Mechanical and Vibrational Properties of α- and β-$MgAl_2Ge_2$ compound: Ab-initio study

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ABSTRACT

$MgAl_2Ge_2$ compound is in the hexagonal $P6_3/mmc$ (α) and trigonal P-3m1 (β) structures. We have been used strass-strain method to predict the second order elastic constants (C_{ij}) and perturbation theory for the vibrational properties of the titled compound within the density functional theory. Our results showed that the compound is satisfy mechanical stability for β-structure confirmed by vibrational calculations. The polycrystalline aggregate behavior estimated using the C_{ij} for mechanically stable β-phase. They are all good agreement with available experimental theoretical data. The calculated phonon dispersion and phonon density of states are also given and discussed.

1. INTRODUCTION

$MgAl_2Ge_2$ is germanides with AB_2X_2 form (so-called 122 stoichiometry) in $CaAl_2Si_2$-prototype (trigonal P-3m1 space group, No. 164) crystal view is given in Fig. 1. In the AB_2X_2 stoichiometry, A is an alkali, alkaline-earth, or rare earth element, B refers to a transition metal or main-group metalloid, and X is an element from groups 13–16 of the periodic table [1]. This large family includes over 700 members and exhibits an exceptional collection of chemical and physical properties like superconductivity at high temperature and large magneto-resistance. Also, $MgAl_2Ge_2$ is considered in α-$MgAl_2C_2$ phase in the hexagonal crystal system with space group $P6_3/mmc$ (No. 194) [2].

We have performed the systematic density functional theory (DFT) calculation to predict the structural, mechanical, and vibrational properties of $MgAl_2Ge_2$ compound in both phases. The structure of this paper is as follows: The method of calculation is given in Section 2, the results and discussion overall conclusions are presented in Section 3.

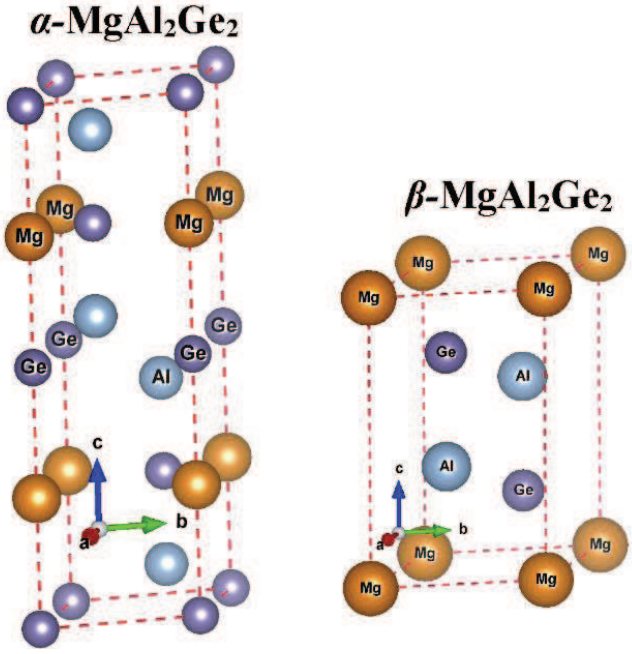

Figure 1. The considered phases for $MgAl_2Ge_2$ compound.

2. METHOD

All calculations have been carried by using the VASP code [3-4] based on the density functional theory (DFT). The electron–ion interaction was considered in the form of the projector-augmented-wave (PAW) method with plane wave up to an energy of 360 eV [5]. Perdew–Burke–Ernzerhof (PBE) type functional [6] within the generalized gradient approximation (GGA) has been used for the exchange and correlation terms in the electron–electron interaction. 13x13x4 and 13x13x6 Gamma-centered k-grids been used for α- and β-phases. The stress-strain method, implemented in the VASP code, was used to predict the second order elastic constants [8]. Also, DFPT & Phonopy have been used for vibtational calculations [9, 10].

3. RESULTS AND DISCUSSION

3.1. Structural properties

$MgAl_2Ge_2$ is considered in α-$MgAl_2C_2$ (hexagonal, $P6_3/mmc$, No. 194) and β-$MgAl_2C_2$ ($CaAl_2Si_2$-type, trigonal P-3m1, No. 164) (See Fig. 1) [1, 2]. The structural parameters and atomic sites for both phase are given in Table 1. The calculated lattice parameters, ground state energies and volumes are listed in Table 2. Our results are good agreement with experimental and theoretical data [1, 2].

Table 1. The structural parameter and atomic sites for α- and β- $MgAl_2Ge_2$ phases.

Phase	Atoms	Positions	Coordinates		
			x	*y*	*z*
***α*-$MgAl_2Ge_2$**	Mg	2b	0	0	¼
	Al	4f	1/3	2/3	~1/12
	Ge	2a	0	0	0
	Ge	2c	1/3	2/3	¼
***β*-$MgAl_2Ge_2$**	Mg	1a	0	0	0
	Al	2d	1/3	2/3	0.6303
	Ge	2d	1/3	2/3	0.2404

Table 2. The calculated lattice parameters (a, c in Å), ground state energy (E_0 in eV/f.u.), and volume (V_0 in Å^3/fu) with available experimental values.

Phase	*a* Å	*c* Å	E_0 *eV/f.u.*	V_0 Å^3/f.u.	*References*
***α*-$MgAl_2Ge_2$**	4.4076	13.7486	-17.1051	115.655	Present
***β*-$MgAl_2Ge_2$**	4.1388	6.8213	-18.3905	101.19	Present
	4.13	6.839		101.0	CASTEP-PBE [1]
	4.117	6.787		99.6	Exp [2]

3.2. Mechanical properties

The mechanical and dynamical behaviors of crystals could be predicting from the second order elastic constants (C_{ij}) [11]. In particular, they also provide about the stability and stiffness of materials [12]. We have used the "stress-strain" method [8] to compute the elastic constants, and the findings are given in Table 3.

Table 3. The calculated elastic constants (C_{ij} in GPa).

Phase	C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}	*Stability*	*References*
α-$MgAl_2Ge_2$	42	80.7	28		71.7	15.5	NO	Present
β-$MgAl_2Ge_2$	111.6	60.3	24.5	-2.2	94.1	26	YES	Present
	113	51	28	-2	87	26		CASTEP-PBE [1]

The traditional mechanical stability conditions for hexagonal and trigonal crystals on the elastic constants are known as [13, 14];

Hexagonal → $C_{11}>0,\ C_{11}-C_{12}>0,\ C_{44}>0,\ (C_{11}+C_{12})C_{33}-2C_{12}^2>0$

Trigonal → $C_{11}-|C_{12}|>0,\ (C_{11}+C_{12})C_{33}-2C_{13}^2>0,\ (C_{11}-C_{12})C_{44}-2C_{14}^2>0.$

Our results are given in Table 2 satisfy Born's stability conditions only for β-phase. We found that the titled compound mechanically unstable in α-phase. The mechanical properties, such as bulk modulus (B), Young's modulus (E), shear modulus (G), Poisson's ratio (ν), Debye temperature (θ_D) and the longitudinal and transverse and average sound velocities are calculated by using the Voigt–Reuss–Hill approximation [15], and are listed in Table 4. They are well agreeing with available literature data [1].

Table 4. Calculated bulk modulus (B in GPa), isotropic shear modulus (G in GPa), Young's modulus (E in GPa), Poisson's ratio (ν), G/B and B/G ratios, Debye temperature (θ_D in K), sound velocities (vl, vt and vm in m/s)

B	G	E	ν	G/B	B/G	θ_D	v_l	v_t	v_m	References
58.3	28.7	73.9	0.29	0.49	2.03	340.9	5132	2798	3121	Present
57.1	29.9	76.4	0.277		1.91					GGA-PBE[1]

The bulk, shear and Youns's modulus give information about mechanical behavior of the poly-crystals [11]. Our calculated results show that this compound has soft nature in *β*-phase. According to criterion, a material is brittle (ductility) if the B/G ratio is less (high) than 1.75 [12]. The calculated value of the B/G (2.03) is higher than 1.75 for the titled compound; hence, the compound will behave in a ductile manner in *β*-phase.

The typical value of Poisson's ratio is about ν = 0.1 for covalent materials and 0.25 for ionic materials. In the present case the value of ν is 0.29 for *β*-phase. Thus, the ionic contributions to the atomic bonding are dominant in *β*-phase.
The present G/B ratio for compound is 0.49. These values are lower than 1.06 for the references fragile compound α-SiO2 [16]. Therefore, this type crystal solid possess low shear deformation resistance and intrinsic damage tolerance.

3.3. Dynamical Properties

The other method gives more information about structural stability is phonon dispersions. The DFPT and Phonopy code were used to calculate dynamical properties for both phase. The results are illustrated in Figure 2. It is found that $MgAl_2Ge_2$ compound dynamically stable in β-phase. α-phase exhibits negative frequencies, which is an indicator of instability.

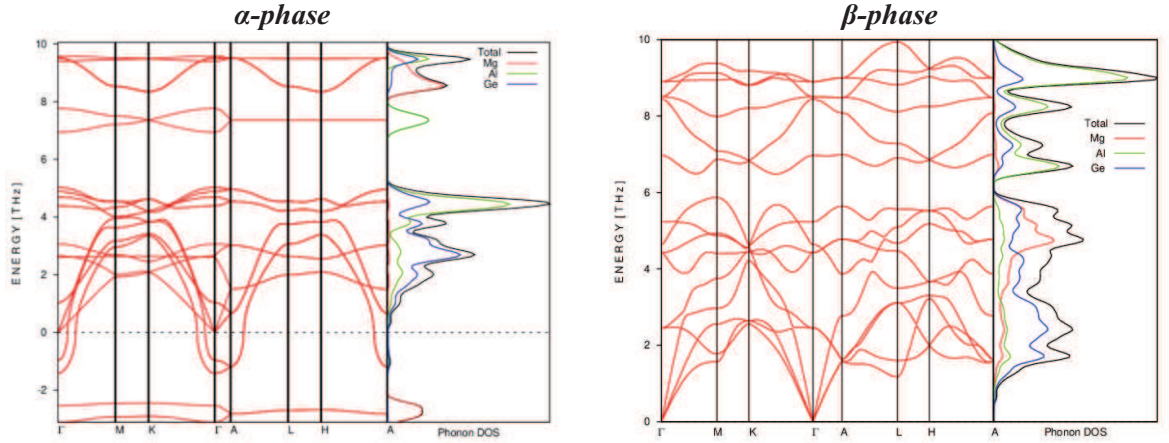

Figure 2. The calculated phonon distribution of $MgAl_2Ge_2$

4. CONCLUSION

We have performed the first principles total energy calculation for hexagonal α-phase and trigonal β-phase $MgAl_2Ge_2$ compound using the plane-wave pseudopotential approach to the density-functional theory within the generalized gradient approximation. The calculated lattice parameters are consistent with the experimental and theoretical values. The calculated second order elastic constants and phonon dispersions show that the compound mechanically and dynamically stable in β-phase. The B/G ratio is 2.03 and the ductile character is dominant.

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