

# First-principle studies of Ca–X (X=Si,Ge,Sn,Pb) intermetallic compounds

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## ABSTRACT

The structural properties, elastic properties, heats of formation, electronic structures, and densities of states of 20 intermetallic compounds in the Ca–X (X=Si, Ge, Sn, Pb) systems have been systematically investigated by using first-principle calculations. Our computational results indicated that with increasing atomic weight of X, the bulk modulus of Ca–X intermetallic compounds decreases gradually. It was also found that Ca<sub>36</sub>Sn<sub>23</sub> and CaPb are mechanically unstable phases. Results on the electronic energy band and densities of states also indicated that Ca<sub>3</sub>Si<sub>4</sub> is an indirect band gap semiconductor with a band gap of 0.598 eV, and Ca<sub>2</sub>Si, Ca<sub>2</sub>Ge, Ca<sub>2</sub>Sn, and Ca<sub>2</sub>Pb are direct band gap semiconductors with band gaps of 0.324, 0.265, 0.06, and 0.07 eV, respectively. In addition, it is found that the absolute values of heats of formation for all Ca–X intermetallics are larger than 30 kJ/mol atom.

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## 1. Introduction

Due to their unique properties and potential technological applications in metallurgy, chemical engineering, aeronautics as well as astronautics, substantial recent efforts have been devoted to the search for intermetallic compounds [1–3]. Among these intermetallic compounds, Ca–X (X=Si, Ge, Sn, Pb) system intermetallic compounds have drawn considerable attention owing to their practical applications in thermoelectric and optoelectric materials and in the design of novel electronic devices [4,5]. Based on earlier results, phase diagrams of Ca–X systems have been investigated by Manfrinetti [6], Palenzona [7,8], Okamoto [9] and Bruzzone [10]. According to these phase diagrams, there are 20 intermetallic compounds, namely Ca<sub>2</sub>Si, Ca<sub>5</sub>Si<sub>3</sub>, CaSi, Ca<sub>3</sub>Si<sub>4</sub>, CaSi<sub>2</sub>, Ca<sub>2</sub>Ge, Ca<sub>5</sub>Ge<sub>3</sub>, Ca<sub>7</sub>Ge<sub>6</sub>, CaGe, CaGe<sub>2</sub>, Ca<sub>2</sub>Sn, Ca<sub>5</sub>Sn<sub>3</sub>, Ca<sub>36</sub>Sn<sub>23</sub>, Ca<sub>7</sub>Sn<sub>6</sub>, CaSn, CaSn<sub>3</sub>, Ca<sub>2</sub>Pb, Ca<sub>5</sub>Pb<sub>3</sub>, CaPb, and CaPb<sub>3</sub>.

Among these 20 types of intermetallic compounds, Ca<sub>2</sub>Si, Ca<sub>2</sub>Ge, Ca<sub>2</sub>Sn, and Ca<sub>2</sub>Pb have been extensively investigated experimentally and theoretically due to their unique semiconductor properties [5–14]. For example, various aspects such as structural properties [5–10,13], energy band structures [5], electronic densities of states [5], dielectric functions [5], and heats of formation [11,12,14] have been explored systematically. As a newly discovered compound Ca<sub>3</sub>Si<sub>4</sub>, its structural properties, energy band structures, transport properties and dielectric functions have been studied by Manfrinetti and Migas et al. It

has been found that Ca<sub>3</sub>Si<sub>4</sub> is an indirect band gap semiconductor with a band gap of 0.35 eV [4,6]. Moreover, it has been reported that Ca<sub>5</sub>Si<sub>3</sub> and CaSi can emerge as promising candidates for hydrogen storage materials [15]. As for other Ca–X system intermetallic compounds, much attention has been focused on their heats of formation [16–18], but systematical first-principle calculations are still lacking. In addition, their elastic properties and electronic structures have hardly been investigated in this context, despite their significant potential applications. Therefore, it is important to perform systematical studies on the Ca–X system intermetallic compounds. In this paper, the structural properties, elastic properties, mechanical stability, thermodynamic stability, heats of formation, electronic structures, and densities of states of the 20 Ca–X system intermetallic compounds have been studied by using first-principle calculations.

## 2. Computational method

Twenty types of Ca–X system intermetallic compounds have been investigated by using density functional theory (DFT) and plane-wave pseudopotential technique implemented in the CASTEP package [19]. In this computational scheme, the ultrasoft pseudopotentials have been employed for the 3p<sup>6</sup>4s<sup>2</sup>, 3s<sup>2</sup>3p<sup>2</sup>, 3d<sup>10</sup>4s<sup>2</sup>4p<sup>2</sup>, 4d<sup>10</sup>5s<sup>2</sup>5p<sup>2</sup>, and 5d<sup>10</sup>6s<sup>2</sup>6p<sup>2</sup> atom configurations of Ca, Si, Ge, Sn, and Pb [20]. Exchange–correlation interaction was described by using the generalized gradient approximation with the Perdew–Burke–Ernzerh parameterization [21]. The **k** point separation in the Brillouin zone of the reciprocal space is 0.04 nm<sup>−1</sup>, that is, 3 × 5 × 3, 4 × 4 × 5, 6 × 6 × 6, 3 × 3 × 2,

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$7 \times 7 \times 7$  for  $\text{Ca}_2\text{Si}$ ,  $\text{Ca}_5\text{Si}_3$ ,  $\text{CaSi}$ ,  $\text{Ca}_3\text{Si}_4$ ,  $\text{CaSi}_2$ ;  $3 \times 5 \times 3$ ,  $4 \times 4 \times 5$ ,  $3 \times 1 \times 3$ ,  $6 \times 6 \times 6$ ,  $7 \times 7 \times 2$  for  $\text{Ca}_2\text{Ge}$ ,  $\text{Ca}_5\text{Ge}_3$ ,  $\text{Ca}_7\text{Ge}_6$ ,  $\text{CaGe}$ ,  $\text{CaGe}_2$ ;  $3 \times 4 \times 2$ ,  $3 \times 3 \times 3$ ,  $2 \times 2 \times 1$ ,  $3 \times 1 \times 2$ ,  $5 \times 5 \times 5$ ,  $4 \times 4 \times 4$  for  $\text{Ca}_2\text{Sn}$ ,  $\text{Ca}_5\text{Sn}_3$ ,  $\text{Ca}_{36}\text{Sn}_{23}$ ,  $\text{Ca}_7\text{Sn}_6$ ,  $\text{CaSn}$ ,  $\text{CaSn}_3$ ;  $3 \times 5 \times 3$ ,  $2 \times 2 \times 4$ ,  $5 \times 5 \times 5$ ,  $6 \times 6 \times 6$  for  $\text{Ca}_2\text{Pb}$ ,  $\text{Ca}_5\text{Pb}_3$ ,  $\text{CaPb}$ ,  $\text{CaPb}_3$ , respectively. The kinetic cutoff energy for plane waves was determined as 400 eV.

To validate the performance of the present first-principle method, benchmark calculations have been performed for the  $\text{CaPb}_3$  phase. The calculated lattice parameter of 4.970 Å agrees well with the experimental value of 4.900 Å [10]. Moreover, the calculated heat of formation for the  $\text{CaPb}_3$  phase is  $-33.5$  kJ/molatoms, which is consistent with experimental data of  $-35.0$  kJ/molatoms [22]. These results indicate that the computational scheme utilized in this work is credible.

### 3. Results and discussion

#### 3.1. Structural properties

In this work, the initial crystal structures have been built on the basis of the experimental crystallographic data of the 20 types of Ca–X system intermetallic compounds [6–8,10,23–33], and then the lattice parameters and internal coordinates of the 20

compounds were optimized by using first-principle calculations. The optimized lattice parameters and mass densities are summarized in Table 1 in comparison with the available experimental data and their corresponding crystal structures. It is clearly seen that all the lattice parameters obtained by using first-principle calculations are very close to the previous experimental values. These agreements of optimized lattice parameters and calculated mass densities with the experimental values provide an additional confirmation that the computational methodology utilized in this paper is suitable and reliable.

#### 3.2. Elastic properties and mechanical stability

The elastic constants  $C_{ij}$  (GPa) and bulk moduli of the 20 Ca–X system intermetallic compounds have been calculated by using DFT calculations. The methodology of the calculation has been described by Nye [34], Ashcroft and Mermin [35]. The elastic constants  $C_{ij}$  (GPa) were determined by applying small strains of order 0.003. Calculated results together with their previous theoretical values [5,18] are shown in Table 2. Mechanical stability of the 20 compounds has been analyzed in terms of their elastic constants. For cubic crystals, the conditions for mechanical stability are given by [36]

$$C_{11} > 0, C_{44} > 0, C_{11} - C_{12} > 0, C_{11} + 2C_{12} > 0 \quad (1)$$

**Table 1**

Calculated and experimental lattice parameters for Ca–X system intermetallic compounds.

System	Phase	At% X	Space group	Lattice parameters (Å)			Mass density (kg/m <sup>3</sup> )	Reference
				a	b	c		
Ca–Si	$\text{Ca}_2\text{Si}$	33.3	<i>Pnma</i>	9.002	7.667	4.799	2170.71	[23]
				8.990	7.647	4.837	2161.61	This work
	$\text{Ca}_5\text{Si}_3$	37.5	<i>I4/mcm</i>	7.640		14.620	2215.61	[24]
				7.635		14.787	2193.46	This work
	$\text{CaSi}$	50.0	<i>Cmcm</i>	4.545	10.728	3.890	2387.09	[25]
				4.560	10.741	3.881	2381.87	This work
	$\text{Ca}_3\text{Si}_4$	57.2	<i>P6<sub>3</sub>/m</i>	8.541		14.906	2460.73	[6]
				8.546		14.903	2458.35	This work
	$\text{CaSi}_2$	66.7	<i>R<math>\bar{3}</math>m</i>	3.887		30.530	2400.57	[26]
				3.880		30.228	2433.10	This work
Ca–Ge	$\text{Ca}_2\text{Ge}$	33.3	<i>Pnma</i>	7.734	4.834	9.069	2992.41	[23]
				7.667	4.866	9.070	2998.20	This work
	$\text{Ca}_5\text{Ge}_3$	37.5	<i>I4/mcm</i>	7.740		14.660	3162.62	[24]
				7.710		14.877	3140.95	This work
	$\text{Ca}_7\text{Ge}_6$	46.2	<i>Pnma</i>	7.409	22.391	8.129	3527.06	[7]
				7.427	22.443	8.085	3529.92	This work
	$\text{CaGe}$	50.0	<i>Cmcm</i>	4.565	10.837	4.005	3777.16	[27]
				4.584	10.877	4.000	3755.49	This work
	$\text{CaGe}_2$	66.7	<i>R<math>\bar{3}</math>m</i>	3.949		30.720	4448.94	[28]
				4.041		30.285	4308.82	This work
Ca–Sn	$\text{Ca}_2\text{Sn}$	33.3	<i>Pnma</i>	7.975	5.044	9.562	3433.84	[29]
				7.958	5.075	9.580	3413.65	This work
	$\text{Ca}_5\text{Sn}_3$	37.5	<i>I4/mcm</i>	8.117		15.429	3635.99	[8]
				8.141		15.500	3598.38	This work
	$\text{Ca}_{36}\text{Sn}_{23}$	39.0	<i>P4/mbm</i>	12.502		22.880	3875.13	[8]
				12.452		23.686	3773.24	This work
	$\text{Ca}_7\text{Sn}_6$	46.2	<i>Pnma</i>	7.869	23.828	8.462	4155.73	[8]
				7.908	23.826	8.547	4094.11	This work
	$\text{CaSn}$	50.0	<i>Cmcm</i>	4.813	11.544	4.351	4362.31	[30]
				4.793	11.613	4.401	4305.09	This work
Ca–Pb	$\text{Ca}_2\text{Pb}$	33.3	<i>Pnma</i>	4.732			62.8.33	[31]
				4.755			6120.24	This work
	$\text{Ca}_5\text{Pb}_3$	37.5	<i>P6<sub>3</sub>mc</i>	8.072	5.100	9.647	4806.09	[29]
				8.000	5.147	9.697	4779.99	This work
	$\text{CaPb}$	50.0	<i>P4/mmm</i>	9.626		6.816	5093.96	[32]
				9.355		7.004	5048.81	This work
	$\text{CaPb}_3$	75.0	<i>Pm<math>\bar{3}</math>m</i>	5.118		4.491	6981.11	[10]
				5.116		4.649	6748.07	This work
	$\text{CaPb}_3$	75.0	<i>Pm<math>\bar{3}</math>m</i>	4.900			9339.19	[33]
				4.970			8952.29	This work

As can be seen from Table 2, all the elastic constants of the cubic structures (CaSn<sub>3</sub> and CaPb<sub>3</sub>) satisfy the above restrictions in Eq. (1), and this indicates that these cubic structures are all mechanically stable.

For tetragonal structures, the mechanical stability criteria can be expressed as follows [36]:

$$C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, C_{11} - C_{12} > 0, C_{11} + C_{33} - 2C_{13} > 0, 2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0 \quad (2)$$

Among the five tetragonal structures, that is, Ca<sub>5</sub>Si<sub>3</sub>, Ca<sub>5</sub>Ge<sub>3</sub>, Ca<sub>5</sub>Sn<sub>3</sub>, Ca<sub>36</sub>Sn<sub>23</sub>, and CaPb, the elastic constants of Ca<sub>5</sub>Si<sub>3</sub>, Ca<sub>5</sub>Ge<sub>3</sub>, and Ca<sub>5</sub>Sn<sub>3</sub> are consistent with the above restrictions in Eq. (2), and these results demonstrate that they are mechanically stable.

However, for the Ca<sub>36</sub>Sn<sub>23</sub> compound,  $C_{11}=95 > 0$ ,  $C_{33}=52.8 > 0$ ,  $C_{44}=-122.7 < 0$ ,  $C_{66}=30.9 > 0$ ,  $C_{11}-C_{12}=77.1 > 0$ ,  $C_{11}+C_{33}-2C_{13}=218 > 0$ ,  $2C_{11}+C_{33}+2C_{12}+4C_{13}=138.2 > 0$ . This implies that the Ca<sub>36</sub>Sn<sub>23</sub> compound does not satisfy the restriction of  $C_{44} > 0$ . Note also that for the CaPb compound,  $C_{11}=39.56 > 0$ ,  $C_{33}=57.31 > 0$ ,  $C_{44}=13.62 > 0$ ,  $C_{66}=-11.13 < 0$ ,  $C_{11}-C_{12}=13.68 > 0$ ,  $C_{11}+C_{33}-2C_{13}=38.75$ ,  $2C_{11}+C_{33}+2C_{12}+4C_{13}=304.4 > 0$ . The calculated elastic constant  $C_{66}$  is negative, violating the mechanical stability criteria in Eq. (2). Although optimized lattice parameters of Ca<sub>36</sub>Sn<sub>23</sub> and CaPb compounds are very close to the experimental data, our calculations reveal that Ca<sub>36</sub>Sn<sub>23</sub> and CaPb structures are mechanically unstable. There are three possible reasons for this: first, existing stress has not been considered in

**Table 2**  
Calculated elastic properties compared to other theoretical values for the single crystalline Ca–X system intermetallic compounds.

System	Phase	$C_{11}$	$C_{12}$	$C_{13}$	$C_{22}$	$C_{23}$	$C_{33}$	$C_{44}$	$C_{55}$	$C_{66}$	$K$
Ca–Si	Ca <sub>2</sub> Si	82.1	19.4	16.9	74.9	31.6	69.1	26.9	18.1	32.2	40.1
	Ca <sub>2</sub> Si										46.0 [5]
	Ca <sub>2</sub> Si										40.0 [5]
	Ca <sub>5</sub> Si <sub>3</sub>	79.6	20.9	27.0			56.4	31.9		39.6	40.0
	CaSi	99.0	26.8	25.7	101.7	26.8	125.6	36.9	50.0	34.5	53.4
	Ca <sub>3</sub> Si <sub>4</sub>	117.8	31.1	23.6			121.7	38.1			57.1
Ca–Ge	CaSi <sub>2</sub>	133.9	47.1	29.9			92.6	43.2			60.7
	Ca <sub>2</sub> Ge	67.1	20.7	23.5	67.5	27.2	67.4	23.6	14.7	31.5	38.3
	Ca <sub>5</sub> Ge <sub>3</sub>	74.4	19.9	24.1			52.4	28.5		39.3	36.8
	Ca <sub>7</sub> Ge <sub>6</sub>	75.1	24.8	26.5	72.4	28.7	72.2	34.8	28.6	31.8	42.2
	CaGe	92.8	23.0	23.9	90.2	22.8	107.7	33.3	44.6	29.2	47.5
	CaGe <sub>2</sub>	87.4	32.3	31.9			72.6	36.4			48.4
Ca–Sn	Ca <sub>2</sub> Sn	36.2	27.7	11.3	58.3	33.2	42.5	14.7	15.0	26.4	24.0
	Ca <sub>2</sub> Sn										29.8 [18]
	Ca <sub>5</sub> Sn <sub>3</sub>	64.9	22.2	20.7			43.6	24.9		34.7	32.2
	Ca <sub>5</sub> Sn <sub>3</sub>										32.6 [18]
	Ca <sub>36</sub> Sn <sub>23</sub>	95.0	17.9	–35.1			52.8	–122.7		30.9	10
	Ca <sub>7</sub> Sn <sub>6</sub>	56.7	23.5	31.9	61.0	31.6	45.0	21.9	24.9	12.3	37.2
	CaSn	76.4	11.3	22.3	82.5	22.3	69.0	20.6	33.3	19.9	37.7
	CaSn										39.0 [18]
	CaSn <sub>3</sub>	74.0	32.8					4.6			46.5
	CaSn <sub>3</sub>										45.9 [18]
Ca–Pb	Ca <sub>2</sub> Pb	31.5	22.3	18.5	54.4	21.5	53.8	16.5	15.6	24.2	27.1
	Ca <sub>5</sub> Pb <sub>3</sub>	64.5	17.5	11.4			46.5	14.5			27.5
	CaPb	31.6	25.9	29.1			57.3	13.6		–11.1	32.3
	CaPb <sub>3</sub>	50.2	29.5					20.2			36.4

$C_{ij}$ , elastic stiffness (in GPa);  $K$ , bulk modulus (in GPa).

**Table 3**  
Polycrystalline bulk modulus, shear modulus, Young's modulus (GPa), Poisson's ratio for Ca–X system intermetallic compounds deduced by Voigt, Reuss, and Hill (VRH) approximations.

System	Phase	$K_V$	$K_R$	$K_H$	$G_V$	$G_R$	$G_H$	$E$	$G/K$	$\nu$
Ca–Si	Ca <sub>2</sub> Si	40.2	40.1	40.2	26.0	24.5	25.3	62.6	0.63	0.2400
	Ca <sub>5</sub> Si <sub>3</sub>	40.6	40.0	40.3	30.1	27.8	28.9	70.0	0.72	0.2103
	CaSi	53.9	53.4	53.6	40.7	39.9	40.3	96.7	0.75	0.1995
	Ca <sub>3</sub> Si <sub>4</sub>	57.1	57.1	57.1	42.5	42.1	42.3	101.8	0.74	0.2029
	CaSi <sub>2</sub>	63.8	60.7	62.3	42.9	42.4	42.6	104.1	0.68	0.2213
Ca–Ge	Ca <sub>2</sub> Ge	38.3	38.3	38.3	22.7	21.3	22.0	55.4	0.57	0.2590
	Ca <sub>5</sub> Ge <sub>3</sub>	37.5	36.8	37.1	28.1	26.1	27.1	65.4	0.73	0.2066
	Ca <sub>7</sub> Ge <sub>6</sub>	42.2	42.2	42.2	28.4	27.6	28.0	68.7	0.66	0.2286
	CaGe	47.8	47.6	47.7	36.2	35.4	35.8	85.8	0.80	0.1999
	CaGe <sub>2</sub>	48.8	48.5	48.7	30.2	29.1	29.6	73.9	0.61	0.2468
	Ca <sub>2</sub> Sn	31.3	24.0	27.7	15.5	12.0	13.8	35.5	0.49	0.2863
Ca–Sn	Ca <sub>5</sub> Sn <sub>3</sub>	33.4	32.1	32.8	24.2	22.3	23.3	56.4	0.70	0.2130
	Ca <sub>36</sub> Sn <sub>23</sub>	15.4	9.7	12.5	–23.2	73.2	25.0	45.0	2.0	–0.0981
	Ca <sub>7</sub> Sn <sub>6</sub>	37.4	37.2	37.3	16.9	14.0	15.4	40.9	0.42	0.3183
	CaSn	37.7	37.7	37.7	26.2	24.8	25.5	62.5	0.67	0.2239
	CaSn <sub>3</sub>	46.5	46.5	46.5	11.0	6.7	8.8	24.9	0.19	0.4107
	Ca <sub>2</sub> Pb	29.4	27.1	28.2	16.4	14.6	15.5	39.3	0.55	0.2679
Ca–Pb	Ca <sub>5</sub> Pb <sub>3</sub>	28.5	27.5	28.0	19.5	18.4	19.0	46.4	0.68	0.2232
	CaPb	33.8	32.2	33.1	6.7	16.6	11.6	31.3	0.35	0.3423
	CaPb <sub>3</sub>	36.4	36.4	36.4	16.3	14.6	15.4	40.6	0.42	0.3141

$K$ , bulk modulus (in GPa);  $G$ , shear modulus (in GPa);  $E$ , Young's modulus (in GPa);  $\nu$ , Poisson's ratio.

the experimental measurement; second, inasmuch as the nearest neighbor distance between Sn–Sn, Sn–Ca and Ca–Ca are 3.023, 3.042 and 3.169 Å [8], respectively, the nature of the interactions between Sn–Sn, Sn–Ca and Ca–Ca may be the reason for mechanical unstability of  $\text{Ca}_{36}\text{Sn}_{23}$ ; third, the magnetism of  $\text{Ca}_{36}\text{Sn}_{23}$  and CaPb may affect the elastic constants. To clarify further the mechanical stability of  $\text{Ca}_{36}\text{Sn}_{23}$  and CaPb, more attention should be paid to this issue.

For hexagonal structures, the mechanical stability restrictions can be expressed as follows [37,38]:

$$C_{11} > 0, C_{44} > 0, C_{11} - C_{12} > 0, (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0 \quad (3)$$

As shown in Table 2, the elastic constants of the hexagonal structures ( $\text{Ca}_3\text{Si}_4$ ,  $\text{CaSi}_2$ ,  $\text{CaGe}_2$ , and  $\text{Ca}_5\text{Pb}_3$ ) can comply with all these stability criteria in (3), and this indicates that all of these structures are mechanically stable.

The mechanical stability criteria orthorhombic structures are as follows [39]:

$$\begin{aligned} C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0, C_{11} + C_{22} \\ - 2C_{12} > 0, C_{11} + C_{33} - 2C_{13} > 0, C_{22} + C_{33} \\ - 2C_{23} > 0, C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23} > 0. \end{aligned} \quad (4)$$

Based on the elastic constants of orthorhombic structures ( $\text{Ca}_2\text{Si}$ ,  $\text{CaSi}$ ,  $\text{Ca}_2\text{Ge}$ ,  $\text{Ca}_7\text{Ge}_6$ ,  $\text{CaGe}$ ,  $\text{Ca}_2\text{Sn}$ ,  $\text{Ca}_7\text{Sn}_6$ ,  $\text{CaSn}$ , and  $\text{Ca}_2\text{Pb}$ )

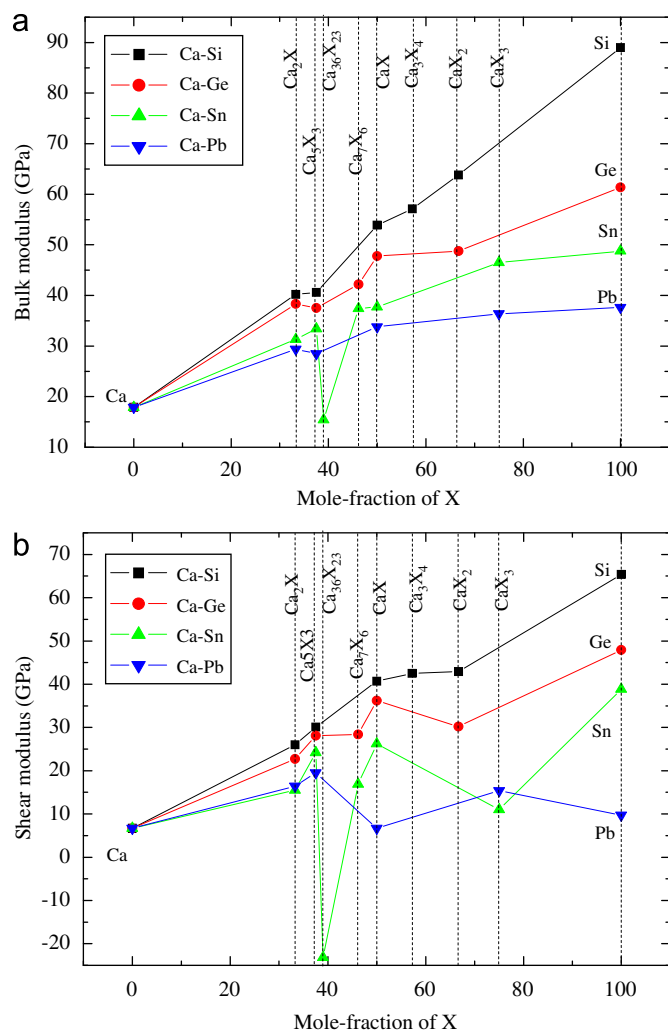
in Table 2, all the orthorhombic structures compounds considered in this paper are mechanically stable.

To further understand the mechanical properties, we have deduced the polycrystalline bulk modulus ( $K$ ), shear modulus ( $G$ ), Young's modulus ( $E$ ), and Poisson's ratio ( $\nu$ ) using Voigt, Reuss, and Hill (VRH) approximations based on their single-crystal elastic constants [40], and the results are shown in Table 3. Fig. 1(a) shows the relationship between bulk modulus and concentration of X. It is clearly shown that the bulk modulus increases nearly monotonously with the increasing concentration of X (in atom%), except that of  $\text{Ca}_{36}\text{Sn}_{23}$ . For the  $\text{Ca}_{36}\text{Sn}_{23}$

**Table 4**

Calculated and experimental heats of formation for Ca–X system intermetallic compounds.

System	Phase	Heat of formation (kJ/mol atoms)	Reference
Ca–Si	$\text{Ca}_2\text{Si}$	–44.8	This work
		–56.1	[11]
		–56.1	[44]
		–47.1	[17]
		–47.2	This work
	$\text{Ca}_5\text{Si}_3$	–55.3	[11]
		–55.3	[44]
		–49.2	[17]
	CaSi	–52.4	This work
		–48.9	[11]
		–49.6	[44]
		–43.5	[17]
		–45.8	This work
	$\text{Ca}_3\text{Si}_4$	–46.0	[11]
		–40.6	[44]
		–40.4	[17]
Ca–Ge	$\text{CaSi}_2$	–37.1	This work
		–37.8	[11]
		–37.8	[44]
	$\text{Ca}_2\text{Ge}$	–31.2	[17]
		–58.9	This work
Ca–Sn	$\text{Ca}_2\text{Ge}$	–60.4	This work
		–61.4	This work
		–64.3	This work
	$\text{CaGe}$	–46.8	This work
		–63.4	This work
		–57.8	[45]
	$\text{Ca}_5\text{Sn}_3$	–66.4	[16]
		–83.1	[12]
		–63.1	This work
		–63.6	[45]
Ca–Pb	$\text{Ca}_3\text{Sn}_{23}$	–65.8	[16]
		–86.6	[12]
		–63.5	This work
		–65.4	[45]
		–66.3	[16]
	$\text{Ca}_7\text{Sn}_6$	–85.8	[12]
		–62.6	This work
		–71.4	[45]
	CaSn	–65.1	[16]
		–75.7	[12]
		–63.0	This work
	$\text{CaSn}_3$	–72.7	[45]
		–66.3	[16]
		–70.2	[12]
		–42.0	This work
Ca–Pb	$\text{Ca}_2\text{Pb}$	–47.8	[45]
		–40.9	[16]
		–37.7	[12]
	$\text{Ca}_5\text{Pb}_3$	–56.4	This work
		–59.0	[22]
		–52.8	This work
	CaPb	–56.0	[22]
		–51.9	This work
		–57.0	[22]
	$\text{CaPb}_3$	–36.8	This work
		–35.0	[22]



**Fig. 1.** Calculated (a) bulk moduli and (b) shear moduli of Ca–X system intermetallic compounds.

compound, the calculated bulk modulus is 15.4 GPa, which is much lower than that of other Ca–X system intermetallic compounds. The bulk modulus of Ca–Si system compounds is larger than that of Ca–Ge, Ca–Sn, and Ca–Pb system compounds. This can be explained by the calculated high bulk modulus of 89 GPa for pure Si. With increasing atomic weight of X, all the bulk moduli of Ca–X system intermetallic compounds decrease gradually. These results are in agreement with the results for the Mg–X (X=Si, Ge, Sn) compounds calculated by Ganeshan et al. [41]. Now, since the valence electron densities of Si, Ge, Sn, and Pb are the same, the decrease in bulk modulus is due to the increase in X atomic radius with the increasing atom weight of X. In addition, the relationship between shear modulus and the concentration of X has been plotted in Fig. 1(b). With the increase in the concentration of X  $c$  (in atom%), the shear modulus for Ca–Si system compounds increases monotonously. The tendency indicates that the hardness of Ca–Si system compounds increases with the increasing of X concentration  $c$ . As for Ca–Ge, Ca–Sn, and Ca–Pb system compounds, the shear modulus changes disorderly. The shear modulus of  $\text{Ca}_{36}\text{Sn}_{23}$  compound is  $-23.2$  GPa, which is also much lower than that of other Ca–Sn system compounds. For all the 20 Ca–X system intermetallic compounds, it is found that the hardness of CaPb compound is the smallest and  $\text{CaSi}_2$  compound is the largest.

In order to further analyze the mechanical properties of the 20 Ca–X system intermetallic compounds, brittleness and ductility properties have also been studied by using the shear modulus to bulk modulus ( $G/K$ ) ratio and Poisson's ratio. According to Pugh [42], if  $G/K$  ratio is larger than 0.57, the material behaves in a brittle manner, otherwise the material behaves in a ductile manner. For our computational scheme, the values of  $G/K$  are

shown in Table 3. In terms of the  $G/K$  values,  $\text{Ca}_2\text{Sn}$ ,  $\text{Ca}_7\text{Sn}_6$ ,  $\text{CaSn}_3$ ,  $\text{Ca}_2\text{Pb}$ ,  $\text{CaPb}$ , and  $\text{CaPb}_3$  are ductile materials, and the ductility of these compounds ranks as follows:  $\text{CaSn}_3 > \text{Ca}_7\text{Sn}_6 > \text{Ca}_2\text{Sn}$ ,  $\text{CaPb} > \text{CaPb}_3 > \text{Ca}_2\text{Pb}$ . All the Ca–Si and Ca–Ge system compounds are brittle materials, and the brittleness of these compounds ranks as follows:  $\text{Ca}_3\text{Si}_4 > \text{CaSi} > \text{Ca}_5\text{Si}_3 > \text{CaSi}_2 > \text{Ca}_2\text{Si}$ ,  $\text{Ca}_7\text{Ge}_6 > \text{CaGe} > \text{Ca}_5\text{Ge}_3 > \text{CaGe}_2 > \text{Ca}_2\text{Ge}$ . For other Ca–Sn system compounds, the brittleness of these compounds ranks as follows:  $\text{Ca}_{36}\text{Sn}_{23} > \text{Ca}_5\text{Sn}_3 > \text{CaSn}$ . According to Frantsevich et al. [43], Poisson's ratio can also be used to distinguish the brittleness from ductility in metal and intermetallic materials. Metals having a Poisson's ratio around  $1/3$  are ductile, whereas metals having a Poisson's ratio less than  $1/3$  are inferred as being brittle. On the basis of the Poisson's ratio shown in Table 3, the brittleness and ductility properties of the 20 compounds determined by Poisson's ratio  $\nu$  criterion are in good agreement with the results estimated by the  $G/K$  ratio.

### 3.3. Thermodynamic stability and heats of formation

In order to investigate further physical properties of our intermetallic compounds, heats of formation of all the 20 compounds have been calculated by using the following formula:

$$E_{\text{form}}^{\text{Ca}_m\text{X}_n} = E_{\text{tot}}^{\text{Ca}_m\text{X}_n} - (mE_{\text{solid}}^{\text{Ca}} + nE_{\text{solid}}^{\text{X}})/(m+n), \quad (5)$$

where  $E_{\text{tot}}^{\text{Ca}_m\text{X}_n}$  represents the total energy of a  $\text{Ca}_m\text{X}_n$  primitive cell that includes  $m$  Ca atoms and  $n$  X atoms with equilibrium lattice parameters,  $E_{\text{solid}}^{\text{Ca}}$  is the total energy of a Ca atom, and  $E_{\text{solid}}^{\text{X}}$  is the total energy of an X (X=Si, Ge, Sn, Pb) atom.

The calculated heats of formation of the 20 compounds together with their available experimental and theoretical data

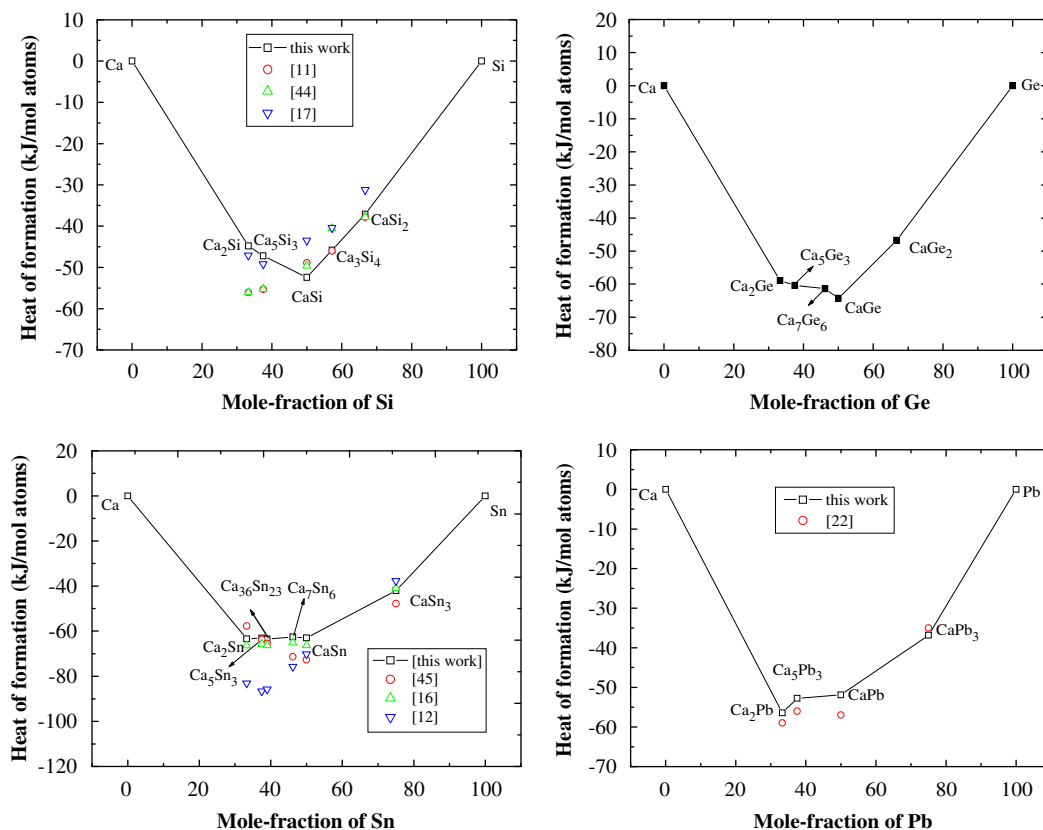


Fig. 2. Calculated heats of formation compared to experimental and theoretical values for Ca–X system intermetallic compounds.



[11,12,16,17,22,44,45] are summarized in Table 4. In order to clearly see the comparison between calculated results and previous data, these results have also been depicted in Fig. 2. As

we can see from Table 4 and Fig. 2, all the Ca–X system intermetallics values of heats of formation are in a very good agreement with the previous experimental and theoretical data.

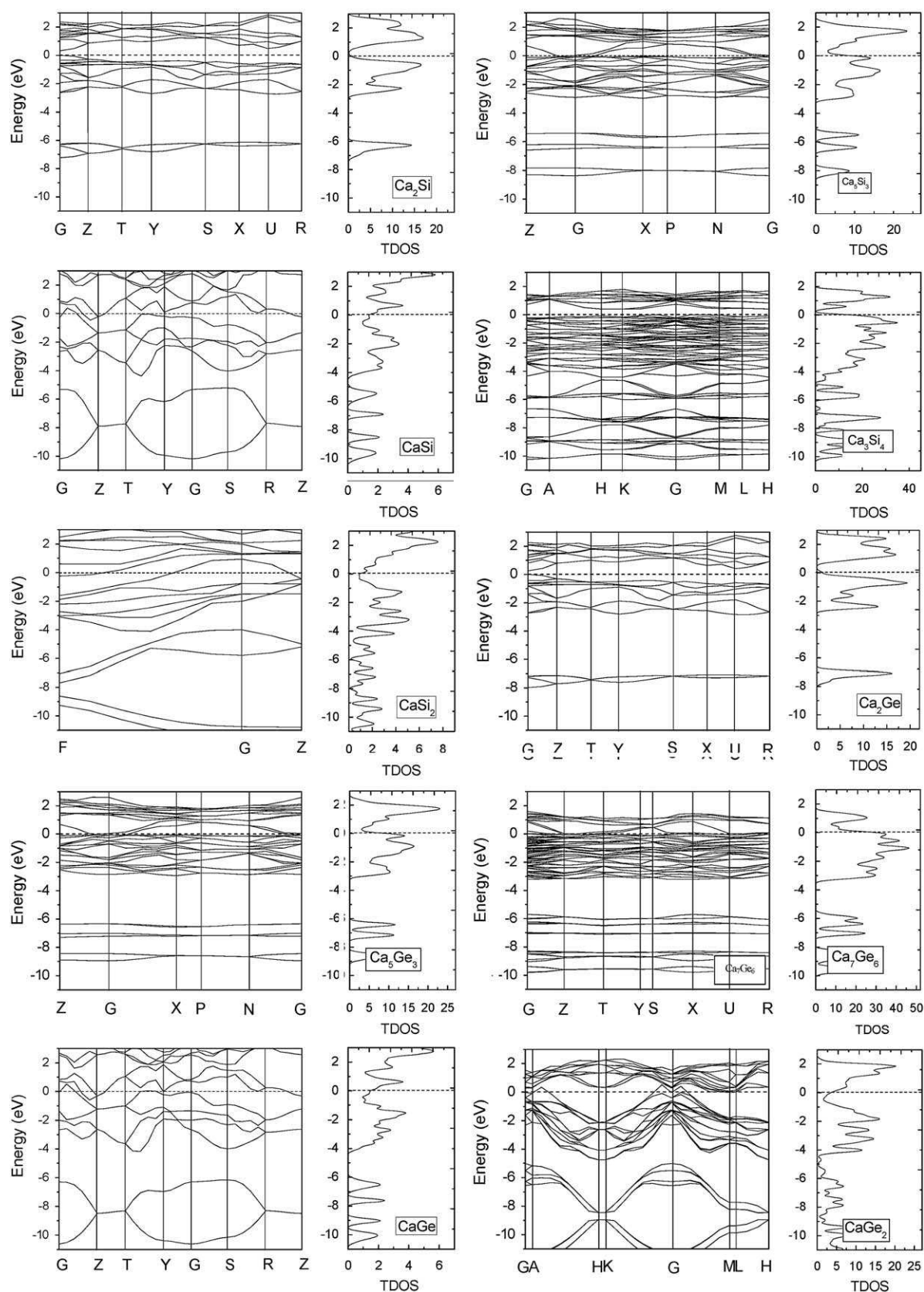


Fig. 3. The electronic energy band structures and densities of states of Ca–X system intermetallic compounds. Zero of the energy corresponds to the Fermi energy.

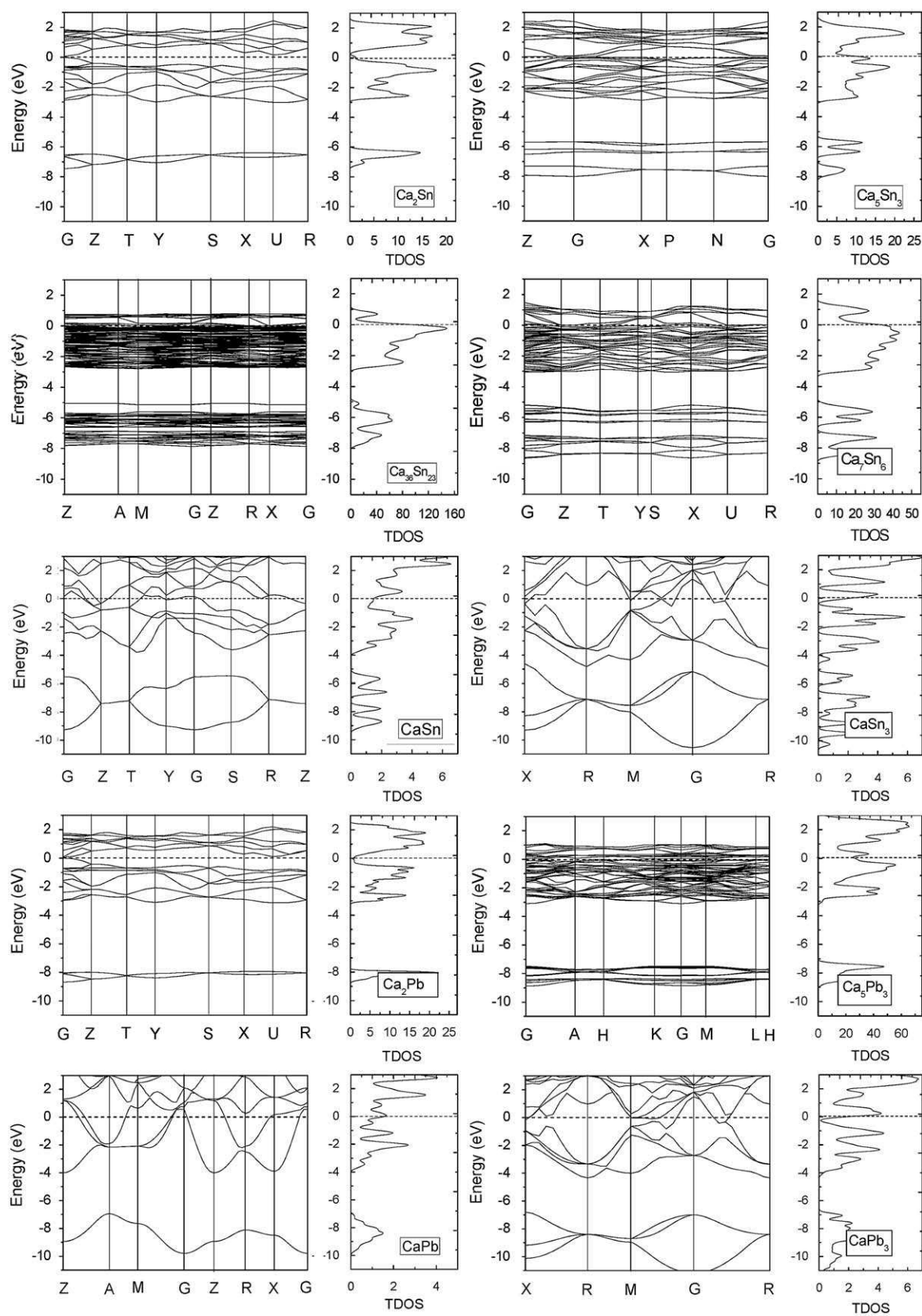


Fig. 3. (Continued)

In addition, all the absolute values of heats of formation are larger than 30 kJ/mol atoms, and these results indicate a very strong chemical interaction between Ca–Si, Ca–Ge, Ca–Sn, and Ca–Pb.

Judging from the obtained negative heats of formation, we can conclude that all the Ca–X system intermetallic compounds are thermodynamically stable.

### 3.4. Electronic energy band structures and densities of states

The electronic energy band structures and densities of states of the 20 Ca–X system intermetallic compounds considered in this work have also been calculated, and the results are shown in Fig. 3. The zero energy represents the Fermi level. As shown in Fig. 3, all the valence band maximum and the conduction band minimum of  $\text{Ca}_2\text{Si}$ ,  $\text{Ca}_2\text{Ge}$ ,  $\text{Ca}_2\text{Sn}$ , and  $\text{Ca}_2\text{Pb}$  are located at G point. The band gaps for  $\text{Ca}_2\text{Si}$ ,  $\text{Ca}_2\text{Ge}$ ,  $\text{Ca}_2\text{Sn}$  and  $\text{Ca}_2\text{Pb}$  are 0.324, 0.265, 0.06 and 0.07 eV, respectively. This indicates that all the  $\text{Ca}_2\text{X}$  intermetallic compounds are direct band gap semiconductors. Moreover, these results are in accordance with other theoretical calculations carried out by Migas and Miglio [5]. As for  $\text{Ca}_3\text{Si}_4$  compounds, the top of the valence band is localized at  $0.7 \times K$ –G and the lowest conduction band minimum is situated at  $0.5 \times H$ –K. The band gap for  $\text{Ca}_3\text{Si}_4$  compounds is 0.598 eV. Therefore,  $\text{Ca}_3\text{Si}_4$  is an indirect band gap semiconductor, and the result is in a fairly good agreement with the discovery reported in Ref. [4]. As for other intermetallics considered in the 20 compounds, their valence band overlaps the conduction band at the Fermi surface in the diagrams. This indicates that all of them are conductors. Electrical properties of the 20 Ca–X system intermetallic compounds are also further elucidated by their corresponding densities of states.

## 4. Conclusions

We have investigated the structural properties, elastic properties, heats of formation, electronic structures, and densities of states of the 20 types of Ca–X (X=Si, Ge, Sn, Pb) system intermetallic compounds using density functional theory. It is found that all bulk moduli of Ca–X system intermetallic compounds decrease with the increasing of X atomic weight. Moreover, most of the 20 intermetallics considered in this work are mechanically stable except those of  $\text{Ca}_{36}\text{Sn}_{23}$  and  $\text{CaPb}$ . The analysis on the electronic structures of the 20 compounds shows that  $\text{Ca}_3\text{Si}_4$  is an indirect band gap semiconductor with a band gap of 0.598 eV, and  $\text{Ca}_2\text{Si}$ ,  $\text{Ca}_2\text{Ge}$ ,  $\text{Ca}_2\text{Sn}$ , and  $\text{Ca}_2\text{Pb}$  are direct band gap semiconductors with band gaps of 0.324, 0.265, 0.06, and 0.07 eV, respectively. In addition, our calculations also revealed that the absolute values of heats of formation of all the Ca–X intermetallics are larger than that of 30 kJ/mol atom, indicating a very strong chemical interaction among Ca–Si, Ca–Ge, Ca–Sn and Ca–Pb.

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