The rise of 212 MAX phase borides: A case study of Zr$_2$PbB$_2$ via DFT study

M. A. Ali$^{1,2,*}$, M. M. Hossain$^{1,2}$, M. M. Uddin$^{1,2}$, A. K. M. A. Islam$^{3,4}$, S. H. Naqib$^{2,4,*}$

$^1$Department of Physics, Chittagong University of Engineering and Technology (CUET), Chattogram-4349, Bangladesh
$^2$Advanced Computational Materials Research Laboratory (ACMRL), Department of Physics, Chittagong University of Engineering and Technology (CUET), Chattogram-4349, Bangladesh
$^3$Department of Electrical and Electronic Engineering, International Islamic University Chittagong, Kumira, Chattogram-4318, Bangladesh
$^4$Department of Physics, University of Rajshahi, Rajshahi-6205, Bangladesh

Abstract

An interesting class of ternary metallic borides, known as 212 MAX phase borides, is the recent advancement of the MAX phase family. This new class exhibits similar level of metallicity but significantly improved mechanical and thermal properties compared to its traditional carbide counterparts, owing to the existence of 2D boron layer by forming 2c-2e type of covalent bonding between the atoms. In this article, results from ab-initio calculations on an unexplored 212 phase, Zr$_2$PbB$_2$, along with other previously studied phases have been reported. The mechanical stability of Zr$_2$PbB$_2$ has been confirmed from the calculation of the stiffness constants. The obtained elastic constants, elastic moduli and Vickers hardness are found to be significantly larger compared to its carbide counterpart Zr$_2$PbC, a trend similar to other 212 borides. The studied compound is brittle like most MAX and MAB phases with a comparatively low Vickers hardness value. The electronic band structure and density of states revealed traditional metallic nature of Zr$_2$PbB$_2$. A number of important thermal parameters are explored, certifying suitability of Zr$_2$PbB$_2$ compared to its carbide counterpart Zr$_2$PbC, similar trend was found for other 212 borides. The obtained results predict that Zr$_2$PbB$_2$ has significant promise to be used as an efficient thermal barrier coating material. We have explored the physical basis of improved thermophysical properties of boride containing 212 compounds compared to their carbide counterparts in this study.

Keywords: MAX phase borides; DFT study; Mechanical properties; Electronic properties; Thermal properties

1. Introduction

The demand of novel materials with better demonstration of their performances in various applications is increasing day by day in association with the advancement of technology. One of the best ways to achieve this goal is the prediction and/or synthesis of materials in addition to the existing ones that are used in various technological applications. Since, the practical use of MAX phases results due to their peculiar physical properties, the prediction, synthesis as well as study of newly synthesized MAX phase materials have received huge interest from both application as well as basic research points of view [1]. The term MAX represents a layered class of solids in

*Corresponding authors: ashrafphy31@cuet.ac.bd; salehnaqib@yahoo.com
which M is a representative from the transition metal group, A is a representative from the IIIA or IVA group in the periodic table and X is C/N/B atom [2–7]. Despite the metallic nature of the MAX phase materials, they are also potential candidates for use as an alternative of high-temperature materials because of their ceramic like characteristics [1,4,8–10]. Long list of their potential applications can be found elsewhere [1,4,11–13].

However, the main focus for the discovery of new MAX phase was limited due only to the extension of either M element or A element [14–23] or reporting of the MAX phase alloys by the combination of M, M’ and A, A’; M, M’ = Ti, Zr, Hf, Ta, ….; A, A’ = Al, Ga, Si, Ge, P, … [24–33]. The atom X was recognized as either C/N for a long time before the groundbreaking work of Khazaei et al. [5] where they have proposed B as an X element. Prior to this proposal, very few attempts were made to extend the MAX phase family by tuning the X elements in comparison with the attempts taken to extend by choosing the M and/or A element(s) for the same. Both the physical and chemical characters of B as well as B containing compounds convey the prospects of the MAX phase borides by replacing C/N by boron [34]. In recent times such systems have been synthesized and are already listed as the promising members of the MAX phases. Significant attention has also been paid to these MAX phase borides [5–7,35–44]. The first report on the hypothetical MAX phase borides [M2AlB (M = Sc, Ti, Cr, Zr, Nb, Mo, Hf, or Ta)] was published by Khazaei et al. [5] where the trend in the electronic structures of the phase stability have been investigated. Gencer et al. [38] reported the electronic and vibrational properties of Ti2SiB. A predictive study of M2AlB (M = V, Nb, Ta) borides was performed by Surucu et al. [39]. First synthesis of the M2SB (M = Zr, Hf and Nb) borides phase was carried out by Rackl et al. [6,40]. Chakraborty et al. [41] predicted the V2AlB boride by B substitution in place of C in the V2AlC. A DFT study of M2AB (M = Ti, Zr, Hf; A = Al, Ga, In) compounds was carried by G. Surucu [42] in which the structural, electronic, anisotropic elastic, and lattice dynamical properties were considered. We have performed a comprehensive investigation of the synthesized borides M2SB (M = Zr, Hf and Nb) in our earlier report [43] where the physical properties of borides were compared with those of carbides. Boron substitutional effect on the carbon-site in Nb2SC MAX phase was studied by S. K. Mitra et al. [44]. Substitution of C and N in place of B-site of the first synthesized MAX boride Nb2SB has also been reported [35]. Physical properties of predicted MAX phase borides Hf2AB (A = Pb, Bi) have been reported by Hossain et al. [37]. Only one MAX phase boride belonging to the 413 sub class has been
investigated by A. Gencer [36]. Miao et al. [7] have predicted MAX phase borides Hf$_2$AB (A = Bi, Pb) where they have calculated the formation energy and investigated their dynamical stability. Miao et al. [7] have also predicted another class of MAX phase materials crystallized with different space group (S.G.: 187, also called sub-space group of conventional MAX phase [7,45]) of the hexagonal system. The traditional MAX phases are crystallized in the S.G.: 194 of the hexagonal system. The study [7] predicted six 212 [Ti$_2$InB$_2$, Hf$_2$AB$_2$ (In, Sn), Zr$_2$AB$_2$ (A = In, Tl, Pb)] MAX phases and two 314 [Hf$_3$PB$_4$, Zr$_3$CdB$_4$] MAX phases among which Ti$_2$InB$_2$ ($P\bar{6}m2$; No. 187) has already been synthesized [45]. Miao et al. [7] was inspired by the discovery of Ti$_2$InB$_2$ [45] and further other layered ternary borides known as MAB phases have been investigated [46–48]. Although, the 212 and 314 MAX phases have layered structure [that crystallize] in hexagonal system, the atomic arrangement in the cell is completely different from conventional MAX phases as shown in Fig. 1. As evident from the figure that there is a 2D layer of B sandwiched in between two Zr layers that significantly contributes in the enhancement of the structural stability and mechanical strength[49].

So far, the physical properties of Ti$_2$InB$_2$ [50,51], Hf$_2$AB$_2$ (A = In, Sn) [52], Zr$_2$AB$_2$ (A = In, Tl) [49], Hf$_3$PB$_4$ [53], and Zr$_3$CdB$_4$ [54] MAX phases have been studied using the density functional theory (DFT) method. For each of the cases, the mechanical properties are found to be enhanced remarkably in comparison with their conventional C/N containing 211 MAX phases. The Debye temperature and melting temperature increased for boron containing 212 phases compared to 211 carbides/nitrides. The minimum thermal conductivity also decreases for the same, the thermal expansion coefficient remains reasonably suitable for coating materials in borides. Thus, the enhanced thermo-mechanical properties of B-containing 212 MAX phases revealed their appropriateness for applications in high-temperature technology compared to the widely used 211 MAX phase carbides. These features of 212 MAX phases are very much motivational and we are interested to study the yet to be investigated stable 212 MAX phase Zr$_2$PbB$_2$.

Therefore, in this study the thermo-mechanical parameters of Zr$_2$PbB$_2$ have been studied by means of the DFT method and the properties are compared with those of other 212 MAX phases as well as with its (Zr$_2$PbB$_2$) 211 counterpart carbide (Zr$_2$PdC).
2. Computational methodology

In this study, the physical properties of Zr$_2$PbB$_2$ have been computed by CAmbridge Serial Total Energy Package (CASTEP) code [55,56] via the plane-wave pseudopotential-based DFT method. The generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) [57] was used to treat exchange and correlations functions. The pseudo-atomic calculations were performed for B - 2s$^2$ 2p$^1$, Pb - 6s$^2$ 6p$^2$, and Zr -5s$^2$ 4p$^6$ 4d$^2$ electronic orbitals. The cutoff energy and k-point [58] was set as 500 eV and 10 × 10 × 4. The geometry was relaxed by Broyden Fletcher Goldfarb Shanno (BFGS) technique [59] whereas density mixing was selected for electronic structure calculations. Furthermore, the self-consistent convergence of the total energy was set to 5 × 10$^{-6}$ eV/atom, the maximum force on the atom was taken as 0.01 eV/Å, the maximum ionic displacement was set to 5 × 10$^{-4}$ Å and a maximum stress was limited to 0.02 GPa. The bulk modulus (B) and shear modulus (G) are calculated using the Hill’s approximation [60,61]. Hill’s values are the average values of the upper limit (Voigt [62]) and lower limit (Reuss [63]) of B: \[ B = (B_V + B_R)/2 \] and G: \[ G = (G_V + G_R)/2 \]. The $B_V$, $B_R$, $G_V$ and $G_R$ have been calculated from the stiffness constants by the following relations: \[ B_V = [2(\alpha_{11} + \alpha_{12}) + C_{33} + 4C_{13}]/9 \]; \[ BR = C2M; C2 = (C_{11} + C_{12})C_{33} - 2C_{13}; M = C_{11} + C_{12} + 2C_{33} - 4C_{13} \]; \[ G_V = [M + 12C_{44} + 12C_{66}]/30 \] and \[ G_R = \left(\frac{5}{2}\right) \frac{C^2_{44}C_{66}}{3B_VC_{44}C_{66} + C^2(C_{44} + C_{66})} \]; \[ C_{66} = (C_{11} - C_{12})/2 \]. The Young’s modulus (Y) has been calculated using the equation: \[ Y = 9BG/(3B + G) \] [64,65]. The Poisson’s ratio ($\nu$) is computed using the equation: \[ \nu = (3B - Y)/(6B) \] [64,65]. The Cauchy pressure (CP) is defined in terms of stiffness constants; \[ CP = (C_{12} - C_{44}) \].

3. Results and discussion

3.1 Structural properties and stability

The structure of conventional MAX phase is well known, but the structure of the B-containing 212 MAX phase is less familiar. To distinguish between the structures, the unit cell of both 212 (Zr$_2$PbB$_2$) and 211 (Zr$_2$PbC) phases is presented in Fig. 1. As seen, there is a clear difference in the atomic arrangements in these structures which is responsible for the different physical behaviors with respect to mechanical, electronic, and thermal properties. Both 212 (Zr$_2$PbB$_2$) and 211 (Zr$_2$PbC) are crystallized in the hexagonal system with different space groups. The 212
MAX phase belongs to the space group $P\bar{6}m2$, (No. 187) [7] while 211 MAX phase belongs to the space group of P63/mmc (194) [4]. The position of M, A and X atoms are different in 212 and 211 MAX phases. The M (Zr) atoms are positioned at $(1/3, 2/3, z_M)$ in 211 phase, whereas it is at $(0.3333, 0.6667, 0.6935)$ for 212 phase. The atomic positions of A (Pb) atoms are $(1/3, 2/3, 3/4)$ and $(0.6667, 0.3333, 0.0)$, respectively for the 211 and 212 phases. The most important difference is the positions and contribution of the X atoms in the bulk crystals. The X (C) atoms occupy the corner position $(0, 0, 0)$ in 211 phase while it (B) occupies two positions: $(0.6667, 0.3333, 0.5)$ and $(0.0, 0.0, 0.5)$ forming a 2D layer sandwiched in between the M layers. Within this 2D layer, the B atoms itself makes a strong covalent bond (B-B) that results in a comparatively more stable structure than that of the 211 MAX phase.

Fig. 1. The unit cells of (a) Zr$_2$PbB$_2$ and (b) Zr$_2$PbC and (c) Phonon dispersion curve of Zr$_2$PbB$_2$.

The unit cell of Zr$_2$PbB$_2$ is optimized to obtain the other physical properties. The cell constants calculated for the optimized structure is given in Table 1. A very good consistency is observed between the values obtained in this study and prior results [7]. This reveals the precision of the parameters used for calculations in this work.

| Phase     | $a$ (Å) | % of deviation | $c$ (Å) | % of deviation | c/a | Reference     |
|-----------|---------|----------------|---------|----------------|-----|---------------|
| Zr$_2$PdB$_2$ | 3.2787  | 0.08           | 8.4282  | 0.15           | 2.57| This work     |
|           | 3.276   |               | 8.415   |                | 2.57| Ref [7]       |
Miao et al [7] have shown that the predicted 212 phases including Zr$_2$PbB$_2$ are thermodynamically stable by calculating the enthalpy with reference to the known competing phases. They have also calculated the phonon dispersion curves in which no imaginary frequency branch exists. The phonon dispersion curve of Zr$_2$PbB$_2$ has also been calculated in this study wherein no imaginary frequency branch exists as shown in Fig. 1 (c). This confirms the dynamical stability of Zr$_2$PbB$_2$ boride like other 212 MAX phase borides. Moreover, the mechanical stability of Zr$_2$PbB$_2$ has also been checked in the following section.

3.2.1 Mechanical properties

To bring out the figure of merit of the 212 MAX phases in light, it is necessary to discuss the possible relevant parameters for disclosing the mechanical properties. During the practical use of materials many of them are subjected to applied forces or loads. Thus, knowledge of the related parameters is essential for the proper selection of the materials, otherwise, crack formation, mechanical failure, fracture introduction or structural deformation may take place. One of the key applications of the MAX phases is as the structural components at high temperatures [66]. The constants used to unveil the mechanical behavior of solids are stiffness constants, tensile strength, elastic moduli, hardness, brittleness/ductility, and fracture toughness, etc. Thus, the aforementioned parameters of Zr$_2$PbB$_2$ have been estimated and discussed [Table 2]. The first step in study of mechanical properties is the calculation of stiffness constants from which all the other mechanical parameters can be calculated. The obtained single crystal elastic constants using the strain-stress method [64,67–70] are tabulated in Table 2 along with those of others 212 MAX phases and their corresponding 211 carbides phases. Study of mechanical stability is one of the ways for assessing the stability of solids under static stress used in practical applications. For this case, the stability of Zr$_2$PbB$_2$ is checked by the well-known stability conditions [71,72] for hexagonal system as follows: $C_{11} > 0$, $C_{11} > C_{12}$, $C_{44} > 0$, $(C_{11} + C_{12})C_{33} - 2(C_{13})^2 > 0$. The titled boride satisfies the above-stated conditions and hence it is predicted to be mechanically stable.

As can be seen in the Table 2, the $C_{11}$ and $C_{33}$ values are not only higher for Zr$_2$PbB$_2$ compared to the corresponding 211 Zr$_2$PbC phase but also higher for other 212 phases compared to their 211 counterparts. In case of $C_{11}$, an increase of 35%, 10%, 22%, 11%, 40%, and 28% is observed for Zr$_2$PbB$_2$, Zr$_2$InB$_2$, Zr$_2$TlB$_2$, Hf$_2$InB$_2$, Hf$_2$SnB$_2$, Ti$_2$InB$_2$, respectively compared to their
corresponding 211 MAX phases. Similarly in case of $C_{33}$, an increase of 13%, 06%, 21%, 2%, 22%, and 14% is noted for Zr$_2$PbB$_2$, Zr$_2$InB$_2$, Zr$_2$TlB$_2$, Hf$_2$InB$_2$, Hf$_2$SnB$_2$, Ti$_2$InB$_2$, respectively compared to their corresponding 211 phases. It is well known that the $C_{11}$ and $C_{33}$ measure bonding strength along the $a$- and $c$-axis. Thus, increase of $C_{11}$ and $C_{33}$ implies the increase of bonding strength along the mentioned directions; consequently, overall bonding strength is expected to be increased for 212 phases that is also reflected from the values of elastic moduli and hardness values presented in Table 2. As we know, the bulk modulus ($B$) measures the resistance against the uniform volume changing hydrostatic pressure whereas the shear modulus ($G$) measures the resistance against shape changing plastic deformation. A comparative stiffness of the solids can be known from the value of the Young’s modulus ($Y$) which gives a measure of the resistance against change in the length. Thus, in case of $B$ [$G(Y)$], an increase of 19%[22%(21%)], 1%[11%(9%)], 17%[18%(17%)], 1%[9%(7%)], 14%[43%(36%)], and 17%[22%(22%)] for Zr$_2$PbB$_2$, Zr$_2$InB$_2$, Zr$_2$TlB$_2$, Hf$_2$InB$_2$, Hf$_2$SnB$_2$, and Ti$_2$InB$_2$ have been found compared to their corresponding 211 phases Zr$_2$PbC, Zr$_2$InC, Zr$_2$TlC, Hf$_2$InC, Hf$_2$SnC, and Ti$_2$InC, respectively.

Now, we focus our attention on the hardness parameters, $H_{Chen}$ and $H_{Miao}$, as calculated from the following equations: $H_{Chen} = 2\left(\frac{G}{B}\right)^2 G^{0.585} - 3$ [73] and $H_{Miao} = \frac{(1-2\nu)E}{6(1+\nu)}$ [74]. The calculated values are presented in Table 2. Like elastic moduli, the hardness parameters of 212 MAX phase borides are also higher than those of 211 MAX phase carbides. An increment of 19%(24%), 20%(18%), 12%(18%), 16%(15%), 75%(71%), and 21%(26%) for $H_{Chen}$ ($H_{Miao}$) is observed in case of Zr$_2$AB$_2$ (A = In, Tl, Pb), Hf$_2$AB$_2$ (A = In, Sn) and Ti$_2$InB$_2$, respectively compared to those of their corresponding 211 MAX phase carbides. Hence, it is evident that the hardness parameters are significantly enhanced for 212 phases in comparison with 211 phases. As discussed so far in this section, the mechanical properties of the 212 MAX phase borides are considerably enhanced compared to their counterpart 211 MAX phase carbides. Thus, a reasonable question is that what features bring about these enhancements in the 212 systems? The possible answer is explored in section 3.5.
Table 2: The stiffness constants, $C_{ij}$ (GPa), elastic moduli $[B, G, Y]$ (GPa), hardness parameters, Pugh ratio, $G/B$, Poisson ratio, $\nu$ and Cauchy Pressure, $CP$ (GPa) of $M_2AB_2$ ($M = Zr, Hf, In; A = In, Ti, Pb$) together with those of $M_2AC$ ($M = Zr, Hf, In; A = In, Ti, Pb$).

| Phase     | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | $B$    | $G$    | $Y$   | $H_{\text{Chen}}$ | $H_{\text{Miao}}$ | $G/B$ | $\nu$ | CP       | Reference   |
|-----------|----------|----------|----------|----------|----------|--------|--------|-------|-----------------|-----------------|--------|-------|----------|-------------|
| Zr$_2$Pb$_2$ | 297      | 57       | 72       | 245      | 76       | 138    | 95     | 232   | 15.55           | 17.73           | 0.69   | 0.22  | -19      | This study  |
| Zr$_2$PbC  | 220      | 66       | 65       | 216      | 80       | 116    | 78     | 191   | 13.08           | 14.28           | 0.67   | 0.23  | -14      | This study  |
| Zr$_2$InB$_2$ | 315      | 46       | 64       | 263      | 82       | 138    | 105    | 251   | 19.11           | 21.24           | 0.76   | 0.20  | -36      | Ref [49]    |
| Zr$_2$InC  | 286      | 62       | 71       | 248      | 83       | 136    | 95     | 231   | 15.87           | 17.94           | 0.70   | 0.22  | -14      | Ref [75]    |
| Zr$_2$TiB$_2$ | 310      | 52       | 61       | 251      | 66       | 135    | 94     | 229   | 15.68           | 17.71           | 0.70   | 0.22  | -21      | Ref [49]    |
| Zr$_2$TiC  | 255      | 60       | 52       | 207      | 63       | 115    | 80     | 195   | 13.98           | 15.06           | 0.70   | 0.22  | -03      | Ref [76]    |
| Hf$_2$InB$_2$ | 343      | 61       | 76       | 278      | 94       | 154    | 114    | 274   | 19.46           | 22.56           | 0.74   | 0.20  | -33      | Ref [52]    |
| Hf$_2$InC  | 309      | 81       | 80       | 273      | 98       | 152    | 105    | 256   | 16.75           | 19.65           | 0.69   | 0.21  | -17      | Ref [75]    |
| Hf$_2$SnB$_2$ | 353      | 65       | 86       | 306      | 110      | 165    | 124    | 297   | 21.02           | 24.84           | 0.75   | 0.20  | -45      | Ref [52]    |
| Hf$_2$SnC  | 251      | 71       | 107      | 238      | 101      | 145    | 87     | 218   | 12.00           | 14.50           | 0.60   | 0.25  | -30      | Ref [77]    |
| Ti$_2$InB$_2$ | 364      | 47       | 58       | 275      | 94       | 147    | 122    | 287   | 23.72           | 26.44           | 0.83   | 0.17  | -47      | Ref [52]    |
| Ti$_2$InC  | 284      | 62       | 51       | 242      | 87       | 126    | 100    | 236   | 19.57           | 20.92           | 0.79   | 0.18  | -25      | Ref [51]    |

Table 3: Calculation of Vickers hardness $H_v$ of Zr$_2$Pb$_2$ using Mulliken analysis. Bond number ($n^\mu$), bond length ($d^\mu$), bond overlap population ($P^\mu$), metallic population ($P^\nu$), bond volume ($v^\nu$), bond hardness ($H_v^\mu$) of $\mu$-type bond are displayed. The values of $H_v$ for other 212 phases are also included.

| Compounds    | Bond | $n^\mu$ | $d^\mu$ (Å) | $P^\mu$ | $P^\nu$ | $v^\nu$ (Å$^3$) | $H_v^\mu$ (GPa) | $H_v$ (GPa) | Reference |
|--------------|------|---------|-------------|--------|---------|-----------------|-----------------|------------|-----------|
| Zr$_2$Pb$_2$ | B-B  | 1       | 1.89298     | 2.12   | 0.00595 | 7.538           | 53.98           | 2.75       | This study |
| Zr$_2$Pb$_2$ | Zr-B | 2       | 2.51753     | 0.24   | 0.00595 | 17.732          | 1.43            |            | [49]      |
| Zr$_2$Pb$_2$ | Zr-B | 2       | 2.51753     | 0.20   | 0.00595 | 17.732          | 1.19            |            | [49]      |
| Zr$_2$InB$_2$ |     |         |             |        |         |                 | 2.92           |            | [49]      |
| Zr$_2$TiB$_2$ |     |         |             |        |         |                 | 2.19           |            | [49]      |
| Hf$_2$InB$_2$ |     |         |             |        |         |                 | 3.94           |            | [52]      |
| Hf$_2$SnB$_2$ |     |         |             |        |         |                 | 4.41           |            | [52]      |
| Ti$_2$InB$_2$ |     |         |             |        |         |                 | 4.05           |            | [52]      |

3.2.2 The brittleness of Zr$_2$Pb$_2$

Although, the MAX phases are metallic in nature but most of them also exhibit brittleness like ceramics. In this section, three widely known formalisms are used to predict brittleness/ductility. First of all, Pugh ratio, ($G/B$) [85] is used that confirms the brittle character of Zr$_2$PbB$_2$ [$G/B < 0.571$ for ductile and $G/B > 0.571$ for brittle solids]. The Poisson’s ratio ($\nu$) also confirmed the brittle character of Zr$_2$PbB$_2$ as $\nu = 0.26$ is a critical value to identify the brittle and ductile materials and $\nu$ is lower than the critical value for brittle solids and for the ductile solids, the values are higher. In addition, the value of $\nu$ also indicates the bonding nature within the solids.
For example, it is typically low (0.10) for covalent solids and high (0.33) for metallic solids. For present case, it ($\nu$) is 0.22, which is close to the average/border line of the limiting values, thus, expecting a mixture of covalent and metallic bonding within $\text{Zr}_2\text{PbB}_2$ like other MAX phases. In fact, it agrees well with the existence of the M-X (covalent) bonding and M-A (ionic) bonding within the MAX phase materials. Moreover, Pettifor [78] addressed the Cauchy pressure ($CP$) to determine the chemical bonding and ductile/brittle nature of solids. A negative value of $CP$ certifies the covalently bonded brittle solids whereas the positive value indicates metallic solids. As evident, $\text{Zr}_2\text{PbB}_2$ belongs to the covalently bonded brittle class of solids.

### 3.3 Electronic band structure (EBS) and density of states (DOS)

Fig. 2 (a) illustrates the EBS of $\text{Zr}_2\text{PbB}_2$ boride in which the electronic paths are shown in the first Brillouin zone. The obtained EBS is similar to the metallic solids due to the overlapping of the valence and conduction bands. This is the characteristics of MAX phase materials that exhibit a good combination of the metallic and ceramics properties [43, 52, 79, 80]. The anisotropic characteristics of the MAX phases are expected due to their layered structure. The EBS also exhibits the anisotropy along the basal plane and $c$-direction of the crystal. The paths $\Gamma$-A, H-K and M-L corresponds to the $c$-direction while the paths A-H, K-$\Gamma$, $\Gamma$-M and L-H are for the basal plane [81]. It is seen that the energy dispersions along the basal plane and the $c$-direction differ significantly, confirming the anisotropic behavior of charge effective masses for the above-mentioned directions, as has been found for other MAX phases [43, 49, 52].

![EBS and DOS](image)

**Fig. 2.** The electronic (a) band structure and (b) density of states of $\text{Zr}_2\text{PbB}_2$. 
Fig. 2 (b) displays the electronic energy density of states (DOS) of Zr$_2$PbB$_2$ which roughly exhibits the usual characteristics of MAX phase materials. The Fermi level is dominantly contributed by the Zr-$d$ electronic states in association with very small contribution from the B-$p$ and Pb-$p$ electronic states. The most strong orbital hybridization is observed between B-$p$ states and Zr-$d$ states that contribute to the formation of strong covalent bonding between them, similar to other MAX phases [12,82,83], specially matched with those of Zr$_2$AB$_2$ (A = In, Tl) [49]. It is worth stating that the Fermi level of Zr$_2$PbB$_2$ resides close to the pseudogap in the TDOS profile. This is an indication of high level of electronic stability.

3.4 Thermal Properties

Recently, the high temperature applications of MAX phases have attracted much attention from both research and applications points of view. Some of the thermal parameters of particular interest can be used to assess the suitability of materials for high temperature applications. In this section, the Debye temperature ($\Theta_D$), minimum thermal conductivity ($k_{\text{min}}$), thermal expansion coefficient, Grüneisen parameter, and melting temperature of Zr$_2$PbB$_2$ have been calculated to assess the its potential for thermal applications.

The elastic properties can be correlated with the thermal properties, for example, phonon dynamics, thermal expansion, thermal conductivity, specific heat, and lattice enthalpy are connected to the Debye temperature. The Debye temperature itself depends on the elastic parameters which determine the sound velocity in a material. The details of the calculations can be found elsewhere [49]. The obtained value of $\Theta_D$ for Zr$_2$PbB$_2$ is 434 K, higher than that of the corresponding 211 Zr$_2$PbC compound (366 K) [Table 4]. The $\Theta_D$ of Zr$_2$PbB$_2$ is also greater than those of Zr$_2$InB$_2$ and Hf$_2$InB$_2$. In reality, the obtained values of $\Theta_D$ for 212 MAX phases are significantly larger compared to those of their C-containing counterparts belonging to the 211 MAX phases, indicating their higher temperature limits for use because the $\Theta_D$ limits the normal modes of thermal vibrations within the solids. Based on the values of $\Theta_D$ we can rank the 212 MAX phases as follows: Ti$_2$InB$_2$ > Zr$_2$InB$_2$ > Hf$_2$SnB$_2$ > Zr$_2$PbB$_2$ > Zr$_2$TlB$_2$ > Hf$_2$InB$_2$.

For the assessment of high temperature application, minimum thermal conductivity ($k_{\text{min}}$) is one of the important parameters. The thermal conductivity attains a constant value (minimum) at high temperature known as the minimum thermal conductivity [84]. Lower the value of $k_{\text{min}}$,
more suitable the solid for use in thermal barrier coating applications as it conducts less amount of heat which is one of the main criteria of TBC materials. The $k_{\text{min}}$ is closely associated with the acoustic wave velocity in the materials and can be calculated by the following model due to Clark [84]:

$$K_{\text{min}} = k_B v_m \left(\frac{M}{n\rho N_A}\right)^2$$

The value of $k_{\text{min}}$ is significantly lowered (21%) for Zr$_2$PbB$_2$ (0.77 W/mK) compared to that of Zr$_2$PbC (0.97 W/mK) as seen in Table 4. As also seen from the Table 4, $K_{\text{min}}$ of Zr$_2$PbB$_2$ is lowest and equal to those of Zr$_2$InB$_2$ and Hf$_2$InB$_2$, certifying a very low capability of heat conduction at high temperatures. Actually, the $K_{\text{min}}$ of 212 phases are lower compared to their 211 counterparts, revealing more appropriateness of 212 phases for the use as TBC materials.

Table 4: Debye temperature, $\Theta_D$, minimum thermal conductivity, $K_{\text{min}}$, Grüneisen parameter, $\gamma$, melting temperature, $T_m$, and thermal expansion coefficient (TEC) of M$_2$AB$_2$ (M = Zr, Hf, In; A = In, Tl, Pb) compounds together with those of M$_2$AC (M = Zr, Hf, In; A = In, Tl, Pb) compounds.

| Phase       | $\rho$ (g/cm$^3$) | $v_l$ (m/s) | $v_t$ (m/s) | $v_m$ (m/s) | $\Theta_D$ (K) | $K_{\text{min}}$ (W/mK) | $\gamma$ | $T_m$ (K) | TEC ($10^6$ K$^{-1}$) | Ref.       |
|-------------|-------------------|-------------|-------------|-------------|----------------|--------------------------|---------|-----------|------------------------|-----------|
| Zr$_2$PbB$_2$ | 8.70              | 5514        | 3304        | 3655        | 434            | 0.77                     | 1.36    | 1613      | 5.3                    | This study |
| Zr$_2$PbC    | 9.04              | 4933        | 2937        | 3252        | 366            | 0.97                     | 1.41    | 1338      | This study             |           |
| Zr$_2$InB$_2$| 6.87              | 6358        | 3907        | 4312        | 516            | 0.92                     | 1.28    | 1693      | 6.5                    | Ref [49]  |
| Zr$_2$InC    | 7.32              | 6004        | 3616        | 3999        | 459            | 1.24                     | 1.36    | 1584      | Ref [75]               |           |
| Zr$_2$TlB$_2$| 8.71              | 5466        | 3284        | 3633        | 433            | 0.77                     | 1.36    | 1660      | 7.1                    | Ref [49]  |
| Zr$_2$TlC    | 8.92              | 4989        | 2993        | 3311        | 372            | 0.89                     | 1.36    | 1430      |                        | Ref [76]  |
| Hf$_2$InB$_2$| 10.86             | 5309        | 3240        | 3578        | 431            | 0.77                     | 1.29    | 1800      | 5.9                    | Ref [52]  |
| Hf$_2$InC    | 11.67             | 5004        | 2999        | 3319        | 383            | 1.04                     | 1.32    | 1691      |                        | Ref [75]  |
| Hf$_2$SnB$_2$| 11.08             | 5459        | 3344        | 3692        | 447            | 0.80                     | 1.28    | 1872      | 5.6                    | Ref [52]  |
| Hf$_2$SnC   | 12.06             | 5121        | 3050        | 3376        | 393            | 1.07                     | 1.49    | 1746      |                        | Ref [93]  |
| Ti$_2$InB$_2$| 05.90             | 7241        | 4545        | 5004        | 633            | 1.19                     | 1.19    | 1858      |                        | Ref [52]  |
| Ti$_2$InC   | 05.91             | 7168        | 4487        | 4942        | 621            | 1.23                     | 1.20    | 1833      | 15.4                   | Ref [51]  |
| Ti$_2$SnB$_2$| 06.08             | 6531        | 4055        | 4471        | 534            | 1.00                     | 1.23    | 1569      |                        | Ref [51]  |

$\rho$ is the crystal density, $v_l$, $v_t$, and $v_m$ are the longitudinal, transverse and average sound velocities, respectively.

Owing to the close connection of Grüneisen parameter ($\gamma$) with specific heat at constant volume, bulk modulus, and TEC, calculation of $\gamma$ is of scientific interest. It is used to reveal the degree of anharmonic effects present in solids. Thus, $\gamma$ has been determined via the relation with Poisson’s
ratio [85]: \( \gamma = \frac{3}{2} \frac{(1+\nu)}{(2-3\nu)} \). As seen, the anharmonic effect is low for Zr\(_2\)PbB\(_2\), in fact, for all the 212 phases compared to their corresponding 211 phases, indicating more appropriateness for their use at elevated temperatures. In addition, the values remain within the predicted limit [0.85 to 3.53] for polycrystalline solids associated with the limiting value of the Poisson’s ratio [0.05–0.46] [86].

One of the mandatory information for the selection of materials for application at high temperature technology is the melting point \( T_m \) that provides an idea of temperature limit for usage. Owing to the combined ceramic properties of MAX phases with metallic properties, they have been recognized as suitable systems for the above-mentioned sectors. Hence, calculation of \( T_m \) for MAX phase is important and has been estimated in this study using the equation relating elastic constants as follows [87]: \( T_m = (3C_{11}+1.5C_{33}+354) \) K. Like other 212 MAX phases, the \( T_m \) of Zr\(_2\)PbB\(_2\) is also larger and it is 20% more than its counterpart Zr\(_2\)PbC. On the other hand, \( T_m \) is the lowest for Zr\(_2\)PbB\(_2\) in comparison with other 212 MAX phase borides (Table 4). Knowledge regarding the decomposition temperature \( (T_d) \) is also pre-requisite regardless of the value of \( T_m \). The MAX phases have a tendency to decompose at a lower temperature than that of \( T_m \). Unfortunately; no information regarding \( T_d \) of Zr\(_2\)PbB\(_2\) as well as other 212 phases is present. An earlier report provided by Cue et al. [88] might be helpful regarding this issue. They have estimated \( T_d \) and \( T_m \) of some MAX phases and shown that \( T_d \) is lower than \( T_m \), for some cases \( T_d \) is close to \( T_m \) [89], thus, one may expect a high \( T_d \) for Zr\(_2\)PbB\(_2\) as well. The value thermal expansion coefficient (TEC) for the Zr\(_2\)PbB\(_2\) compound is lower than those of other 212 MAX phases and their 211 counterparts, as shown in Table 4. It is essential to note that the TEC of Zr\(_2\)PbB\(_2\) phase is much lower than that of a commonly used TBC material, Y\(_4\)Al\(_{12}\)O\(_9\) [90]. This result provides a further indication of the possible use of Zr\(_2\)PbB\(_2\) as a TBC material.

### 3.5 Why are the thermo-mechanical properties for 212 phases enhanced?

From the analysis of the above-mentioned results it is obvious that the thermo-mechanical properties are significantly upgraded when we go from the 211 MAX phase carbides to the 212 MAX phase borides. Why are the properties enhanced for 212 phases? The answer lies in the structure. Though, both 212 and 211 phases belong to the MAX family but their structures are not exactly the same. The 212 phases are crystallized in the space group P-6m2, (No. 187) [7,45]
while the 211 phases are crystallized in the space group P6₃/mmc (No. 194) [4,91] as shown in Fig. 1 (a and b). The bonding nature within these two structures is also different. For the 212 phases, there is a very strong covalent bonding among the B atoms by forming a 2D layer of and contributing as 2c-2e type of bonding as shown in Fig. 3 (a and b). In addition, there is also strong covalent bonding between M (Zr atoms for Zr₂PbB₂) and X (B atoms for Zr₂PbB₂) similar to the 211 phases (Zr and C are M and X atoms for Zr₂PbC) as well as comparatively weak M – A bonding (Pb is the A atom in case of Zr₂PbC). There is no covalent bond between the C atoms in the 211 phase, although strong covalent bonds between M- X atoms is formed as well as the M-A bonds. Owing to the existence of the very strong B-B covalent bonding within the 2D layer of B atoms, the structure becomes more stable, and the overall cohesive energy is enhanced significantly for the 212 phases in comparison with the 211 phases. It is noted that, for 211 MAX phase borides, B-B bonding does not exist [5,6,35,37,43,92]. Our statements will be further clarified by the calculation of Mulliken population analysis given in Table 5. As seen in Table 5, charge is transferred from Zr to B (0.54/0.55) and Pb (0.01). The charge transfer mechanism confirms the existence of ionic character as observed for the C-containing MAX phase Zr₂PbC. In this carbide, charge is transferred from Zr to C (0.79) and Pb (0.06) [Table 5]. Table 5 also shows the bond overlap population (BOP) analysis for both the compounds. The value of BOP indicates the nature bonding/anti-bonding states within the solids depending on the positive/negative values. A negative value of BOP stands for anti-bonding whereas positive value for bonding states. It is clear from the Table 5 that no anti-bonding exists within the considered MAX phases. In addition, the value of BOP is also an indicator of bonding strength, higher the BOP, stronger the bonding. As evident from Table 5, the B-B bonding exhibits the largest BOP value, confirming very strong covalent bonding formed by the 2c-2e channel. The M (Zr) - X (B/C) bonding in the Zr₂PbC is stronger than that of Zr₂PbB₂ with the BOP values of 1.03 and 0.24/0.20, respectively. Due to the existence of very strong B-B bonding, the bonding strength as well as mechanical parameters and hardness values are higher for Zr₂PbB₂ compared to Zr₂PbC. Similar results are also reported for other known 212 phases [49,51,52].
Fig. 3. Formation of B-B covalent bonding within Zr$_2$PbB$_2$.

Table 5: Mulliken atomic and bond overlap populations of Zr$_2$PbB$_2$ and Zr$_2$PbC MAX compounds.

| Compound | Atomic population | Bond overlap population |
|----------|-------------------|-------------------------|
|          | Atom  | s   | p   | d   | Total | Charge (e) | EVC (e) | Bond | Bond number $n^\mu$ | Bond length $d^\mu$ (Å) | Bond population $p^\mu$ |
| Zr$_2$PbB$_2$ | B    | 0.98 | 2.58 | 0.00 | 3.55 | -0.55 | B-B | 1 | 1.89298 | 2.12 |
|           | B    | 0.97 | 2.57 | 0.00 | 3.54 | -0.54 | Zr-B | 2 | 2.51753 | 0.24 |
|           | Zr   | 2.15 | 6.46 | 2.84 | 11.45 | 0.55 | Zr-B | 2 | 2.51753 | 0.20 |
|           | Zr   | 2.15 | 6.46 | 2.84 | 11.45 | 0.55 |       |    |                  |                  |
|           | Pb   | 1.42 | 2.55 | 10.04 | 14.01 | -0.01 |       |    |                  |                  |
| Zr$_2$PbC | C    | 1.48 | 3.30 | 0.00 | 4.79 | -0.79 | Zr-C | 4 | 2.31654 | 1.03 |
|           | Zr   | 2.36 | 6.58 | 2.74 | 11.58 | 0.42 |       |    |                  |                  |
|           | Pb   | 1.44 | 2.58 | 10.04 | 14.06 | -0.06 |       |    |                  |                  |

4. Conclusions

The thermo-mechanical properties of Zr$_2$PbB$_2$ are explored via DFT calculations with an intension to shed light on the enhanced thermo-mechanical properties of recently added 212 MAX phase borides in comparison with their 211 carbide counterparts. The titled MAX phase is mechanically stable. The values of elastic constants and moduli of 212 phases are higher than...
those of the 211 phase carbides. The Vickers hardness is also higher for the same. The study of thermo-mechanical properties reveals the appropriateness of the 212 phase borides compared to their carbide counterparts. Existence of very strong B-B bonding contributes to the enhancement of the thermo-mechanical properties for the 212 compounds. We hope, the results presented in this paper will stimulate further research into the 212 MAX phases which exhibits better characteristics for applications in the thermo-mechanical sectors compared to many other conventional MAX compounds.

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