High Temperature Mid-IR Polarizer via Natural In-Plane Hyperbolic Van der Waals Crystals

Nihar Ranjan Sahoo, Saurabh Dixit, Anuj Kumar Singh, Sang Hoon Nam, Nicholas X. Fang,* and Anshuman Kumar*

Integration of conventional mid to long-wavelength infrared (IR) polarizers with chip-scale platforms is restricted by their bulky size and complex fabrication. Van der Waals materials-based polarizer can address these challenges due to its nonlithographic fabrication, ease of integration with chip-scale platforms, and room temperature operation. In the present work, mid-IR optical response of the sub-wavelength thin films of α-phase molybdenum trioxide (α-MoO₃) is investigated for application toward high temperature mid-IR transmission and reflection type thin film polarizer. To the authors’ knowledge, this is the first report of above room temperature mid-IR optical response of α-MoO₃ to determine the thermal stability of the proposed device. It is found that the α-MoO₃-based polarizer retains high extinction ratio with peak value exceeding 10 dB, up to a temperature of 140 °C. The experimental findings are explained by natural in-plane hyperbolic anisotropy of α-MoO₃ in the mid-IR, high temperature X-ray diffraction and Raman spectroscopic measurements. This work opens up new avenues for naturally in-plane hyperbolic van der Waals thin films to realize sub-wavelength IR optical components without lithographic constraints.

1. Introduction

Recently, a new class of van der Waals (vdW) layered materials have been shown to possess natural hyperbolic anisotropy in mid-infrared (IR) spectral region.[1–4] Hyperbolic anisotropy is an extreme type of optical anisotropy in which the real part of dielectric permittivity holds the opposite sign in different crystallographic directions. As a result, within a hyperbolic spectral region, the vdw material behaves like a metal in one crystal direction and a dielectric in the other crystal direction. Unlike artificial hyperbolic metamaterials[5]—where in-plane hyperbolic anisotropy is invoked by lithographic patterning, natural hyperbolicity of these vDW materials is attributed to structural anisotropy of crystal unit cell. In particular, hexagonal boron nitride (h-BN),[3] α-phase molybdenum trioxide (α-MoO₃),[6] and α-phase vanadium pentoxide (α-V₂O₃)[2] are natural hyperbolic materials (NHMs) which exhibit Reststrahlen Bands (RBs)—the spectral region between longitudinal optical (LO) and transverse optical (TO) phonons—in the mid-IR spectral region and show hyperbolicity due to interaction of optical phonons with photons (light–matter interaction). Phonons have a relatively long lifetime compared to plasmons resulting in lower optical losses than their analogous plasmonic-based metamaterials[7–9] in which photons are coupled with plasmons. Many NHMs[1–3] exhibit hyperbolic anisotropy in mid-IR spectral region (3–30 µm) which has diverse applications like polarized IR imaging,[10] molecular sensing,[11,12] free space communication,[13] and quantum interference.[14] Unlike h-BN, which possesses uniaxial hyperbolic anisotropy (i.e., εₓₓ ≠ εᵧᵧ ≠ εᵣᵣ), α-MoO₃ exhibits in-plane hyperbolic anisotropy (i.e., εₓₓ ≠ εᵧᵧ ≠ εᵣᵣ) which is particularly beneficial for planar mid-IR optical devices.[15,16] With this motivation, there has been recent interest in developing flat optics based on vdw layered materials which can be integrated with chip-scale platforms using vdW integration, operational at room temperature, and does not involve complex lithographic fabrication techniques.[17–20]

We present an application of α-MoO₃ in the mid-IR spectral region, that is, from 545–1000 cm⁻¹ (around 10–18 μm), as a thin film polarizer that reflects the light with one state of polarization while transmitting the light with its orthogonal state of polarization. Here, single-crystal α-MoO₃ thin films are synthesized using physical vapor deposition (schematically shown in Figure 1a) and are transferred on top of potassium bromide (KBr) window, purchased from Edmund Optics, using mechanical exfoliation technique. In-plane anisotropy of the synthesized α-MoO₃ thin film is confirmed using polarization-resolved Raman spectroscopy. We optimize the mid-IR optical responses of α-MoO₃, mainly transmittance and reflectance, as a function of the thickness. Optimum thickness of α-MoO₃ based IR polarizer is found to lie in the range of 2.5–3.5 μm for which the extinction ratio (ER) is obtained more than 75

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N. R. Sahoo, S. Dixit, A. K. Singh, A. Kumar
Laboratory of Optics of Quantum Materials
Physics Department
Indian Institute of Technology Bombay
Mumbai, Maharashtra 400076, India
E-mail: anshuman.kumar@iitb.ac.in
S. H. Nam, N. X. Fang
Department of Mechanical Engineering
Massachusetts Institute of Technology
Cambridge MA 02139, USA
E-mail: nicfang@mit.edu

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and 10 dB in a broad mid-IR spectral region, respectively for reflection and transmission geometry with remarkable operational bandwidth and degree of polarization (DOP) in long-wavelength IR regime. Moreover, to the best of our knowledge, this is the first work where the optical response of $\alpha$-MoO$_3$ is studied above room temperature, to determine the operating temperature tolerance for the $\alpha$-MoO$_3$ thin-film based polarizer device. We observe that the ER and DOP of $\alpha$-MoO$_3$ thin films retain their values up to a temperature of 140 °C. We explain these experimental results through extensive full wave simulations of Maxwell’s equations and via complementary measurements using temperature dependent X-ray diffraction and Raman spectroscopy.

2. Results and Discussion

We first confirm the structure of our fabricated crystals. Representative high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analysis of synthesized thin films are shown in Figure 1b–d. The estimated values of in-plane lattice constants are around 3.69 and 3.97 Å. Further structural information of synthesized thin films is investigated via X-ray diffraction (XRD) pattern (shown in Figure 1e) which shows sharp diffraction peaks at the 2θ values of 12.48°, 25.48°, and 38.76° corresponding respectively to (020), (040), and (060) planes of $\alpha$-MoO$_3$.[21] Out of plane lattice constant is found around 14.14 Å using Bragg’s Law.[22] The values of lattice constants evaluated from XRD, HRTEM, and SAED match closely with the lattice parameters of the orthorhombic phase of MoO$_3$ (i.e., $\alpha$-MoO$_3$).[1,21] Scanning electron micrograph (SEM) image of the synthesized $\alpha$-MoO$_3$ thin films on the silicon substrate is shown in Figure 1f, which reveals the rectangular shape of flake. Chemical composition of the thin films is examined using X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy (XPS) spectrum exhibits binding energies of Mo 3d doublets at 232.7 eV (for 3d$_{5/2}$) and 235.8 eV (for 3d$_{3/2}$) which is associated with the VI oxidation state of molybdenum (Figure 1g). These peaks indicate negligible oxygen vacancies in the synthesized $\alpha$-MoO$_3$ thin films.[23] These investigations substantiate the fact that the chemical and structural properties of our fabricated rectangular-shaped $\alpha$-MoO$_3$ thin films using thermal physical deposition technique are as expected.

Next, we explore the anisotropy of $\alpha$-MoO$_3$ thin films using polarization-resolved Raman spectroscopy. The $\alpha$-MoO$_3$ unit cell follows the $D_{3h}^5$ space group[24] which consists of 4 Mo and 12 O (total 16 atoms). Hence, there are 48 phonon...
modes at the center of the Brillouin zone having the following decomposition:\cite{25}

\begin{equation}
\Gamma^{vb} = 8A_g \oplus 4B_{2g} \oplus 4B_{1g} \oplus 8B_{1u} \oplus 4A_u \\
\oplus 7B_{2u} \oplus 7B_{3u} \oplus 3B_{1u}
\end{equation}

Out of these modes, \(A_{1g}, B_{2g}, B_{2g} \) and \(B_{3g} \) are Raman active modes. Since \(\alpha-\text{MoO}_3 \) has an orthorhombic crystal structure, it has different Raman modes associated with phonons along different crystallographic directions. Here, we focus on the \(B_{2g} \) mode (at 282 cm\(^{-1}\)) which is the wagging mode of O-Mo-O atoms, \(A_g \) mode for the translational vibration of MoO\(_6\) chain along the \(y\)-crystal direction (called \(A_{1g} \) mode) at 157 cm\(^{-1}\), and \(A_{2g} \) mode from asymmetric stretching of O-Mo-O atoms along the \(x\)-crystal direction is at 818 cm\(^{-1}\) (called \(A_{2g} \) mode).\cite{26} If \(e_i \) and \(e_j \) are the polarization unit vectors along the incident and scattered light, then Raman intensity is given by \(I = |e_i \cdot R \cdot e_j|^2 \).

The angular dependence of the Raman intensity for \(A_g \) and \(B_{2g} \) modes can be obtained from

\begin{equation}
R(A_g) = \begin{pmatrix}
A & 0 & 0 \\
0 & B & 0 \\
0 & 0 & C
\end{pmatrix}
\end{equation}

\begin{equation}
R(B_{2g}) = \begin{pmatrix}
0 & 0 & E \\
0 & 0 & 0 \\
E & 0 & 0
\end{pmatrix}
\end{equation}

Here, \(A, B, C, \) and \(E \) represent the strength of Raman tensor's elements. Intensity of these Raman modes can be theoretically captured via the Raman tensor:\cite{26, 28}

\begin{equation}
I(A_g) \propto (A \cos^2 \beta + B \sin^2 \beta)^2
\end{equation}

\begin{equation}
I(B_{2g}) \propto E^2 \sin^2 2\beta
\end{equation}

Here, \(\beta\) represents the angle between the [100] crystal direction and the polarization state of laser. In Figure 2a, our experimental Raman spectra show \(A_{1g}, B_{2g} \) and \(A_{2g} \) modes at 156, 282, and 818 cm\(^{-1}\) respectively for \(\beta = 0^\circ, 45^\circ, \) and \(90^\circ \). These characteristic Raman modes of \(\alpha-\text{MoO}_3 \) show a variation in the Raman intensities as a function of \(\beta\), which is attributed to the dependence of Raman intensity tensor on the polarization state of incident laser light and the crystallographic directions. Figure 2b–d present polar plots for theoretical and experimental Raman intensities of \(A_{1g}, B_{2g} \) and \(A_{2g} \) respectively. Theoretical variation of Raman intensities of these modes is calculated using Equation (4). \(B_{2g} \) mode has the angular periodic intensity variation of \(90^\circ \) (four lobes), and the orientation of two-lobed \(A_g \) modes are orthogonal to each other. For \(A_{1g}, A_{2g} \) mode, the ratio of \(A \) and \(B \) are taken as 0.35 and 2 in the Equation (4), respectively, to fit our experimental polarization-resolved Raman data. Here, the condition \(A > B \) results in the formation of a two-lobed main axis parallel to the \(x\)-axis (i.e., [100] direction). On the other hand, \(A < B \) leads to a two-lobed main axis perpendicular to the \(x\)-axis. These results validate that synthesized \(\alpha-\text{MoO}_3 \) flakes exhibit the expected crystallographic orientation with strong in-plane anisotropy, which is crucial for the functioning of our proposed IR polarizer.

The optical response of a thin film depends on its thickness and hence it is a vital parameter for the polarizer. Therefore, we consider different thicknesses of \(\alpha-\text{MoO}_3 \) thin film from the flakes transferred using mechanical exfoliation technique and investigate their mid-IR optical responses. Thicknesses of \(\alpha-\text{MoO}_3 \) thin films are measured using a profilometer and are shown in Figure S2, Supporting Information for three representative samples D1, D2, and D3, respectively. The mechanical exfoliation technique results in the transfer of vdW flakes with nonuniform thicknesses. For instance for samples D1, D2, and D3 thicknesses are found to be in

![Figure 2. Polarization resolved Raman scattering spectroscopy. a) Polarization resolved Raman spectra of \(\alpha-\text{MoO}_3 \) thin film at \(\beta = 0^\circ \) (green), \(45^\circ \) (blue), and \(90^\circ \) (red) exhibiting characteristic phonon energies of \(\alpha-\text{MoO}_3 \). Polar plot of angle resolved normalized Raman intensities for b) \(A_{1g}, c) B_{2g} \) and d) \(A_{2g} \) modes of \(\alpha-\text{MoO}_3 \).](image-url)
Next, we explore the mid-IR optical responses of α-MoO$_3$ thin films. α-MoO$_3$ exhibits three RBs in the spectral range of 544.6 to 850.1 cm$^{-1}$ (RB-1), 821.4 to 963 cm$^{-1}$ (RB-2), and 956.7 to 1006.9 cm$^{-1}$ (RB-3), where the real part of dielectric permittivity is negative along [001], [100] and [010] crystal direction of α-MoO$_3$, respectively.[27] Due to the in-plane hyperbolic anisotropy of α-MoO$_3$ along [100] and [001] crystallographic directions in the RBs, α-MoO$_3$ reflects light which is linearly polarized along one direction. In contrast, the light with an orthogonal polarization state gets transmitted as shown schematically in Figure 3a. Hence, α-MoO$_3$ exhibits anisotropic reflectance and transmittance for s- and p-polarized light in the RB-1 and RB-2, respectively, making it a suitable candidate for reflecting as well as transmitting type mid-IR polarizer.

We validate this concept using a finite element method based on full-wave numerical simulation, COMSOL MULTIPHYSICS,[28] for a representative thickness of 2.5 μm. We plot the magnitude of normalized electric field distribution at the frequency 620 cm$^{-1}$ (i.e., RB-1) for incident electric field polarization along [100] and [001] crystal directions of α-MoO$_3$ (shown in Figure S3, Supporting Information). When the incident electric field is along [001] direction (s-polarized), it is majorly reflected by α-MoO$_3$, and a small amplitude of the incident light is transmitted. In contrast, when the incident electric field is along [100] direction (p-polarized), a small amplitude of the incident electric field is reflected by α-MoO$_3$, and majorly transmits the incident electric field. We further develop a transfer matrix method (TMM) based semi-analytical model to estimate the optical responses for p- and s- polarized light incident on α-MoO$_3$ as a function of thickness and frequency. Details of the model parameters with reflectance and transmittance color plots are provided in Section S1, Supporting Information. The findings from TMM corroborate our numerical simulation results. To quantify the performance of α-MoO$_3$ based polarizer, we define ER as

$$\text{ER} = 10 \log \frac{I_p}{I_s}$$

where $I_p$ and $I_s$ are the reflectances (transmittances) of p-polarized and s-polarized light respectively. Figure 3b,c presents ER as a function of thickness and frequency for reflected and transmitted light, respectively, which are calculated using the TMM approach. Optimum thickness of the α-MoO$_3$ based polarizer for large ER and bandwidth is found to be in the range of 2.5 to 3.5 μm. Corresponding theoretical reflectances and transmittances color plots as a function of frequency and thickness have been shown in Figure S4, Supporting Information. At higher α-MoO$_3$ thicknesses, Fabry–Pérot (FP) modes appear for p-polarized incident light within RB-1 spectral region.[29] Furthermore, the theoretical transmittance for s-polarized light in RB-1 spectral region is significantly small (0.001) obtaining which is practically difficult due to noise. Therefore, a reduction of experimental ER is expected in the RB-1 spectral region for transmission as well reflection mode.

Figure 3. Figures of merit of mid-IR polarizer in the transmission and reflection geometry. a) Schematic illustration of α-MoO$_3$ thin film as a reflecting and transmitting type polarizer device. b,c) shows theoretical ER as a function of thickness and frequency for reflected and transmitted light respectively. d,e) represent the ER and DOP of IR polarizer based on α-MoO$_3$ thin films in reflection and transmission geometry, respectively, for Samples D1–D3. Solid lines and dashed lines correspond to ER and DOP respectively.
Figure 3d,e represents the ER and DOP, respectively which is obtained from the experimentally observed polarization-resolved reflectance and transmittance spectra for samples D1–D3 in both RBs of α-MoO3. These spectra show some deviation from their theoretical counterpart (Figure S4, Supporting Information). This discrepancy can be attributed to multiple factors. First, there are optical losses in the KBr substrate due to contamination from the flake transfer method. Second, we obtain a range of thicknesses from the mechanical exfoliation technique. Since FP modes, observed for p-polarized light in RB-1 spectral region, strongly depend on the thickness of α-MoO3, range of thickness might lead to modulation of FP modes and consequently the optical responses for p-polarized light in RB-1 spectral region. Hence the theoretical spectrum deviates from the experimental spectrum. We believe that with an improvement in transfer technique, this discrepancy can be resolved and some performance metrics close to the theoretical limit can be obtained.

To evaluate the operational bandwidth of the proposed IR polarizer, we chose characteristic parameters like ER, so that the experimentally occurred optical losses are compensated in both polarization states of light and give us realistic operational parameters. The ER thresholds for RB-1 and RB-2 spectral regions are considered as 7.5 and 10 dB, respectively, to evaluate the operational bandwidth. In the reflection geometry (Figure 3d), a shift of operational spectral bandwidth is observed in the ER spectra toward lower frequency as we go from D1 to D3. This is due to the higher thicknesses of α-MoO3 from flake D1 to D3, which leads to the change in frequency of FP modes in the RB-1 spectral region resulting in the shift of operational bandwidth in the RB-1 spectral region. Optimum thickness is closest to that of sample D2, which provides a larger operational bandwidth (2.75 µm) compared to D1 (0.73 µm) and D3 (2.04 µm) in the RB-1, a trend which is consistent with our theoretical predictions. However, we observe no significant change in the operational bandwidth in the RB-2 spectral region for samples D1–D3 and operational bandwidth is found around 1.0 µm. Furthermore, the DOP spectrum, given by \((I_s - I_p)/(I_s + I_p)\), is also shown for D1–D3 in Figure 3d. The DOP informs us about the state of polarization of output light in which ±1 represents completely polarized light, and 0 represents unpolarized light. In the proposed operational bandwidths, DOP is observed to be more than 0.75 and ~0.85 in RB-1 and RB-2, respectively, suggesting nearly linear polarized light at the output. In our configuration, ± signs in DOP correspond to s- and p-polarization state of output light respectively.

Experimentally measured figures of merit in transmission geometry, displayed in Figure 3e, show almost similar bandwidths for samples D1 and D2 for ER values of 7.5 and 10 dB in RB-1 and RB-2, respectively. However, ER remains below 7.5 dB in most of RB-1 for D3. This is because sample D3 majorly consists of flakes with thickness around 4.0 µm, which is suboptimal, as discussed earlier. FP modes in the higher thicknesses lead to increased absorption of p-polarized light in RB-1 and result in the reduction of transmittance, which is evident from reflectance and transmittance spectra shown in Figure S5, Supporting Information. Consequently, we observe the reduction of ER for sample D3. Operational bandwidths in transmission geometry are found nearly the same for D1 and D2 in RB-1 (around 4.5 µm) and RB-2 (around 1.5 µm) spectral region. These operational bandwidths in RB-1 and RB-2 spectral regions for reflection and transmission geometry have been tabulated in Table 1 for samples D1–D3. Similarly, DOP in the proposed bandwidth for transmission geometry is found more than ~0.75 and 0.85 in RB-1 and RB-2, respectively, suggesting nearly linear polarized light at the output. Optimum thickness of α-MoO3 for large ER and operational bandwidth is found to be around 2.5 to 3.5 µm.

For the first time to our knowledge, our work explores the above room temperature thermal tolerance of the optical responses of α-MoO3 thin films. Temperature threshold is a critical parameter for optical devices in the mid-IR since the environment and intense IR sources can induce heating and raise the temperature of the polarizer material. In the mid-IR spectral region, optical phonons govern the optical response of α-MoO3 and the lifetime of optical phonons typically decreases with the increase in temperature.\(^{30}\) Hence, an enhancement in the optical losses within the material is expected at elevated temperatures, which may lead to deterioration in device performance. Second, at high temperatures, the optical phonon frequencies can also shift,\(^ {33}\) which may limit the bandwidth of the device. To ensure the temperature stability of α-MoO3 thin film, we first perform temperature-dependent X-ray diffraction up to 160 °C, which is shown in the Figure S6, Supporting Information. We found a maximum of around 0.4% out of plane lattice expansion which is reversible on cooling down to room temperature. Subsequently, we perform temperature-dependent polarization-resolved FTIR reflectance and transmittance investigation of samples D1–D3 for temperature range from 25 to 140 °C. Polarization-resolved reflectance and transmittance of D1–D3 are shown in Figures S7 and S8, Supporting Information. It is worth mentioning that the temperature of heatable stage in our FTIR system is limited to 140 °C and hence we are not able to examine the threshold of α-MoO3-based mid-IR polarizer. We observe only a slight variation in the optical responses when the temperature is increased from 25 to 140 °C, which might be associated with the reduction of phonon lifetimes.\(^ {30}\) Although the observed intensities are nearly constant within 8–10% w.r.t. temperature, we have not observed any monotonic trend of intensities. It could be due

| Table 1. Operational bandwidth for Samples D1–D3 in both RBs of α-MoO3 in reflection and transmission geometry. |
| Samples | Reflection bandwidth [cm\(^{-1}\)] | Transmission bandwidth [cm\(^{-1}\)] |
|--------|-----------------|-----------------|
| D1     | 694–731         | 892–977         |
|        | 545–726         | 810–924         |
| D2     | 571–678         | 900–977         |
|        | 545–726         | 815–928         |
| D3     | 545–613         | 892–972         |
|        | 586–608         | 847–948         |
to the noise resulting from the finite thickness KBr. Furthermore, knife-edge aperture of the FTIR with rough edges might also invoke diffraction-originated noise in the spectrum. These noises mask the expected small variations in the intensities, and hence the presence of any monotonic trend w.r.t. temperature cannot be resolved.

The ER in the reflecting type polarizer as a function of temperature and frequency is shown in Figure 4a–c for samples D1–D3, respectively. We found that ER remains above the threshold values in RB-1 and RB-2 spectral region for the temperature up to 140 °C. Furthermore, DOP for samples D1–D3 are also found nearly similar to room temperature values for temperature up to 140 °C as shown in Figure 4d–f. Similarly, ER and DOP for samples D1–D3 of transmission type polarizer are shown in Figure 5a–c, and Figure 5d–f, respectively, where ER for D1 and D2 withhold its threshold up to temperature 140 °C (Figure 5a,b) in RB-1 spectral region. Furthermore, the operational bandwidths in both RBs remains almost similar in the entire temperature range. Since sample D3 exhibits ER below threshold even at room temperature due to the higher α-MoO$_3$ thickness, ER of this sample also remains below threshold in most of RB-1 spectral region at higher temperatures as shown in Figure 5c. Moreover, DOP in the transmission type polarizers for samples D1 and D2 remains more than −0.75 and 0.85 in RB-1 and RB-2, respectively, up to 140 °C. Additionally, we investigate optical responses of flake D1 as a function of heating time to examine the stability with operational time duration at 140 °C (shown in Figure S9, Supporting Information), which suggests the performance of α-MoO$_3$ based mid-IR polarizer is stable also as a function of this variable. From these temperature-dependent FTIR investigations, we conclude that α-MoO$_3$ thin film based reflecting and transmission type IR polarizers can retain their figures of merit (ER and DOP) up to 140 °C while retaining similar operational bandwidths in both RBs. Temperature dependent XRD studies confirm that α-MoO$_3$ crystal structure can withstand temperature 140 °C with a reversible 0.4% of out the plane lattice expansion.

3. Conclusion

In this work, we investigated the optical properties of large-scale fabricated single crystal α-MoO$_3$ films for application toward mid-IR polarizer in reflection and transmission geometry. Our polarization-resolved Raman studies confirm the inherent in-plane anisotropic nature of the synthesized flakes. Polarization properties of α-MoO$_3$ films in the mid-IR region are attributed to their strong in-plane hyperbolic anisotropy. We found optimum thickness of α-MoO$_3$ films for efficient mid-IR polarizer to be in the range of 2.5 to 3.5 μm in which ER is observed to be more than 7.5 dB in RB-1 and more than 10 dB in RB-2 spectral region. Operational bandwidth at optimum thickness is found around 2.75 and 1.0 μm in RB-1 and RB-2 spectral region, respectively, for reflection type polarizer and around 4.5 and 1.5 μm in RB-1 and RB-2 spectral region, respectively, for transmission type polarizer. To the best of our knowledge, temperature-dependent studies for the optical response of α-MoO$_3$ thin films in the mid-IR have been
carried out above room temperature for the first time. This study confirms that our proposed \( \alpha \)-MoO\(_3\) based polarizer device retains excellent reflectance and transmittance characteristics with a temperature tolerance up to \((140 ^\circ C)\). This work affirms the potential of sub-wavelength vdW thin film of \( \alpha \)-MoO\(_3\) for miniaturized mid-IR optical devices without using any complicated lithography techniques and can be easily integrated onto the chip-scale platform. This study further opens up the application arena of vdW natural hyperbolic crystals for lithography-free alternatives for other exotic optical functionalities such as quantum interference,\(^{14}\) sensing,\(^{32}\) planar hyperlensing,\(^{33}\) and thermal emission control.\(^{34}\)

Although we have focused on the mid-IR polarizer application of \( \alpha \)-MoO\(_3\), a promising field—twist-optics\(^{35-40}\)—has shown a plethora of unusual polaritonic phenomena via introducing twist-angle within a stack of biaxial hyperbolic vdW crystals. The far-field optical response of such Moiré systems can be useful for infrared optical devices relying on twist angle dependent optical chirality,\(^{41}\) cross polarization transmittance, and anomalous refraction.\(^{42}\) Further functionality can be explored in heterostructures of these in-plane hyperbolic crystals with other photonic materials such as SiC\(^{43,44}\) where the exotic phenomena of switching of forbidden directions has been reported.

4. Experimental Section

Deposition of \( \alpha \)-MoO\(_3\) Thin Films: Fabrication of \( \alpha \)-MoO\(_3\) thin films had been carried out here using thermal physical evaporation technique\(^{21}\) in a two-zone split-furnace as shown schematically in the Figure 1a. Briefly, 0.1 g of MoO\(_3\) powder (Sigma-Aldrich) with a purity of 99.99 had been kept in a cleaned quartz boat at zone-1 (800 \(^\circ C\)) and a cleaned silicon substrate was kept around 15 cm away at zone-2 (600 \(^\circ C\)) as shown in the Figure 1a. Heating rate for both zones was kept around 10 \(^\circ C\) min\(^{-1}\). Furnace was kept at target temperature for 120 min and then cooled down to room temperature naturally. This process resulted in the deposition of flakes on a silicon substrate and free-standing thick single-crystal flakes on the wall of the quartz tube. Next, the mechanical exfoliation technique of free-standing flakes of \( \alpha \)-MoO\(_3\) using scotch-tape was used to obtain the desired thickness of \( \alpha \)-MoO\(_3\) thin film and transfer it on a KBr window, act like substrate in this case, using thermal release tape.

Structural Characterization of \( \alpha \)-MoO\(_3\) Thin Films: HR-TEM and SAED pattern was obtained by FEI Tecnai G2, F30 with an acceleration voltage of 300 kV. Temperature-dependent structural properties of \( \alpha \)-MoO\(_3\) thin films were studied from Rigaku X-ray diffractometer using Cu-K\(\alpha\) radiation (1.541 Å), operated at 40 kV of potential and 40 mA of current, in the 2\(\theta\)-\(\omega\) mode with a scan rate of 6 \(^\circ\) min\(^{-1}\). The samples were heated at a rate of 10 \(^\circ C\) min\(^{-1}\) with 10 min of stay time at target temperature. Morphology of \( \alpha \)-MoO\(_3\) thin-films on silicon substrate was observed using JEOL-JSM scanning electron microscope operated at an accelerating voltage of 20 kV in the secondary electron mode.

XPS was performed using Kratos Analytical, Axis Supra for elemental composition analysis. The spectrometer was calibrated with respect to the binding energy of 1 s of carbon at 285.0 eV. Thickness profiles of various deposited and transferred flakes were investigated using Bruker’s DekTak XT stylus profilometer. Raman spectroscopy was carried out in back-scattering geometry using Horiba’s Jobin Yvon Lab-Ram 800 at room temperature. A 532 nm solid-state laser line was used as an excitation source and a 100× long working distance objective with a numerical aperture (NA) of 1.25 was used for focusing the laser beam to a spot size of \( \approx 0.5 \mu \)m. Raman spectrometer was initially calibrated using Raman active optical mode of crystalline silicon.
at 520.70 cm$^{-1}$. An analyzer was placed in the path of back-scattered light before the spectrometer’s entrance, which allowed to analyze the Raman shift parallel or perpendicular to incident laser light. Rotation of flake method was adopted using rotational stage keeping the polarization state of incident laser light fixed.

**FTIR Spectroscopy:** Mid-infrared optical response of the α-MoO$_3$ thin films were studied in the 520–1000 cm$^{-1}$ spectral region using Bruker Hyperion-3000 FTIR microscope equipped with Bruker Vertex 80 spectrometer. Temperature-dependent studies were carried out up to 140 °C with an interval of 20 °C using a Hyperion heatable sample holder, and a Pt100 resistor was connected for sensing the current temperature. Temperature control unit used a digital PID algorithm for controlling the temperature. Stay time at the target temperature was kept at 10 min. The IR light was illuminated using a 15× Cassegrain objective with a NA of 0.40 and an average off-normal incidence angle of about 17°. Spectrum was recorded with the help of a wideband MCT (mercury cadmium telluride) detector at the spectral resolution of 2 cm$^{-1}$ and 256 number of scan. Flakes were kept in such a manner that the X-axis of the FTIR instrument was parallel to the [100] direction of α-MoO$_3$. The polarization-dependent studies were carried out using a KRS-5 based IR polarizer. Here, reflectance spectra were collected with respect to the gold background in the back-scattering geometry, and transmittance spectra were collected with respect to the air background. A knife-edge aperture was set with an area 90 μm × 130 μm for the selection of area on α-MoO$_3$ flake. All FTIR spectra were smoothed by weighted adjacent averaging from nine points to remove noise.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

2D materials, hyperbolic in-plane anisotropy, mid-IR polarizer, natural hyperbolic materials, van der Waals crystals

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