Theoretical calculations of structural, electronic, and elastic properties of $CdSe_{1-x}Te_x$: A first principles study

M Shakil[1,†], Muhammad Zafar[2], Shabbir Ahmed[2], Muhammad Raza-ur-rehman Hashmi[2], M A Choudhary[2], and T Iqbal[1]

[1] *Department of Physics, Hafiz Hayat Campus, University of Gujrat, Gujrat* 50700, *Pakistan*
[2] *Simulation Laboratory, Department of Physics, the Islamia University of Bahawalpur, Bahawalpur* 63100, *Pakistan*

(Received 17 January 2016; revised manuscript received 6 April 2016; published online 9 June 2016)

The plane wave pseudo-potential method was used to investigate the structural, electronic, and elastic properties of $CdSe_{1-x}Te_x$ in the zinc blende phase. It is observed that the electronic properties are improved considerably by using LDA + U as compared to the LDA approach. The calculated lattice constants and bulk moduli are also comparable to the experimental results. The cohesive energies for pure CdSe and CdTe binary and their mixed alloys are calculated. The second-order elastic constants are also calculated by the Lagrangian theory of elasticity. The elastic properties show that the studied material has a ductile nature.

Keywords: first principles calculations, density functional theory, II–VI semiconductors, structural, electronic, and elastic properties

PACS: 61.72.uj, 73.20.At, 62.20.de **DOI:** 10.1088/1674-1056/25/7/076104

1. Introduction

One of the basic features of the solar cell is its ability to absorb effectively a wide spectrum of photons contained in the solar radiation. This feature depends on the intrinsic optical and electronic properties of the semiconductor material, and one critical parameter is the energy band gap. The II–VI chalcogenides and their mixed ternary alloys show semiconducting properties.[1,2] These chalcogens and their alloys are especially suitable for the conversion of solar energy to electrical energy in photovoltaic or photo electrochemical devices. For a selected composition range of the solid solution of CdSe and CdTe, the band-gap and lattice parameters can be changed by altering the relative amount of chalcogenides in the $CdSe_xTe_{1-x}$ compound. For thin films of $CdSe_{1-x}Te_x$, the crystal structure and band-gap can be adjusted by changing the concentrations of Se and Te. The band gap of this material can be varied from 1.39 eV to 1.72 eV by appropriately adjusting the atomic composition (x) from 0 to 1.[3] This range of band gap is important for photovoltaic conversion, because the ideal band gap for the solar cell is 1.4 eV. Therefore $CdSe_{1-x}Te_x$ ternary thin films are widely used in solar cells,[4,5] solar control, and photovoltaic applications.[6,7] They can also be used for the photo-assisted decomposition of water,[8] etc. Normally, CdSe and CdTe exhibit hexagonal wurtzite and cubic zinc blende (ZB) structures, respectively. A structural phase transition is expected in the $CdSe_{1-x}Te_x$ pseudo-binary system as a function of the composition. A number of investigations have reported that these films do not have a single phase over the entire composition range and the presence of either the cubic or hexagonal phase depends on the proportion of selenium and tellurium in the pseudo-binary system. Murali and Jayasutha reported the hexagonal phase for the $CdSe_{1-x}Te_x$ films deposited on a substrate by brush plating at different temperatures.[9] However, a few experimental results were inconsistent with the above discussed results. Uthanna and Reddy,[10] Mangalhara *et al.*,[11] and Islam *et al.*[12] have observed the presence of only the cubic phase in the $CdSe_{1-x}Te_x$ films over the entire composition range.

A large number of theoretical and experimental results[1–12] have been reported for $CdSe_{1-x}Te_x$. However, all the studies focused on pure CdSe and CdTe. In this study, the electronic properties of ternary alloys (i.e. $CdSe_{1-x}Te_x$) are calculated by the LDA+U approach based on density functional theory (DFT) and the elastic properties are reported for the first time. It is envisaged that the elastic properties have significant influences on the devices.

2. Computational details

To simulate the various physical properties of $CdSe_{1-x}Te_x$ alloys, we employed the plane wave pseudo potential method to solve the Kohn–Sham equations. The well known and versatile DFT based Quantum ESPRESSO code[13] was used to study the properties within the framework of DFT[14] and this method produces consistent results for the physical properties of different materials. For the exchange–correlation (XC) potential, the local density approximation (LDA)[15] of Perdew and Zunger (pz)[16] was applied. The ultrasoft pseudo-potential (USPP) was used to describe the interaction between the ionic cores and the valance electrons. Plane waves with a cutoff energy of 30 Ry were used to characterize

†Corresponding author. E-mail: shakil101@yahoo.com; m.shakil@uog.edu.pk

© 2016 Chinese Physical Society and IOP Publishing Ltd

the electronic wave functions, and the Brillouin zone integrations were performed using an $8 \times 8 \times 8$ Monkhorst–Pack[17] grid of k-point mesh. In the present study, $CdSe_{1-x}Te_x$ was modeled at various compositions with a step of 0.25 using eight atoms per unit cell. A partial substitution of an element by another in a compound can cause drastic changes in the physical properties of the parent material. In this study, CdSe is the parent material and Se is partially substituted by Te. The total energy for each concentration was calculated and it was found that CdSe and CdTe are more stable in the zinc-blende structure. The equilibrium lattice parameters and bulk modulli of $CdSe_{1-x}Te_x$ were obtained by calculating the total energy at different lattice constants and fitting the data to Murnaghan's equation of states. As LDA and GGA both calculated a very small energy gap, a Hubbard U correction[18] was incorporated with LDA for the determination of the electronic band structure of $CdSe_{1-x}Te_x$. The elastic constants and moduli were calculated by the Lagrangian theory of elasticity.[19]

3. Results and discussion

3.1. Structural properties

As a starting step, the total energy was calculated as a function of the lattice constant for binary compounds CdSe, CdTe and their mixed alloys. The energy versus lattice constant data are plotted in Fig. 1. The data were fitted to Murnaghan's equation of state[20] to determine the equilibrium lattice constant a_0 and the bulk modulus B. The optimized results are summarized in Table 1 to compare with other theoretical and experimental data. The optimized results for a_0 and B are presented in Fig. 2 along with Vegard's law. To study the alloys, it is assumed that all atoms in the crystals are located at their ideal sites. It is also assumed, according to Vegard's law, that any compound has a linear variation in lattice constant with composition x.[21] Our calculated lattice parameters at different compositions for $CdSe_{1-x}Te_x$ alloys are found to vary exactly linearly, consisting with the law. The calculated lattice parameters of the CdX compound increase in the following sequence: $a_0(\mathrm{CdSe}) < a_0(\mathrm{CdSe_{0.75}Te_{0.25}}) < a_0(\mathrm{CdSe_{0.50}Te_{0.50}}) < a_0(\mathrm{CdSe_{0.25}Te_{0.75}}) < a_0(\mathrm{CdTe})$. The reason is that the tetrahedral covalent radius of Te (0.134 nm) is larger than that of Se (0.115 nm).[22] The cohesive energy is a measure of the strength of the forces which for the ZB structure of CdX is calculated as

$$E_{\mathrm{coh}}^{\mathrm{AB}} = E_{\mathrm{atom}}^{\mathrm{A}} + E_{\mathrm{atom}}^{\mathrm{B}} - E_{\mathrm{total}}^{\mathrm{AB}}, \tag{1}$$

where $E_{\mathrm{coh}}^{\mathrm{AB}}$ is the total energy of CdSe and CdTe with equilibrium lattice constants, and $E_{\mathrm{atom}}^{\mathrm{A}}$ and $E_{\mathrm{atom}}^{\mathrm{B}}$ are the energies of the isolated Cd and Se/Te atoms in the free state, respectively. The calculated cohesive energies, listed in Table 1, are very close to the experimental values.[23] The accuracy of the cohesive energies calculated by Quantum ESPRESSO is encouraging as shown by this comparatively satisfactory result, confirming that the calculated results in this work are reliable. Further analysis of these results shows that CdSe has relatively higher structural stability than CdTe due to the larger absolute value of the cohesive energy.

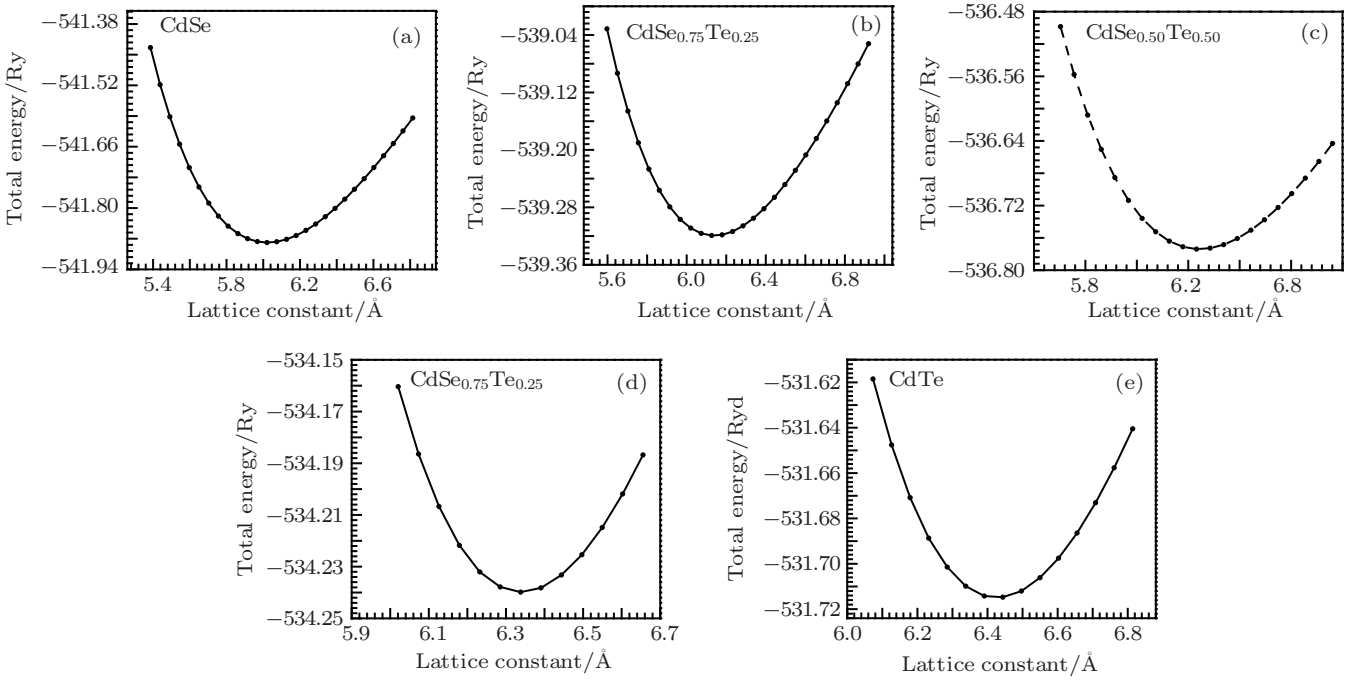


Fig. 1. Structural optimization plots for $CdSe_{1-x}Te_x$ alloys in the ZB phase: (a) $x = 0.00$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$, (e) $x = 1.00$.

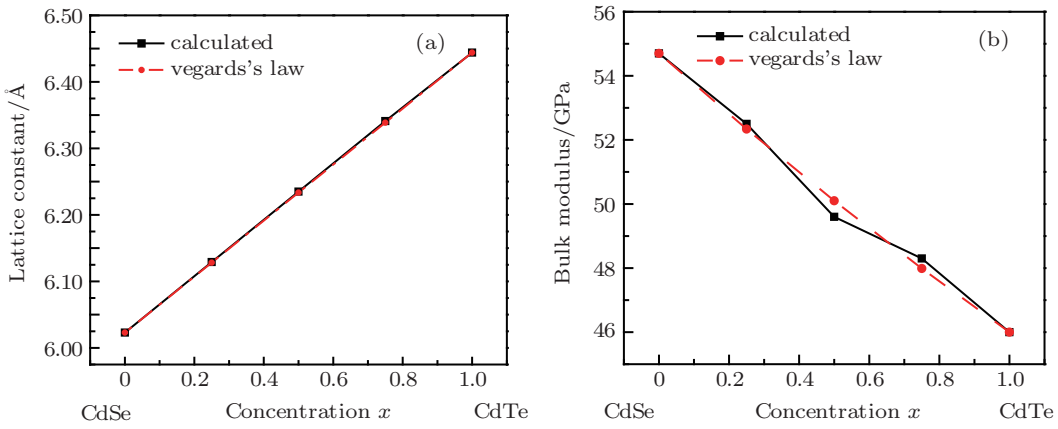


Fig. 2. (color online) Variations of the calculated (a) lattice constants and (b) bulk moduli with x for $CdSe_{1-x}Te_x$ alloys.

Table 1. Calculated lattice parameters and bulk moduli of $CdSe_{1-x}Te_x$ alloys compared with experimental and other theoretical results.

Composition	Lattice constant/Å			Bulk modulus/GPa			Cohesive energy/eV	
x	This work	Exp.	Theor.	This work	Exp.	Theor.	This work	Exp./Theor. (LDA)
0.00	6.023	6.05[a]	6.037[b]	54.700	53[a]	58.9[b]	6.8073	4.91[a]/7.05[e]
	6.129			52.338			6.5468	
	6.235			50.100			6.3347	
0.25	6.341			47.988			6.1613	
0.50	6.444	6.48[c]	6.583[d]	46.000	44[c]	43.28[d]	6.0181	6.31[a]/4.45[e]
0.75								
1.00								

[a] Ref. [23], [b]Ref. [24], [c]Ref. [25], [d]Ref. [26], [e]Ref. [27].

3.2. Electronic properties

The applications of the studied materials require precise knowledge of the energy band gaps along with the aligned placement of main conduction band (CB) valleys. Band gaps and band structures provide esteemed information for the fabrication and development of electronic, opto-electronic, and magneto-electronic devices. To explore the electronic properties of CdSe, CdTe compounds and their alloys, we calculated the band structure at high symmetry points in the first Brillouin zone in the ZB structure within LDA and LDA+U at equilibrium lattice constants. As the valence band maximum (VBM) and the conduction band minimum (CBM) locate at the same point, $CdSe_{1-x}Te_x$ has a direct energy band gap. This direct energy band gap decreases from CdSe ($x = 0$) to CdTe ($x = 1$). The obtained results of this study are compared with the experimental and other theoretical results in Table 2. In the case of LDA, the band gaps are smaller than the experimental values, since the LDA approach underestimates the band gaps for all materials of interest. While in the case of LDA+U, the energy band gaps are very close to the experimental results. The value of U (in eV) decreases from CdSe ($x = 0$) to CdTe ($x = 1$) as listed in Table 2. The band structures obtained with LDA and LDA+U are depicted in Fig. 3. In this figure, we notice that the band gap varies linearly with the composition (0.25, 0.5, and 0.75). Figure 3 also shows that the bottom of the conduction bands and the top of the valence bands are situated at the Γ point in the Brillouin zone, resulting in a direct band gap. To elucidate the nature of the electronic band structure, we calculated the total and partial density of states (PDOS) of the $CdSe_{1-x}Te_x$ alloys and present the results in Fig. 4. The first part VB1 is due to the s states of Se and Te. The second part VB2 is due to the 3d states of Cd. Whereas the uppermost valence band, VB3, is formed due to Se and Te p states along with Cd s states between -6 eV and 0 eV except for CdSe where this range is from -4 eV to 0 eV. While the Se/Te s states (VB1) are in the range from -12.0 eV to -10.0 eV. Similarly, the lowest CB is dominated by Cd s and p chalcogen states. It can be seen from the plot that the Te s state is closer to the Cd d state as compared to the Se s state. It can be observed clearly from Fig. 4 that when x changes from 0.0 to 1.00, the density of states (DOS) is changed. In general, the band gap of CdTe is smaller than that of CdSe, but in our case (by LDA), it is larger as shown in Table 2. Similar behavior has been reported.[28,29] It is recovered with the help of the LDA+U approach. It confirms that the Te incorporation into CdSe induces an obvious band gap narrowing. It is necessary to point out that the VBM is always in the Fermi level and it has no obvious shift, which can be clearly seen in Fig. 3.

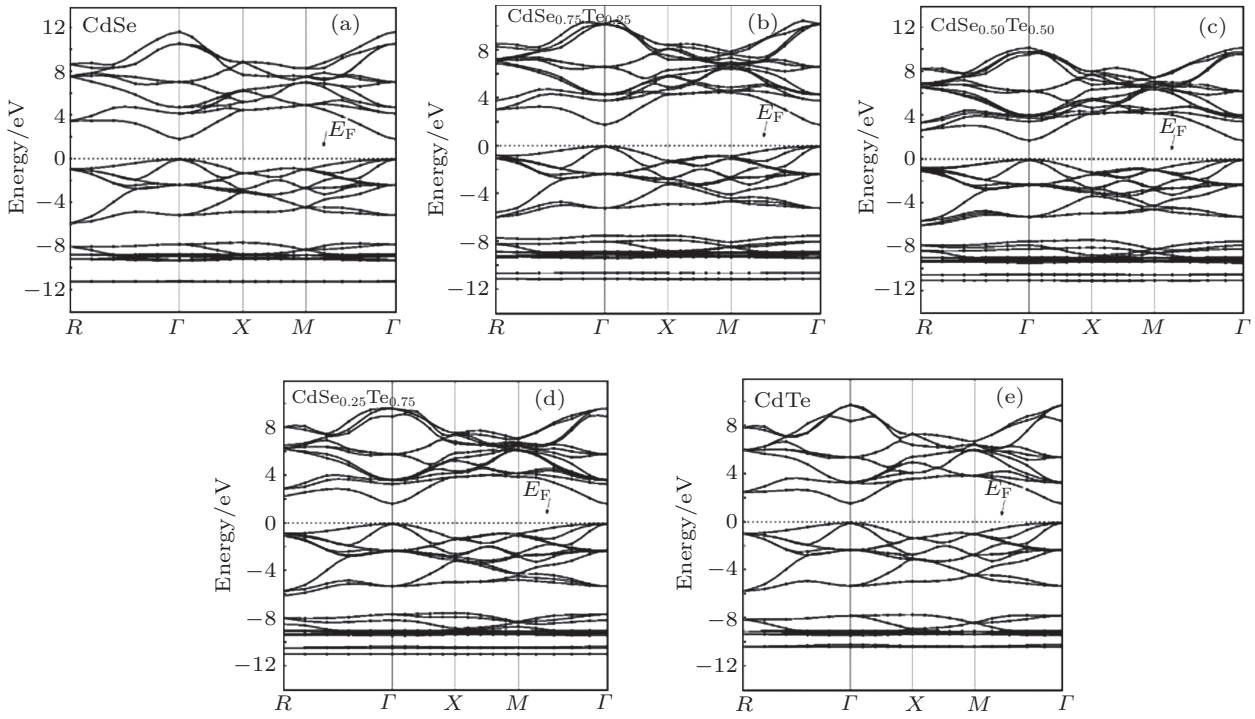


Fig. 3. Electronic band structures of $CdSe_{1-x}Te_x$: (a) $x = 0.00$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$, (e) $x = 1.00$.

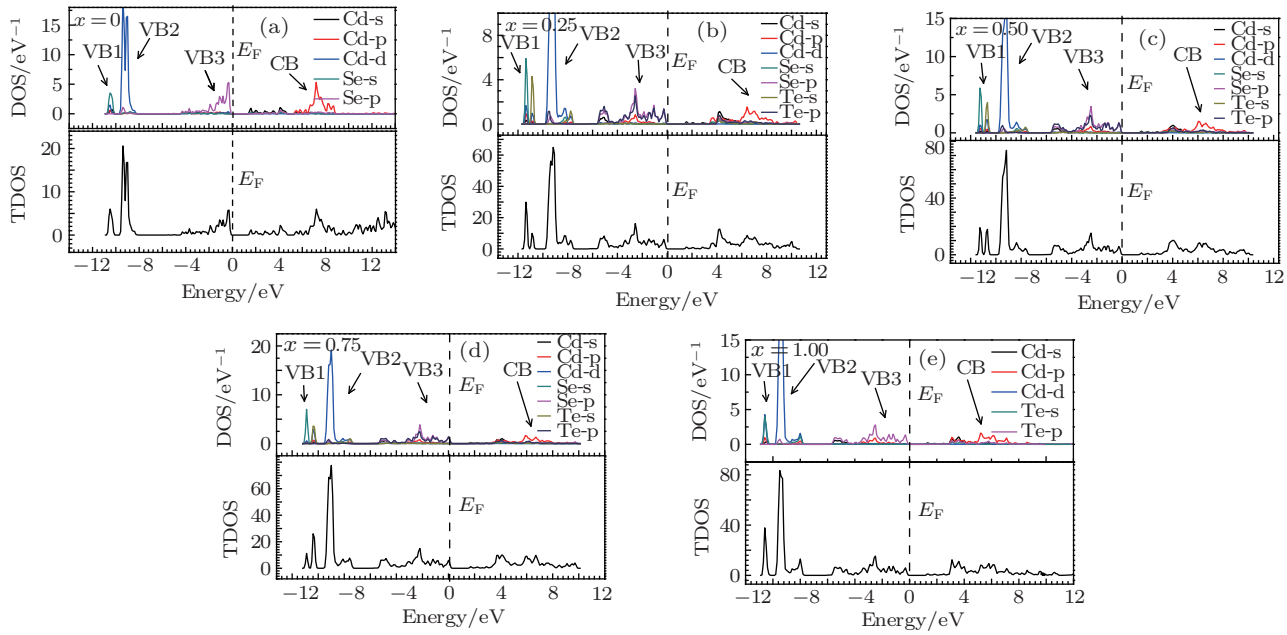


Fig. 4. (color online) Total and partial DOSs of $CdSe_{1-x}Te_x$: (a) $x = 0.00$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$, (e) $x = 1.00$.

Table 2. Comparison of calculated band gaps of $CdSe_{1-x}Te_x$ alloys with experimental and theoretical results in the ZB structure.

Composition x	Calculated LDA+U E_g/eV	U/eV	Calculated LDA E_g/eV	Theoretical LDA E_g/eV	Theoretical LDA-correc. E_g/eV	Experimental E_g/eV
0.00	1.8544	4.70	0.4811	0.42[a]	1.84[b]	1.9[c], 1.73[d]
0.25	1.7959	4.45	0.5209			
0.50	1.7258	4.20	0.5458			
0.75	1.6741	3.95	0.5801			
1.00	1.6186	3.70	0.6079	0.6[e]	1.68[b]	1.6[c], 1.55[d]

[a]Ref. [24], [b]Ref. [30], [c]Ref. [23], [d]Ref. [32], [e]Ref. [31].

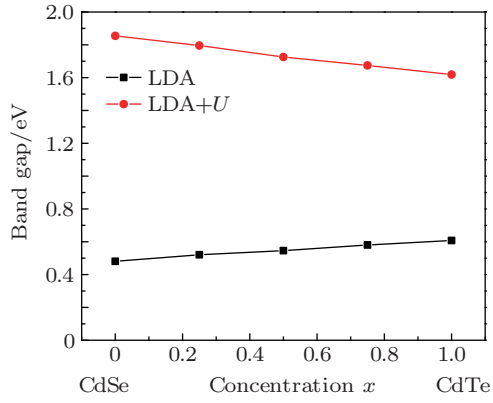


Fig. 5. (color online) Variation of energy gap of $CdSe_{1-x}Te_x$ with the concentration of Te.

3.3. Elastic properties

The elastic constants are important and necessary parameters to describe the response to an applied macroscopic stress and especially important because they are correlated to numerous physical properties, such as the elasticity, mechanical stability, and stiffness of the materials. The cubic crystals have only three independent elastic constants, i.e., C_{11}, C_{12}, and C_{44}. They can be determined by computing the stress generated by applying a small strain to an optimized unit cell. For three structures, we carried out calculations with strains in the range of -0.05 to 0.05 for each distortion. The systems were fully relaxed after each distortion in order to reach the equilibrium state with approximately zero forces on all atoms. In this work, we calculated the second-order elastic constants by the analysis of change in calculated stress resulting from change in the strain. The obtained results are given in Table 3, which show good agreement with other theoretical and available experimental results. The deliberated results about bulk moduli by energy minimization and from the elastic constants are comparable. It confirms the accuracy and consistency of our calculated elastic constants. The bulk modulus of CdTe is smaller than that of CdSe, which approves the legitimacy of the known empirical relation proposed by Cohen[33] $B = 1761 \times d^{-3.5}$, where d is the nearest-neighbor distance in angstroms. The traditional and well known mechanical stability conditions of elastic constants for cubic crystals are $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, and $C_{12} < B < C_{11}$.[34] For $CdSe_{1-x}Te_x$ semiconductor alloys, the obtained elastic constants are given in Table 3 and plotted in Fig. 6 which satisfy the above stability criteria, and thus corroborate the mechanical stability of the structure. Since the elastic anisotropy of materials has an imperative application in engineering, it is highly associated with the possibility to induce micro-cracks in the material. To enumerate the elastic anisotropy of the alloy, we computed the anisotropy factor A from the elastic constants using the following expression:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}. \tag{2}$$

For an absolutely isotropic material, A is equal to 1, while any value smaller or larger than 1 indicates an anisotropic material. The magnitude of deviancy from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. From the computed anisotropy factors given in the Table 3, one can see that A is greater than 1.0 and we cannot consider $CdSe_{1-x}Te_x$ as elastically isotropic. Once the elastic constants C_{11}, C_{12}, and C_{44} are calculated, the related properties, namely, the shear modulus G, the Young modulus E, and the Poisson ratio v can be estimated under Voigt–Reuss–Hill approximations[35] using the following relations:

$$E = \frac{9GB}{G + 3B}, \tag{3}$$

$$\upsilon = \frac{1}{2}\left(\frac{3B - 2G}{3B + G}\right), \tag{4}$$

where $B = (C_{11} + 2C_{12})/3$ is the bulk modulus, and $G = (G_R + G_V)/2$ is the isotropic shear modulus. Here G_R is the Reuss shear modulus corresponding to the lower bound of G, and G_V is the Voigt shear-modulus corresponding to the upper bound of G; they can be written as $G_V = (C_{11} - C_{12} + 3C_{44})/5$ and $5/G_R = 4/(C_{11} - C_{12}) + 3/C_{44}$. The calculated elastic moduli for polycrystalline $CdSe_xTe_{1-x}$ are also given in Table 3.

Table 3. Comparison of calculated elastic constants of $CdSe_{1-x}Te_x$ alloys with other results in ZB structure.

Composition x	C_{11}	C_{12}	C_{44}	B	E	G	B/G	v	A
0.00	74.2	49.9	24.0	58.01	52.00	18.25	3.01	0.35	1.98
	81.2[a]	47.8[a]	22.9 [a]		45.8[a]	11.3[a]			
	58.8 [b]	48.9 [c]	25.2 [b]		36.8[b]	13.3[b]			
0.25	67.1	47.8	23.2	54.19	48.11	16.02	3.15	0.35	2.40
0.50	63.6	45.0	22.3	50.79	46.34	15.73	2.95	0.35	2.39
0.75	59.7	41.5	21.5	47.61	44.44	15.22	2.88	0.34	2.36
1.00	58.9	38.0	21.1	44.95	44.87	15.91	2.67	0.33	2.02
	68.1[a]	39.3[c]	22.1[c]	45.25[d]	49.5[c]	15.2[e]			
	57.37[d]	39.19[d]	21.3[d]		40.85[d]	15.13[d]			

[a]Ref. [38], [b]Ref. [36], [c]Ref. [39], [d]Ref. [40], [e]Ref. [27].

The shear modulus is related to the resistance to plastic deformation and the bulk modulus is associated with the resistance to fracture. Pugh[36] introduced the new criteria about the brittleness and hardness of a material which is related to the ratio of the bulk modulus to the shear modulus (B/G). A high (low) value of B/G means a ductile (brittle) material. The critical value which separates ductility from brittleness is about 1.75. The results infer that none of the $CdSe_{1-x}Te_x$ compounds are brittle. Poisson's ratio v provides further information for dealing with the characteristic of the bonding forces. The values 0.5 and 0.25 are the upper and lower boundaries for central force solids, respectively.[37] Since the measured Poisson ratio is between these values, so the inter-atomic forces are central in these compounds.

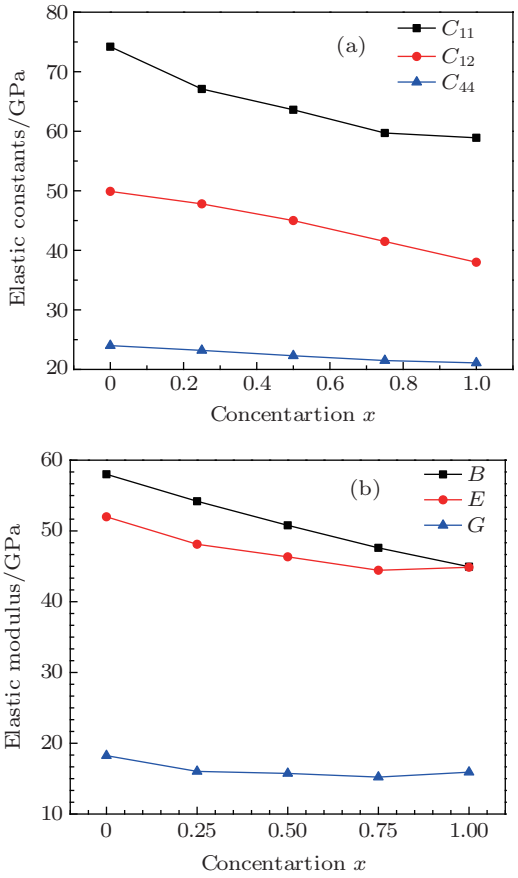


Fig. 6. (color online) Variation of (a) elastic constants and (b) elastic modulus in $CdSe_{1-x}Te_x$ at various concentrations of tellurium in ordered alloys.

4. Conclusions

Employing the pseudo-potential technique based on DFT within LDA and LDA+U, we have investigated the structural, electronic, and elastic properties of the binary and ternary alloy of CdSe and CdTe. The material was chosen because of its vast field of application. This study reveals the composition dependent changes in the ground state properties such as lattice constants (a_0), bulk moduli, and elastic properties of $CdSe_{1-x}Te_x$ semiconductor alloy. The calculated results are in good agreement with the theoretical and experimental results. This study gives confirmations of the LDA+U approach that was used to improve the underestimated electronic band gaps of Cd-based selenium, tellurium and ternary semiconductor alloys. The simulated band structures and DOSs show that the $CdSe_{1-x}Te_x$ alloys are semiconductor in nature with a small direct band gap. For this calculation, strong intra-correlation factor U for Cd 4d electrons was used and the results with the LDA+U approach are comparable to the experimental results. No deviation in lattice constant from Vegard's law is observed for $CdSe_{1-x}Te_x$. A linear dependence on composition x is observed for the bulk modulus and lattice constant of the studied alloys. The B/G value reflects that the studied material has a ductile nature for the whole concentration.

Acknowledgements

The authors gratefully acknowledged the support provided by Prof. Dr. M. A. Choudhary regarding fruitful discussions. We are also thankful to Prof. Dr. S. A. Ahmad due to providing access to simulation facilities at the simulation laboratory, Department of Physics, the Islamia University of Bahawalpur, Pakistan.

References

[1] Zafar M, Ahmed S, Shakil M and Choudhary M A 2014 *Chin. Phys. B* **23** 106108
[2] Zafar M, Ahmed S, Shakil M, Choudhary M A and Mahmood K 2015 *Chin. Phys. B* **24** 076106
[3] Muthukumarasamy N, Balasundaraprabhu R and Jayakumar S 2004 *Physica Status Solidi a* **201** 2312
[4] Hodes G, Manassen J and Cahen D 1980 *J. Am. Chem. Soc.* **102** 5962
[5] Muthukumarasamy N, Velumani S, Balasundaraprabhu R, Jayakumar S and Kannan M D 2010 *Vacuum* **84** 1216
[6] Sebastian P J and Sivaramakrishnan V 1990 *J. Phys. D: Appl. Phys.* **23** 1114
[7] Kumar L, Singh B P, Misra A and Misra S C K 2005 *Physica B* **363** 102
[8] Velumani S, Mathew X, Sebastian P J 2003 *Solar Energy Materials and Solar Cells* **76** 359
[9] Murali K R and Jayasuthaa B 2009 *Solar Energy* **83** 891
[10] Uthanna S and Reddy P J 1983 *Solid State Commun.* **45** 979
[11] Mangalhara J P, Thangaraj R and Agnihotri O P 1989 *Solar Energy Materials* **19** 157
[12] Islam R, Banerjee H D and Rao D R 1995 *Thin Solid Films* **266** 215
[13] Paolo G and Stefano B 2009 *J. Phys.: Condens. Matter* **21** 395502
[14] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864
[15] Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244
[16] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
[17] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
[18] Anisimov V I, Zaanen J and Andersen O K 1991 *Phys. Rev. B* **44** 943
[19] Wallace D C 1998 *Thermodynamics of Crystals, Dover Books on Physics* (New York: Dover Publications)
[20] Murnaghan F D 1944 *Proc. Natl. Acad. Sci. USA* **30** 44
[21] Vegard L 1921 *Zeitschrift für Physik* **5** 17
[22] Pyykkö P 2012 *Phys. Rev. B* **85** 024115
[23] Madelung O, Schultz M and Weiss H 1982 *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology* (Berlin: Springer-Verlag)
[24] Ameri M and Fodil M 2012 *Materials Sciences & Applications* **3** 768

[25] Cardona M, Madelung O, Habeke G and Rössler U 1982 *Semiconductors Physics of Group IV Elements and III–V Compounds* (Hellwege K H and Madelung O, Ed) Landolt-Bornstein, New series, Group III, 17
[26] Al-Douri Y, Reshak A H, Baaziz H, Charifi Z, Khenata R, Ahmad S and Hashim U 2010 *Solar Energy* **84** 1979
[27] Guo L, Zhang S, Feng W, Hu G and Li W 2013 *J. Alloys Compd.* **579** 583
[28] Ouendadji S, Ghemid S, Meradji H and Hassan F E H 2010 *Computational Materials Science* **48** 206
[29] Fleszar A and Hanke W 2005 *Phys. Rev. B* **71** 045207
[30] Khan I, Ahmad I, Aliabad H and Maqbool M 2012 *Computational Physics* (physicscompph) arXiv:12010870
[31] Rozale H, Lazreg A, Chahed A and Ruterana P 2009 *Superlattices and Microstructures* **46** 554
[32] Patil S and Pawar P 2012 *Biological and Physical Sciences* **2** 1472
[33] Cohen M L 1985 *Phys. Rev. B* **32** 7988
[34] Shein I R and Ivanovskii A L 2008 *J. Physics: Condens. Matter* **20** 415218
[35] Chung D and Buessem W 1967 *J. Appl. Phys.* **38** 2535
[36] Pugh S F 1954 *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **45** 823
[37] Dao M, Chollacoop N, Van Vliet K, Venkatesh T and Suresh S 2001 *Acta Materialia* **49** 3899
[38] Sharma S, Verma A S, Sarkar B K, Bhandari R and Jindal V K 2011 *AIP Conference Proceedings* **1393** 229
[39] Deligoz E, Colakoglu K and Ciftci Y 2006 *Physica B* **373** 124
[40] Kheloufi N and Bouzid A 2016 *J. Alloys Compd.* **659** 295