Structural determination and physical properties of CuB_2: a first principles study

Engin Deligoz*, Havva Bogaz Ozisik, Haci Ozisik

Department of Physics, Faculty of Arts and Sciences, Aksaray University, TR-68100 Aksaray, Turkey

**e-mail corresponding author*: edeligoz@aksaray.edu.tr

Keywords: CuB_2, Structural Properties, First Principles

ABSTRACT

The structural determination, thermodynamic and mechanical properties of CuB_2 compound are systematically investigated by first-principles within the density functional theory (DFT). The titled compound is considered in AlB_2, ReB_2, and OsB_2-type structures. The two different flavor PAW potentials (LDA-CA and GGA-PBE) are used to determine the properties. The mechanical stability is confirmed via the calculated elastic constants for in the ReB_2 phases. In order to gain some further information, we have predicted the bulk modulus, shear modulus, Young's modulus, Poison ratio (v), Anisotropy factor (*A*), sound velocities, and Debye temperature for the titled compound in the stable structure and the reasonable values are found. The obtained results are compared with the available data.

1. INTRODUCTION

Ultra hard materials are used in many applications, from cutting and polishing tools to wear-resistant coatings [1]. Unfortunately, almost all ultra-hard materials (diamond, cubic BN, etc.) are expensive because they either occur naturally in limited supplies or have to be made at high pressure synthetically [2]. A number of compounds are currently being investigated for their potential use as hard materials [1-3]. A promising approach to design super hard or hard materials is to combine transition metals possessing a high bulk modulus with small, covalent bond forming atoms such as boron, carbon, nitrogen or oxygen [4].

In this study, the structural determination and mechanical Cupper diboride (CuB_2) are systematically investigated by first-principles within the density functional theory (DFT). Three structures are considered (AlB_2-, ReB_2-, and OsB_2-types) [2, 5]. The method of calculation is given in Section 2, the results and overall conclusions are presented and discussed in Section 3.

2. METHOD

All calculations have been carried by using the VASP code [6-7] 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 500 eV [8], an adequate value for studying the physical properties. The Perdew–Burke–Ernzerhof (PBE) within the generalized gradient approximation (GGA) [9] and Ceperley- Alder (CA) type functional within the local density approximation (LDA) [10] has been used for the exchange and correlation terms in the electron–electron interaction. 8x8x4, 4x8x4, and 4x8x4 Monkhorstand Pack [11] grid of k-points has been used for AlB_2, ReB_2, and OsB_2-type structures, respectively. The second order elastic constants were predicted by using the stress-strain method implemented in the VASP code [12].

3. RESULTS AND DISCUSSION

3.1. Structural properties

CuB_2 compound is considered in the AlB_2-, ReB_2-, and OsB_2-type structures [1, 3]. The optimized lattice parameters are listed in Table 1.

Table 1. The calculated lattice parameters (a, b, c in Å) and cohesive energies (E_{coh} in eV/fu) for CuB_2 compound.

Structure	PP	*a*	*B*	*c*	E_{coh}	References
AlB_2	GGA-PBE	2.981		3.3952	-15.9789	Present
	LDA-CA	2.9479		3.2661	-18.461	Present
ReB_2	GGA-PBE	2.9369		7.117	-15.9356	Present
	LDA-CA	2.8987		6.8427	-18.543	Present
OsB_2	GGA-PBE	5.7834	2.4766	3.9801	-15.8059	Present
	LDA-CA	5.7541	2.4067	3.878	-18.28	Present

It can be clearly seen that the AlB_2-type is the most stable phase among the considered crystal phases.

3.2. Mechanical properties

The elastic constants of solids provide a link between the mechanical and dynamical behaviors of crystals and give important information concerning the nature of forces operating in solids [13]. In particular, they provide information on the stability and stiffness of materials. We have used the "stress-strain" relations [12] to compute the elastic constants, and the findings are given in Table 2.

Table 2. The calculated elastic constants (C_{ij} in GPa) for CuB_2 compound.

Structure	*PP*	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	C_{22}	C_{23}	C_{55}	*Stability*
AlB_2	GGA-PBE	434.8	125.5	88.2	227.5	-22.3	154.7				No
	LDA-CA	474.8	139.5	117.7	254.8	-31.2	167.6				No
ReB_2	GGA-PBE	351.5	109.2	79.1	497.1	91.5	121.1				Yes
	LDA-CA	387.7	118	111.4	581.8	129.8	134.9				Yes
OsB_2	GGA-PBE	457.8	114.8	64.2	382.9	-14.1	131.9	250.3	32.9	48.9	No
	LDA-CA	534.6	88.8	77.4	456.3	-20.6	144.2	340	36.6	61.4	No

Although energetically the most favorable phase is AlB_2, only the ReB_2-type satisfy the stability conditions [14, 15] for CuB_2 compound. The mechanical properties, such as bulk modulus (B), Young's modulus (E), shear modulus (G), Poisson's ratio (ν), Debye temperature (θ_D in K), the longitudinal, transverse, average elastic wave velocity (v_l, v_t, v_m in m/s) and Zener anisotropy factor (A) which are functions of the elastic constants, are calculated by using the Voigt–Reuss–Hill approximation [16] and the result are listed in Table 3. Unfortunately, no experimental or other theoretical works exist on these properties for comparison with our results.

Table 3. Calculated bulk modulus (B in GPa), shear modulus (G in GPa), Young's modulus (E in GPa), Poisson's ratio (ν), B/G ratio, G/B ratio, Debye temperature (θ_D in K), The longitudinal, transverse, average elastic wave velocity (v_l, v_t, v_m in m/s), Shear anisotropic factors (A_1, A_2, and A_3) for CuB_2 in ReB_2-type structure.

B	G	E	ν	G/B	B/G	θ_D	v_l	v_t	v_m	A_1	A_2	A_3
191.4	118.6	294.8	0.2432	0.619	1.613	753.6	8106	4722	5238	0.53	0.53	1

Bulk modulus, Shear modulus (G), Poisson's ratio (ν), Young's modulus (E) which are the most interesting elastic properties for applications, are often measured for polycrystalline materials when investigating their hardness. 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 0.24 for CuB_2 in ReB_2 phase. Thus, the ionic contributions to the atomic bonding are dominant for the case. The present values of G/B ≈ 0.6 strongly support the ionic contribution to inter-atomic bonding.

According to criterion, a material is brittle (ductility) if the B/G ratio is less (high) than 1.75. The calculated value of the B/G (1.613) is less than 1.75 for the titled compounds; hence, CuB_2 will behave in a brittle manner in the ReB_2 phase. For a completely isotropic material, the factor *A* takes the value of 1. When the value of *A* is smaller or greater than unity, it is a measure of the degree of elastic anisotropy. The results show that the compound has relatively shear anisotropy.

4. CONCLUSION

In summary, we have performed the first principles total energy calculation for CuB_2 using the plane-wave pseudopotential approach to the density-functional theory within the generalized gradient approximation. The B/G ratio is 1.613 and the brittle character is dominant. The G/B ratio ≈0.6 and the ionic character dominant. ReB_2 has

relatively elastic anisotropic character. We hope that our other predicted results will be serving as a reliable reference for the future experimental and theoretical studies.

ACKNOWLEDGEMENTS

The numerical calculations reported in this paper were partially performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources) and at Aksaray University ASUBTAM-HPC system.

REFERENCES

[1] Sarin V.K., Mari D., Llanes L., Nebel C.E., Comprehensive hard materials, Amsterdam, Elsevier, 2014, vols. 1–3.

[2] E. Deligoz, K. Colakoglu, and Y.O. Ciftci, Chin. Phys. B 21:10 (2012) 106301.

[3] H.B. Ozisik, K. Colakoglu, E. Deligoz, Journal of Physics and Chemistry of Solids, 73:4, 2012, 593-598

[4] R.B. Kaner, J.J. Gilman, S.H. Tolbert, Science 2005, 308:5726, 1268-1269.

[5] E. Deligoz, K. Colakoglu, and Y.O. Ciftci, Sol. State. Comm. (2009), 149, 1843-1848

[6] G. Kresse, J. Furthmüller, Phys. Rev. B, 1996, 54:11169.

[7] G. Kresse, D. Joubert. Phys. Rev. B, 1999, 59:1758.

[8] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.

[9] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev.Lett., 1996, 77, 3865.

[10] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).

[11] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188-5192.

[12] Y.L. Page, P. Saxe, Phys. Rev. B 65 (2002) 104104.

[13] E. Ateser, H. Ozisik, K. Colakoglu and E. Deligoz, Comp. Mater. Sci., 50 (2011) 3208.

[14] M. Born, Math. Proc. Camb. Phil. Soc. (1940), 36, 160.

[15] H.B. Ozisik, K. Colakoglu, G. Surucu, H. Ozisik, Computational Materials Science (2011), 50:3, 1070-1076.

[16] R. Hill: Proc. Phys. Soc. London 65 (1952) 349.