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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 $Ca_{36}Sn_{23}$ and CaPb are mechanically unstable phases. Results on the electronic energy band and densities of states also indicated that Ca_3Si_4 is an indirect band gap semiconductor with a band gap of 0.598 eV, and Ca_2Si, Ca_2Ge, Ca_2Sn, and Ca_2Pb 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.

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_2Si, Ca_5Si_3, CaSi, Ca_3Si_4, $CaSi_2$, Ca_2Ge, Ca_5Ge_3, Ca_7Ge_6, CaGe, $CaGe_2$, Ca_2Sn, Ca_5Sn_3, $Ca_{36}Sn_{23}$, Ca_7Sn_6, CaSn, $CaSn_3$, Ca_2Pb, Ca_5Pb_3, CaPb, and $CaPb_3$.

Among these 20 types of intermetallic compounds, Ca_2Si, Ca_2Ge, Ca_2Sn, and Ca_2Pb 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_3Si_4, 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_3Si_4 is an indirect band gap semiconductor with a band gap of 0.35 eV [4,6]. Moreover, it has been reported that Ca_5Si_3 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 $3p^6 4s^2$, $3s^2 3p^2$, $3d^{10} 4s^2 4p^2$, $4d^{10} 5s^2 5p^2$, and $5d^{10} 6s^2 6p^2$ 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 $0.04\,nm^{-1}$, that is, $3\times5\times3$, $4\times4\times5$, $6\times6\times6$, $3\times3\times2$,

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$7\times7\times7$ for Ca_2Si, Ca_5Si_3, CaSi, Ca_3Si_4, $CaSi_2$; $3\times5\times3$, $4\times4\times5$, $3\times1\times3$, $6\times6\times6$, $7\times7\times2$ for Ca_2Ge, Ca_5Ge_3, Ca_7Ge_6, CaGe, $CaGe_2$; $3\times4\times2$, $3\times3\times3$, $2\times2\times1$, $3\times1\times2$, $5\times5\times5$, $4\times4\times4$ for Ca_2Sn, Ca_5Sn_3, $Ca_{36}Sn_{23}$, Ca_7Sn_6, CaSn, $CaSn_3$; $3\times5\times3$, $2\times2\times4$, $5\times5\times5$, $6\times6\times6$ for Ca_2Pb, Ca_5Pb_3, CaPb, $CaPb_3$, 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 $CaPb_3$ 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 $CaPb_3$ phase is −33.5 kJ/mol atoms, which is consistent with experimental data of −35.0 kJ/mol atoms [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^3)	Reference
				a	*b*	*c*		
Ca–Si	Ca_2Si	33.3	*Pnma*	9.002	7.667	4.799	2170.71	[23]
				8.990	7.647	4.837	2161.61	This work
	Ca_5Si_3	37.5	*I*4/*mcm*	7.640		14.620	2215.61	[24]
				7.635		14.787	2193.46	This work
	CaSi	50.0	*Cmcm*	4.545	10.728	3.890	2387.09	[25]
				4.560	10.741	3.881	2381.87	This work
	Ca_3Si_4	57.2	$P6_3/m$	8.541		14.906	2460.73	[6]
				8.546		14.903	2458.35	This work
	$CaSi_2$	66.7	$R\bar{3}m$	3.887		30.530	2400.57	[26]
				3.880		30.228	2433.10	This work
Ca–Ge	Ca_2Ge	33.3	*Pnma*	7.734	4.834	9.069	2992.41	[23]
				7.667	4.866	9.070	2998.20	This work
	Ca_5Ge_3	37.5	*I*4/*mcm*	7.740		14.660	3162.62	[24]
				7.710		14.877	3140.95	This work
	Ca_7Ge_6	46.2	*Pnma*	7.409	22.391	8.129	3527.06	[7]
				7.427	22.443	8.085	3529.92	This work
	CaGe	50.0	*Cmcm*	4.565	10.837	4.005	3777.16	[27]
				4.584	10.877	4.000	3755.49	This work
	$CaGe_2$	66.7	$R\bar{3}m$	3.949		30.720	4448.94	[28]
				4.041		30.285	4308.82	This work
Ca–Sn	Ca_2Sn	33.3	*Pnma*	7.975	5.044	9.562	3433.84	[29]
				7.958	5.075	9.580	3413.65	This work
	Ca_5Sn_3	37.5	*I*4/*mcm*	8.117		15.429	3635.99	[8]
				8.141		15.500	3598.38	This work
	$Ca_{36}Sn_{23}$	39.0	*P*4/*mbm*	12.502		22.880	3875.13	[8]
				12.452		23.686	3773.24	This work
	Ca_7Sn_6	46.2	*Pnma*	7.869	23.828	8.462	4155.73	[8]
				7.908	23.826	8.547	4094.11	This work
	CaSn	50.0	*Cmcm*	4.813	11.544	4.351	4362.31	[30]
				4.793	11.613	4.401	4305.09	This work
	$CaSn_3$	75.0	$Pm\bar{3}m$	4.732			62.8.33	[31]
				4.755			6120.24	This work
Ca–Pb	Ca_2Pb	33.3	*Pnma*	8.072	5.100	9.647	4806.09	[29]
				8.000	5.147	9.697	4779.99	This work
	Ca_5Pb_3	37.5	$P6_3mc$	9.626		6.816	5093.96	[32]
				9.355		7.004	5048.81	This work
	CaPb	50.0	*P*4/*mmm*	5.118		4.491	6981.11	[10]
				5.116		4.649	6748.07	This work
	$CaPb_3$	75.0	$Pm\bar{3}m$	4.900			9339.19	[33]
				4.970			8952.29	This work