Electronic structure, elastic and thermodynamic properties of SnS from theoretical study

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In this work, first-principles methods based on density functional theory are used to study the structural, electronic and elastic properties of rock-salt SnS in detail. Thermodynamic properties of SnS under high temperature and high pressure were studied by using the quasi-harmonic Debye model. The results show that the optimized structural parameters are in good agreement with the experimental and other theoretical values. The band structure and density of states of SnS are obtained by calculation and analysis. Based on the quasi-harmonic Debye method, the pressure and temperature dependencies of the equilibrium volume, the bulk modulus, the Debye temperature and so on are obtained.

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1. Introduction

SnS has excellent photoelectric conversion properties, it is a kind of efficient, cheap and environmentally friendly solar photoelectric conversion material [1-3]. SnS can be used as an absorber layer for solar cells with thin films. It has the advantages of less chemical consumption and less material consumption, and the photoelectric conversion efficiency is as high as about 20% [4]. The excellent properties of SnS have attracted the attention of many people, and they have been studied by adopting different methods. Makinistian et al have used the density functional theory method to study the energy band and density of states of orthorhombic IV-VI compounds (GeS, GeSe, α -SnS and SnSe) [5]. The orthorhombic structure observed by Ehm et al. [6] was transformed into a monoclinic γ -SnS structure (P21/C) at about 18.15 GPa, and then the angular dispersion synchrotron powder diffraction could reach 38.5 GPa. Undoubtedly, all other research can only be carried out on the basis of the fundamental physical properties of known materials. However, there are many properties, such as electronic structure, elasticity, thermodynamics, etc., which are not well known in previous studies. Therefore, the main purpose of this study is to use density functional theory to calculate the structural, electronic properties, elastic and thermodynamic properties of SnS at high temperature and high pressure.

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2. Methods

In the present work, all the calculations are performed using the CASTEP code, based on the density functional theory [7]. The Vanderbilt ultrasoft pseudopotential [8] is used with the cutoff energy of 500 eV for the considered structure. The *k* point meshes of $7 \times 7 \times 7$ for cubic structure SnS is generated using the Monkhorst-Pack scheme. The electronic exchange-correlation potentials are described within the generalized gradient approximation (GGA) proposed by Perdew et al.[9].

3. Calculation results and discussion

3.1. Structural optimization

It is known that the rock-salt SnS crystal belongs to the cubic crystal structure, the space group is FM-3M, and the lattice constant is: a = b = c = 5.80 Å. We obtained the coordinates of Sn (0.5, 0.5, 0.5) and the coordinates of S (0, 0, 0) by consulting the literature. Fig. 1 illustrates the structure of SnS.



Fig. 1. The unit cell model of SnS.

By setting a series of different lattice constants, we obtain the primitive cell models of different volumes, and calculate the corresponding total energy E of the system and the original cell volume V, so as to obtain the required E-V curve, as shown in Fig 2.



Fig. 2. Relationship between total energy and volume of SnS.

Then, the Birch-Murnaghan equation of state (EOS) equation of state is used for fitting [10], and the lattice constant, bulk modulus B_0 and the first derivative of bulk modulus B_0' in equilibrium state are obtained. This equilibrium unit cell is calculated by the following equation:

$$\Delta E(V) = E - E_0 = B_0 V_0 \left[\frac{V_n}{B_0'} + \frac{1}{1 - B_0'} + \frac{V_n^{1 - B_0}}{B_0' (B_0' - 1)} \right]$$
(1)

where E_0 is the equilibrium energy of the system at 0 GPa, and the volume of the equilibrium unit cell at 0 GPa is represented by V_0 . The variation of the normalized volume V_n with the pressure *P* satisfies the following relation:

$$P = -\frac{dE}{dV} = \frac{B_0}{B'_0} [V_n^{-B'_0} - 1]$$
(2)

where B_0 and B_0 ' are the bulk modulus at zero pressure and the first derivative of the bulk modulus, respectively. The fitting results are shown in Table 1 along with the experimental and theoretical values. It can be seen from the table that our calculated SnS lattice constant a = b = c = 5.8286 Å is close to the experimental value and better than the existing theoretical value. The calculated bulk modulus B_0 of SnS is 54.25 GPa, and the first derivative of the bulk modulus is 4.4598. However, there is no other theoretical value or its experimental value to compare with.

Table 1. Calculated lattice constant a (Å), volume $V(Å^3)$, bulk modulus B (GPa) and its first pressure derivativ B' for SnS, compared to available experimental and theoretical values.

| | a (Å) | $V(\text{\AA}^3)$ | B_0 (GPa) | B_0 ' |
|----------------------|--------|-------------------|-------------|---------|
| Present work | 5.8286 | 198.013 | 54.25 | 4.4598 |
| Cal.[11] | 5.85 | 200.202 | | |
| Exp. ^[12] | 5.80 | 195.112 | | |

3.2. Electronic properties

The band structure is shown in Fig. 3, the Fermi level is located at 0 eV, where the valence band corresponds to the energy level below the Fermi level, and the part above the Fermi level corresponds to the conduction band, and the bottom of the conduction band and the top of the valence band is located at the R axis of the energy band, from which we conclude that the SnS of this structure belongs to a direct bandgap semiconductor. The calculated band gap of SnS crystal is 0.46 eV at 0 GPa.

Furthermore, by studying the band structure of SnS under different pressures, we obtain Fig. 4. Its band gap is enlarged and reaches a maximum value of 0.619 eV at a pressure of 40 GPa. We believe that this is because the interatomic spacing of the system decreases after pressurization, which increases the charge density between atoms, strengthens the mutual repulsion between electrons, increases the entire equivalent potential field, and increases the band gap.

| Present work | | | | | | | |
|---------------------|-------|-------|-------|-------|-------|--|--|
| P(GPa) | 0 | 10 | 20 | 30 | 40 | | |
| E _g (eV) | 0.460 | 0.495 | 0.457 | 0.523 | 0.619 | | |

Table 2. Band gaps of SnS under different pressures.







Fig. 4. Variation of the band gap of SnS under different pressures.

Fig. 5 shows the calculated results of the density of states (DOS), which includes the total density of states and the partial density of states of the s and p orbitals of Sn, S. We note that the lowest valence bands are calculated in the energy range from -15 eV to -10 eV, these energy bands are basically dominated by the S-3s state with a small amount of Sn-5s and Sn-5p states. The Sn-5s state is dominant in the -10 eV to -5 eV region of the central valence band. In the region near the Fermi level E_F , the S-3p state is dominated, which means that the S atom can strongly absorb electrons. The 5s and 5p states of Sn atoms also participate in the formation of these valence bands, but the density values of these states are smaller compared to the S-3p states. The conduction band is mainly composed of Sn-5p orbitals, and the S-3p states also have a certain contribution.



Fig. 5. Total density of states and partial density of states of SnS.



Fig. 6. Variation of total density of states of SnS at 0, 20, 40 GPa.

Fig. 6 shows the total density of states of SnS at different pressures. It can be seen that with the increase of pressure, due to the action of external force, the valence band and conduction band tend to widen, while the intensity decreases slightly.

3.3. Elastic properties

To gain further insight into the mechanical stability of SnS, we calculated the elastic constants (C_{11} , C_{12} , C_{44}) of SnS. If this structure is stable, according to Born's theorem, the mechanical stability of cubic crystal solid materials under isotropic pressure can be judged according to the following conditions [13]

$$C_{11} - C_{12} > 0, C_{11} > 0, C_{44} > 0 \text{ and } C_{11} + 2C_{12} > 0$$
 (3)



Fig. 7. Elastic constant of SnS as a function of pressure.

The elastic constants (0-30 GPa) of SnS under different pressures are listed in Table 3. From Table 3, we can see that the calculated elastic constants (C_{11} , C_{12} , C_{44}) of SnS are positive and satisfy the above mechanical stability criterion, which indicates that SnS crystals can exist stably under the condition of P < 30 GPa. However, we currently have no experimental or theoretical data available for comparison of elastic constants at different pressures. At the same time, according to the data, we obtain the relationship between the elastic constant and the pressure, as shown in Fig. 7. From the figure, we can find that the elastic constants C_{11} and C_{12} increase with the increase of pressure, in which C_{11} changes rapidly with the increase of pressure, while the elastic constant C_{44} changes less obviously or even decreases slightly with the increase of pressure.

Table 3. Elastic constants $C_{ij}(GPa)$, bulk modulus B(GPa), shear modulus G(GPa), Young's modulus E(GPa), B/G ratio, Poisson's ratio v and compression factor k (1/GPa) of SnS under different pressures.

| Р | C_{11} | C_{12} | C ₄₄ | В | G | Ε | B/G | v | k |
|----|----------|----------|-----------------|--------|-------|--------|-------|--------|--------|
| | | | | | | | | | |
| 0 | 136.05 | 15.18 | 20.09 | 55.47 | 31.82 | 133.01 | 1.743 | 0.1004 | 0.0180 |
| 10 | 237.66 | 24.97 | 17.07 | 95.87 | 39.24 | 232.91 | 2.443 | 0.0951 | 0.0104 |
| 20 | 327.84 | 27.84 | 13.57 | 127.84 | 44.73 | 323.48 | 2.856 | 0.0783 | 0.0078 |
| 30 | 413.73 | 31.97 | 9.65 | 159.22 | 48.85 | 409.15 | 3.260 | 0.0717 | 0.0063 |

In Table 3, we also list the elastic properties of SnS, such as bulk modulus *B*, shear modulus *G*, Young's modulus *E* and Poisson's ratio *v*, which change with the increases of pressure. The obtained bulk modulus *B* (55.47 GPa) at 0 K and 0 GPa agrees with the value given in Table 1 (54.25 GPa). It can be seen from Fig. 8 that *B*, *G*, and *E* of SnS will increase linearly with the increase of pressure under different pressures. Among them, *E* and *B* change rapidly with the increase of pressure, while *G* changes is relatively slow. In addition, we also noticed that the calculated bulk modulus *B* and Young's modulus *E* are much larger than the shear modulus *G*, which means that the shear deformation of SnS is more likely to occur. Combined with the analysis of Fig. 8, this shows that C_{11} and *B*, *E* are more sensitive to pressure changes than other elastic constants. At the same time, it can also be concluded that SnS become more and more difficult to compress with increasing pressure, which may be because SnS has a cubic crystal structure with high microscopic symmetry. Therefore, the research results show that its resistance to volume deformation is strong.



Fig. 8. B, G, E of SnS as a function of pressure.

B/G = 1.75 was evaluated as the critical value for judging material brittleness/toughness. If B/G > 1.75, the material behaves ductile; otherwise, the material becomes brittle [14]. Interestingly, from Table 3 we can see that the B/G = 1.743 of SnS at 0 GPa is slightly lower than 1.75. This indicates the brittle nature of this crystal. However, the B/G ratio increased from 1.743 to 3.26 as the pressure increased to 30 GPa, indicating that the increase in pressure caused SnS to transition from brittleness to ductility with a gradual increase in ductility.

Fig. 9 shows the variation of Poisson's ratio v and compressibility k with pressure. It can be seen that with the increase of pressure, both Poisson's ratio v and compressibility k decrease, which indicates that under high pressure, Sn ions the distance between S ions becomes smaller, and the SnS becomes more and more difficult to compress.



Fig. 9. Poisson's ratio v and compressibility k of SnS as a function of pressure.

3.4. Thermodynamic properties

When studying the thermodynamic properties of SnS, we set the temperature range to 0-1000 K and the pressure variation range to 0-20 GPa. The following calculations are performed by the GIBBS code [15].

The relationship between V/V_0 and pressure of SnS at different temperatures (V_0 is the structural parameter of zero pressure equilibrium) is shown in Fig. 10. It can be seen from the figure that as the pressure increases, the value of V/V_0 decreases continuously. At P < 5 GPa, the difference between the relative volumes is not large with the change of temperature. When P > 5GPa, the difference in V/V_0 gradually manifested at different temperatures. At the same time, at a given pressure, with increasing temperature, V/V_0 decreases very little; while at constant temperature, V/V_0 decreases almost linearly with the increase of pressure, which indicates that when the pressure is increased, V/V_0 decreases almost linearly. SnS is more easily compressed than at elevated temperatures.



Fig. 10. Relationship between V/V_0 and pressure of SnS at different temperatures.



Fig. 11. V_0 as a function of temperature T at P = 0 GPa (a) and V as a function of pressure at T = 0, 200, 400, 600, 800 and 1000 K (b).

Fig. 11 The transition of the equilibrium volume V_0 with the temperature *T* at zero pressure and the change of the volume *V* with the pressure *P* at different temperatures. As shown in Fig. 11(a), at zero pressure, when T > 100 K, the equilibrium volume of the crystal increases rapidly. While in Fig. 11(b), at different temperatures, the volume *V* decreases almost linearly with the increase of pressure. From this, we can conclude that the crystal volume is more susceptible to pressure changes than to temperature changes.

As shown in Fig. 12(a), the bulk modulus B increases almost linearly with the increase of pressure at different temperatures.



Fig. 12. Relationship between B, P and T of SnS.

By observing Fig.12(b), it is known that the bulk modulus of SnS are 54.30 GPa, 53.48 GPa, and 34.17 GPa at zero pressure when the temperature is 0 K, 100 K, and 1000 K, respectively. When, the bulk modulus changes slowly, but it decreases significantly at high temperature, which also shows that the hardness of SnS is greatly reduced at high temperature. The comprehensive analysis shows that the bulk modulus of SnS is greatly affected by the pressure, and the hardness of SnS will decrease significantly in the high temperature range.

Table 4 is the entropy S, Debye temperature Θ and heat capacity C_v of SnS crystal obtained at different temperatures and pressures. It can be seen that when the pressure is constant, as the temperature increases, S and C_v also become larger, and then become smaller; when the temperature remains unchanged, as the pressure increases, they become larger, while S and C_v become smaller. Moreover, with the increase of pressure, S changes faster at low temperature than at high temperature, and rises faster with the change of pressure, which also increases the stiffness of the crystal.

| T/K | | P/GPa | | | | |
|-----|----------------|--------|--------|--------|--------|--------|
| | | 0 | 5 | 10 | 15 | 20 |
| 100 | S | 23.77 | 18.76 | 15.70 | 13.60 | 12.04 |
| | Θ | 279.82 | 325.90 | 361.47 | 390.87 | 416.08 |
| | C _v | 34.74 | 30.92 | 28.06 | 25.78 | 23.92 |
| 300 | S | 72.26 | 64.48 | 59.42 | 55.69 | 52.76 |
| | Θ | 272.90 | 321.39 | 358.11 | 388.18 | 413.89 |
| | C _v | 47.88 | 47.14 | 46.51 | 45.95 | 45.44 |
| 500 | S | 98.60 | 89.90 | 84.36 | 80.30 | 77.11 |
| | Θ | 264.66 | 316.02 | 354.02 | 384.90 | 411.12 |
| | $C_{ m v}$ | 49.20 | 48.90 | 48.66 | 48.44 | 48.24 |
| 700 | S | 116.96 | 107.35 | 101.44 | 97.18 | 93.84 |
| | Θ | 255.48 | 310.28 | 349.75 | 381.42 | 408.21 |
| | $C_{ m v}$ | 49.56 | 49.400 | 49.27 | 49.15 | 49.05 |
| 900 | S | 131.53 | 120.77 | 114.50 | 110.04 | 106.57 |
| | Θ | 244.94 | 304.20 | 345.22 | 377.81 | 405.24 |
| | $C_{ m v}$ | 49.70 | 49.60 | 49.52 | 49.45 | 49.39 |

Table 4. Entropy S ($J \cdot mol^{-1}K^{-1}$), Debye temperature Θ (K) and heat capacity C_v ($J \cdot mol^{-1}K^{-1}$) of SnS at different temperatures and pressures.



Fig. 13. Variation of heat capacity C_v and C_p with temperature under different pressures.

Fig. 13 shows the thermal capacity C_v and C_p of SnS as a function of temperature at different pressures. It can be seen that C_v and C_p are very similar in the low temperature region, where when P = 0 GPa, T = 100 K, C_v and C_p are 34.74 and 35.06 J.mol⁻¹K⁻¹, respectively. And they all increase sharply with the increase of temperature at low temperature, which is in line with Debye's law. But the difference is that the C_P also increases slightly at high temperature, while the C_V converges to the Dulong-Petit limit. As the pressure increases, C_p gradually decreases and C_V tends to be constant. This shows that under high pressure and high temperature, the effect of pressure and temperature on C_P is weak, and the effect on C_V is even smaller.

4. Conclusions

In summary, we have presented a theoretical study of the structural, elastic and thermal properties of SnS using GGA-PBE and quasi-harmonic Debye model. Our theoretical results of lattice constant is found to be in good agreement with experimental data. Through calculations, the elastic constants, bulk modulus, shear modulus, Young Modulus, Poisson's ratio, B/G of SnS are also calculated for the first time. The analyses on the band structure and the density of states reveal that SnS a direct bandgap semiconductor. Through the quasi-harmonic Debye method, the pressure and temperature dependences of the equilibrium volume, the bulk modulus, the Debye temperature and so on are obtained. The results show that pressure and temperature have significant effects on these thermal properties.

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