HIGH PRESSURE STUDY OF ZIRCONIUM DIBORIDE USING FIRST PRINCIPLE DFT

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Abstract: Elastic properties of a solid are correlated with various fundamental physical properties so values of these elastic constants help us to understand the mechanical properties for practical applications in various areas of technology and science. High Pressure structural changes in terms of lattice parameters, density of states, enthalpy, fermi energy, elastic constants, Debye temperature, Poisson Ratio etc of hexagonal P6mmm phase of Zirconium Diboride (ZrB_2) have been calculated and represented under High Pressure up to 400 GPa first time which is equivalent to the core pressure of the earth by using Quantum ESPRESSO under Density Functional Theory (DFT) in order to understand stability, deformation and possible structural phase transformation in extreme pressure conditions for future industrial and scientific applications. Our calculated results are well optimized to achieve stable structure at minimum enthalpy for unit cell with well convergence threshold limit of 10^{-12} Ry and 60 Ry of kinetic energy cutoff and having charge density cut-off of 540 Ry under variable-cell relaxation method in all directions for good approximations. The calculated results using First-Principle (ab-initio) DFT approximations of Hohenberg-Kohn-Sham are in well agreement with other theoretical and experimental results. Pseudopotentials used is Vanderbilt type and ultrasoft. Our results at low pressure are very similar to other reported experiments and theoretical calculations. However, we have calculated various properties and showed electronic density of states at extreme pressure first time and at varying high pressure ranges. Speed of sound in pressure-generated stressed-state, Young, Bulk & Shear Modulus – all in Voigt-Reuss-Hill approximations have also been presented.

IndexTerms - Quantum ESPRESSO; DFT; Elastic Constants; Zirconium Diboride; First Principle Calculations

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I. INTRODUCTION

Transition-metal diborides are attractive towards not only in scientific and industrial application perspective but also in fundamental science and technological applications, due to unique physical as well as chemical properties like extremely high-melting point, high hardness level, high-thermal conductivity, inertness behavior towards chemicals etc [1-6]. The crystal structure of transition metal diborides is similar to Aluminum diboride (Space Group P6/mmm) in which metal and boron atoms sitting at (0, 0, 0) and (1/3, 2/3, 1/2) sites, when the co-planar graphite type Boron layers seen to be present with the close-packed metal sheets. After the discovery of AlB_2 structured MgB_2 [7], to explore potential applications and unique behaviors of materials, high-pressure study is being emerged in material science research as pressure could significantly change the electronic bonding state to alter the physical, chemical, magnetic, thermodynamical and optical properties and potentially induce the phase transition at structural level. There is a lack or less research reports on the existence of pressure driven phase transitions in terms of Transition Metal Diborides. The compressibility measurements by using X-ray diffraction techniques for TiB_2 up to 65 GPa [8] ZrB_2 and VB_2 up to 50 GPa [9] and HfB_2 up to 30 GPa [10] were performed and some related mechanical characteristics were investigated but no obvious phase transitions were observed in any of these compounds. Ma et al [11] reported orthorhombic structure of MgB_2 stable above 190 GPa through simulations. The thermodynamic properties of TiB_2 [12] and elastic and electronic properties of NbB_2 under pressure [13] were calculated and the results do not suggest structural transformations over a wide range of pressure (0-200 GPa). In our DFT ab-initio calculations up to 400 GPa so as to comparative analysis to the pressure at the core of the earth, we explored for potential high-pressure polymorphs of the boride and its various properties. In a paper of Meiguang Zhang et al [14] extensively explored the high-pressure structures of transition-metal diborides (TMB_2, TM = Sc, Ti, Y, and Zr) stabilized with the AlB_2 -type structure at ambient pressure by using first-principles structural prediction. They found two novel high-pressure structures and the phase transformation mechanism were discussed: (i) a monoclinic structure (C2/m, Z = 4) for ScB_2 and YB_2 stable above 208 and 163 GPa respectively; and (ii) a tetragonal R-$ThSi_2$ -type phase (I4 1 /amd, Z = 4) for TiB_2 stable above 215 GPa. Their calculations show that the electron transfer from transition-metals TM to B under pressure might be the main cause for the structural phase transitions. Further phonon and hardness calculations suggest that R-$ThSi_2$ phase of TiB_2 is quenchable to ambient pressure and possesses excellent mechanical property with a Vickers hardness of 29.8 GPa. ZrB_2 is quite stable and persists on the ambient-pressure AlB_2-type structure up to at least 300 GPa. They attribute the strong covalent hybridization between the transition-metal Zr and B to this ultrastability. In our study we extended pressure limit up to 400 GPa to explore the research.

Zirconium diboride (ZrB_2) can be manufactured by reactive hot pressing of ZrB+B powder mixture [15]. This is an important member of Ultra-high temperature ceramics (UHTCs) [16] with physically stable at high temperatures (in excess of 3000 K) [17]. In extensive way, it crystallizes in the hexagonal (space group P6/mmm) AlB_2 type structure up to at least 300 GPa due to strong covalent hybridization between the transition-metal Zr and B with c and a are close to be equal [14]. In this arrangement, the hexagonal nets of metal atoms and triangle nets of pure boron atoms are alternately stacked along the c-axis. Hence, the crystal structures of ZrB_2 compound can be considered as a layered structure [14]. It possesses high thermal and electrical conductivity hence be used as thermal protection materials for a variety of extreme chemical and thermal environments, including hyper-sonic flight and atmospheric re-entry [17-18]. High-pressure research is leading to the identification of novel behavior of solids and the exploration of potential technological materials [19], since pressure could significantly alter the electronic bonding state to modify the physical properties and/or then induce the structural phase transition. However, the high-pressure behaviors of AlB_2-type compounds are least studied, and there is lack of confirmed reports on the existence of pressure-induced phase transitions. Experimentally, the measurements by using X-ray diffraction techniques for Transition Metal Diborides (TMB_2) in which ZrB_2 up to 50 GPa were performed and some related mechanical characteristics were investigated, but no obvious phase transitions were observed in any of these compounds. Theoretically, Ma et al. first reported a non-superconducting high-pressure orthorhombic polymorph (Imma, Z=4) of MgB_2 stable above 190 GPa through ab-initio evolutionary simulations [20-26]. In solid state physics, the electronic band structure (BS) of a solid describes the range of energies that an electron within the solid may have (called energy bands, allowed bands or simply bands) and ranges of energy that it may not have (called band gaps or forbidden bands). Band theory derives these bands and band gaps by examining the allowed quantum mechanical wave functions. For an electron in a large, periodic lattice of atoms or molecules. Band theory has been successfully used to explain many physical properties of solids and forms the foundation of the understanding in material science. Band structure calculations and other simulation and DFT calculations take advantage of the periodic nature of a crystal lattice exploiting its symmetry [27-36]. The density of states function g (E) is defined as the number of electronic states per unit volume, per unit energy for electron energies near (E). The density of states function is important for calculations of effects based on band theory. It appears in calculations for optical absorption where it provides both the number of excitable electrons and the number of final states for an electron. It appears in calculations of electrical conductivity where it provides the number of mobile states, and in computing electron scattering rates where it provides the number of final states after scattering.

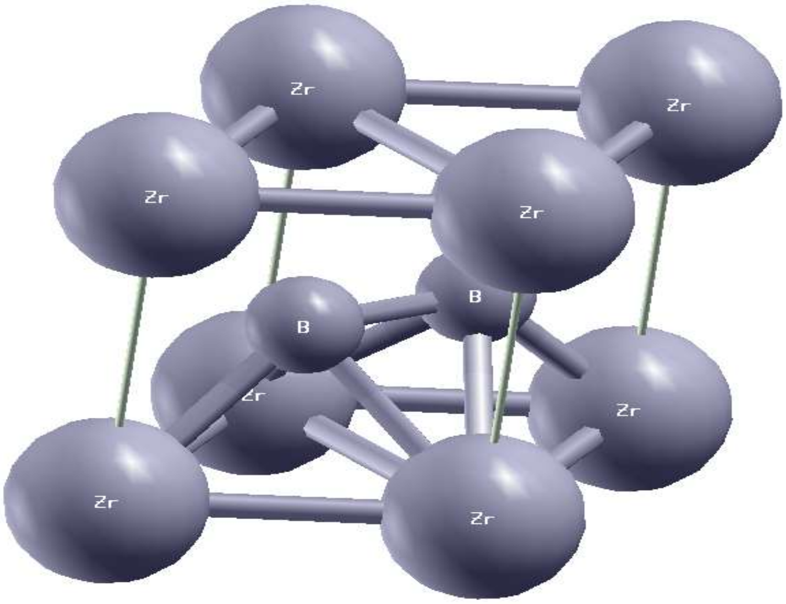


Figure 1. Graphical representation shown covalent bonds between Zr and B in ZrB_2 structure

Superhard materials are used in various industrial applications due to their superior properties of low compressibility, thermal conductivity, refractive index, chemical inertness, and high hardness. The superhard materials are strong covalently bonded compounds formed by light atoms B, C, N, and O, such as diamond [37], c-BN [38], B_6O [39], etc. The compounds formed by TM and light atoms usually possess high valence electron density and directional covalent bonds, and these covalent bonds are strong enough to inhibit creation and movement of dislocations, which greatly improve their mechanical properties and create high hardness. Based on this design criterion, the recent design of new intrinsically potential superhard materials has focused on TM borides, e.g., ReB_2 [40], OsB_2 [41], WB_4 [42,43], CrB_4 [44] and so on. The obtained results exhibit that these materials all have large bulk and shear moduli. Up to now, in the Zr-B system, three binary phases [45,46], i.e., ZrB, ZrB_2, and ZrB_{12}, have been synthesized experimentally among them, ZrB with the NaCl-type cubic structure has a high melting up to now. Also it's thermal conductivity, and its thermal stability are in the temperature range from 1073 to 1523 K [47]. ZrB_2 is an AlB_2 -type hexagonal structure and has properties of both ceramics and metals, and its melting temperature has been reported to be either 3313 [47] or 3523 K [47-48]. ZrB_2 also possesses electrical conductivity, thermal conductivity, and chemical corrosion resistance [49-50]. ZrB_2 ceramic products have been considerably used in making high-temperature structural and functional materials [51-52]. ZrB_{12} with a cubic structure was formed by reaction at T = 2303 K [53], and it presents a wide range of interesting characteristics such as high temperature resistance, superconductivity and large hardness. The crystal structure and related physical properties of ZrB, ZrB_2 and ZrB_{12} have been investigated theoretically [54–62]. By using the first-principles calypso algorithm for crystal structure prediction, Zhang et al [63] predicted two orthorhombic Cmcm and Amm2 structures of ZrB_4 and they also showed that these two phases are potentially superhard materials because of large shear modulus (229 and 236 GPa) and high hardness (42.8 and 42.6 GPa). Very recently, Chen et al [64] systemically investigated the elasticity, hardness and thermal properties of ZrB_n (n = 1, 2, 12) by using the first-principles calculations of plane-wave ultra-soft pseudo-potential technology based on the density functional theory. However, there is no experimental report on the synthesis of Zirconium triborides. In the work of Gangtai Zhang et al [65], the crystal structures of ZrB_3 are extensively investigated by the first-principles particle swarm optimization algorithm (PSO) on crystal structural prediction [66–69].

The k-point optimization under a Plane-wave basis-set is good approximation since we used high number of k-point with high mesh (887) and our cut-off energy is up to 10^{-12} is very low to get accurate values. Using some external computational codes and tools like thermo_pw [70], pwGUI, XcrysDen [71] we also represented different variations in thermodynamical, electronic and physical properties with respect to pressure. Our results at low pressure are very similar to other reported experiments and theoretical calculations [72-74, 9-

10, 20-21]. However, we have calculated various properties first time at varying high pressure ranges so could not compare with any data due to unavailability of the similar research in the same condition. Speed of sound in pressure-generated stressed-state, Young, Bulk & Shear Modulus, Poisson ratios – all in Voigt-Reuss-Hill approximations have been presented at high pressure.

II. COMPUTATIONAL METHOD

Computer simulations are an integral part of contemporary basic and applied research in the sciences. Computation is becoming as important as theory and experiment. Computational, theoretical and experimental methods are all equally essential in research and studies of solid materials. Moreover, the ability "to compute" forms part of the essential accumulation of researchers. This ability often combines knowledge from many different subjects, in our case essentially from the physical sciences, numerical mathematics, computing languages, topics from high performance computing and some knowledge of computers. These theoretical calculations are based on use of density functional theory with the generalized gradient approximation. We have used Unified Pseudopotential Format (UPF) plane-wave (pw) Perdew-Burke-Ernzerhof (PBE) [77] exchange-correlational pseudo-potential (pp) density functional theory (DFT) as implemented in the Quantum ESPRESSO codes [75-76] under Vanderbilt ultrasoft as implemented in pp [78] within combination of nonlinear core-correction and semicore state-sp in valence. The gound state at absolute temperature, properties of ZrB_2 have been studied using this approach. We calculated the electronic band structure (BS) in different B-Z (Brillouin Zones) symmetries and Density of states (dos) vs Energy for ZrB_2. Quantum ESPRESSO is mainly based on DFT theory (electron-ion interaction), plane wave and pseudopotentials (electron-electron interaction). It calculates the ground state energy and Kohn-Sham orbital for various types of structural optimizations. Three main components of the method are PWSCF (plane wave self-consistent field), CP (Car-Parinello), FPMD (first principle molecular dynamics). For calculations, irreducible k-points were generated according to the Monkhorst-Pack scheme [79]. The Kohn-Sham [80] single-particle functions were expanded on a basis of plane-wave set with a kinetic energy cut-off of 60 Ry. Brillouin-zone was sampled with k-point mesh in order to get converged ground state energy. The Zirconium Diboride ZrB_2 considered in the present work under pressure, it transforms to AlB_2-type (P6mmm) structure. The exchange and correlation effects have been treated within the GGA. The lattice parameter, bulk modulus and pressure derivative of the bulk modulus were determined by the standard procedure of computing the total energy for different volumes and fitted to Murnaghan's equation of state [81]. The evolutionary variable-cell high-pressure structure predictions were performed at different pressure ranges from 0 GPa to 400 GPa. The present first-principles optimization procedure and properties calculations using BFGS (Broyden-Fletcher-Goldfarb-Shanno) algorithm method is applied for pressure control to allow the variation of both the shape and the volume of the cell under fully relaxation of cell in all directions. The kinetic energy cutoff is 60 Ry and charge cutoff is 540 Ry which are calculated sufficient values for good approximations. Brillouin zone integration is performed using a discrete value of upto 9 9 7 Monkhorst–Pack k-point sampling with a shearing width 10^{-2} Ry for the start unit cell. For the geometry optimizations and properties calculations, exchange–correlation effect is mainly taken into account using the PBE form of the generalized gradient approximation (GGA).

III. RESULTS

Table 1. Calculated values of Elastic Constants of ZrB_2 upto 400 GPa

P (in GPa)	**Elastic Constants (in Kbar)**					
	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
0	5766.4714	580.82953	1248.17608	4478.44049	2602.76670	2592.82030
10	6280.96224	710.03538	1496.84577	4934.31282	2848.95313	2785.95313
20	6882.49339	885.82721	1802.93464	5474.96700	3139.29654	2998.33309
30	7437.26248	1058.84465	2097.85743	5977.90358	3406.97462	3189.20892
40	7944.30198	1219.99300	2376.16861	6438.86154	3649.64022	3362.15449
50	8469.18516	1385.58583	2788.01311	6881.64533	3940.51454	3541.79966
60	8972.33971	1559.90912	3091.47424	7337.99339	4181.52202	3706.21529
70	9460.89512	1735.23265	3391.91706	7786.53134	4413.88249	3862.83123
80	9936.75635	1911.62038	3689.14713	8228.70339	4638.46865	4012.56799
90	10401.30286	2088.99609	3943.17571	8666.13906	4855.99825	4156.15338
100	10855.54476	2267.21860	4274.26168	9099.77703	5067.07569	4294.16308
400	19547.83208	8027.57366	11909.42966	20790.29042	9338.84356	5760.12921

Table 2. Calculated values of Thermodynamical and various physical properties of ZrB_2 upto 400 GPa

P (in GPa)	Debye Temperature (K)	Average Debye sound speed (m/s)	V_P (m/s)	V_B (m/s)	V_G (m/s)	Bulk Modulus (B)	Young Modulus (E)	Shear Modulus (G)	Poisson Ratio (n)
0	937.415	6824.834	9592.107	6331.592	6240.160	2458.70924	5412.11726	2388.21153	0.13309
10	972.000	6985.993	9899.427	6611.001	6381.221	2763.87373	5894.36469	2575.08382	0.14450
20	1004.079	7154.452	10233.256	6920.767	6528.161	3133.60496	6450.80783	2788.15922	0.15682
30	1033.938	7295.208	10519.948	7189.693	6650.806	3482.98858	6956.46716	2980.43685	0.16702
40	1059.698	7413.975	10766.169	7421.823	6754.274	3806.93290	7411.80511	3152.90868	0.17539
50	1082.137	7501.521	11009.118	7682.497	6828.978	4193.08246	7688.00403	3218.30773	0.18713
60	1104.646	7599.187	11226.721	7893.532	6913.65	4529.72949	8300.55746	3474.91551	0.19435
70	1125.549	7688.15	11428.436	8090.134	6990.648	4860.71460	8716.53901	3629.30568	0.20085
80	1145.103	7769.944	11616.686	8274.305	7061.336	5186.85435	9117.16646	3777.58961	0.20674
90	1163.511	7845.757	11793.400	8447.675	7126.766	5508.62437	9504.42864	3920.61099	0.21211
100	1180.920	7916.414	11960.047	8611.581	7187.666	5826.43466	9879.74084	4058.94296	0.21703
400	1405.461	8469.596	14275.781	11211.949	7652.947	13595.39192	16441.82975	6334.12915	0.29788

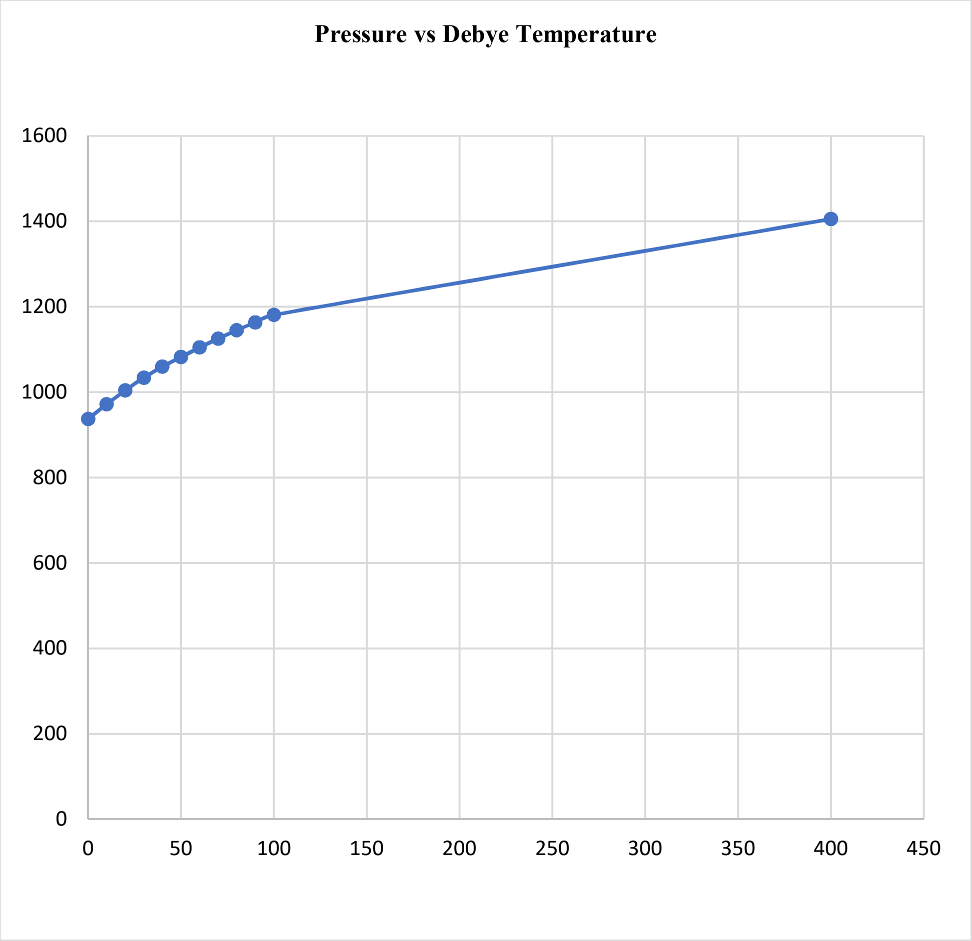


Figure 2. Variation in Debye temperature at different high pressure ranges upto 400 GPa

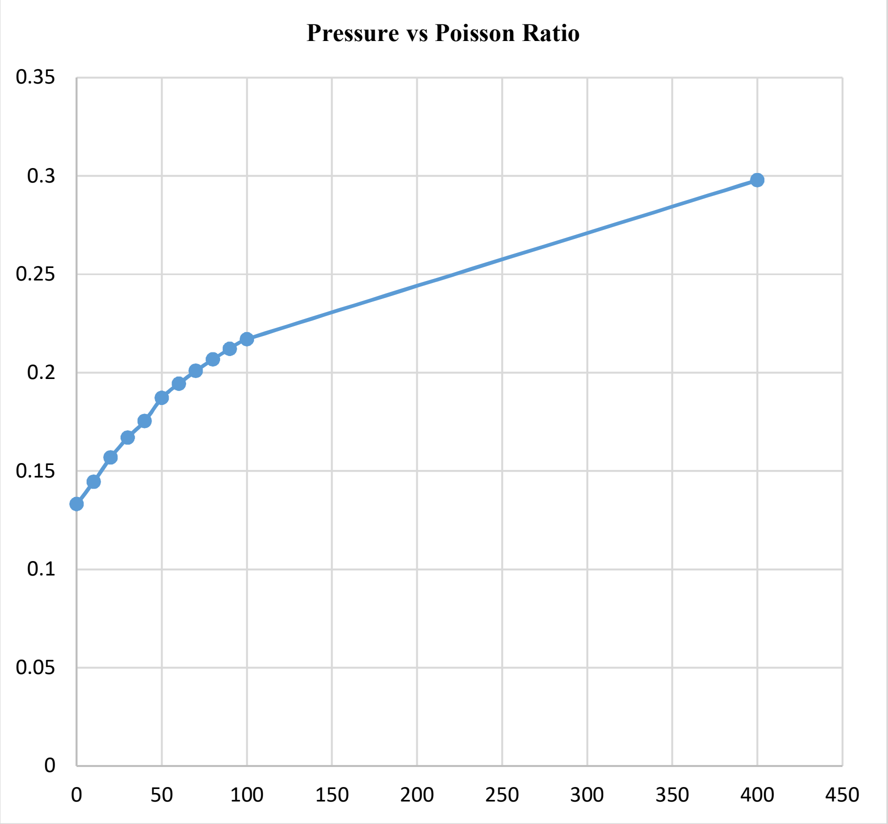
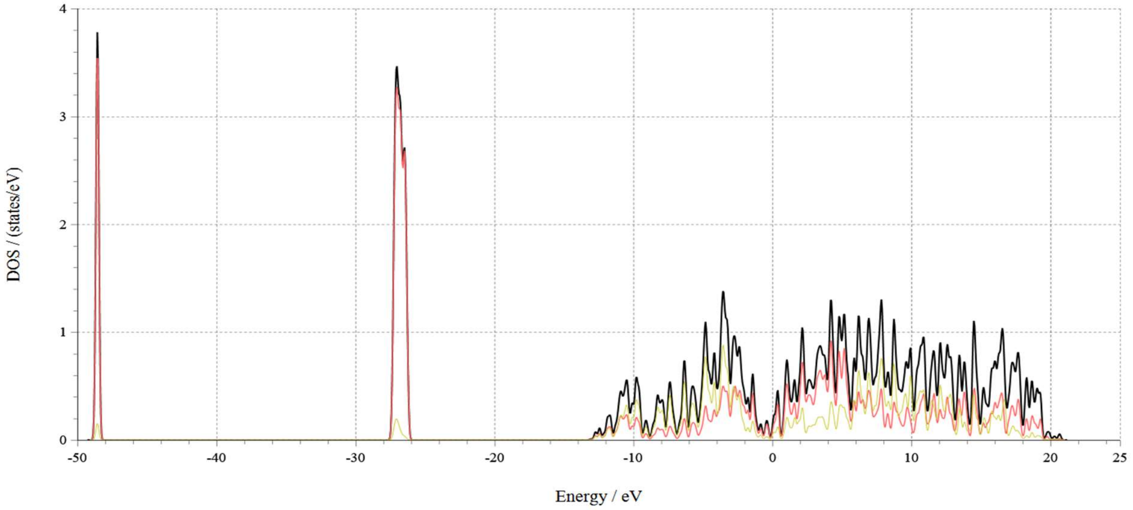


Figure 3. Variation in Poisson Ratio at different high pressure ranges upto 400 GPa

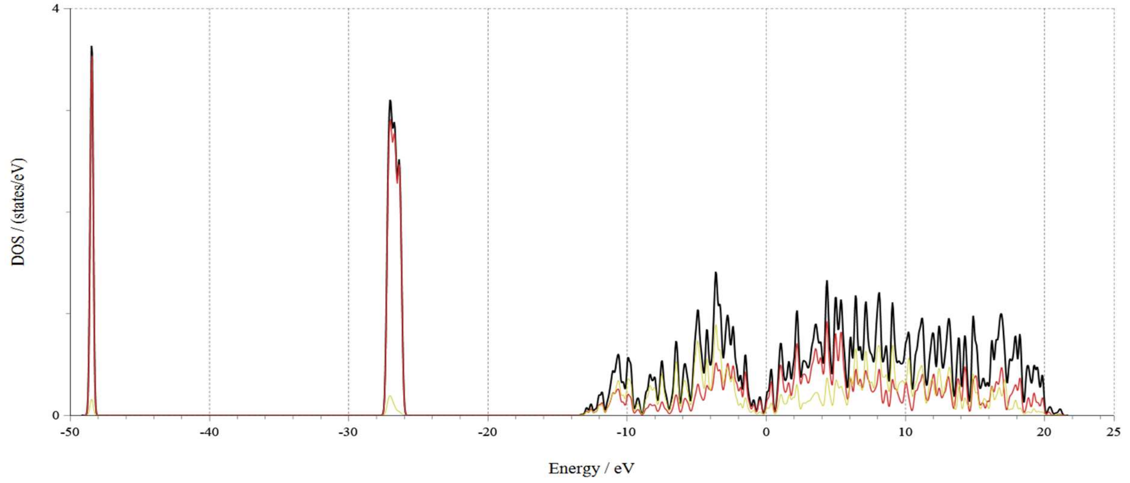
Table 3. Calculated values of various properties in external pressure upto 4000 Kbar (400 GPa)

Pressure (in Kbar)	**a (in Å)**	**c (in Å)**	**Fermi Energy (eV)**	**Unit Cell Volume (Å)^3**	**Density (g/cm^3)**	**Total energy (Ry)**	**Final Enthalpy (Ry)**
0	3.17049	3.53852	15.9997	30.8039	6.08317	-111.742	-111.742
100	3.13166	3.48840	16.6621	29.6283	6.32453	-111.739	-111.603
200	3.09803	3.44553	17.2552	28.6389	6.54303	-111.733	-111.47
300	3.06815	3.40843	17.7941	27.7867	6.74369	-111.723	-111.34
400	3.04120	3.37575	18.2901	27.0390	6.93018	-111.711	-111.215
500	3.02218	3.33587	18.2524	26.3894	7.10077	-111.695	-111.09
600	2.99967	3.30942	18.6660	25.7888	7.26616	-111.680	-110.97
700	2.97874	3.28523	19.0554	25.2442	7.42291	-111.664	-110.853
800	2.95922	3.26303	19.4241	24.7460	7.57233	-111.647	-110.739
900	2.94094	3.24256	19.7745	24.2880	7.71515	-111.629	-110.626
1000	2.92366	3.22350	20.1103	23.8623	7.85279	-111.610	-110.516
4000	2.60291	2.94940	28.1535	17.3055	10.8281	-110.944	-107.768

Density of states of ZrB2 at 0 GPa



Density of states of ZrB2 at 10 GPa (Yello for Boron, Red for Zr)



Density of states 150 GPa

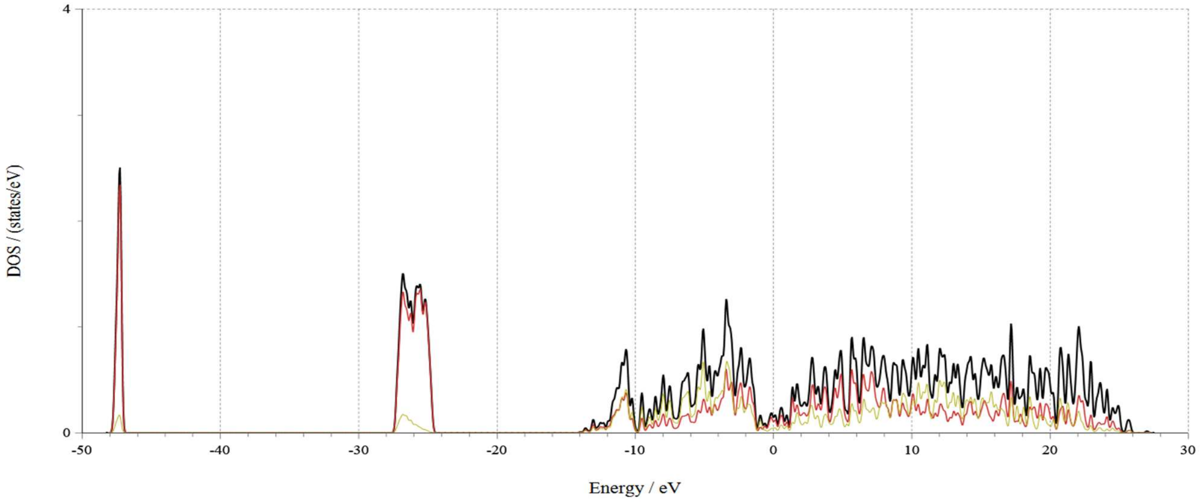


Figure 4. Variation in Density of states under external pressure (0 GPa, 10 GPa & 150 GPa) for ZrB_2

IV. DISCUSSION AND CONCLUSIONS

(i) Calculated results at absolute temperature of Poisson Ratio vs Pressure shows that there is a stability of ZrB_2 upto 400 GPa. It shows some abnormal behavior above 400 GPa and some phase instability is shows at this pressure range. It is an indication of deformation and phase transformation above 400 GPa and hence we considered the limit of the pressure upto 400 GPa which is equivalent to the pressure at the core of the earth. Debye temperature vs temperature also verifies the fact of phase transformation at the pressure higher than 400 GPa.

(ii) Different modulus of elasticity at absolute temperature shows that there is a stability of ZrB_2 upto 400 GPa and some phase instability is shows at higher pressure.

(iii) Results also verify the fact that the elastic properties of a solid are closely correlated with various fundamental physical properties, such as Debye temperature, Poisson ratio, Modulus of elasticity, interatomic bonding, equation of states, Debye temperature, density, Fermi energy, enthalpy and so on.

(iv) The independent elastic constants of ZrB_2 have been calculated using the stress–strain relation by codes as implemented in Quantum ESPRESSO using thermos_pw codes and shows that increasing pressure also increases these values monotonically upto 400 GPa.

(v) Density of states shows that peaks are lowers in higher pressure and shifted towards higher energy hence fermi energy increases at higher pressure. These DoS curve also indicates phase transformations beyond 400 GPa.

In our DFT ab-initio study it is observed that Zirconium Diboride is potential substitution for diamond and other High Pressure survivor materials as it is highly resistant to High Pressure upto 400 GPa and the material can be used in supersonic aerospace, space shuttle, Nuclear Protective Shielding and high end cutting tools. The calculated data are very useful for further study on this ceramic and for industrial applications.

V. ACKNOWLEDGEMENT

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