Physical Science International Journal

24(12): 60-71, 2020; Article no.PSIJ.56771
ISSN: 2348-0130

Structural Optimization and the Study of the Electronic, Mechanical, Thermodynamic and Phonon Properties of Mg_2sn from First Principle

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Authors' contributions

This work was carried out in collaboration among all authors. Author ISO proposed the article, provided all necessary resources for the acquisition of the data and training on how to use the software (Quantum Espresso) supervised and made the necessary corrections to the manuscript. Author TPC wrote the literature of the manuscript, performed the calculations with the aid of the aforementioned software and managed the analysis of the study. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/PSIJ/2020/v24i1230232
Editor(s):
(1) Dr. Suraya Hani Bt Adnan, Universiti Tun Hussein Onn Malaysia, Malaysia.
(2) Dr. Lei Zhang, Winston-Salem State University, USA.
(3) Dr. Thomas F. George, University of Missouri, USA.
Reviewers:
(1) Hermes José Loschi, The University of Zielona Gora, Poland.
(2) Bankole Adebanji, Ekiti State University, Nigeria.
Complete Peer review History: http://www.sdiarticle4.com/review-history/56771

Original Research Article

Received 24 October 2020
Accepted 29 December 2020
Published 31 December 2020

ABSTRACT

First principles pseudopotential method based on density functional theory is used to investigate the Structural, Mechanical, Phonon, Thermodynamic and Electronic properties of Mg_2Sn. The equilibrium properties including lattice constant, bulk modulus, pressure derivative cohesive energy, young modulus, shear modulus were determined. The results obtained were compared with available experimental and other available results. Mg_2Sn was found to be brittle in nature with a non-metallic properties as shown by the value of the Cauchy pressure of -4.03. The Phonon dispersion curve of Mg_2Sn was obtained utilizing the PBE-GGA exchange-correlation potential as employed in the Vienna Ab-Initio Simulation Package (VASP) computer code. The gap separating the acoustic and the optical branch of the curve was found to be about $50cm^{-1}$ at X-point. The

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thermodynamic properties of the material was investigated in the temperature of 0-800K. At room temperature, the calculated value of the specific heat capacity (C_v) is 71.28J/mol which is in good agreement with experimental and other results. Mg_2Sn was found to a narrow gap semiconductor with an indirect bandgap of magnitude of 0.175eV.

Keywords: Psuedopotential; phonon; density of state; thermodynamic; plane waves; pseudopotential; density functional theory.

1. INTRODUCTION

Magnesium is known to be the eight most common element in the Earth crust and the fourth most common element in the Earth (after iron, oxygen and silicon), making up to 13% of the planet's mass and large fraction of the planet's mantle.

Magnesium and its alloys have an excellent combination of properties of which some are excellent strength-to-weight ratio, good fatigue and impact strengths and relatively large thermal and electricalconductivities [1] and excellent biocompatibility [2]. Because of the above mentioned properties, Magnesium has applications in areas such as aerospace, Electronics, automotive and biomedical applications.

The stannide, germanide and silicide alloys of magnesium generally denoted as Mg_2X where X = Sn, Ge and Si, are a family of group II-IV compounds that are narrow gap semiconductors. These narrow gap semiconducting compounds show many advantages for potential TE (Thermoelectric) applications due to the abundance of constituents, low density, non-toxicity and environmental friendliness [3].

Among various Mg alloys, the Mg-Sn binary system is a typical precipitating, hardening system. It is a candidate for high strength wrought material due to high strength, excellent corrosion resistance, high temperature superplastic deformation and extrusion capability at moderate temperature. In addition, Mg_2Sn phase has a melting point of 1043K which resist dislocation slipping at high temperature and improves the mechanical properties at elevated temperature [4]. Apart from its promising thermoelectric properties, Mg_2Sn compound has attracted interest as an electrode material for rechargeable lithium cells and for its catalytic properties.

The electronic and optical properties of Mg_2Sn have recently been studied by Uma Shankar Sharma [5], where the refractive index of Mg_2Sn wasfound to be 1.01. The work of Yu Rong Jin et [6] all has suggested that $Mg_2Sn$is a promising mid- temperature thermoelectric material with maximum ZT value of 1.1 (for p-type Mg_2Sn) with carrier concentration of$9.8\ x\ 10^{19}\ cm^3$.

In this present work, the structural, electronic, mechanical, thermodynamic and phonon properties of Mg_2Sn has been thoroughly investigated using quantum Espresso from first principle calculations and the values obtained are compared with other available studies.

2. METHODOLOGY AND COMPUTA TIONAL DETAILS

The first principle calculation of this work was performed using Quantum Espresso package [7]. The exchange and correlation were described by Perdew-Burke-Erzerhof(PBE) functional in form of GGA [8]. PAW method was also used to generate the pseudopotential for the elements (Mg and Sn). The convergence of the total electronic energy as computed in plane wave pseudopotential code is determined by two important computational parameters, which are the number of basis functions (plane wave cut-off) and the number of K-points (k-spacing).

The number of basis functions was determined by running series of self-consistence calculations for different values of kinetic energy cut-off (ecutwfc) starting from fifty (50Ry) to hundred (100Ry) at an interval of 5Ry. The converged value of the ecutwfc is 80Ry. The value of the k-points was also varied from a value of 4 k-pointmesh to 16 k-point mesh at an interval of 2 k-point mesh. The two values help in determining accurately the electronic ground state properties of the system studied in the present work. A self-consistent ab-initio calculation using the full-potential linearized augmented plane wave (FP-LAPW) method within the framework of the spin-polarized density functional theory (DFT) was used to study the structural, electronic, mechanical, thermodynamic and phonon properties of Mg_2Sn.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

The antifluorite structure of Mg_2Sn with space group $Fm\bar{3}m$ which has a faced centered cubic symmetry was studied in this present work. The crystal structure is shown in Fig. 1a below with the magnesium atoms in blue and tin atoms in ash colour.

The total energies as a function of lattice parameter are fitted to Murnaghan equation of state and the graphs of energy vs volume and pressure vs volume are shown in Fig.1. b-c, the equilibrium lattice constant (a), bulk modulus (B_0) and pressure derivative for Mg_2Sn were determined. The results obtained are shown in Table1. It can be seen that the result is in good agreement with available experimental and theoretical values.

3.2 Mechanical Properties

In order to get a full view of the mechanical properties of a material, the elastic constants of the material must be considered. Since Mg_2Sn have a cubic structure, it is defined by three independent elastic constants which are $C_{11}, C_{12}\ and\ C_{44}$ and they are shown in Table 2 below. From Table 2, we can say that Mg_2Sn is mechanically stable because it satisfies the well-known "Born stability criteria" for a cubic crystal [9].

$$C_{11} - C_{12} > 0;\ C_{11} + 2C_{12} > 0;\ C_{44} > 0 \quad (3.0.1)$$

Generally, the elastic constant C_{11} characterizes the x direction resistance to the linear compression, C_{44} is the most significant parameter, which indirectly determines the indentation hardness of a solid. A large C_{44} implies a strong resistance to monoclinic shear in the (1 0 0) plane.

Cauchy pressure, $C_{12} - C_{44}$, can be used to describe the angular character of atomic bonding in metals and compounds [10]. The negative value of the Cauchy-pressure implies that the material is non-metallic with directional bonding and if positive, the material is expected to be metallic. From Table 2, it is evident that the calculated value of the Cauchy-pressure of Mg_2Sn at ambient conditions is negative, which indicates a non-metallic behavior of the material (i.eMg_2Sn is predicted to be a brittle material similarly as many non-metals).

The elastic modulus, including bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (υ) and also the B/G factor of Mg_2Snadopting the Voigt-Reuss-Hill average approximation are presented in Table 3.

The correlation between the elastic properties of single crystals and an aggregate is made by employing the Voigt and Reuss continuum the ories [11]. Moreover, Hill demonstrated that the arithmetic average of the Voigt and Reuss values gives a better approximations for the elastic properties of materials. For cubic system, Voigt and Reuss bounds of B and G can be expressed as follows [12]:

$$B_v = B_R = \frac{(C_{11}+2C_{12})}{3} \quad (3.0.2)$$

$$G_v = \frac{(C_{11}-C_{12}+3C_{44})}{5} \quad (3.0.4)$$

$$G_R = \frac{5(C_{11}-C_{12})C_{44}}{[4C_{44}+3(C_{11}-C_{12})]} \quad (3.0.5)$$

And the arithmetic mean of B and G can be obtained as follow:

$$B = \frac{1}{2}(B_V + B_R)\ \ and\ G = \frac{1}{2}(G_R + G_V) \quad (3.0.6)$$

Young's modulus and Poisson's ratio are major elasticity related to characteristic property of a material, which are calculated using the following formula:

$$E = \frac{9GB}{3B+G}\ \ and\ \ \upsilon = \frac{3B-2G}{2(3B+G)} \quad (3.0.7)$$

From Table3 above, the calculated values for bulk modulus (B), young modulus (E), shear modulus (G) and Poisson ratio (υ) are in close relation with experimental and other theoretical values.

The ratio of bulk modulus to shear modulus (B/G), proposed by Pugh [13], has been applied extensively to assess brittle or ductile behavior of materials. A high ratio, B/G, is associated with the ductile behavior of materials, whereas a low value corresponds to the brittle nature of materials. The critical value that separates ductile from brittle materials is 1.75. We see from the table above that Mg_2Sn is brittle in nature.

3.3 Phonon Properties

An important branch of solid state physics is lattice dynamics, which concerns itself with the vibrations of atoms about their equilibrium sites

in a solid. These vibrations are almost responsible for the thermal properties (like heat capacity, thermal conductivity, thermal expansion and so on) of a material [14].

In this present work, the calculation of phonon dispersion curve of Mg2Sn was performed utilizing the PBE-GGA exchange-correlation potential as employed in the Vienna Ab-Initio Simulation Package (VASP) computer code. The phonon dispersion curves are the aforemen tioned material is shown in Fig. 1d.

From Fig. 1d. there is a gap separating the acoustic branch and the optical branch of the curve. This gap was found to be about 50cm^{-1} at X-point. The states of lower energy (acoustic) are dominated by the tin and those of higher energy (optical) by the magnesium due to their important mass difference. The results obtained in this present work is in good relationship obtained by J bourgeois et al. [15].

3.4 Thermodynamic Properties

The thermodynamic properties of Mg_2Sn which entails the specific capacity (C_v), the Debye vibrational Energy, Debye free Energy, Debye entropy, the Debye temperature and sound velocity were successfully investigated in this present work. The calculations were performed in the temperature range of 0-800K.

Fig. 1e-1h below show the result of specific heat capacity at constant volume, the Debye entropy, Debye Free Energy, and Debye Vibrational Energy of Mg_2Sn. From Fig. 1e. the specific heat capacity at constant volume increases rapidly as temperature increases and it approaches the Dulong-Petit limit at a very high temperature. At low temperature, C_v is proportional toT^3.

As temperature increases, the entropy of Mg_2Sn increases as seen in Fig. 1f. The free energy in Fig. 1g. below decreases as the temperature increases. From Fig. 1h, it is clear that the Debye vibrational energy increases as the temperature is increased. At room temperature (300K), the calculated value of the specific heat capacity (C_v), Debye temperature (θ_D) and the sound velocity of Mg_2Sn are presented in Table 4.

3.5 Electronic Properties

The Electronic band structure calculation for Mg_2Sn was done using pseudo -potential and plane wave basis set method within the Density functional theory (DFT), treating exchange-correlation functional with generalized gradient approximation (GGA) in the form of PredewBerke- Erzndof (PBE) functional as implemented in Quantum Espresso package.

Fig. 1i. and Fig. 1j, below show the band structure of Mg_2Sn with the corresponding density of state (DOS).

From Fig. 1i, we see that the conduction band minimal state is at X-point which implies that Mg_2Sn has an indirect bandgap. The calculated bandgap for Mg_2Sn is 0.175eV. The obtained result for the bandgap is in close agreement with 0.142eV obtained by Guangsha. S. and Emmanouil K. [16].

The DFT method in LDA/GGA is well known to underestimate the electronic band gap between materials [17]. An efficient method for the prediction of fundamental band gaps in solids using density functional theory (DFT) as proposed by M. K.Y. Chan and G. Ceder [18] is advisable.

The semiconducting character of this material can be determined from the total density of states (DOS) and the individual contribution of different orbitals in the partial density of states (PDOS). Fig. 1. j-k below show the total density of state (DOS) and the partial density of state (PDOS) of Mg_2Sn.

The density of state (DOS) provides numerical information on the states that are available at each energy level. The value of zero density of states indicates thatthere are no available states for occupation in an energetic level [19].

Detailed features of the total density of state (DOS) are shown by the partial density of state (PDOS) since it gives information about the origin of the bands. The fermi level (E_F) is set at zero point as shown in the Figs. 1(j-k) below. The bands after (conduction band) the fermi energy are dense compared to that before the fermi energy (valence band). As a result of this, the conduction band contains more peaks. From Fig. 1k below, we see that we see that the Sn-3p state dominates the valence band while the Mg-2s state dominates the conduction.

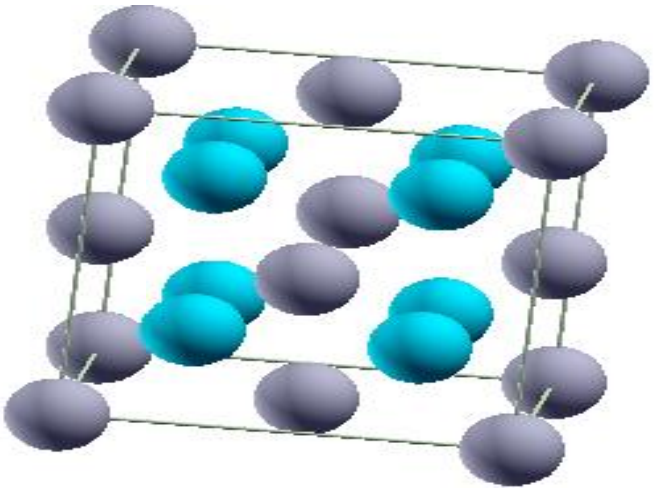

Fig. 1a. Mg_2Sn conventional unit cell the magnesium atoms are shown in blue and tin atoms in ash colour

Table 1. Structural parameters of Mg_2Sn

Mg_2Sn	Lattice parameter(Å)	Bulk modulus(B_0) (GPa)	Pressure derivative($B_0^{'}$) (GPa)
Present	6.83	42.86	4.26
Calculated	6.76 [20]	46.34 [21]	4.35 [22]
Others	6.82 [23]	40.61[24]	4.19 [25]

Table 2. Calculated elastic constants (C_{11}, C_{12} and C_{44}) and cauchy-pressure ($C_{12} - C_{44}$) of Mg_2Sn

Mg_2Sn	C_{11}(GPa)	C_{12}(GPa)	C_{44}(GPa)	$C_{12} - C_{44}$
Present	71.98	28.29	32.40	-4.03
Experimental [26]	82.40	20.80	36.60	-15.80
Others [27]	69.98	26.37	32.03	-5.66

The values given in the above are in good agreement with experimental values and other recent works

Table 3. Voigt-reeuss-hill average of the two approximation of bulk modulus (B), young modulus (E), shear modulus (G) and poisson ratio (v)

Mg_2Sn	$Bulk\ modulus\ (B)$ $in\ GPa$	Young modulus (E) in GPa	Shear modulus (G) in GPa	Poisson ratio (v)	B/G
Present	42.86	68.29	27.66	0.23	1.55
Experimental [28]	41.30	80.30	34.20		1.21
Others [29]	40.95	71.50	29.57		1.36

Table 4. The specific heat capacity (C_v), debye temperature (θ_D) and the sound velocity of Mg_2Sn

Mg_2Sn	Specific-heat capacity (C_v) (J/mol)	Debye temperature θ_D(K)	Sound velocity (m/s)
Present	71.28	310.51	3112.50
Calculated	72.50 [30]	336.8 [30]	2960 [31]
Others	74.8 [32]	307.6 [32]	3000

The values gotten for the heat capacity, Debye temperature and sound velocity are seen to be in close agreement with available experimental and other results

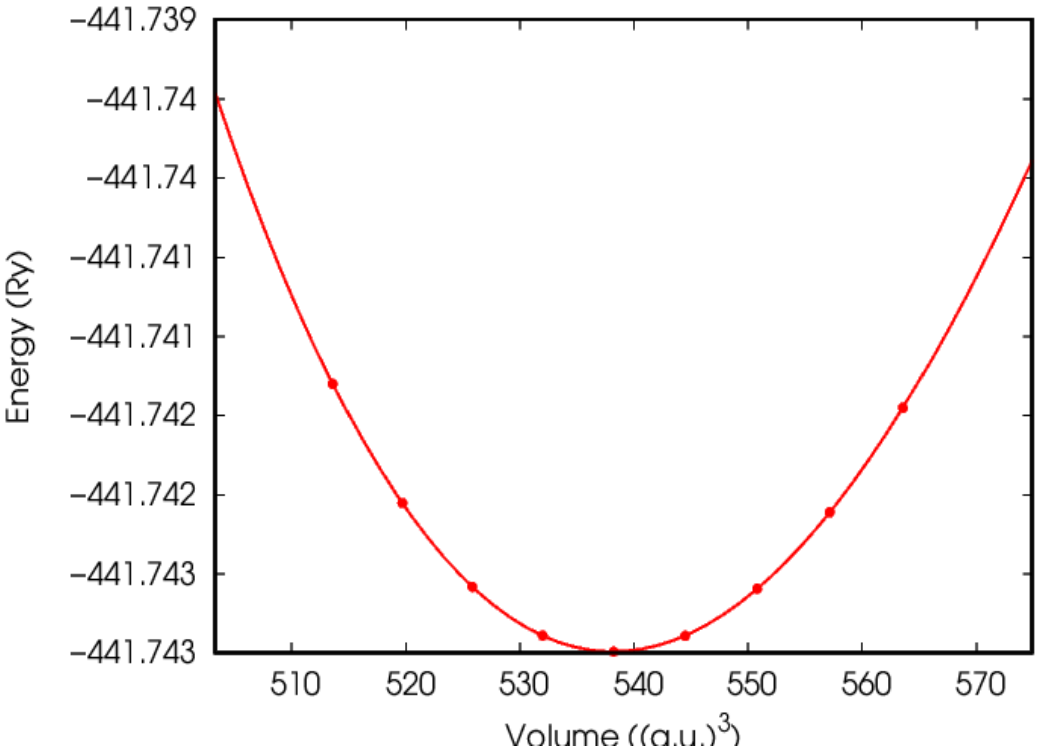

Fig. 1b. Graph of energy of Mg_2Sn against volume

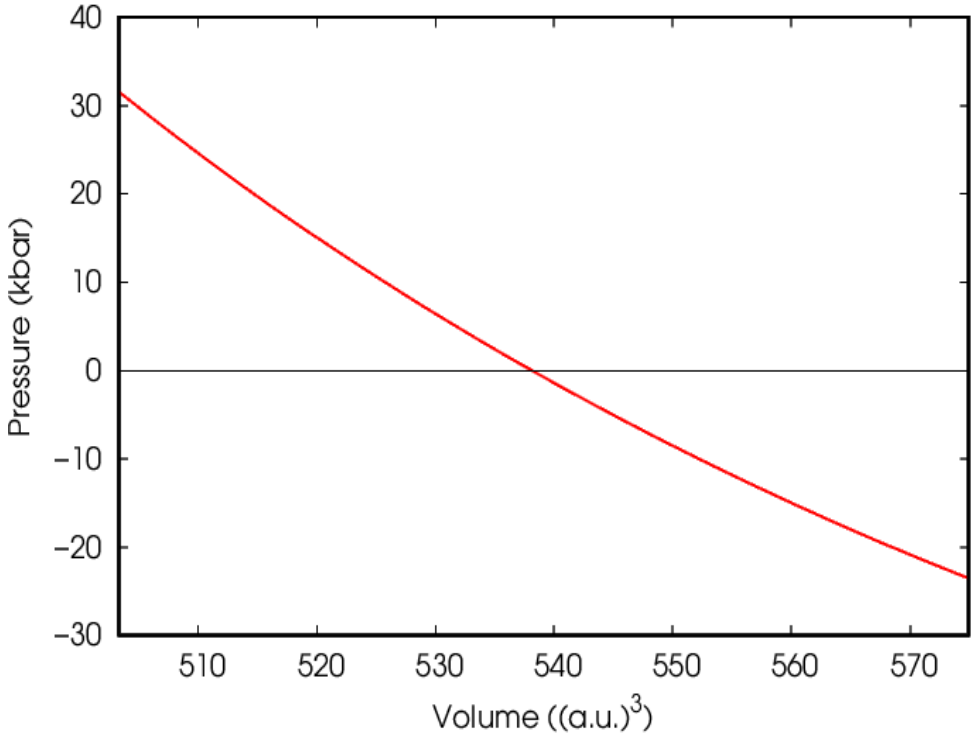

Fig. 1c. Graph of pressure of Mg_2Sn against volume

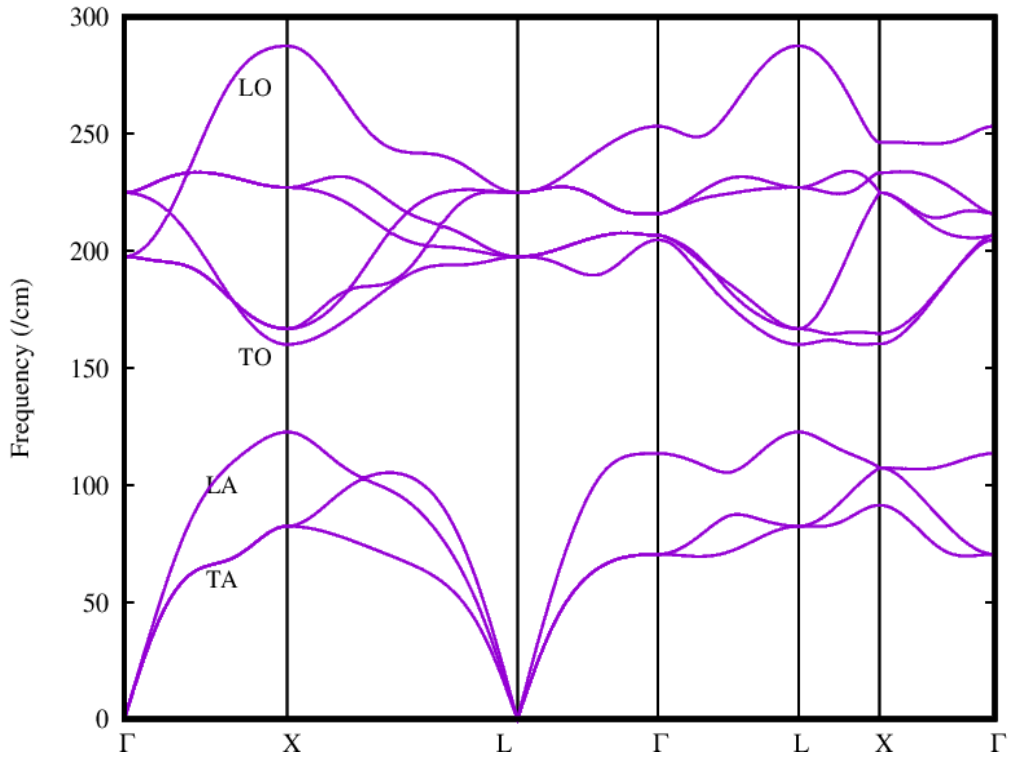

Fig. 1d. The phonon dispersion curve of Mg_2Sn

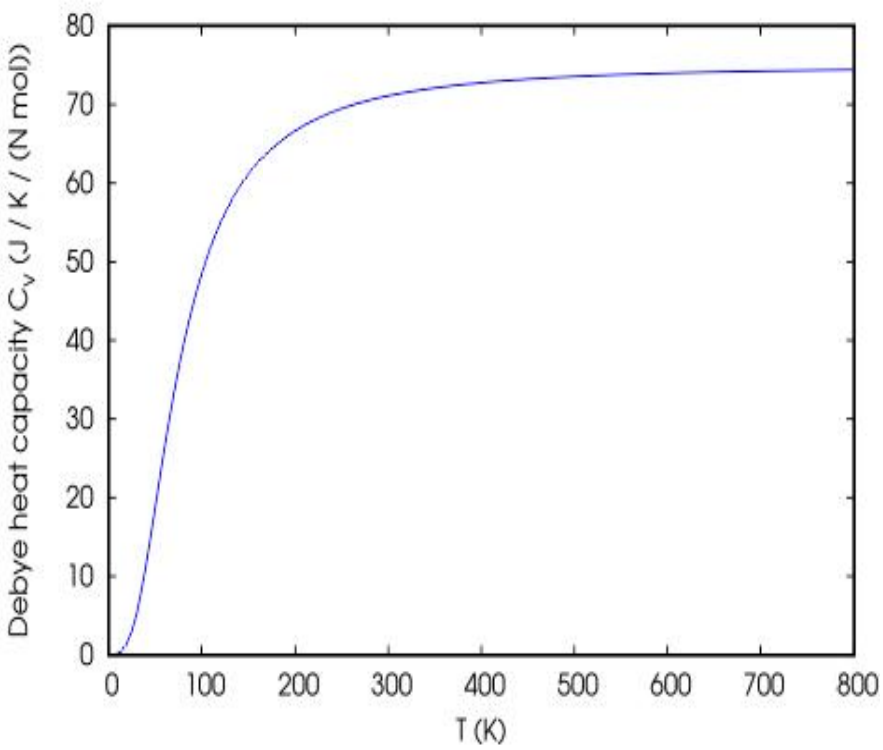

Fig. 1e. the specific heat capacity of Mg_2snin the temperature range of 0-800K

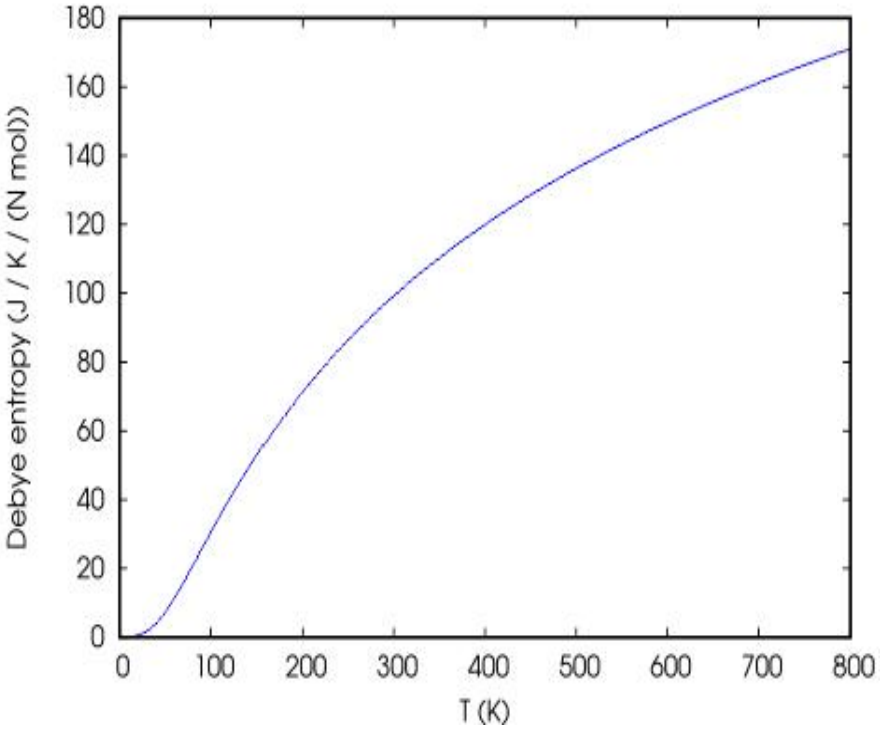

Fig. 1f. The entropy of Mg_2Snin the temperature range of 0-800K

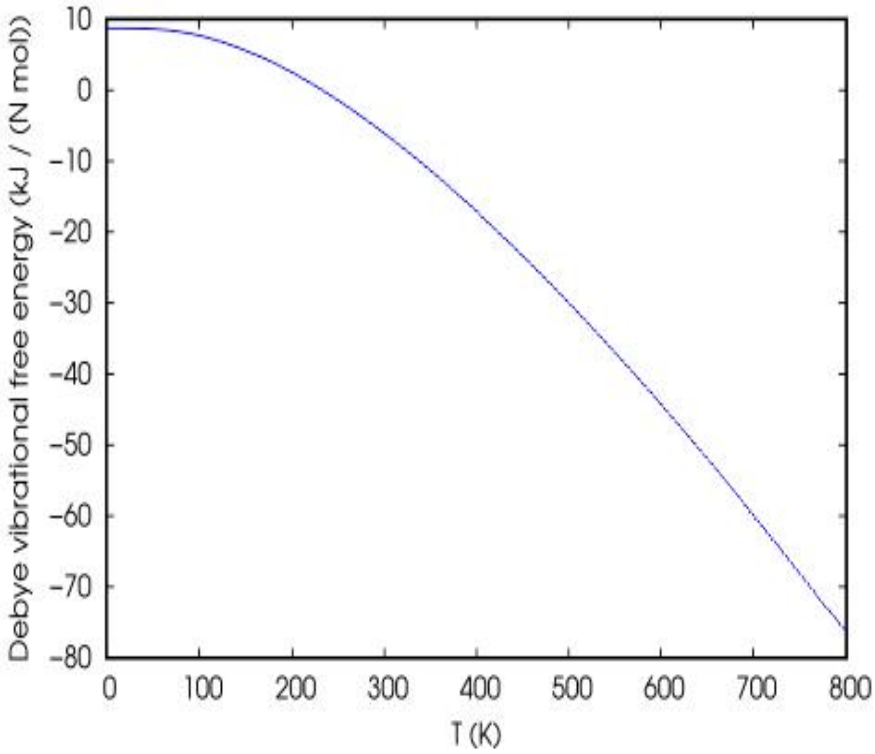

Fig. 1g. Debye free energy of Mg_2Sn in the temperature range of 0-800K

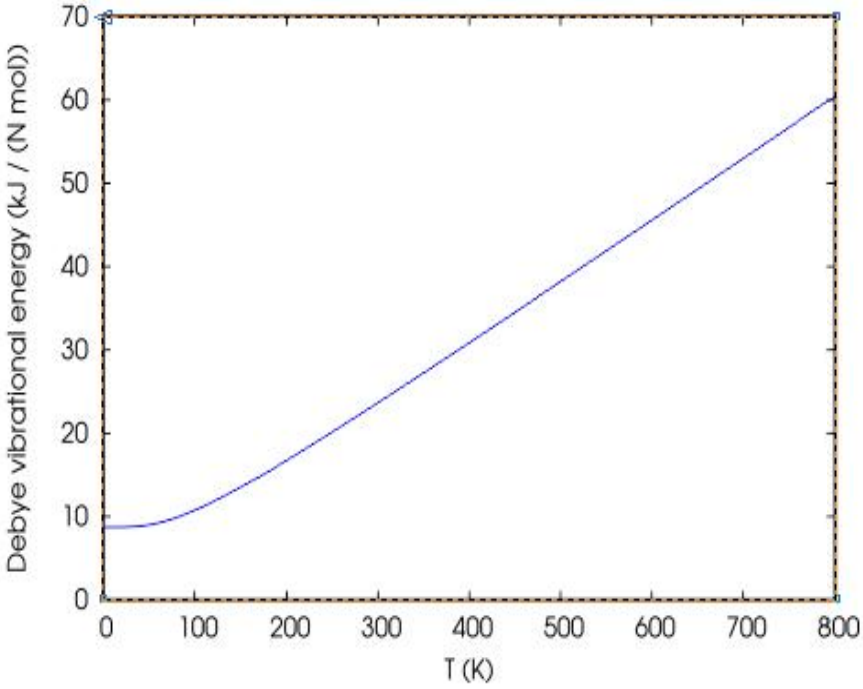

Fig. 1h. Debye vibrational energy of Mg_2Sn in the temperature range of 0-800K

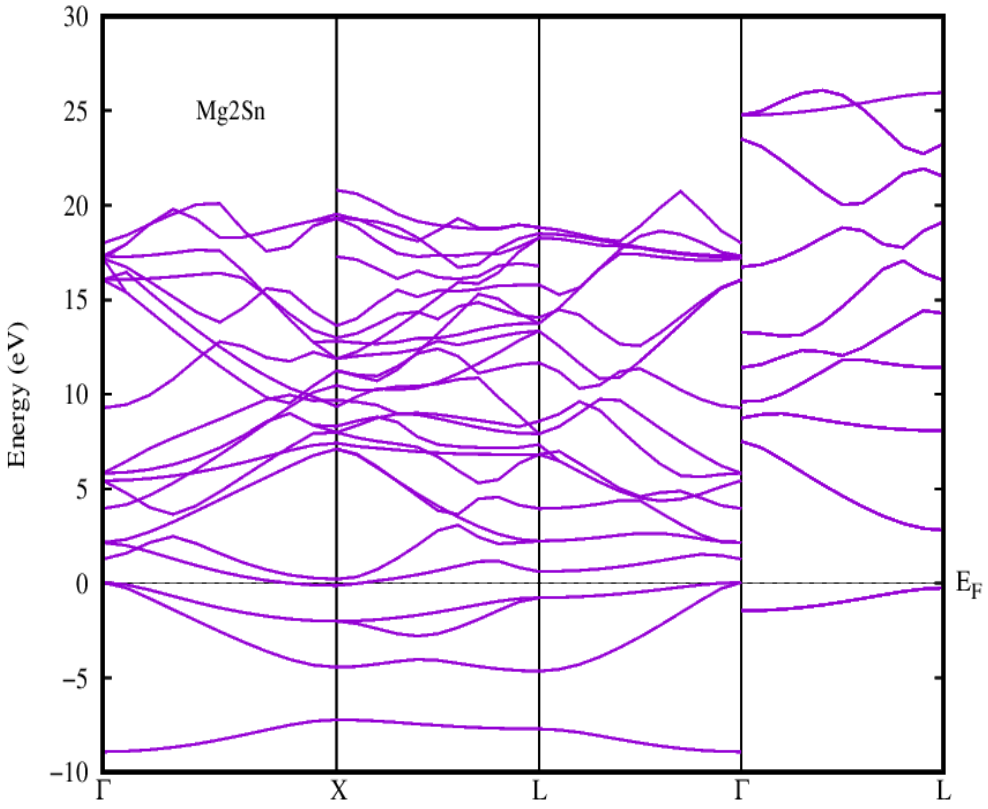

Fig. 1i. The electronic band structure of Mg_2Sn

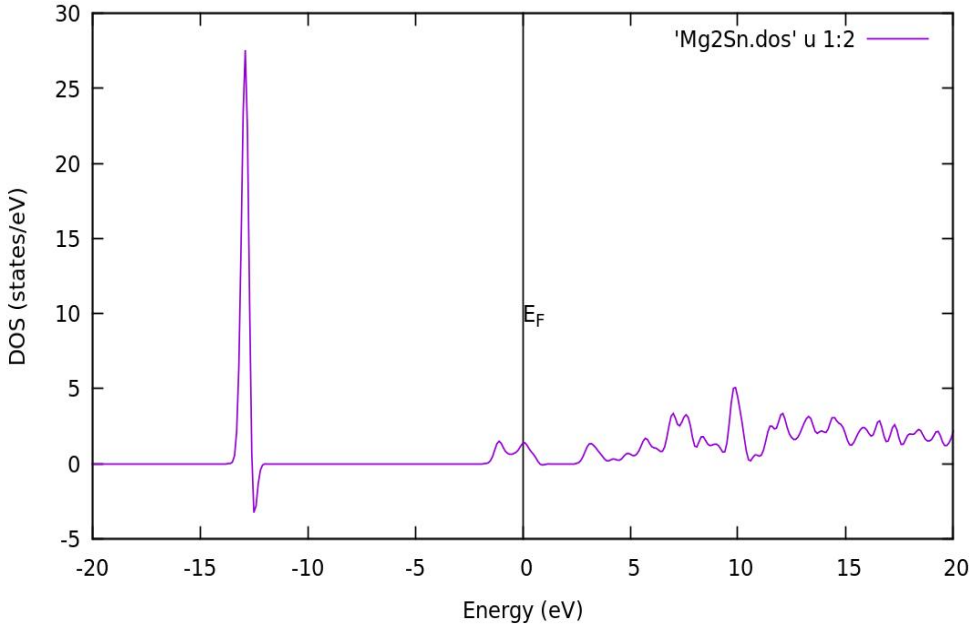

Fig. 1j. Total density of state (DOS) of Mg_2Sn

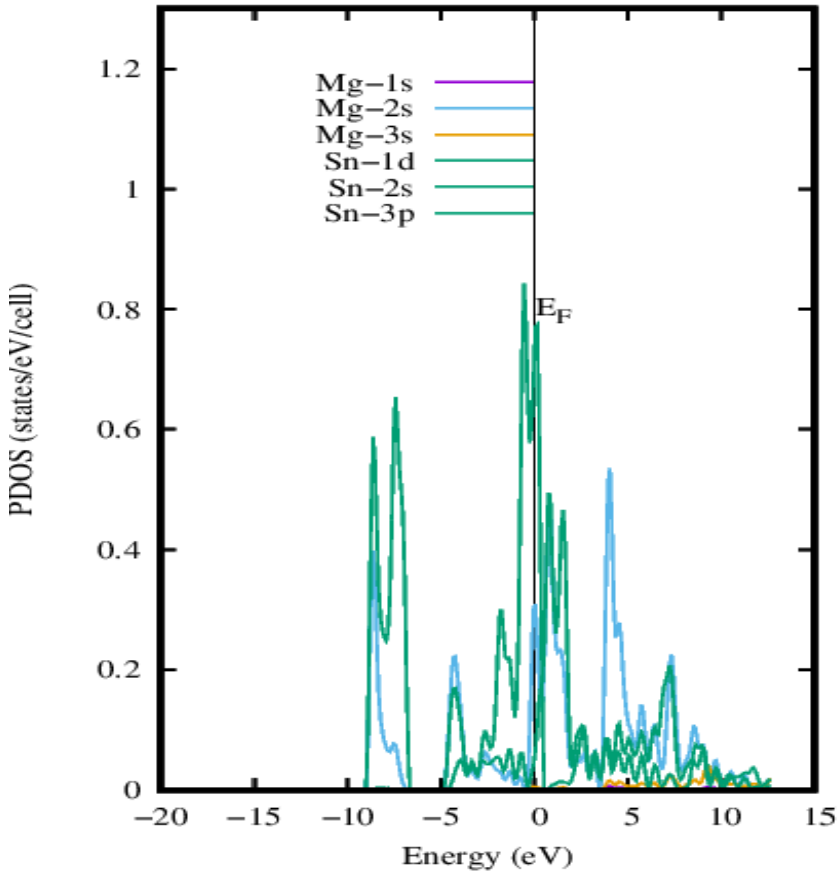

Fig. 1k. The partial density of state (PDOS) of Mg_2Sn

5. CONCLUSION

The first principle calculation using Quantum Espresso package was successfully employed to optimize the structural properties and study the mechanical, phonon, thermodynamic and electronic properties of Mg_2Sn.

The lattice parameter of the material was found to be 6.83 Å which is in good agreement with available results. Mg_2Sn was found to be mechanically stable by satisfying the well-known "Born stability criteria". The B/G ratio of the material was found to be 1.55, which shows that Mg_2Sn is brittle in nature. . The ground state properties and the elastic stiffness constants of this material are in good agreement with experimental and other results. From the phonon dispersion curve obtained in this work, the material is seen to be thermodynamically stable. The specific heat capacity and Debye temperature of Mg_2Sn was found to be 71.28J/mol and 310.5K which is in good agreement with experimental and other available results. From the electronic band structure, Mg_2Sn was found to a narrow gap semiconductor with indirect bandgap of magnitude of 0.1751eV.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
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