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Ab-initio Calculations of Structural, Electronic, Optical, Dynamic and Thermodynamic Properties of HgTe and HgSe

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Abstract In present work, using the density functional theory within local density approximation, the structural optimization, electronic band structure, density of electron states, optical, dynamic and thermodynamic properties of HgTe and HgSe were investigated. It was found that HgTe and HgSe show semiconducting property with a direct band gap at high symmetry point gamma with the value of 0.99 eV since conduction band does not interact with uppermost state of valance band because of existence of heavy holes. Real and imaginary parts of dielectric function as a function of photon energy were studied and photon wavelength dependence of refractive index was compared with experimental result. Also, temperature dependent thermodynamic properties such as Helmholtz free energy, internal energy, entropy and specific heat have been worked. The calculated and experimental results are in a good agreement.

Keywords Density Functional Theory, Electronic Structure, Optical Properties, Dynamic Properties

1. Introduction

Many semiconductors of $A^{II}B^{VI}$ type crystallize in the form of zinc-blende structure. Among those HgTe and HgSe are special because of their different band end structure[1-3]. Mercury chalcogenides are to be used in optoelectronic and spintronic applications[1,4]. Besides, conduction bands of HgTe and HgSe are non-parabolic and can be well explained by Kane model[5]. The cubic HgTe and HgSe are technologically interesting materials with applications in quantum electronics[6]. Compared to other II-IV group semiconductors, few experimental and theoretical studies on these compounds have been performed[7-10]. Delin and Klüner, using an all-electron full-potential linear muffin-tin orbital method, found that in the zinc-blende structure both HgSe and HgTe are semimetals[6]. Arora and Ahujawe reported energy bands, density of states (DOS) and band gaps of these chalcogenides via using Hartree–Fock and density functional theory[11]. Penna et al. calculated the electronic structure of the binary compounds CdTe and HgTe with density functional theory local density approximation (DFT-LDA), empirical pseudopotential method (EPM) and a new full-Brillouin zone (FBZ) k.p method[12]. Rajput and Browne studied lattice dynamics of II-VI compounds by the adiabatic bond charge model[13]. Cordona et al. studied the electronic band structure and the phonon dispersion relations of the zinc-blende (ZB) type mercury chalcogenides[9]. Thermal properties of mercury chalcogenides were also calculated[10].

There is no comprehensive study about HgTe and HgSe by using density functional theory as far as we know. So we investigated structural and volume optimization, electronic band structure, density of states, optical properties, dynamic and thermodynamic properties for these compounds.

2. Computational Methods

The physical properties of HgTe and HgSe crystals were investigated using ABINIT[14] code within the local density approximation based on the density functional theory. The self-consistent pseudopotentials, generated by FHI98PP code[15] with the Ceperley-Alder Perdew-Wang scheme[16], were used for all ab initio calculations. The conjugate gradient minimization method[17] was employed in order to solve the Kohn-Sham equations[18]. The exchange-correlation effects were taken into account within the Ceperley-Alder Perdew-Wang local density functional pseudopotentials (CAPW-LDA-1992)[19]. Plane waves were used as the basis set for the electronic wave functions. For mercury atom the 5d and 6s electrons, for tellurium atom the 5s and 5p electrons and for selenium atom the 4s and 4p electrons were considered as the true valence. First of all, in all calculations total energy of this materials were optimized with respect to cutoff energy and Monkhorst-Pack mesh grid.

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The obtained total energy calculations were done to a good convergence at 25 Hartree of cutoff energy and 60 k points using 8x8x8 Monkhorst-Pack mesh grid[20] in HgTe and HgSe crystals for structural optimization and electronic band structure. The Brillouin zones of these compounds have been sampled with a 8x8x8 Monkhorst-Pack mesh grid with 60 k points for the calculations of dynamic and thermodynamic properties and a 10x10x10 Monkhorst-Pack mesh grid 110 k points for the calculations of optical properties.

3. Structural Properties

All the calculations of HgTe and HgSe crystals involve two atoms per face centered cubic unit cell and they have space group symmetry with space group number 216. Firstly, total energy optimization with respect to cutoff energy was performed and value of cutoff energy was calculated as 25 Hartree (Ha) for both compounds as seen in figure 1. Secondly number of k points was optimized by total energy and was calculated as 60 for both HgTe and HgSe as shown in figures 2a and 2b. One of the two atoms (Hg) was placed at the 0.0, 0.0, 0.0 while the other (Te/Se) at 0.5, 0.5, 0.5.

Thirdly, lattice and volume parameter optimization were performed according to total energy. Volume parameters were calculated as 447.739 and 424.484 of cubic Bohr respectively as in figure 3. The calculated values of lattice parameters for HgTe and HgSe compounds are 12.144 and 11.556 Bohr, while experimental ones are 12.21 and 11.49 Bohr respectively. As seen, there is a good agreement between calculated and experimental results for lattice parameters. Then, calculated results were used for calculation of all physical properties of these compounds. Total energy was investigated as a function of volume in figure 3 and as a function of pressure of unit cell for HgTe and HgSe crystals as seen in figure 4. It is seen from figures 3 and 4 that minimum values total energies are -67.62 and -68.875 Ha for these compounds. Figure 5 shows pressure as a function of volume of unit cell for HgTe and HgSe crystals.

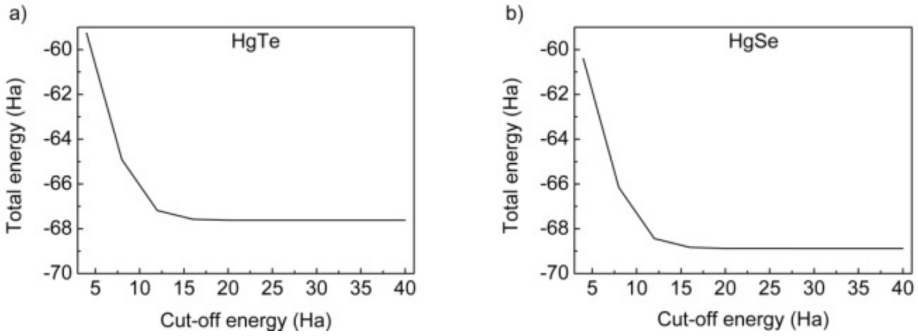

Figure 1. Cut-off energy-total energy optimization for a) HgTe and b) HgSe

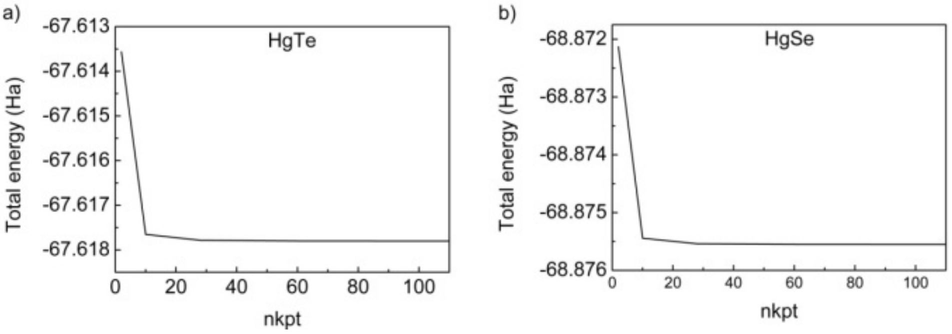

Figure 2. Number of k points (nkpt) - calculated total energy optimization for a) HgTe and b) HgSe

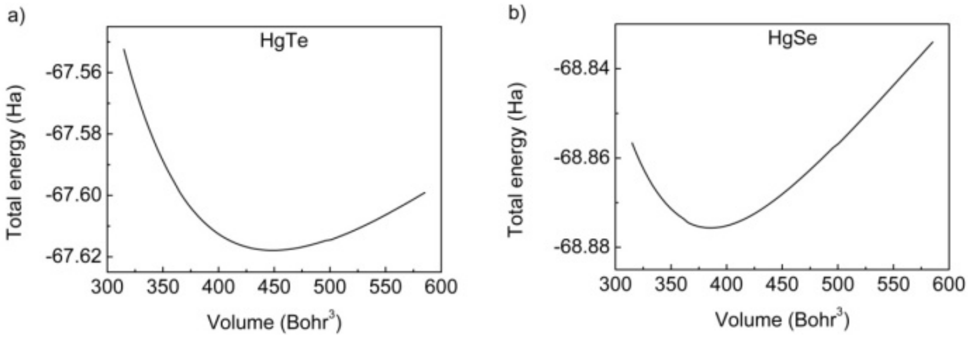

Figure 3. Total energy-volume dependence for unit cells of HgTe and HgSe

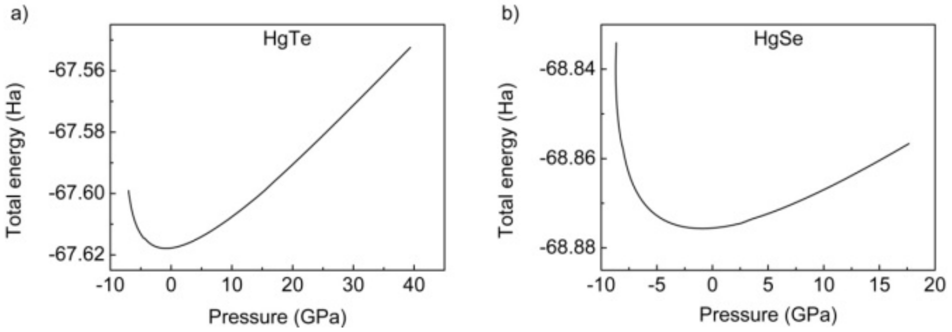

Figure 4. Total energy-pressure dependence for unit cells of HgTe and HgSe

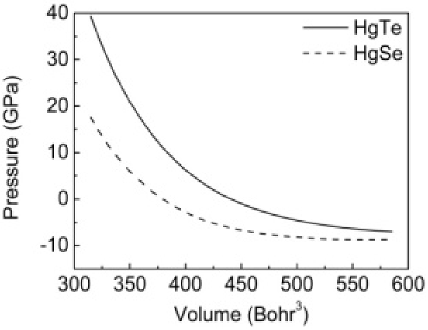

Figure 5. Pressure-volume dependence for unit cells of HgTe and HgSe

4. Electronic Properties

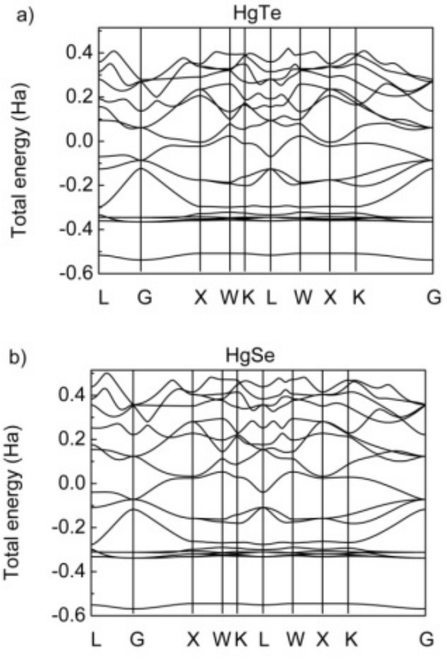

Figure 6. Electronic band structure for a) HgTe and b) HgSe

Pseudopotential method based on density functional theory within local density approximation was used for electronic structure calculations of mercury tellurium and mercury selenide. Calculated electronic band structure for HgTe and HgSe are given as in figures 6a and 6b. Both HgTe and HgSe crystals have nine valence bands. Additional nine conduction bands were used for band structure calculations. According to band structure calculations, both HgTe and HgSe crystals have a direct band gap at high symmetry gamma (Γ) point with the value of 0.99 eV. As seen in these figures, at gamma points, bottom of conduction band and top of valance band seems to be touching. But in $A^{II}B^{VI}$ type semiconductors, conduction band does not interact with uppermost state of valance band because of existence of heavy holes. Instead, it interacts with other lower states of valance band, so making these structures semiconductor. A comprehensive study about band structure of these compounds can be found in[1]. Moreover, the DOS' for these compounds are shown in figure 7.

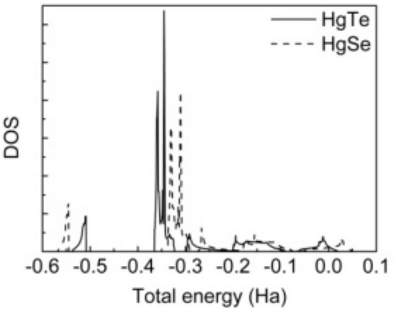

Figure 7. DOS for HgTe and HgSe

5. Optical Properties

HgTe and HgSe crystals are optic crystals and they exhibit the symmetry of the point group 216. The calculated real (ε_1) and imaginary (ε_2) parts of these compounds are given in figure 8.

As seen from these figures, the real part of linear dielectric function, ε_1, goes to its maximum value at 0 eV of photon energy for both HgTe and HgSe. Furthermore, one can see from figure 8 that the static dielectric constants for HgTe and HgSe crystals are 15.0 and 13.5, respectively. The main peak values in the imaginary parts of linear dielectric functions calculated in present work are at 1.9, 4 and 5.7 eV for HgTe and 2.0, 5.0 and 6.6 eV for HgSe. The energy loss functions (L), for both volume and surface, are presented in figures 9 for the compounds HgTe and HgSe. The maximum of calculated surface is at 10 eV, while maxima for volume loss functions are at 14, 18.8, 23.5, 27 and 32 eV for HgTe. On the other hand, maxima of calculated surface are at 11, 13, 16 and 20 eV, while for volume loss functions are at 12, 14.5, 16.5, 20, 21.6, 23.6, 26.4 and 34.6 eV for HgSe. The calculated extinction coefficients (k), absorption coefficients (α), and reflectivities (R) for HgTe and HgSe are shown in figure 10a, 10b and 10c, respectively.

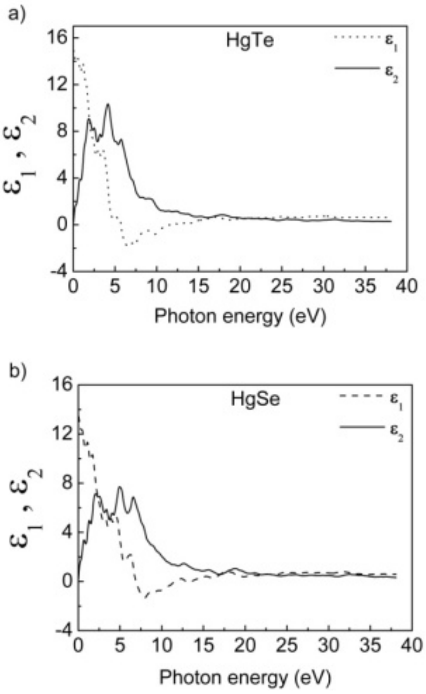

Figure 8. Real and imaginary parts of dielectric function for a) HgTe and b) HgSe

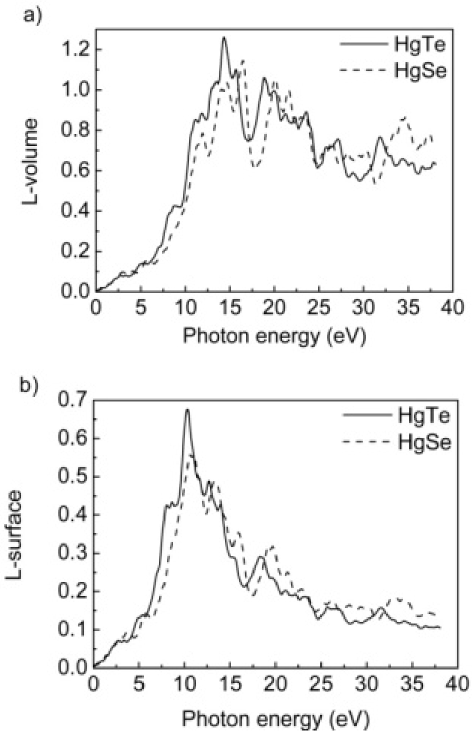

Figure 9. Loss functions of HgTe and HgSe as a function of photon energy for a) volume and b) surface

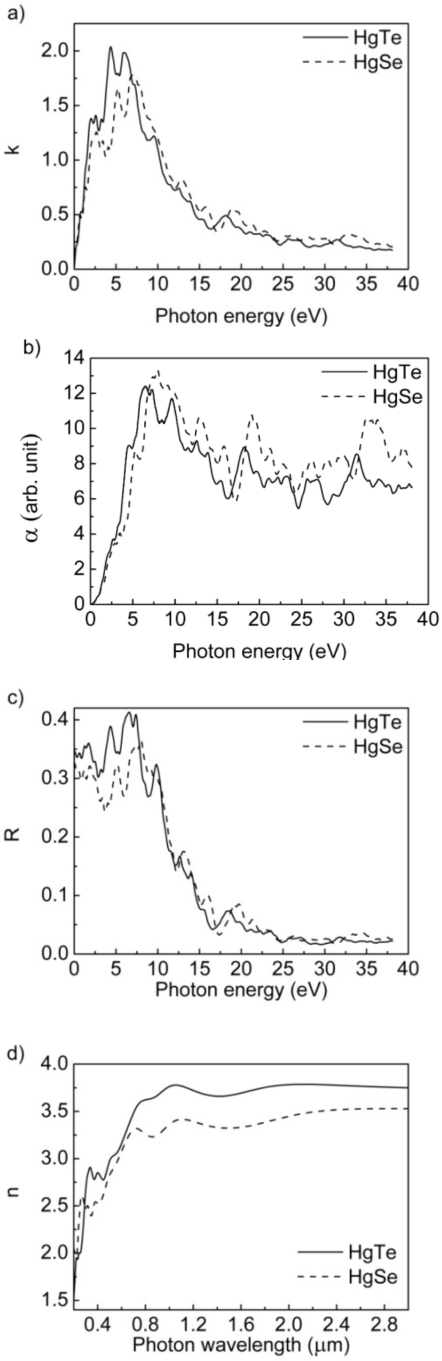

Figure 10. The calculated a) extinction coefficients, b) absorption coefficients and c) reflectivities as a function of photon energy, d) spectral dependence of refractive index (n) on wavelength

One can see from these figures that a crystal of these compounds is virtually optically transparent in 0-0.9 eV photon energy range. The photon energy ranges of 1-4 eV and 1-7 eV are characterized by strong absorption, while 4-10 and 7-12 eV photon ranges are characterized for appreciable reflectivity for HgTe and HgSe, respectively. Figure 10d represents the spectral dependence of calculated refractive index for HgTe and HgSe crystals in the wavelength range of 0-1.2 μm which is in good agreement with experimental data[21]. The refractive index decreases with the transition from strong absorption region towards the long waves, in other words, a normal dispersion occurs as seen from the figures. The maximum in the dependence of n=n(λ) has been obtained at the wavelengths of λ=1.98 μm and λ=2.85 μm, while the calculated values of refractive indices are 3.78 and 3.65 for HgTe and HgSe, respectively.

6. Dynamic and Thermodynamic Properties

In mercury tellurium and mercury selenide crystals, unit cell contains two atoms at zero pressure. In the end of crystallization of HgTe and HgSe at zero pressure, while the Hg atom is located at the point of (0.0, 0.0, 0.0), Te/Se atom is located at the point of (0.5, 0.5, 0.5), in the reduced coordinates, inside the unit cell. Figure 11 and 12 show the phonon band structures and phonon density of states for these crystals.

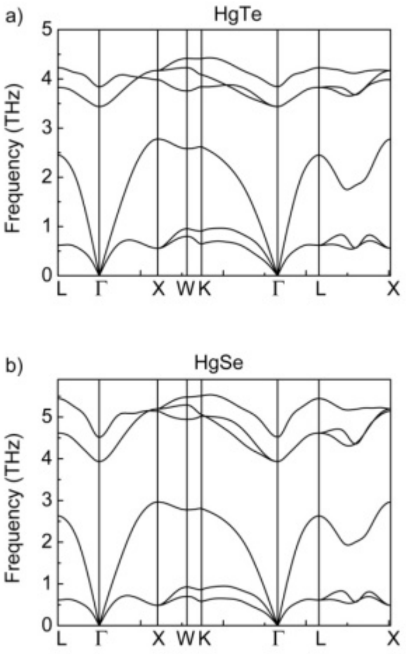

Figure 11. Phonon band structures for a) HgTe and b) HgSe

There are two atoms per unit cell for HgTe and HgSe crystals, six phonon branches totally appear.

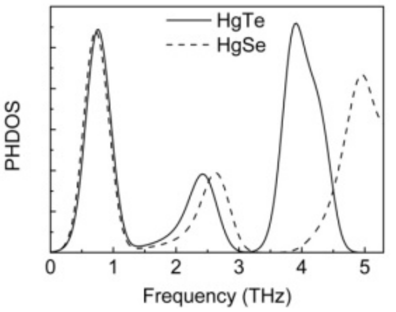

Figure 12. Phonon density of states for HgTe and HgSe

While three of them are the acoustic branches, the remaining three are the optical branches. Some of the branches are degenerate along more symmetrical directions inside Brillouin zone of HgTe and HgSe crystals. The direction from the high symmetry point Γ to X and the direction from the Γ to L, respectively, are more symmetrical compared to the other directions in figure 11 for HgTe and HgSe. So, transverse acoustic (TA) modes and transverse optic (TO) modes for both compounds are degenerate along these symmetry directions. When the symmetry is broken along the other directions the degeneracy in the modes disappear. A similar symmetry effect can also be seen in the electronic band structure of these crystals in figure 6. As seen in these figures, two of top valence levels are also degenerate along the directions of Γ to X and Γ to L. As expected, acoustic phonon dispersion curves are the linear as a function of wave vector **k** for small values of k. We have calculated that the frequency values of TO and longitudinal optic (LO) modes at the center of BZ are 3.44 and 3.84 THz for HgTe, while for HgSe these values are 3.96 and 4.52 THz, respectively. Calculated frequency values of the modes for HgTe are 0.63 THz (TA), 2.44 THz (LA), 3.84 THz (TO) and 4.21 THz (LO) at the high symmetry point L and 0.56 THz (TA), 2.78 THz (LA-longitudinal acoustic), 4 THz (TO) and 4.17 THz (LO) at the high symmetry point X. Meanwhile, obtained frequency values for HgSe are 0.62 THz (TA), 2.63 THz (LA), 4.62 THz (TO) and 5.44 THz (LO) at the high symmetry point L and 0.50 THz (TA), 2.98 THz (LA), 5.13 THz (TO) and 5.21 THz (LO) at the high symmetry point X. There is a gap between the acoustic and the optic phonon branches. As seen from figure 11, acoustic and optic modes do not interact along all symmetry directions. Moreover, phonon densities of states for mercury tellurium and mercury selenide are shown in figure 12. Thermodynamic properties of HgTe and HgSe crystals have been calculated using phonon band structure calculations. The entropy (S), the constant-volume specific heat (C), and the phonon contributions to Helmholtz free energy (F) and internal energy (E) as a function of temperature for HgTe and HgSe crystals are given in figure 13. The contribution of phonons, that is, the contribution of lattice to the internal energy and free energy do not vanish at zero temperature as shown in Fig. 13a and 13b. The contributions of phonons to free energy, F0, at zero temperature are 3.25 and 3.71 kJ/mol for HgTe and HgSe, respectively. Meanwhile, these contributions to internal energy, E_0, at zero temperature are 3.19 and 3.76 kJ/mol for HgTe and HgSe, respectively. That is, zero-point oscillations manifest themselves. We have calculated the dependence of the entropy on temperature from phonon band structure calculations. Figure 13c shows the curves of entropy as a function of temperature. Finally, the constant-volume specific heat for HgTe and HgSe crystals is given in figure 13d. The constant-volume specific heat is calculated from phonon band structure calculations. The specific heat approaches limit values of 49.71 and 49.57 at 830 K for HgTe and HgSe, respectively, which extremely close to the value of 49.91, the classical limit of specific heat, for mercury tellurium and mercury selenide.

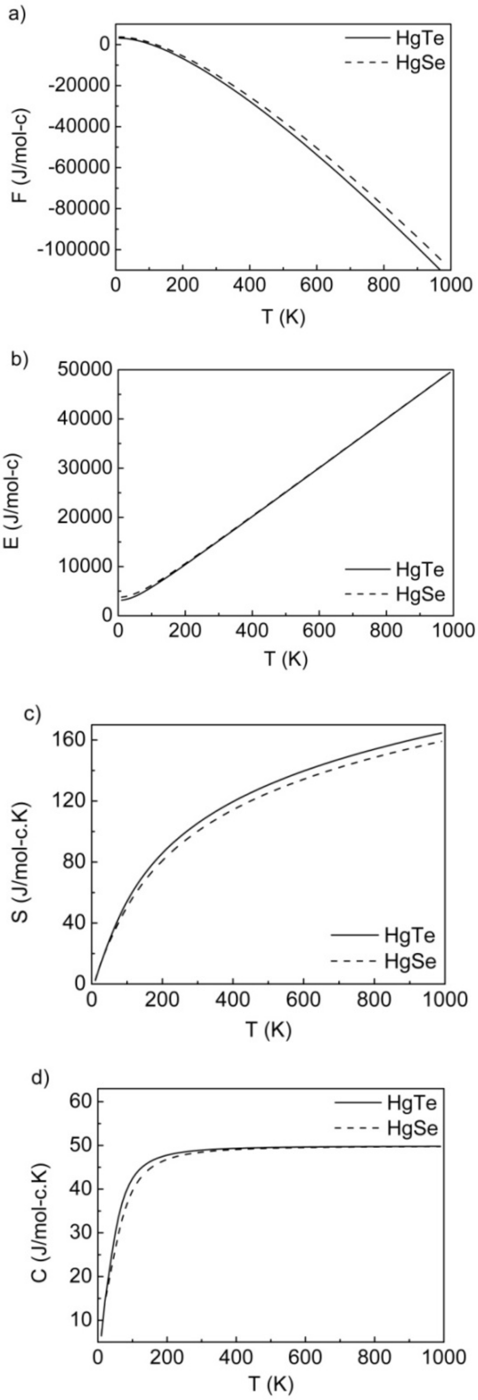

Figure 13. a) Helmholtz free energy, b) internal energy, c) entropy and d) constant volume specific heat for HgTe and HgSe as a function of temperature

7. Conclusions

Structural and volume optimization, electronic band structure, density of states, optical properties, dynamic and thermodynamic properties of HgTe and HgSe were investigated by using ABINIT[14] code within the local density approximation based on the density functional theory. HgTe and HgSe show semiconducting property with a direct band gap at high symmetry point gamma with the value of 0.99 eV.

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REFERENCES

[1] Gawlik K. U., Kipp L., Skibowski M., Orlowski N. and Manzke R., 1997, HgSe: Metal or Semiconductor?, Phys. Rev. Lett. 78, 3165-3168.

[2] Einfeldt S., Goschenhofer F., Becker C. R. and Landwehr G., 1995, Optical properties of HgSe, Phys. Rev. B 51, 4915-4925.

[3] Janowitz C., Orlowski N., Manzke R. and Golacki Z., 2001, On the band structure of HgTe and HgSe - view from photoemission , J. Alloys Compounds, 328, 84-89.

[4] Chantis A. N., Schilfgaarde M. V. and Kutani T., 2006, Erratum: Ab Initio Prediction of Conduction Band Spin Splitting in Zinc Blende Semiconductors[Phys. Rev. Lett. 96, 086405 (2006)], Phys. Rev. Lett. 96, 086405.

[5] B.M. Askerov, Electron Transport Phenomena in Semiconductors, World Scientific (Translated from Russian), 23, 1985.

[6] Delin A., Klüner T., 2002, Excitation spectra and ground-state properties from density-functional theory for the inverted band-structure systems β-HgS, HgSe, and HgTe, Phys. Rev. B, 66, 035117.

[7] Kumar V., Shrivastava A. K. and Jha V., 2010, Bulk modulus and microhardness of tetrahedral semiconductors, J. Phys. Chem.Solids 71, 1513-1520.

[8] Boutaiba F., Zaoui A. and Ferhat M., 2009, Fundamental and transport properties of ZnX, CdX and HgX (X=S, Se, Te) compounds, Superlattice Microstruct. 46, 823-832.

[9] Cardona M., Kremer R. K., Lauck R., Siegle G., Muñoz A. and Romero A. H., 2009, Electronic, vibrational, and thermodynamic properties of metacinnabar β-HgS, HgSe, and HgTe, Phys. Rev. B 80, 195204.

[10] Verma A. S., Singh R. K. and Rathi S. K., 2009, Thermal property of binary tetrahedral semiconductors, Physica B 404, 4051-4053.

[11] Arora G., Ahuja B.L., 2008, Electronic structure of some mercury chalcogenides using Compton spectroscopy, Radiat. Phys. and Chem. 77, 9–17.

[12] Penna M., Marnetto A., Bertazzi F., Bellotti E., Goano M., 1996, Empirical Pseudopotential and Full-Brillouin-Zone k.p Electronic Structure of CdTe, HgTe, and Hg1-xCdxTe , Journal of Electronic Materials, Vol. 53, 14.

[13] Rajput B. D., Browne D. A., 2002, Lattice dynamics of II-VI materials using the adiabatic bond-charge model , Phys. Rev. B, 66, 035117.

[14] Gonze X., Beuken J. M., Caracas R., Detraux F., Fuchs M., Rignanese G. M., Sindic L., Verstrate M., Zerah G., Jollet F., Torrent M., Roy A., Mikami M., Ghosez P., Raty J. Y. and Allan D. C., 2002, First-principles computation of material properties: the ABINIT software project, Computational Materials Science 25, 478-492.

[15] Fuch M. and Scheffler M. Comput. 1999, Ab initio pseudopotentials for electronic structure calculations of poly-atomic systems using density-functional theory, Phys. Commun. 119, 67-68.

[16] Perdew J. P. and Wang Y., 1992, Accurate and simple analytic representation of the electron-gas correlation energy, Phys. Rev. B 45, 13244-13249.

[17] Payne M. C., Teter M. P., Allan D. C., Arias T. A. and Joannopoulos J. D. 1992, Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients, Rev. Mod. Phys. 64, 1045-1097.

[18] Kohn W. and Sham L. J. 1965, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140, A1133-A1138.

[19] Perdew J. P., Burke K. and Ernzerhof M., 1996, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865-3868.

[20] Monkhorst H. J. and Pack J. D., 1976, Special points for Brillouin-zone integrations, Phys. Rev. B 13, 5188-5192.

[21] Polyanskiy M. (2012), Refractiveindex.info HgTe (Mercury telluride) SOPRA N&K Database.[Online]. Available: http://refractiveindex.info/?group=CRYSTALS&material=HgTe