Elastic and thermodynamic properties of α-Bi₂O₃ at high pressures: Study of mechanical and dynamical stability

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ABSTRACT

The elastic and thermodynamic properties of the monoclinic polymorph of bismuth oxide (α-Bi₂O₃); aka mineral bismite, have been theoretically investigated both at room pressure and under hydrostatic compression by means of first principles calculations based on density functional theory. In this work, the elastic stiffness coefficients, elastic moduli, Poisson’s ratio, B/G ratio, elastic anisotropy indexes (A₀, A₁, A₂, A₃, A₄₅) and directional dependence of Young modulus and linear compressibility have been obtained. Vickers hardness, and sound wave velocities have been calculated. Our simulations show that bismite has a high elastic anisotropy, α-Bi₂O₃ is a ductile material whose elastic anisotropy increases under compression and presents a stronger ability to resist volume compression than shear deformation at all pressures. Besides, it has a very small minimum thermal conductivity, which is well suited for thermoelectric applications. Finally, the mechanical and dynamical stability of bismite at high pressure has been studied and it has been found that α-Bi₂O₃ becomes mechanically unstable at pressures beyond 19.3 GPa and dynamically unstable above 11.5 GPa. These instabilities could be responsible for the amorphization of bismite observed experimentally between 15 and 20 GPa.

1. Introduction

Bismuth trioxide has been extensively studied due to its high polymorphism and technological importance [1]. The stable phase of Bi₂O₃ at room conditions is the α phase, which occurs in nature as mineral bismite. α-Bi₂O₃ crystallizes in a monoclinic crystalline structure (space group: P2₁/c No. 14, Z = 4) and this phase presents the lowest symmetry of all the known polymorphs of bismuth trioxide [1,2]. The structure of α-Bi₂O₃ can be described as layers of bismuth atoms parallel to the (100) plane of the monoclinic cell, separated by layers of oxygen atoms (see Fig. 1) [1]. Noteworthy, recent studies on α-Bi₂O₃ have focused on its use as a photocatalyst, a gas sensor and a supercapacitor [3–7].

The structural, vibrational, optical, electric and magnetic properties of α-Bi₂O₃ have been studied under different conditions of temperature or pressure [1,8–23]. These studies report that this material has unusual magnetic and electrical properties such as the existence of internal magnetic fields and a longitudinal magnetoelectric effect [9,10]. In addition, shock compression experiments have demonstrated that bismite can be used as thermite mixtures for high pressure (HP) applications [8]. In this context, powder X-ray diffraction and Raman scattering experiments have shown that α-Bi₂O₃ undergoes an amorphization at HP between 15 and 20 GPa depending on the hydrostatic conditions [16,22,23].

Despite the technological applicability of α-Bi₂O₃, its elastic properties are barely known and, to the best of our knowledge, only its axial compressibilities, bulk modulus at zero pressure, and sound velocity are recently known [8,16]. The present work reports a theoretical study of the elastic and thermodynamic properties of bismite both at room pressure (0.0001 GPa) and at HP up to ~20 GPa. This study has allowed us to discuss the mechanical stability of this sesquioxide at HP. Besides, we report lattice dynamics ab initio calculations at different pressures. In particular, the knowledge of the phonon dispersion curves (PDCs) at different pressures has allowed us to study the dynamical stability of bismite at HP. We will show that the monoclinic structure of Bi₂O₃ becomes dynamically unstable prior to become mechanically unstable. These instabilities likely cause the amorphization experimentally observed in α-Bi₂O₃ between 15 and 20 GPa.
We have also studied the mechanical properties of simulations some tests were performed using small strains in order to with the density functional theory (DFT) [24] employing the plane-wave scheme (PAW) [26] has allowed us to describe the full nodal atoms and small (red) spheres O atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2. Calculation methods

\textit{Ab initio} simulations of \(\alpha\)-Bi\(_2\)O\(_3\) under compression were carried out with the density functional theory (DFT) [24] employing the plane-wave pseudopotential method implemented in the VASP code (Vienna \textit{Ab initio} Simulation Package) [25]. The use of the projector-augmented wave scheme (PAW) [26] has allowed us to describe the full nodal character of the all-electron charge density in the core region taking into account 15 valence electrons (5d\(^{10}\)6s\(^2\)4p\(^3\)) for bismuth and 6 valence electrons (2s\(^2\)2p\(^3\)) for oxygen. The exchange-correlation energy was computed within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzenhof functional for solids (PBEsol) [27]. A \(6\times4\times4\) Monkhorst–Pack grid of special k-points was used for integrations over the Brillouin zone (BZ). In order to obtain accurate results for a precise description of the electronic properties, the basis set of plane waves was developed up to an energy cutoff of 520 eV. In this way, a high convergence in total energy (better than 1 meV per formula unit) was obtained. Our calculations do not take into account the spin-orbit interaction because those calculations are computationally very demanding and it has been previously shown that spin-orbit interaction is small in \(\alpha\)-Bi\(_2\)O\(_3\) [23].

DFT calculations are a well-tested method that describes properly the properties of semiconductors under compression [28]. For that purpose, the structure of bismite was fully relaxed to its optimized way, the structural parameters were obtained, as well as a set of related through the calculation of forces on atoms and stress tensors. In this purpose, the structure of bismite was fully relaxed to its optimized

Finally, the dynamical stability of \(\alpha\)-Bi\(_2\)O\(_3\) was studied with \textit{ab initio} DFT-based lattice-dynamics simulations at the zone centre (Γ point) and along high symmetry directions of the BZ by using the PHONON code [34]. To calculate the dynamical matrix using the harmonic approximation with the direct force constant approach, highly converged results on forces are required [34,35]. The PDGs were obtained with a supercell of size \(2\times2\times3\) (320 atoms) that gave a good description of the phonon branches.

3. Results and discussion

3.1. Elastic properties and mechanical stability of bismite

\(\alpha\)-Bi\(_2\)O\(_3\) has 13 independent second-order elastic constants (\(C_{ij}\)) which, in the Voigt notation, are: \(C_{11}, C_{12}, C_{13}, C_{15}, C_{22}, C_{23}, C_{25}, C_{33}, C_{35}, C_{44}, C_{46}, C_{55}\) and \(C_{66}\) [36]. When the crystal is loaded under external hydrostatic compression, the elastic stiffness coefficients, \(B_{ij}\), must be employed instead of \(C_{ij}\) elastic constants. The \(B_{ij}\) coefficients for a monoclinic crystal, in the Voigt notation, under an external hydrostatic pressure, \(P\), are: \(B_{11} = C_{11} - P, B_{12} = C_{12} + P, B_{13} = C_{13} + P, B_{15} = C_{15}, B_{22} = C_{22} - P, B_{23} = C_{23} + P, B_{25} = C_{25}, B_{33} = C_{33} - P, B_{35} = C_{35}, B_{44} = C_{44} - P, B_{46} = C_{46}, B_{55} = C_{55} - P\) and \(B_{66} = C_{66} - P\) [37]. Note that the values of \(B_{ij}\) and \(C_{ij}\) are equal when \(P = 0\) GPa (value close to room pressure).

3.1.1. At room pressure

Table 1 lists the calculated \(C_{ij}\) elastic constants for \(\alpha\)-Bi\(_2\)O\(_3\) at 0 GPa. Elastic constants are referred to an orthonormal coordinate system \((x, y, z)\) [36]. These orthonormal axes, following the IRE (Institute of Radio Engineers) convention, are related to the monoclinic crystal lattice vectors \((a, b, c)\) in the following way: \(x\)-axis is parallel to \(\alpha\)–axis, \(z\)-axis is parallel to \(c\)-axis, and \(y\)-axis is perpendicular to \((yz)\) plane. \(C_{11}, C_{22}\) and \(C_{33}\) elastic constants indicate the resistance of the material to be elongated or compressed along \(x, y\) and \(z\) directions, respectively. For \(\alpha\)-Bi\(_2\)O\(_3\), \(C_{33} > C_{11} > C_{22}\) indicates that unidirectional compressibility increases in the following sequence of directions: [001] < [100] < [010]. On the other hand, elastic constants \(C_{44}, C_{55}\) and \(C_{66}\) are related to the resistance to shear deformation. In our

<table>
<thead>
<tr>
<th>(\alpha)-Bi(_2)O(_3)*</th>
<th>(C_{ij}) (in GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>114.0</td>
<td></td>
</tr>
<tr>
<td>59.1</td>
<td></td>
</tr>
<tr>
<td>57.1</td>
<td></td>
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<tr>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>84.3</td>
<td></td>
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<tr>
<td>30.4</td>
<td></td>
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<tr>
<td>2.6</td>
<td></td>
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<tr>
<td>150.3</td>
<td></td>
</tr>
<tr>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>36.4</td>
<td></td>
</tr>
<tr>
<td>46.4</td>
<td></td>
</tr>
<tr>
<td>71.3, 65.3, 68.3</td>
<td></td>
</tr>
<tr>
<td>36.0, 30.9, 33.4</td>
<td></td>
</tr>
<tr>
<td>92.5, 80.0, 86.3</td>
<td></td>
</tr>
<tr>
<td>0.28, 0.30, 0.29</td>
<td></td>
</tr>
<tr>
<td>1.98, 2.12, 2.04</td>
<td></td>
</tr>
<tr>
<td>4.35, 7.73, 0.80, 0.84, 2.32, 0.93</td>
<td></td>
</tr>
<tr>
<td>5.36, 4.44, 4.90</td>
<td></td>
</tr>
</tbody>
</table>

* Our \textit{ab initio} calculations.

Table 1

\(\alpha\)-Bi\(_2\)O\(_3\) elastic moduli \(B, G\), and \(E\) (in GPa), Poisson’s ratio (\(\nu\)), \(B/G\) ratio, and Vickers hardness (\(H\), in GPa) are obtained in the Voigt, Reuss and Hill approximations, labeled respectively with subscripts \(V, R\), and \(H\). The percentage of anisotropy in both compression (\(A_P\)) and shear (\(A_S\)), as well as the shear anisotropic factors (\(A_1, A_2, A_3\)) and the universal anisotropy index (\(A_U\)) are also included. Data are calculated at 0 GPa.

![Crystalline structure for \(\alpha\)-Bi\(_2\)O\(_3\). Large (blue) spheres represent Bi atoms and small (red) spheres O atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image-url)
particular case, $C_{66} > C_{55} > C_{44}$ denotes that the [010](001) shear is easier than the [001](100) shear which is easier than the [010](001) shear. $C_{11}, C_{22}$ and $C_{33}$ are greater than $C_{44}, C_{55}$ and $C_{66}$ in bismite. This indicates that this material has a greater resistance to unidirectional compression than to shear deformation. Finally, elastic constants with mixed compression/shear coupling ($C_{15}, C_{25}$ and $C_{35}$) along with elastic constant $C_{46}$ related to shear deformation have the smallest values in bismite.

The calculated elastic constants for α-Bi$_2$O$_3$ can be compared to those experimentally obtained for glass Bi$_2$O$_3$ using the pulse echo overlap technique [38]. The value of $C_{11}$ in the glass ($C_{11} = 86.5$ GPa) is 26% smaller than the theoretical average ($C_{11} + C_{22} + C_{33}$)/3 in the crystal. The value of $C_{44}$ in the glass ($C_{44} = 26.5$ GPa) is 30% smaller than the theoretical average ($C_{44} + C_{55} + C_{66}$)/3 in the crystal. These results clearly suggest that the crystalline phase is stiffer than the glass, as observed in a number of compounds [39], and give confidence to our calculated results to continue exploring the mechanical properties of bismite from a theoretical ground.

The knowledge of the elastic constants at 0 GPa allows us to study the mechanical stability of the monoclinic structure. In this context, the mechanical stability of a crystal at zero pressure requires that the whole set of elastic constants, $C_{ij}$, satisfies the Born stability criteria [40]. These stability criteria for monoclinic crystals with 13 independent elastic constants, taking into account that $C_{ij}$ matrix must be positive-definite, are given by the following conditions:

$$m_1 = C_{11} > 0$$

(1)

$$m_2 = C_{11}C_{22} - C_{12}^2 > 0$$

(2)

$$m_3 = (C_{22}C_{33} - C_{23}^2)C_{11} - C_{23}C_{11}^2 + 2C_{22}C_{12}C_{13} - C_{22}C_{12}^2 > 0$$

(3)

$$m_4 = C_{44} > 0$$

(4)

$$m_5 = C_{44}C_{66} - C_{46}^2 > 0$$

(5)

$$(6)$$

Values of $m_i$ ($i = 1–6$) at 0 GPa are given in Table 2. As it can be observed, all the stability criteria are satisfied at 0 GPa; thus, the monoclinic structure of bismite is mechanically stable at room pressure. This result is in good agreement with the fact that mineral bismite is found at room conditions.

The elastic moduli can be obtained from the elastic stiffness coefficients $B_0$ and the components of the elastic compliances tensor $S_{0i}$. In particular, the bulk modulus, $B$, and shear modulus, $G$, have been calculated with the expressions [41]:

$$B_V = \frac{B_{11} + B_{22} + B_{33} + 2(B_{12} + B_{23} + B_{13})}{9}$$

(7)

$$\frac{1}{B_V} = S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{13})$$

(8)

$$B_H = \frac{B_V + B_0}{2}$$

(9)

Table 2

<table>
<thead>
<tr>
<th>$m_i$ (GPa)</th>
<th>114.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_1$ (GPa$^2$)</td>
<td>61.1 $10^4$</td>
</tr>
<tr>
<td>$m_2$ (GPa$^2$)</td>
<td>74.4 $10^4$</td>
</tr>
<tr>
<td>$m_3$ (GPa$^2$)</td>
<td>30.0</td>
</tr>
<tr>
<td>$m_4$ (GPa$^2$)</td>
<td>261.4 $10^5$</td>
</tr>
<tr>
<td>$m_5$ (GPa$^2$)</td>
<td>13.2 $10^5$</td>
</tr>
</tbody>
</table>

The elastic moduli in α-Bi$_2$O$_3$ at 0 GPa are tabulated in Table 1. It must be stressed that the Hill bulk modulus, $B_{H0} = 68.3$ GPa is in rather good agreement with the theoretical value (B$_0 = 72.8$ GPa) obtained from our structural data calculated with VASP. This agreement (there is only a 6% difference) suggests the consistency of our calculations. On the other hand, our Hill bulk modulus is 20% smaller than the experimental value of $B_0 = 85.4$ GPa previously reported [16]. It must be stressed that the last two values for $B_0$ were obtained from a 3rd order Birch-Murnaghan equation of state [16]. Besides, our calculated value for $B_{H0}$ is 36% smaller than the bulk modulus obtained from shock compression experiments ($B_{H0} = 106$ GPa) [8]. In this context, it should be commented that the small value of the first derivative of the bulk modulus, $B'_0 = 1.28$ found in the shock compression work results in a greater value for $B_0$ due to the strong correlation between $B_0$ and $B'_{0}$ [46]. The fact that the bulk modulus is greater than the shear modulus indicates that α-Bi$_2$O$_3$ presents a stronger ability to resist volume compression than shear deformation at 0 GPa.

The Poisson’s ratio, ν, is connected with the way structural elements are packed and provides information about the characteristics of the bonding forces and chemical bonding [47]. The ν ratio has been calculated with the expression [45]:

$$\nu_X = \frac{1}{2} \left( \frac{3B_X - 2G_X}{3B_X + G_X} \right)$$

(14)

The subscript X in Eq. (13) refers to the symbols V, R, and H. The Poisson’s ratio in α-Bi$_2$O$_3$, with the Hill approximation, is ν = 0.29 at 0 GPa (see Table 1). Since ν > 0.25 the interatomic bonding forces are predominantly central and the ionic bonding prevails against covalent bonding in bismite at room pressure [48,49].

The B/G ratio was proposed by Pugh as a relationship which relates empirically the plastic properties of a material with its elastic moduli [50]. This relationship quantifies the ratio between the resistance to fracture and the resistance to plastic deformation. A value of the B/G ratio higher (lower) than 1.75 is associated with a ductile (brittle) material. In our calculations, we have found a value of B/G = 2.04 for α-Bi$_2$O$_3$ at 0 GPa (see Table 1) which indicates that bismite is ductile at room pressure.

It is well known that microcracks may be induced in materials due

| $\kappa_i$ (10$^{-3}$ GPa$^{-1}$) | 2.36 | 8.79 | 4.15 |
| $\kappa_0$ (10$^{-3}$ GPa$^{-1}$) | 1.53 (1) | 7.84 (2) | 2.50 (1) |
| $\kappa_{0'}$ (10$^{-3}$ GPa$^{-1}$) | 2.07 (1) | 6.64 (3) | 4.41 (1) |

This work

Ref. [16]

Ref. [16]

Table 3

Axial compressibilities, $\kappa_i$, $\kappa_0$ and $\kappa_{0'}$ in α-Bi$_2$O$_3$ obtained from the elastic constants at 0 GPa. The axial compressibilities reported in Ref. [16], obtained from a Murnaghan equation of state fit of data, are also given for comparison.
Fig. 2. (left) Directional dependence of the Young modulus, in units of GPa, and (right) spatial dependence of the linear compressibility, in units of TPa^{-1}, in bismite at 0 GPa. The Young modulus and linear compressibility in a given direction are shown as a green surface. Data plotted with the ELATE software [54]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

### Table 4
Maximum and minimum values for the Young modulus, $E$, and linear compressibility, $\kappa$. The anisotropy ratio (maximum value/minimum value) and direction of minimum and maximum value for $E$ and $\kappa$ are also included. Data are calculated at 0 GPa with the ELATE software [54].

<table>
<thead>
<tr>
<th>Young modulus (GPa)</th>
<th>Linear compressibility (TPa^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{min}}$</td>
<td>$E_{\text{max}}$</td>
</tr>
<tr>
<td>$\kappa_{\text{min}}$</td>
<td>$\kappa_{\text{max}}$</td>
</tr>
</tbody>
</table>

| value | 53.4 | 127.0 | 1.7 | 8.8 |
| anisotropy ratio | 2.4 | 5.1 |
| direction of minimum and maximum value | (0, 1, 0) | (0.30, 0) | (0.89, 0) | (0, 1, 0) |

* In Cartesian coordinates ($x$, $y$, $z$).

### Table 5
Density ($\rho$ in g/cm$^3$), longitudinal ($v_{\text{long}}$) and transverse ($v_{\text{trans}}$) wave velocities (in m/s), Debye temperature ($\theta_v$ in K), and minimum thermal conductivity ($\kappa_{\text{min}}$ in W m$^{-1}$ K$^{-1}$) in $\alpha$-Bi$_2$O$_3$ at 0 GPa. The labels $V$, $R$, and $H$ refer to the Voigt, Reuss and Hill approximations, respectively.

| $\rho$      | 9.539 |
| $v_{\text{long}}$ (V, R, H) | 3537.0, 3341.3, 3440.5 |
| $v_{\text{trans}}$ (V, R, H) | 1943.6, 1798.7, 1872.5 |
| $\theta_v$ (V, R, H) | 2166.5, 2008.1, 2088.8 |
| $\kappa_{\text{min}}$ (V, R, H) | 0.47, 0.43, 0.45 |

To elastic anisotropy [51]. We have evaluated this anisotropy using different anisotropy indexes. Firstly, we have calculated the percentage of anisotropy in both compressibility and shear moduli with expressions $A_B = (B_V - B_A)/(B_V + B_A)$ and $A_G = (G_V - G_A)/(G_V + G_A)$, respectively [52]. A value of 0% indicates no anisotropy, while a value of 100% is associated with the largest anisotropy. In $\alpha$-Bi$_2$O$_3$, $A_B = 4.35$% and $A_G = 7.73$% at 0 GPa (see Table 1). These results indicate a larger anisotropy in shear than in compression in bismite at room pressure. Secondly, we have calculated the shear anisotropic factors that provide a measure of the degree of anisotropy in the bonding between atoms in different planes [47]. The formulas that define the shear anisotropy factors are the following:

$$ A_1 = \frac{4B_4}{B_{11} + B_{33} - 2B_{13}} $$  \hspace{1cm} (15)

$$ A_3 = \frac{4B_{13}}{B_{22} + B_{33} - 2B_{23}} $$  \hspace{1cm} (16)

$$ A_3 = \frac{4B_{13}}{B_{11} + B_{22} - 2B_{12}} $$  \hspace{1cm} (17)

where $A_1$ is the factor for the (100) shear planes between the $\langle 011 \rangle$ and $\langle 010 \rangle$ directions, $A_2$ is for the (010) shear planes between the $\langle 101 \rangle$ and $\langle 001 \rangle$ directions, and $A_3$ is for the (001) shear planes between the $\langle 110 \rangle$ and $\langle 010 \rangle$ directions [47]. For an isotropic crystal the shear anisotropy factors must be one. A value of $A_1$, $A_2$ or $A_3$ smaller or greater than one is a measure of the elastic anisotropy of the crystal. In $\alpha$-Bi$_2$O$_3$, $A_1 = 0.80$, $A_2 = 0.84$ and $A_3 = 2.32$ at 0 GPa (see Table 1). These results indicate that bismite exhibits a larger anisotropy in $A_3$ and shows more distinct performance in $\langle 001 \rangle$ planes than in $\langle 100 \rangle$ and $\langle 010 \rangle$ planes. Thirdly, we have also calculated the anisotropy of the material by using the universal elastic anisotropy index $A_U$ defined by: $A_U = S(G_V/G_R) + (B_V/B_R) - 6$ [53]. For a locally isotropic crystal, $A_U$ must be zero, so the deviation of $A_U$ from zero is a measure of the degree of elastic anisotropy for the crystalline structure. We have found that $\alpha$-Bi$_2$O$_3$ is elastically anisotropic because it has an $A_U$ value above zero at 0 GPa (see Table 1).

The anisotropy in the monoclinic cell of bismite can also be estimated by the axial compressibilities $\kappa_a$, $\kappa_b$ and $\kappa_c$. These compressibilities have been obtained by using the expressions [36]:

$$ \kappa_a = S_{11} + S_{12} + S_{13} $$  \hspace{1cm} (18)

$$ \kappa_b = S_{12} + S_{22} + S_{23} $$  \hspace{1cm} (19)

$$ \kappa_c = S_{13} + S_{23} + S_{33} $$  \hspace{1cm} (20)

where $S_{ij}$ are the components of the elastic compliances tensor. Table 3 includes the values for $\kappa_a$, $\kappa_b$ and $\kappa_c$, obtained at 0 GPa using Eqs. (18)-
Fig. 3. Theoretical pressure evolution of the elastic constants, $C_{ij}$, in $\alpha$-Bi$_2$O$_3$. Solid lines connecting the calculated data points are guides to the eyes.

Fig. 4. Theoretical pressure evolution of the elastic stiffness coefficients, $B_{ij}$, in $\alpha$-Bi$_2$O$_3$. Solid lines connecting the calculated data points are guides to the eyes.
and Hill (triangles) approximations. Solid lines connecting the calculated data points are guides to the eyes.

The results are shown in Fig. 2 with a 3D parametric surface. For an absolutely isotropic medium this surface must be a sphere. It is clearly evident that \( \kappa \) compressibility, the Vickers hardness, can be obtained with the expression

\[ H_v = 0.92(\frac{G}{B})^{1/3}G^{0.708} \]

(20). It is found that \( \kappa_b > \kappa_c > \kappa_a \); i.e., the \( b \)-axis is the most compressible one and the \( a \)-axis the less compressible one. Our theoretical results (see Table 3) are in good agreement with those given in Ref. [16] obtained from equation of state fits. Therefore, this result again gives us confidence about the correctness of our simulations. The elastic anisotropy of bismite given by the different anisotropy indexes is in agreement with the anisotropy observed in the axial compressibilities, since \( \kappa_a/\kappa_b > 1 \) and \( \kappa_b/\kappa_c > 1 \).

To conclude with the study of the anisotropy, we have obtained the directional dependence of both the Young modulus, \( E \), and the linear compressibility, \( \kappa \), for bismite at 0 GPa using the ELATE program [54]. The results are shown in Fig. 2 with a 3D parametric surface. For an absolutely isotropic medium this surface must be a sphere. It is clearly evidenced that \( \alpha\)-\( \text{Bi}_2\text{O}_3 \) is highly anisotropic. The direction of minimum \( E \), in Cartesian coordinates (\( x \), \( y \), \( z \)), is (0, 1, 0) [see Table 4]. This indicates that the direction with the smallest stiffness is along the \( b \)-axis. The stiffest direction is (0.30, 0, 0.95). This direction is in the (010) plane at an angle of 17.5° to the \( z \)-axis. The directions for maximum and minimum values of \( E \) (\( E_{max} \) and \( E_{min} \)) are correlated with the fact that \( C_{33} > C_{11} > C_{22} \). The high anisotropy is also evidenced quantitatively by the ratio \( E_{max}/E_{min} = 2.4 \). On the other hand, the linear compressibility takes maximum and minimum values of \( \kappa_{max} = 8.8 \text{ GPa}^{-1} \) and \( \kappa_{min} = 1.7 \text{ GPa}^{-1} \) (see Table 4). The anisotropy ratio in linear compressibility is also quite high, \( \kappa_{max}/\kappa_{min} = 5.1 \). The direction of maximum compressibility is (0, 1, 0), that is, the \( b \)-axis. We note that \( \kappa_{max} \) has the same value as the axial compressibility \( \kappa_b = 8.79 \times 10^{-4} \text{ GPa}^{-1} \) (see Table 3). The direction of minimum compressibility is (0.89, 0, 0.45). This direction is in the (010) plane at an angle of 27.0° to the \( x \)-axis and 49.3° to the \( a \)-axis.

Another common mechanical magnitude to characterize materials is hardness. It is known that hardness is a complex variable which involves elasticity and plasticity in a material. It has been recently proposed that the Vickers hardness, \( H_v \), can be obtained with the expression of Tian et al. [55]:

The values of \( H_v \) in \( \alpha\)-\( \text{Bi}_2\text{O}_3 \) at 0 GPa in the Voigt, Reuss and Hill approximations are included in Table 1. Bismite has a value of \( H_v = 4.90 \text{ GPa} \) at 0 GPa in the Hill approximation. Consequently, this sesquioxide can be considered as a relatively soft material because \( H_v \) is smaller than 10 GPa. The soft behavior of \( \alpha\)-\( \text{Bi}_2\text{O}_3 \) is related with its ductile behavior at 0 GPa, as previously shown.

Finally, we have calculated the average sound velocity, \( v_{max} \) in \( \alpha\)-\( \text{Bi}_2\text{O}_3 \) from the known elastic moduli [56]. This velocity is a quantity which provides information on the elastic moduli, elastic anisotropy, and other thermodynamic properties. In polycrystalline materials \( v_m \) can be obtained by the expression [57]:

\[ v_m = \left[ \frac{1}{3} \left( \frac{2}{v_{max}} + \frac{1}{v_{lon}} \right) \right]^{-1/3} \]

In Eq. (22), \( v_{trans} \) and \( v_{lon} \) are the transverse and longitudinal elastic wave velocities of the polycrystalline material:

\[ v_{lon} = \left( B + \frac{4}{3}G \right)^{1/2} \]

\[ v_{trans} = \left( \frac{G}{\rho} \right)^{1/2} \]

where \( \rho \) is the density of the material and \( B \) and \( G \) are the elastic moduli. Table 5 shows the density and wave velocities \( v_m, v_{lon} \) and \( v_{trans} \) in \( \alpha\)-\( \text{Bi}_2\text{O}_3 \) at 0 GPa. The obtained value of \( v_m \) in the Hill approximation (2088.8 m/s) at 0 GPa is similar to that obtained for porous \( \alpha\)-\( \text{Bi}_2\text{O}_3 \) \( (v_m = 2111 \pm 432 \text{ m/s}) \) in shock compression experiments [8], and 39% smaller that obtained by the calculated Hugoniot for bulk \( \alpha\)-\( \text{Bi}_2\text{O}_3 \) \( (v_m = 3432 \text{ m/s}) \) in dynamic experiments [8].
3.1.2. At high pressure

The HP evolution of the elastic constants, $C_{ij}$, and of the elastic stiffness coefficients, $B_{ij}$, in $\alpha$-$\text{Bi}_2\text{O}_3$ are given in Figs. 3 and 4, respectively. We report the HP dependence of $B_{ij}$ and $C_{ij}$, although only $B_{ij}$ are valid at any pressure, because $B_{ij}$ are obtained from the $C_{ij}$. As it can be observed, $B_{11}$, $B_{22}$, $B_{33}$, $B_{12}$, $B_{13}$, $B_{15}$ and $B_{23}$ ($B_{55}$ and $B_{35}$) increase (decrease) with pressure in the whole pressure range studied. On the other hand, $B_{44}$, $B_{66}$, $B_{25}$ and $B_{46}$ increase with pressure up to 4.5, 15.5, 11.2 and 10.3 GPa, respectively, and then decrease as pressure increases. It must be noted that $B_{35}$ changes its sign at 14.0 GPa.

From the HP dependence of the elastic stiffness coefficients, the HP evolution of the $B$, $G$, and $E$ elastic moduli, $\nu$ Poisson’s ratio, and $B/G$ ratio for $\alpha$-$\text{Bi}_2\text{O}_3$ is calculated (Fig. 5). For the sake of simplicity, only the HP dependence of the elastic moduli in the average Hill approximation will be commented. As it can be seen, $B_{\text{H}}$ increases under compression, reaches a maximum value of 118.3 GPa at 12.6 GPa, and then it decreases under pressure. Similarly, $G_{\text{H}}$ increases with pressure achieving a maximum value of 87.3 at 1.6 GPa and decreases above that pressure. In turn, $E_{\text{H}}$ decreases with pressure in the whole pressure range studied. Finally, $\nu$ also increases with pressure, reaching a value of 0.42 at 18.1 GPa. It must be stressed that the HP increase of $\nu$ indicates that the ductility and the metallic behavior increase under compression. This metallization can be understood as a decrease of the ionic character of the material. In this sense, the effect of pressure on bismite is the increase of atomic coordination and progressive reduction of interatomic bond directionality. We note that bond directionality decreases in the sequence covalent-ionic-metallic of bond character.

It can also be observed that the $B/G$ ratio increases at HP in $\alpha$-$\text{Bi}_2\text{O}_3$, reaching a value of 6.1 at 18.1 GPa. Since the $B/G$ ratio is related to the Poisson’s ratio [49], the increase in $B/G$ also indicates an increment of the ductility under compression.
Fig. 6 shows the evolution with pressure of the different anisotropy indexes previously defined for bismite. The compression and shear anisotropy factors ($A_b$, $A_c$), $A_2$ shear anisotropy factor, and $AU$ universal anisotropy factor increase significantly under compression. This denotes a considerable increment of the elastic anisotropy in $\alpha$-Bi$_2$O$_3$ with pressure. On the other hand, $A_1$ and $A_2$ shear anisotropy factors have a small variation with pressure.

Fig. 7 presents the HP dependence of the Vickers hardness in $\alpha$-Bi$_2$O$_3$. Clearly, $H_v$ decreases as pressure increases because the $G$ elastic modulus and, consequently, the $G/B$ ratio decrease with pressure. Therefore, bismite becomes softer as pressure increases; a result which is related to the increase of its ductility ($B/G$ ratio), as previously commented.

The HP dependence of the sound velocities for $\alpha$-Bi$_2$O$_3$ is given in Fig. 8. The calculated $v_{\text{lon}}$, obtained with elastic moduli in the Hill approximation, increases with pressure reaching a maximum value of 3761.7 m/s at 9.7 GPa and decreases above that pressure. Moreover, the calculated velocities $v_{\text{trans}}$ and $v_m$ in all approximations decrease as pressure increases, thus reflecting the decrease of $G$.

It must be stressed that the crystalline structure of a compound in a given structure is stable if it is mechanically and dynamically stable [58–60]. Taking into account that we have evaluated the mechanical stability of bismite at room pressure in section 3.1.a) through the Born stability criteria, and that bismite is also dynamically stable at room pressure [23], now we evaluate in this section the mechanical stability of bismite at HP on the basis of the theoretically calculated elastic constants at HP.

When a non-zero stress is applied to the crystal, a generalization of the Born stability criteria is required [61,62]. The generalized Born stability criteria for monoclinic crystals are obtained by replacing in Eqs. (1)–(6) the $C_{ij}$ elastic constants by the $B_{ij}$ elastic stiffness coefficients. These criteria are given by:

$$M_1 = B_{11} > 0$$  
$$M_2 = B_{11}B_{22} - B_{12}^2 > 0$$  
$$M_3 = (B_{22}B_{33} - B_{23}^2)B_{11} - B_{13}B_{23}^2 + 2B_{23}B_{12}B_{11} - B_{22}B_{13}^2 > 0$$  
$$M_4 = B_{44} > 0$$  
$$M_5 = B_{11}^2B_{33} - B_{13}B_{33}B_{13}^2 + 2B_{13}B_{23}B_{13}^2 - 2B_{12}B_{13}B_{23}^2 - 2B_{12}B_{23}B_{13}^2 + 2B_{23}B_{12}B_{13}^2 - B_{22}B_{33} - B_{23}B_{33} - 2B_{13}B_{23}^2 + 2B_{22}B_{13}B_{33} + B_{33}B_{23} - B_{22}B_{33}B_{23}^2 - B_{13}B_{23}B_{13}^2 + 2B_{12}B_{13}B_{33} - B_{22}B_{13}B_{23}^2 - B_{13}B_{23}B_{13}^2 + 2B_{12}B_{13}B_{33} - B_{22}B_{13}B_{23}^2 - B_{13}B_{23}B_{13}^2 + 2B_{12}B_{13}B_{33} > 0$$  
$$M_6 = B_{44}B_{33} - B_{43}B_{34} > 0$$

Fig. 9 reports the evolution of the generalized stability criteria in $\alpha$-Bi$_2$O$_3$ under compression. At HP up to 23 GPa, all stability criteria are satisfied except $M_5$ (Eq. (29)), which is violated at 19.3 GPa. Therefore, our simulations show that $\alpha$-Bi$_2$O$_3$ becomes mechanically unstable above 19.3 GPa. This value is consistent with the quick increase of the $AB$, $AG$ and $AU$ anisotropy factors above 16 GPa in $\alpha$-Bi$_2$O$_3$ (see Fig. 6), which is typically observed when a compound approaches the mechanical instability [63].

3.2. Dynamical stability of bismite

In this section, we will focus on the study of the dynamical stability of the monoclinic structure of $\alpha$-Bi$_2$O$_3$ at HP. For that purpose, we have
performed lattice dynamics calculations and have evaluated the PDC at different pressures (see Fig. 10). It can be observed that our calculations do not show any phonon branch with imaginary frequencies at any point of the BZ in α-Bi2O3 at 0 GPa in good agreement with a previous report [23]. Therefore, bismite is dynamically stable at room pressure as previously commented. However, imaginary frequencies (below 0 in the ordinate scale of Fig. 10) are developed above 11.5 GPa. Therefore, our theoretical calculations predict that bismite becomes dynamically unstable at HP (above 11.5 GPa) before becoming mechanically unstable (above 19.3 GPa).

To conclude this section, we want to comment that our results on the mechanical and dynamical stability of bismite at HP allow us to understand previous works that have studied the behavior of Bi2O3 under compression [16,22,23,64,65]. In this context, a phase transition was not observed experimentally at room temperature, additionally, a pressure-induced amorphization of Bi2O3 at 0 GPa in good agreement with a previous report [23]. Therefore, bismite is dynamically stable at room pressure as previously commented. However, imaginary frequencies (below 0 in the ordinate scale of Fig. 10) are developed above 11.5 GPa. Therefore, our theoretical calculations predict that bismite becomes dynamically unstable at HP (above 11.5 GPa) before becoming mechanically unstable (above 19.3 GPa).

To conclude this section, we want to comment that our results on the mechanical and dynamical stability of bismite at HP allow us to understand previous works that have studied the behavior of Bi2O3 under compression [16,22,23,64,65]. In this context, a phase transition was not observed experimentally at room temperature, probably due to the hindrance of the pressure-driven phase transition at room temperature. Additionally, a pressure-induced amorphization of α-Bi2O3 was observed between 15 and 20 GPa depending on the hydrostatic conditions [16,22,23]. Noteworthy, the experimental amorphization of α-Bi2O3 under compression is consistent with the results of the present theoretical study of the mechanical and dynamical stability of α-Bi2O3 which suggest that amorphization could be caused by the dynamical and mechanical instabilities theoretically predicted to occur on α-Bi2O3 under purely hydrostatic pressure above 11.5 and 19.3 GPa, respectively. The difference between experimental and theoretical pressure values for the onset of the pressure-induced amorphization could be ascribed to the non-purely hydrostatic compression of α-Bi2O3 in the reported experiments, which could favor a larger stability of the monoclinic phase [16,22,23].

3.3. Thermodynamic properties of bismite

To conclude this work, we want to calculate some thermodynamic properties of bismite, such as the Debye temperature and the minimum thermal conductivity, from the knowledge of the average sound velocity, \( v_m \). The Debye temperature, \( \theta_D \), corresponds to the upper limit of phonon frequency in a crystal lattice and it can be calculated with the semi-empirical formula [57]:

\[
\theta_D = \frac{h}{k_B} \left( \frac{3nN_A}{M} \right)^{1/3} v_m
\]  

(31)

In Eq. (31) \( h \) is the Planck's constant, \( k_B \) is the Boltzmann's constant, \( n \) is the number of atoms in the molecule, \( N_A \) is the Avogadro’s number, \( \rho \) is the density, \( M \) is the molecular weight, and \( v_m \) is the average sound velocity. The value of \( \theta_D = 245.7 \text{K} \) in the Hill approximation, for α-Bi2O3 at 0 GPa (see Table 5), is 22% smaller than the estimated value of \( \theta_D = 316 \text{K} \), obtained from shock compression data using Lindeman’s melting law [8]. A decrease of \( \theta_D \) with pressure, clearly following the decrease of \( v_m \) with pressure, is observed in bismite (see Fig. 11(a)).

On the other hand, the thermal conductivity is a property that allows modeling the heat transfer in solids. The theoretical minimum of the thermal conductivity has been estimated by using the expression given by Clarke [66]:

\[
\kappa_{\text{min}} = k_B v_m \left( \frac{M}{\eta n N_A} \right)^{2/3}
\]  

(32)

and the expression given in Long's model [67]:

\[
\kappa_{\text{min}} = \left( \frac{1}{3} \left( \sqrt{2 + 2\nu^2} + \frac{1 - 2\nu^2}{2} + \frac{1}{1 - \nu^2} \right) \right)^{-1} \cdot \frac{k_B \theta_D^2}{\rho} \left( \frac{E}{\rho} \right)^{1/2}
\]  

(33)

where \( m \) is the number of atoms per volume. Both expressions give the same result for \( \kappa_{\text{min}} \) and take into account the anisotropic elasticity of monoclinic α-Bi2O3. The value of \( \kappa_{\text{min}} \) in the Hill approximation, for α-Bi2O3 at 0 GPa, is 0.45 W m\(^{-1}\) K\(^{-1}\) (see Table 5). Therefore, this sesquioxide can be considered as a low \( \kappa \) material interesting for thermoelectric applications [68]. As shown in Fig. 11(b), \( \kappa_{\text{min}} \) in the Hill approximation increases slightly as pressure increases from 0 to 1.6 GPa and then decreases as pressure increases. It should be stressed that the calculated value of \( \kappa_{\text{min}} = 0.45 \text{W m}^{-1} \text{K}^{-1} \) is smaller than the thermal conductivity measured at room temperature for α-Bi2O3 which turns out to be 1.3 W m\(^{-1}\) K\(^{-1}\) [69]. Therefore, we consider that there is room for improvement in the decrease of the thermal conductivity of bismite both at room pressure and at HP conditions for thermoelectric applications [70].

4. Conclusions

In the present work, the elastic and thermodynamic behavior of α-Bi2O3 has been studied theoretically both at room pressure and under hydrostatic compression. The values at room pressure and the HP dependence of the elastic moduli, Poisson’s ratio, \( B/G \) ratio and elastic anisotropy indexes of bismite are reported as well as a study of the directional dependence of Young modulus and linear compressibility at 0 GPa.

Our results show that this sesquioxide: i) is ductile at all pressures and has a larger resistance to volume compression than to shear deformation; ii) shows an intrinsic elastic anisotropy which increases with pressure; iii) is relatively soft at room pressure and its hardness decreases under compression. Besides, its average sound velocity and
Debye temperature decrease with increasing pressure. Moreover, we have found that α-Bi$_2$O$_3$ is a material with a very low thermal conductivity that could be useful for thermoelectric applications both at low and high pressures.

Finally, the study of the mechanical and dynamical stability of the monoclinic structure of bismuth oxide at high pressure shows that this low and high pressures.

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