%$ ^{18}O ; therefore, even the more unreliable profiles still indicate a significant ^{18}O enrichment compared to the 0.2% natural abundance. The ^{18}O enrichment is likely primarily limited by background oxygen sources: although the $^{18}\text{O}_2$ precursors are 97–99% enriched, this purity may be diluted in the growth chamber by ^{16}O species in oxygen or water molecules that may persist during evacuation of the system. The native oxide of the Mo precursor is another likely source of ^{16}O . The oxygen isotope fraction in the α - MoO_3 flakes may also depend on thermodynamic and/or kinetic factors that may affect isotope-dependent oxide growth and which require further investigation for the case of α - MoO_3 [62,63]. Regardless, the relatively high obtained enrichment levels illuminate the effectiveness of our reactive vapor transport technique to control both the metal- and oxygen-isotope ratios in large-area α - MoO_3 crystals.

Figure 5(c) shows the Raman spectra of the different isotopic α - MoO_3 permutations to elucidate how isotope enrichment modifies the phonon properties. The A_g mode at 995 cm^{-1} intensifies for ^{98}Mo -enriched crystals compared to naturally abundant α - MoO_3 , potentially due to reduced isotope scattering. All Raman peaks redshift modestly; for instance, A_g 995 cm^{-1} shifting by less than 2 cm^{-1} . This shift is smaller than reported ^{92}Mo and ^{100}Mo -enriched α - MoO_3 , where larger changes in average atomic mass induce $3\text{--}4\text{ cm}^{-1}$ shifts in either direction [37]. In contrast, ^{18}O -enrichment induces a more significant spectral redshift: A_g 995 cm^{-1} moves to 947 cm^{-1} , a shift of nearly 50 cm^{-1} . The intensity of this peak reduces, most likely due to increased phonon scattering by the now co-existing ^{16}O and ^{18}O species. Effects compound in the dual-element isotope-enriched sample, resulting in a 945 cm^{-1} high-energy A_g peak with moderate intensity. Although the Reststrahlen bands can-

TABLE II. Mean crystal dimensions as measured by optical microscopy and optical profilometry.

Growth pressure (Torr)	Length (mm)	Width (mm)	Thickness (μm)
150	0.37 ± 0.28	0.07 ± 0.04	8.1 ± 4.4
360	0.62 ± 0.31	0.08 ± 0.03	8.6 ± 4.0
490	2.7 ± 1.6	0.36 ± 0.23	11 ± 7.7
740	6.0 ± 3.0	1.3 ± 0.9	20 ± 8.8

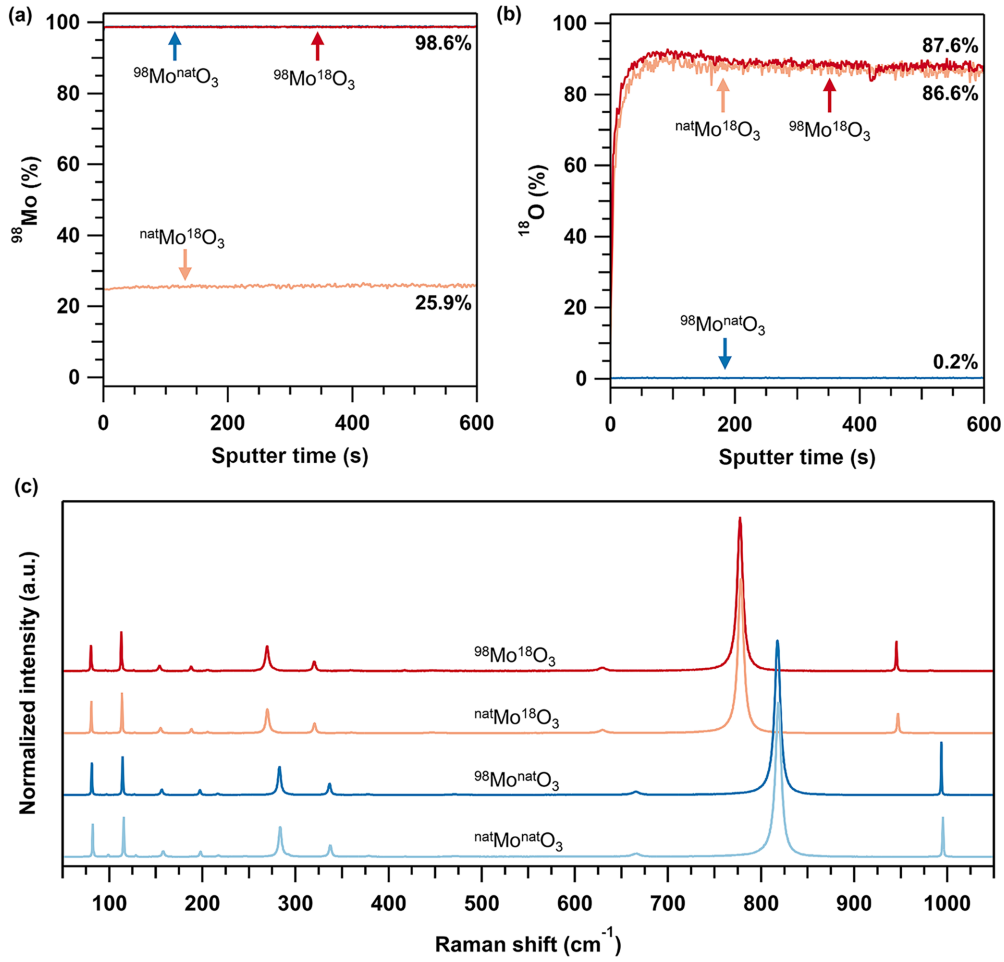


FIG. 5. Dual-element isotope enrichment of α - MoO_3 . Depth profiles of (a) ^{98}Mo and (b) ^{18}O isotope fractions collected by ToF-SIMS. In (a), the $^{98}\text{Mo}^{\text{nat}}\text{O}_3$ and $^{98}\text{Mo}^{18}\text{O}_3$ profiles overlap. (c) Offset Raman spectra of the naturally abundant and isotope-enriched α - MoO_3 flakes after intensity normalization to the $\sim 819 \text{ cm}^{-1}$ α - MoO_3 peak.

not be extracted directly from Raman spectra of α - MoO_3 , our results are consistent with the expected universal softening of phonon modes, which applies to the Raman-inactive TO and LO phonon modes that bound the Reststrahlen bands [31,37]. Therefore, incorporating ^{18}O induces stronger α - MoO_3 Reststrahlen band tunability than Mo isotopes can, where precisely modifying isotope fractions could realize broad spectral control of HPhP modes.

The stronger dependence of the Raman mode frequencies on the O isotope enrichment compared to the Mo component can be understood in part using the simplified case of a diatomic chain of Mo and O atoms. We can approximate the optical phonon mode frequency at two limiting positions of the dispersion [39]:

$$\omega_{\text{opt}}(K \rightarrow 0) \cong \sqrt{2C \left(\frac{1}{m_{\text{light}}} + \frac{1}{m_{\text{heavy}}} \right)}, \quad (1)$$

$$\omega_{\text{opt}}\left(K \rightarrow \frac{\pi}{a}\right) = \sqrt{\frac{2C}{m_{\text{light}}}}, \quad (2)$$

where K is the wavevector, C is the bond spring constant, m_{light} and m_{heavy} are the two atomic masses, and $\frac{\pi}{a}$ is the

Brillouin zone boundary with interplanar spacing a . Through the additive relationship of the reciprocal atomic masses in Eq. (1), m_{light} becomes increasingly dominant in systems with wide atomic mass disparities like Mo–O. Therefore, in both equations, the optical phonon frequencies are primarily dependent on the mass of the lighter atom, or O in this case. To capture structure-specific effects, we will explore the relative contributions of Mo and O lattice sites towards governing individual phonon mode behaviors in a forthcoming study [64].

Conclusions. Using reactive vapor transport, we have developed a method to rapidly synthesize α - MoO_3 flakes with control over both the O and Mo isotopic fractions. Our technique efficiently consumes limited $^{18}\text{O}_2$ sources to enable high-yield growth using less than 1 standard L of gaseous O_2 . Chemical and structural characterization reveals the high crystalline and stoichiometric quality. We vary the flake size and morphology by modifying the growth pressure, with synthesis at near-atmospheric pressure producing large crystals comparable with those reported by other growth methods. ToF-SIMS analyses quantify the obtained isotopic fractions as 98.6% ^{98}Mo and up to 87.6% ^{18}O . We find that ^{18}O enrichment facilitates significant phonon mode tunability that exceeds the capabilities of Mo-isotope engineering. To the

best of our knowledge, this is the first reported synthesis of highly ^{18}O -enriched $\alpha\text{-MoO}_3$ —a capability critical to exploring cutting-edge phonon-derived phenomena in $\alpha\text{-MoO}_3$ including enhanced thermal conductivity and tunable HPhP modes.

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Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Data availability. The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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