First-principles investigations on Pb–Ba intermetallic compounds

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\textbf{A B S T R A C T}

To better clarify and understand the ground-state physical properties of Pb–Ba intermetallic compounds, phase stabilities, elastic properties and electronic structures of Pb–Ba intermetallic compounds have been investigated by using first-principles calculations within local density approximation. The formation enthalpies of these compounds indicate that they are thermodynamically stable. The bulk modulus $B$, shear modulus $G$, Young’s modulus $E$ and Poisson’s ratio $\nu$ were evaluated. The brittle and ductile properties were discussed by using $B/G$ and $\nu/E$ ratio. The hardness was estimated by using a semi-empirical equation. The mechanical anisotropy was characterized by calculating several different anisotropic indexes and the 3D figures of directional dependences of reciprocals of elastic moduli. Finally, the electronic structures were also discussed.

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1. Introduction

Due to their industrial application in thermoelectric and optoelectronic materials \[1\], the Pb-based alloys had been studied for many years. The Pb–X phases ($X = \text{alkaline earths}$), which the X elements are all divalent, have a progressive trend in their atomic radii and electronegativities \[2\]. The introduction of alkaline earths to lead alloys leads a structural hardening by precipitation of intermetallics. Among these Pb–X phases, the formation enthalpies, thermodynamic properties and elastic properties for Pb–Ca phases have been studied \[3–5\]. For Pb–Ba phases, there are five intermetallic compounds in the experimental Pb–Ba phase diagram \[6\]: the congruent melting points of Ba$_2$Pb$_3$ and BaPb$_3$ are 1243 K and 883 K, respectively; Ba$_2$Pb, BaPb and Ba$_3$Pb$_5$ form by peritectic reaction. The crystalline structures of Pb–Ba compounds were previously determined: Ba$_2$Pb$_3$ has the body-centered tetragonal structure with $a = 9.038$, $c = 16.843$ Å; BaPb has the orthorhombic structure with $a = 5.29$, $b = 12.60$, $c = 4.78$ Å; Ba$_3$Pb$_5$ is trigonal with $a = 7.287$, $c = 25.770$ Å; Ba$_2$Pb$_3$ crystallizes in the Pu$_3$Pd$_5$-type structure with $a = 11.148$, $b = 9.049$, $c = 11.368$ Å; Ba$_2$Pb crystallizes in the CoSi$_2$-type structure with $a = 8.640$, $b = 5.71$, $c = 10.61$ Å \[6–8\]. The phase relations and thermodynamic properties were assessed, the results were shown that BaPb has the lowest formation enthalpy (–73 ± 2 kJ/mol) while Ba$_3$Pb$_5$ possesses the largest one (–44 ± 2 kJ/mol) with the order of formation enthalpy: BaPb$_3$ < Ba$_2$Pb$_3$ < Ba$_2$Pb < Ba$_3$Pb$_5$ < BaPb \[2,4\]. For Ba$_2$Pb both the conduction band minimum and valence band maximum are at the one point with the respective band gap of 0.18 eV \[9\]. However, though their significant potential applications, systematical investigations on elastic properties and electronic structures for Pb–Ba intermetallic compounds are still lacking up to now.

First-principles calculations based on density functional theory have been confirmed to be a powerful tool to investigate accurately the physical and chemical properties of crystalline materials \[10–13\]. The calculations provide a possibility to explain and predict the physical properties of solids which are previously inaccessible by experiments. In the present work, the systematical first-principles calculations of thermodynamic and elastic properties for Pb–Ba intermetallic compounds, including formation enthalpies, elastic constants and electronic structures, were performed in order to understand deeper their ground-state properties. Based on the calculated elastic constants, the elastic anisotropy and the hardness were also investigated and discussed.

2. Computational method

The Pb–Ba intermetallic compounds in present work were investigated by using first-principles method implemented in CASTEP (Cambridge sequential total energy package) package \[14\], which is based on density functional theory (DFT). The core-valence interactions were described as Ultra-soft pseudopotentials. The exchange–correlation energy was treated with local density approximation (LDA) CA-PZ function \[15,16\]. The valence
electrons configurations of Pb 5d106s26p2 and Ba 5s25p6 are considered. The k points in the first irreducible Brillouin zone were 8 × 8 × 4, 8 × 12 × 8, 10 × 4 × 10, 9 × 9 × 3, 9 × 12 × 6 for BaPb3, Ba3Pb, BaPb, Ba5Pb3, and Ba3Pb, respectively. The cutoff energy was selected as 400 eV after convergence tests. The separation of the reciprocal space was around 0.01 Å−1 and the SCF (self-consistent field) tolerance was set as $5 \times 10^{-7}$ eV/atom.

3. Results and discussion

3.1. Structural properties

The crystal structures of the considered Pb–Ba intermetallic compounds based on the experimental crystallographic data [6,7] are shown in Fig. 1. The lattice parameters and internal coordinates of these compounds are listed in Tables 1 and 2, respectively. In order to investigate the ground-state physical properties of Pb–Ba intermetallic compounds, the geometry optimizations were performed. The optimized lattice parameters and atomic coordinates, together with the available experimental data [6–8], are listed in Tables 1 and 2, respectively. The calculated results of Pb–Ba intermetallic compounds agree very well with the available experimental data, which indicates that the calculations in the present work are reasonable and reliable.

3.2. Phase stability

To determine the relative stability of Pb–Ba compounds, the formation enthalpies (ΔH) have been investigated by employing the following relation:

$$\Delta H(\text{Ba}, \text{Pb}_y) = \frac{E_{\text{total}}(\text{Ba}, \text{Pb}_y) - xE_{\text{bulk}}(\text{Ba}) - yE_{\text{bulk}}(\text{Pb})}{x + y} \tag{1}$$

ΔH is the formation enthalpy, respectively. $E_{\text{total}}(\text{Ba}, \text{Pb}_y)$ is the total cell energy of a BaPb, primitive cell including x Ba atoms and y Pb atoms; $E_{\text{bulk}}$ is the chemical potential of Ba or Pb atom in the bulk state. The formation enthalpies of the Pb–Ba intermetallic compounds, together with their available experimental [2] and other theoretical calculated data [4], are depicted in Table 3. Fig. 2(a) plots a comparison of formation enthalpies obtained by the present calculation, CALPHAD model and experiment. It can be seen in Fig. 2(a) that the present calculated and other theoretical calculated values or experimental values are plotted in the x- and y-axis, respectively; and the solid line implies a perfect agreement between the present calculated and other theoretical or experimental values, while two dashed lines are represented an error bar of ±5.0 kJ/mol (note: in this paper, the unit kJ/mol means kJ/mole of atoms.). With regard to all the intermetallic compounds in the Pb–Ba binary system, the first-principles calculated formation enthalpies agree well with those from the CALPHAD approach and experimental approach with a small deviation (<5.0 kJ/mol).

Generally speaking, a negative formation enthalpy usually means an exothermic process and a more negative formation enthalpy corresponds to a better phase stability. The calculated formation enthalpies of the Pb–Ba compounds as a function of the mole fraction of Ba are shown in Fig. 2(b). The calculated formation enthalpies for the Pb–Ba intermetallic compounds follow the order: BaPb3 > Ba5Pb > Ba3Pb > BaPb3 > BaPb. The most negative formation enthalpy of BaPb (−74.382 kJ/mol) implies it has the most phase stability in these Pb–Ba intermetallic compounds.

We have also investigated the relationship between the formation enthalpies (ΔH) and the congruent melting temperatures ($T_m$) of Pb–Ba intermetallic compounds. Fig. 3 shows the calculated formation enthalpies (ΔH) compared with their melting temperatures ($T_m$) of Pb–Ba intermetallic compounds [2,9,17]. It is interesting to note that for these compared compounds the formation enthalpy is more negative if the compound has a higher melting temperature. It can be expected since a more negative formation enthalpy is an indicator of a greater stability and stronger interatomic bonding. Stronger bonding leads to higher melting temperature [18]. Such correlations between formation enthalpy of solids and their melting temperatures have been observed experimentally in many binary systems [18,19]. In the considered Pb–Ba system, BaPb has the highest melting temperature (1258 K) [17], followed by Ba5Pb (1243 K) [2], Ba2Pb (1201 K) [9], Ba3Pb5 (999 K) [2] and BaPb3 (883 K) [2].

3.3. Elastic constants and polycrystalline moduli

The elastic constants can be obtained by calculating the total energy as a function of appropriate lattice deformation. To calculate the elastic constants $C_{ij}$, a serial of deformed cells (strain) $\epsilon^{(i)}$ are introduced and optimized to calculate the tensor of elastic constants. The elastic strain energy U is given by the following [20]:

$$U = \Delta E/V_0 = 1/2 \sum_{i=1}^{6} \sum_{j=1}^{6} C_{ij}\epsilon_i\epsilon_j \tag{2}$$

where $\Delta E$ is the energy difference; $V_0$ is the volume of the original cell; $C_{ij}$ is the elastic constants; $\epsilon_i$ and $\epsilon_j$ are strain. The number of independent elastic constants is different due to the different crystal structure. There are six, nine and six independent elastic constants for trigonal, orthorhombic and tetragonal structures, respectively.

![Fig. 1. Crystal structures of the Pb–Ba intermetallic compounds. The gray and green balls represent Pb atoms and Ba atoms, respectively.](image-url)
Table 1
Calculated and experimental lattice parameters for Pb–Ba intermetallic compounds.

<table>
<thead>
<tr>
<th>Phase</th>
<th>At% of Ba</th>
<th>Crystal structure</th>
<th>Space group</th>
<th>Lattice parameters (Å)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaPb₃</td>
<td>25.0</td>
<td>Trigonal</td>
<td>R₃mH</td>
<td>a=7.200, c=25.735, b=25.770</td>
<td>Present [7]</td>
</tr>
<tr>
<td>Ba₃Pb₅</td>
<td>37.5</td>
<td>Orthorhombic</td>
<td>Cmcm</td>
<td>a=11.089, c=8.962, b=11.285</td>
<td>Present [6]</td>
</tr>
<tr>
<td>BaPb</td>
<td>50.0</td>
<td>Orthorhombic</td>
<td>Cmcm</td>
<td>a=5.235, c=12.506, b=4.746</td>
<td>Present [7]</td>
</tr>
<tr>
<td>Ba₅Pb₃</td>
<td>62.5</td>
<td>Tetragonal</td>
<td>I₄/mcm</td>
<td>a=8.967, c=16.810, b=9.038</td>
<td>Present [7]</td>
</tr>
<tr>
<td>Ba₂Pb</td>
<td>66.7</td>
<td>Orthorhombic</td>
<td>Pnma</td>
<td>a=8.575, c=10.540, b=8.640</td>
<td>Present [8]</td>
</tr>
</tbody>
</table>

Table 2
Calculated and experimental unit cell-internal parameters (Wyckoff positions) for Pb–Ba intermetallic compounds.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Unit cell-internal parameters (Wyckoff positions)</th>
<th>Present work (x, y, z)</th>
<th>Experiment (x, y, z) (Ref.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaPb₃</td>
<td>Ba1:3a (0.0000, 0.0000, 0.0000)</td>
<td>0.0000, 0.0000, 0.0000</td>
<td>0.0000, 0.0000, 0.0000 (7)</td>
</tr>
<tr>
<td>Ba₂Pb₅</td>
<td>Ba1:4c (0.0000, 0.6173, 0.2500)</td>
<td>0.2070, 0.0000, 0.0000</td>
<td>0.0000, 0.2070, 0.0000 (6)</td>
</tr>
<tr>
<td>BaPb</td>
<td>Pb1:4c (0.0000, 0.4204, 0.2500)</td>
<td>0.0000, 0.0000, 0.2500</td>
<td>0.0000, 0.0000, 0.2500 (7)</td>
</tr>
<tr>
<td>Ba₅Pb₃</td>
<td>Pb1:4a (0.0000, 0.0000, 0.2500)</td>
<td>0.0000, 0.2130, 0.2500</td>
<td>0.0000, 0.2130, 0.2500 (6)</td>
</tr>
<tr>
<td>Ba₂Pb</td>
<td>Ba2:4c (0.8435, 0.2500, 0.0794)</td>
<td>0.9785, 0.2500, 0.6818</td>
<td>0.9785, 0.2500, 0.6818 (8)</td>
</tr>
</tbody>
</table>

Table 3
Comparison of the calculated, CALPHAD modeled (at 300 K) and measured (at 300 K) formation enthalpies ΔH (kJ/mol) for Pb–Ba intermetallic compounds.

<table>
<thead>
<tr>
<th>Pb</th>
<th>BaPb₃</th>
<th>Ba₃Pb₅</th>
<th>BaPb</th>
<th>Ba₅Pb₃</th>
<th>Ba₂Pb</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>-43.510</td>
<td>-57.639</td>
<td>-74.382</td>
<td>-68.584</td>
<td>-62.857</td>
<td>0</td>
</tr>
<tr>
<td>CALPHAD [4]</td>
<td>-47.202</td>
<td>-59.844</td>
<td>-76.223</td>
<td>-68.993</td>
<td>-64.240</td>
<td></td>
</tr>
<tr>
<td>Experiment [2]</td>
<td>-44 ± 2</td>
<td>-60 ± 2</td>
<td>-73 ± 2</td>
<td>-69 ± 2</td>
<td>-67 ± 2</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Comparison of the calculated formation enthalpies in this work and the values by CALPHAD and experiment (a) for Pb–Ba compounds, and the calculated formation enthalpies as a function of the mole fraction of Ba (b). The solid line shows unity (y = x) while the dotted lines present an error range of ±5.0 kJ/mol.
The elastic constants are obtained from the curvature of the functional of the energy versus strain. The strains used in this work are listed in Table 4. The obtained independent elastic constants are listed in Table 5. The elastic compliance matrices calculated directly from elastic constants are listed in Table 6.

For various crystals, the elastic constants need to satisfy the generalized stability criteria: \( C_{11} > C_{12}, (C_{11} + C_{12})C_{33} - 2C_{13} > 0, (C_{11} - C_{12})C_{44} - 2C_{14} > 0 \) for the trigonal crystal [21]; \( C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, C_{11} > C_{12}, C_{11} + C_{33} - 2C_{13} > 0, 2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0 \) for the tetragonal crystal [22]; \( C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0, C_{11} + C_{22} - 2C_{12} > 0, C_{11} + C_{13} - 2C_{12} > 0, C_{22} + C_{33} - 2C_{23} > 0, C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23} > 0 \) for the orthorhombic crystal [23].

From Table 5, it is obvious that, the calculated elastic constant \( C_{14} \) (–0.81 GPa) of trigonal BaPb\(_{3}\) is negative. The opposite and reverse alignments were in use for trigonal crystals before 1952, which lead to different signs for one of the elastic constants. The sign of \( C_{14} \) depends on exactly how the crystallographic axes are oriented [24]. However, the elastic constants of BaPb\(_{3}\) still satisfies the mechanical stability criteria with \( C_{11} = 66.704, C_{12} = 26.13, (C_{11} + C_{12})C_{33} - 2C_{13} = 5882.35 > 0, (C_{11} - C_{12})C_{44} - 2C_{14} = 865.26 > 0 \). As for the three orthorhombic crystals (Ba\(_{3}\)Pb\(_{5}\), PbPb and Ba\(_{3}\)Pb), the elastic constants are consistent with the restrictions to the orthorhombic crystal. For the tetragonal crystal (Ba\(_{3}\)Pb\(_{5}\)), all the elastic constants meet the mechanical stability criteria. These results reveal that Pb–Ba intermetallic compounds are mechanically stable.

The elastic constant \( C_{11} \) characterizes the x direction resistance to linear compression [25]. It is obvious that the calculated \( C_{11} \) for BaPb\(_{3}\) is larger than the other Pb–Ba compounds, which indicate that BaPb\(_{3}\) is very incompressible under uniaxial stress along the x axis. Ba\(_{3}\)Pb\(_{5}\) is compressible along the x axis due to the smallest \( C_{11} \) (36.99 GPa). The elastic constant \( C_{33} \) represents the resistance to linear compression along the z axis. It can be considered that the x axis is more compressible than the z axis for BaPb\(_{3}\), BaPb\(_{3}\) and Ba\(_{3}\)Pb due to their calculated higher \( C_{11} \) than \( C_{13} \). For the BaPb and Ba\(_{3}\)Pb, \( C_{11} \) is larger than \( C_{33} \), which means that the z axis is more compressible than the x axis. Moreover, it is well known that the elastic constant \( C_{44} \) is the most significant parameter. A large \( C_{44} \) implies a strong resistance to monoclinic shear in the (1 0 0) plane [26]. The highest \( C_{44} \) for BaPb\(_{3}\) than that for the other Pb–Ba compounds means that BaPb\(_{3}\) has the strongest ability to resist shear distortion in the (1 0 0) plane.

It is well known that the mechanical properties are mainly determined by the elastic modulus. The polycrystalline elastic properties, including bulk modulus \( B \), shear modulus \( G \), Young’s modulus \( E \) and Poisson’s ratio \( \nu \), can be calculated by Voigt–Reuss–Hill (VRH) approximation:

\[
B = \frac{1}{2}(B_V + B_K)
\]

\[
G = \frac{1}{2}(G_V + G_K)
\]

\[
E = \frac{9BG}{3B + G}
\]

\[
\nu = \frac{3B - 2G}{6B + 2G}
\]

where \( B_V \), \( B_K \), \( G_V \), and \( G_K \) are bulk modulus and shear modulus in the Voigt and Reuss approximations, respectively. The results are tabulated in Table 7. The results of elastic moduli as a function of the mole fraction of Ba are shown in Fig. 4. Firstly, we have calculated the bulk moduli of cubic Pb and Ba, the results are 46.03 GPa and

![Fig. 3. The melting temperatures compared with calculated formation enthalpies of Pb–Ba intermetallic compounds.](image-url)
Table 5
The calculated elastic constants for Pb–Ba intermetallic compounds.

<table>
<thead>
<tr>
<th>Phase</th>
<th>C11 (GPa)</th>
<th>C12</th>
<th>C13</th>
<th>C14</th>
<th>C22</th>
<th>C23</th>
<th>C24</th>
<th>C33</th>
<th>C34</th>
<th>C45</th>
<th>C56</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaPb3</td>
<td>66.70</td>
<td>26.13</td>
<td>25.99</td>
<td>-0.81</td>
<td>77.92</td>
<td>21.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba3Pb2</td>
<td>60.21</td>
<td>24.08</td>
<td>20.79</td>
<td>61.20</td>
<td>19.22</td>
<td>73.39</td>
<td>21.20</td>
<td>22.20</td>
<td>21.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaPb</td>
<td>56.40</td>
<td>21.23</td>
<td>23.73</td>
<td>53.82</td>
<td>19.18</td>
<td>52.82</td>
<td>10.94</td>
<td>33.49</td>
<td>11.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba3Pb5</td>
<td>47.81</td>
<td>17.16</td>
<td>16.90</td>
<td>-0.94</td>
<td>19.46</td>
<td>18.34</td>
<td>19.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba2Pb</td>
<td>36.99</td>
<td>12.66</td>
<td>27.48</td>
<td>41.23</td>
<td>17.81</td>
<td>46.62</td>
<td>12.61</td>
<td>12.98</td>
<td>18.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6
The elastic compliance matrix of Pb–Ba compounds calculated from the elastic coefficients using the strain–stress method.

<table>
<thead>
<tr>
<th>Phase</th>
<th>S11</th>
<th>S12</th>
<th>S13</th>
<th>S14</th>
<th>S22</th>
<th>S23</th>
<th>S24</th>
<th>S33</th>
<th>S34</th>
<th>S45</th>
<th>S56</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaPb3</td>
<td>0.01897</td>
<td>-0.00572</td>
<td>-0.00442</td>
<td>0.00093</td>
<td>0.01578</td>
<td>0.04688</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba3Pb2</td>
<td>0.02077</td>
<td>-0.00689</td>
<td>-0.00408</td>
<td>0.02009</td>
<td>-0.00331</td>
<td>0.01565</td>
<td>0.04716</td>
<td>0.04504</td>
<td>0.04650</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaPb</td>
<td>0.02361</td>
<td>-0.00636</td>
<td>-0.00830</td>
<td>0.02306</td>
<td>-0.00552</td>
<td>0.02467</td>
<td>0.09145</td>
<td>0.02986</td>
<td>0.08541</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba3Pb5</td>
<td>0.02729</td>
<td>-0.00534</td>
<td>-0.01259</td>
<td>0.04838</td>
<td>0.05452</td>
<td>0.05529</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba2Pb</td>
<td>0.04839</td>
<td>-0.00304</td>
<td>-0.02736</td>
<td>0.02924</td>
<td>-0.00938</td>
<td>0.04116</td>
<td>0.07931</td>
<td>0.07703</td>
<td>0.05371</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

9.60 GPa, respectively. The experimental and theoretical bulk moduli for Pb are 44.8 GPa [27] and 46.2 GPa [28], respectively; while the experimental bulk modulus for Ba is 10.5 GPa [29]. The bulk modulus of Pb is very larger than that of Ba. The present calculated bulk moduli of Pb and Ba are in good agreement with the available experimental and theoretical data, which provide a confirmation that the computational methodology utilized in the present work is suitable. It is obvious that, from Fig. 4(a), the bulk modulus, shear modulus and Young’s modulus for Pb–Ba intermetallic compounds decrease roughly with the increasing mole fraction of Ba. As we known, the shear modulus is more pertinent to hardness than the bulk modulus. The calculated shear modulus of Ba3Pb5 is the largest among Pb–Ba intermetallic compounds, which indicate that Ba3Pb5 should have the highest hardness. The Young’s modulus for the Pb–Ba compounds follows the order BaPb3 > Ba3Pb5 > BaPb > Ba5Pb3 > Ba5Pb2. Young’s modulus is defined as the ratio of stress and strain and can also be used as a measure of the stiffness of a solid: when the value of Young’s modulus is large, the material is stiff [30]. In the present work, BaPb3 is stiffer than the other considered compounds due to its higher value of Young’s modulus (54.68 GPa).

According to Pugh [31], a larger B/G value (>1.75) for a solid represents ductile while a smaller B/G value (<1.75) usually means brittle. Moreover, the Poisson’s ratio ν is consistent with B/G, which refers to a ductile compound usually has a large ν (>0.26) [32]. The values of B/G are larger than 1.75 and values of ν are larger than 0.26 for BaPb3, BaPb and Ba2Pb in Table 7, which indicate that they are ductile and Ba5Pb2 is the most ductile phase. The values of B/G and ν for Ba3Pb5 and Ba3Pb3 are less than 1.75 and 0.26, respectively. It shows that they are brittle and Ba5Pb3 has the most brittleness. In general, hardness is related to the elastic and plastic properties of a material. The hardness of polycrystalline materials can be predicted by a relatively simple semi-empirical equation of hardness, and the expression is as follow [33]:

\[ H_v = 0.92 \left( \frac{G}{B} \right)^{1.137} G^{0.708} \]  

(4)

Table 7 lists the calculated Vickers hardness of Pb–Ba intermetallic compounds. The calculated hardness is less than 10 GPa. Ba3Pb5 has the highest hardness while Ba5Pb2 possesses the smallest one. It is consistent with the result predicted from shear modulus. G, G/B and Hv as a function of the mole fraction of Ba were plotted.

![Fig. 4](image-url)

The elastic moduli (B, G, and E) (a) and the change trend among G, G/B, Hv (b) as a function of the mole fraction of Ba. Note that Hv value is magnified by 5 times to the initial value.
in Fig. 4(b). The $H_T$ value is multiplied by the factor of 5 for a better comparison. It can be concluded from Fig. 4(b) that $G/B$ is more relative to hardness than the shear modulus $G$ because of the power index of $G/B$ larger than that of $G$. Therefore, Ba$_3$Pb owns the smallest $H_T$ (2.41 GPa) due to its minimal $G/B$ value. For the Pb–Ba compounds, there are no or less available experimental and theoretical studies available on hardness. We hope our study could provide a useful guidance for future study.

3.4. Anisotropy of elastic moduli

As a significant parameter of a material, elastic anisotropy is closely related to the possibility of inducing micro-cracks in the material. The elastic anisotropy can be described by the universal anisotropic index $A^U$ and the percent anisotropy in shear and compression ($A_c$ and $A_p$). The universal elastic anisotropy index $A^U$ and the percent anisotropy for a crystal with any symmetry can be expressed as follows [34,35]:

$$A^U = \frac{S_{CC} - S_{RR}}{S_{CC} + S_{RR}} - 6 \geq 0$$

$$A_p = \frac{B_p - B_R}{B_p + B_R}, \quad A_c = \frac{G_c - G_R}{G_c + G_R}$$

where $B_p$ ($G_p$) and $B_R$ ($G_R$) are the bulk modulus (shear modulus) in the Voigt and Reuss approximations, respectively, $A^U$ of a solid is zero if the solid is isotropic. The large deviation of $A^U$ from zero indicates the highly anisotropic mechanical properties. $A^U$ represents a universal measure to quantify the single crystal elastic anisotropy [34]. $A_c = A_p = 0$ refers the elastic isotropy, while $A_c = A_p = 1$ means the maximum elastic anisotropy [36]. Furthermore, since the investigated crystal systems in present work include the trigonal (Ba$_3$Pb$_3$), orthorhombic (Ba$_3$Pb$_5$, BaPb and Ba$_3$Pb), and tetragonal (Ba$_3$Pb$_3$) structures, the shear anisotropic factors also need consider describing the elastic anisotropy. Therefore, the shear anisotropic factors $A_1$, $A_2$, $A_3$ are calculated and discussed. The shear anisotropic factors are defined as [37]:

$$A_1 = \frac{4C_{14}}{C_{11} + C_{33} - 2C_{13}}$$

$$A_2 = \frac{4C_{45}}{C_{22} + C_{33} - 2C_{23}}$$

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}}$$

The values of $A_1$, $A_2$ and $A_3$ should equate to 1.0 for an isotropic crystal. Otherwise, it is an anisotropic crystal. The results of elastic anisotropy are listed in Table 8. It is found that the trigonal Ba$_3$Pb$_3$ has the smallest $A^U$ value among the Pb–Ba intermetallic compounds. The elastic moduli of Ba$_3$Pb$_3$ are not strongly dependent on the different directions and the calculated $A_c$ and $A_p$ values support this conclusion. Though $A_c$, $A_1$, $A_2$ and $A_3$ determine the anisotropy of the shear modulus, the values of $A_1$, $A_2$ and $A_3$ are quite different from $A_c$ [35]. The calculated $A_1$, $A_2$ and $A_3$ values seem to support the supposition that the shear moduli of the Pb–Ba intermetallic compounds have a strong directional dependence. Moreover, it is noticed that the values of $A_p$ are smaller than $A_c$ for all considered Pb–Ba intermetallic compounds, which indicate that these Pb–Ba compounds are slightly anisotropic in compressibility. However, the universal anisotropic index $A^U$ is the best indicator among these anisotropic indexes, which can provide unique and consistent results for the mechanical anisotropic properties of the Pb–Ba intermetallic compounds. It can be concluded from the calculated $A^U$ in Table 8 that the order of the elastic anisotropy for the calculated Pb–Ba compounds is BaPb > Ba$_3$Pb$_3$ > Ba$_3$Pb$_5$ > BaPb > Ba$_3$Pb$_5$. The three-dimensional (3D) surface construction is a valid method to describe the elastic anisotropic behavior of a solid completely. The 3D figures of the directional dependences of reciprocals of bulk modulus and Young’s modulus for the Pb–Ba compounds are different due to their various crystal structures [21].

For trigonal system,

$$1 - \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{11} + \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{12} = \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{13} - S_{13}$$

$$1 - \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{11} + \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{12} = \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{13} + S_{13} - S_{12}$$

(10)

For orthorhombic system,

$$1 - \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{11} + \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{12} = \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{13} - S_{13}$$

$$1 - \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{11} + \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{12} = \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{13} + S_{13} - S_{12}$$

(11)

For tetragonal system,

$$1 - \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{11} + \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{12} = \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{13} - S_{13}$$

$$1 - \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{11} + \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{12} = \left( \frac{B}{11} \right)^{\frac{1}{3}} S_{13} + S_{13} - S_{12}$$

(12)

where $S_{ij}$ is the usual elastic compliance constant, which is obtained from the inverse of the matrix of the elastic constants. $l_1$, $l_2$ and $l_3$ are the direction cosines. The results are shown in Figs. 5 and 6 for the bulk and Young’s moduli, respectively. The surface in each graph denotes the magnitude of $B$ and $E$ along different directions. The 3D figure appears as a spherical shape for an isotropic structure, while the deviation from the spherical shape exhibits the content of anisotropy [13]. From Fig. 5, it can see that the 3D figure of the bulk modulus for the trigonal BaPb$_3$ has a deviation in shape from the sphere, indicating that the bulk modulus for BaPb$_3$ show slightly anisotropic. The nonspherical nature in Fig. 6 shows that the Young’s modulus for BaPb$_3$ also is anisotropic and the $x$-axis is more anisotropic than the $z$-axis because of the values of $C_{13}$ larger than $C_{12}$ for BaPb$_3$. For the orthorhombic Ba$_3$Pb$_5$ and Ba$_3$Pb$_5$, the bulk modulus and Young’s modulus show anisotropic for different orien-
tations: the 3D figures are evident deviate in shape from the sphere along x-axis and z-axis owing to the $C_{33}$ larger than the $C_{11}$ for Ba$_3$Pb$_5$ and Ba$_2$Pb, which may result in the x-axis is more anisotropic than the z-axis in Ba$_3$Pb$_5$ and Ba$_2$Pb. As for the orthorhombic BaPb, the 3D surface of Young’s modulus along x-axis, y-axis and z-axis deviate from the spherical shape largely, which means BaPb is

Fig. 5. The surface construction of the bulk modulus for the Pb–Ba compounds. The magnitude of bulk at different directions is represented by the contour. For all graphs, the units are in GPa.

Fig. 6. The directional dependence of the Young’s modulus for the Pb–Ba compounds. The magnitude of Young’s modulus at different directions is represented by the contour. The units are in GPa.
highly anisotropic. The 3D figures of the bulk modulus and Young's modulus for the tetragonal Ba₃Pb₂ are characterized by more anisotropic along the z axis than that along the x axis.

Debye temperature $\Theta_D$ is a fundamental parameter for thermodynamic properties of a material, which is related to elastic constants, thermal expansion and specific heat. The vibrational excitations only yield from acoustic vibrations at the low temperatures. Based on elastic constant evaluations, Debye temperature can be estimated from the average sound velocity by the following equation [38]:

$$\Theta_D = \frac{\hbar}{k} \left( \frac{3n}{4\pi} \frac{N_A\rho}{M} \right)^{\frac{1}{3}} v_m$$

(13)

where $\hbar$ and $k$ are the Planck constant and Boltzmann's constant, respectively; $N_A$ is the Avogadro's number. $M$ is the molecular weight. $n$ is the number of per formula unit and $\rho$ is the density. The average sound velocity $v_m$ can be calculated as follows [39]:

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_L^2} + \frac{1}{v_T^2} \right) \right]^{\frac{1}{2}}, \quad v_L = \left[ \frac{B + 4G}{3} / \rho \right]^{\frac{1}{2}}, \quad v_T = \left( \frac{G}{\rho} \right)^{\frac{1}{2}}$$

(14)

where $v_L$ is the longitudinal velocity and $v_T$ is the transverse sound velocity. The calculated Debye temperatures for the Pb–Ba intermetallic compounds are listed in Table 9. The elastic wave velocities of these compounds are relatively small because of their small mechanical moduli and large densities. The largest $\Theta_D$ is 160.74 K for Ba₃Pb₂ while the lowest one is 135.38 K for Ba₂Pb₃. The order of $\Theta_D$ for Pb–Ba compounds is: Ba₃Pb₂ > BaPb₂ > BaPb > Ba₃Pb₁ > BaPb. The Debye temperature reflects the thermal conductivity: a higher Debye temperature means a larger associated thermal conductivity. From the order of $\Theta_D$ for Pb–Ba compounds, Ba₃Pb₂ has the largest thermal conductivity, while Ba₂Pb possesses the lowest one. There is no experimental and theoretical data available for Debye temperatures of the Pb–Ba compounds so far. Therefore, our calculated results can provide support for future works on Pb–Ba compounds.

### Table 9

<table>
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<th>Compound</th>
<th>BaPb₂</th>
<th>Ba₃Pb₂</th>
<th>BaPb</th>
<th>Ba₃Pb₁</th>
<th>Ba₂Pb</th>
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<td>$\rho$</td>
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<td>1603.41</td>
<td>1516.85</td>
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<tr>
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<td>1779.94</td>
<td>1690.40</td>
<td>1732.16</td>
<td>1601.23</td>
</tr>
<tr>
<td>$\Theta_D$</td>
<td>154.76</td>
<td>160.74</td>
<td>147.34</td>
<td>147.22</td>
<td>135.38</td>
</tr>
</tbody>
</table>

3.5. Electronic structure

The electronic energy band structures near Fermi level of the Pb–Ba intermetallic compounds considered in the present work have also been investigated and the results are shown in Fig. 7. The zero energy means the Fermi level. It can be seen from Fig. 7 that band structures near Fermi level for these compounds are concentrated in the range of $-4$ to $2$ eV. Both the top valence band and the lowest conduction band of Ba₂Pb are situated at $0.4 \times -G - Z$ in Fig. 7. Therefore, Ba₂Pb is a direct band gap semiconductor with the band gap of 0.195 eV, it is in good agreement with the theoretical result (0.18 eV) calculating by WEIN2K code [9]. As for other considered compounds, their valence bands overlap the conduction bands at the Fermi surface, which indicate that they are conductors.

To illustrate the basic features of the chemical bonding in Pb–Ba intermetallic compounds, the total density of states (TDOS) and partial density of states (PDOS) were also investigated. Fig. 8 depicts the TDOS and PDOS of Pb–Ba intermetallic compounds. The DOS shown in Fig. 8 reveal that the part of TDOS, which the energy ranges from $-4$ eV to $2$ eV, are mainly contributed by Pb 6p and Ba 5d states, while the part of TDOS near the energy of $-8$ eV are primarily contributed by Pb 6s states. It indicates that the 6p states of Pb hybridize strongly with the Ba 5d states in the region ranging from $-4$ eV to $2$ eV.

Moreover, the TDOS below the Fermi level (ranging from $-4$ eV to $0$ eV) for the Pb–Ba intermetallic compounds were analyzed. It is found that the bonding electron numbers of these Pb–Ba intermetallic compounds per atom are 1.990 for BaPb₂, 1.992 for Ba₃Pb₂, 2.013 for BaPb, 2.006 for Ba₂Pb, and 1.999 for Ba₃Pb₁, respectively. Larger bonding electron numbers correspond to the stronger...
charge interaction [40], and the phase stability of the compound will be better. Thus, BaPb has the best phase stability than others in the Pb–Ba intermetallic compounds.

4. Conclusions

Phase stability, elastic moduli, hardness, elastic anisotropy properties, Debye temperatures, and electronic structures of the Pb–Ba intermetallic compounds were investigated and discussed by using the first-principles calculations. The formation enthalpies indicate that the phase stabilities of these compounds follow the order: BaPb₃ < Ba₃Pb < Ba₂Pb < Ba₂Pb₃ < BaPb. The elastic properties, including bulk modulus B, shear modulus G, Yong’s modulus E and Poisson’s ratio ν, were calculated. The results of elastic constants reveal these compounds are mechanically stable. The hardness for all the calculated compounds is less than 10 GPa. The elastic anisotropy was characterized by calculating several different anisotropic indexes and factors (A¹, A², A₃, A₄, and A₅), and the results indicated that the Pb–Ba intermetallic compounds show anisotropic mechanical properties and the order of elastic anisotropy is BaPb > Ba₂Pb > Ba₂Pb₃ > BaPb > Ba₃Pb. The Debye temperature was also predicted. The analysis on the electronic structures shows that BaPb is a direct band gap semiconductor with the band gap of 0.195 eV. The higher phase stability of BaPb relative to other Pb–Ba compounds can be attributed to its higher bonding electron numbers.

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References


