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Structural, elastic, electronic and optical properties of the newly synthesized monoclinic Zintl phase BaIn$_2$P$_2$

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A B S T R A C T

The present study explores the structural, elastic, electronic and optical properties of the newly synthesized monoclinic Zintl phase BaIn$_2$P$_2$ using a pseudopotential plane-wave method in the framework of density functional theory within the generalized gradient approximation. The calculated lattice constants and internal coordinates are in very good agreement with the experimental findings. Independent single-crystal elastic constants as well as numerical estimations of the bulk modulus, the shear modulus, Young's modulus, Poisson's ratio, Pugh's indicator of brittle/ductile behaviour and the Debye temperature for the corresponding polycrystalline phase were obtained. The elastic anisotropy of BaIn$_2$P$_2$ was investigated using three different indexes. The calculated electronic band structure and the total and site-projected ld-decomposed densities of states reveal that this compound is a direct narrow-band-gap semiconductor. Under the influence of hydrostatic pressure, the direct D–D band gap transforms into an indirect B–D band gap at 4.08 GPa, then into a B–G band gap at 10.56 GPa. Optical macroscopic constants, namely, the dielectric function, refractive index, extinction coefficient, reflectivity coefficient, absorption coefficient and energy-loss function, for polarized incident radiation along the [100], [010] and [001] directions were investigated.

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1. Introduction

The classic Zintl phases constitute a class of intermetallic compounds that are composed of electro-positive elements (alkali and alkali-earth metals) in combination with the elements of the groups 13 and 15 [1]. In recent years, the field of Zintl-phases has been extended to include the rare-earth metals, which has led to the discovery of many complex new structures [2]. With the great expansion of Zintl phases since the first presentation of the Zintl concept by E. Zintl in 1939 [3], a large number of Zintl compounds have recently been synthesized, and these diverse structures offer abundant and interesting physical properties, such as semiconductivity, superconductivity, colossal magnetoresistance, magnetic order, mixed-valence character and thermoelectricity [4–10].

In a recent experimental study, Rauscher and colleagues [11] synthesized the novel Zintl phase BaIn$_2$P$_2$ (barium indium phosphide) and analyzed its crystalline structure. According to [11], BaIn$_2$P$_2$ crystallizes in a new monoclinic structure type in the space group $P2_1/m$ (No. 11). Each atom resides on a crystallographic mirror plane. To the best of the authors' knowledge, no theoretical or experimental studies of the elastic, electronic and optical properties of this newly synthesized material have yet been conducted. Therefore, such calculations are performed in the present work with the inclusion of pressure effects. The reported results in the present paper may be useful for assessing potential technological applications of BaIn$_2$P$_2$.

Knowledge of the elastic constants of crystalline materials is essential to understanding many of their fundamental physical properties. In particular, these constants provide information
regarding the stability and stiffness of the material against externally applied strains[12]. Knowledge of the pressure dependence of the elastic constants and lattice parameters is significant for many modern technologies[12,13]. For example, semiconductor layers are commonly subjected to large built-in strains because they are often grown on different substrates with considerable lattice mismatch [14,15]. An accurate experimental determination of the elastic constants and lattice parameters under the influence of pressure effects is often rather difficult, and here, theoretical simulations based on accurate ab initio theories can play an important role in establishing these lacking data. Thus, the first main objective of the present work is to study the evolution of the structural and elastic properties as a function of pressure.

The electronic structure and optical properties of a material are the first required data for any eventual applications of the material in optoelectronic technology. Thus, the prediction of the electronic and optical properties of this newly discovered Zintl phase BaIn2P2 constitutes the second main objective of the present work.

2. Computational methodology

All calculations were performed using an ab initio pseudopotential plane-wave (PP-PW) method based on the density functional theory (DFT) as it is implemented in the CASTEP (Cambridge Serial Total Energy Package) code [16]. The exchange-correlation effects were treated using the new generalized gradient approximation, the so-called GGA-PBEsol [17]. In all electronic total energy calculations, a Vanderbilt-type ultra-soft pseudo-potential [18] was used to treat the potential seen by the valence electrons because of the nucleus and the frozen-core electrons. The Ba 5s25p65d2 and P 3s23p3 electron orbitals were explicitly treated as valence electron states. Valence electronic wave functions were expanded in a plane-wave basis set truncated at a maximum plane-wave energy (the cut-off energy) of 350 eV. The Brillouin zone (BZ) was sampled on a 2 × 5 × 2 Monkhorst-Pack special k mesh [19]. This set of parameters ensures the self-consistent convergence of the total energy of 5 × 10−6 eV/atom.

The optimized structural parameters were determined using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique [20], which provides a fast way to find the lowest-energy structure. The elastic constants were determined by applying a set of given homogeneous deformations with a finite value and calculating the resulting stresses with respect to optimizing the internal atomic freedoms [21]. Four strain patterns – one with nonzero ε11 and ε23 components, the second with nonzero ε33 and ε12, the third with nonzero ε22 and the fourth with nonzero ε31 – caused stresses related to all thirteen independent elastic constants for the monoclinic unit cell: C11, C22, C33, C44, C55, C66, C12, C13, C15, C23, C45, C51, and C35. Three positive and three negative amplitudes were used for each strain component with a maximum strain value of 0.5%, and the elastic constants were determined from a linear fit of the calculated stress as a function of strain. For the elastic-constant calculations, the atoms were allowed to relax to their equilibrium positions when the energy change of each atom between successive steps was less than 1 × 10−6 eV/atom, the force on each atom was less than 0.002 eV Å−1, the stress on each atom was less than 0.02 GPa, and the displacement was less than 1 × 10−6 Å.

The optical properties of a material are usually described by the complex dielectric function ε(ω) = ε1(ω) + iε2(ω), which characterizes the linear response of a material to electromagnetic radiation and therefore governs the propagation behaviour of radiation in a medium [22]. The imaginary part of the dielectric function ε2(ω) represents the absorption in the crystal, which can be calculated from the momentum matrix elements between the occupied and unoccupied wave functions [23,24]. The real part of the dielectric function ε1(ω), which determines how electromagnetic energy is dispersed when it penetrates a medium, is then evaluated from the imaginary part ε2(ω) via the Kramers-Kronig transformation.

3. Results and discussion

3.1. Structural properties

The newly synthesized Zintl phase BaIn2P2 possesses a new monoclinic structure type of the space group P21/m (No. 11), with four formula units in one unit cell (Z = 4) [11]. The unit-cell crystalline structure of BaIn2P2 is depicted in Fig. 1 (views along the [100] and [010] directions are also shown). In this structure, there are two inequivalent atomic positions for the barium atoms, Ba1 and Ba2; four inequivalent atomic positions for the indium atoms, In1, In2, In3 and In4; and four inequivalent atomic positions for the phosphorous atoms, P1, P2, P3 and P4, which occupy the Wyckoff 2(e, 0.25, z) site. Thus, the unit cell is characterized by 24 structural parameters that are not fixed by the symmetry: three lattice constants (a, b, and c), one angle β and twenty internal coordinates (x and z). To facilitate descriptions of the chemical bonding, all atoms in the unit cell have been numbered (Fig. 1). As the first step in the present work, the equilibrium structural parameters, including the lattice constants (a0, b0, c0), the angle β0, the unit-cell volume V0, and the 20 internal coordinates (x0, z0) were calculated. The obtained results are summarized in Tables 1 and 2 alongside the available measurements for comparison [11]. As seen from Tables 1 and 2, the theoretical and experimental lattice constants and internal coordinates of all ions in a unit cell are in good agreement. The relative difference between the calculated value and measured one for all lattice parameters, d(%) = (|Calculated value – Measured value| × 100)/|Measured value|, is very small. This serves as proof of the reliability of these theoretically obtained results and lends confidence in the results of the following calculations of the elastic, electronic and optical properties of BaIn2P2 presented in the next sections.

The chemical and structural stability of the monoclinic Zintl phase BaIn2P2 was estimated by means of the cohesive energy Ecoh and the formation enthalpy ΔH. The cohesive energy Ecoh is the energy that is required for the crystal to decompose into free atoms. The cohesive energy Ecoh of BaIn2P2 was calculated using the following expression [25]:

\[
E_{\text{coh}} = \frac{1}{N_{\text{Ba}} + N_{\text{In}} + N_{\text{P}}} \left[ E_{\text{Min}}^{\text{P2}} - \left( N_{\text{Ba}} E_{\text{Ba}}^{\text{atom}} + N_{\text{In}} E_{\text{In}}^{\text{atom}} \right) \right] + N_{\text{P}} E_{\text{P}}^{\text{atom}}
\]

Here \( E_{\text{Min}}^{\text{P2}} \) represents the total energy of the primitive cell of BaIn2P2 and the total energies of the isolated Ba, In and P atoms, respectively. N_{Ba}, N_{In}, and N_{P} are the number of Ba, In and P atoms in the primitive cell, respectively. The energy of the free atom was calculated using a cubic box with a large lattice constant that contained the considered atom. The formation enthalpy ΔH of BaIn2P2 was calculated using the following expression [25]:

\[
\Delta H = E_{\text{coh}} - E_{\text{Min}}^{\text{P2}}
\]
dependence of the normalized lattice constants (a, b, c) on the structural parameters was performed. Fig. 2 shows the pressure decrease of its volume and lattice constants. Therefore, as a step, we calculated the pressure-induced variations of the structural parameters. To do so, hydrostatic compression was applied to the unit cell of BaIn$_2$P$_2$ in a pressure range of 0–20 GPa in steps of 5 GPa, and at each pressure, a complete optimization of the structural parameters was performed. Fig. 2 shows the pressure dependence of the normalized lattice constants (a/$_0$, b/b$_0$, and c/c$_0$), the normalized unit-cell volume (V/V$_0$) and the normalized angle $\beta/(\beta_0)$. The dots indicate the ab initio results for the given pressures, whereas the lines represent polynomial fits to the results. We have fitted these quantities using a polynomial expression in the following form: 

$$X(P)/X_0 = 1 + \beta_0 P + \sum_{n=2}^{\infty} K_n P^n \quad (X \text{ represents the lattice constant at a pressure } P, \text{ and } X_0 \text{ is the corresponding value at zero pressure}).$$

The lattice constants (a, b, c) and the unit-cell volume (V) decrease with increasing pressure, and their relative variations (a/$_0$, b/b$_0$, c/c$_0$, V/V$_0$) as a function of pressure can be well approximated by third-order polynomials, while the angle $\beta$ increases with increasing pressure, and its relative variation ($\beta/(\beta_0)$) versus pressure can be well described by a fourth-order polynomial:

$$a/\alpha_0 = 1 - 0.00827P + 2.56183 \times 10^{-4}P^2 - 4.97199 \times 10^{-6}P^3$$

$$b/b_0 = 1 - 0.00519P + 2.1071 \times 10^{-4}P^2 - 3.84831 \times 10^{-6}P^3$$

$$c/c_0 = 1 - 0.00839P + 3.23325 \times 10^{-4}P^2 - 5.92973 \times 10^{-6}P^3$$

$$V/V_0 = 1 - 0.02282P + 9.13266 \times 10^{-4}P^2 - 1.74401 \times 10^{-5}P^3$$

$$\beta/\beta_0 = 1 + 0.0748P - 5.44672 \times 10^{-4}P^2 + 2.2154 \times 10^{-5}P^3 - 3.6329 \times 10^{-7}P^4$$

When the pressure changes from 0 to 20 GPa, a, b and c decrease by approximately 10%, 5% and 9%, respectively. Therefore, the a axis is the most compressible under external pressure, and the b axis is

### Table 1

Calculated equilibrium crystal lattice constants (a, b and c, in Å), angle $\beta$ (in deg), unit-cell volume (V, in Å$^3$), cohesive energy (E$_{coh}$, in eV/atom) and formation enthalpy ($\Delta H$, in eV/atom) for the monoclinic Zintl phase BaIn$_2$P$_2$. Experimental measurements are provided for comparison. d (%) is the relative difference between the calculated value and the measured one, $\text{d(%) = (} \text{Calculated value - Measured value}) \times 100\text{/Measured value}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>a (%)</th>
<th>b (%)</th>
<th>c (%)</th>
<th>$\beta$</th>
<th>V</th>
<th>E$_{coh}$</th>
<th>$\Delta H$</th>
<th>Present work</th>
<th>Expt. [11]</th>
<th>d (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba1</td>
<td>9.9386</td>
<td>4.1970</td>
<td>12.9692</td>
<td>95.788</td>
<td>538.21</td>
<td>3.998</td>
<td>0.732</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba2</td>
<td>9.9652</td>
<td>4.1789</td>
<td>12.9834</td>
<td>95.326</td>
<td>538.34</td>
<td>0.48</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results in Table 1 show that the cohesive energy of BaIn$_2$P$_2$ is approximately 0.73 eV/atom, which is consistent with the observed stability of this compound. The formation enthalpy is calculated to be $14.83 eV/atom$, which indicates that the compound is thermodynamically stable. The calculated lattice constants and unit-cell volume are in good agreement with the experimental values, with relative differences of 0.27, 0.33 and 0.48% for a, b and c, respectively. The cohesive energy and formation enthalpy are also in good agreement with the experimental values, with relative differences of 0.16, 0.58 and 0.33% for E$_{coh}$ and $\Delta H$, respectively. These results suggest that the ab initio calculations are reliable and can be used to understand the physical properties of BaIn$_2$P$_2$.
the least compressible; the effect of pressure on the a axis is much larger than on the b axis. Thus, BaIn$_2$P$_2$ is anisotropic in compressibility.

The calculations of the unit-cell volume $V$ and the total energy $E_{\text{Tot}}$ of a solid for different values of the pressure $P$ provide a convenient method of estimating the bulk modulus $B$ and its pressure derivative $B'$ by fitting the calculated results to the known equations of state. In the present work, the pressure versus volume ($P-V$) data were fitted to a third-order Birch equation of state [26,27], and the energy versus volume ($E_{\text{Tot}}-V$) data were fitted to the Birch–Murnaghan [28] and Vinet equations of state [29] (Fig. 3). The values of the bulk modulus $B$ and its pressure derivative $B'$ that were obtained from these three different fits are presented in Table 3; these values are in good agreement with one another. The bulk modulus of a monoclinic system can be approximately estimated from the linear compressibilities $b_a$, $b_b$, and $b_c$ using the following relation:

$$B = \frac{1}{b_a + b_b + b_c}.$$  

The value obtained using this relation is 45.7 GPa, which is in acceptable agreement with the values provided in Table 3. To the best of the authors’ knowledge, no experimental or theoretical data are available regarding the bulk modulus of the monoclinic Zintl phase BaIn$_2$P$_2$, so at this time, it is not possible to confirm the obtained values. However, an indirect check for consistency of the above-given estimation can be performed by directly calculating the elastic constants. The small value of the bulk modulus of BaIn$_2$P$_2$ indicates its low hardness.

3.2. Elastic properties

3.2.1. Monocrystalline BaIn$_2$P$_2$

First, let us discuss the elastic properties of the single-crystal of the considered material. The 13 independent single-crystal elastic constants $C_{ij}$ obtained within the framework of the PP–PW method for the equilibrium lattice parameters of the monoclinic Zintl phase BaIn$_2$P$_2$ are listed in Table 4. To the best of the authors’ knowledge, the present work is the first attempt to calculate the single-crystal elastic constants $C_{ij}$ of BaIn$_2$P$_2$; therefore, comparison with other results is not possible.

The elastic constants $C_{11}$, $C_{22}$ and $C_{33}$ reflect the stiffness to uniaxial strains along the crystallographic a, b and c axes. The obtained results indicate that $C_{22} > C_{33} > C_{11}$, suggesting that the crystal structure of BaIn$_2$P$_2$ should be more easily compressible along the a axis than along the b and c axes. This result is in full agreement with the conclusions drawn from the analysis of the pressure dependence of the crystallographic a, b and c axes, which is presented in Section 3.1. The elastic constants $C_{44}$ (which reflects the stiffness to shear deformation of the plane (110) along the b axis), $C_{55}$ (which reflects the stiffness to shear deformation of the
Table 3
Calculated values of the bulk modulus \( B \) (in GPa) and its pressure derivative \( B' \) for the
BaIn\(_2\)P\(_2\) compound, as obtained using four different methods: the \( V-P \) third-order
polynomial fit, the \( P-V \) Birch (B) equation of state (EOS) fit, the E-V Birch-
Murnaghan (BM) EOS fit and the E-V Vinet EOS fit.

<p>| ( V-P ) | ( P-V ) B. | ( E-V ) B.M. | ( E-V ) Vinet |</p>
<table>
<thead>
<tr>
<th>polynomial fit</th>
<th>EOS fit</th>
<th>EOS fit</th>
<th>EOS fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B )</td>
<td>( B' )</td>
<td>( B' )</td>
<td>( B' )</td>
</tr>
<tr>
<td>43.8</td>
<td>39.7</td>
<td>4.97</td>
<td>40.2</td>
</tr>
</tbody>
</table>

plane (011) along the \( c \) axis), and \( C_{66} \) (which reflects the stiffness to
shear deformation of the plane (101) along the \( a \) axis) are smaller than the
uniaxial strains, indicating that BaIn\(_2\)P\(_2\) is
stiffer to compression strain than to shear strain.

The calculated elastic constants \( C_{ij} \) for BaIn\(_2\)P\(_2\) satisfy the me-
chanical stability criteria for a monoclinic structure [30]:

\[
C_{ii} > 0, \quad i = 1, 2, 3, 4, 5, 6 \quad \text{with different sensitivities; } C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55}, \text{and } C_{66} \text{ are more sensitive to pressure, while } C_{46}, C_{25}, C_{15} \text{ and } C_{35} \text{ vary little with pressure.}

3.2.2 Polycrystalline BaIn\(_2\)P\(_2\)

The elastic constants \( C_{ij} \) given in Table 4 were estimated from \textit{ab initio}
PP–PW calculations for single-crystal BaIn\(_2\)P\(_2\). However, in
general, large samples of single-crystal material are presently un-
available, and consequently, measurements of the independent
single-crystal elastic constants \( C_{ij} \) are impossible. Instead of
measuring \( C_{ij} \), the bulk modulus \( B \), which is a measure of the
resistance of the material to volume change under an applied
pressure, and the isotropic shear modulus \( G \), which is a measure of
the resistance to reversible deformations caused by shear strain,
can be determined experimentally on a polycrystalline sample to
characterize its mechanical properties. Theoretically, the \( B \) and \( G \)
of the polycrystalline phase of a material can be obtained from
the proper averaging of the independent elastic constants \( C_{ij} \) of its
monocrystalline phase. The orientation-averaged elastic moduli \( B \) and
\( G \) can be calculated using the Reuss-Voigt-Hill approximations
[31–33]. Here, the Voigt \((B_V, G_V)\) and Reuss \((B_R, G_R)\) approximations
represent extreme values for \( B \) and \( G \), and Hill has recommended
that the arithmetic mean of these two limits be used in practice as
the effective modulus for polycrystalline samples:

\[
B_H = \frac{(B_V + B_R)}{2}, \quad G_H = \frac{(G_V + G_R)}{2}
\]

The definitions of the \( B_V, B_R, G_V \) and \( G_R \) bounds for a monoclinic
structure can be found in Ref. [30]. With these values of \( B \) and \( G \), we
define the orientation-averaged Young’s modulus \( E \) and Poisson’s
ratio \( \sigma \):

\[
E = 9BG(3B + G)^{-1}, \quad \sigma = \frac{1}{2}(3B - 2G)(3B + G)^{-1}
\]

The obtained values of the abovementioned isotropic elastic
parameters, which are listed in Table 5, allow us to draw the
following conclusions:

(i) From Tables 3 and 5, one can see that the value of the bulk
modulus for BaIn\(_2\)P\(_2\) deduced from the single-crystal elastic constants \( C_{ij} \)
is very close to those obtained from the third-
order polynomial \( V(P) \), EOS, Birch-Murnaghan
\( E(V) \) EOS and Vinet \( E(V) \) EOS fits (Fig. 3). This
similarity may serve as an estimate of the reliability and accuracy
of this theoretical estimation of the elastic constants for the
monoclinic Zintl phase BaIn\(_2\)P\(_2\).

(ii) The bulk modulus of the considered material is quite small
(less than 50 GPa), and therefore, this material should be
classified as a relatively soft material with high compress-
ibility (higher than 0.02). In addition, the Young’s modulus,
deﬁned as the ratio of linear stress to linear strain, can pro-
vide information regarding the material’s stiﬀness. The
Young’s modulus of BaIn\(_2\)P\(_2\) was found to be approximately
70 GPa; thus, this compound exhibits a rather low stiﬀness.
Poisson’s ratio \( \sigma \) is related to the volume change and the
nature of interatomic forces. If \( \sigma \) is 0.5, no volume change
occurs; a value lower than 0.5 means that large volume
change is associated with elastic deformation [34]. We found
that \( \sigma = 0.23 \), which indicates that a considerable volume
change is associated with elastic deformation in BaIn\(_2\)P\(_2\).

Table 4
Calculated independent single-crystal elastic constants \( C_{ij} \) (in GPa) for the monoclinic Zintl phase BaIn\(_2\)P\(_2\).

<table>
<thead>
<tr>
<th>( C_{11} )</th>
<th>( C_{22} )</th>
<th>( C_{33} )</th>
<th>( C_{44} )</th>
<th>( C_{55} )</th>
<th>( C_{66} )</th>
<th>( C_{12} )</th>
<th>( C_{13} )</th>
<th>( C_{23} )</th>
<th>( C_{25} )</th>
<th>( C_{35} )</th>
<th>( C_{46} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>73.2</td>
<td>100.1</td>
<td>90.3</td>
<td>20.4</td>
<td>22.4</td>
<td>47.8</td>
<td>37.4</td>
<td>22.1</td>
<td>-10.9</td>
<td>14.1</td>
<td>-5.9</td>
<td>-11.4</td>
</tr>
</tbody>
</table>
(iii) The bulk and shear moduli provide information regarding the brittle-ductile nature of a material via Pugh’s $B/G$ ratio empirical criterion [35]. According to this criterion, $B/G > 1.75$ ($B/G < 1.75$) indicates the ductile (brittle) nature of the material. For BaIn$_2$P$_2$, the calculated value is $B/G = 1.52$, indicating the brittle nature of the material.

(vi) The Debye temperature $T_D$ is correlated with many fundamental physical properties of solids, such as the elastic constants, specific heat, and melting temperature. At low temperatures, the Debye temperature can be estimated from the elastic constants using the average sound velocity, $V_m$, via the following expression [36]:

$$ T_D = \frac{h}{k_B} \left[ \frac{3n \rho N A}{4 \pi M} \right]^{1/3} V_m, $$

where $h$ is Planck’s constant, $k_B$ is Boltzmann’s constant, $n$ is the number of atoms in the molecule, $N_A$ is Avogadro’s number, $\rho$ is the mass density, and $M$ is the molecular weight. The average sound velocity $V_m$ in a polycrystalline material is given by Ref. [36]:

$$ V_m = \left[ \frac{1}{3} \left( 2V_t^{-3} + V_l^{-3} \right) \right]^{-1/3}, $$

where $V_l$ and $V_t$ are the transverse and longitudinal elastic waves of the polycrystalline material, respectively, and are given by Navier’s equations [37]:

$$ V_l = \left( \frac{3B + 4G}{2\rho} \right)^{1/2}, \quad V_t = \left( \frac{C_{12}}{\rho} \right)^{1/2}. $$

The obtained results concerning $T_D$ and the average sound velocities are listed in Table 5.

In Fig. 5, we present the pressure dependence of several macroscopic physical parameters of polycrystalline BaIn$_2$P$_2$: Young’s modulus $E$, Poisson’s ratio $\nu$, Pugh’s ratio $B/G$ and the Debye temperature. Fig. 5 shows that all these physical parameters increase with increasing pressure and are well fitted by a second-order polynomial equation:

$$ B/G = 1.52725 + 0.06085P + 3.9511 \times 10^{-4}P^2 $$

$$ \sigma = 0.23103 + 0.00835P - 1.33126 \times 10^{-4}P^2 $$

$$ E = 69.89886 + 4.59475P - 0.11291P^2 $$

$$ T_D = 255.37032 + 5.92401P - 0.17068P^2 $$

The results indicate that BaIn$_2$P$_2$ is prone to brittleness below 3.6 GPa and is strongly prone to ductility above 3.6 GPa. The results also indicate that the Debye temperature increases with increasing pressure.

3.2.3. Elastic anisotropy

Another interesting physical parameter with respect to the elastic properties of solids is the elastic anisotropy. The elastic anisotropy reflects different bonding natures in different crystallographic directions and has important implications because it is correlated with the possibility of inducing microcracks in materials. Hence, it is important to estimate the elastic anisotropy of a solid to identify methods of improving its mechanical durability. At present, a variety of approaches have been proposed for the numerical

![Table 5](#)

<table>
<thead>
<tr>
<th>$B_s$</th>
<th>$B_r$</th>
<th>$B$</th>
<th>$G$</th>
<th>$E$</th>
<th>$\sigma$</th>
<th>$V_l$</th>
<th>$V_t$</th>
<th>$V_m$</th>
<th>$T_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.6</td>
<td>40.8</td>
<td>43.2</td>
<td>30.8</td>
<td>26.2</td>
<td>28.5</td>
<td>1.52</td>
<td>70.1</td>
<td>0.230</td>
<td>3917</td>
</tr>
</tbody>
</table>

Fig. 4. Calculated pressure dependence of the independent elastic constants $C_{ij}$ of the monoclinic Zintl phase BaIn$_2$P$_2$. The symbols indicate the calculated results. The lines represent the results of fitting these theoretical results to a second-order polynomial.
Fig. 5. Calculated pressure dependence of Pugh’s ratio $B/G$, Young’s modulus $E$, Poisson’s ratio $\nu$ and the Debye temperature for the monoclinic Zintl phase BaIn$_2$P$_2$. The symbols indicate the calculated results. The lines represent the results of fitting these theoretical results to a second-order polynomial.

3.3. Electronic structure and chemical bonding

The calculated band structure and its corresponding total and site-projected $l$-decomposed density (DOS) diagrams for the monoclinic Zintl phase BaIn$_2$P$_2$ are depicted in the left and right panels of Fig. 7, respectively. The band structure was calculated along special lines connecting the following high-symmetry points in the Brillouin zone (Fig. 8): $Z(0, 0, 0.5)$, $T(0, 0, 0)$, $Y(0, 0.5, 0)$, $A(-0.5, 0.5, 0)$, $B(-0.5, 0.0, 0)$, $D(-0.5, 0.5, 0.5)$, $E(-0.5, 0.5, 0.5)$ and $C(0, 0.5, 0.5)$ (the coordinates are given in terms of unit vectors of the reciprocal lattice). The calculated band-gap energy $E_g$ is 0.28 eV and is of a direct character because both the valence-band maximum (VBMa) and the conduction-band minimum (CBMi) occur at the same point, $D$, in the Brillouin zone. Notably, the band-

estimation of the elastic anisotropy. Here, we used three different indexes to estimate the elastic anisotropy of the BaIn$_2$P$_2$ compound:

(i) One method of measuring the elastic anisotropy is to consider the percentage of anisotropy in the compression and shear modes [38]:

$$A_{\text{Comp}} = \frac{B_V - B_R}{B_V + B_R} \times 100, \quad A_{\text{Shear}} = \frac{G_V - G_R}{G_V + G_R} \times 100$$

where $B$ and $G$ are the bulk and shear moduli, respectively, and the subscripts $V$ and $R$ represent the Voigt and Reuss bounds, respectively. For crystals, these values can range from zero, which represents perfect isotropy, to 100%, which represents the maximum anisotropy. The percentages of anisotropy in the compression and shear modes of BaIn$_2$P$_2$ at zero pressure are approximately 6% and 8%, respectively. Thus, according to this index, BaIn$_2$P$_2$ is somewhat anisotropic in both the compression and shear modes.

(ii) The above elastic anisotropy criteria quantify the degree of anisotropy from a single bulk or shear contribution. To quantify the extent of the anisotropy accurately, a novel, more universal index $A_{\text{II}}$ has been proposed by Ranganathan and Ostoj-Starzewski [39] to measure the single-crystal anisotropy accounting for both bulk and shear contributions, where $A_{\text{II}}$ is defined as follows: $A_{\text{II}} = 5G_V/G + B_V/B_R - 6$. For isotropic crystals, the universal index is equal to zero ($A_{\text{II}} = 0$); the deviation of $A_{\text{II}}$ from zero defines the extent of the anisotropy of a crystal. The obtained universal index for BaIn$_2$P$_2$ at zero pressure is approximately $A_{\text{II}} \approx 1$, which reveals that this material is characterized by some anisotropy.

(iii) Three-dimensional (3D) illustration of the elastic moduli is an effective method of visualizing the details of the elastic anisotropy of a material along its crystallographic directions. In a 3D representation, an isotropic system would exhibit a spherical shape, and the deviation from a spherical shape indicates the degree of anisotropy. To illustrate the elastic anisotropy of the investigated material, a three-dimensional representation of the directional dependence of the Young’s modulus and linear bulk modulus is presented in Fig. 6, using the relations given in Ref. [40]. Clearly, Fig. 6 exhibits obvious deviations of the Young’s modulus and linear bulk modulus surfaces from a spherical shape, so one can conclude that the monoclinic Zintl phase BaIn$_2$P$_2$ possesses obvious elastic anisotropy. To provide a better understanding of the origin of the changes in the Young’s modulus and linear bulk modulus along different directions, we also visualize them along the $(X = Y)Z$, $XY$, $XZ$ and $YZ$ planes in Fig. 6. From these cross sections, one can see that the Young’s modulus exhibits less anisotropy in the $X$ plane compared to the other planes. For the linear bulk modulus, the lesser elastic anisotropy is observed for the $XY$ and $YZ$ planes, while the other planes exhibit strong elastic anisotropy. Finally, the values of the linear bulk modulus along the $X$, $Y$ and $Z$ axes are approximately 105, 174 and 109 GPa, respectively, and they are consistent with those obtained using the linear compressibility: $B_a = \beta_a^{-1} = 121$ GPa, $B_b = \beta_b^{-1} = 193$ GPa and $B_c = \beta_c^{-1} = 119$ GPa, where the change in the $a$, $b$ or $c$ lattice parameter is measured as a function of hydrostatic pressure. This good agreement verifies the reliability of our calculations.
gap value $E_g$ obtained using DFT is, as a rule, somewhat underestimated. Thus, the $E_g$ value given above can serve as a minimum estimate of the true band gap. Unfortunately, no data concerning experimental measurements of the band gap of the investigated compound have been reported so far. The band gaps calculated using DFT with the common approximations LDA and GGA are likely to be approximately 30\%–50\% smaller than experimental values [41]. Therefore, the real band gap of BaIn$_2$P$_2$ is expected to be less than 0.4 eV, and the monoclinic Zintl phase BaIn$_2$P$_2$ can be classified as a narrow-band-gap semiconductor.

Fig. 6. Illustration of the directional dependence of Young’s modulus $E$ (a) and the linear bulk modulus (b) and their cross sections in various planes for the monoclinic Zintl phase BaIn$_2$P$_2$. The distance between zero and any point on the surface is equal to the elastic modulus in that direction.

Fig. 7. The calculated band structure of BaIn$_2$P$_2$ (left panel) and DOS diagrams (right panel) for the monoclinic Zintl phase BaIn$_2$P$_2$. 
The effective charge-carrier mass is one of the main factors that determines the transport properties and electrical conductivity of a material. Generally speaking, the smaller the effective masses of the carriers are, the faster the photogenerated carriers are. Consequently, a light effective mass can promote the migration of carriers and suppress the recombination of carriers. Here, the effective charge-carrier mass \( m^* \) was evaluated by fitting the \( E-k \) diagram near the valence-band maximum (VBM) and conduction-band minimum (CBM) with a paraboloid; the effective mass \( m^* \) at a given point along the direction given by \( k \) is:

\[
\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2}
\]

The effective masses for electrons and holes calculated from the electronic energy band dispersions at points of interest in the Brillouin zone for \( \text{BaIn}_2\text{P}_2 \) are summarized in Table 5. The effective electron mass is indicated by the subscript “e” \( (m_e^*) \), and the hole mass is indicated by “h” \( (m_h^*) \). We obtained the following results: \( m_e^*(D\rightarrow E) = 0.01, m_h^*(D\rightarrow B) = 0.126, m_e^*(D\rightarrow E) = 0.081 \) and \( m_h^*(D\rightarrow B) = 0.064 \). The dependence of the effective mass on the crystallographic direction demonstrates the anisotropy of this property. The relatively larger value of the effective mass along the \( D \rightarrow B \) direction reflects the greater flatness of the conduction band along this direction.

The composition of the calculated band structure (Fig. 7, left panel) can be deduced from the DOS diagrams (Fig. 7, right panel). The total DOS spectrum of \( \text{BaIn}_2\text{P}_2 \) exhibits six well-defined regions below the Fermi level \( (E_F) \), which are labelled V1, V2, V3, V4, V5 and V6. The narrow deep structure V1, which is centred at approximately \(-27.6 \text{ eV}\), is attributed to the Ba 6s states. The group of bands V2, which is peaked at approximately \(-14.3 \text{ eV}\), is dominantly composed of the In 4d states. The bundle of bands V3 originates mainly from the Ba 5p states. The group of valence bands V4, which is centred at approximately \(-10 \text{ eV}\), contains principally P 3s states, with a slight contribution from the In 5s and Ba 6s states. The group of valence bands V5, which is centred at approximately \(-5 \text{ eV}\), is a mixture of P 3p states and In 5s and 5p states. These are followed by the group of valence bands V6, which extends from \(-3.75 \text{ eV}\) up to \( E_F \) and is formed by the hybridization of the P 3p and In 5p orbitals and a small contribution from the Ba 5d states. The group of conduction bands, which is labelled C1, contains a mixture of the empty P 3p states, In 5s and 5p states and Ba 5d states. It is worth noting here that we calculated the distributions of states for all inequivalent positions of each element of \( \text{BaIn}_2\text{P}_2 \), and essentially no noticeable difference among them was noted.

The application of hydrostatic pressure significantly affects the electronic structure of a solid, leading to variation in the value of the fundamental band gap (the lowest-energy band gap) and sometimes its character, as well. The pressure dependence of the investigated compound is illustrated in Fig. 9. For pressures less than 4.08 GPa, \( \text{BaIn}_2\text{P}_2 \) has a direct band gap \( D-D \), which increases with increasing pressure. When the pressure is higher than 4.08 GPa, the top of the valence band (TVB) moves from the D-point to the B-point in the Brillouin zone, whereas the bottom of the conduction band (CBB) is still located at the D-point until the pressure reaches 10.56 GPa, when it moves to the \( \Gamma \)-point. Therefore, for pressures \( P \) such that \( 4.08 \text{ GPa} < P < 10.56 \text{ GPa} \), \( \text{BaIn}_2\text{P}_2 \) has an indirect \( B-D \) band gap, which is not sensitive to pressure variations within this range. For pressures higher than 10.56 GPa, the fundamental gap of \( \text{BaIn}_2\text{P}_2 \) becomes an indirect \( B-\Gamma \) band gap, and it decreases with increasing pressure. We note here that the pressure dependence of the selected band-gap energies is not consistent with a polynomial fit; this is because of the change in the type of the TVB and CBB points in the Brillouin zone under the influence of pressure variations.

To illustrate the bonding features, the charge-density distributions were calculated. The left panel of Fig. 10 depicts the calculated contour plots of the charge-density distributions in the (040) plane. The most interesting aspect of this figure is the presence of a
directional bonding between the In atoms (In−In) and between the In and P atoms (In−P). The bonding between P and In is primarily covalent with some ionic features. There is only a weak directional bonding between the Ba and P atoms. The charge surrounding the Ba site is partially shifted toward the P atom, and this is consistent with the greater electronegativity of P compared to Ba. The spherical charge distribution around the Ba atoms clearly suggests a primarily ionic bonding between the Ba and P atoms with a somewhat covalent character.

To accentuate the redistribution of the charge density $\rho$ of the $\text{BaIn}_2\text{P}_2$ compound, the point-by-point charge density difference, $\delta \rho = \rho(\text{BaIn}_2\text{P}_2) - \rho(\text{Ba atoms}) - \rho(\text{In atoms}) - \rho(\text{P atoms})$, on the (040) plane is plotted in the right panel of Fig. 10. From the right panel of Fig. 10, one can see that there is a loss of charge from the P and In cores and a redistribution of this charge into the interstitial charge. The value of the charge-density difference is negative at the P and In sites, while positive values are exhibited between the P and In sites, indicating that common charges exist between P and In and that covalent bonds are therefore formed between In and P atoms.

To further investigate the electronic structure of the considered material, we calculated the charge transfer using Hirshfeld population analysis (HPA) [42]. The obtained results are summarized in Table 6. One can observe that Ba and In atoms donate electrons and P atoms accept electrons. A lower atomic charge difference implies relatively lower ionicity and higher covalency in the corresponding chemical bonds. The chemical bonding between In and P is more covalent than that between Ba and P.

### 3.4. Optical properties

Fig. 11 shows the calculated dependence of the imaginary part $\varepsilon_2(\omega)$ and the real part $\varepsilon_1(\omega)$ of the dielectric function $\varepsilon(\omega)$ on the photon energy for three polarizations of the electric field $\vec{E}$ of the incident light with respect to the crystallographic axes $\vec{E}/\langle 100 \rangle$, $\vec{E}/\langle 010 \rangle$ and $\vec{E}/\langle 001 \rangle$ for the monoclinic $\text{BaIn}_2\text{P}_2$ compound. Both the absorptive parts ($\varepsilon_2(\omega)$) and the dispersive parts ($\varepsilon_1(\omega)$) of the complex dielectric functions exhibit a noticeable anisotropy for $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$, and they are smaller for the $\langle 100 \rangle$ polarization. The absorption edge is slightly shifted toward lower energies for the $\langle 100 \rangle$ polarization. Because the imaginary part of the dielectric function, $\varepsilon_2(\omega)$, is proportional to the crystal absorption spectrum, with the aid of the DOS diagrams (Fig. 7), it is possible to assign the absorption peaks between 0.28 and 5 eV to the electronic transitions from the occupied group of valence bands V6 (P 3p, In 5p and Ba 4d states) to the empty group of conduction bands C1 (P 3p, In 5s5p and Ba 5d states). It is well known that DFT underestimates the band gaps, and consequently, the calculated optical spectra will be shifted toward lower energies relative to the experimental spectra. To fix this error, sometimes the optical spectra are rigidly shifted toward higher energies up to the experimentally determined location by introducing a scissor operator. Because no experimental data are available for the considered material, this rigid-shift technique has not been applied. The calculated static dielectric constant $\varepsilon_1(0)$ was found to be 15.181 for $\vec{E}/\langle 100 \rangle$, 13.93 for $\vec{E}/\langle 010 \rangle$, and 13.99 for $\vec{E}/\langle 001 \rangle$. The static dielectric constant $\varepsilon_1(0)$, because it is an important optical constant, was calculated at various pressures. The results are shown in Fig. 13, where it can be seen that $\varepsilon_1(0)$ increases when the pressure increases for the three light polarizations.

The calculated refractive-index ($n(\omega)$) and extinction-coefficient ($k(\omega)$) spectra in the energy range from 0 to 30 eV for three incident radiation polarizations along the $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ directions for the investigated material are depicted in Fig. 12(a) and (b). Certain differences in the intensities of the calculated refractive-index and extinction-coefficient spectra for different polarizations are evident in Fig. 12(a) and (b), which emphasizes the anisotropic optical properties of the material. The refractive index $n(\omega)$ is at a maximum (in the lower energy limit) for the $\langle 001 \rangle$ polarization, is at a minimum for the $\langle 100 \rangle$ polarization, and takes on an intermediate value for the $\langle 010 \rangle$ polarization. The values of the static refractive index $n(0)$ are 3.90, 3.72 and 3.75 for incident radiation polarized along the $\langle 100 \rangle$, $\langle 010 \rangle$ and $\langle 001 \rangle$ directions, respectively. When the photon energy increases, the refractive index $n(\omega)$ displays a broad maximum with three humps in the visible part of the spectrum for incident radiation polarized along the $\langle 010 \rangle$ direction. It then decays abruptly to its minimum level. The values of the refractive index $n(\omega)$ are less than one for photon energies higher than 5.6 eV. The local maxima of the extinction coefficient $k(\omega)$ correspond to the zeroes of $\varepsilon_2(\omega)$. The refractive index $n(\omega)$, because it is an important optical constant, was calculated at various pressures. The results are shown in Fig. 13, where it can be seen that $n(\omega)$ increases when the pressure increases for the three light polarizations.

The absorption coefficient $a(\omega)$ is a parameter that characterizes the decay of the light intensity spreading over a unit distance in a

![Fig. 10. Charge-density distribution in eÅ⁻¹ (right panel) and charge-density difference on the (040) plane for the monoclinic Zintl phase $\text{BaIn}_2\text{P}_2$.](image)
Fig. 11. Real (upper graph) and imaginary (lower graph) parts of the dielectric function for incident radiation polarized along the three different crystal directions in the monoclinic Zintl phase BaIn2P2.

The effects of hydrostatic pressure on the lattice parameters, elastic constants, fundamental band gap, and optical constants were also investigated. The shrinkage of the BaIn2P2 compound along the crystallographic axes (a, b and c) was computed, and it was found to be correlated with the elastic constants C_{11}, C_{22} and C_{33}.

The results reported here represent the first attempt at an ab initio investigation of the physical properties of the BaIn2P2 compound, and we hope that these theoretical results can assist in offering a theoretical basis for experiments and applications involving BaIn2P2.

4. Conclusions

We have used the PP-PW method based on DFT with the GGA-PBEsol approach to predict some physical properties of the monoclinic Zintl phase BaIn2P2. After an accurate geometrical optimization of the crystal structure, the elastic, electronic and optical properties of the material were carefully calculated in detail.

Analysis of the single-crystal and polycrystalline elastic parameters revealed that the investigated material is mechanically stable and has a relatively small bulk modulus and a brittle character.

The BaIn2P2 compound exhibits noticeable elastic anisotropy, which can be visualized in detail by plotting the three-dimensional dependence of Young’s modulus and the linear bulk modulus on the direction in the BaIn2P2 crystal structure and its two-dimensional cross sections in various planes. Electronic-structure analysis demonstrated that BaIn2P2 is a narrow-band-gap semiconductor; the band gap was evaluated to be 0.28 eV. The real and imaginary parts of the dielectric function, the refractive indexes, the absorption coefficient, the reflectivity spectra and the electron-loss function were calculated for the (100), (010) and (001) polarizations. The optical properties exhibit noticeable anisotropy.

The energy-loss function was found to be correlated with the elastic constants, fundamental band gap, and optical constants along the crystallographic axes (a, b and c) was computed, and it was found to be correlated with the elastic constants C_{11}, C_{22} and C_{33}.

The results reported here represent the first attempt at an ab initio investigation of the physical properties of the BaIn2P2 compound, and we hope that these theoretical results can assist in offering a theoretical basis for experiments and applications involving BaIn2P2.

Fig. 12. Calculated optical constants: refractive index n(ω), extinction coefficient k(ω), absorption coefficient a(ω), reflectivity R(ω) and energy-loss function L(ω) for the monoclinic Zintl phase BaIn2P2.
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References