

Theoretical Investigations on Phase Stability of Tetragonal and Cubic Ga₃Zr under High Pressure

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Abstract. By using density functional theory (DFT) calculations, the phase stability of Ga₃Zr with tetragonal (*D*0₂₂) and cubic (*L*₁₂) structures under high pressure have been investigated. The equilibrium configurations have been obtained after geometry optimizations. The lattice parameters and formation energy are calculated and compared between the both structures under various pressures. The results show that: *D*0₂₂-Ga₃Zr is more stable under ambient pressure, however, Ga₃Zr will transform into *L*₁₂ cubic structure when the pressure goes up more than 28.48~36.34GPa, approximately.

Introduction

The properties of materials are usually related to their circumstances. Besides the factor of temperature, pressure also significant influences the properties of materials. For some substances, structural transition may be induced under high pressure. In recent years, by using density functional theory (DFT) calculation method, the theoretical studies about pressure induced phase transition have been commonly performed. For example, the pressure-induced *B*4-*B*1 (wurtzite to rock salt) transition of GaN was investigated, the critical pressure was predicted about 44.8 GPa, which agreed with previous calculation values of 42.9~51.8 GPa [1]. By using *ab initio* molecular dynamics simulation, the high-pressure induced transition of GaN from zinc blende (*B*3) to rock salt (*B*1) structure was investigated, and the critical pressure was predicted about 34 GPa [2]. Gallium selenide (GaSe) would crystallize in ϵ structure at zero pressure, and transform into *B*1 cubic phase under appropriate pressure (~17 GPa) [3]. For the ternary compound CuGaSe₂, its space group was predicted to change from *I* $\bar{4}2d$ to *Fm* $\bar{3}m$ at 11.87 GPa, which was close to experimental result (~13GPa) [4].

Besides the above gallium-containing semiconductor materials, the DFT calculations are also performed to investigate Ga-Zr intermetallics. For Ga₃Zr and Ga₂Zr, the crystallochemical affinity and optical functions [5], and their band structure, density of states, and crystal chemistry [6] were studied by using all-electron full potential linearized augmented plane wave (FP-LAPW) method. Furthermore, the phase equilibriums of Ga-Zr system were investigated by combining experimental investigation and thermodynamic modeling, the formation enthalpies phases of Ga-Zr intermetallics (including Ga₃Zr, Ga₂Zr, etc.) were computed via first-principles calculations, and the calculated phase diagram and thermodynamic properties agreed well with the available experimental data [7].

Under ambient conditions, the compound Ga₃Zr exhibit tetragonal structure (*D*0₂₂, *I*4/*mmm*) [7, 8], and the cubic structure (*L*₁₂, *Pm* $\bar{3}m$) is a metastable phase. It is natural to doubt that, when the pressure changes, Ga₃Zr may transform from an original structure into another structure. However, according to our knowledge, the high pressure induced structural transition of Ga₃Zr is rarely reported. The present work is conducted to clarify the phase stability of *D*0₂₂- and *L*₁₂-Ga₃Zr under high pressures.

Computational Methodology

The DFT calculations in present work were conducted using CASTEP package [9, 10], and plane-wave ultrasoft pseudopotentials [11, 12] were employed. The valence electrons considered in the pseudopotentials were Ga $3d^{10}4s^24p^1$, Zr $4s^24p^64d^25s^2$, respectively. The exchange correlation (XC) energy was treated with two different forms: generalized gradient approximation (GGA) functionals of PBE [13], and local density approximation (LDA) functional of CAPZ [14, 15]. The convergence threshold in the self consistent field (SCF) procedure was set as 5.0×10^{-7} eV/atom. In the minimization with Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm, the convergence tolerances for the energy, force, stress and displacement were set as 5.0×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa and 5×10^{-4} Å, respectively. After the validation of convergence tests, the cutoff energy on the plane wave basis was set as 350 eV, the k -points grids were set as $20 \times 12 \times 20$, $40 \times 40 \times 22$, $24 \times 24 \times 24$ and $24 \times 24 \times 10$ for bulk α -Ga (A11, *Cmca*)[16], hcp-Zr (A3, *P6₃/mmc*)[17], $L1_2$ - and $D0_{22}$ -Ga₃Zr respectively. The above k -points settings make the separation of the reciprocal space around 0.01Å^{-1} .

After fully optimizations, the calculated equilibrium lattice constants and previous experimental data are listed in Table 1, the elastic constants (C_{ij}) and formation energy $\Delta E_f(\text{Ga}_3\text{Zr})$ are listed in Table 2. For the both XC potentials, the calculated lattice constants agree well with the available experimental data, their deviations are in the ranges of $-1.4\% \sim 5.1\%$ and $-3.8\% \sim 2.6\%$ for GGA-PBE and LDA-CAPZ potentials, respectively. For $D0_{22}$ -Ga₃Zr, our calculated lattice parameters with GGA-PBE potential are very close to the results ($a = 3.9875 \text{Å}$, $c = 8.7961 \text{Å}$) in previous DFT calculation [7]. Besides that, our calculated formation energy $\Delta E_f(D0_{22}\text{-Ga}_3\text{Zr})$ is also accordance with the previous calculation [7]. Therefore, the calculation parameters adopted in our work are validated, and the calculations accuracy is adequate.

Moreover, the “over-binding effect” of LDA potential reported in other calculations [18-22] is also shown in our calculations, the lattice constants calculated with LDA-CAPZ potential is slightly smaller than the results of GGA-PBE potential.

Table 1 Crystallographic data, lattice constants of bulk Ga, Zr and Ga₃Zr.

Phase	Space group (#)	Pearson symbol	Strukturbericht designation	Lattice constants (Å)	
				Present Calc.	Expt.
α -Ga	<i>Cmca</i> (64)	<i>oC8</i>	A11	$a=4.5776$, $b=7.7406$, $c=4.5727^a$ $a=4.4177$, $b=7.4829$, $c=4.4271^b$	$a=4.519$, $b=7.658$, $c=4.526$ [16]
hcp-Zr	<i>P6₃/mmc</i> (194)	<i>hP2</i>	A3	$a=3.2298$, $c=5.1711^a$ $a=3.1468$, $c=5.0793^b$	$a=3.2331$, $c=5.1480$ [17]
Tetragonal Ga ₃ Zr	<i>I4/mmm</i> (139)	<i>tI8</i>	$D0_{22}$	$a=3.9160$, $c=9.1713^a$ $a=3.8220$, $c=8.9522^b$	$a=3.963$, $c=8.730$ [7] $a=3.971$, $c=8.729$ [8]
Cubic Ga ₃ Zr	<i>Pm$\bar{3}m$</i> (221)	<i>cP4</i>	$L1_2$	$a=4.1245^a$ $a=4.0218^b$	

Note: Superscripts "a" and "b" denote the results with exchange correlation functionals of GGA-PBE and LDA-CAPZ, respectively.

Table 2 Elastic constants (C_{ij}) and formation energy (ΔE_f) of $L1_2$ - and $D0_{22}$ - Ga_3Zr .

Phases	Data source	Elastic properties (GPa)							ΔE_f (Ga_3Zr) (kJ/mol)
		C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B_0	
$D0_{22}$ - Ga_3Zr	Present calculation with GGA-PBE	181.16	85.14	47.26	180.68	75.79	113.76	99.89	-46.304
	Present calculation with LDA-CAPZ	219.37	105.39	59.36	215.49	88.98	135.32	121.96	-52.606
	Other calculation with GGA-PBE in Ref. [7]	--	--	--	--	--	--	--	-53.727 ^a
$L1_2$ - Ga_3Zr	Present calculation with GGA-PBE	133.30	78.06	--	--	42.06	--	96.47	-43.923
	Present calculation with LDA-CAPZ	149.19	95.33	--	--	50.32	--	113.28	-50.433

Note: ^a An approximate value of first-principle calculation with GGA-PBE potential under 0 GPa in Ref. [7].

Results and Discussion

Formation Energy. For the compound A_mB_n , the formation energy per atom (ΔE_f) can be ascertained as [23]:

$$\Delta E_f(A_mB_n) = \frac{1}{m+n} [E_{total}(A_mB_n) - mE_{bulk}(A) - nE_{bulk}(B)], \quad (1)$$

where E_{total} denotes the total energy per formula for the compound A_mB_n , and E_{bulk} denotes the total energy per atom for elementary materials of bulk A and B. Under various pressures ranging from 0 to 60 GPa, the $\Delta E_f(Ga_3Zr)$ in both structures were calculated after the crystal structures had been fully optimized. In the pressure range of 0~60 GPa, 13 different pressures with the interval of 5 GPa are considered in our present study, respectively. However, for the simplicity, only the results under pressures with 10 GPa intervals are presented in Table 3. The formation energy and equilibrium volume under other pressures are illustrated in Fig. 1 and Fig. 2.

 Table 3 Lattice parameters (a , c , a/c), equilibrium volume per atom (V_0) and formation energy (ΔE_f) of $L1_2$ - and $D0_{22}$ - Ga_3Zr under various pressures.

Phases	Parameters	XC potentials	Pressure (GPa)						
			0	10	20	30	40	50	60
$D0_{22}$	a (Å)	GGA-PBE	3.9160	3.8164	3.7439	3.6866	3.6392	3.5981	3.5622
		LDA-CAPZ	3.8220	3.7395	3.6769	3.6263	3.5832	3.5460	3.5132
	c (Å)	GGA-PBE	9.1713	8.8806	8.6734	8.5120	8.3769	8.2630	8.1640
		LDA-CAPZ	8.9522	8.7076	8.5248	8.3790	8.2569	8.1518	8.0598
	c/a	GGA-PBE	2.34	2.33	2.32	2.31	2.30	2.30	2.29
		LDA-CAPZ	2.34	2.33	2.32	2.31	2.30	2.30	2.29
V_0 (Å ³ /atom)	GGA-PBE	17.58	16.17	15.20	14.46	13.87	13.37	12.95	
	LDA-CAPZ	16.35	15.22	14.41	13.77	13.25	12.81	12.43	
ΔE_f (kJ/mol)	GGA-PBE	-46.304	55.225	149.738	239.096	324.468	406.554	485.875	
	LDA-CAPZ	-52.606	42.424	131.678	216.593	298.030	376.576	452.664	
$L1_2$	a (Å)	GGA-PBE	4.1245	4.0062	3.9213	3.8548	3.8002	3.7537	3.7125
		LDA-CAPZ	4.0218	3.9233	3.8501	3.7910	3.7419	3.6992	3.6619
	V_0 (Å ³ /atom)	GGA-PBE	17.54	16.07	15.07	14.32	13.72	13.22	12.79
		LDA-CAPZ	16.26	15.10	14.27	13.62	13.10	12.65	12.28
	ΔE_f (kJ/mol)	GGA-PBE	-43.923	57.210	151.034	239.639	324.144	405.341	483.772
		LDA-CAPZ	-50.433	43.989	132.426	216.458	296.974	374.585	449.715

Note: For the calculations of formation energy, the reference states are α -Ga and hcp-Zr under zero pressure and zero temperature.

Comparing with the results of LDA-CAPZ potential, the lattice parameters, atomic volume, and formation energies obtained with GGA-PBE are slightly larger, and the difference always exists under various pressures from 0 GPa to higher pressures, which suggests the numerical errors strongly depends on the exchange-correlation functional [24].

Generally speaking, the formation energy of a natural compound should be negative, which suggests that the chemical compound is more thermodynamic stable than the elementary substances. In present work, the formation energies are calculated on the basis of elementary substances (α -Ga and hcp-Zr). At zero pressure, the calculated $\Delta E_f(DO_{22}\text{-Ga}_3\text{Zr})$ is more negative than $\Delta E_f(L1_2\text{-Ga}_3\text{Zr})$, which convicts that $DO_{22}\text{-Ga}_3\text{Zr}$ is more stable than $L1_2\text{-Ga}_3\text{Zr}$ at ambient pressure.

Phase Stability. The elementary substances under zero pressure are adopted as reference states in our calculations. When the pressure increases, the formation energies of DO_{22} - and $L1_2\text{-Ga}_3\text{Zr}$ rapidly change toward positive side. More importantly, the difference [$\Delta E_f(L1_2\text{-Ga}_3\text{Zr}) - \Delta E_f(DO_{22}\text{-Ga}_3\text{Zr})$] of both structures gradually decrease with the pressure varying from 0 GPa to higher pressures. It is reasonable to propose that, although the $DO_{22}\text{-Ga}_3\text{Zr}$ is more stable than $L1_2\text{-Ga}_3\text{Zr}$ at ambient pressure, the priority of DO_{22} structure gradually becomes dimmer with pressure increasing. Thus, the structural transition from DO_{22} to $L1_2$ can be anticipated when the pressure changes to an enough high point. The relations between the formation energy difference, atomic volume and high pressure are shown in Fig. 1 and Fig. 2, respectively.

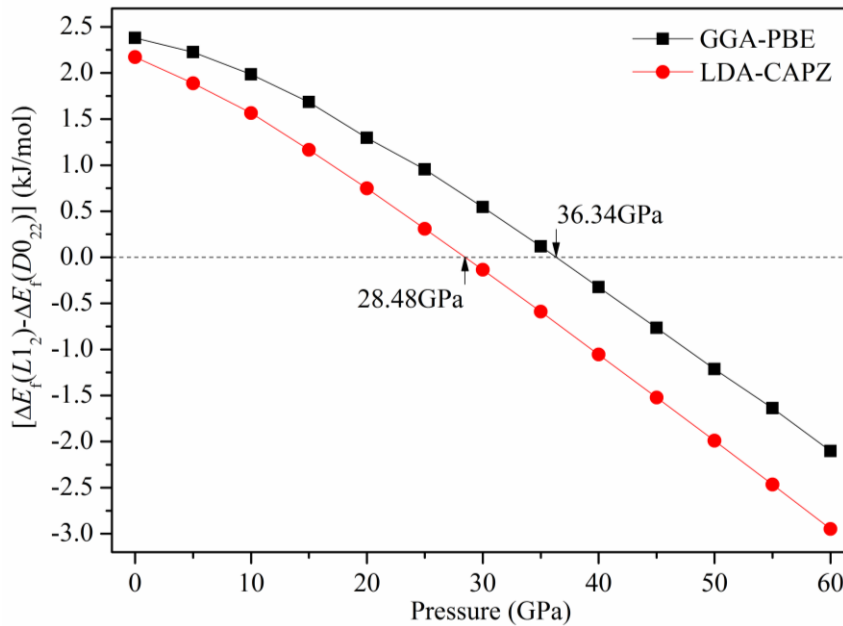


Figure 1. Calculated formation energy difference [$\Delta E_f(L1_2\text{-Ga}_3\text{Zr}) - \Delta E_f(DO_{22}\text{-Ga}_3\text{Zr})$] as a function of pressure, the critical pressures corresponding to the structural transition are labelled by arrows.

In order to compare the phase stability between the both structures, the Gibbs free energy should be used. Because all calculations in our work are performed under the temperature $T=0$ K, so the relative stability of different structures can be deduced from the pressure dependence on enthalpy [25, 26]. In Fig. 1, the values of [$\Delta E_f(L1_2\text{-Ga}_3\text{Zr}) - \Delta E_f(DO_{22}\text{-Ga}_3\text{Zr})$] are positive when the pressure less than 28.48 GPa or 36.34 GPa with GGA-PBE or LDA-CAPZ functionals. So, $DO_{22}\text{-Ga}_3\text{Zr}$ is more stable when pressure less than 28.48~36.34 GPa. It is consistent with the previous argument that, in the (Al, Ga)-(Ti, Zr, Hf) systems, either the DO_{22} or the DO_{23} structures are stable; the $L1_2$ appears more often to be metastable [27]. The pressure corresponding to [$\Delta E_f(L1_2\text{-Ga}_3\text{Zr}) - \Delta E_f(DO_{22}\text{-Ga}_3\text{Zr})$] approaching zero should be critical pressure, it shows that $DO_{22}\text{-Ga}_3\text{Zr}$ will transform into $L1_2$ structure when the pressure is over 28.48 GPa and 36.34 GPa calculated with functionals of GGA-PBE and LDA-CAPZ, respectively. The volume per atom will drop about $\Delta V/V = 1.0\sim 1.1\%$ as shown in Fig. 2.

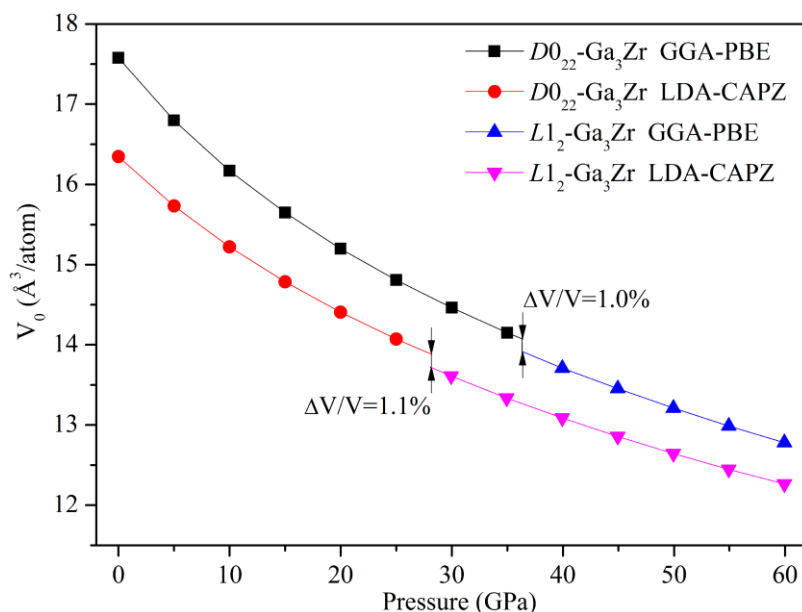


Figure 2. Calculated volume-pressure relationship for $D0_{22}$ - and $L1_2$ -Ga₃Zr.

Summary

The structure, formation energy, phase stability of $D0_{22}$ - and $L1_2$ -Ga₃Zr have been investigated with external pressure varying from 0 GPa to 60 GPa by using DFT calculations. The results show that (1) comparing with $L1_2$ -Ga₃Zr, the $D0_{22}$ -Ga₃Zr is more stable when pressure less than 28.48~6.34 GPa; (2) the phase stability of Ga₃Zr depends on the external pressure, when pressure goes up enough high (the critical pressure is about 28.48~6.34 GPa), the phase transition will happen, and $D0_{22}$ -Ga₃Zr will transform into $L1_2$ -Ga₃Zr. Mean while, the volume will drop about 1 along with the phase transition.

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