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1 Introduction

Metal oxyhalides are a family of emerging two-dimensional materials with a general formula of MOX (O: oxygen; X: halogen; M: metal) and usually present layered structures composed of buckling M–O bilayers sandwiched by two X layers.¹ Due to their diverse chemical compositions, these bulk layered compounds possess a variety of unique properties. TiOX is a Mott–Hubbard insulator, which implies resonating valence bonds and high temperature superconductivity under doping^{2,3} as well as strain-induced insulator-to-metal transformations.^{4,5} Likewise, VOCl has been considered as a multiorbital Mott insulator⁶ and shows an antiferromagnetic order at low temperatures.⁷ FeOCl is also a low-temperature antiferromagnet^{8,9} and indicates potential applications in environmental management.^{10–12} Recently, two-dimensional materials have received continuous attention owing

Pressure-mediated structural phase transitions and ultrawide indirect-direct bandgaps in novel rare-earth oxyhalides[†]

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Ultrawide bandgap semiconductors are fundamentally important in solid-state lighting, transparent electrodes and power electronics, but their 2D forms are rarely reported and less studied. By means of *ab initio* simulations, we predict new trigonal YOBr and monolayered crystals with ultrawide bandgaps and exceptional properties. It is demonstrated that trigonal YOBr is energetically, dynamically and mechanically stable and shows lower energy compared with other known experimental phases. We present that, under hydrostatic pressure, the bulk YOBr crystal undergoes a structural transformation from $R\bar{3}m$ to P4/nmm, accompanied by an indirect-direct band transition. By further exploring relevant metal oxyhalides MOX (M = Sc/Y and X = Cl/Br), we suggest that, owing to the small exfoliation energy, the monolayers promise experimental fabrication by mechanical cleavage, as for graphene. These MOX monolayers possess excellent stability, large bandgaps and high carrier mobilities. We reveal interesting indirect-direct bandgap transitions in uniaxially strained ScOCl and trigonal YOBr monolayers. In addition, we highlight that remarkable ultraviolet light absorption and appreciable band edges render these MOX monolayers great candidates for potential applications in UV-electronics and photocatalysis. Our findings open a new avenue to explore phase transitions in rare-earth oxyhalides under pressure/strain and provide promising ultrawide-bandgap semiconductors for future optoelectronic devices.

to their novel tunable properties and various potential applications.^{13–20} 2D forms of metal oxyhalides possess exceptionally different properties from their bulk counterparts. For instance, the CrOX monolayers have been predicted to exhibit large ferromagnetic ordering, great spin polarization and high Curie temperature,^{21,22} while 2D BiOX, InOI and GaOI were suggested as promising photocatalysts^{23,24} and UV photodetectors.²⁵

As important members of the layered metal oxyhalides family, rare-earth oxyhalides have many interesting properties and useful functionalities. Bulk ScOCl and ScOBr were found to crystallize in an orthorhombic FeOCl-type structure (space group no. 59, *Pmmn*).^{26,27} Many of the lanthanide oxide halides share the same crystal symmetry as tetragonal PbFCl (space group no. 129, *P4/nmm*),^{28,29} while some of them have trigonal YOF- or SmSI-type structure (space group no. 166, $R\bar{3}m$).²⁶ The trigonal and tetragonal YOCl crystals have been experimentally prepared.³⁰ However, for bulk YOBr, only a tetragonal phase has been reported.³⁰ To date, the existence of the trigonal YOBr crystal is still unknown; the possible phase transitions and underlying mechanisms in these YOX crystals remain unclear. In addition, a comprehensive understanding of their 2D forms is still lacking.

In this work, using *ab initio* calculations, we investigated the crystal structures and phase transitions of the bulk YOX

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crystals, as well as the exceptional properties of MOX monolayers. We first identified trigonal YOBr as a new stable compound according to the calculated formation energy, elastic tensors and phonon dispersions. Pressure-induced phase-transitions in bulk YOX crystals from $R\bar{3}m$ to P4/nmmhave been revealed from the equation of states. Furthermore, we suggested that the MOX monolayers are highly stable ultrawide bandgap semiconductors with high carrier mobility and should be prepared experimentally from mechanical exfoliation. Under uniaxial strains, indirect-direct bandgaps can be realized in the ScOCl and trigonal YOBr monolayers. Strong light absorption in ultraviolet wavelengths and appreciable band edges of these MOX monolayers indicate that they have great potential applications in UV electronic devices and photocatalysts.

2 Computational details

All of the calculations were performed using a plane-wave basis projector-augmented wave method³¹ as implemented in the Vienna Ab initio Simulation Package (VASP).32 The density functional dispersion correction (D3-Grimme)³³ was adopted for the van der Waals (vdW) interactions. A kinetic energy cutoff of 450 eV was set for plane-wave basis. The convergence criterion of total energy was 10⁻⁶ eV in self-consistent calculations and that of residual forces on atoms was 10^{-2} eV Å $^{-1}$ for geometry optimization. Uniform k-grids with a reciprocal spacing of 0.02 were generated to sample the Brillouin zones. A vacuum spacing of 20 Å along the z axis was applied to avoid interactions between adjacent slabs. Phonon calculations were performed using a $6 \times 6 \times 1$ supercell with density functional perturbation theory,³⁴ for which the PHONOPY code³⁵ was employed. The 4 \times 4 \times 1 supercell was used to simulate the adsorption of the water molecule. The exchange-correlation functional was given by generalized gradient approximation (GGA) by Perdew-Burke-Ernzerhof (PBE)³⁶ and with corrections for strong correlation of 3d electrons in the Dudarev method³⁷ (GGA+U) or the hybrid functional by Heyd-Scuseria-Ernzerhof (HSE06).³⁸ The U values for the 3d electrons of Sc and Y are 10 and 5.7 eV, respectively, which were determined by adjusting electronic bandgaps to available data from previous theoretical study³⁹ and our HSE06 calculations. Time-dependent Hartree-Fock calculations (TDHF)^{40,41} on top of the HSE06 functional were adopted to obtain accurate dielectric functions.

3 Results and discussion

3.1 Bulk crystals under pressure

Bulk ScOCl and ScOBr crystallize in a FeOCl-type orthorhombic structure (Fig. 1(a)). YOCl and YOBr crystals possibly possess a PbFCl-type tetragonal structure (P-YOX, Fig. 1(b)) and YOF- or SmSI-type trigonal structure (R-YOX). Both the YOF- and SmSI-type structures (Fig. S1, ESI†) have the same $R\bar{3}m$ symmetry with tightly bound slabs. Each slab consists of homoatomic layers with the same sequence of X–M–O–O–M–X. The difference between two structures is only the stacking configuration

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Fig. 1 Crystal structures of the (a) orthorhombic ScOX with space group no. 59, *Pmmn*, (b) tetragonal YOX with space group no. 129, *P4/nmm* (P-YOX) and (c) trigonal YOX with space group no. 166, $R\bar{3}m$ (R-YOX), where the top and bottom parts are the top and side views, respectively. The unit cells are highlighted by solid lines. Metal, oxygen and halogen atoms are shown in yellow, blue and red, respectively. First Brillouin zones of (d) tetragonal and (e) trigonal YOX crystals.

of slabs (*i.e.*, ABC stacking for YOF and ACB stacking for SmSI). As the discrepancy of the calculated total energy between two structural types of bulk YOCl and YOBr is less than 1 meV, consequently, the YOF-type structures (Fig. 1(c)) with lower energy were used in the following calculations. The calculated lattice parameters and electronic bandgaps are listed in Table S1 (ESI[†]). Comparing with experiments, the GGA-PBE approach reproduces better lattice parameters than the GGA+*U* methods, therefore, all structural properties were calculated using the GGA-PBE functional, while the electronic band structures and effective mass were predicted from the GGA+*U* calculations, unless stated otherwise.

Since the trigonal phase of YOBr has never been prepared by experimentalists, we first assessed its lattice-dynamical stability from the predicted phonon dispersion spectrum. As shown in Fig. 2(a), no imaginary frequencies have been observed, indicating that the bulk R-YOBr crystal is dynamically stable. We then calculated elastic stiffness tensors based on Hooke's Law by performing six finite distortions on the crystals.⁴² The bulk, shear, Young's modulus and Poisson ratio are summarized in Table S2 (ESI[†]). Under the Born elastic stability conditions,⁴³ all of the ScOX and YOX crystals, including bulk R-YOBr, are mechanically stable. Interestingly, it is also found that the ground-state total energy of bulk R-YOX is always lower than that of P-YOX crystals as shown in Fig. 2(c), suggesting that trigonal R-YOBr is also energetically stable.



Fig. 2 (a) Phonon dispersions of R-YOBr bulk crystals. Total energy vs. volume for trigonal and tetragonal phases of (b) YOCl and (c) YOBr. Phase-transition pressures P_t are estimated by the common tangents. Electronic band structures and density of states of (d) R-YOBr and (e) P-YOBr crystals. The dashed line at 0 eV indicates the Fermi energy. The band edges are denoted by the arrows.

As the proposed trigonal R-YOBr crystal shows great dynamical, mechanical and energetical stability, it is thus expected to be synthesized from an experiment.

As external pressure often induces unexpected physical phenomena in the crystal,^{44–48} here we explored structural phase trainsitions of bulk YOBr and YOCl under hydrostatic pressure from the simulated equations of states (EOS). Fig. 2 describes the calculated total energy of the tetragonal and trigonal YOX phases at different volumes and the EOS fits according to the Murnaghan equation:⁴⁹

$$E(V) = E_0 + B_0 V_0 \left[\frac{(V/V_0)^{1-B'_0}}{B'_0(B'_0 - 1)} + \frac{1}{B'_0} \frac{V}{V_0} - \frac{1}{B'_0 - 1} \right],$$

where E_0 and V_0 are equilibrium energy and volume at zero pressure; B_0 and B_0' are bulk modulus and its pressurederivative at P = 0, respectively. B_0 and B_0' are determined by $B = -V(\partial P/\partial V)_T$ and $B' = (\partial K/\partial P)_T$, where $P = -(\partial E/\partial V)_S$. The Murnaghan equation remains satisfactory as the ratio V/V_0 is above ~90%.⁵⁰ Since our ground-state calculations were performed effectively at T = 0, the Gibbs free energy G = E + pV - TS is equal to the enthalpy H = E + pV. Consequently, a phase transition occurs at the pressure where the enthalpy change between initial and final phases is zero. That is, the transition pressure (P_t) could be given by the common tangent construction of the E-V curves. We eventually obtained the P_t values of ~1.58 and ~0.50 GPa for the phase transitions from $R\bar{3}m$ to P4/nmm in bulk YOCl and YOBr crystals, respectively. P_t is

Table 1 Physical quantities for trigonal (R) or tetragonal (P) structures of bulk crystals at zero pressure: equilibrium volume (V), structural parameters c/a and total energy (E_{tot}) in two formula units. B_0 is the bulk modulus calculated by fitting thermodynamic equations of the state (EOS) curve. Phase-transition pressures (P_t) are defined in the text. $\Delta V/V_0$ is the relative change of volume between R and P phases, where V_0 is the equilibrium volume of R-YOX at zero pressure

	YOCI		YOBr	
	R	Р	R	Р
$V(Å^3)$	116.50	100.63	126.20	122.77
c/a	2.46	1.69	2.60	2.17
$E_{\rm tot}$ (eV)	-46.13	-45.99	-44.77	-44.76
B_0 (GPa)	28.8	75.4	31.6	29.1
		R–P phase transitio	n	
$\Delta V/V_0$ (%)		-13.62		-2.72
$P_{\rm t}$ (GPa)		1.58		0.50

more evident in the enthalpy-pressure curves of two phases as shown in Fig. S2 (ESI[†]). The above energy-volume curves also present some other static properties, which are listed in Table 1. We noticed that the trigonal phases (R-YOX) possess lower ground-state energy and more loose structures. That is, the trigonal structures are more stable at zero temperature and pressure, while the tetragonal structures (P-YOX) are the highpressure phases. Compared with bulk YOCl, YOBr shows a much smaller difference between the trigonal and tetragonal phases on total energy, equilibrium volume and compressibility, resulting in a lower phase-transition pressure. As further illustrated in Fig. 2(d) and (e), the pressure-induced phase-transition in YOBr also accompanies a indirect-direct electronic band transformation, where the high-pressure tetragonal phase is presented by a direct bandgap semiconductor and the low-pressure trigonal one has a weakly indirect bandgap. The changes of the top valence bands are a contribution from the p electrons of oxygen and halogen atoms of YOBr, which is an obvious indication of atomic motions of anions (Table S3, ESI⁺) during the structural phasetransition under pressure and thus results in possible orbital reconstructions. The valence band maximum (VBM) is governed by the p electrons of O and Br atoms, where the conduction band minimum (CBM) is dominated by the Y-d electrons. As shown in Table S3 (ESI[†]), R-YOBr possesses shorter Y-Br bonds and longer Y-O bonds in comparison to P-YOBr, indicating that the Br atoms of R-YOBr and O atoms of P-YOBr could receive more electrons from Y atoms, and therefore the DOS of Br-p in R-YOBr and O-p in P-YOBr below the Fermi level are slightly larger, while the slightly different DOS on their CBM may be due to the different chemical bondings of O-Y-O.

3.2 Preparation and stability of monolayers

One of the mostly-used methods to fabricate 2D materials is mechanical cleavage or liquid exfoliation. To assess the possibility of preparing these monolayers from an experiment, we simulated the cleavage process (Fig. S3, ESI†) and estimated the exfoliation energy as shown in Fig. 3(a). Compared with the benchmark material graphite (0.31 J m⁻² in our previous work⁵¹), the calculated exfoliation energy of ScOX and R-YOX monolayers is much smaller, suggesting that they should be experimentally exfoliated from their bulk layered crystals, as for graphene. We also noticed that the tetragonal phases of YOX have a larger exfoliation energy than the trigonal ones, as the latter have longer interlayer distances and thus are easier for



Fig. 3 Calculated (a) exfoliation energy and (b) formation energy of MOX monolayers. The dashed line indicates the data of graphene.

mechanical cleavage. Obviously, the exfoliation energy of the P-YOCl (0.69 J m⁻²) is the largest among these crystals, but it is smaller than that of the experimentally prepared Ca_2N (1.08 J m⁻²) monolayer.⁵² Therefore, all of these 2D crystals are promising for fabrication in the lab. These findings also demonstrate the weak vdW interactions of ScOX and YOX monolayers, leading to great potential as heterostructural materials.

To confirm the energetic stability of the monolayers, we calculated their formation energy according to:

$$\Delta H = (E_{\rm t} - n_{\rm M} E_{\rm M} - n_{\rm O} E_{\rm O} - n_{\rm X} E_{\rm X})/n,$$

where E_t is the total energy of the MOX monolayers; E_M , E_O , and E_X are the total energy of rare-earth crystals, gaseous O_2 and Cl_2 molecules, as well as Br solids, respectively. As shown in Fig. 3(b), negative ΔH values are in the range of -3.2 to -2.8 eV, demonstrating that the formation of MOX monolayers is favourable. Moreover, single-layered R-YOX crystals with lower formation energy than the P-YOX monolayers indicate better thermodynamic stability of trigonal phases. Hence, all of the following calculations were performed for ScOX and R-YOX monolayers. Furthermore, the dynamical stability of ScOX and R-YOX was testified through phonon dispersion curves. As illustrated in Fig. S4 (ESI†), negligible imaginary frequencies (-2.9 to -4.1 cm⁻¹) were observed around the Γ points, suggesting that all of these monolayers are dynamically stable.

3.3 Monolayers under strain

Surprisingly, different from typically layered materials $(e.g. MoS_2)$ with diverse layer-dependent bandgaps, quantum confinement has little impact on the electronic bandgaps of these MOX crystals, as all of the MOX monolayers present very close bandgap values in comparison with their bulk counterparts (Tables S1 and S4, ESI⁺). The calculated electronic band structures and density of states are illustrated in Fig. 4. Apparently, the ScOX monolayers are ultrawide indirect bandgap semiconductors and R-YOX monolayers show weakly-indirect gaps. It is observed that the conduction band minima (CBM) of these 2D crystals are at Γ points and mainly contributed by the M-d and O-p orbitals, while their valence band maxima (VBM) locate at Y points for ScOX monolayers and around Γ points for the R-YOX monolayers, which are dominant by the p orbitals from oxygen and halogen atoms. It is interesting to note that the shapes of conduction bands in YOCl and YOBr monolayers are very similar, suggesting that they should have very close electron effective mass as confirmed by our prediction in Table S5 (ESI⁺). Due to the moderate effective mass and smallest deformation potential constant, the ScOBr monolayer exhibits a relatively higher hole mobility of $\sim 4086 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ along the x direction, while the R-YOBr monolayer possesses minimum effective mass and deformation potential constant, leading to the highest electron mobilities of \sim 2051 cm² V⁻¹ s⁻¹ and 1803 cm² V⁻¹ s⁻¹ along zigzag and armchair directions, respectively. The carrier mobilities of ScOBr and R-YOBr monolayers are higher than those of black phosphorus films,⁵³ while those of ScOCl and R-YOCl are comparable to that of the MoS₂ monolayer.⁵⁴ Since all MOX monolayers are ultrawide bandgap



Fig. 4 Band structures and total/partial density of states of (a) ScOCl, (b) ScOBr, (c) R-YOCl and (d) R-YOBr monolayers calculated by GGA+*U*. The Fermi level is set to zero indicated by the dashed line. The band edges are denoted by the arrows.

semiconductors with a broad bandgap range and high carrier mobilities, they have immense potential for electronic and optoelectronic devices in high-power, high-temperature, highfrequency and anti-radiation environments.

Strain engineering is an effective approach to modulate the crystal structures and electronic band structures of $2D^{55-57}$ and bulk⁵⁸⁻⁶⁰ materials. First, we confirmed that phase transitions between trigonal and tetragonal YOX monolayers are unlikely to occur under uniaxial strains, because the energy of P-YOX is always higher than that of R-YOX (Fig. S5, ESI[†]) which is different compared with their bulk crystals. Hence we continued to explore the strain effect on the electronic band structures of ground-state monolayers. In Fig. 5, the bandgaps of MOX monolayers under uniaxial strains demonstrate irregular variations, but large strain essentially decreases the bandgaps as a whole, except for the R-YOCl monolayer which exhibits a monotonic decrease of the bandgap from compressive to tensile strain. The strain response of ScOCl and ScOBr monolayers looks very similar. Interestingly, there are indirect-to-direct bandgap transitions in the ScOCl and R-YOBr monolayers under uniaxial strains. To further understand these phenomena and transitions, we calculated the band edges with respect to strains (Fig. S6, ESI⁺). Obviously, under strain, the decreasing bandgap of the R-YOCl monolayer is owing to almost monotonic shifts of the VBM and CBM, while the non-monotonic shifts of band edges (especially the VBM) result in irregular variations of bandgaps in the other MOX. Furthermore, it is noted that the strain-induced indirect-direct bandgap transitions are dominated by the top valence bands which consist of the p electrons of oxygen and halogen atoms (Fig. S7, ESI[†]). Therefore, the electronic properties of MOX monolayers can be effectively adjusted by applying external strain, which may lead to promising applications in flexible electronic devices.

3.4 Optical absorption and photocatalysis

Optical property is one of the most important physical characteristics of semiconductors. The calculations of dielectric



Fig. 5 Bandgaps of (a) ScOCl, (b) ScOBr, (c) R-YOCl and (d) R-YOBr monolayers under uniaxial strains from GGA+*U* calculations.

constants were performed using the time-dependent Hartree-Fock (TDHF) method, for TDHF calculations could provide a more valid and reliable optical response, which was certified in our previous work.⁶¹ As shown in Fig. 6(a and b), all of the MOX monolayers possess strong absorption in the ultraviolet spectrum. Many peaks within the energy range can be observed. The optical absorption edges of ScOCl and ScOBr monolayers are at the photon energy of about 3.8 and 3.0 eV along the x direction and then the absorption intensity varies with the increase of photon energy. It can be observed that several peaks appear in the range below the HSE06 bandgaps (6.4 and 5.3 eV), which is due to excitonic effects. The major peaks of ScOX monolayers appear in the range slightly higher than the bandgaps, approaching the maximum adsorption of 25-30%. In contrast, R-YOX monolayers exhibit optical absorption edges at the photon energy near their bandgaps and the maximum adsorption is up to 25%. Our results indicate that all absorption peaks of these 2D MOX along in-plane polarizations are located in the photon energy range above 3.1 eV, which is desirable for the practical applications in optoelectronic devices in the UV spectrum. Particularly, in the solar-blind spectrum region (200-280 nm) with the photon energy of 5.3-6.5 eV, MOX (especially YOX) monolayers possess favorable absorption. Since solar-blind deep-ultraviolet photodetection systems are commonly operated in harsh environments⁶² and ultrawide bandgap materials are usually suitable for highervoltage, high-frequency and high-temperature applications, the MOX possess a natural potential for solar-blind ultraviolet optoelectronic devices. Besides, the ScOX exhibits significant anisotropic absorption coefficients, resulting in possible utilization in polarized light sensors.

Ultrawide bandgap semiconductors were recently used as highly efficient photocatalytists for water splitting, which has a record external quantum efficiency of up to 96% when they were irradiated with ultraviolet light.⁶³ Fig. 6(c) depicts the





band edge alignments of MOX monolayers with respect to vacuum, as compared with the electrochemical potentials of the standard hydrogen electrode (-4.44 eV) and oxygen redox couple (-5.67 eV).⁶⁴ All of the MOX monolayers possess appreciable band edges, which cover the redox potentials in acidic (pH = 0) water, indicating their possibility to split water. Furthermore, the water redox potentials are greatly affected by the pH values.⁶⁴ The standard reduction potential for H^+/H_2O is derived from $E_{H^+/H_2O} = -4.44 + pH \times 0.059$ eV, while the oxidation potential for O_2/H_2O is expressed as E_{O_2/H_2O} = $-5.67 + pH \times 0.059$ eV. Thus, we also considered band alignments with the water redox potentials in a neutral (pH = 7) environment. The band edges of MOX monolayers are still in the appropriate positions. As most of the photocatalytic water splitting reactions occur at the surfaces of catalysts, we evaluated the adsorption energy of water molecules on the 2D MOX surfaces, which is defined as $E_{ad} = E(H_2O/MOX) - E(H_2O) - E(MOX)$, where $E(H_2O/MOX)$ is the total energy of the water-adsorbed MOX, and $E(H_2O)$ and E(MOX) are the total energy of an isolated water molecule and the pure 2D MOX, respectively. The results suggest that the adsorption energy of 2D MOX (-0.16, -0.15, -0.14 and -0.14 eV per water molecule for ScOCl, ScOBr, R-YOCl and R-YOBr, respectively.) is even smaller than that of the 2D InSe photocatalyst (-0.05 eV).65 The negative values imply the strong adsorption ability, which is favourable for the water-splitting reaction. Therefore, 2D MOX are potential candidates for photocatalytic water splitting under UV light irradiation in deep space.

4 Conclusion

In summary, based on *ab initio* calculations, we developed a comprehensive understanding of the crystal structures, phase stability, electronic structures and optical properties of rare-earth oxyhalides MOX (M = Sc/Y and X = Cl/Br). A new trigonal YOBr with the space group of $R\bar{3}m$ has been predicted and identified to be dynamically, mechanically and energetically stable. From the equation of states, we have shown that bulk YOCl and YOBr crystals undergo structural phase transitions from $R\bar{3}m$ to P4/nmm at moderate hydrostatic pressures of

1.58 and 0.5 GPa, respectively, which could be easily verified in diamond anvil cells by experiments. The calculated exfoliation energy of the MOX crystals is small enough (< 0.69 J m⁻²) for the experimental preparation of the monolayers by mechanical cleavage or liquid exfoliation. We have further demonstrated that 2D ScOX/R-YOX monolayers possess excellent stability, ultrawide bandgaps and high carrier mobilities. More interestingly, indirect-to-direct bandgap transitions could be realized in the ScOCl and R-YOBr monolayers under uniaxial strains. It has been highlighted that the MOX monolayers show strong ultraviolet light absorbance and appropriate band edges for photocatalytic water splitting. The exceptional properties of MOX monolayered crystals suggest their great potential applications in UV electronics.

Conflicts of interest

The authors declare that they have no conflict of interest.

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