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Influence of substitution impurities on electronic properties of CaSe nanostructures – a quantum chemical study

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Abstract: The realistic structures of pure, Te, S and Mg substituted CaSe nanostructures are successfully optimized and simulated using density functional theory along with B3LYP/ LanL2DZ basis set. Structural stability of CaSe nanostructures is characterized in terms of calculated energy, chemical potential, vibration studies and chemical hardness. The point symmetry group and dipole moment of pure, Te, S and Mg substituted CaSe nanostructures are also reported. The electronic properties are discussed in terms of ionization potential, electron affinity and HOMO-LUMO gap of CaSe nanostructures. The results of the present work provide information to tailor CaSe nanostructures by substituting proper impurities. The structural stability and electronic properties can be enhanced with substituting proper impurities in CaSe nanostructures which find its potential application in microelectronics, catalyst and in luminescence materials.

Keywords: calcium selenide; nanostructures; electron affinity; chemical hardness; electronic properties.

Introduction

The alkaline-earth chalcogenides have closed shell ionic systems which crystallize in rock salt type structure. The unique properties of calcium selenide (CaSe) are one among the large family of alkaline-earth chalcogenides which has numerous technological applications. CaSe finds its potential application in microelectronics, catalyst and luminescence [1-3]. Due to its luminescence property CaSe is used in infrared-sensitive devices. In spite of its numerous applications, only little information is explored about the structural and electronic properties of CaSe. From the previously reported literatures, CaSe has a direct band gap material with a band gap of 5 eV. In spite of the applications of CaSe, only few works are reported about its mechanical and electronic properties. Mechanical properties and electronic structure of CaSe are also recorded in computational point of view. Pandey et al. studied band gap of CaSe using Hartree – Fock calculation and it is reported to be 11.6 eV and after correction it is calculated to be 8.56 eV [4]. Marinelli et al. [5, 6] studied direct band gap of CaSe nanostructures and found to be 11.4 eV using ab initio method. The band gap value remains higher than the experimental value of 5 eV reported from optical measurement [7]. Khena ta et al. reported indirect band gap of CaSe which is reported to be 2.08 eV [8]. The experimental indirect band gap was reported to be 3.85 eV by Banu et al. [9]. In recent years, the focus is on electronic and structural [10-14] properties of CaSe nanostructures.

The motivation behind the present work is to tailor electronic properties and structural stability of CaSe nanostructures with substitution impurities to enhance the electronic properties. The promising method to study the electronic properties and structural stability of CaSe nanostructures is density functional theory (DFT). In the present work the structural stability and electronic properties of CaSe nanostructures are studied and reported.

Computational Methods

The pure CaSe nanostructures, Te, S and Mg substituted CaSe nanostructures are completely optimized using Gaussian 09W package [15]. The atomic number of calcium and selenium is twenty and thirty four respectively. In the existing work, different impurities are substituted in pure CaSe nanostructures and nanostructures are optimized with the help of Becke's three-parameter hybrid functional (B3LYP) along with suitable basis set LanL2DZ [16-18]. While simulating CaSe nanostructures selection of basis set is an important criterion. LanL2DZ basis set is a good choice for effective output with pseudo potential approximation [19]. Moreover, it is suitable for H, Hf-Bi and Li-La elements. Gauss Sum 3.0 package [20] is used to plot density of states (DOS) spectrum of CaSe nanostructures.

Results and Discussion

The existing work mainly focus on dipole moment (DM), ionization potential (IP), chemical hardness (CH), HOMO – LUMO gap, chemical potential (CP), calculated energy and electron affinity (EA) to fine-tune electronic properties of CaSe nanostructures with substitution impurities such as sulfur, tellurium, magnesium and defect structured CaSe nanostructure.

Figure 1(a) – 1(b) represents pure, Te, S, Mg substituted CaSe nanostructures and defect CaSe nanostructures respectively. The intrinsic CaSe nanostructure consists of eight Ca atoms and eight Se atoms to form 3d cubic like structure. Te substituted CaSe nanostructure has eight Ca atoms, six Se atoms and two Se atoms are replaced with two Te atoms. Similarly, S substituted CaSe nanostructure contains eight Ca atoms, six Se atoms and two S atoms are substituted instead of two Se atoms. Mg substituted CaSe nanostructure has six Ca atoms, eight Se atoms and two Mg atom are substituted instead of two Ca atoms.

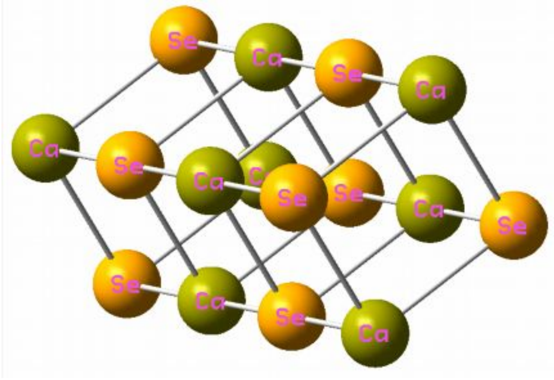


Figure.1 (a) Structure of pure 3D-CaSe nanostructure

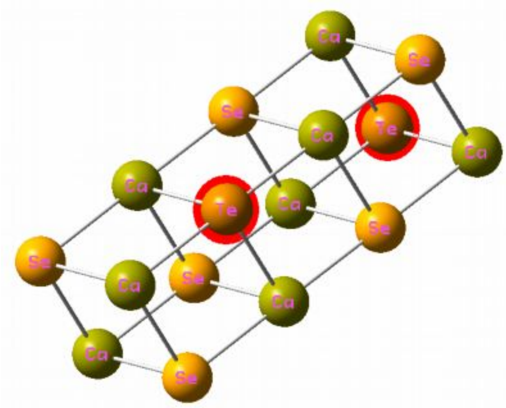


Figure.1 (b) Structure of Te substituted 3D- CaSe nanostructure

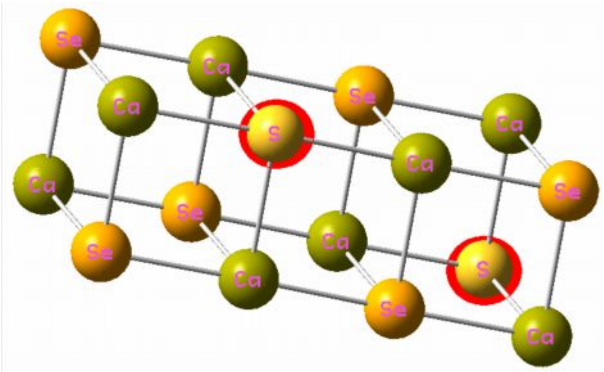


Figure.1 (c) Structure of S substituted 3D-CaSe Nanostructure

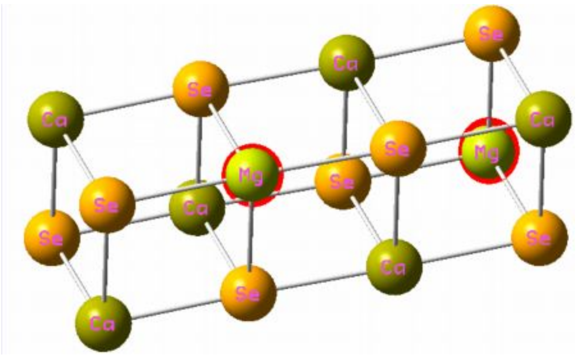


Figure.1 (d) Structure of Mg substituted 3D-CaSe nanostructure

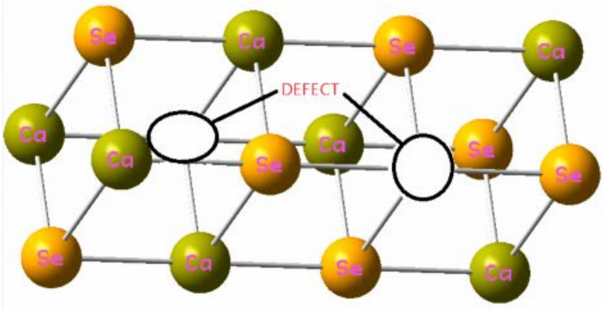


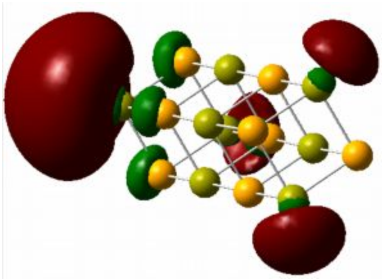
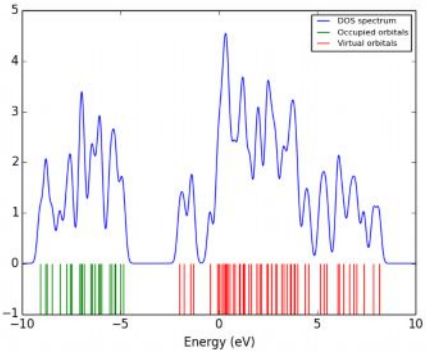
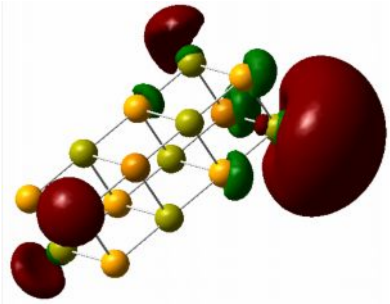
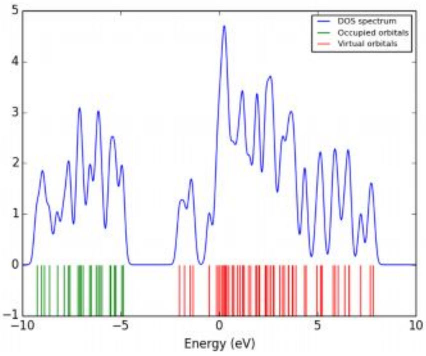
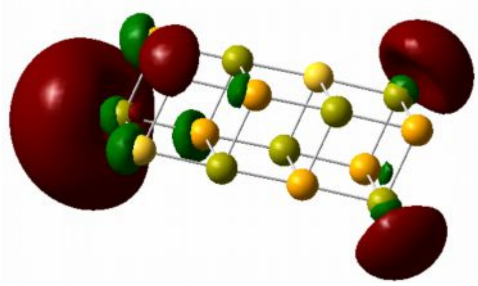
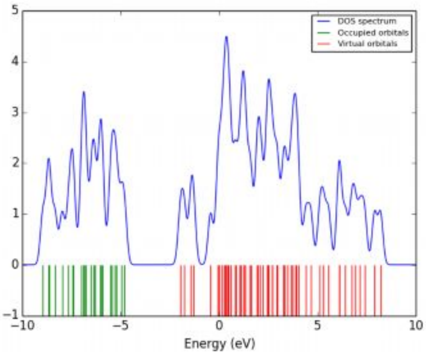
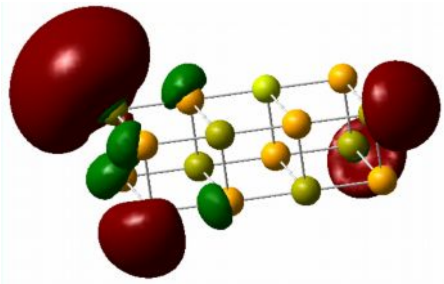
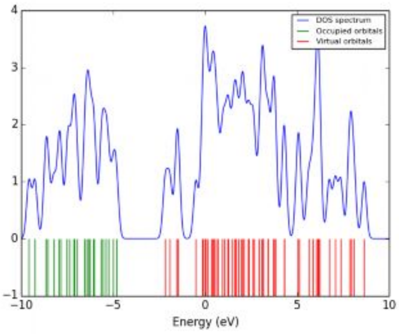
Figure.1 (e) Structure of defect CaSe nanostructure

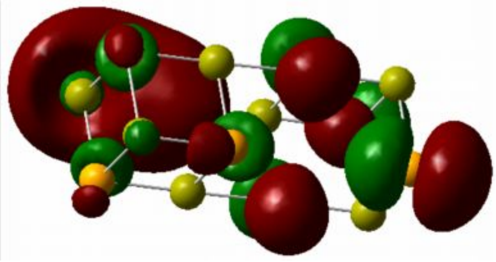
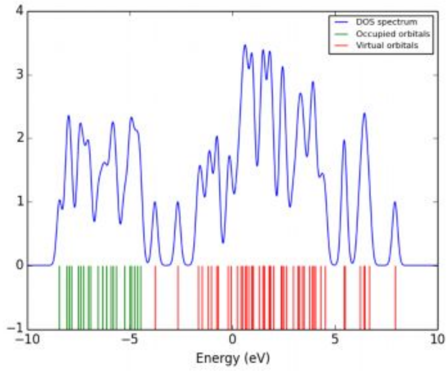
Table.1 Energy, Point symmetry and Dipole moment of CaSe nanostructures

Nanostructures	**Energy (Hartrees)**	**Dipole moment (Debye)**	**Point Group**
Intrinsic CaSe	-366.29	0.63	C_1
Te substituted CaSe	-363.64	0.75	C_1
S substituted CaSe	-368.17	0.59	C_1
Mg substituted CaSe	-295.03	1.98	C_1
Defect CaSe	-320.42	9.83	C_1

Structural stability of CaSe nanostructures can be discussed using calculated energy. The calculated energy, point group (PG) and dipole moment (DM) of all possible CaSe nanostructures are tabulated in Table 1. The calculated energy of intrinsic CaSe nanostructure is -366.29 Hartrees. The calculated energy of Te substituted CaSe nanostructures is -363.64 Hartrees which is lower than intrinsic CaSe. This infers that the structural stability decreases due to the substitution of Te in CaSe nanostructure. Similarly the structural stability drastically decreases for Mg substituted CaSe nanostructure, since the calculated value is very low in the order of -295.03 Hartrees compared to intrinsic CaSe nanostructure. The calculated energy of defect CaSe nanostructure is found to be low around -320.42 Hartrees. The stability decreases due to removal of one Ca atom and one Se atom from intrinsic CaSe nanostructures. The structural stability of S substituted CaSe nanostructure increases due to the substitution of two S atoms instead of two Se atoms and the value is calculated to be -368.17 Hartrees which is higher than the pure CaSe nanostructure. The dipole moments of intrinsic CaSe, Te, S substituted CaSe nanostructures are calculated to be 0.63, 0.75 and 0.59 Debye respectively which is low. This infers that the charge distributions are uniform inside the nanostructures and the atoms are well packed in three CaSe nanostructures. In contrast, Mg substituted CaSe and defect CaSe nanostructures have high value of DP which is 1.98 and 9.83 Debye respectively. It reveals that the charge distributions are not uniform in these CaSe nanostructures. All CaSe nanostructures has point group of C_1 which has only one symmetry operation, E.

Table.2 HOMO-LUMO gap and density of states of CaSe nanostructures

Nano Structures	**HOMO – LUMO Visualization** LUMO HOMO	**E_g (eV)**	**HOMO, LUMO and DOS Spectrum**
Intrinsic CaSe		**2.85**	
Te substituted CaSe		**2.88**	
S substituted CaSe		**2.84**	
Mg substituted CaSe		**2.66**	

Defect CaSe		**0.7**	

The electronic properties of CaSe nanostructures can be described by lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [21-24]. Almost all the possible CaSe nanostructures has same energy gap value in the range of 2.66 – 2.88 eV except for defect CaSe nanostructures which is 0.7 eV as shown in Table 2. The density of states (DOS) and visualization of HOMO – LUMO are shown in Table 2. The substitution impurities have not much influence in the band gap compared with pure CaSe nanostructures.

The CaSe nanostructures show a semiconducting behavior. The energy required to move the electrons from HOMO to LUMO level should be more. From the density of states spectrum the localization of charges are seen more in LUMO level than HOMO level. The substitution impurity completely modifies the density of charges in HOMO and LUMO level. Electronic properties of CaSe nanostructures can be fine-tuned with the help of substitution impurities.

Ionization potential, electron affinity, chemical potential and chemical hardness of CaSe nanostructures

The electronic properties of CaSe nanostructures can also be analyzed by electron affinity (EA) and ionization potential (IP) [25, 26]. Figure 2 shows the EA and IP of CaSe nanostructures.

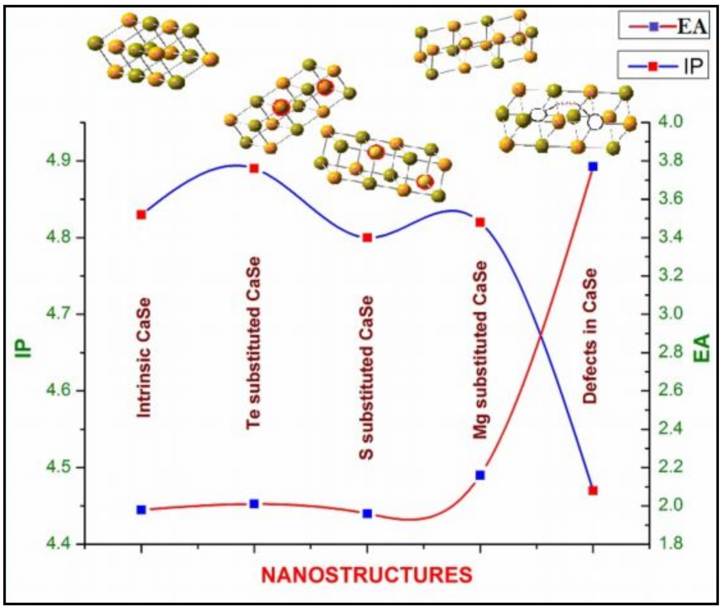


Figure. 2 IP and EA of CaSe nanostructures

The energy required to remove electron from CaSe nanostructures is known as IP. On other hand the change in energy due to addition of electron to CaSe nanostructures is EA. Almost same IP values are recorded for all CaSe nanostructures and the value is around 4.8 eV. Meanwhile different trends are observed in EA which is in the range of 1.96 – 3.77 eV. EA play an important role in plasma Physics and also in chemical sensors. The energy required to remove the electron is more for all CaSe nanostructures except for defect structure. In defect structure Ca and Se are already removed giving rise to delocalization of orbitals around the defect which gives rise to easy removal of electrons from CaSe nanostructures. Hence IP for defect CaSe nanostructure is found to be low. In contrast EA values for all CaSe nanostructures are low, whereas for defect CaSe nanostructure it is more.

Table.3 Chemical potential and chemical hardness of CaSe nanostructures

Nano Structures	Chemical potential (eV)	Chemical hardness (eV)
Intrinsic CaSe	-3.40	1.42
Te substituted CaSe	-3.45	1.44
S substituted CaSe	-3.38	1.42
Mg substituted CaSe	-3.49	1.33
Defects in CaSe	4.12	0.35

Chemical potential (CP) and chemical hardness (CH) are related to IP and EA. The structural stability of CaSe nanostructures can be calculated in terms of CH and CP [21, 27]. CP and CH can be calculated as $\mu = -(IP+EA)/2$ and $\eta = (IP-EA)/2$ respectively. Almost same values of CP are observed for all CaSe nanostructures which is 3.4 eV with corresponding CH value around 1.4 eV except for defect CaSe nanostructures as shown in Table 3. Moreover the energy gap of intrinsic CaSe, Te, S and Mg substituted CaSe nanostructures has almost same value. The effective fragment potential (EFP) model is useful to reveal the effect of chemical potential and chemical hardness. In some cases CP is represented by electronegativity which is applicable to semiconductor Physics.

Vibrational Studies of CaSe nanostructures

The structural stability of CaSe nanostructures is mainly concerned with vibrational studies. CaSe nanostructures are said to be more stable when there is no imaginary frequency. Table 4 represents the vibrational frequency and IR intensity for CaSe nanostructures [28-29].

Table.4 Vibrational Frequency and IR Intensity of CaSe nanostructures

Nano Structures	Frequency (cm^{-1})		IR intensity (km/mole)	
Intrinsic CaSe	533.44	339.19	195.94	173.76
Te substituted CaSe	539.8	333.11	148.34	133.61
S substituted CaSe	539.22	349.46	193.3	135.24
Mg substituted CaSe	446.87	306.52	166.03	110.78
Defects in CaSe	370.65	425.83	48.76	48.05

The pure CaSe nanostructure has the IR intensity of 195.94 and 173.76 km/mole with corresponding vibrational frequency at 533.44 and 339.19 cm^{-1} followed by the Te substituted CaSe nanostructure has the vibrational frequency recorded at 539.8 and 333.11 cm^{-1} along with IR intensity of 148.34 and 133.61 km/mole respectively. The prominent IR intensity of S substituted CaSe nanostructure is 193.3 and 135.24 km/mole with vibrational frequency of 539.22 and 349.46 cm^{-1} respectively. Mg substituted CaSe nanostructure has vibrational frequency at 446.87 and 306.52 cm^{-1} with IR intensity of 166.03 and 110.78 km/mole respectively. In the case of defect CaSe nanostructures the vibrational frequency is observed at 370.65 and 425.83 cm^{-1} with corresponding IR intensity of 48.76 and 48.05 km/mole respectively. For all CaSe nanostructures, molecular stretching vibrational mode is observed. The vibrational spectrums of CaSe nanostructures are shown in Figure 3(a) – 3(e).

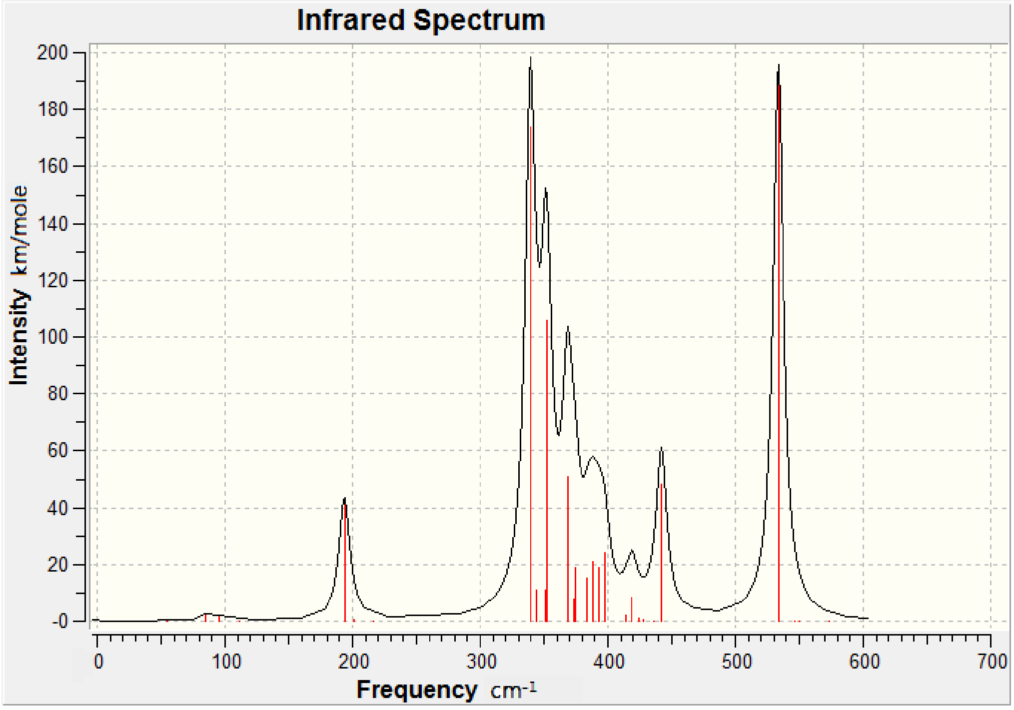


Figure.3 (a) pure 3D-CaSe nanostructure

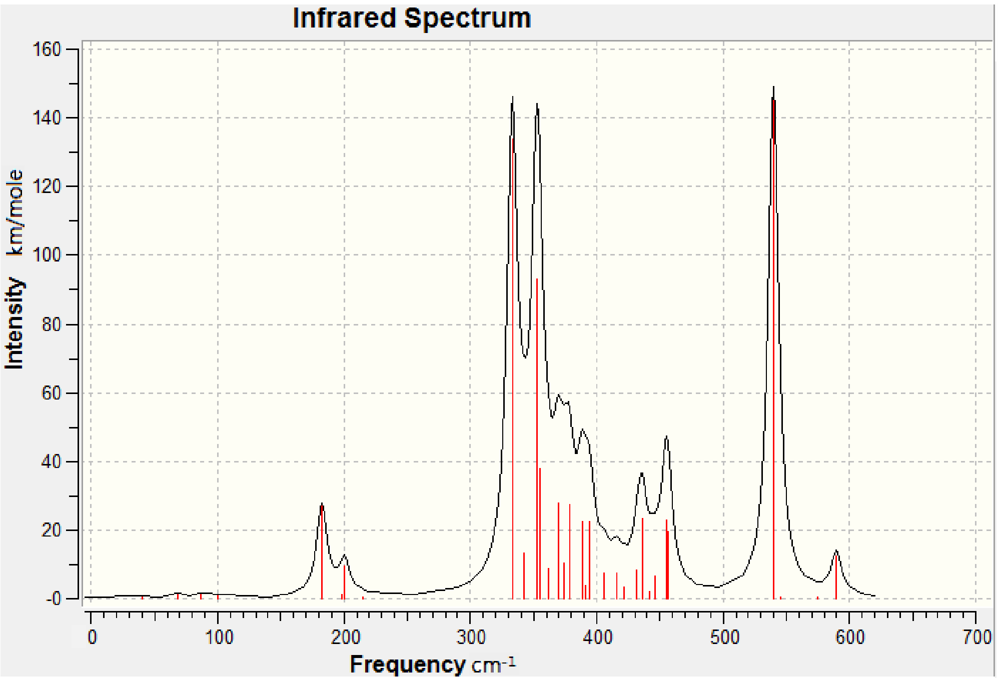


Figure.3 (b) Te substituted 3D- CaSe nanostructure

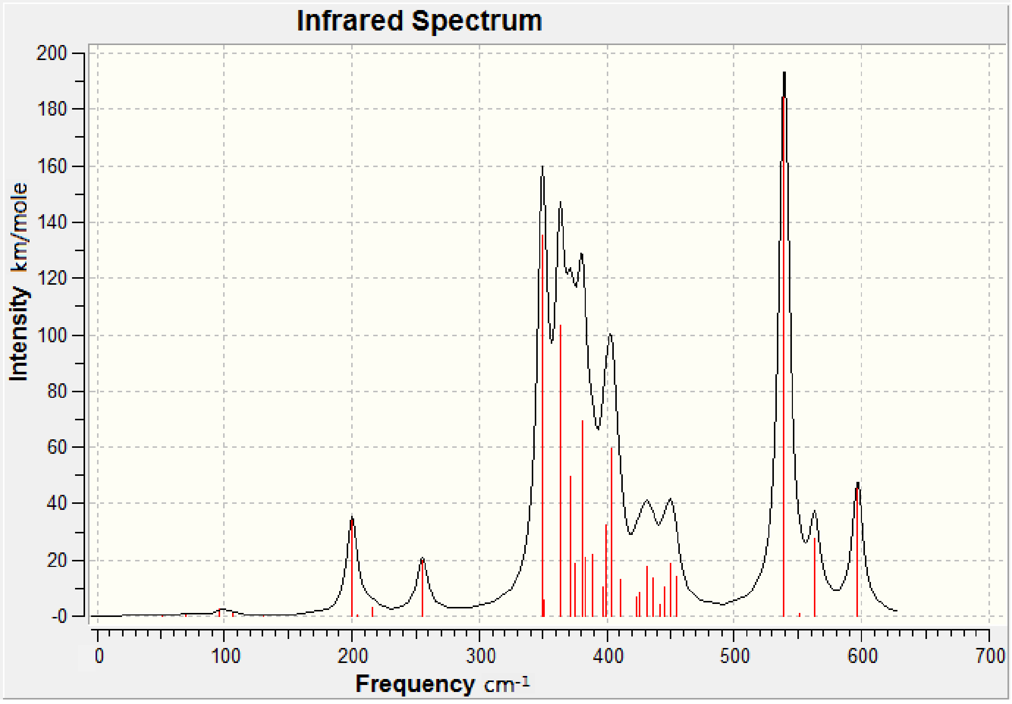


Figure.3 (c) S substituted 3D- CaSe nanostructure

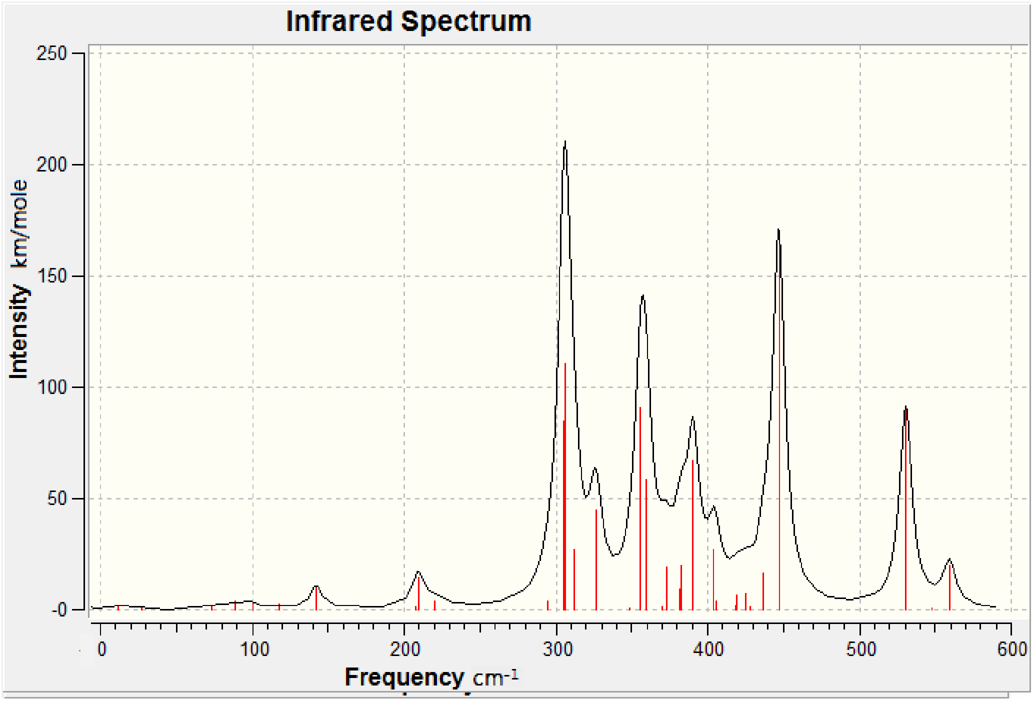


Figure.3 (d) Mg substituted 3D- CaSe nanostructure

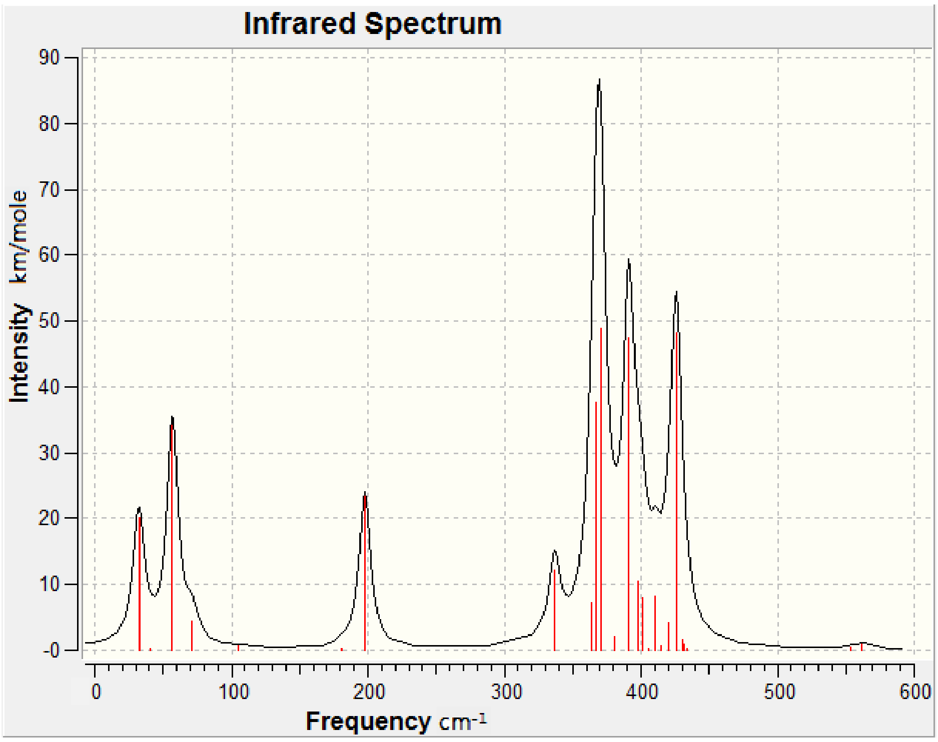


Figure.3 (e) defect CaSe nanostructure

Conclusion

In conclusion, the realistic structures of pure, Te, S and Mg substituted CaSe nanostructures are successfully optimized and simulated with B3LYP/LanL2DZ basis set. The structural stability of CaSe nanostructures is discussed with the help of chemical hardness, calculated energy, vibrational studies and chemical potential. Point symmetry group and dipole moment of pure and Te, S and Mg substituted CaSe nanostructures are also reported. Using HOMO-LUMO gap, ionization potential, density of states spectrum and electron affinity, the electronic properties of CaSe nanostructures are described. The results of the present work will give an insight to enhance the structural stability and electronic properties of CaSe nanostructures with substitution impurities such as Te, S and Mg in CaSe nanostructure. The electronic properties and structural stability of CaSe nanostructures can be tailored with substitution impurity and defect structure which find its potential application in microelectronics, catalyst and luminescence materials.

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