Pressure dependent elastic, electronic, superconducting, and optical properties of ternary barium phosphides (Ba$M_2$P$_2$; $M$ = Ni, Rh): DFT based insights

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Abstract
Density functional theory based investigations of structural, elastic, electronic band structure, and optical properties of superconducting ternary phosphides (Ba$M_2$P$_2$; $M$ = Ni, Rh) have been carried out. Calculated ambient condition properties are compared with experimental and theoretical results, where available. Pressure dependent electronic density of states at the Fermi level, $N(E_F)$, and the Debye temperature, $\theta_D$, have been explored and their effect on the superconducting transition temperature have been disclosed. $N(E_F)$ shows nonmonotonic pressure dependence in BaNi$_2$P$_2$. Pressure dependence of $N(E_F)$ for BaRh$_2$P$_2$, on the other hand, is systematic. Pressure dependence of $N(E_F)$ affects superconducting transition temperature significantly. Debye temperature increases with increasing pressure. Variation of optical parameters with photon energy show metallic behavior complementing the features of electronic band structure calculations. Absorption coefficient of BaNi$_2$P$_2$ exhibits strong optical absorption in ultraviolet region, while BaRh$_2$P$_2$ absorbs photons over a wider energy band including the entire visible range. Reflectivity spectra for both BaNi$_2$P$_2$ and BaRh$_2$P$_2$ reveal that they are strong reflectors of visible light and BaNi$_2$P$_2$ in particular holds significant promise to be used as coating material to reduce solar heating.

Keywords: density functional theory (DFT), ternary phosphide superconductors, effect of pressure, electronic band structure, optical constants

(Some figures may appear in colour only in the online journal)

1. Introduction
The ternary low $T_c$ phosphides, Ba$M_2$P$_2$ ($M$ = Ni, Rh), belong to the transition metal 122 compounds famous for exhibiting superconductivity over a wide range of critical temperatures and fascinating electronic ground states with varying degree of electronic correlations and complexity [1]. The short hand nomenclature ‘122’ originates from the stoichiometry of the materials. Compounds belonging to this group have a chemical formula $AT_2Pn_2$, where $A$ = alkaline-earth or rare-earth atom; $T$ = transition metal atom; $Pn$ = P, As, or Sb—one of the three pnictogens. The discovery of superconductivity with comparatively high transition temperature in layered iron oxypnictide (La[O$_{1-x}$F$_x$]FeAs with $x = 0.05$–0.12; $T_c = 26$ K) in early 2008 [2] induced a great deal of excitement within the condensed matter physics community [3]. Soon in the same year, superconductivity was found in a doped 122 compound (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ [4] with a high $T_c$ of 38 K. Since then, variety of 122 compounds has been discovered with different $T_c$s with and without Iron [1]. Not only that, superconductivity was also found in iron-free 122 phosphide and antimonide compounds [1, 5, 6]. Subsequently, it was found that these 122-compounds exhibit a number of intriguing electronic features, such as
superconductivity [4], heavy fermion behavior [7], Kondo correlations [8], coexistence of superconductivity and magnetic orders and charge and spin density waves [1, 4, 7–10].

Quite generally, the 122 compounds with Fe show higher superconducting critical temperatures. At the same time, the role of magnetic order on superconductivity in these systems is still ambiguous [1]. Moreover, a number of investigations on iron-based pnictides suggest that Fe atoms themselves carry no magnetic moment in these compounds [1], making the role of the transition metals in AF$_2$P$_2$ rather fascinating. 122 compounds assume ThCr$_2$Si$_2$-type crystalline structure. Superconductivity is realized in doped AF$_2$As$_2$ on the A site (where A = Ba, Sr, Ca, Eu), under applied pressure in AF$_2$As$_2$, and at ambient pressure in the stoichiometric iron-free and iron-containing BaNi$_2$P$_2$, LaRu$_2$P$_2$, CsFe$_2$As$_2$, and KFe$_2$As$_2$ metallic ternaries [11]. So far numerous work have been done on the 122-type iron-based pnictides, to get insight into the underlying physics leading to superconductivity in AF$_2$P$_2$-compounds, including the role of the transition metals and their relevance to magnetic order. Furthermore, efforts on compounds without iron have also been made, both from experimental and theoretical point of views [1]. For compounds without Fe, LaRu$_2$P$_2$, for example, superconducting transition takes place at 4.0 K [12]. Superconducting transition temperature for BaNi$_2$As$_2$, on the other hand is 0.7 K [11]. This can be contrasted with the $T_c$ of 38 K for isostructural (Ba$_1$+$\delta$K)$_2$Fe$_2$As$_2$. Understanding of all these diverse behaviors, as the rare-earth, transition metal and pnictogen atoms are varied, present a serious challenge to the condensed matter physics community.

In this study we focus our attention on two low-$T_c$ members of the 122 family, namely, BaNi$_2$P$_2$ ($T_c = 3.0$ K) [13] and BaRh$_2$P$_2$ ($T_c = 1.0$ K) [14, 15]. The role of these two elements on widely different values of superconducting transition temperatures of BaNi$_2$P$_2$ and BaRh$_2$P$_2$ is worth investigating. The structural features of BaNi$_2$P$_2$ is known through the early experimental work of Keimes et al. [16]. Terashima et al. [17] have studied the de Haas van Alphen (dHvA) oscillation in BaNi$_2$P$_2$. Ieda and co-workers [18], on the other hand, have reported the angle-resolved photoemission spectroscopy (ARPES) results of BaNi$_2$P$_2$. Both these studies together revealed that the Fermi surface of this 122 compound has hole and electron sheets with three strong dimensional features. A number of theoretical studies exist for BaNi$_2$P$_2$. For example, electronic band structure of this compound was investigated by several groups [1, 19, 20]. All these band structure calculations reveal that the shallow valence electronic bands are constituted mainly from the Ni 3$d$ orbitals with strong admixture with the P $p$ electronic states.

In 2009, heat capacity, resistivity, and uniform magnetic susceptibility studies showed bulk superconductivity in BaIr$_2$P$_2$ ($T_c = 2.1$ K) and BaRh$_2$P$_2$ ($T_c = 1.0$ K) single crystals with ThCr$_2$Si$_2$-type crystalline structure [14, 15]. These two compounds were known since the early work of Wurth et al. [21] and Lohken et al. [22], even though their superconducting state remained unexplored. These two compounds (and BaNi$_2$P$_2$) are isostructural to LaRu$_2$P$_2$ and altogether they amply highlight the realization of superconductivity in a large variety of layered transition metal pnictides. The density functional theory (DFT) based investigation by Shein and Ivanovskii on ternary 122 phosphides [23] indicates that the electronic energy density of states at the Fermi level, $\rho(E_F)$, is markedly larger for BaRh$_2$P$_2$ in comparison with that for BaIr$_2$P$_2$, although the $T_c$ of the former is very much lower than that of the latter. This led Shein and Ivanovskii [23] to suggest that the increase in $T_c$ from 1.0 K for BaRh$_2$P$_2$ to 2.1 K for BaIr$_2$P$_2$ can be related to the difference in the phonon spectrum of these compounds. Existing experimental [14, 15, 24] and theoretical studies [24, 25] on 122 ternary phosphide superconductors imply that the strength of the interlayer P–P bonding plays a prominent part for superconductivity in these systems.

It is hard to overstate the role of pressure in understanding, modifying, and exploring the superconducting correlations in elements, compounds and solid solutions. It is the concept of chemical pressure that led to the discovery of Y123 (YBa$_2$Cu$_3$O$_x$; the first superconducting compound with a transition temperature above the boiling point of liquid nitrogen) high-$T_c$ cuprate superconductor [26]. The pressure dependence of the superconducting transition temperature can yield a wealth of information regarding the structural, lattice dynamical, and electronic band structure related features (e.g., the electronic energy density of the states at the Fermi level) directly linked to the emergence of superconductivity [27–29]. To the best of our knowledge, pressure dependent ab-initio study on superconducting 122 ternary phosphides is scarce in the existing literature. This is one of the main motivations for this pressure dependent ab-initio study of BaNi$_2$P$_2$ and BaRh$_2$P$_2$ compounds. As far as we are aware of, there is no investigation on the optical properties of these two systems. From a number of recent investigations on layered ternaries belonging to different classes, we have found that these compounds often possess attractive optical features which are suitable for variety of optoelectronic device applications [30–36]. Therefore, we have undertaken this project also to investigate the energy dependent optical constants of BaNi$_2$P$_2$ and BaRh$_2$P$_2$ in detail. It is worth noting that energy dependent optical response of a material is intimately related to the underlying electronic band structure and provides us with valuable information that complements the band structure calculations.

The rest of this paper has been structured as follows. Section 2 consists of a description of the theoretical formalism employed in calculations of the physical properties. In section 3 we have presented, analyzed and discussed the results of calculations. Finally, in section 4, the main results are summarized and important conclusions are made.

2. Computational methodologies

We have employed DFT based approach with periodic boundary conditions to calculate structural and electronic properties of BaM$_2$P$_2$ ($M = \text{Ni, Rh}$). In this approach the ground state energy of a compound is obtained via the
solution of Kohn–Sham equation [37]. In this study, in view of the known characteristics of BaM2P2 (M = Ni, Rh) and various exchange-correlation functionals [11, 13–16, 38, 39], we have used the GGA incorporating the Perdew–Burke–Emzerhof (PBE) functional [39] as contained within the CAMbridge Serial Total Energy Package (CASTEP) software [40]. This particular functional is well known for its general applicability and gives rather accurate results for diverse class of metallic crystalline solids. We have also used Vanderbilt-type ultra-soft pseudopotentials to take into account of the electron-ion interactions [41]. Vanderbilt-type ultra-soft pseudopotential relaxes the norm-conserving criteria but at the same time produces a smooth and computation friendly procedure to minimize the computational time without significantly compromising the accuracy of the results. Broyden Fletcher Goldfarb Shanno (BFGS) geometry optimization [42] technique was used to optimize the crystal structure for the given symmetry (I4/mmm, space group No. 139). The following electronic states have been considered for the band structure calculations: Ba [5p 5d 6s], Ni [3p 3d 4s], Rh [4p 4d 5s], P [3s 3p]. An energy cut-off of 500 eV was used for the expansion of the plane wave basis set. k-point sampling within the first Brillouin zone (BZ) was carried out with the Monkhorst-Pack grid scheme [43]. For precise k-space integration, 15 × 15 × 7 and 12 × 12 × 6 k-point grids were used to sample the BZ for BaNi2P2 and BaRh2P2, respectively. The tolerance levels for computational convergence were set to ultra-fine. We have calculated the single crystal elastic constants by the ‘stress-strain’ method contained within the CASTEP code, where elastic responses of the optimized structure corresponding to various stress components are considered. The bulk modulus, B and the modulus of rigidity (shear modulus), G were calculated from the estimated single crystal elastic constants, C_{ij}. Elastic constants and moduli are linked to the average velocity of sound in a crystalline solid. This sound velocity, on the other hand depends on the Debye temperature. Utilizing this link, the Debye temperatures of BaM2P2 have been calculated at different pressures. The electronic band structure has been investigated using the optimized geometry of BaM2P2. Major optical constants were obtained by considering both interband and intra-band photon induced electronic transition probabilities. The imaginary part, \( \varepsilon_2(\omega) \), of the complex dielectric function, \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) was calculated from the matrix elements of electronic transition between occupied and unoccupied electronic states by employing the CASTEP supported formula given by,

\[
\varepsilon_2(\omega) = \frac{2e^2}{\Omega \varepsilon_0} \sum_{k\omega} \left| \langle \psi_v^\dagger | \mathbf{\hat{p}} - \mathbf{\hat{F}} | \psi_i \rangle \right|^2 \delta(E_k^v - E_k - E)
\]

In this equation, \( \Omega \) is the volume of the unit cell, \( \omega \) is the angular frequency of the incident electromagnetic wave (photon), \( e \) is the electronic charge, \( \psi_i, \psi_v \) are the conduction and valence band wave functions at a fixed wavevector \( k \). The delta function enforces conservation of energy and momentum during the photon induced optical transition. It should be mentioned that equation (1) has been written for interband transitions. Equation (1) is also valid for intraband optical transitions with relevant changes in the energy level/ band indices. The real part of the dielectric constant \( \varepsilon_1(\omega) \) of the dielectric function can be extracted from the corresponding imaginary part \( \varepsilon_2(\omega) \) via the Kramers-Kronig equations. Once these two parts of the energy dependent dielectric constant are known, all the other optical parameters can be evaluated from those [44]. This methodology has been employed extensively by a volume of earlier studies to accurately calculate the frequency dependent optical constants for compounds belonging to diverse classes of materials with widely varying electronic band structures [30–36, 45].

3. Theoretical results

3.1. Structural and elastic properties

As mentioned earlier BaM2P2 compounds crystallize in ThCr2Si2-type structure belonging to the space group I4/mmm (body centered tetragonal). Figure 1 shows the schematic crystal structure of BaM2P2. The optimized lattice constants and cell volumes under different uniform pressure are presented in table 1. Ambient condition theoretical and experimental results from earlier studies [16, 20, 21, 23, 46, 47] are also given in this table, where available. It is seen that the optimized structural parameters under ambient condition agree well with prior results [16, 20, 21, 23, 46, 47]. In fact the zero-pressure values of the lattice parameters and cell volumes obtained here agree to a better extent with the experimental values compared to some of the other theoretical estimates [23, 46]. Due to the tetragonal structural symmetry the compounds under study possess six independent single crystal elastic constants (C_{ij}), designated by C_{11}, C_{33}, C_{44}, C_{66}, C_{12}, and C_{13}. We have tabulated the calculated C_{ij} for BaM2P2 at different pressures in table 2 together with the existing theoretical estimates [47, 48]. A crystal with given symmetry is elastically or mechanically stable if the elastic energy

![Figure 1. Schematic crystal structure of BaM2P2. The different crystallographic directions are also shown.](image-url)
corresponding to an arbitrary strain within the elastic limit is positive. This requirement leads to the following four necessary and sufficient conditions for mechanical stability of tetragonal systems [49]:

$$C_{11} > |C_{12}|; 2C_{13}^2 < C_{33}(C_{11} + C_{12}); C_{44} > 0; C_{66} > 0$$

(2)

From the tabulated values of $C_{ij}$ and the conditions for stability, it is evident that both BaNi$_2$P$_2$ and BaRh$_2$P$_2$ are mechanically stable. Among the six independent elastic constants, $C_{11}$ ($=C_{22}$) and $C_{13}$ measure the elastic response of the compound due to uniaxial stresses. $C_{44}$ and $C_{66}$ arise in reaction to shearing stresses. $C_{12}$ and $C_{13}$, on the other hand measure the response due to an axial stress with respect to a strain along a perpendicular axis. The elastic moduli can be calculated from the calculated values of $C_{ij}$.

In table 2, it is interesting to note that at zero pressure $C_{12}$ of BaNi$_2$P$_2$ shows a negative value. This is not entirely unusual. For example, compounds where atoms have mixed valency can show negative off-diagonal elastic constants together with mechanical stability [50]. In some cases, negative elastic constant implies existence of internal stress inside the compound. At finite pressures, all the elastic constants are positive and increase with increasing pressure up to 15 GPa. At higher pressure (20 GPa), some of the elastic constants exhibit slightly decreasing trend. This may imply that a gradual tendency towards pressure induced structural instability might set in for BaM$_2$P$_2$ at high pressures above 20 GPa. It is worth mentioning that the structural stability criteria (equation (1)) are fulfilled at all the pressures considered herein. At the same time, lattice constants and cell volumes of BaM$_2$P$_2$ decrease systematically with increasing pressure (table 1) with no sign of any abrupt change in the decreasing trend indicative of structural phase transition. From table 2 it is seen that, $C_{11} > C_{33}$ at all pressures for both the compounds. The difference becomes more prominent as pressure increases. This indicates that the structure is stiffer along the [100] and [010] directions in comparison to that along the [001] direction, as far as the uniaxial stiffness is

| Pressure (GPa) | Compound       | $a$(Å) | $b$(Å) | $c$(Å) | $V$(Å$^3$) | Reference     |
|---------------|----------------|--------|--------|--------|------------|---------------|
| 0             | BaNi$_2$P$_2$  | 3.941  | 3.941  | 12.008 | 186.532    | This work     |
| 5             |                | 3.869  | 3.869  | 11.751 | 175.883    |               |
| 10            |                | 3.806  | 3.806  | 11.573 | 167.661    |               |
| 15            |                | 3.762  | 3.762  | 11.392 | 161.195    |               |
| 20            |                | 3.724  | 3.724  | 11.236 | 155.815    |               |

| Pressure (GPa) | Compound       | $a$(Å) | $b$(Å) | $c$(Å) | $V$(Å$^3$) | Reference     |
|---------------|----------------|--------|--------|--------|------------|---------------|
| 0             | BaRh$_2$P$_2$  | 4.001  | 4.001  | 12.619 | 202.05     | This work     |
| 5             |                | 3.953  | 3.953  | 11.279 | 191.912    |               |
| 10            |                | 3.915  | 3.915  | 11.984 | 183.737    |               |
| 15            |                | 3.885  | 3.885  | 11.733 | 177.169    |               |
| 20            |                | 3.862  | 3.862  | 11.488 | 171.412    |               |

| Pressure (GPa) | Compound       | $C_{11}$ | $C_{13}$ | $C_{44}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | References     |
|---------------|----------------|----------|----------|----------|----------|----------|----------|---------------|
| 0             | BaNi$_2$P$_2$  | 124.702  | 107.218  | 38.14    | 23.975   | −21.29   | 27.96    | This work     |
| 5             |                | 161.658  | 113.81   | 51.62    | 32.953   | 7.14     | 60.743   |               |
| 10            |                | 220.55   | 140.88   | 65.76    | 39.13    | 59.723   | 112.363  | This work     |
| 15            |                | 228.461  | 184.239  | 78.459   | 44.091   | 62.686   | 116.329  | This work     |
| 20            |                | 222.052  | 124.660  | 89.318   | 48.744   | 54.954   | 108.578  | This work     |
| 0             | BaRh$_2$P$_2$  | 162.586  | 104.518  | 39.607   | 68.094   | 57.621   | 57.547   | This work     |
| 5             |                | 205.048  | 128.131  | 53.598   | 100.885  | 90.481   | 77.339   | This work     |
| 10            |                | 233.863  | 162.046  | 62.839   | 121.715  | 115.035  | 91.363   | This work     |
| 15            |                | 259.092  | 187.261  | 73.135   | 137.568  | 136.694  | 112.054  | This work     |
| 20            |                | 278.497  | 185.347  | 81.518   | 150.532  | 156.95   | 130.868  | This work     |
| 0             |                | 147.26   | 89.79    | 26.81    | 53.39    | 57.75    | 60.50    | Theo. [47]   |
concerned. Such behavior is directly related to the strength of the chemical bonding in the respective crystallographic directions within the compound. Table 2 also shows that $C_{44} > C_{66}$, at all pressures. The principle implication of this result is that, the [100] (010) shear should be more effective in changing the shape than the [100] (001) shear for BaM$_2$As$_2$ compounds. All these qualitative and quantitative features of $C_{ij}$ strongly reflect the layered features of the crystal structure under consideration. From the values of $C_{ij}$ it becomes evident that chemical bondings within the $ab$-plane are stronger than those along $c$-direction.

As mentioned earlier, various elastic moduli, the Poisson’s ratio and the Pugh’s ratio can be estimated from the calculated single crystal elastic constants $C_{ij}$. Table 3 shows these polycrystalline elastic moduli and ratios of BaM$_2$P$_2$ at different applied pressures. The Voigt approximation [51] asserts that isotropic bulk and shear moduli can be extracted from linear combinations of single crystal elastic constants [51–54]. The Voigt approximated bulk and shear moduli have been denoted by $B_V$ and $G_V$, respectively. Reuss, on the other hand, derived [55] different values of isotropic bulk and shear moduli from the single crystal elastic constants [52–54] using different criteria. Reuss approximated elastic moduli are denoted by $B_R$ and $G_R$. Subsequently, Hill [56] concluded that, the Voigt and Reuss approximated estimates are actually the upper and lower limits of the polycrystalline elastic moduli. A more realistic measure of the bulk and shear moduli are therefore, the arithmetic averages given by, $B = (B_V + B_R)/2$ and $G = (G_V + G_R)/2$, respectively. Both Young’s modulus, $Y$, and Poisson’s ratio, $n$, are related to the bulk modulus and to the shear modulus [52–54]. The Pugh’s ratio, expressed as $B/G$, is another useful elastic indicator which is also presented in table 3.

The pressure dependent variation of elastic moduli and ratios reveal several new interesting features of BaM$_2$P$_2$. The bulk, shear and the Young moduli show conventional pressure dependence, namely, all these parameters increase with increasing pressure (except at 20 GPa for BaNi$_2$P$_2$). Such increase is natural, since applied pressure makes the crystal stiffer. The intriguing part is revealed in the pressure dependence of the Pugh’s and Poisson’s ratios.

We have $B > G$, for both the compounds, implying that they are prone to mechanical failure due to shape deformation. In comparison to many other metallic layered ternaries and their solid solutions, the calculated elastic moduli of BaM$_2$P$_2$ are rather small [36, 57–61], indicating that these compounds are relatively soft in nature. The ratio between polycrystalline bulk and shear moduli is known as the Pugh’s ratio [62] which is an important indicator of mechanical behavior of solids. A large value of this ratio indicates ductile behavior; whereas a low value indicates brittleness. The brittle to ductility boundary is marked by a critical Pugh’s ratio of 1.75. From table 3 it is observed that applied pressure increases this ratio quite rapidly. For BaNi$_2$P$_2$, the Pugh’s ratio at zero pressure is 1.20, implying ductility, at a pressure of 5 GPa this value increases to 1.72, close to the ductile to brittle boundary, for further increase in pressure, Pugh’s ratio exceeds 1.75 and the compound is predicted to show highly brittle behavior. For BaRh$_2$P$_2$, the Pugh’s ratio implies brittleness throughout but pressure increases its value systematically. Therefore, we conclude that the brittleness of BaRh$_2$P$_2$ increases with increasing applied pressure. The Poisson’s ratio is another significant measure that gives us information not only about mechanical behavior but also about the underlying atomic bonding characteristics of a compound. It is known that $n = 0.25$ is the lower limit for solids where central-force field dominates [63]. The Poisson’s ratio of BaNi$_2$P$_2$ shows strong pressure dependence. It rises sharply at low pressure. Poisson’s ratio of BaNi$_2$P$_2$ under ambient condition implies that non-central force dominates in electronic bondings in this compound, while the ratio at 5 GPa indicates the dominance of central forces in BaNi$_2$P$_2$. For BaRh$_2$P$_2$, the pressure dependence of $n$ is significantly weaker. At all pressures including ambient the dominant bonding is central in nature. The brittle to ductile boundary is marked by a Poisson’s ratio of ~0.31 [64]. This suggests that BaNi$_2$P$_2$ becomes brittle as pressure increases. The same pressure induced trend in observed for BaRh$_2$P$_2$. Relatively low values of Poisson’s ratio for BaM$_2$P$_2$ indicate that the

| Pressure (GPa) | Compound | $B_V$ | $B_R$ | $B$ | $G_V$ | $G_R$ | $G$ | $Y$ | $B/G$ | $N$ | References |
|---------------|----------|-------|-------|-----|-------|-------|-----|-----|-------|-----|------------|
| 0             | BaNi$_2$P$_2$ | 47.32 | 46.23 | 46.77 | 41.52 | 36.32 | 38.92 | 91.41 | 1.20  | 0.17 | This       |
| 5             | BaNi$_2$P$_2$ | 77.15 | 77.11 | 77.13 | 47.81 | 41.27 | 44.54 | 112.05 | 1.72  | 0.26 | This       |
| 10            | BaNi$_2$P$_2$ | 127.87 | 126.43 | 127.15 | 53.89 | 40.85 | 47.37 | 126.42 | 2.70  | 0.33 | This       |
| 15            | BaNi$_2$P$_2$ | 136.87 | 136.77 | 136.82 | 63.26 | 54.86 | 59.06 | 154.89 | 2.32  | 0.31 | This       |
| 20            | BaNi$_2$P$_2$ | 123.67 | 119.04 | 121.35 | 65.25 | 40.78 | 53.01 | 138.83 | 2.32  | 0.31 | This       |
| 0             | BaRh$_2$P$_2$ | 86.12 | 82.35 | 84.23 | 46.59 | 43.19 | 44.89 | 114.35 | 1.88  | 0.27 | This       |
| 5             | BaRh$_2$P$_2$ | 114.28 | 106.84 | 110.56 | 61.15 | 54.85 | 58.02 | 148.14 | 1.92  | 0.27 | This       |
| 10            | BaRh$_2$P$_2$ | 136.14 | 129.55 | 132.85 | 71.61 | 64.61 | 68.11 | 174.51 | 1.96  | 0.28 | This       |
| 15            | BaRh$_2$P$_2$ | 158.56 | 152.14 | 155.35 | 79.74 | 71.05 | 75.39 | 194.67 | 2.08  | 0.29 | This       |
| 20            | BaRh$_2$P$_2$ | 175.52 | 164.34 | 169.93 | 84.29 | 71.12 | 77.71 | 202.29 | 2.17  | 0.30 | This       |
| 0             | BaRh$_2$P$_2$ | 82.42 | 77.75 | 80.08 | 35.11 | 31.19 | 33.15 | 87.39 | 2.44  | 0.31 | Theo. [47]|

Table 3. Polycrystalline bulk modulus $B_V$, $B_R$, $B$ (in GPa), shear modulus $G_V$, $G_R$, $G$ (in GPa), Young modulus $Y$ (in GPa), Pugh’s ratio $B/G$ and Poisson’s ratio $n$ for BaM$_2$P$_2$. 
atomic packing density should be comparatively low in these compounds; a characteristic of materials with substantial covalent and/or ionic bonding(s).

Measure of elastic anisotropy is a technologically important parameter. Elastic anisotropy affects variety of mechanical processes [65] such as the evolution and growth of plastic deformations in crystals, propagation of cracks under external or nonequilibrium internal perturbations, microscale cracking in ceramic compounds, alignment or misalignment of quantum dots, enhanced mobility of charged defects, plastic relaxation in thin films, etc. Hence, it is instructive to investigate the elastic anisotropy of compounds to understand their behavior under different conditions for possible engineering applications. Elastic anisotropy of crystals is characterized by a number of anisotropy factors. Herein we have calculated a number of anisotropy factors of BaMnP2 in the body centered tetragonal form. The widely used anisotropic factors for tetragonal crystal structures are the three shear anisotropy indices, namely, \( A_1, A_2 \) and \( A_3 \). Furthermore, the anisotropy indices for the bulk and shear moduli, \( A_B \) and \( A_G \), respectively, are also estimated. The universal anisotropic index, \( A_U \), an indicator applicable to all crystal systems irrespective of the structural symmetry, has been computed. The set of relations employed to connect the anisotropy indices to the elastic constants and moduli are shown below [66, 67]:

\[
A_1 = \frac{C_{44}(C_{11} + 2C_{13} + C_{33})}{C_{11}C_{33} - C_{13}^2}, \quad \text{for the (010) or (100) plane.}
\]

\[
A_2 = \frac{C_{44}(C_4 + 2C_{13} + C_{33})}{C_4C_{33} - C_{13}^2}, \quad \text{for the (1\overline{1}0) plane,}
\]

where \( C_k = C_{66} + \frac{(C_{11} + C_{12})}{2} \).

\[
A_3 = \frac{2C_{66}}{C_{11} - C_{12}}, \quad \text{for the (001) plane.}
\]

\[
A_B = \frac{B_V - B_R}{B_V + B_R} \times 100; \quad A_G = \frac{G_V - G_R}{G_V + G_R} \times 100.
\]

\[
A_U = \frac{5G_V}{G_R} + \frac{B_V}{B_R} - 6.
\]

All these anisotropy indices and their pressure dependences are enlisted in table 4.

From physical ground, shear anisotropy indices determine the degree of anisotropies in the bonding strengths between atomic species located at different crystal planes. A value of \( A_i = 1 \) (\( i = 1, 2, 3 \)) suggests completely isotropic nature; deviation from unity suggests otherwise.

The variations of anisotropy indices are quite interesting in the sense that these parameters show nonmonotonic pressure dependence for BaNi3P2. The anisotropy parameters increase steadily up to 10 GPa, decrease till 15 GPa and then increase sharply at 20 GPa. These are indicative of pressure dependent anisotropic change in the bonding characteristics and possible tendency towards structural phase transition at high pressures for BaNi3P2. The behavior for BaRh3P2, on the other hand, is rather systematic. All the anisotropic indicators increase systematically except \( A_B \). \( A_B \) of BaRh3P2 is nonmonotonic but the extent of variation is smaller than that for BaNi3P2.

The ratio between \( B \) and \( C_{44} \) can quantify the machinability of a material via the machinability index, \( \mu_M = B/C_{44} \) [68]. \( \mu_M \) provides us with a value that gives a measure of degree of ease with which a particular compound can be machined (e.g., cut or put into different desired shapes). A higher value corresponds to a better machinability. The pressure dependent \( \mu_M \) of BaNi3P2 exhibits nonmonotonic behavior with the highest value of 1.94 at 10 GPa. \( \mu_M \) of BaRh3P2 shows very weak dependence on applied pressure and lies between 2.06 to 2.12 at different pressures.

### 3.2. Debye temperature

The Debye temperature, \( \theta_D \), correlates with many important thermo-physical properties of solids, such as heat capacity, bonding strengths, phonon thermal conductivity, vacancy formation energy, melting temperature etc. This temperature also sets the characteristic energy scale which involves the electron-phonon coupling and formation of Cooper pairs in superconductors. At low temperatures the vibrational excitations in a crystal arise from the acoustic modes. Therefore, at low temperatures \( \theta_D \) calculated from the elastic constants is closely related to that obtained from the analysis of heat capacity measurements. Among several available methods for estimating \( \theta_D \), Anderson method is simple and straightforward, which depends mainly on the average sound velocity in a solid and can be expressed as [69]:

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

where \( h \) and \( k_B \) are the Planck’s and Boltzmann’s constants, respectively, \( N_A \) is the Avogadro’s number, \( ρ \) denotes the density of the compound, \( M \) refers to the molecular weight and \( n \) is the number of atoms in the molecule. The sound wave, in a crystalline solid, propagates with an average velocity \( \mu_m \) which can be determined from,

\[
\mu_m = \left[ \frac{1}{3} \left( \frac{1}{v_l^2} + \frac{2}{v_t^2} \right) \right]^{-1/3}
\]

In equation (4), \( v_l \) and \( v_t \) are the longitudinal and transverse sound wave velocities, respectively. These two velocities can be determined from the expressions given below [69]:

\[
v_l = \left[ \frac{3B + 4G}{3ρ} \right]^{1/2}
\]

and

\[
v_t = \left[ \frac{G}{ρ} \right]^{1/2}
\]

The estimated Debye temperature \( \theta_D \) under different pressures along with the respective sound wave velocities \( v_l, v_t, \) and \( \mu_m \) for BaMnP2 are enlisted in table 5.

Both Debye temperature and sound velocity increase systematically with pressure. This is mainly a consequence of
pressure induced stiffening of the crystal. The agreements between previously determined \( \theta_D \) and the present estimations are excellent [47, 48, 70]. A pressure induced change in the Debye temperature is predicted to change a number of important physical properties of \( \text{BaM}_2\text{P}_2 \). For example, increase in Debye temperature leads to an increase in the phonon thermal conductivity, crystal stiffness and melting temperature of solids [71, 72].

### 3.3. Electronic band structure

Electronic band structure calculations are one of the most important features of crystalline solids which almost completely determine the charge transport and optical characteristics of materials. The band structure exhibits how the energy \( (E) \) of the allowed electronic states changes with the momentum \( (\nabla k) \) in the reciprocal lattice space. These \( E(k) \) plots within the Brillouin zone are also known as the electronic dispersion curves. The electronic band structures at some selected pressures for \( \text{BaM}_2\text{P}_2 \) at different pressures are shown in figure 2.

The band structures of \( \text{BaM}_2\text{P}_2 \) reveal clear metallic character as a number of bands cross the Fermi level and there are significant valence and conduction band overlaps. The bands around \( E_F \) show dispersive features with varying degree. Among all these bands the ones running along \( A-M \) show non-dispersive feature. This implies that effective mass of charge carriers are large in this direction and there is anisotropy in the charge transport with respect to propagation direction. The band structure across the Fermi level also shows electron- and hole-like character. Therefore, the topography of the Fermi surface should contain both electron- and hole-sheets. Application of pressure has significant effect on the band structure. The pressure induced shift in the band structure is seen both below and above the Fermi energy. The energy shifts in the bands are mixed in character. Some of the bands show a decreasing trend in energy with increasing pressure; in some bands an opposite trend is seen. The degree of dispersion for the bands near the Fermi energy also varies with pressure. This implies that the transport properties of \( \text{BaM}_2\text{P}_2 \) will be affected significantly due to pressure. To explore the matter in greater depth, we have shown the orbital partial density of states (PDOS) and total density of states (TDOS) of \( \text{BaM}_2\text{P}_2 \) in figure 3 with different applied pressures.

Figure 3(a) shows that the Ba 5d, Ni 3d, and P 3p states contribute significantly to the total electronic density of states at the Fermi level, \( N(E_F) \) of \( \text{BaNi}_2\text{P}_2 \). Significant overlap in energy among these orbitals implies hybridization and tendency towards formation of covalent bondings. These three electronic states also contribute strongly in the

### Table 4. Pressure dependent variation of elastic anisotropy indices of \( \text{BaM}_2\text{P}_2 \).

| Pressure (GPa) | Compound      | \( A_1 \) | \( A_2 \) | \( A_3 \) | \( A_B \) | \( A_G \) | \( A_U \) |
|---------------|---------------|----------|----------|----------|----------|----------|----------|
| 0             | \( \text{BaNi}_2\text{P}_2 \) | 0.87     | 1.24     | 0.33     | 1.16     | 6.68     | 0.74     |
| 5             |               | 1.39     | 1.88     | 0.43     | 0.02     | 7.34     | 0.79     |
| 10            |               | 2.08     | 2.83     | 0.49     | 0.56     | 13.76    | 1.61     |
| 15            |               | 1.77     | 2.22     | 0.53     | 0.03     | 7.11     | 0.76     |
| 20            |               | 3.16     | 4.09     | 0.66     | 1.91     | 23.08    | 3.04     |
| 0             | \( \text{BaRh}_2\text{P}_2 \) | 1.10     | 1.02     | 1.29     | 2.24     | 3.78     | 0.44     |
| 5             |               | 1.28     | 1.10     | 1.76     | 3.36     | 5.43     | 0.64     |
| 10            |               | 1.23     | 1.01     | 2.05     | 2.48     | 5.14     | 0.59     |
| 15            |               | 1.36     | 1.09     | 2.25     | 2.06     | 5.76     | 0.65     |
| 20            |               | 1.71     | 1.29     | 2.48     | 3.29     | 8.47     | 0.99     |

### Table 5. The crystal density \( \rho \) (gm/cm\(^3\)), transverse \( (\nu_t) \) (m/s), longitudinal \( (\nu_l) \) (m/s), and average sound velocity \( \nu_m \) (m/s) and Debye temperature \( \theta_D \) (K) of \( \text{BaM}_2\text{P}_2 \) at different pressures.

| Pressure (GPa) | Compound      | \( \rho \) | \( \nu_t \) | \( \nu_l \) | \( \nu_m \) | \( \theta_D \) | Reference |
|---------------|---------------|-----------|-----------|-----------|-----------|-------------|-----------|
| 0             | \( \text{BaNi}_2\text{P}_2 \) | 5.63      | 2629.25   | 4183.48   | 2681.73   | 301.10      | This      |
| 5             |               | 5.97      | 2731.41   | 4779.35   | 2810.51   | 321.80      | This      |
| 10            |               | 6.27      | 2748.64   | 5507.02   | 2855.17   | 332.17      | This      |
| 15            |               | 6.52      | 3009.69   | 5747.89   | 3114.23   | 367.10      | This      |
| 20            |               | 6.74      | 2804.45   | 5335.24   | 2903.17   | 346.11      | This      |
| 0             | \( \text{BaRh}_2\text{P}_2 \) | 5.68      | 2513.23   | 4761.23   | 2876.93   | 323.70      | Theo. [48]|
| 0             |               | 6.65      | 2598.14   | 4652.32   | 2679.78   | 292.97      | This      |
| 5             |               | 7.00      | 2878.98   | 5178.61   | 2967.45   | 354.77      | This      |
| 10            |               | 7.32      | 3050.35   | 5524.86   | 3143.96   | 354.77      | This      |
| 15            |               | 7.59      | 3151.63   | 5803.30   | 3252.19   | 375.58      | This      |
| 20            |               | 7.84      | 3148.33   | 5904.04   | 3252.19   | 375.58      | This      |
| 0             |               | 6.58      | 2244.54   | 4345.97   | 2512.93   | 273.91      | Theo. [47]|

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M M Mridha and S H Naqib

Phys. Scr. 95 (2020) 105809
Figure 2. The electronic band structure of (a) BaNi$_2$P$_2$ and (b) BaRh$_2$P$_2$ at different representative pressures (black, cyan, and red lines are for pressures of 0, 10, 20 GPa, respectively). The Fermi energy is marked by the horizontal line placed at 0 eV. For clarity, the band structures at 5 and 15 GPa are not shown.
formation of the valence band (VB) states below the Fermi level. Ba 6s and Ni 3p electronic states contribute in the conduction band (CB) above $E_F$. The main contributor for the conduction states is the Ba 5d orbital. In addition to several closely spaced peaks in the TDOS in the CB, there are two intense peaks in the VB centered on $-2.0 \text{ eV}$ and $-4.0 \text{ eV}$. These two peaks are due to the Ni 3d and P 3p electronic states. These peaks are expected to play significant roles in determining the optical properties of BaNi$_2$P$_2$. The TDOS profile near the Fermi level is split for BaNi$_2$P$_2$. The Fermi level lies slightly towards the antibonding (i.e., higher energy) peak. Finite value of $N(E_F)$ for BaNi$_2$P$_2$ confirms its metallic character.

Figure 3(b) illustrates the PDOS and TDOS features of BaRh$_2$P$_2$. It is seen that significant contribution to the $N(E_F)$ comes from the Ba 4d, Rh 5s 4d, and P 3p electronic states. There is large overlap among the PDOS due to Rh 5s 4d and P 3p orbitals around the Fermi energy. Therefore, the transport and bonding properties of BaRh$_2$P$_2$ are controlled by these electronic states and their hybridization. The TDOS at $E_F$ for BaRh$_2$P$_2$ is comparable to that for BaNi$_2$P$_2$. The Fermi level of BaRh$_2$P$_2$ lies quite close to a sharply rising peak in the TDOS little above $E_F$. This shows that electronic stability of BaRh$_2$P$_2$ is somewhat lower than that for BaNi$_2$P$_2$. Two large peaks in the TDOS are found at around $-5 \text{ eV}$ and $-2.5 \text{ eV}$ in the VB. These peaks, together with the peak at $\sim 0.6 \text{ eV}$ in the CB are expected to contribute strongly to the matrix elements for optical transitions.

Pressure affects the band structure. It appears that pressure enlarges the bandwidths of VB and CB for both BaNi$_2$P$_2$ and BaRh$_2$P$_2$. The TDOS at the Fermi level also changes moderately with pressure. We discuss this pressure induced change in the TDOS and its implication on superconductivity in the next section.

From the band structure we see that the $E(k)$ curves crossing the Fermi level do not show marked change in the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{The PDOS and TDOS of (a) BaNi$_2$P$_2$ and (b) BaRh$_2$P$_2$ at different representative pressures (solid, short-dashed, and long-dashed lines are for pressures of 0, 5, 10 GPa, respectively). For clarity, DOS curves for 15 and 20 GPa are excluded.}
\end{figure}
slopes (figure 2) and as a result the change in the electronic density of states at the Fermi level do not change to a very large extent with pressure (figure 3). The position of the Fermi level with respect to the peaks in the DOS also remains fairly unchanged. All these features indicate that the possibility of electronic topological transitions in the electronic structure is low for the compounds under consideration, at least up to an applied pressure of 20 GPa.

3.4. Effect of pressure on superconductivity

$\text{BaM}_2\text{P}_2$ exhibits conventional phonon mediated superconductivity. Phase coherent Cooper pairs are formed and a symmetrical energy gap appears above and below the Fermi level at the superconducting transition temperature, $T_c$. For conventional superconductors Cooper pairs are formed due to attractive electron-phonon interaction. From weakly to moderately strongly coupled superconductors McMillan $T_c$-equation [73] can be employed to estimate $T_c$ with high degree of accuracy. The expression for $T_c$ is given below.

$$T_c = \frac{\theta_D}{1.45} \exp \left\{-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right\}$$  \hspace{1cm} (7)

In equation (7), $\lambda$ denotes the electron-phonon coupling constant and $\mu^*$ signifies the repulsive Coulomb pseudopotential. The electron-phonon coupling constant can be expressed in a number of ways, namely, (i) via electron-phonon spectral density, (ii) via the Hopfield parameter, average phonon energy and electronic density of states at the Fermi level, and finally (iii) via the product of electronic density of states at the Fermi level and the electron-phonon interaction energy [74–76]. Among these, the third one has the simplest functional structure where the electron-phonon coupling constant can be expressed as $\lambda = N(E_F)V_e\text{ph}$ with $V_e\text{ph}$ representing the electron-phonon interaction energy responsible for Fermi surface instability and Cooper pairing [74, 77]. Precise calculation of the electron-phonon spectral density, the Hopfield parameter and $V_e\text{ph}$ is a challenging task [75, 76] because these parameters involve detailed microscopic treatment of coupled system of electrons and phonons. The level of difficulty is further raised since $V_e\text{ph}$ is affected by structural details and lattice anharmonicity in non-trivial fashion [74, 75]. Due to these difficulties, sometimes only the effect of the characteristic phonon energy and the DOS at the Fermi level are considered to study the change in $T_c$ due to pressure or doping [75, 76, 78]. This is not an entirely unreasonable approximation, since $\theta_D$ and $N(E_F)$ are the two major factors which determine $T_c$ [75, 76, 78, 79]. Moreover, in a number of conventional superconductors it has been found that $\lambda$ varies almost linearly with the electronic density of states at the Fermi level [79], implying that the change in $V_e\text{ph}$ with composition or pressure can be relatively low. We adopt this approximation in calculating the pressure dependence of the superconducting transition temperature of $\text{BaM}_2\text{P}_2$ in this section.

One can calculate the pressure dependence of $T_c$ by taking into account of the pressure dependent variation of $\theta_D$ and $N(E_F)$ for $\text{BaM}_2\text{P}_2$ ($M = \text{Ni, Rh}$). These variations are shown in figure 4. First, we calculate the ambient pressure $\lambda$ for $\text{BaM}_2\text{P}_2$. This is done by using the experimentally determined $T_c$ of $\text{BaM}_2\text{P}_2$ ($M = \text{Ni, Rh}$) as the input parameter in equation (7). The zero pressure electron-phonon coupling constants are found to be 0.60 and 0.45 for $\text{BaNi}_2\text{P}_2$ and $\text{BaRh}_2\text{P}_2$, respectively. In these calculations, the value of the Coulomb pseudopotential, $\mu^*$ has been selected to be 0.13, a typical value for many different superconducting compounds [73, 77, 74]. In our approximated scheme, any variation in the $V_e\text{ph}$ due to pressure has not been considered. Therefore, the changes in $\lambda = N(E_F)V_e\text{ph}$ due to pressure become a linear function of $N(E_F)$. Equipped with the computed pressure dependent values of $\theta_D$ and approximated values of pressure dependent $\lambda$, we have calculated $T_c(P)$ employing equation (7). The results of these calculations are depicted in figure 5. Figure 5 shows that $T_c$ varies non-monotonically with pressure for $\text{BaNi}_2\text{P}_2$, whereas for $\text{BaRh}_2\text{P}_2$, $T_c$ decreases with increasing pressure which flattens at high pressures.
3.5. Optical properties of BaNi$_2$P$_2$ and BaRh$_2$P$_2$

Study of optical properties is important for understanding the response of a material to incident electromagnetic wave. How various optical parameters behave at different spectral frequencies or energies are also important to unlock possible optoelectronic and photovoltaic device applications of the compounds under investigation. In this regard, the optical response of a material to infrared, visible and ultraviolet spectra is particularly pertinent. A number of energy dependent optical parameters, e.g., real and imaginary part of dielectric constant \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \), extinction coefficient \( k(\omega) \), energy loss function \( L(\omega) \), energy dependent refractive index \( n(\omega) \), the(extinction coefficient \( k(\omega) \), energy loss function \( L(\omega) \), real and imaginary parts of the optical conductivity \( \sigma_1(\omega) \) and \( \sigma_2(\omega) \), respectively), reflectivity, \( R(\omega) \), and the absorption coefficient \( \alpha(\omega) \), are investigated to elucidate the response of BaM$_2$P$_2$ to incident photons with different energies. The energy dependent optical parameters are shown in figure 5.

The top panels of figure 5 exhibit the dielectric constants. The real part of the dielectric constant is related to the polarizability of the compound, the imaginary part, on the other hand gives a measure of the loss within the compound. \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) of BaNi$_2$P$_2$ show clear metallic character, consistent with electronic band structure. The peak in the \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) of BaNi$_2$P$_2$ at \( \sim 8.0 \text{ eV} \) arises from the optical transitions from the electronic states around \(-2.0 \text{ eV}\) to \(-4.0 \text{ eV}\) in the VB to the states around \(5.0 \text{ eV}\) in the CB (figure 3(a), the TDOS plot). Similarly the weak peaks in the \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) of BaRh$_2$P$_2$ at \( \sim 7.5 \text{ eV} \) originate from the electronic states around \(-6.0 \text{ eV}\) to \(-1.5 \text{ eV}\) in the VB to the states around \(1.5 \text{ eV}\) in the CB (figure 3(b), the TDOS plot). The second pair of panels illustrates the complex refractive indices of BaNi$_2$P$_2$ and BaRh$_2$P$_2$. The real part of the refractive index determines the phase velocity of propagation the electromagnetic wave inside the material. The imaginary part, often termed as the extinction coefficient, in contrast, measures the attenuation as the electromagnetic wave as it propagates through the compound. The real parts are quite high in the visible range of the optical spectra for both BaNi$_2$P$_2$ and BaRh$_2$P$_2$. The third pair of panels from the top shows the absorption spectra for BaNi$_2$P$_2$ and BaRh$_2$P$_2$. The optical absorption spectra of BaNi$_2$P$_2$ and BaRh$_2$P$_2$ are quite different although both show clear metallic character. The absorption coefficient for BaNi$_2$P$_2$ is significantly higher, characterized by prominent peaks at \( \sim 8.0 \text{ eV} \) and \( \sim 18.0 \text{ eV} \) in the ultraviolet region. Overall, BaNi$_2$P$_2$ absorbs ultraviolet (UV) radiation very effectively over an extended energy range from \(7.0 \text{ eV}\) to \(20.0 \text{ eV}\). The absorption capability of BaRh$_2$P$_2$ is relatively low. A prominent peak in the absorption coefficient is located \(\sim 10.0 \text{ eV}\) in the mid-UV region. The fourth pair of panels in figure 6 shows the reflectivity spectra of the compounds under consideration. BaNi$_2$P$_2$ has very interesting reflectivity characteristics. The reflectivity is very high, above 90% for the visible photons. The spectra also exhibit two distinct peaks. The first one is broad and the reflectivity remains above 80% in the energy range from \(10.0 \text{ eV}\) to \(20.0 \text{ eV}\) in the mid-UV region. The second peak is much sharper at resides around \( \sim 23.0 \text{ eV}\) is the in the high energy region of the UV. The reflectivity of BaRh$_2$P$_2$ is significantly lower. This spectra show a peak around \( \sim 10.0 \text{ eV} \) where the reflectivity approaches almost 70%. The next pair of panels shows the optical conductivities. Optical conductivity once again confirms the metallic nature of the compounds. Optical conductivity of BaNi$_2$P$_2$ is significantly higher than that of BaRh$_2$P$_2$. The last (bottom) pair of panels of figure 6 shows the loss function of BaNi$_2$P$_2$ and BaRh$_2$P$_2$. This particular optical parameter shows how a fast charged particle loss its energy via exciting plasmon modes as it passes through the compound. We see a strong plasma peak at \( \sim 24.0 \text{ eV} \) for BaNi$_2$P$_2$. For BaRh$_2$P$_2$, multiple plasma peaks are observed. Peaks at \( \sim 12.5 \text{ eV} \) and \( \sim 19.0 \text{ eV} \) are prominent.

It is interesting to notice that at the plasma frequency, absorption, reflectivity and optical conductivity fall sharply. Above the plasma frequency, the compounds under consideration become transparent and show insulating character.

Like the other properties considered in this study, pressure affects the energy dependent spectra for optical constants. The energy dependent structures in the optical constants depend on the energy dependent features of the electronic energy density of states. The height and energy widths of various peaks in the optical parameters depend on the joint DOS of the electronic orbitals involved in optical transitions. Since pressure affects the band structure and the PDOS and TDOS profiles, there are resulting pressure related changes in the optical parameter spectra. But as far as practical optoelectronic applications are concerned, these are almost exclusively under ambient condition. Therefore, we have only shown the ambient pressure behavior of the optical constants in this section.
Figure 6. Dielectric constants, refractive indices, absorption coefficients, reflectivities, optical conductivities, and loss functions of BaNi$_2$P$_2$ (panels in the left column) and BaRh$_2$P$_2$ (panels in the right column) compounds.
4. Discussion and conclusions

Detailed analyses of pressure dependent structural and elastic properties of BaNi$_2$P$_2$ and BaRh$_2$P$_2$ in the ThCr$_2$Si$_2$-type body centered tetragonal structure have been performed. The pressure dependent single crystal elastic constants ensure mechanical stability up to 20 GPa (the upper limit of the pressure considered). Both BaNi$_2$P$_2$ and BaRh$_2$P$_2$ possess significant elastic anisotropy. Various anisotropy indices vary non-monotonically with pressure indicating the anisotropic nature in the atomic bonding strengths and layered nature of BaM$_2$P$_2$ ($M = $ Ni, Rh). BaNi$_2$P$_2$ shows pressure induced ductile to brittle transition. BaRh$_2$P$_2$, on the other hand remains brittle for pressures up to 20 GPa. The Poisson’s ratios of BaM$_2$P$_2$ imply low packing density and mixed bonding character, dominated by covalent and ionic contributions. The machinability indices of the compounds under study at different pressures are quite high; comparable to those of many MAX phase nanolaminates [80]. BaRh$_2$P$_2$ is more machinable compared to BaNi$_2$P$_2$. The Debye temperature, an important thermo-physical parameter of solids, was calculated from the elastic constants and crystal density. This particular method for calculating the Debye temperature from various elastic constants and moduli has been used widely to estimate $\theta_D$ for variety of compounds with different electronic ground states and bonding characteristics [57, 80–83]. We have found that $\theta_D$ is almost identical for both BaNi$_2$P$_2$ and BaRh$_2$P$_2$, and shows conventional increasing trend with increasing pressure.

The electronic band structures and the PDOS and TDOS features of BaNi$_2$P$_2$ and BaRh$_2$P$_2$ are investigated in detail. The electronic band widths increase with increasing pressure. This is due to increase in the orbital overlap at increased pressure. The TDOS at the Fermi level for BaNi$_2$P$_2$ vary weakly with change in pressure but for BaRh$_2$P$_2$, $N(E_F)$ decreases with increasing pressure up to 15 GPa. Above 15 GPa, the variation flattens. We have calculated the pressure dependent superconducting transition temperature of BaNi$_2$P$_2$ and BaRh$_2$P$_2$. Variation of the electron-phonon coupling constant with pressure has been estimated. $T_c$ of BaNi$_2$P$_2$ varies non-monotonically with pressure. The overall variation is small. For BaRh$_2$P$_2$, $T_c$ decreases steadily with increasing pressure. This decrement is largely due to the reduction in the $N(E_F)$ with increasing pressure. The ambient pressure electron-phonon coupling constants for BaNi$_2$P$_2$ and BaRh$_2$P$_2$ are quite close to those for other isostructural APd$_4$As$_2$ ($A =$ Ba, Sr, Ca) ternaries [81, 84]. Since $N(E_F)$ of BaNi$_2$P$_2$ and BaRh$_2$P$_2$ are comparable at zero pressure, the larger value of $\lambda$ of BaNi$_2$P$_2$ implies that the matrix element of the electron-phonon interaction energy is higher in this compound.

The energy dependent optical parameters confirm the metallic character of the compounds under study and are consistent with the electronic band structure, TDOS, and PDOS features. It is found that BaNi$_2$P$_2$ absorbs UV photons very effectively over an extended spectral range from 7.0 eV to 20.0 eV. This compound also reflects the visible radiations very effectively. Therefore, BaNi$_2$P$_2$ can be used as an efficient absorber of UV radiation and also as a reflecting coating material to reduce solar heating.

To summarize, we have investigated pressure dependent elastic, electronic, and superconducting properties of BaNi$_2$P$_2$ and BaRh$_2$P$_2$ via DFT based calculations. The optical properties at ambient pressure have also been investigated. The compounds under study, particularly BaNi$_2$P$_2$, have attractive optical features suitable for possible applications.

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Data availability

The data sets generated and/or analyzed in this study are available from the corresponding author on reasonable request.

Author contributions

M M M performed the theoretical calculations and contributed in the analysis. S H N designed the project, analyzed the results, and wrote the manuscript. Both the authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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