

TUNING OPTICAL RESPONSE OF MIXED CdS_xSe_{1-x} VIA FULL POTENTIAL MBJLDA APPROACH

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Abstract: First-principles calculations based on density functional theory (DFT) for CdSe in pristine form and with S-disorder have been reported to check out the optical response. The modified Becke-Johnson approach was considered to overcome the underestimation of standard DFT derived electronic energy gap. The incorporation of S-disorder in CdSe has hardly any effect on dielectric response in low energy (> 2 eV) region, however, for higher energies. The observed optical response for both compounds is good enough to raise the candidature of CdSe for optoelectronic devices.

Keywords: Band structure, DFT, mBJLDA, Chalcogenides.

Introduction: The optoelectronic applications of chalcogenide semiconductors are growing rapidly due to their potential use in photodetectors, light emitting diodes and solar cells etc. [1-4]. The experimental findings as well as numerous industrial applications initiated comprehensive theoretical studies of structural, optical and electronic properties of Zn and Cd based chalcogenides. Ghahramani et al. [5] reported band structure calculations of the frequency-dependent second and third harmonic response functions of ZnSe, ZnTe, and CdTe using linear combination of Gaussian orbitals technique and found that the effects of weak optical transitions are much more pronounced in the second and third order optical response functions than in the linear response. Kheloufi et al. [6] studied the ground state properties of CdS_xTe_{1-x} ($x = 0, 0.25, 0.5, 0.75, 1$) ternary semiconductor materials and calculated Born effective charges along with dielectric constants from density functional perturbation theory (DFPT).

Cadmium selenide (CdSe) is II-VI type semiconducting material which at normal temperature and pressure crystallizes in the hexagonal, wurtzite structure. However, it can also crystallize in the cubic, zinc-blende structure; although these are metastable under normal conditions yet by selecting suitable substrates and molecular-beam epitaxy (MBE) technique, it is possible to grow it in these structures [7]. Samarth et al. [8] presented the dielectric function spectra of ZnSe and CdSe as obtained by vacuum

ultraviolet ellipsometry measurement and analyzed it with parametric semiconductor model. Mixed CdSe semiconductor passivated with CdS have been used in the manufacture of photovoltaic and optoelectronic devices [9-10] already. Beside the study of optical response of pristine CdSe, the *sp*-element disorder in it has not been explored much in detail. With the great potential of mixed CdSe and CdS semiconductors for photovoltaics, we have targeted S-disorder in CdSe in this work and planned to examine the tuning of band gap and optical response of $\text{CdS}_x\text{Se}_{1-x}$ ($x = 0.03$) via full potential calculations.

Theory: Cubic CdSe has zinc blende structure with a band gap 1.73 eV [11]. The electronic structure calculations of binary CdSe alloys in pristine and disordered forms were carried out using the highly precise all electrons full potential linearized augmented plane wave (FPLAPW) method [12] based on density functional theory (DFT) [13] as implemented in WIEN2k [14]. The exchange and correlation (XC) potentials were constructed using the generalized gradient approximation (GGA) within the parameterization of Perdew-Burke-Ernzerhof (PBE) [15]. In FPLAPW calculations, the core states were treated fully relativistically while valence states and semi-core states were examined semi-relativistically. The plane wave cut off parameters were decided by $R_{\text{MT}}k_{\text{max}} = 8$ (where k_{max} is the largest wave vector of the basis set such that k_{max} controls the accuracy of the calculation).

In many semiconductors, LDA and GGA strongly underestimate the value of the energy gap. Thus, for present case too, the improved values for the band gaps are usually obtained by mBJLDA potential as developed by Tran and Blaha [16] after modifying Becke-Johnson potential. The Fourier expansion of potential in the interstitial region was expanded upto $G_{\text{max}} = 14 \text{ a.u.}^{-1}$ and the maximum value of partial waves inside the atomic sphere was $l_{\text{max}} = 10$. The calculations were based on the supercell approach where one Se atom at (0,0,0) in the $(2 \times 2 \times 2)$ supercell of CdSe is replaced by S-atom which corresponds to 3.1 % doping. The non-overlapping muffin-tin radii (RMT) of Cd, Se and S were chosen as large as possible to obtain nearly touching spheres and to ensure minimize interstitial space. The energy convergence criterion was set to 10^{-4} Ry and the charge convergences were also monitored along with it. The *k*-space integration was carried out using the modified tetrahedron method [17] with 50 *k*-points in the irreducible Brillouin zone (IBZ) for doping of 3.1 %. The final calculations were performed with the theoretical lattice constant and relaxed structure.

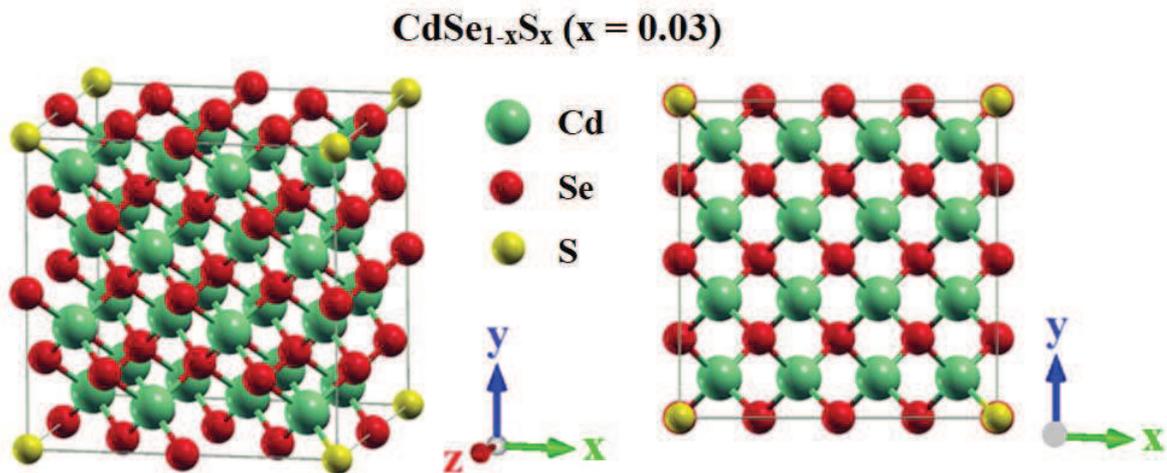


Fig. 1: A $(2 \times 2 \times 2)$ supercell for simulating $\text{CdSe}_{1-x}\text{S}_x$ ($x = 0.03$) semiconductor. The right panel shows the front view of the supercell.

Results: Cubic CdSe in zinc blende structure [11] belongs to *space group*, $216 = F\bar{4}3m$, contains two formula units (eight atoms) such that the Se atom is present at (0,0,0) and Cd atom is at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The

3.1 % S-disorder in CdSe can be designed by creating 2x2x2 supercell of the same and then replacing the Se atom present at the origin by S as shown in Fig. 1.

It is important to extract suitable lattice parameters for CdSe and CdSe_{1-x}S_x (x = 0.03). To cater this need, the lattice parameters for both were optimized in the neighbourhood of experimental lattice parameters of CdSe [11] in cubic configuration (Fig. 2). These optimized parameters, listed in Table 1, were used further to find ground state properties of studied semiconducting compounds.

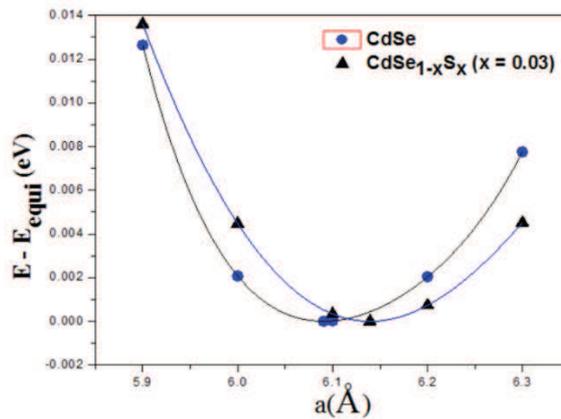


Fig.2: Total energy versus lattice parameter of CdSe_{1-x}S_x (x = 0, 0.03) semiconductors. The solid lines show a polynomial fit for determining the equilibrium lattice constants.

Table 1: Calculated Optimized Lattice Parameter (Å⁰) Compared With Experimental Values, Cohesive Energy (E_v), Band Gap By GGA And Mbjlda (E_v) Compared With Experimental Values

Semiconductor	Experimental lattice parameter	Optimized lattice parameter	Band gap GGA	Band gap mBJLDA	Experimental Band gap (eV)
CdSe	6.05	6.015	0.46	1.70	1.74*
CdSe _{0.97} S _{0.03}	-	5.999	0.41	0.92	-

*Ref. 11

The total DOS for CdSe_{1-x}S_x (x = 0, 0.03) is depicted in Fig. 3 which shows the clear semiconductor nature for both compounds. There exists an electronic band gap for both at Fermi level (E_F) with valence band filled up to E_F. The calculations for band gap have been performed within GGA as well as mBJLDA approaches. The experimental band gap for pristine CdSe is 1.74 eV [11] whereas within GGA, it comes out 0.46 eV only. This clearly shows the limitation of GGA to predict the band structure of semiconducting CdSe compound in agreement with the experiment. In order to improve the band gap, mBJLDA approach plays an important role by catching the essentials of orbital dependent potentials with orbital independent terms. The observed band gap (1.70 eV) using mBJLDA for CdSe is in excellent agreement with the experimental value [11]. We have also found that for CdSe_{0.97}S_{0.03} compound, the band gap decreases to 0.92 eV in comparison to pristine CdSe within mBJLDA approach.

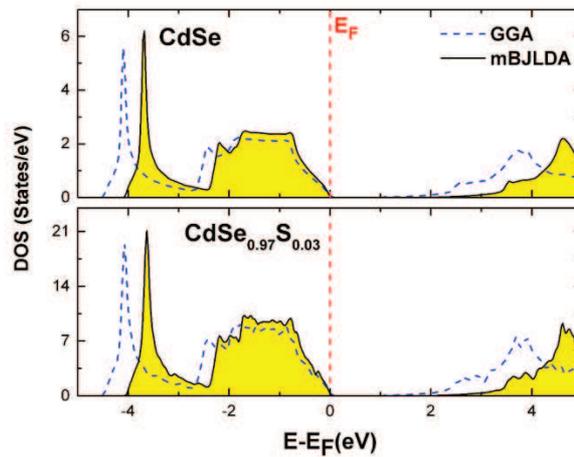


Fig.3: Calculated total DOS of CdSe_{1-x}S_x (x=0, 0.03) with GGA and mBJLDA

In pristine CdSe, the valence band is extended up to E_F due to the availability of Cd-p and Se-p states, however in conduction band, Cd-s states are most dominant. In case of CdSe_{1-x}S_x (x = 0.03), S-p states also contribute in the total DOS up to E_F. Further, in conduction band S-s states increases the unoccupied states in the bottom of conduction band. The importance of mBJLDA in correcting the band gap is also verified by plotting the band structure which is as shown in Fig. 4. On comparison among band structures from GGA and mBJLDA approaches, it is found that the various bands in valence band are unshifted, however, in conduction band, mBJLDA derived unoccupied bands get shifted towards higher energy as compared to that for GGA. Thus, it is confirmed that mBJLDA can produce the band levels more accurately as compared to GGA formalism. The band gap of CdSe is direct along Γ - Γ direction and the valence band is extended upto Fermi level. The presence of direct band gap makes CdSe an interesting material for optoelectronic devices.

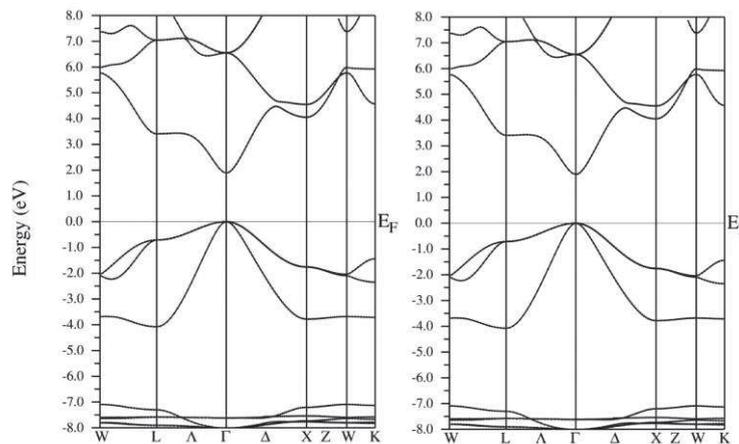


Fig. 4: The Band Structure and Total Density of States for CdSe Binary Alloys within mBJLDA Approach

Finally, for analyzing optical response, we have plotted real and imaginary parts of dielectric function $\epsilon(\omega)$ within the mBJLDA approach for CdSe_{1-x}S_x (x=0, 0.03) in energy range; E = 0-8 eV in Fig. 5. The results have been quoted without applying any scissor effect in energy. Both CdSe_{1-x}S_x (x=0, 0.03) show qualitative similar $\epsilon(\omega)$ spectra, implying that the optical response is robust even with the presence of S-disorder in CdSe. The similar dielectric response was expected due to identical DOS for both compounds. Four peaks in the $\epsilon_1(\omega)$ spectra are clearly visible. With S-disorder, the peaks in $\epsilon_2(\omega)$ spectra show slight blue shifting. The fundamental optical gaps for both compounds are ~ 2 eV which

can be identified by almost zero magnitude of $\varepsilon_2(\omega)$ till the threshold energy ~ 2 eV. This gap leads to Γ - Γ direct optical transitions between top of the valence band and bottom of conduction band. The transition is also corresponding to first optical absorption. After fundamental absorption, there are three more higher energy absorption edges present in $\varepsilon_2(\omega)$ spectra.

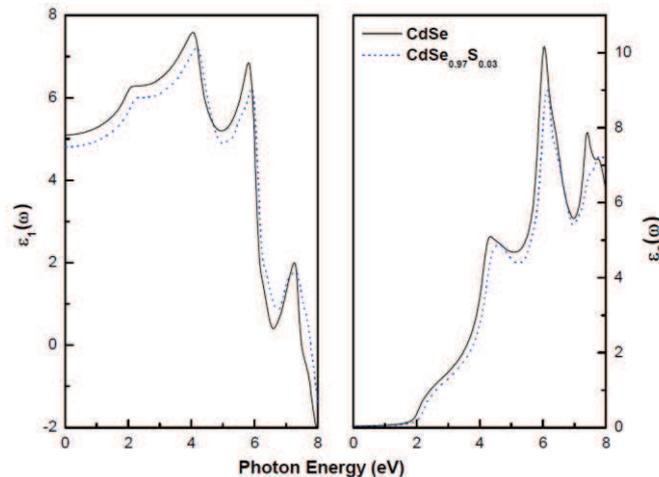


Fig. 5: Calculated real and imaginary part of dielectric function $\varepsilon(\omega)$ of $\text{CdSe}_{1-x}\text{S}_x$ ($x = 0, 0.03$)

Conclusion: A first principles approach based on DFT have been utilized for $\text{CdSe}_{1-x}\text{S}_x$ ($x = 0, 0.03$) in order to check the dependence of band gap and optical response on sp-element; S-disorder. The simulated band gap of pure CdSe was corrected with the help of mBJLDA approach and obtained the same in excellent agreement with available experimental data. The band gap of $\text{CdSe}_{0.97}\text{S}_{0.03}$ is 0.92 eV, which is less as compared to its value for pure case. The direct band gap along Γ - Γ is identified from band structure plot. The incorporation of S-disorder in CdSe has hardly any effect on dielectric response, predicting the robustness of the optical properties with S-disorder. The observed optical response for both compounds is helpful in making them the potential candidates for optoelectronic devices.

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References:

1. R. L. Byer, "New Applications Emerge for Nonlinear Optical Materials", *Photonics Spectra*, (1995) 103-104.
2. J.I. Contreras-Rascon, J. Díaz-Reyes, J.E. Flores-Mena, M. Galvan-Arellano, L.A. Juarez-Moran and R.S. Castillo-Ojeda, "Characterization of CBD- $\text{CdSe}_{1-y}\text{S}_y$ deposited at low-temperature for photovoltaic applications", *Current Appl. Phys.* 15 (2015) 1568.
3. F. Xu, X. Ma, S.M. Kauzlarich and A. Navrotsky, "Enthalpies of formation of $\text{CdS}_x\text{Se}_{1-x}$ solid solutions", *J. Mater. Res.* 24 (2009) 1368.
4. P. O. Brien, J. McAleese, "Developing an understanding of the processes controlling the chemical bath deposition of ZnS and CdS", *J. Mater. Chem.* 8 (1998) 2309.
5. E. Ghahramani, D. J. Moss, and J. E. Sipe, "Full-band-structure calculation of first, second and third-harmonic optical response coefficients of ZnSe, ZnTe, and CdTe", *Phys. Rev. B*, 43, 9700 (1991).
6. N. Kheloufi and A. Bouzid, "Ground state properties from first principle calculations of $\text{CdS}_x\text{Te}_{1-x}$ ternary semiconductors materials", *J. Alloys Compds* 659 (2016) 295.
7. N Samarth, H. Luo, J K. Furdyna, S. B. Qadri and Y. R. Lee, A. K. Ramdas and N. Otsika, "Growth of cubic (zinc blende) CdSe by molecular beam epitaxy", *Appl. Phys. Lett.* 54 (1989) 2680.

8. Y.W. Jung, J.J. Yoon, J.S. Byun, Y.D. Kim, "Dielectric function analysis of ZnSe and CdSe using parametric semiconductor model", *Microelectronics Journal* 39 (2008) 570.
9. M.A. Contreras, A.M. Gabor, A.L. Tennant, A. Asher, J.R. Tuttle and R. Noufi, "Accelerated publication 16.4% total-area conversion efficiency thin-film polycrystalline MgF₂/ZnO/CdS/Cu (In, Ga) Se₂/Mo solar cell", *Progr. Photovolt.* 2 (1994) 287.
10. T.B. Tang, "Semiconductors used in optoelectronic devices—An overview", *Journal of Electronic Materials, Electron. Mater.* 4 (1975) 1229.
11. S. Ninomiya and S. Adachi, Optical properties of cubic and hexagonal CdSe", *J. Appl. Phys.* 78 (1995) 4681.
12. G. K. H. Madsen, and P. Blaha, "Efficient linearization of the augmented plane-wave method", *Phys. Rev. B* 64 (2001) 195134.
13. M. Weinert, E. Wimmer, and A. J. Freeman, "Total-energy all-electron density functional method for bulk solids and surfaces", *Phys. Rev. B* 26 (1982) 4571.
14. P. Blaha, K. Schwarz, G. Madsen, and D. K. J. Luitz, in "Wien2k, An Augmented Plane Wave plus Local orbitals program for calculating crystal properties", (Publisher, Vienna University of technology, Austria, 2001), ISBN: 3-9501031-1-2.
15. J.P. Perdew, K. Burke, and M. Ernzerhof, "Generalized Gradient Approximation Made Simple", *Phys. Rev. Lett.* 77 (1996) 3865.
16. F. Tran and P. Blaha, "Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential", *Phys. Rev. Lett.* 102 (2009) 226401.
17. P. E. Blöchl, O. Jepsen and O. K. Andersen, "Improved tetrahedron method for Brillouin-zone integrations", *Phys. Rev B* 49 (1994) 16223.
