Structural, elastic, electronic properties and heats of formation of Ca–Zn intermetallics from first principles calculations

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ABSTRACT

Structural, elastic and electronic properties, as well as heats of formation, of seven Ca–Zn intermetallic compounds have been studied by using first principles methods. It was found that with increasing Zn concentration, the bulk moduli and shear moduli of Ca–Zn intermetallic compounds increase monotonically. Our results also indicate that Ca_3Zn, Ca_5Zn_3, and $CaZn$ are ductile, while $CaZn_2$, $CaZn_5$, $CaZn_{11}$, and $CaZn_{13}$ are brittle. Furthermore, calculations of the electronic properties and heats of formation indicate that seven Ca–Zn intermetallic compounds, considered in this work, are all conductors and thermodynamically stable.

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1. Introduction

There is tremendous interest in the Ca–Zn system and its inter-metallic compounds because of their outstanding physical and chemical properties [1–3]. The Ca–Zn phase diagram is based on the work of Messing et al. [4], who investigated the system by means of differential thermal analysis supplemented by X-ray diffraction and vapor effusion measurements. They found that the Ca–Zn system contains eight intermetallic compounds, namely Ca_3Zn, Ca_7Zn_4, $CaZn$, $CaZn_2$, Ca_7Zn_{20}, $CaZn_5$, $CaZn_{11}$, and $CaZn_{13}$. Later in 1990, based on the crystallographic data reported by Fornasini and Merlo [5] and Bruzzone et al. [6], Itkin and Alcock [7] revised the Ca–Zn phase diagram by replacing Ca_7Zn_4 and Ca_7Zn_{20} with Ca_5Zn_3 and $CaZn_3$, respectively.

In order to understand the physical and chemical properties of Ca–Zn intermetallic compounds, lots of experimental and theoretical works focusing on their crystallographic data [5,6,8–13], thermodynamics [14–22], electronic properties [23–25], and elastic properties [26] have been carried out. For example, the crystal structures and lattice parameters of these eight Ca–Zn system inter-metallic compounds have been reported, in particular Ca_3Zn, $CaZn$ and $CaZn_3$ by Fornasini et al. [5,8]; Ca_5Zn_3 by Bruzzone et al. [6]; $CaZn_2$ by Schulze and Wieting [9]; $CaZn_5$ by Haucke [10] and

Messing et al. [4]; $CaZn_{11}$ by Iandelli and Palenzona [11]; and $CaZn_{13}$ by Ketelaar [12] and Iandelli and Palenzona [11], among others. The compositions of the compounds and the temperature of the invariant reactions were given by Messing et al. [4] and Itkin and Alcock [7]. As for their thermodynamic properties, Chiotti et al. [14] reported that the enthalpy of fusion of $CaZn_2$ was about 12.9 kJ/mol measured with an adiabatic calorimeter. At 800 °C, Chiotti and Hecht [15] measured Zn vapor pressures by using the dew-point method for samples with greater than 50 at.% Zn and by the Knudsen effusion method for samples with lower Zn concentrations. Delcet and Egan [16] investigated the Ca activities in the liquid Ca–Zn alloys by using electro-motive force measurements on CaF_2 solid electrolyte cells. An excellent review paper about the thermodynamic properties of the Ca–Zn compounds has also been given by Notion et al. [17]. By using a computerized optimization procedure, Brubaker and Zhong et al. investigated the phase equilibria and thermodynamics properties of the Ca–Zn system, and they concluded that the $CaZn_3$ is a congruent melting compound [18–20]. Recently, the thermodynamic assessment of the Ca–Zn system, by using the Modified Quasichemical Model with a maximum short-range ordering composition at a ratio of Zn/Ca = 2:1, has been performed by Spencer et al. [2]. Rahman and Medraj [22] calculated the phase diagram and thermodynamic properties of the Ca–Zn system, and they found that the activities of both Ca and Zn components show some deviations from theoretical values. In addition, Hafner and Tegze [23] investigated the structural properties of amorphous Ca–Zn alloys by using molecular dynamics

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Table 1
Calculated and experimental lattice parameters for Ca–Zn system intermetallic compounds.

Phase	X (at.%)	Pearson symbol	Space group	Prototype	Lattice parameters (Å)			Mass density (kg/m^3)	Reference
					a	b	c		
Ca$_3$Zn	25	$oC16$	$Cmcm$	BRe$_3$	4.150	13.528	10.186	2199.91	[8]
					4.051	13.363	10.112	2252.37	This work
Ca$_5$Zn$_3$	37.5	$tI32$	$I4/mcm$	Cr$_5$B$_3$	7.963		15.407	2696.03	[6]
					7.802		15.620	2770.36	This work
CaZn	50.0	$oC8$	$Cmcm$	CrB	4.202	11.610	4.442	3232.44	[8]
					4.333	11.661	4.215	3289.01	This work
CaZn$_2$	66.7	$oI12$	$Imma$	CeCu$_2$	4.591	7.337	7.667	4393.87	[9]
					4.576	7.369	7.537	4464.63	This work
CaZn$_5$	83.3	$hP6$	$P6_3/mmc$	CaCu$_5$	5.405		4.183	5758.14	[4,10]
					5.399		4.200	5747.97	This work
CaZn$_{11}$	91.7	$tI48$	$I4_1/amd$	BaCd$_{11}$	10.699		6.830	6554.27	[11]
					10.652		6.776	6559.55	This work
CaZn$_{13}$	92.9	$cF112$	$Fm\bar{3}c$	NaZn$_{13}$	12.130			6552.63	[11,12]
					12.176			6550.42	This work

simulations based on pseudopotential-derived inter-atomic forces. Moreover, electronic density of states of CaZn$_5$, CaZn$_2$, CaZn, Ca$_3$Zn and projected density of states of Ca$_5$Zn$_3$ have also been calculated by Tegze and Hafner [24] and Lee et al. [25]. Although substantial efforts in addressing structural and thermodynamic properties of Ca–Zn intermetallic compounds have been made, up to date their elastic properties and electronic structures have hardly been reported in the literature. Systematic first-principle calculations are still lacking in this area. To fill this gap, in this contribution, we have systematically studied the structural, elastic and electronic properties, as well as heats of formation of seven Ca–Zn intermetallic compounds (except for CaZn$_3$) by using first principles calculations.

2. Computational method

Our investigations have been performed by using CASTEP, which is based on the density functional theory (DFT) and plane-wave pseudopotential technique [27]. In this computational study, the ultrasoft pseudopotentials have been employed for the 3p^{6}4s^2 and 3d^{10}4s^2 atom configurations of Ca and Zn, respectively [28]. The generalized gradient approximation and the Perdew–Burke–Ernzerhof method of parameterization were utilized to describe the exchange–correlation interaction [29]. The **k** point separation in the Brillouin zone of the reciprocal space is 0.04 nm^{-1}, that is, $6 \times 6 \times 2$, $3 \times 3 \times 2$, $6 \times 2 \times 6$, $5 \times 3 \times 3$, $5 \times 5 \times 6$, $2 \times 2 \times 4$, $4 \times 4 \times 4$ for Ca$_3$Zn, Ca$_5$Zn$_3$, CaZn, CaZn$_2$, CaZn$_5$, CaZn$_{11}$, and CaZn$_{13}$, respectively. The kinetic cutoff energy for plane waves was determined as 400 eV, and the reliability of this method has been demonstrated in our previous works [30–32].

3. Results and discussion

3.1. Structural properties

Based upon the experimental crystallographic data [4,6,8–12], the initial crystal structures of the seven Ca–Zn intermetallic compounds have been established, and their lattice parameters and internal coordinates were optimized by using first principles calculations. The calculated lattice parameters and their corresponding crystal structures are shown in Table 1, which is in a good agreement with the available experimental values. Fig. 1 shows the present theoretically calculated mass densities compared to experimental values of the seven Ca–Zn intermetallic compounds with increasing Zn concentration c (in at.%). As can be seen from Fig. 1, the overall shapes are very similar, although a small amount of mismatch exists for most of the Ca–Zn system intermetallic compounds.

3.2. Elastic properties and mechanical stability

Table 2 presents calculated elastic constants C_{ij} (GPa) and bulk moduli of the seven Ca–Zn intermetallic compounds considered in this work. The mechanical stability of the seven compounds is being discussed here based on their elastic constants. For the

seven Ca–Zn intermetallic compounds, we observed that CaZn$_{13}$ has a cubic structure, Ca$_5$Zn$_3$ and CaZn$_{11}$ have tetragonal structures, CaZn$_5$ has a hexagonal structure, and Ca$_3$Zn, CaZn$_2$ and CaZn have orthorhombic structures.

For cubic crystals, the mechanical stability criteria can be given as follows [33]:

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

As we can see from Table 2, the elastic constants of the cubic structure CaZn$_{13}$ satisfy all the above constraints in (1), which indicates that CaZn$_{13}$ is mechanically stable.

For tetragonal structures, the conditions for mechanical stability are also given in Ref. [33]:

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

As shown in Table 2, the elastic constants of tetragonal structures Ca$_5$Zn$_3$ and CaZn11 are consistent with the above restrictions in (2), and these results demonstrate that these structures are mechanically stable.

The mechanical stability criteria for hexagonal structures can be expressed as follows [34,35]:

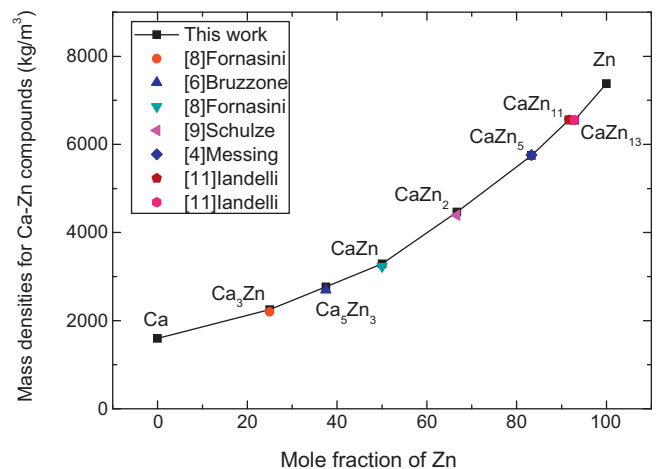$$C_{11} > 0, \quad C_{44} > 0, \quad C_{11} - C_{12} > 0, \quad (C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0 \tag{3}$$

Fig. 1. Calculated mass densities compared to their respective experimental values for Ca–Zn intermetallic compounds.

Table 2
Calculated elastic parameters (in GPa) for the single crystalline Ca–Zn system intermetallic compounds.

Phase	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	K
Ca_3Zn	40.5	19.3	12.4	37.4	14.6	45.2	9.6	11.8	19.0	24.021.5 [26]
Ca_5Zn_3	42.8	19.3	20.8			34.3	13.9		19.1	26.6
$CaZn$	39.8	28.0	23.4	51.1	18.9	66.9	2.5	25.6	18.7	32.5
$CaZn_2$	102.0	11.5	34.0	82.0	22.6	76.4	27.8	36.7	15.4	43.4
$CaZn_5$	110.9	38.9	21.4			178.1	43.6			61.3
$CaZn_{11}$	149.8	32.7	36.4			150.1	46.1		42.4	73.4
$CaZn_{13}$	157.7	32.6					44.5			74.3

As can be seen from Table 2, all the values of elastic constants for the hexagonal $CaZn_5$ compound obey these mechanical stability restrictions in (3).

From Ref. [36], the mechanical stability criteria of orthorhombic structures are given as follows:

$$C_{11} > 0, \quad C_{22} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{55} > 0, \quad C_{66} > 0,$$
$$C_{11} + C_{22} - 2C_{12} > 0, \quad C_{11} + C_{33} - 2C_{13} > 0, \quad C_{22} + C_{33}$$
$$-2C_{23} > 0, \quad C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23} > 0. \tag{4}$$

For orthorhombic structures Ca_3Zn, $CaZn_2$ and $CaZn$, their calculated elastic constants are all consistent with the above restrictions in (4), which indicate that the three intermetallic compounds are all mechanically stable.

According to the above analysis, all the seven Ca–Zn intermetallic compounds considered in this work are mechanically stable.

Based on their single-crystal elastic constants, we have also calculated the polycrystalline bulk moduli (K), shear moduli (G), Young's moduli (E), and Poisson's ratio (ν) by using the Voigt, Reuss, and Hill (VRH) approximations [37]. The obtained results are presented in Table 3. In addition, the relationship between bulk moduli and shear moduli with concentration of Zn is plotted in Fig. 2. We found that with increasing Zn concentration (in at.%), the bulk moduli and shear moduli increase monotonically. Moreover, similar to the case of the same Zn concentration, we can clearly see that the bulk moduli of the seven Ca–Zn intermetallic compounds are larger than their respective shear moduli. This can be explained by the high values of calculated bulk moduli of 75 GPa for pure Zn.

In addition, we have also studied the brittleness and ductility properties by using the shear moduli to bulk moduli (G/K) ratio. The calculated G/K ratio and Poisson's ratio are summarized in Table 3. The relationship that links empirically plastic properties

of pure metals with their elastic moduli was first proposed by Pugh [38], after that, it has been used for compounds successfully [39,40]. According to Pugh' theory, if G/K ratio is larger than 0.57, the material behaves in a brittle manner, otherwise the material behaves in a ductile manner. Based on the calculated G/K ratio, we conclude that Ca_3Zn, Ca_5Zn_3, and $CaZn$ are ductile, and the ductility of the three compounds ranks as follows: $CaZn > Ca_5Zn_3 > Ca_3Zn$. Moreover, the ductile behavior of Ca_3Zn compound is consistent with the reported results made by Widom et al. [26]. As for $CaZn_2$, $CaZn_5$, $CaZn_{11}$, and $CaZn_{13}$, they are brittle, and the brittleness of these compounds ranks as follows: $CaZn_5 > CaZn_{13} > CaZn_{11} > CaZn_2$.

3.3. Thermodynamic stability and heats of formation

By using the optimized crystal structures, ground state total energies for the seven Ca–Zn intermetallic compounds and pure Ca and Zn have been calculated, and then heats of formation of these intermetallic compounds have been investigated by using the following expression:

$$E_{form}^{Ca_mZn_n} = \frac{E_{tot}^{Ca_mZn_n} - (mE_{solid}^{Ca} + nE_{solid}^{Zn})}{m + n} \tag{5}$$

where $E_{form}^{Ca_mZn_n}$ is the atomic heats of formation for a Ca_mZn_n compound, $E_{tot}^{Ca_mZn_n}$ stands for the total energy of a Ca_mZn_n primitive cell, which includes m Ca atoms and n Zn atoms with equilibrium lattice parameters. E_{solid}^{Ca} is the total energy of a Ca atom in the pure cubic Ca metal with equilibrium lattice parameters, and E_{solid}^{Zn} is the total energy of a Zn atom in the pure hexagonal Zn metal with equilibrium lattice parameters. Since the influence of pressure on the considered compounds is ignored and the energies are calculated
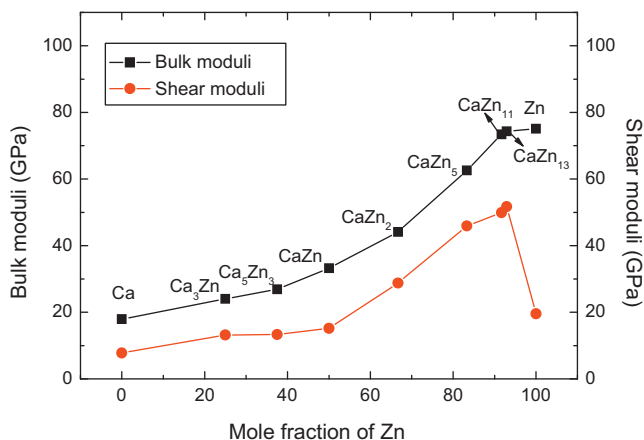
Fig. 2. Calculated bulk moduli and shear moduli of Ca–Zn intermetallic compounds.
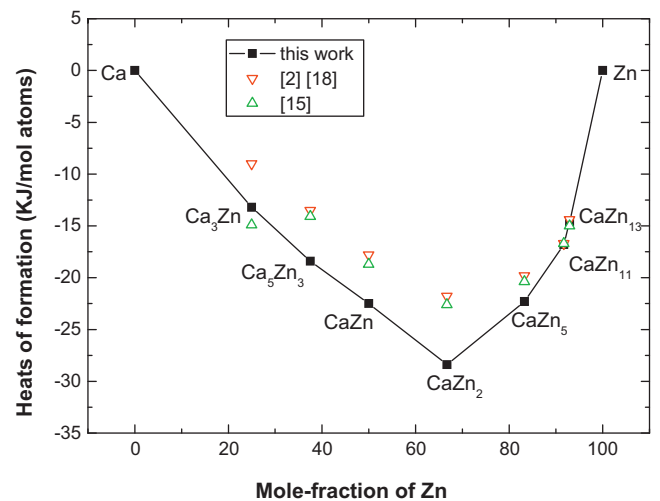
Fig. 3. Calculated heats of formation compared to experimental and theoretical data for Ca–Zn intermetallic compounds.
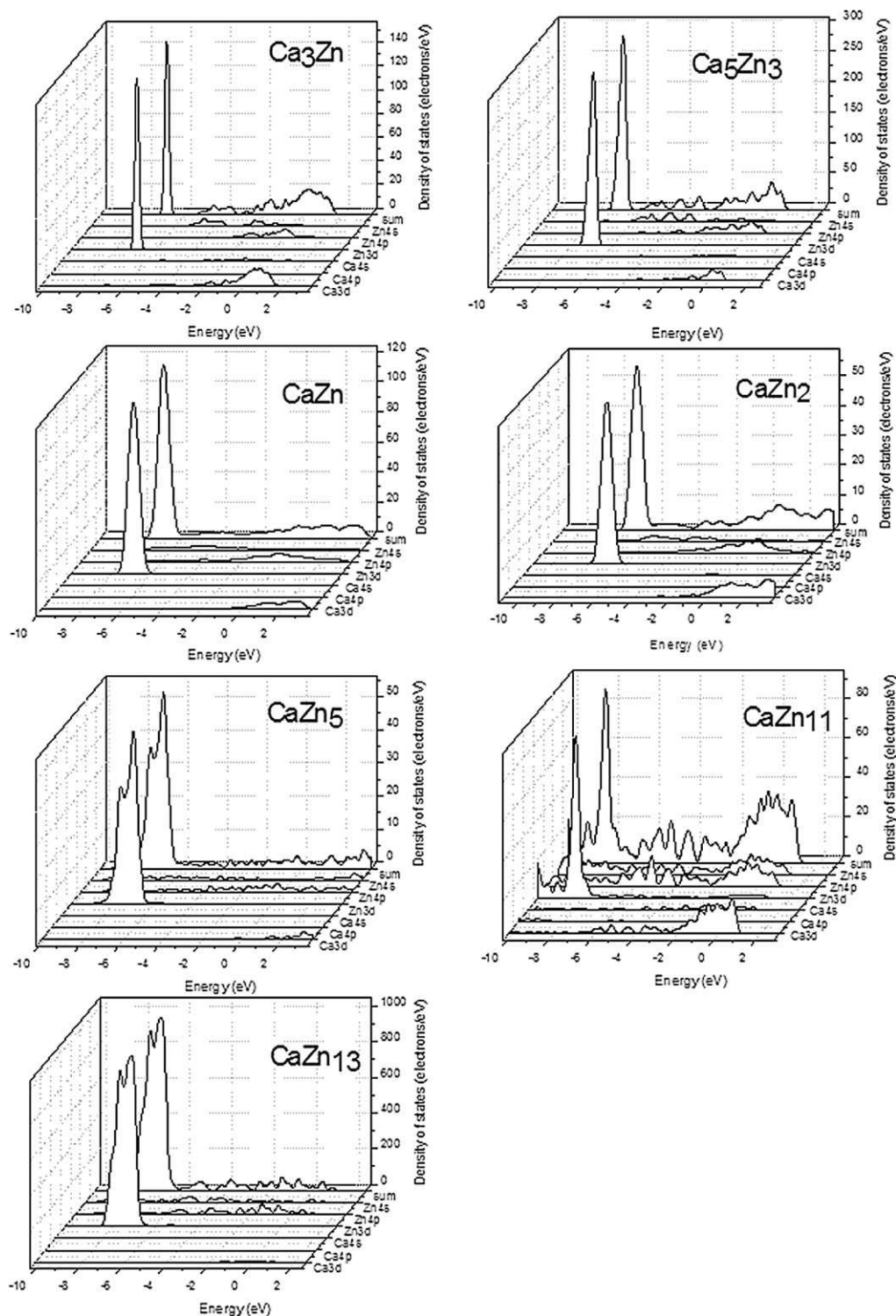
Fig. 4. PDOS plots calculated for Ca–Zn intermetallic compounds.

at 0 K without any entropic contributions, the energy of formation is taken to be heats of formation, and they are equal to the enthalpy of formation.

The calculated heats of formation of the seven Ca–Zn intermetallic compounds are presented together with the theoretically data from Spencer et al. [2] and Brubaker [18] and the experimental data from Chiotti and Hecht [15] in Table 4. For further comparisons, these results are also illustrated in Fig. 3. As can be seen from Table 4 and Fig. 3, a reasonable consistency has been

achieved between our calculated heats of formation for the seven compounds with the previously reported theoretically and experimental data. The heats of formation for Ca_3Zn, Ca_5Zn_3, $CaZn$, $CaZn_2$, $CaZn_5$, $CaZn_{11}$, and $CaZn_{13}$ are −13.2, −18.4, −22.5, −28.4, −22.3, −16.8, and −14.6 kJ/mol atom, which indicate that they are all thermodynamically stable. Compared with our previous investigation [31], we found that the chemical interaction of the Ca–Zn system is smaller than that of Ca–X (Si, Ge, Sn, Pb) systems. In Refs. [19] and [41], Zhong et al. and Volkovich et al. also deduced that the heats of

Table 3
Polycrystalline bulk moduli (in GPa), shear moduli (in GPa), Young's moduli (in GPa), Poisson's ratios for Ca–Zn system intermetallic compounds deduced by Voigt, Reuss, and Hill (VRH) approximations.

Phase	K_V	K_R	K_H	G_V	G_R	G_H	E	G/K	ν
Ca$_3$Zn	24.021.5 [26]	24.0	24.0	13.26.3(2) [26]	12.3	12.7	32.4	0.55	0.27440.37 [26]
Ca$_5$Zn$_3$	26.9	26.6	26.7	13.3	12.2	12.8	33.1	0.49	0.2940
CaZn	33.2	32.5	32.8	15.2	7.5	11.3	30.5	0.46	0.3450
CaZn$_2$	44.1	43.4	43.7	28.8	25.6	27.2	67.6	0.65	0.2424
CaZn$_5$	62.6	61.3	61.9	45.9	43.1	44.5	107.7	0.73	0.2103
CaZn$_{11}$	73.4	73.4	73.4	49.9	49.1	49.5	121.2	0.68	0.2248
CaZn$_{13}$	74.3	74.3	74.3	51.7	50.3	51	124.5	0.70	0.2206

K, bulk moduli; G, shear moduli; E, Young's moduli; ν, Poisson's ratio.

formation of the compounds in the Sr–Zn system should be higher than those of the Ca–Zn system.

3.4. Electronic structures

By using the density functional theory technique, partial density of states (PDOS) of the seven Ca–Zn intermetallic compounds have been calculated, and the results are plotted in Fig. 4. Zero energy in the plotted figures corresponds to the Fermi energy. As can be see from the PDOS diagrams, for Ca$_3$Zn, Ca$_5$Zn$_3$, CaZn, and CaZn$_2$, the largest contribution comes from Zn 4p and Ca 3d states to the density of states. For CaZn$_5$ and CaZn$_{13}$, the density of states is mainly dominated by Zn 4p states. Zn 4s, 4p, 3d states and Ca 4s, 3d states are all contribute to the density of states of CaZn$_{11}$. For all the seven Ca–Zn intermetallic compounds, the Zn 3d states are much localized at the energy of −7 eV. Moreover, it can be find that the values of density of states for all the seven Ca–Zn intermetallic compounds at Fermi energy are not zero, and these results indicate that the seven Ca–Zn intermetallic compounds, considered in this work, are all conductors.

Table 4
Calculated and experimental heats of formation for Ca–Zn system intermetallic compounds.

Phases	Heats of formation (kJ/mol atoms)	References
Ca$_3$Zn	−13.2	This work
	−9.1	[2]
	−14.9	[15]
	−9.1	[18]
Ca$_5$Zn$_3$	−18.4	This work
	−13.5	[2]
	−14.1	[15]
	−13.5	[18]
CaZn	−22.5	This work
	−17.8	[2]
	−18.7	[15]
	−17.8	[18]
CaZn$_2$	−28.4	This work
	−21.8	[2]
	−22.6	[15]
	−21.8	[18]
CaZn$_5$	−22.3	This work
	−19.8	[2]
	−20.4	[15]
	−19.8	[18]
CaZn$_{11}$	−16.8	This work
	−16.7	[2]
	−16.7	[15]
	−16.7	[18]
CaZn$_{13}$	−14.6	This work
	−14.4	[2]
	−15.0	[15]
	−14.4	[18]

4. Conclusions

The structural, elastic and electronic properties, as well as heats of formation of seven Ca–Zn intermetallic compounds (Ca$_3$Zn, Ca$_5$Zn$_3$, CaZn, CaZn$_2$, CaZn$_5$, CaZn$_{11}$, and CaZn$_{13}$) have been investigated systematically by using first principles calculations. It was found that with increasing Zn concentration (in at.%), the bulk moduli and shear moduli of Ca–Zn intermetallic compounds increase monotonically. According to the calculated shear/bulk moduli (G/K) ratios, we have found that Ca$_3$Zn, Ca$_5$Zn$_3$, and CaZn are ductile materials and CaZn$_2$, CaZn$_5$, CaZn$_{11}$, and CaZn$_{13}$ are brittle materials. Results on the computed electronic properties indicated that the seven Ca–Zn intermetallic compounds considered in this work are all conductors. In addition, compared with our previous work [31], it was found that the chemical interaction of the Ca–Zn system is smaller than that in Ca–X (Si, Ge, Sn, Pb) systems.

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