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THE STRUCTURAL, MECHANICAL AND THERMODYNAMICAL PROPERTIES OF Cu_2MnSnS_4: A FIRST-PRINCIPLES STUDY

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First-principle calculations of structural, elastic and thermal properties of Cu_2MnSnS_4 compound is performed in the framework of the Density Functional Theory. The lattice constant, mulliken population analysis and ground state energy are calculated. Based on the calculated results, it is found that the bonds between S atoms and other three atoms (Cu, Mn, Sn) exhibit the feature of covalent bond. Also, elastic properties of the compound including bulk modulus B, shear modulus G, Young's modulus E and Poisson's ratio ν are calculated. The results reveal that Cu_2MnSnS_4 is mechanically a ductile and anisotropic. The thermodynamical properties such as heat capacity, Debye temperature and entropy were calculated employing the quasi-harmonic Debye model at different temperatures (0-1000K) and pressures (0-40GPa) using the quasi-harmonic Debye model for the first-time.

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1. Introduction

In recent years, in order to deal with the increasing serious energy crisis and environmental pollution, research on new materials is of pressing need and of great significance. Quaternary semiconducting compounds of the I_2-II-IV-VI_4 type, where I = Cu, Ag, II = Zn, Cd, Hg, Mn, Fe or Co, IV = Si, Ge, Sn or Pb and VI = S, Se or Te, have been investigated by different groups [1-3] because of their attractive semiconducting properties and potential applications in thin film solar cells. Cu_2MnSnS_4 (CMTS) belonging to Cu-based quaternary chalcogenide semiconductor, it has direct band gap energy of between 1.0 eV and 1.4 eV, a large absorption coefficient of over 10^4 cm^{-1}, which is regarded as one of the promising absorber materials [4-6].

The crystallographic parameter values of the Cu_2MnSnS_4 have been reported by using the melt and anneal technique and X-ray powder diffraction measurements [7, 8], respectively. The magnetic behavior of various I_2-(Mn,Fe,Co)-IV-VI_4 have been measured[9-11]. The crystallography structure of Cu_2MnSnS_4 was a stannite with space group $I\bar{4}2m$ (No. 121) [12, 13]. As reported by several authors, the CMTS compound has a suitable band gap. Liang et al. reported a value close to 1.1 eV for CMTS [6], but Cui et al also reported the value around 1.3 eV [14]. The band gap of the Cu_2MnSnS_4 thin film is about 1.29 eV determined by the UV-vis-NIR absorption spectra measurement, which indicates it has potential applications in solar cells [15]. However, the available information related to structural, mechanical and thermal properties for the Cu_2MnSnS_4 compound is very scarce. The knowledgement of the crystallographic parameters as well as mulliken population

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analysis are important to study their basic crystal properties.

In this work, we have investigated the structural, elastic and thermodynamical properties of Cu_2MnSnS_4 compound using density function theory. The present work helps in further understanding of the basic properties, compensates the lack of theoretical data for Cu_2MnSnS_4 compound and also provides reference data for the future experimental and theoretical work on these intermetallic compounds.

2. Calculations method

In this paper, all the results of Cu_2MnSnS_4 crystal were obtained by using a plane-wave basis set for the electronic wave functions and periodic boundary conditions, as implemented in the CASTEP package. The exchange-correlation energy is evaluated in the generalized gradient approximation (GGA) Perdew-Burke-Ernerhof (PBE) functional [16-19]. The calculations were performed following the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique. The interaction between the valence electrons and the core-electrons is described by ultra-soft pseudo-potentials. In order to satisfy the calculation accuracy and ensure the calculation speed, the plane wave cut off energy is 440eV, and the whole Brillouin zone is calculated by the K point grid of 5×5×5. Convergence shows that the brillouin zone sampling and the kinetic energy cut-off are sufficient for crystal optimization.

The thermodynamic properties are studied within the quasi-harmonic Debye model implemented in the Gibbs program [20-23]. We use the density function theory to calculate the total energy (E) of crystal for a grid of volume of the unit cell(V) at T = 0 K, P = 0 GPa. The final optimal curve of total energy is obtained by minimizing the energy verses volume by Birch–Murnaghan equation of state [24]. Using this, the thermodynamic properties such as the bulk modulus, specific heats, and Debye temperature at non-zero temperature and pressure are calculated.

3. Result and discussion

3.1. structure and elastic properties

The structure was solved in the space group $I\bar{4}2m$ (No.121), which describes the structure of the compound Cu_2MnSnS_4 (Fig.1). The Fig.1 shows the unit cell of the studied phase. This structure is based on a stannite-type arrangement of sulfur and metal atoms, in which each cation is tetrahedrally coordinated to four atoms of sulfur. In order to investigate the ground-state properties of Cu_2MnSnS_4 alloy, the geometry optimizations are performed first with full relaxation of the cell shape and atomic positions. The results of first-principles calculations of the structural properties of the compound are presents in Table 1, together with the available experimental values [8，25-27]. The comparison shows that our results are in reasonable agreement with experimental values. Pseudo-atomic valence states had been set as Cu-$3d^{10}4s^1$, Mn-$3d^5 4s^2$, Sn-$5p^2$, S-$3p^4$.

To analyze the chemical bonding information, the mulliken population analysis of Cu_2MnSnS_4 crystal is shown in Table 1. One can see from Table 1, the Cu atom and S atom got the charges, the Mn atom and Sn atom lost the charges at the same time when the structure was in the process of optimization. By mulliken population's analysis, the interaction between S atoms and Mn atoms is stronger than the other two interactions(S-Cu and S-Sn). In the case of Cu_2MnSnS_4, the bonds between S atoms and other three atoms exhibit the feature of covalent bond. The bond length increases with the rising of atomic number, the situation is similar to that of ternary semiconductors [28].

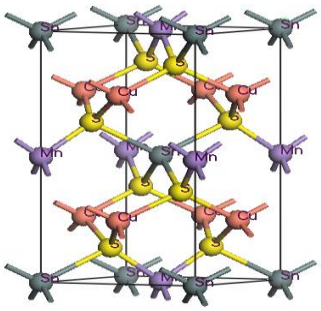

Fig.1.Unit cell of the Cu_2MnSnS_4 phase.

Table1. Lattice constants and Mulliken population analysis of Cu_2MnSnS_4 crystal.

Lattice constants/Å			Calculated value			Experimental value		
a			5.627			5.518[8], 5.458[25],5.49[26],5.514[27],		
c			10.659			10.807[8], 10.827[25],10.82[26],10.789[27],		
Atom	s	p	d	Total	Charge/e	bond	Population	Bond length/ Å
Cu	0.64	0.65	9.76	11.05	-0.05	S-Cu	0.41	2.328
Mn	0.38	0.5	6.03	6.91	0.09	S-Mn	0.63	2.169
Sn	1.44	1.55	0.00	2.99	0.99	S-Sn	0.02	2.676
S	1.83	4.42	0.00	6.25	-0.25			

3.2. Mechanical properties

The Poisson ratio (ν), elastic constants C_{ij}(GPa), bulk modulus (B) and other mechanical parameters have been calculated and simulated by using GGA-PBE method are listed in Table 2. The elastic constants of stannite structure have C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66} six independent components. If the stannite structure is mechanically stable, the above six components must obey the Born stability criteria[28-31]:$C_{11}>0$, $C_{33}>0$, $C_{44}>0$, $C_{66}>0$, $(C_{11}-C_{12})>0$, $(C_{11}C_{33}-C_{13}^2)>0$, and $[(C_{11}+C_{12})C_{33}- 2C_{13}^2]>0$. As shown in Table 2, all of the elastic constants for the compound satisfies these criteria mentioned above, indicating that these compounds are mechanically stable.

All these stannites studied are more resistive to volume compression than to shear due to $B_H > G_H$. Considering that a solid with a larger B_H/G_H (> 1.75) and ν(> 0.26) values is ductile, otherwise it is brittle[30,32]. As seen from the results, the values of B_H/G_H ratio for Cu_2MnSnS_4 compounds are larger than the critical value (1.75), thus indicating this semiconductor is ductile. In addition, Zener's anisotropy index $A = 2C_{44}/(C_{11} - C_{12})$=1.77[30] is studied. For isotropic case $A = 1$, while the deviations from unity measure the degree of elastic anisotropy. Our results show that the compound under consideration is highly anisotropic.

Table 2. Calculated mechanical parameters of Cu_2MnSnS_4 compound

Elastic stiffness constants C_{ij}(GPa)	C_{11}	89.557	Young modulus (GPa)	*X*	42.545
	C_{12}	59.523		*Y*	42.545
	C_{13}	54.289		*Z*	37.856
	C_{33}	77.396	Poisson ratios	*Exy*	0.4165
	C_{44}	26.643		*Exz*	0.4093
	C_{66}	34.743		*Eyx*	0.4165
Bulk modulus (GPa)	Voigt	65.856		*Eyz*	0.4093
	Reuss	65.081		*Ezx*	0.3642
	Hill	65.469		*Ezy*	0.3642
Shear modulus(GPa)	Voigt	23.500	Lame lambda(GPa)	Voigt	50.190
	Reuss	20.794		Reuss	51.219
	Hill	22.147		Hill	50.704
Universal anisotropy index		0.663	Compressibility(GPa^{-1})		0.015

3.3. Thermodynamic properties

The thermal properties of a crystal determine the suitable conditions for initiating and maintaining the quality of crystal growth. Through the quasi-harmonic Debye model, we have investigated the thermal properties of the Cu_2MnSnS_4 over a range of pressures from 0GPa to 40GPa and a range of temperatures from 0K to 1000K.

As very important parameters, the heat capacities of a substance not only provide essential insight into the vibrational properties but are also mandatory for many applications. Our calculation of the heat capacities C_p and C_v of Cu_2MnSnS_{42} versus temperature at different pressures (0GPa and 40GPa) are shown in the following Fig.2. The heat capacity C_v [33] can be written in the form of

$$C_v = 3nk\left[4D\left(\frac{\theta}{T}\right) - \frac{3\theta T}{e^{\frac{\theta}{T}} - 1}\right]$$

where *n* is the number of atoms per unit, $D(\theta/T)$ represents the Debye integral. From the figure, the heat capacities increase with increasing temperature, because phonon thermal softening occurs when the temperature increases. The constant volume heat capacity C_v and the constant pressure capacity C_p are very similar in appearance and both of them are proportional to T^3 at low temperatures. At high temperatures, the heat capacity tends to the Petit and Dulong limit, which is a common feature for all solids at high temperature This results show that the interactions between ions in the nano-laminates have great effect on heat capacities especially at low temperature. From Fig. 2 it is clear that when T< 400 K, the heat capacity (C_v) depends on both temperature and pressure, whereas at high temperatures, C_v approaches approximately 99.55 J mol^{-1} K^{-1}.

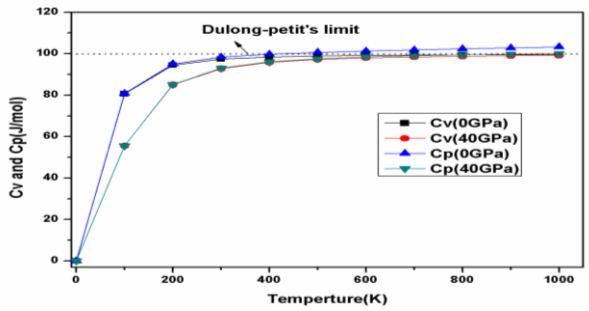

Fig. 2. Heat capacity of Cu_2MnSnS_4 versus temperature under different pressure

The entropy(S) of Cu_2MnSnS_4 versus temperature and pressure are shown in Fig.3 (a). The entropies are variable by power exponent with increasing temperature. The $\theta_D(k)$ is related to heat capacity, melting temperature and the thermal vibration frequency of a solid. The variation of the Debye temperature $\theta_D(k)$ as a function of pressure and temperature illustrated by our results is displayed in Fig. 3 (b). We observe that $\theta_D(k)$ decreases non-linearly with increasing temperature for Cu_2MnSnS_4. The variation of $\theta_D(k)$ with temperature and pressure reflects the fact that the thermal vibration frequency of the atoms in Cu_2MnSnS_4 changes slowly with temperature but changes rapidly with pressure.

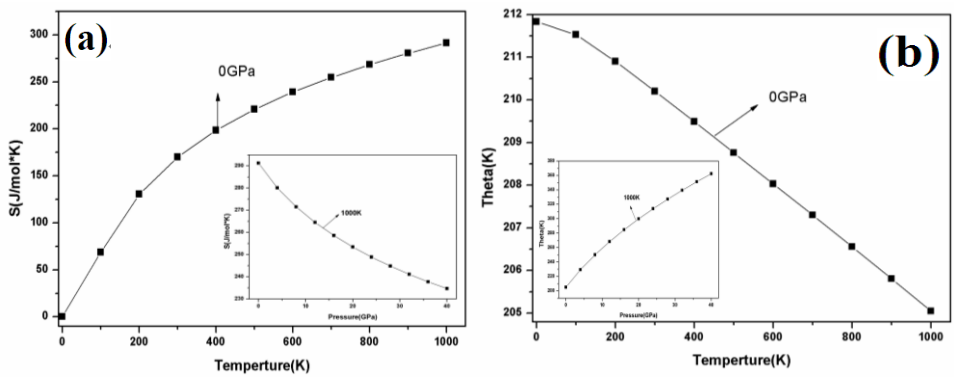

Fig.3 The entropy (a) and Debye temperature (b) versus temperature and pressure

4. Conclusions

Owing to the lack of reported values of the elastic and thermal properties of Cu_2MnSnS_4. The parameters of the basic properties of Cu_2MnSnS_4 crystal have been calculated by using the plane wave pseudo-potential density functional theory as well as quasi-harmonic Debye model. The calculated lattice constants (*a, c*) have been discussed which are in good agreement with the experimental data. Furthermore, the Zener's anisotropy index A and B_H/G_H are studied, which indicate Cu_2MnSnS_4 is a anisotropic and ductile material.

The first-time results on temperature and pressure dependence Debye temperature, entropy and heat capacities are obtained and discussed. The results indicated: the heat capacity (C_v) decreased

with the pressure increasing at same temperature, while increase with temperature increasing under the same pressure. In addition, the thermal expansion coefficient increases exponentially with the temperature up to 400K.

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References

[1] H Katagiri, K. Jimbo, W.S Maw, K. Oishi, M.Yamazaki, H. Araki, A.Takeuchi. Thin. Solid. Films. **517**, 2455 (2009)
[2] Y.Shapira, E.J McNiff, N.F Oliveira, E.D Honig, K. Dwight, A.Wold, Phys. Rev. B **37**, 411(1988)
[3] G.H McCabe, T.Fries, M.T Liu, Y.Shapira, L.R Ram-Mohan, R.Kershaw, A.Wold, C.Fau, M. Averous, E.J McNiff. Phys. Rev. B **56**, 6673 (1997)
[4] M. Quintero, E. Moreno, S. Alvarez, J. Marquina, C. Rinc´on, E. Qunitero, P. Grima, J. A. Heano , M. A. Mac´ıas, Rev. LatinAm. Metal. Mat. **34**, 28 (2014)
[5] L. Chen, H. Deng, J. Tao, W. Zhou, L. Sun, F. Yue, P. Yang , J. Chu, J. Alloys Compd. **640**, 23 (2015)
[6] X. Liang, P. Guo, G. Wang, R. Deng, D. Pan ,X. Wei, RSC Adv. **2**, 5044 (2012)
[7] A.M Lamarche, A.Willsher, L.Chen, G. Lamarche, J.C Woolley, J. Solid State Chem. **94**, 313 (1991)
[8] M. A Macias, M.Quintero, E.Moreno, Revista Latinoamericana De Metalurgia Y Materiales **34**,1 (2014)
[9] L.Guen, W. S Glaunsinger, .J. Solid State Chem. **35**(1), 10 (1980)
[10] X. L Chen, A. M Lamarche, G.Lamarche, J. Magn. Magn. Mater. **118**(1–2).119(1993)
[11] E.Quintero, M.Quintero, E.Moreno, L.Lara, M.Morocoima, F.Pineda, P.Grima, R.Tovar, P.Bocaranda, J.A Henao, M.A Macías, J. Phys.Chem. Solids **71**,993 (2010)
[12] F.López-Vergara, A.Galdámez, V.Manríquez, J.Solid. State. Chem. **198**,386 (2013)
[13] T.Bernert, A.Pfitzner, Zeitschrift Für Kristallographie **220**(11), 968 (2009)
[14] Y. Cui, R. Deng, G. Wang, D. Pan, J. Mater. Chem. **22**, 23136 (2012)
[15] L. L Chen, H. M Deng, K. Z Zhang, Mater. Sci. Forum **814**,39 (2015)
[16] P. P.John, B.Kieron, E. Matthias, Phys. Rev. Lett. **77**(18), 3865(1996)
[17] L. Guo, G. Hu, W.J. Feng, S.T. Zhang, Acta Phys.-Chim.Sin. **29**(5), 929(2013)
[18] J.H. Yuan, B. Gao, W.Wang, J. F. Wang, Acta Phys. Chim.Sin. **31**(7), 1302(2015)
[19] Y.J Dong, Y.L Gao, chalcogenide letters, **13**(11), 515(2016)
[20] M. A Blanco, E.Francisco, V. Lua˜na, Comput. Phys. Commun.**158,** 57 (2004)
[21] M. A Blanco, A. M Penda's, E.Francisco, J. M Recio, R.Franco, J. Mol. Struct. Theochem. **368**, 245(1996)
[22] M.Fl´orez, J .M Recio, E.Francisco, M. A Blanco, A. M Pend´as, Phys. Rev.

B **66,** 144112(2002)
[23] E.Francisco, J. M Recio, M. A Blanco, A. M Pend´as J. Phys. Chem. **102,** 1595(1998)
[24] F. Birch, J. Geophys. Res. **83** 1257(1978)
[25] F.López-Vergara, A.Galdámez, V. Manríquez, Phys. Stat. Solidi. **251**(5), 958(2014)
[26] X. Wang ,X. Gu , H. Guan , F. Yu. Chalcogenide Letters **12**(3), 99(2015)
[27] T. Fries, Y. Shapira, F. Palacio, M. C. Mor´on, G. J.McIntyre, R. Kershaw, A. Wold, E. J. McNiff Jr., Phys. Rev. B **56**, 5624(1997)
[28] Y.J. Dong, Y.L. Gao. J. Yunnan Normal University, **36**(5), 14(2016)
[29] M. Born, K. Huang, Clarendon Press, Oxford, (1954)
[30] S. Yip, J. Li, M. Tang, J.Wang, Mater.Sci.Eng., **A317(1–2)** 236 (2001)
[31] J.Wang, S. Yip, S. R Phillpot, D. Wolf, Phys.Rev.Lett. **71** 4182 (1993)
[32] M. V Schilfgarde, N.Newman, T.J Peshek, Photo Spec Confer. IEEE 001297 (2009)