Elastic properties, hardness, and anisotropy in baddeleyite IVTMO_2 ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$)

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In this article, we used plane-wave density functional theory to investigate the elasticity, anisotropy, and minimum thermal conductivities of baddeleyite type IVTMO_2 (m-TiO_2 , m-ZrO_2 , and m-HfO_2). The elastic constants and modulus, Poisson's ratio, hardness, sound speed, Debye temperature, and minimum thermal conductivities at high temperature were calculated. These calculations show that m-MO_2 is not superhard, with a hardness range of about 8–13 GPa. Among these materials, m-TiO_2 is the hardest, while m-HfO_2 is the least hard. Their elastic and plastic anisotropy are given in detail. Moreover, the m-HfO_2 thin film is the most likely to develop microcracks during preparation because it has the highest elastic anisotropy. Among the three dioxides, m-HfO_2 is the best thermal barrier because it has the lowest thermal conductivity.

INTRODUCTION

Triplet group-IVB transition metal dioxides (IVTMO_2) such as TiO_2 , ZrO_2 , and HfO_2 have attracted a great deal of attention in recent years [1–5] because of their extraordinary physical and chemical characteristics, including their high bulk modulus, high thermodynamic stability, high melting point, low diffusivity, and excellent adherence to supports. These compounds can form in a variety of crystal structures depending on the pressure, temperature, dopant content, and growth conditions, and they have wide applications ranging from superhard protective coatings to catalyst substrates. Furthermore, IVTMO_2 is a suitable replacement for high-performance microelectronic gate dielectrics [6,7].

There are many investigations on the properties of IVTMO_2 . For example, Cava *et al.* [8] found that doping Ta_2O_5 with TiO_2 increased its relative dielectric constant by four times. Debernardi [9] investigated the structural and vibrational properties of TiO_2 and HfO_2 , finding that the fluorite phases of both metal dioxides were structurally unstable. Zhao *et al.* [10] investigated the crystallization and phase transformation from tetragonal to monoclinic in ZrO_2

and HfO_2 thin films. Other researchers have investigated the transformation from monoclinic phase to tetragonal phase in HfO_2 [5], as well as its mechanical [11], optical, and elastic properties [12]. Even with this range of study, some properties of IVTMO_2 , particularly their mechanical properties, are not well understood. For example, elastic anisotropy in thin films usually leads to microcracks, and differences in thermal expansion between a film and matrix might induce a dropping of the film from the matrix.

Zhao *et al.* [10] reported that bulk ZrO_2 has three crystalline structures at normal pressure: cubic (2300–2680°C), tetragonal (1170–2300°C), and monoclinic (<1170°C). Bulk HfO_2 has only two crystalline structures: tetragonal (1750–2800°C) and monoclinic (<1750°C). The most abundant polymorph of TiO_2 found in nature is rutile, and at room temperature it is stable up to 12 GPa, where it directly converts to the baddeleyite-type (monoclinic) phase [13]. Because m-HfO_2 has a larger bulk modulus than the other two metal dioxides [12], it was expected to have high hardness. The bulk modulus was once thought to be good predictor of hardness. Although it is true that a hard material must have a high modulus [14], it is a common misconception that an incompressible material is a hard one. For example, osmium has only a twentieth the hardness of diamond, though its bulk modulus is comparable to diamond, making it one of the most incompressible materials known.

It is now well recognized that high bulk and shear moduli do not guarantee high hardness. Other factors—including high electron density, short bond length, high degree of covalent bonding, and near-isotropic deformation—usually dominate a material's intrinsic hardness [15]. Thus, it is important to thoroughly investigate baddeleyite-type IVTMO_2 (we henceforth refer to these m-MO_2 materials as m-TiO_2 , m-ZrO_2 , and m-HfO_2), especially their hardness, elasticity, and anisotropy. To our best knowledge, there are no systemic studies of monoclinic metal dioxides, which are stable at room temperature. In the past decade,

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first-principles calculations have been widely applied to predict the properties of materials and to guide the development of new materials. In the current study, we used first-principles calculations to investigate the elasticity, anisotropy, hardness, and minimum thermal conductivity of $m\text{-MO}_2$.

CALCULATION METHODS AND THEORY

Calculation parameters and model

The $m\text{-MO}_2$ has space groups of $P21/c$, and all the M atoms are group-IVB transition elements: Ti, Zr, or Hf. These materials have a hexagonal structure, high melting temperature, and four electrons in their outer shell. Thus, $m\text{-TiO}_2$, $m\text{-ZrO}_2$, and $m\text{-HfO}_2$ should have similar properties. The Wyckoff sites are $e3$: $4e$ (0.25, 0, 0.25), $4e$ (0.95, 0.22, 0.46), and $4e$ (0.538, 0.75, 0.46) for M, O(1), and O(2), respectively. Fig. 1 shows the crystal structure of $m\text{-MO}_2$.

We performed first-principles calculations based on density functional theory (DFT) [16] by using CASTEP [17] software. The exchange and correlation potentials were calculated with both the local density approximation (LDA) [18] and the Perdew–Burke–Ernzerhof method based on the generalized gradient approximation (GGA) [19]. The crystal wave function was expanded by the plane wave basis set, and the interaction potential for the ion core and valence electron was determined using the ultrasoft pseudopotential (USPP) [20] and the norm-conserving pseudopotential (NCPP) [21]. The plane wave cut-off energy in wave vector (K) space was 770 eV. We then performed Brillouin-zone integration with $8 \times 8 \times 8$ special Monkors–Park K points [22]. For structural optimization, we used the Broyden–Fletcher–Goldfarb–Shanno algorithm [23–26] to optimize the crystal structure model and the position of the atom in the lattice determining the stable structure with the lowest energy. When the total energy

was stabilized to within 5×10^{-6} eV, the force acting on each atom of cells after optimization was less than $0.01 \text{ eV } \text{\AA}^{-1}$, the residual stresses of the cell was less than 0.02 GPa, and the tolerance offset was less than $5 \times 10^{-4} \text{ \AA}$. Convergence was therefore achieved.

Elastic properties and their anisotropies

With the geometry optimized for each degree of freedom in the crystal structure, the lattice parameters agree with the experimental values. Next, the elastic constants and elastic modulus were calculated for each ground-state crystal through linear fitting of stress–strain curves. In general, the elastic constants were calculated using the stress–strain curve or ensemble averages of the fluctuations in stress. Here the elastic constants with respect to the finite strain are defined as follows [27]:

$$C_{ijkl} = \left(\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}} \right)_x,$$

where σ_{ij} and e_{kl} are the applied stress and Eulerian strain tensor, and X and x are the coordinates before and after the deformation, respectively. From this we obtain:

$$C_{ijkl} = c_{ijkl} + \frac{P}{2} (2\delta_{ij}\delta_{kl} - \delta_{ii}\delta_{jk} - \delta_{ik}\delta_{jl}),$$

$$c_{ijkl} = \left(\frac{1}{V(x)} \frac{\partial^2 E(x)}{\partial e_{ij} \partial e_{kl}} \right)_x,$$

where δ and C_{ijkl} are the finite strain and the second-order derivatives of total energy with respect to the infinitesimal strain, respectively. Because the stress and strain tensors are symmetric, the elastic constants have 21 independent components for the triclinic phase, and they are reduced to 13 components for the monoclinic phase. Thus, for baddeleyite-type MO_2 , the elastic stiffness constants matrix is given by:

Figure 1 The crystal structure of monoclinic $m\text{-MO}_2$ ($M=\text{Ti}$, Zr , or Hf). The small red spheres are O atoms, and the large blue spheres are M atoms.

$$C_{ij} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{bmatrix}.$$

The corresponding matrix of elastic compliance constants is given by:

$$S_{ij} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & S_{15} & 0 \\ S_{12} & S_{22} & S_{23} & 0 & S_{25} & 0 \\ S_{13} & S_{23} & S_{33} & 0 & S_{35} & 0 \\ 0 & 0 & 0 & S_{44} & 0 & S_{46} \\ S_{15} & S_{25} & S_{35} & 0 & S_{55} & 0 \\ 0 & 0 & 0 & S_{46} & 0 & S_{66} \end{bmatrix}.$$

To calculate the bulk modulus and shear modulus, we used the models of Voigt and Reuss, respectively. The bulk modulus and shear modulus for monoclinic structure are given by [28]:

$$B_V = (1/9)[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})], \quad (1)$$

$$G_V = (1/15)[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{45} + C_{63}) - (C_{12} + C_{13} + C_{23})], \quad (2)$$

$$B_R = [S_{11} + S_{22} + S_{33}] + 2(S_{12} + S_{13} + S_{23})^{-1}, \quad (3)$$

$$B_R = (1/15)[4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})]^{-1}. \quad (4)$$

Based on extreme value principle, Hill [29] proved that Voigt's and Reuss's models are the upper and lower limits of the elastic constant, respectively. The arithmetic mean Voigt–Reuss–Hill (VRH) value is closer to the experimental result.

$$B = (B_V + B_R)/2, \quad (5)$$

$$G = (G_V + G_R)/2. \quad (6)$$

Using Hill's bulk modulus and shear modulus, we obtained the Young's modulus and Poisson ratio for each material in its polycrystalline form:

$$E = (9BG)/(3B + G), \quad (7)$$

$$\nu = \frac{3B - 2G}{2(3B + G)}. \quad (8)$$

When studying the mechanical properties of a thin film, the influence of microcracks and lattice distortion are often considered. Elastic anisotropy is often the essential prereq-

uisite for microcracks and lattice distortion. Thus, research on elastic anisotropy helps in designing materials with better mechanical durability. To quantitatively study the anisotropy of a single crystal, we calculated the universal anisotropic index A^U [30], which describes the anisotropy of elasticity for single crystals:

$$A^U = 5G_V/G_R + B_V/B_R - 6 \geq 0, \quad (9)$$

where $A^U = 0$ refers to a locally isotropic single crystal. A nonzero A^U corresponds to some degree of elastic anisotropy.

Alternatively, the elastic anisotropies in percentages [31] are expressed as follows:

$$\begin{aligned} A^B &= (B_V - B_R) / (B_V + B_R), \\ A^G &= (G_V - G_R) / (G_V + G_R), \\ A^E &= (E_V - E_R) / (E_V + E_R), \end{aligned} \quad (10)$$

where B_V , B_R , G_V , G_R , E_V , and E_R are the upper (subscript V) and lower (subscript R) limits of the bulk, shear, and Young's moduli, respectively. For an isotropic crystal, A^B , A^G , and A^E must be zero because any values greater than zero represent some degree of elastic anisotropy.

CALCULATED RESULTS AND DISCUSSION

Structural parameters

Table 1 gives the optimized geometric parameters. The LDA potential field underestimates the lattice constants, while the GGA potential field overestimates the lattice constants, so we used both methods with the USPP and the NCPP. Because m-TiO₂ is a high-pressure phase, an external stress of 20 GPa was applied to the material in the calculation. Table 1 reveals that the structural parameters of the three m-MO₂ materials calculated by both the LDA and GGA agree well with the experimental results.

In the LDA, the nuclei are assumed to be far from each other. Thus, electrons move in the crystal lattice approximately like they are in a homogeneous field. Thus, the LDA can be suitable for modeling all kinds of ground-state properties, especially elastic properties, the equation of states, and phase transitions at high pressure and high temperature. In the GGA, a charge gradient is introduced to modify the local changes in charge density. The GGA-calculated structures, energies, and gaps agree well with experimental data. In the USPP, a generalized orthogonal normalization condition is introduced, which makes the wave functions smoother, so fewer basal plane waves and only a small cut-off energy are required. Otherwise, calculations with the NCPP require high cutoff energies to avoid reducing ac-

Table 1 Structural parameters of the three m-MO₂ materials. m-MO₂ structural constants a , b , c (Å); β (°); volume V (Å³); density ρ (g cm⁻³). 1: USPP; 2: NCPP

		m-TiO ₂			m-ZrO ₂				m-HfO ₂			
		LDA	GGA	Expt. ^a	LDA	GGA	Expt. ^b	Expt. ^c	LDA	GGA	Expt. ^d	Expt. ^e
a	1	4.567	4.661	4.598	5.090	5.193	5.146	5.21	5.219	5.333	5.119	5.113
	2	4.535	4.630		5.090	5.203			4.953	5.000		
b	1	4.808	4.866	4.849	5.178	5.238	5.212	5.26	5.358	5.411	5.169	5.172
	2	4.782	4.839		5.200	5.259			5.060	5.060		
c	1	4.723	4.832	4.736	5.248	5.382	5.313	5.37	5.333	5.483	5.297	5.295
	2	4.693	4.802		5.246	5.396			5.103	5.181		
β	1	98.69	98.96	98.6	99.55	99.67	99.22	80.53	99.26	99.789	99.18	99.18
	2	98.56	98.87		99.42	99.68			99.71	100.11		
V	1	102.5	108.2	104.2	136.4	144.3	140.7	145.2	147.2	155.9	138.4	138.2
	2	100.6	106.3		137.0	145.5			126.1	129.1		
ρ	1	5.21	4.93	5.09	6.03	5.70	5.82	5.64	9.55	9.02	10.10	10.12
	2	5.30	5.02		6.00	5.65			11.15	10.89		

Data are from a: [32]; b: [33]; c: [34]; d: [35]; e: [36].

curacy. The NCPP usually gives the correct charge density and is adaptive for self-consistent calculations.

Elastic properties

Elastic constants characterize how a crystal lattice reacts to external stress within the elastic limit. Table 2 shows the elastic constants and elastic moduli of the three dioxides. A monoclinic system has thirteen independent elastic constants, and its mechanical stability criteria are as follows [28]:

$$C_{ii} > 0, (i = 1-6), [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0, (C_{33}C_{55} - C_{35}^2) > 0, (C_{44}C_{66} - C_{46}^2) > 0, (C_{22} + C_{33} - 2C_{23}) > 0. \quad (11)$$

The elastic constants given in Table 2 meet these criteria, indicating that the three dioxides are mechanically stable.

The LDA potential field overestimates the elastic constants, and the GGA potential field underestimates them. Thus, we give both two data sets in Table 2. In brief, we only analyze the data from the LDA and USPP.

All m-MO₂ show $C_{22} > C_{11} > C_{33}$, agreeing with others' calculated results [11,12,35,36] and experimental data [37]. This relationship shows that the resistance to compression decreases in the order of these directions $y \rightarrow x \rightarrow z$. It also manifests that the binding strength between adjacent atomic bonds on {010} planes is the highest, and that on {001} planes is the lowest. For m-TiO₂, $C_{66} > C_{55} > C_{44}$ means that its resistance to shear deformation is strongest on {001} planes and weakest on {100} planes. For m-ZrO₂ and m-HfO₂, their resistance to shear deformation is weakest on {010} planes.

Table 2 lists the Cauchy pressure and its average values,

where $cp1 = C_{23} - C_{44}$, $cp2 = C_{13} - C_{55}$, and $cp3 = C_{12} - C_{66}$. If the interatomic forces can be described by a potential that only depends on the distance between atoms, and if all atoms in an unstrained crystal occupy centers of inversion symmetry in the lattice, then the Cauchy pressure vanishes: $C_{23} = C_{44}$, $C_{13} = C_{55}$, $C_{12} = C_{66}$. This form of the potential excludes torsional, or bending forces (present in covalent crystals) and interatomic forces that vary with atomic volume (present in metals). Because Cauchy pressure—also defined as the difference between the two particular elastic constants—is an indicator of ductility: if the pressure is positive (negative), then the material should be ductile (brittle). A greater magnitude of Cauchy pressure with a positive (negative) sign indicates greater ductility (brittleness). The Cauchy pressures in Table 2 show that m-HfO₂ is the most ductile among the three dioxides.

Table 2 lists some parameters for the polycrystalline dioxides: the bulk modulus B , shear modulus G , Young's modulus E , Pugh modulus ratio G/B , and Poisson's ratio.

According to Pugh's criterion [40], materials with a Pugh modulus ratio $G/B > 0.57$ show brittleness, while materials with $G/B < 0.57$ show ductility. In the LDA calculation, the G/B in Table 2 indicates that m-TiO₂, m-ZrO₂, and m-HfO₂ all show ductility, and the order of G/B is TiO₂ > ZrO₂ > HfO₂, indicating that m-TiO₂ has the highest directing property of bonds, while m-HfO₂ has the lowest; this result agrees with the analysis of Cauchy pressure.

Poisson's ratio ν is the ratio of transverse strain to longitudinal strain in a material, reflecting its volume change with uniaxial deformation; ν can also effectively demonstrate the condition of atomic binding force. Poisson's ratio

Table 2 Elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Pugh modulus ratio G/B , Poisson's ratio ν , and Cauchy pressures $cp1$, $cp2$, $cp3$ with their average values. 1: USPP; 2: NCPP

		m-TiO ₂		m-ZrO ₂					m-HfO ₂			
		LDA	GGA	LDA	GGA	a	b	Expt. ^c	LDA	GGA	d	e
C_{11}	1	477	439	337	335	369	347	361	336	299	337	341
	2	496	457	354	333				420	431		
C_{22}	1	642	554	426	355	402	364	408	430	377	428	393
	2	663	581	425	351				503	456		
C_{33}	1	353	283	313	295	295	274	258	289	225	195	288
	2	364	312	230	251				292	310		
C_{44}	1	138	103	98	79	93	88	100	104	89	120	867
	2	141	113	96	73				118	97		
C_{55}	1	105	94	83	72	79	108	81	78	72	74	94
	2	117	100	87	68				103	98		
C_{66}	1	199	169	137	111	125	122	126	137	120	146	132
	2	207	177	127	108				172	156		
C_{12}	1	251	212	175	141	162	164	142	202	157	235	165
	2	260	222	178	143				198	177		
C_{13}	1	159	108	123	98	87	102	55	148	85	143	107
	2	168	119	102	94				110	103		
C_{15}	1	62	56	34	27	25	28	-21	46	32	64	42
	2	64	61	39	27				47	39		
C_{23}	1	227	198	154	129	142	156	196	179	144	123	159
	2	235	207	152	137				168	165		
C_{25}	1	-4	-1	-11	-4	-7	-17	31	-3	-6	24	-8
	2	-9	-2	-6.3	-1.7				-13	-11		
C_{35}	1	26	11	11	-0.1	-1	11	-18	27	10	57	0
	2	21	21	15	2.9				14	9		
C_{46}	1	-12	-11	-16	-15	-18	-44	-23	-14	-15	-13	-10
	2	-13	15	-14	-15				-21	-21		
B	1	284	235	220	189	212	212	176	223	175	178	204
	2	296	250	194	183				228	225		
G	1	136	116	104	91	105	98	90	93	86	86	99
	2	143	124	96	84				122	115		
E	1	351	300	270	235	269	254	230	246	222	223	255
	2	369	319	247	219				311	295		
G/B	1	0.48	0.49	0.48	0.48	0.49	0.46	0.51	0.42	0.49	0.49	0.48
	2	0.48	0.50	0.49	0.46				0.54	0.51		
ν	1	0.29	0.29	0.29	0.29	0.29	0.30	0.28	0.31	0.29	0.29	0.29
	2	0.29	0.23	0.29	0.30				0.27	0.28		
$cp1$	1	89		56					75			
$cp2$	1	54		40					70			
$cp3$	1	52		38					65			
Avg.	1	65		45					70			

Data are from a: [37]; b:[38]; c: [39]; d: [11]; e: [12].

can formally take values of 1 ($B \ll G$) to 0.5 ($B \gg G$), which respectively are the lower limit, where the material does not change its shape, and the upper limit, where the volume remains unchanged. For central force solids, Poisson's ratio is bounded by the lower limit of 0.25 and the upper limit of 0.5. When ν is 0.25–0.5, the atomic binding force is a central force. Table 2 shows that the central force of the m-MO₂ is the atomic binding force.

Hardness

Hardness is the ability of a material to resist elastic deformation, plastic deformation, or failure under external force. External forces applied to a solid material can cause translations or rotations, or they can induce stresses that produce strain in the material. These strains manifest in volume, shape, and rotational changes. The stress and strain tensors of a material are expressed in terms of the elastic stiffness constants C_{ij} . The magnitude of each elastic constant increases as a solid's resistance to elastic deformation increases [41].

However, hardness cannot yet be calculated exactly. There are several models for estimating hardness. For example, Gao *et al.* [42] proposed a formula for covalent compounds that suits diamond-like superhard materials quite well. Chen *et al.* [43,44] modeled hardness for polycrystalline materials and bulk metallic glasses with the Vickers hardness equation $2((G/B)^2G)0.585-3$. Tian *et al.* [45,46] established a microscopic theory of hardness with $0.92(G/B)^{1.137}G^{0.708}$. Here we evaluated the hardness of m-MO₂ with both Chen's and Tian's methods.

In Table 3, the values of Vickers hardness calculated with the LDA are slightly larger than those calculated with the GGA for m-TiO₂ and m-ZrO₂, and the values from Tian's model are larger and closer to experimental data than those from Chen's. Even so, the theoretical values from both Chen's and Tian's models are smaller than the experimental data, indicating that other factors should be accounted for in determining hardness.

Table 3 Hardness of m-MfO₂ evaluated with 1. Chen's model and 2. Tian's model

		H_v (GPa)		
		LDA	GGA	Expt.
m-TiO ₂	1	12.0	11.1	
	2	12.9	11.9	
m-ZrO ₂	1	9.6	8.9	12.5 ^a
	2	10.7	9.7	
m-HfO ₂	1	7.2	8.8	11.4 ^b
	2	8.6	9.6	

Data are from a: [47]; b: [12].

These results also show that the m-MO₂ are not superhard materials; a superhard material must have an H_v greater than 40 GPa, and usually it must be nearly isotropic—otherwise, it will preferentially deform in a specific direction [48]. Figs 2 and 3 show their high anisotropy. The order of hardness (m-HfO₂ < m-ZrO₂ < m-TiO₂) agrees with the order of anisotropy (m-HfO₂ > m-ZrO₂ > m-TiO₂). All the dioxides have moderate hardness, ~10 GPa. m-TiO₂ is the hardest (12.9 GPa from LDA; 11.9 GPa from GGA); m-ZrO₂ is the second hardest (10.7 GPa from LDA; 9.7 GPa from GGA); and m-HfO₂ is the least hard (8.6 GPa from LDA; 9.6 GPa from GGA). The calculated values of hardness for m-ZrO₂ and m-HfO₂ agree with the experimental data.

Minimum thermal conductivity

At present, MO₂ materials are usually prepared as thin films. Because the binding force between a thin film and its matrix is affected by high temperatures, it is important to research the thermal conductivities of MO₂ materials.

The acoustic wave velocity of a material is closely related to its thermal conductivity. Thermal conductivity declines as temperature increases, so knowing its minimum thermal conductivity $\kappa_{\min}$ is significant to the material's use as temperature rises. Here, we calculated the thermal conductivities in multi-crystal systems of the three m-MO₂ based on Clark Model [49] and Cahill Model [50]:

$$\text{Clark model: } \kappa_{\min} = 0.87k_B M_a^{-2/3} E^{1/2} \rho^{1/6}, \quad (12)$$

$$\text{Cahill model: } \kappa_{\min} = \frac{k_B}{2.48} p^{2.3} (\nu_t + 2\nu_l), \quad (13)$$

where E is Young's modulus, ρ is the density, k_B is the Boltzmann constant, $M_a = [M/(n \cdot N_A)]$ is the average mass of atoms in the lattice, M is the molar mass, n is the number of atoms in a molecule, N_A is Avogadro's number, p is the number of atoms in a unit volume, and ν_t and ν_l are the average waves of the acoustic transverse and longitudinal waves, respectively, expressed by

$$\nu_t = \sqrt{G/\rho}; \quad \nu_l = \sqrt{(B + 4G/3)/\rho}.$$

Cahill's model produced slightly larger values than Clarke's model. Cahill's model considers the atomic number density and the phonon spectrum, while Clarke's model does not account for contributions to conductivity from optical phonons [51]. Thus, Clarke's model will underestimate the thermal conductivity. Also, the data obtained by Cahill's model should be closer than Clarke's model to the

Figure 2 (a) 3D bulk moduli and (b) projections for 1. m-TiO₂, 2. m-ZrO₂, and 3. m-HfO₂; solid red curves represent the xy -plane, dashed green curves represent the yz -plane, and dotted blue curves represent the xz -plane.

Figure 3 (a) 3D Young's moduli and (b) projections for 1. m-TiO₂, 2. m-ZrO₂, and 3. m-HfO₂; solid red curves represent the xy -planes, dashed green curves represent the yz -plane, and dotted blue curves represent the xz -plane.

Table 4 Transverse speed v_t (km s⁻¹), longitudinal speed v_l (km s⁻¹), minimum thermal conductivity $\kappa_{\min}$ [W m⁻¹ K⁻¹], and Debye temperature Θ_D (K) with the USPP

	m-TiO ₂			m-ZrO ₂			m-HfO ₂			
	LDA	GGA	Expt. ^a	LDA	GGA	Exp. ^b	LDA	GGA	c	Expt. ^d
v_t	5.11	4.86		4.16	3.99		3.13	3.09	2.944	
v_l	9.55	8.90		7.71	7.37		6.03	5.70	5.425	
v_m	5.70	5.42		4.64	4.45		3.50	3.45	3.285	
$\kappa_{\min}$ (Clark)	2.23	2.06	1.6	1.67	1.47	2.2	1.15	1.08		1.4
$\kappa_{\min}$ (Cahill)	2.47	2.27		1.76	1.68		1.29	1.23		
Θ_D	831	776		615	579		452	437	431	

Data are from a: [53] (this experimental value is for films); b: [54]; c: [11]; d: [55].

real values. The mass density of the material is used to calculate its Debye temperature [52].

$$\Theta_D = \frac{h}{k} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m, \quad (14)$$

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}. \quad (15)$$

Table 4 lists some calculated data, including the acoustic wave speed, minimum thermal conductivity, and Debye temperature. For all three m-MO₂, the values of minimum thermal conductivity and Debye temperature calculated from the LDA and GGA deviate slightly from each other, especially for m-TiO₂. Table 4 shows that, for a calculation with either LDA or GGA, the values from Cahill's model are slightly larger than those from Clark's model. This difference occurs because Cahill's model considers the atomic number density and the phonon spectrum, while Clarke's model does not account for contributions to conductivity from optical phonons. Thus, Clarke's model will underestimate the thermal conductivity. Also, the calculations from Cahill's model should be closer than Clarke's model to the real values [56]. In Cahill's model, the minimum thermal conductivity is largest in m-TiO₂ and smallest in m-HfO₂. The experimental data for ZrO₂ and HfO₂ are 2.2 and 1.4, respectively. These values are only slightly larger than the minimums we calculated here, indicating that our calculations are reasonable. Among the m-MO₂, m-TiO₂ had the highest Debye temperature, indicating it might have a higher melting temperature.

Anisotropy

Elastic anisotropy

According to Equations (9) and (10), the universal aniso-

tropic index A^U is 0.40, 0.50, and 0.72, for m-TiO₂, m-ZrO₂, and m-HfO₂, respectively, which indicates that the order of anisotropy is m-HfO₂ > m-ZrO₂ > m-TiO₂. The shear anisotropic factors $\{A^B, A^G, A^E\}$ are $\{0.008, 0.046, 0.041\}$, $\{0.022, 0.034, 0.032\}$, and $\{0.053, 0.057, 0.057\}$ for m-TiO₂, m-ZrO₂, and m-HfO₂, respectively. None of these data are zero, so all three dioxides are elastically anisotropic. Because all these data are nonzero, the details of anisotropy cannot be found. To clarify the elastic anisotropies for m-TiO₂, m-ZrO₂, and m-HfO₂, we plotted three-dimensional (3D) surfaces of the moduli in Figs 2 and 3. Their formulas are as follows [57]:

$$B^{-1} = (S_{11} + S_{12} + S_{13})l_1^2 + (S_{12} + S_{22} + S_{23})l_2^2 + (S_{13} + S_{23} + S_{33})l_3^2 + (S_{15} + S_{25} + S_{35})l_3l_1 \quad (16)$$

$$E^{-1} = l_1^4 S_{11} + 2l_1^2 l_2^2 S_{12} + 2l_1^2 l_3^2 S_{13} + 2l_1^3 l_3 S_{15} + 2l_2^4 S_{22} + 2l_2^2 l_3^2 S_{23} + 2l_1 l_2^2 l_3 S_{25} + l_3^4 S_{33} + 2l_1 l_3^3 S_{35} + l_2^2 l_3^2 S_{44} + 2l_1 l_2^2 l_3 S_{45} + l_1^2 l_3^2 S_{55} + l_1^2 l_2^2 S_{66}, \quad (17)$$

where S_{ij} are the compliance constants, and l_1 , l_2 , and l_3 are the directional cosines.

In a 3D representation, an isotropic system must be spherical, and deviation from that spherical shape indicates the degree of anisotropy. Figs 2 and 3 show that m-TiO₂ has the smallest anisotropy, while m-HfO₂ has the largest. This result agrees with the calculated A^U , A^B , and A^E .

Note that the bulk modulus of m-HfO₂ shows the largest anisotropy. Its B_y/B_x and B_y/B_z are greater than four, far larger than those of m-TiO₂ and m-ZrO₂.

A material with greater anisotropy is usually more likely to develop microcracks. As such, more care is required when preparing m-HfO₂ thin films than the other dioxides. Moreover, the high A^U of m-HfO₂ means it cannot be superhard: an ideal superhard material is isotropic; otherwise, it will preferentially deform in a specific direction [48]. For example, diamond and c-BN have an A^U of 0.06 and 0.19, respectively [58], far less than that of m-HfO₂.

Figure 4 (a1, a2 and a3) 3D minimum thermal conductivities for m- MO_2 (M = Ti, Zr, or Hf). (b1, b2 and b3) $k_{\min}$ for the xy-, yz-, and xz-planes, respectively. The solid red curve represents m- TiO_2 , the dotted green curve represents m- ZrO_2 , and the dashed blue curve represents m- HfO_2 .

Figure 5 Tensile and shear stress–strain curves for the three materials in various crystal orientations.

From Clark's model, based on the calculated values of minimum thermal conductivity, we plotted the anisotropic graph for m- MO_2 in Fig. 4. Comparing this with Figs 2, 3, and 4, we find that the bulk modulus is more anisotropic than Young's modulus, which in turn is more anisotropic than the minimum thermal conductivity.

Plastic anisotropy and ideal strength

To investigate the mechanisms of mechanical deformation in the dioxides, we calculated and plotted the stress–strain curves on the [100], [010], and [001] crystal orientations for tension and along the (001)[010], (001)[100], (100)[010] directions for shear, as shown in Fig. 5. All three

compounds exhibit similar anisotropy of tensile strength. The ideal tensile strengths along the [100] directions are much larger than those in the other two directions. The anisotropic ratios of ideal tensile strength tend to decrease as follows: m-TiO₂ $\sigma_{[100]}$ (30 GPa) : $\sigma_{[010]}$ (20 GPa) : $\sigma_{[001]}$ (14 GPa) $\approx$ 1:0.67:0.47, m-ZrO₂ $\sigma_{[100]}$ (34 GPa) : $\sigma_{[010]}$ (25 GPa) : $\sigma_{[001]}$ (21 GPa) $\approx$ 1:0.74:0.62, and for m-HfO₂ $\sigma_{[100]}$ (40 GPa) : $\sigma_{[010]}$ (30 GPa) : $\sigma_{[001]}$ = 26 GPa $\approx$ 1:0.75:0.65. The ratios of $\sigma_{[100]}$: $\sigma_{[010]}$: $\sigma_{[001]}$ indicate that these materials have high tensile plastic anisotropy in the [100] direction, which have the relatively high values. For m-TiO₂, its strength along its weakest direction is $\sim$ 53% lower than that along the strongest direction, indicating strongly anisotropic tension in the [100] direction.

When shear strain is applied, the ideal Hellmann–Feynman stress–strain curves have the maximum ideal shear strength in three directions. Fitting the linear parts of the stress–strain curves (strains < 0.02) shown in Fig. 5, we obtained the shear moduli of the three oxides: m-TiO₂ ($G_{[001](010)}$ = 126 GPa, $G_{[001](100)}$ = 162 GPa, $G_{[100](010)}$ = 230 GPa); m-ZrO₂ ($G_{[001](010)}$ = 150 GPa, $G_{[001](100)}$ = 149 GPa, $G_{[100](010)}$ = 215 GPa); and m-HfO₂ ($G_{[001](010)}$ = 161 GPa, $G_{[001](100)}$ = 151 GPa, $G_{[100](010)}$ = 224 GPa). These results explicitly reveal that the three oxides have anisotropic shear moduli, and the maximum moduli are consistently along the [100] (010) directions. The ideal shear strengths are as follows: m-TiO₂ $\sigma_{[001](100)}$ = 11 GPa, m-ZrO₂ $\sigma_{[001](100)}$ = 9 GPa, and m-HfO₂ $\sigma_{[001](100)}$ = 14 GPa; m-ZrO₂ is the weakest system. The ideal shear strength basically scales with the calculated hardness: m-TiO₂ (12–21 GPa), m-ZrO₂ (10–15 GPa), and m-HfO₂ (9–12 GPa). The anisotropy ratios of shear strength in the dioxides are as follows: m-TiO₂ ($\sigma_{[001](010)}$ (11 GPa) : $\sigma_{[001](100)}$ (12 GPa) : $\sigma_{[100](010)}$ (17 GPa) = 1:1.09:1.55), m-ZrO₂ ($\sigma_{[001](010)}$ (10 GPa) : $\sigma_{[001](100)}$ (11 GPa) : $\sigma_{[100](010)}$ (18 GPa) = 1:1.10:1.80), m-HfO₂ ($\sigma_{[001](010)}$ (20 GPa) : $\sigma_{[001](100)}$ (14 GPa) : $\sigma_{[100](010)}$ (18 GPa) = 1:0.70:0.9). For m-TiO₂ and m-ZrO₂, the maximum anisotropy ratio is along the [100](010) directions, while for m-HfO₂ it is along the [001](010) directions.

Anisotropy of slowness

Acoustic speed is closely linked with the elastic constants; it can be easily measured experimentally, and it is usually obtained using the Christoffel equation [52]:

$$\begin{bmatrix} \alpha & \delta & \varepsilon \\ \delta & \beta & \zeta \\ \varepsilon & \zeta & \gamma \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \rho v^2 \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix},$$

where ρ is the density and v is the acoustic speed. The el-

ements of the monoclinic phase are expressed as follows:

$$\begin{aligned} \alpha &= C_{11}l_1^2 + C_{66}l_2^2 + C_{55}l_3^2 + 2C_{15}l_3l_1, \\ \beta &= C_{66}l_1^2 + C_{22}l_2^2 + C_{44}l_3^2 + 2C_{46}l_3l_1, \\ \gamma &= C_{55}l_1^2 + C_{44}l_2^2 + C_{33}l_3^2 + 2C_{35}l_3l_1, \\ \delta &= (C_{46} + C_{25})l_2l_3 + (C_{12} + C_{66})l_1l_2, \\ \varepsilon &= C_{15}l_1^2 + C_{46}l_2^2 + C_{35}l_3^2 + (C_{13} + C_{55})l_3l_1, \\ \zeta &= (C_{23} + C_{44})l_2l_3 + (C_{25} + C_{46})l_1l_2. \end{aligned}$$

One way to describe wave propagation is slowness, the reciprocal of acoustic speed. When acoustic waves propagate only on the (100), (010), and (001) planes, the Christoffel equation can be solved analytically for cubic, hexagonal, trigonal, tetragonal, and orthorhombic phases. For monoclinic and triclinic phases, the equation can be solved analytically. Fortunately, it can be solved numerically on the three planes. Fig. 6 shows the plotted numerical solution.

The Christoffel equation has three solutions on each plane: S1, S2, and S3; here, S1 > S2 > S3. One can know the vibration modes—for example, the transverse, longitudinal, or pure shear—of S1, S2, and S3 for cubic, hexagonal, trigonal, tetragonal, and orthorhombic phases. In the monoclinic and triclinic phases, the vibration modes are related to all plastic constants C_{ij} . Thus, the acoustic wave in the monoclinic and triclinic phase can combine all possible vibration modes.

The slowness of m-TiO₂ on the xy -plane is nearly isotropic. In each m-MO₂, the order of anisotropy in slowness is $A(xy\text{-plane}) < A(yz\text{-plane}) < A(zx\text{-plane})$. And this order for the materials is $A(\text{m-TiO}_2) < A(\text{m-ZrO}_2) < A(\text{m-HfO}_2)$. The faster the acoustic wave propagates, the more isotropic the slowness appears to be.

CONCLUSIONS

We studied the elasticity, anisotropy, hardness, and minimum thermal conductivity of monoclinic transition metal dioxides: m-HfO₂, m-ZrO₂, and m-TiO₂. The calculated results show that all three m-MO₂ are mechanically stable and that their central force is the atomic binding force. Moreover, all three dioxides show elastic anisotropy in order of m-HfO₂ > m-ZrO₂ > m-TiO₂. m-TiO₂ has the highest hardness and directing property of bonds, while m-HfO₂ has the lowest of both. m-HfO₂ has the lowest G/B , indicating that it is the most ductile among the m-MO₂. The dioxides are not superhard: they only have moderate hardness of $\sim$ 8–13 GPa. We also calculated their Debye temperatures and minimum thermal conductivities. m-HfO₂ can be used as a heat-insulating coating because of its low minimum

Figure 6 Slowness of m-MO₂. Deviation from a circle represents anisotropy. (a) Slowness of m-TiO₂ on the xy-, yz-, and zx-planes (from left to right); (b) slowness of m-ZrO₂ on the xy-, yz-, and zx-planes (from left to right); (c) slowness of m-HfO₂ on the xy-, yz-, and zx-planes (from left to right).

thermal conductivity.

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Authors contributions Chen ZQ conceived the idea of this study. Li CM assisted in designing the method and analyzing the data. Li F and Hu M carried out the calculation procedure. Chen ZQ prepared the manuscript and Li F assisted in writing. Chen ZQ revised it and coordinated this work. All authors discussed the results and commented on the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 本文用平面波密度泛函理论研究了斜锆石型IVTMO₂ (m-TiO₂, m-ZrO₂和m-HfO₂)的弹性, 各向异性以及最小热导率. 通过计算给出了弹性常数及其模量、泊松比、硬度、声速及德拜温度高温下的最小热导率. 结果表明, m-MO₂不是超硬材料, 其硬度范围为8–13 GPa. m-TiO₂是其中最硬的, 而m-HfO₂的硬度最小. 同时还对弹性及塑性的各向异性进行了详细的分析, 表明由于m-HfO₂具有最强的各向异性, 在制作薄膜时最容易产生微裂纹. 值得指出的是, 在三种氧化物中, m-HfO₂由于具有最小的高温热导率而最有可能作为热障材料应用.