ISSN 1996-3343

Asian Journal of Applied Sciences

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Asian Journal of Applied Sciences 7 (8): 721-728, 2014
ISSN 1996-3343 / DOI: 10.3923/ajaps.2014.721.728

Structural Stability and Electronic Properties of Neutral, Anionic and Cationic Nickel Selenide and Cobalt Selenide Nanostructures: A DFT Approach

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ABSTRACT

The transition metal chalcogenide nanostructures of NiSe and CoSe in different states namely cationic, anionic and neutral are completely simulated and optimized successfully by B3LYP/LanL2DZ basis set. Stability of transition metal chalcogenide structures has been conversed by using calculated energy and vibrational studies. Electronic properties of NiSe and CoSe are studied in terms of HOMO-LUMO gap, electron affinity and ionization potential. The point symmetry and dipole moment of NiSe and CoSe are also reported. This study is concentrated in enhancing electronic properties of transition metal chalcogenide which is most applicable to solar cells, lithium ion batteries and as catalyst.

Key words: Nickel selenide, cobalt selenide, HOMO, LUMO, nanostructures

INTRODUCTION

Nickel selenide (NiSe) is a semiconductor which shows excellent electronic and magnetic properties. NiSe has several applications in materials science field particularly in solar cells and in chemical sensors, because the band gap of NiSe lies between nickel oxide and nickel sulphide (Wang *et al.*, 2005). Recently, $NiSe_2$ new application exhibit due to electrochemical properties (Xue and Fu, 2006). So many researches are focused especially on these semiconductors over the past one decade (Steigerwald and Brus, 1990). The nanostructures of NiSe and CoSe can be synthesized by solvothermal process (Yang *et al.*, 2001), mechanical alloying (Campos *et al.*, 2003), hydrothermal (Zhuang *et al.*, 2006), ultrasonic synthesis (Ge and Li, 2003), elemental direct reactions (Henshaw *et al.*, 1997), solid-state synthesis (Bonneau *et al.*, 1991) chemical method, molecular precursors (Brennan *et al.*, 1992) and chemical vapour deposition method. Cobalt selenide (CoSe) is one of the most significant transition metal chalcogenide which is much attention in many engineering applications such as in solar cells and catalysts (Lai *et al.*, 2011; Feng and Alonso-Vante, 2012; Liu *et al.*, 2012). The inspiration behind the study is to improve superior electronic properties of stable nanostructures, using Density Functional Theory (DFT). Even though some of transition metal chalcogenides works are reported with the help of DFT studies (Sriram and Chandiramouli, 2013), the present study deals with two distinct transition metal chalcogenides, NiSe and CoSe nanostructures in neutral, cationic and anionic states.

COMPUTATIONAL DETAILS

The neutral, cationic and anionic nanostructures of NiSe and CoSe are optimized and simulated through NW Chem package (Valiev *et al.*, 2010) with Becke's three- parameter hybrid function-(B3LYP) method in combination with LanL2DZ basic set (Mahfouz *et al.*, 2011; Droghetti *et al.*, 2012; Bouklah *et al.*, 2012; Groenewold *et al.*, 2008; Chandiramouli, 2013). The atomic number of Nickel, Cobalt and Selenide are 28, 27 and 34, respectively. LanL2DZ gives adequate output through pseudo potential approximation (Srinivasaraghavan *et al.*, 2013) Nanostructures stability and electronic properties are calculated by DFT electron density functional. Two dissimilar transition metal chalcogenides NiSe and CoSe are optimized and simulated with the help of NW Chem package.

RESULTS AND DISCUSSION

The optimized nanostructures of NiSe and CoSe are shown in Fig. 1a-d. The present study mainly deals with two different isomers. For each nanostructure, energy is calculated by changing its charge state as cationic, anionic and neutral. Table 1 contains Dipole moment (DP), point group

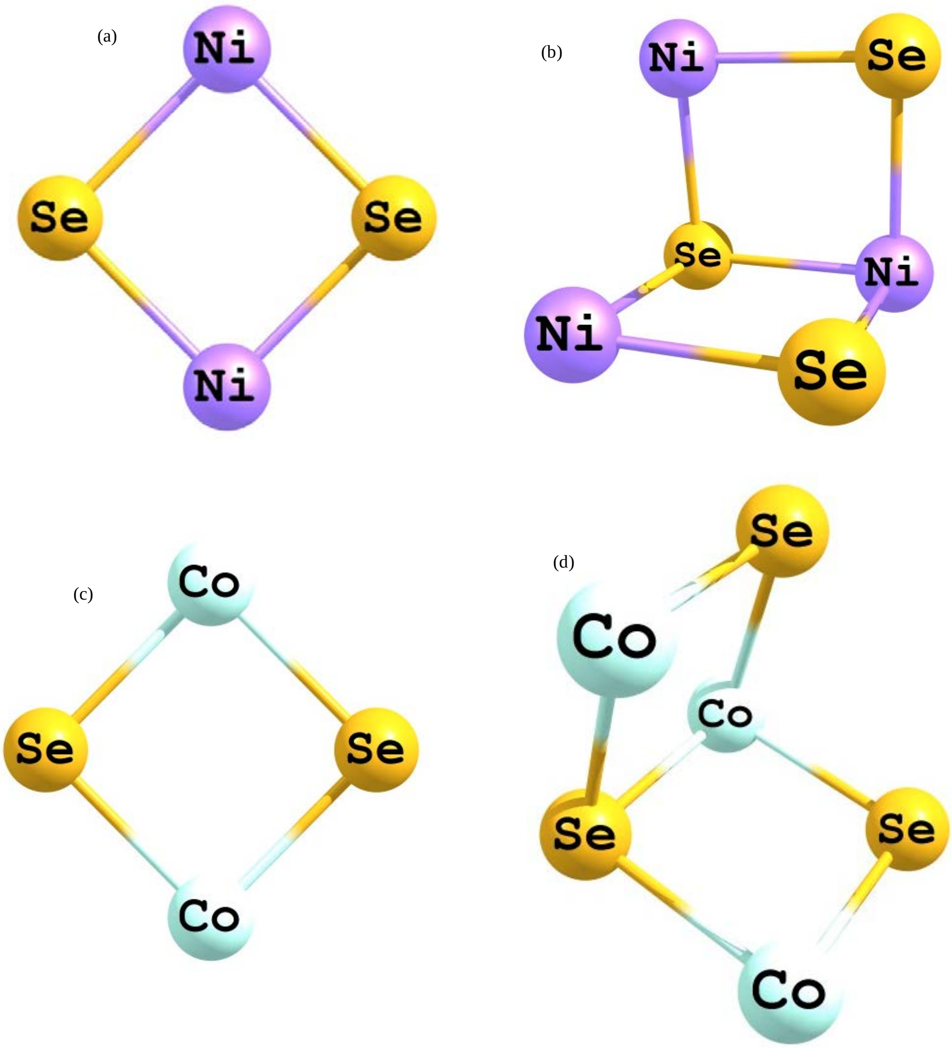

Fig. 1(a-d): (a) $NiSe_2$, (b) $NiSe_3$, (c) $CoSe_2$ and (d) $CoSe_3$

Table 1: Energy, point symmetry and dipole moment of NiSe and CoSe nanostructures

Nanostructures	Size	Charge state	Energy (Hartrees)	DM (Debye)	Point symmetry
NiSe	2	0	-357.00	0.0006	C_S
		1	-356.71	0.0028	C_S
		-1	-357.074	0.0006	C_S
	3	0	-535.44	2.093	C_1
		1	-535.44	2.09	C_1
		-1	-535.50	1.55	C_1
CoSe	2	0	-308.46	0.0009	C_S
		1	-308.18	0.0007	C_S
		-1	-308.53	0.0005	C_S
	3	0	-462.66	2.29	C_1
		1	-462.38	2.09	C_1
		-1	-462.38	2.09	C_1

symmetry and calculated energy. Stability of CoSe and NiSe are discussed using calculated energy. The energy value of $NiSe_2$, $NiSe_3$, $CoSe_2$ and $CoSe_3$ are -357, -535.44, -308.46 and -462.66 Hartrees, respectively. The possible three charge states of corresponding nanostructures energy are observed almost to be same value, the variation is observed only in the decimal part. By the addition of atom, stability of both transition metal chalcogenides NiSe and CoSe increases. The dipole moment of nanostructures are also found to be nearly equal for neutral, cationic and anionic as shown in Table 1. Low DM values are observed in the case of $NiSe_2$ and $CoSe_2$ with the range of 0.0005-0.0028 Debye. Therefore uniform charge distribution are seen inside the nanostructures. In contrast, DM of $NiSe_3$ and $CoSe_3$ nanostructure is found to be high in the range from 1.55-2.09 Debye due to less uniform charge distribution. The point symmetry of all the above mentioned nanostructures is C_1 and C_S which infers asymmetry in the structure.

Electronic properties of NiSe and CoSe nanostructures: The electronic properties of NiSe and CoSe nanostructures can be elucidated by Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) (Arivazhagan and Jeyavijayan, 2011; Xavier and Gobinath, 2012). Alpha represents due to spin up electrons and beta represents due spin down electrons in the nanostructures. The alpha and beta HOMO-LUMO gap for NiSe and CoSe nanostructures are in the range from 1.35-2.49 eV. Alpha energy gap of neutral, cationic and anionic $NiSe_2$ are 1.73, 2.18 and 2.46 eV, respectively. Beta cationic and anionic $NiSe_2$ HOMO-LUMO gap are 2.33 and 2.42 eV, respectively. The remaining $NiSe_3$, $CoSe_2$ and CoSe nanostructures energy gap are tabulated in Table 2. The discussed transition metal chalcogenides nanostructure has semiconductor nature which is applicable to solar cell application.

Ionization potential and electron affinity of NiSe and CoSe nanostructures: Electronic Affinity (EA) and Ionization Potential (IP) plays an important role in electronic properties of both NiSe and CoSe nanostructures. The energy required to expel the electron from nanostructures is known as IP whereas the energy released by adding electron to nanostructures is denoted as EA (Zhan *et al.*, 2003). From Table 3 cationic $NiSe_2$, $NiSe_3$ and $CoSe_2$, $CoSe_3$ has high IP and EA value with the range of 8.74-12.49 eV which can be tailored for engineering applications. Neutral $NiSe_2$, $NiSe_3$ and $CoSe_2$, $CoSe_3$ has moderate IP and EA value starting from 3.36-5.83 eV which is suitable

Table 2: HOMO-LUMO gap of NiSe and CoSe nanostructures

Nanostructures	Size	Charge state	HOMO (eV)	Alpha LUMO (eV)	Gap (eV)	HOMO (eV)	Beta LUMO (eV)	Gap (eV)
NiSe	2	0	-4.10	-5.83	1.73	-	-	-
		1	-10.31	-12.49	2.18	-10.14	-12.47	2.33
		-1	2.25	-0.21	2.46	2.25	-0.17	2.42
	3	0	-3.37	-5.72	2.35	-	-	-
		1	-8.74	-11.19	2.45	-9.29	-11.13	1.84
		-1	1.77	0.07	1.70	1.79	-0.70	2.49
CoSe	2	0	-3.62	-5.49	1.87	-	-	-
		1	-9.79	-12.12	2.33	-9.46	-11.38	1.92
		-1	2.22	-0.21	2.43	2.35	0.05	2.30
	3	0	-3.81	-5.63	1.82	-3.36	-5.55	2.19
		1	-8.98	-11.01	2.03	-	-	-
		-1	1.20	-0.15	1.35	-	-	-

Table 3: Ionization potential and electron affinity of CsCl nanostructures

			Electronic properties	
Nanostructures	Size	Charge state	IP (eV)	EA (eV)
NiSe	2	0	5.63	3.81
		1	11.01	8.98
		-1	0.15	1.20
	3	0	5.49	3.62
		1	12.12	9.79
		-1	0.21	2.22
CoSe	2	0	5.72	3.37
		1	11.19	8.74
		-1	0.07	1.77
	3	0	5.83	4.10
		1	12.49	10.31
		-1	0.21	2.25

for chemical sensors and plasma physics. In contrast the remaining possible anionic transition metal chalcogenide has low value ranging from 0.07-2.25 eV which is less likely applicable to engineering materials.

Vibrational studies of NiSe and CoSe nanostructures: The stability of NiSe and CoSe can also be discussed by vibrational studies. Salient feature of stability of the system is the imaginary frequency should not be entitled (Bandyopadhyay, 2012). Vibrational frequency and IR intensity of NiSe and CoSe are charted in Table 4. Neutral $NiSe_2$ has the vibrational frequency at 456.67 and 427.03 cm^{-1} with IR intensity 17.19 and 16.83 km mol^{-1}, respectively. The remaining cationic and anionic $NiSe_2$ has not much difference observed as shown in Table 4. The calculated vibrational spectrum for neutral states of NiSe and CoSe are shown in Fig. 2a-d.

The prominent IR intensity of $NiSe_3$ is 31.54 and 27.6 km mol^{-1} with vibrational frequency at 440.41 and 449.06 cm^{-1}, respectively. IR intensity of $CoSe_2$ is observed at 4.24 and 4.17 km mol^{-1} with corresponding vibrational frequency of 427.97 and 450.05 cm^{-1}. $CoSe_3$ has

Table 4: Vibrational frequency and IR intensity of NiSe and CoSe nanostructures

			Frequency (cm^{-1})		IR intensity (km mol^{-1})	
Nanostructures	Size	Charge state	NiSe	CoSe	NiSe	CoSe
NiSe	2	0	456.67	427.03	17.19	16.83
		1	480.82	464.05	17.51	15.09
		-1	434.48	479.02	4.77	3.92
	3	0	440.41	449.06	31.54	27.60
		1	461.25	463.13	29.37	13.33
		-1	573.80	436.70	7.58	4.93
CoSe	2	0	427.97	450.05	4.24	4.17
		1	472.22	441.82	13.11	10.18
		-1	451.58	430.73	5.40	4.78
	3	0	460.75	462.41	14.43	6.50
		1	309.77	460.86	118.65	8.63
		-1	453.33	463.45	12.86	10.52

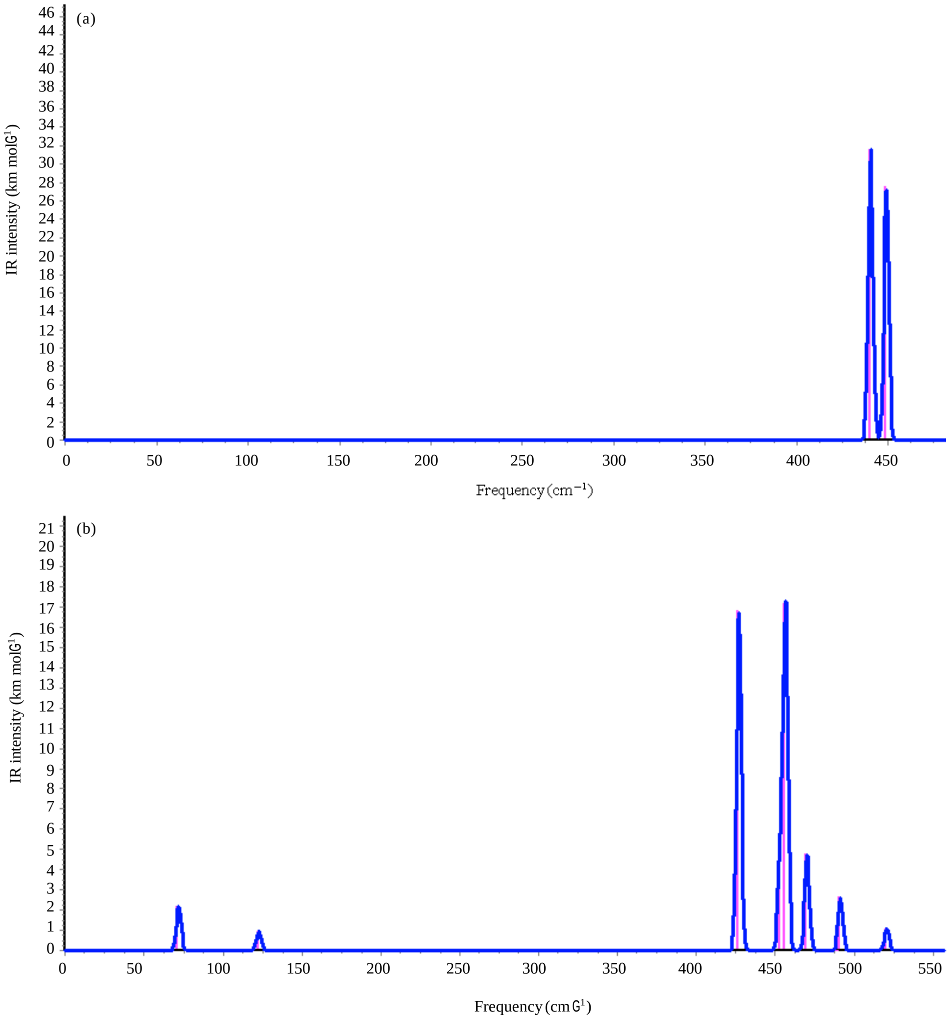

Fig. 2(a-d): Countinue

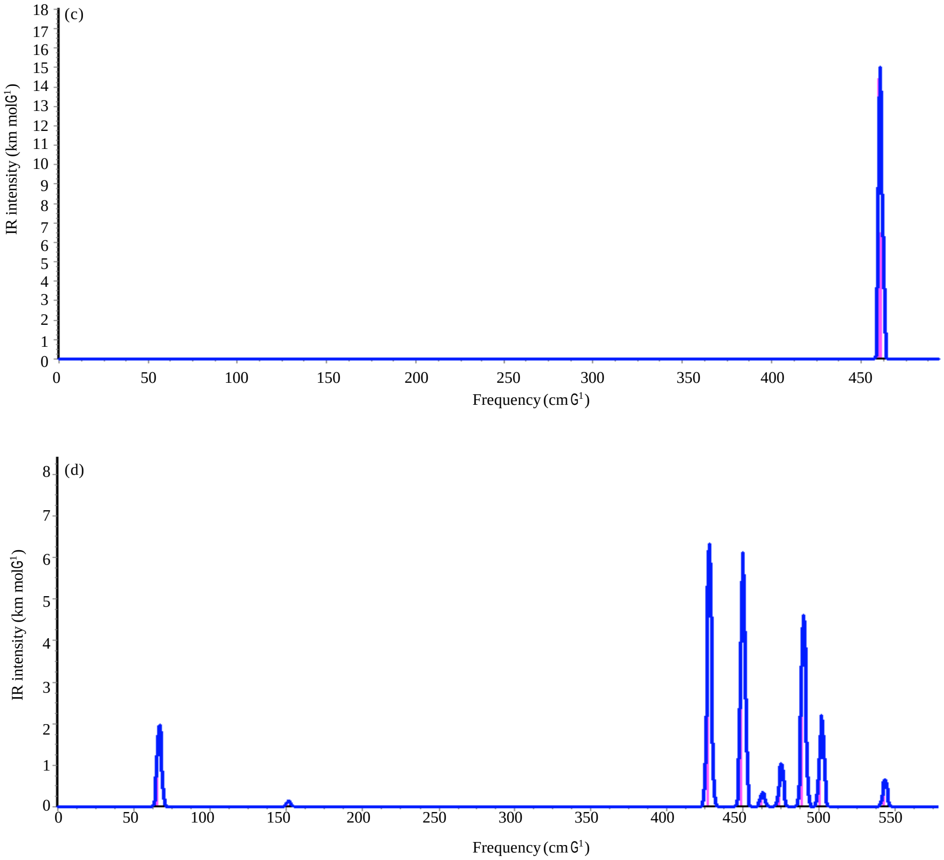

Fig. 2(a-d): (a) Neutral $CoSe_2$, (b) $CoSe_3$, (c) $NiSe_2$ and (d) $NiSe_3$ nanostructures

the vibrational frequency of 460.75 and 462.41 cm^{-1} along with IR intensity of 14.43 and 6.5 km mol^{-1}, respectively. For all the above mentioned nanostructures molecular stretching mode is observed.

CONCLUSION

The transition metal chalcogenide NiSe and CoSe nanostructures with cationic, anionic and neutral charge state are successfully optimized and simulated using DFT with B3LYP/LanL2DZ basis set. Stability of NiSe and CoSe are discussed by vibrational studies and calculated energy. Using HOMO-LUMO gap, EA and IP, electronic properties of NiSe and CoSe nanostructures are studied. Point symmetry and dipole moment of NiSe and CoSe nanostructures are also reported. In the present study, by enhancing electronic properties of NiSe and CoSe nanostructures can be invoked in tailoring nanomaterials which finds its engineering applications in solar cells and as catalysts.

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