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Effect on the structural stability and electronic properties of impurity substituted sodium selenide nanostructures – A quantum chemical study

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Abstract: The realistic pure, tellurium, sulfur, potassium and caesium substituted NaSe nanostructures are simulated and optimized successfully with B3LYP/LanL2DZ basis set. Structural stability of NaSe are analysed by chemical hardness, calculated energy and chemical potential. Electronic properties of NaSe nanostructures are evaluated by ionization potential, HOMO – LUMO gap and electron affinity. The dipole moment and point group of pure and impurity substituted NaSe nanostructures are also reported. The present work paves way to tailor NaSe nanostructures with substitution impurities to enhance the structural stability and electronic properties for engineering applications.

Keywords: Sodium selenide, dipole moment, chemical hardness, chemical potential, HUMO-LUMO.

Introduction

Recent development in nanomaterial synthesis leads to preparation of nanowires, nanotubes, nanorods and nanowires for the past one decade [1-5]. Chalcogen includes S, Se or Te but not O. Chalcogenides are recognised group of inorganic chemistry which finds its applications widely in chalcogenide glasses, solar cells, optical fibers and catalyst. Most of the nanomaterials reveal the properties of technological value especially in semiconductor industries. Among the semiconducting materials, nitrides and chalcogenides find its importance. One among the important chalcogenide materials is sodium selenides (NaSe). NaSe is a colourless solid synthesized by the reaction of selenium and solution of sodium combined together with ammonia [6]. Sodium selenide can be used in many applications particularly in paper and pulp industry for kraft process followed by photographic industry to prevent developer solutions, bleaching in textile industry, sulphur dyes and detergents. NaSe exhibit important physical and chemical properties. Chemically it is very stable and being unreactive with most of the reducing agents.

The objective of the present study is to invoke the structural stability and electronic properties of NaSe nanostructures and incorporating the impurities to enhance the physical and chemical properties. With this as objective, survey was conducted and it reveals that not much work has been carried out in sodium selenide. Density functional theory (DFT) is a promising method to study the stability and electronic properties of nanostructures. DFT can be utilized for fine adjustment of nanostructures and electronic properties of NaSe nanostructures [7-9]. Various nanostructures of NaSe are optimized and simulated successfully and the results are reported.

Computational Methods

NWChem package is utilized to optimize NaSe nanostructures successfully[10]. In simulating nanostructures choosing the basis set is very important criterion, since the atomic number of sodium and selenium is eleven and thirty four respectively, Becke's three-parameter hybrid functional (B3LYP) with LanL2Z basis set is utilized to optimize NaSe nanostructures [11-15]. In the present work, different dopant elements are substituted in pure nanostructures of sodium selenide nanostructures and these combinations of compounds have been optimized with LanL2DZ basis set which produce good throughput with pseudo potential approximation [16].

Results and Discussion

The present work primarily focus on ionization potential (IP), dipole moment (DM), chemical hardness, chemical potential, HOMO-LUMO gap, electron affinity and calculated energy to enhance NaSe nanostructures substituted with different elements namely tellurium, sulphur, potassium and caesium.

Figure.1 (a) Structure of pure 3D-NaSe Nanostructures

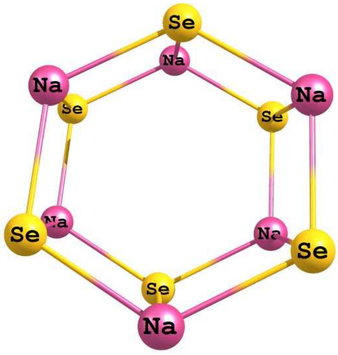


Figure.1 (b) Structure of Te substituted 3D- NaSe nanostructures

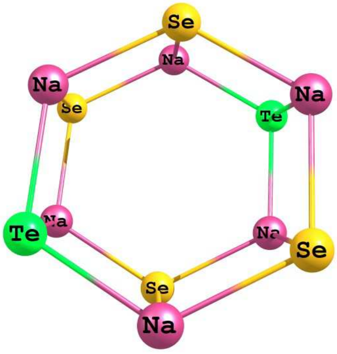


Figure.1 (c) Structure of S substituted 3D-NaSe nanostructures

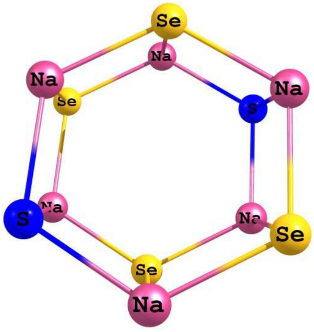


Figure.1 (d) Structure of K substituted 3D-NaSe nanostructures

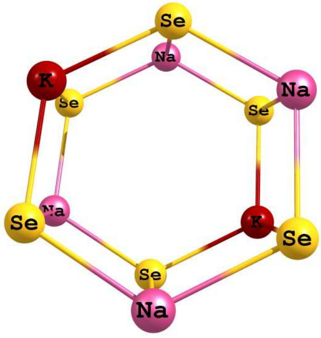


Figure.1 (e) Structure of Cs substituted 3D-NaSe nanostructures

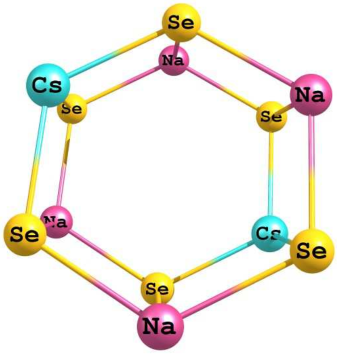


Table.1 Energy, Point symmetry and Dipole moment of NaSe nanostructures

Nanostructures	**Energy (Hartrees)**	**Dipole moment (Debye)**	**Point Group**
Pure NaSe	-56.88	0.098	C_1
Te substituted NaSe	-54.51	0.092	C_1
S substituted NaSe	-58.62	0.1	C_1
K substituted NaSe	-112.64	0.092	C_1
Cs substituted NaSe	-95.79	0.074	C_1

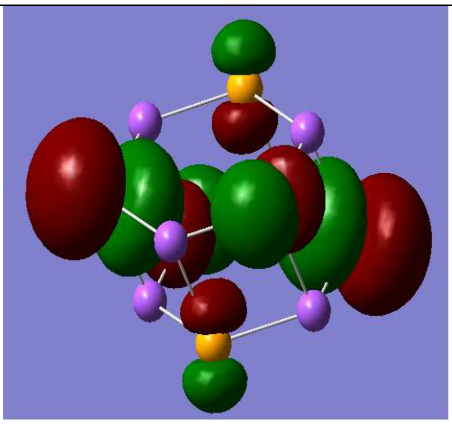
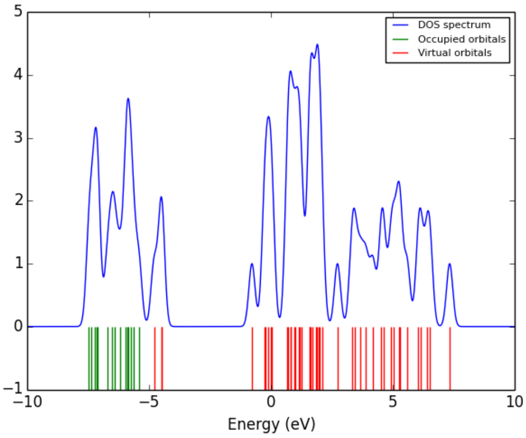
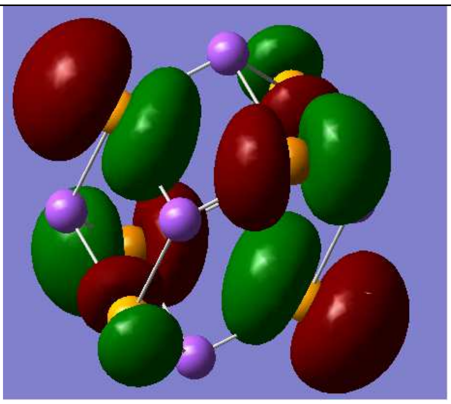
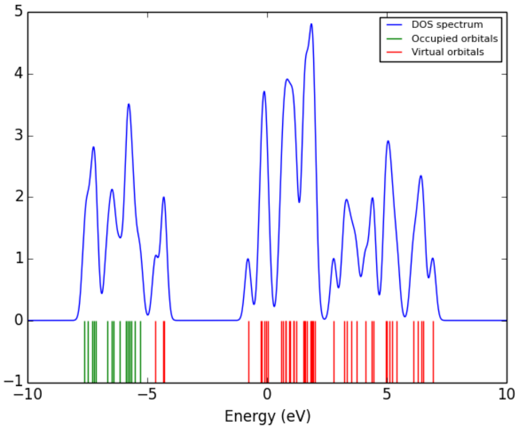
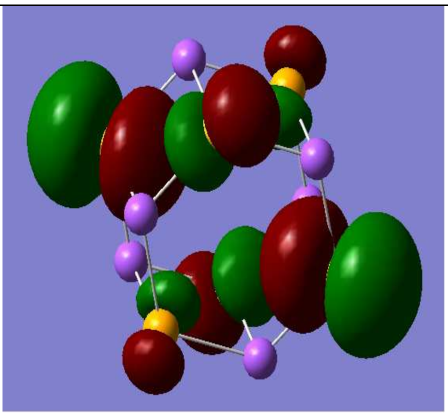
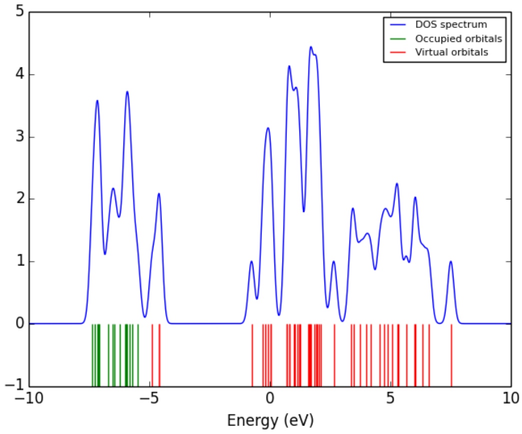
Figure 1(a) – 1(e) represents the nanostructures of pure, Te, S, K, Cs substituted NaSe structures. The pure form of NaSe nanostructure consists of six Na atoms with six Se atoms to form benzene like structure. Te substituted NaSe nanostructure contains six Na atoms, four Se atoms and two Te atoms, two Te atoms are substituted in place of Se atoms. Similarly S substituted NaSe nanostructure is built by six Na atoms, four Se atoms and two S atoms. K substituted NaSe nanostructure is formed by four Na atoms, six Se atoms and two K atoms. Likewise, Cs substituted NaSe nanostructure has six Se atoms, four Na atoms and two Cs atoms, two Cs atoms replace Na atoms.

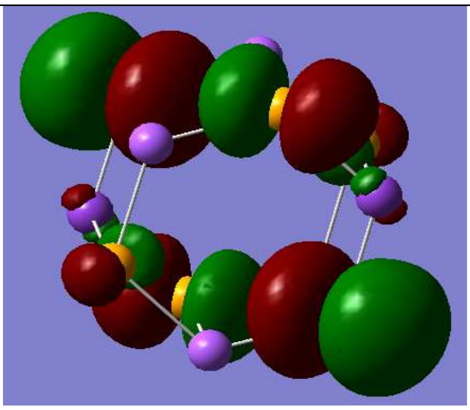
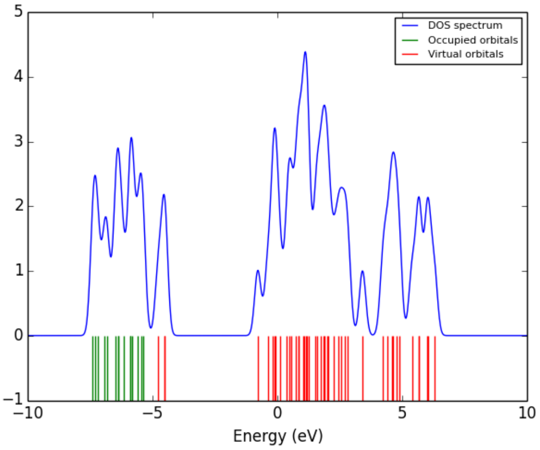
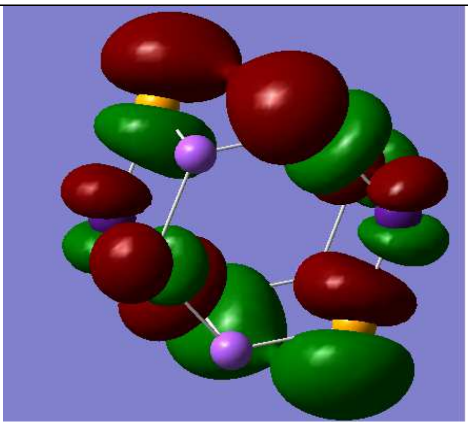
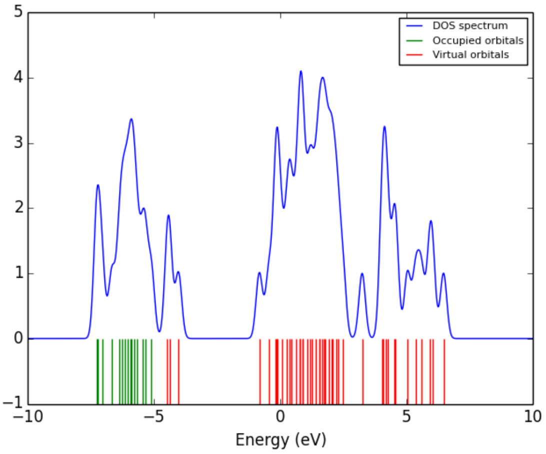
The structural stability of NaSe nanostructures can be analysed using calculated energy. The calculated energy, dipole moment (DM) and point group of all the above mentioned NaSe nanostructures are tabulated in Table 1. The calculated energy of pure NaSe is -56.88 Hartrees. When two Te atoms is substituted in NaSe nanostructures instead of two Se atoms, calculated energy changes to -54.51 Hartrees which is lower than pure NaSe nanostructure. The stability of Te substituted NaSe nanostructure decreases with Te substitution. The calculated energy of S substituted NaSe, K substituted NaSe and Cs substituted NaSe nanostructures are -58.62, -112.64 and -95.79 Hartrees respectively. The calculated energy of these nanostructures is high compared to the pure form of NaSe. The stability increases with the substitution of S, K and Cs atoms. The dipole moment of all NaSe nanostructures are found to be almost of same value and ranges from 0.074 to 0.1 Debye. The low value of DM infers that the atoms are perfectly packed and distribution of charges is uniform inside the nanostructures. All the structures of NaSe have point group of C_1 which refers high asymmetry in the structure.

HOMO-LUMO gap and density of states of NaSe nanostructures

The electronic properties of NaSe nanostructures can be analysed by highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [17,18]. Almost all the nanostructures has same energy gap in the range of 0.62 – 0.64 eV as shown in Table 2. Table 2 visualizes the HOMO-LUMO and density of states (DOS) spectrum in NaSe nanostructures. The energy gap value is not much affected by substitution impurities. The nanostructure of NaSe shows a semiconducting behaviour with narrow gap. Even applying a low energy will excite the electron from HOMO level to LUMO level. The localization of charges is seen more in the LUMO level than in HOMO level from DOS spectrum. This implies that a minimum energy can move the electrons from HOMO to LUMO level. More density of charges is seen in different energy interval of LUMO level. This refers to the localization of charges in the LUMO level. The substitution of impurities in NaSe structures completely modifies the density of charges in energy interval. The electronic properties can be fine-tuned with the substitution of impurities in NaSe nanostructures.

Table. 2 HOMO-LUMO Gap of NaSe nanostructures

Nano structures	**HOMO – LUMO Visualization** LUMO HOMO	**E_g (eV)**	**HOMO, LUMO and DOS Spectrum**
Pure NaSe		0.62	
Te substituted NaSe		0.64	
S substituted NaSe		0.63	

K substituted NaSe		0.62	
Cs substituted NaSe		0.63	

Ionization potential, Electron affinity, chemical potential and chemical hardness of NaSe nanostructures

The electronic properties of NaSe nanostructures can also be studied by Ionization potential (IP) and Electron affinity (EA) [19]. Figure 2 shows the IP and EA of NaSe nanostructures. The IP and EA ranges from 5.1 eV to 5.5 eV for different structures of NaSe. S substituted NaSe requires more energy to remove the electron from the structure, in contrast, Cs substituted NaSe requires less energy to remove the electron from the nanostructure. Since caesium atom has more number of electrons than sodium, the removal of electron from this structure is easier. The energy released due to the addition of electrons to the NaSe nanostructures are referred as EA. EA of NaSe nanostructures values range from 4.46 – 4.86 eV. Among all the impurity substituted NaSe nanostructures there is no much variation in EA is noticed.

The structural stability of NaSe nanostructures can also be explored in terms chemical potential (CP) and chemical hardness (CH) [20]. The significant formula for CH and CP is $\eta = (IP-EA)/2$ and $\mu = -(IP+EA)/2$ respectively. Almost same trends are observed in CP with the value ranging from 4.78 – 5.18 eV. However, CH does not show much difference in the value, it is in the order of 0.3 eV. Table 3. represents CH and CP of NaSe nanostructures.

Figure 2. IP and EA of NaSe Nanostructures

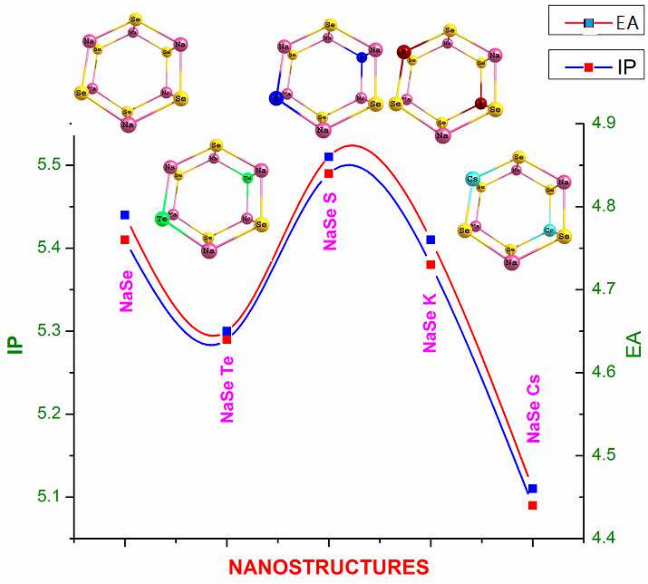


Table.3 Chemical potential and chemical hardness of NaSe nanostructures

Nano structures	Chemical potential (eV)	Chemical hardness (eV)
Pure NaSe	-5.1	0.31
Te substituted NaSe	-4.97	0.32
S substituted NaSe	-5.18	0.32
K substituted NaSe	-5.07	0.31
Cs substituted NaSe	-4.78	0.32

CP and CH are highly related to ionization potential and electron affinity. When the hardness of the material is high, HOMO – LUMO gap is also relatively high. The model of effective fragment potential (EFP) is used to explore the effect of CP and CH [21, 22]. CP also denotes the electronegativity which plays a vital role in semiconductor physics.

Conclusion

Using DFT, pure and impurity substituted NaSe nanostructures are successfully optimized with B3LYP/LanL2DZ basis set. The structural stability of NaSe nanostructures are analysed by chemical potential, calculated energy and chemical hardness. The electronic properties of NaSe nanostructures are discussed in terms of ionization potential, electron affinity, HOMO-LUMO gap and density of states spectrum. The dipole moment and point symmetry of different structures of NaSe are also reported. The present work provides the insight for tailoring NaSe nanostructures to enhance the structural stability and electronic properties with substitution impurities which finds its potential importance in engineering applications.

References

1. Rao C N R, Mueller A and Cheetham A K., The chemistry of nanomaterials, Wiley-VCH, Weinheim., 2004, 5(12), 1913-1914.
2. Rao C N R, Deepak F L, Gundiah G and Govindaraj A., Inorganic nanowires, Progress in Solid State Chemistry., 2003, 31, 5-147.
3. Wang Z L., Advanced materials, Adv. Mater., 2003, 15(5), 351-345.

4. Tenne R and Rao C N R, Inorganic nanotubes, Philosophical Transactions of the royal society of London, series A: Mathematical, Physical and ssEngineering Sciences., 2004, 362(1823), 2099-2125.
5. Rao C N R and Nath M.,Inorganic nanotubes, J. Chem. Soc. Dalton Trans., 2003, 1-24.
6. Brauer G., Handbook of Preparative Inorganic Chemistry, 2nd Ed., Academic Press, 1963, 1,1-1906.
7. Sriram S and Chandiramouli R., DFT studies on the stability of linear, ring, and 3D structures in CdTe nanoclusters, Res Chem Intermed., 2013, DOI: 10.1007/s11164-013-1334-6.
8. Nagarajan V and Chandiramouli R., Structural Stability and Electronic Properties of Neutral, Anionic and Cationic Cesium Chloride Nanostructures – A DFT Study, Res J Pharm Biol Chem Sci, 2014, 5(1), 365-379.
9. Nagarajan V and Chandiramouli R., Quantum Chemical Studies on ZrN Nanostructures, Int.J. ChemTech Res.,2014, 6(1), 21-30.
10. Valiev M, Bylaska E. J, Govind N, Kowalski K, Straatsma T.P, Van Dam H.J.J, Wang D, Nieplocha J, Apra E, Windus T.L, De JongW. A NWChem: a comprehensive and scalable open-source solution for large scale molecular simulations. Comput Phys Commun., 2010, 181, 1477–1489.
11. Chandiramouli R., A DFT study on the structural and electronic properties of Barium Sulfide nanoclusters, Res. J. Chem. Environ., 2013, 17, 64-73.
12 Droghetti A, Alfè D, and Sanvito S., Assessment of density functional theory for iron(II) molecules across the spin-crossover transition, J. Chem. Phys., 2012, 137, 124303-124312.
13. Mohammed Bouklah, Houria Harek, Rachid Touzani, Belkheir Hammouti and Yahia Harek., DFT and quantum chemical investigation of molecular properties of substituted pyrrolidinones, Arabian J. Chem., 2012, 5, 163-166.
14. Wei Huang et al., CO chemisorption on the surfaces of the golden cages, J. Chem. Phys., 2009, 131, 234-305.
15. Groenewold Gary S, Gianotto Anita K, McIlwain Michael E, Van Stipdonk Michael J, Kullman Michael, Moore David T, Polfer Nick, Oomens Jos, Infante Ivan, Visscher Lucas, Siboulet Bertrand and de Jong Wibe A., Infrared Spectroscopy of Discrete Uranyl Anion Complexes, J. Phys. Chem., 2008, 112 A, 508-521.
16. Srinivasaraghavan R, Chandiramouli R, Jeyaprakash B.G. and Seshadri S., Quantum chemical studies on CdO nanoclusters stability, Spectrochim. Acta, Part A., 2013, 102, 242-249.
17. John Xavier R and Gobinath E., Experimental and theoretical spectroscopic studies, HOMO–LUMO, NBO and NLMO analysis of 3,5-dibromo-2,6-dimethoxy pyridine, Spectrochim. Acta, Part A., 2012, 97, 215-222.
18. Sriram S, Chandiramouli R, Balamurugan D and A. Thayumanvan., A DFT study on the structural and electronic properties of ZnTe nanoclusters, Eur. Phys. J. Appl. Phys., 2013, 62, 30101.
19. Zhan C.G, Nichols J.A and Dixon D.A., Ionization Potential, ElectronAffinity, Electronegativity, Hardness, and Electron Excitation Energy: Molecular Properties from Density Functional Theory Orbital Energies, J. Phys. Chem., 2003, 107 A, 4184-4195.
20. Pearson R G., Ionization potentials and electron affinities in aqueous solution, J. Am. Chem. Soc., 1986, 108, 6109-6114.
21. Safi B, Balawender R and Geerlings P., Solvent effect on electronegativity, hardness, condensed Fukui functions, and softness, in a large series of diatomic and small polyatomic molecules: use of the EFP model, J. Phys. Chem. A., 2001,105,11102.
22. Safi B, Choho K, De Proft F and Geerlings P., Theoretical Study of the Basicity of Alkyl Amines in Vacuo and in Different Solvents : A Density Functional Approach, Chem. Phys. Lett., 1999, 300, 85-92.

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