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Density Functional Study on Structural Stability and Electronic Properties of Neutral, Anionic and Cationic MgSe Nanostructures

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The realistic neutral, cationic and anionic states of pristine and Cr incorporated MgSe nanostructures are optimized and simulated successfully with the help of DFT method along with B3LYP/LanL2DZ basis set. The structural stability of MgSe nanostructures are studied using formation energy, chemical hardness. Point symmetry, dipole moment and chemical potential of neutral, cationic and anionic states of pristine and Cr substituted MgSe nanostructures are also studied. The electronic properties such as ionization potential, electron affinity and HOMO-LUMO gap are determined for pristine and Cr substituted MgSe nanostructures. The present work gives the insights on the structural stability and electronic properties of MgSe nanostructure with the incorporation of Cr atoms and the influence of cationic and anionic charge states on MgSe nanostructures are explored.

Keywords: Magnesium selenide, Nanostructures, Stability, Formation energy, Chemical hardness.

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1. INTRODUCTION

Nowadays, chalcogenide nanostructures with well-known morphologies have considerable attention among research community owing to their significant electrical, optical, magnetic and structural properties as related to conventional polycrystalline materials [1, 2]. Synthesis of nanostructured materials with economic and simple methods has significance in the area of fabrication of nano-scale devices [3]. The chemical and physical properties of these materials can be fine-tuned by varying the particle size [4-6]. Magnesium selenide (MgSe) is one of the most prominent wide band gap semiconducting selenides, which can be synthesized by numerous sophisticated physical methods. Wang et al. [7] have reported the structural properties of magnesium selenide films deposited on zinc telluride substrates with the help of molecular epitaxy method. MgSe thin film exhibits rock salt at higher thickness and zinc blend structure at lower thickness. Jiang et al. [8] have investigated MgSe crystal structure, which depends on substrate orientation and growth temperature in chemical vapor deposition method. Feng et al. [9] synthesized MgSe thin films on ZnSe/GaAs substrate along (001) plane with the influence of molecular beam epitaxy method. Drief et al. [10] reported the elastic, electronic and optical properties of MgSe nanostructure using density functional theory (DFT) method.

Magnesium chalcogenides are generally wide band gap semiconductors, which can be utilized in optoelectronic [11] and luminescent devices [12] to cover longer wavelength. MgSe is a key component in II-VI semiconductor alloys having p and n type doping ability [12]. These compounds can crystallize in zinc blende, rock-salt and wurtzite structures. Noor et al. [13] synthesized Cr-doped MgTe and MgSe semiconductors and calculated its half-metallic ferromagetism using *ab initio* exchange correlation effects. The inspiration behind the present work is to study the electronic properties and structural stability of MgSe nanostructures using DFT method. The literature survey was conducted with the help of Cross Ref and SCOPUS database and it was known that very limited work are reported in studying the electronic properties of MgSe nanostructures. DFT method is an efficient method to study the electronic properties and structural stability of MgSe nanostructures [14-16]. Apart from this many works have been carried out with density functional theory on both theoretically as well as experimentally [17, 18]. In the present work, neutral, cationic and anionic states of MgSe nanostructure are optimized and the electronic properties & structural stability of pristine and Cr substitution on MgSe nanostructures are studied and reported.

2. COMPUTATIONAL DETAILS

The realistic neutral, cationic and anionic states of MgSe nanostructures are optimized and studied successfully with the help of Gaussian 09 package [19]. In the present work, Becke's three-parameter hybrid functional in combination with Lee-Yang-Parr correlation functional (B3LYP), LanL2DZ basis set has been used. The atomic number of magnesium and selenium is twelve and thirty four respectively. The most important criteria for simulating MgSe nanostructure is the selection of proper basis set. The LanL2DZ basis set is a good choice among others, which provides high throughput with pseudo potential approximation for MgSe nanostructures [20, 21]. The density of states (DOS) spectrum and HOMO-LUMO gap for neutral, cationic and anionic MgSe nanostructures are calculated through Gauss Sum 3.0 package [22]. While optimizing MgSe nanostructures, the convergence range is achieved in the order of 10^{-5} eV.

3. RESULTS AND DISCUSSION

The main objective of the present work is to study the dipole moment (DM), ionization potential (IP), chemical potential (CP), electron affinity (EA), chemical

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hardness (CH) and HOMO-LUMO gap of MgSe nanostructures. The electronic properties of MgSe nanostructures with the incorporation of chromium as dopant are also studied. Figure 1 (a) & 1 (b) represents pristine and Cr incorporated MgSe nanostructures respectively.

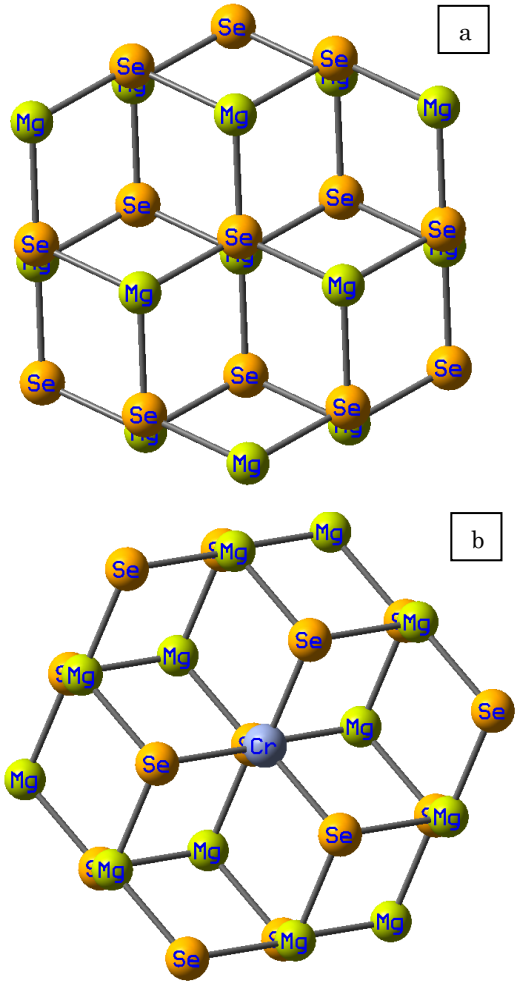


Fig. 1 – Pristine MgSe nanostructure (a) and Cr substituted MgSe nanostructure (b)

The pristine MgSe nanostructure contains thirteen Mg atoms and thirteen Se atoms. Cr incorporated MgSe nanostructure consists of twelve Mg atoms, thirteen Se atoms and one Mg atom is replaced with one Cr atom.

3.1 Structural Stability and Electronic Properties of MgSe Nanostructures

The structural stability of neutral, cationic and anionic MgSe nanostructures is described in the terms of formation energy,

$$E_{\text{form}} = 1/n[E_{(\text{MgSe nanostructure})} - p\,E_{(\text{Mg})} - q\,E_{(\text{Se})}]$$

where $E_{(\text{MgSe nanostructures})}$ refers to the total energy of MgSe nanostructures, $E_{(\text{Mg})}$ and $E_{(\text{Se})}$ represent the corresponding energies of isolated magnesium and selenium atoms. p and q represents the number of magnesium and selenium atoms respectively. n refers the total number of atoms in MnSe nanostructure. The point group, dipole moment and formation energy of pristine and Cr substituted MgSe nanostructures are tabulated in Table 1.

Table 1 – Formation energy, dipole moment and point symmetry of MgSe nanostructures

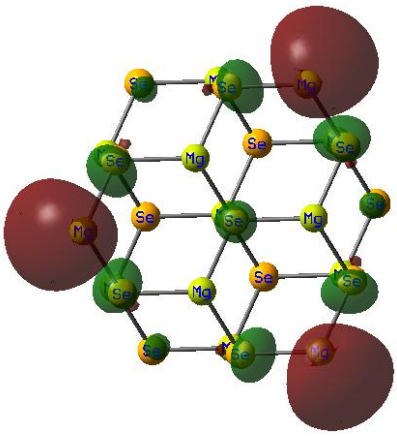
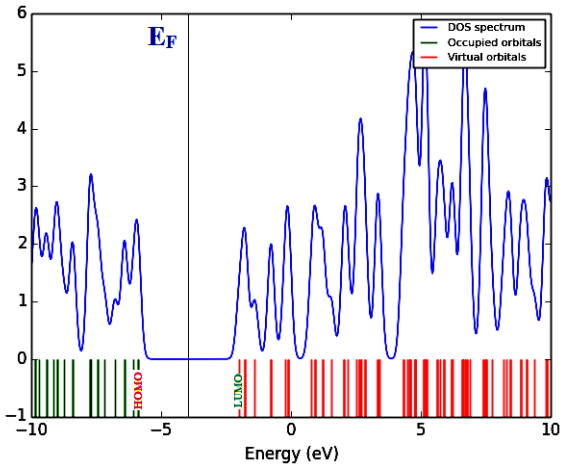
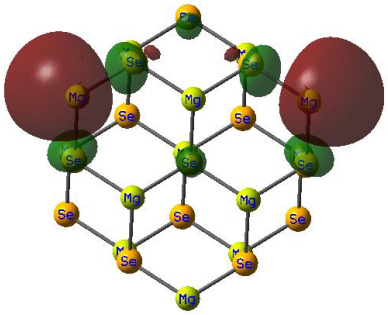
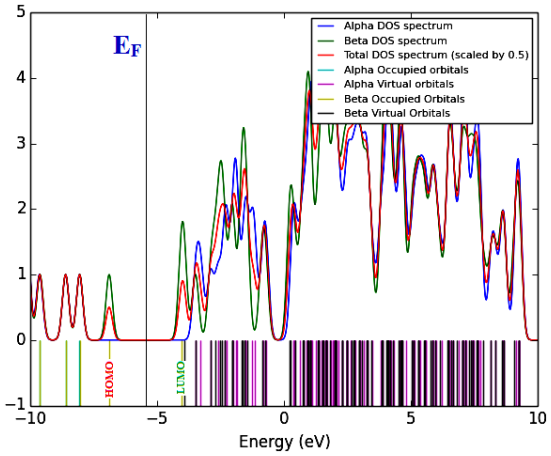
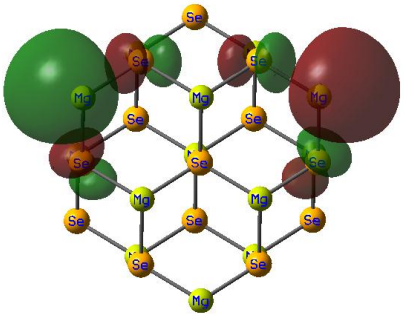
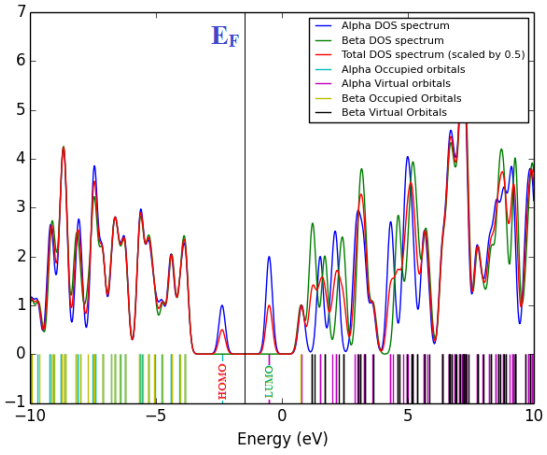
Nanostructures	Formation Energy (eV)	DM (Debye)	PG
Pristine MgSe nanostructure	– 2.54	37.32	C_3V
Cationic MgSe		21.11	C_3V
Anionic MgSe		28.94	C_3V
Cr substituted MgSe	– 2.75	37.31	C_3V
Cationic Cr substituted MgSe		35.15	C_3V
Anionic Cr substituted MgSe		37.36	C_3V

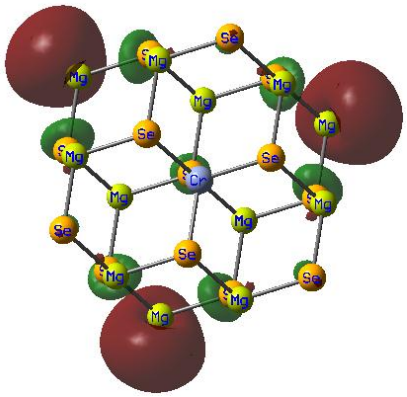
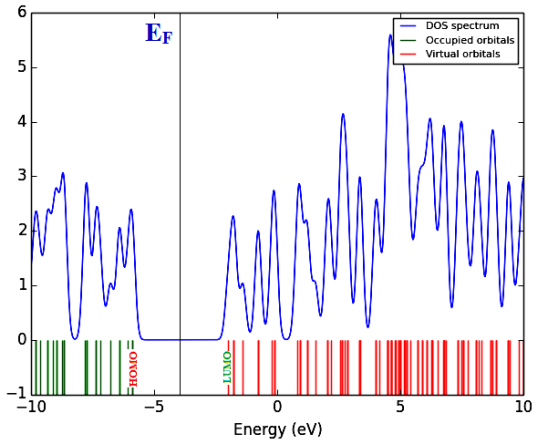
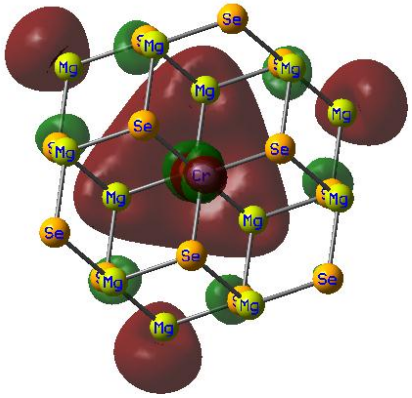
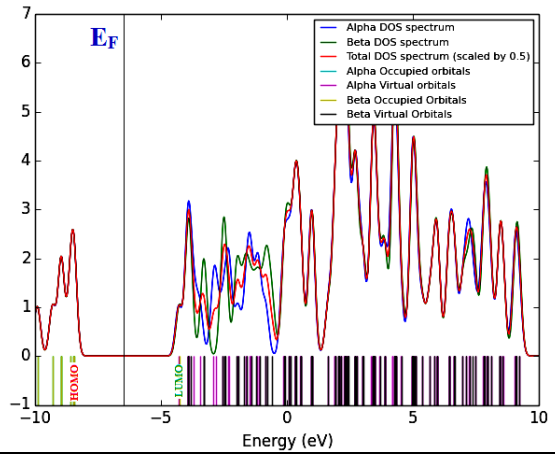
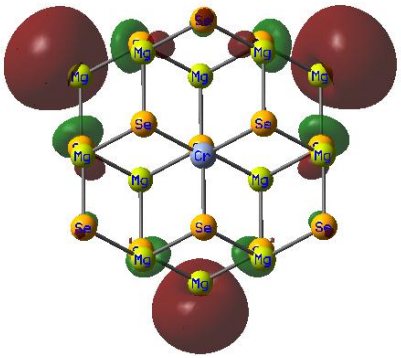
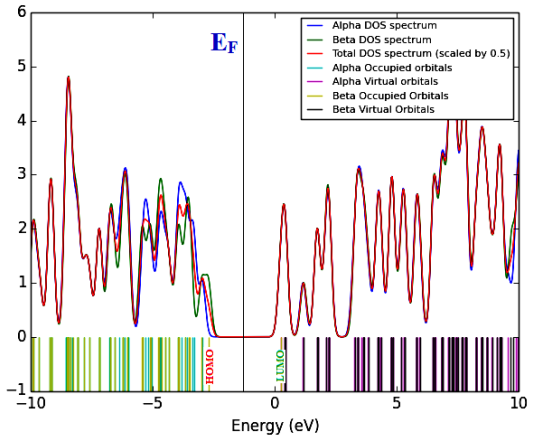
The formation energy of pristine and Cr incorporated MgSe nanostructures are found to be – 2.54 and – 2.75 eV respectively. The stability of MgSe nanostructures mainly depends on formation energy. The structural stability of MgSe nanostructure is directly proportional to the formation energy. The stability of MgSe nanostructure is improved with the substitution of Cr as dopant. The dipole moment of neutral, cationic and anionic states of pristine MgSe nanostructures is 37.32, 21.11 and 28.94 Debye respectively. Furthermore, the corresponding DM values of neutral, cationic and anionic states for Cr substituted MgSe nanostructure is 37.31, 35.15 and 37.36 Debye. Moreover, the dipole moment found to decrease for cationic and anionic states. It indicates the uniform charge distribution along pristine and Cr substituted MgSe nanostructure, whereas the charge distribution is not uniform in the case of neutral state. The point symmetry of MgSe nanostructure is found to be C_{3V}, which exhibits linear, rotation and quadratic symmetry operation.

The electronic properties of MgSe nanostructures can be analyzed in terms of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [23]. Alpha gap results due to the spin up electron in MgSe nanostructures and beta gap arises owing to the spin down electron in MgSe nanostructures. The HOMO-LUMO gap value for pristine and Cr substituted MgSe nanostructures for all the three states are tabulated in Table 2. The HOMO-LUMO gap value for neutral, cationic and anionic states of pristine MgSe nanostructures are 3.92, 4.58 and 1.87 eV respectively. In that order, the HOMO-LUMO gap value for Cr substituted MgSe nanostructures are 3.91, 4.14 and 3.21 eV. This implies that the conductivity of pristine and Cr substituted MgSe nanostructures decreases in cationic state. Due to the shrinkage of cationic MgSe nanostructure, it results in the widening of band gap. In contrast, the conductivity of pristine and Cr substituted MgSe nanostructures increases in anionic states. Thus, the cationic and anionic states influence the electronic properties of MgSe nanostructures. Visualization of HOMO-LUMO gap and DOS spectrum for MgSe

nanostructures are shown in Table 2. In general, magnesium chalcogenides exhibits wide band gap. Furthermore, more energy is required to move the electrons from HOMO level to LUMO level. From the observation of density of states spectrum, the localization of charges is recorded to be more in LUMO level rather than HOMO level along MgSe nanostructures. With the influence of Cr impurity, the density of charges in both HOMO and LUMO levels can be tailored. Thus, it is evident that the electronic properties of MgSe nanostructures can be modified with the incorporation of Cr atom.

Table 2 – HOMO-LUMO gap and density of states spectrum of MgSe nanostructures

Nanostructures	HOMO-LUMO Visualization	E_g (eV)	HOMO, LUMO and DOS spectrum
Pristine MgSe nanostructure		3.92	
Cationic MgSe		4.58	
Anionic MgSe		1.87	

Cr substituted MgSe		3.91	
Cationic Cr substituted MgSe		4.14	
Anionic Cr substituted MgSe		3.21	

3.2 Ionization Potential, Electron Affinity, Chemical Hardness and Chemical Potential of MgSe Nanostructures

The electronic properties of MgSe nanostructure can also be described in terms of electron affinity (EA) and ionization potential (IP) [24-29]. Figure 2 refers the EA and IP of MgSe nanostructures. The change in the energy owing to the addition of electrons in MgSe nanostructure is known as EA and the amount of energy required to detach the electron from MgSe nanostructure is referred as IP. Various trends are observed for electron affinity and ionization potential for MgSe nanostructures as represented in Figure 2. The transfer of electron between the base material and target vapor plays an important role in chemical sensors, which arises due to the electron affinity of the base material. The electron affinity for neutral, cationic and anionic states of pristine MgSe nanostructure is found to be 1.98, 3.47 and 0.50 eV respectively. The corresponding EA values for neutral, cationic and anionic states of Cr substituted MgSe nanostructure are 1.98, 4.3 and 0.25 eV. Thus, the addition of electrons in cationic states of MgSe nanostructure results in drastic energy variation. Similar trends are observed in ionization potential for cationic MgSe nanostructures. It implies that more energy is required to detach electrons from cationic states of MgSe nanostructure due to strong binding of electrons with nucleus.

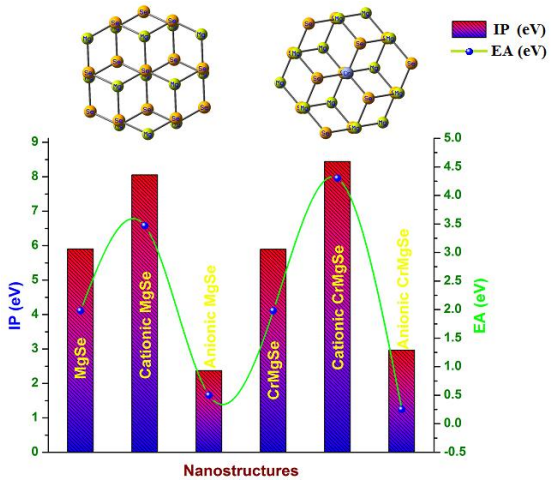


Fig. 2 – IP and EA of MgSe nanostructures

The chemical properties of MgSe nanostructures can also be illustrated in terms of chemical potential (CP) and chemical hardness (CH) [30-33]. CH and CP can be calculated using the equation $\eta = (IP - EA)/2$ and $\mu = -(IP + EA)/2$ respectively, which is tabulated in Table 3. The effect of chemical hardness and chemical potential can also be analyzed with the help of effective fragment potential model for MgSe nanostructures. In most of the cases, chemical hardness is represented as electronegativity, which is one of the significant factors in semiconductor physics. Different trends are observed on both CH and CP. Moreover, depending upon the charge states, chemical hardness as well as chemical potential gets modified.

Furthermore, the cationic states of MgSe nanostructures are found to have high value of CH and CP and anionic states is observed to have low value of CH and CP. Therefore, the structural stability of MgSe nanostructure mainly depends on cationic and anionic states of MgSe nanostructure and the structural stability can be improved with the substitution of Cr atoms in MgSe nanostructure.

Table 3 – Chemical potential and chemical hardness of MgSe nanostructures

Nanostructures	Chemical potential (eV)	Chemical hardness (eV)
Pristine MgSe nanostructures	– 3.94	1.96
Cationic MgSe	– 5.76	2.29
Anionic MgSe	– 1.43	0.93
Cr substituted MgSe	– 3.93	1.95
Cationic Cr substituted MgSe	– 6.37	2.07
Anionic Cr substituted MgSe	– 1.60	1.35

4. CONCLUSIONS

The realistic structures for neutral, cationic and anionic states of pristine and Cr substituted MgSe nanostructures are successfully simulated using B3LYP/LanL2DZ basis set. The structural stability of MgSe nanostructures are investigated with the help of formation energy, chemical potential and chemical hardness. Point symmetry group and dipole moment of pristine and Cr substituted MgSe nanostructures are also reported. From the observations of electron affinity, DOS spectrum, HOMO-LUMO gap and ionization potential, the electronic properties of MgSe nanostructures can be studied. The findings from the present work infer that the structural stability and electronic properties of MgSe nanostructures can be tailored by incorporation of Cr atoms as dopant. Furthermore, the electronic properties and structural stability of MgSe nanostructure can be fine-tuned, which find its potential application in opto-electronic and luminescent devices.

REFERENCES

1. K. Zhou, R. Wang, B. Xu, Y. Li, *Nanotech.* **17**, 3939 (2006).
2. C. Qian, F. Kim, L. Ma, F. Tsui, P. Yang, J. Liu, *J. Am. Chem. Soc.* **126**, 1195 (2004).
3. M.A. Mahdi, J.J. Hassan, S.S. Ng, Z. Hassan, *J. Cryst. Growth.* **359**, 43 (2012)
4. A.U. Uable, *Mater. Chem. Phys.* **121**, 555 (2010).
5. A.U. Uable, D.M. Chaudhari, J.S. Kantale, V.A. Mitkari, M.S. Nikam, W.J. Gawande, P.P. Patil, *J. Alloy. Compd.* **509**, 9249 (2011).
6. G.J. Snyder, E.S. Toberer, *Mat. Mater.* **7**, 105 (2008).
7. H.M. Wang, J.H. Chang, T. Hanada, K. Arai, T. Yao, *J. Cryst. Growth.* **208**, 253 (2000).
8. F. Jiang, Q. Liao, G. Fan, C. Xiong, X. Peng, C. Pan, N. Liu, *J. Cryst. Growth.* **183**, 289 (1998).
9. P.X. Feng, J.D. Riley, R.C.G. Leckey, L. Ley, *J. Phys. D: Appl. Phys.* **34**, 1293 (2001).
10. F. Drief, A. Tadjer, D. Mesri, H. Aourag, *Catal. Today* **89**, 343 (2004).
11. M.W. Wang, M.C. Phillips, J.F. Swenberg, E.T. Yu, J.O. McCaldin, T.C. McGill, *J Appl. Phys.* **73**, 4660 (1993).
12. R. Pandey, S. Sivaraman, *J. Phys. Chem. Solidi* **52**, 211 (1991).
13. N.A. Noor, S.M. Alay-e-Abbas, M.U. Sohaib, S.M. Ghulam Abbas, A. Shaukat, *J. Magn. Magn. Mater.* **374**, 164 (2015).
14. V. Nagarajan, R. Chandiramouli, *J. Chem. Sci.* **127**, 1785 (2015).
15. V. Nagarajan, R. Chandiramouli, *J. Inorg. Organomet. Polym. Mater.* **25**(6), 1529 (2015).
16. V. Nagarajan, V. Saravanakannan, R. Chandiramouli, *Int. J. Chem. Tech. Res.* **8**, 1991 (2015).
17. V. Nagarajan, R. Chandiramouli, *Appl. Surf. Sci.* **344**, 65 (2015).
18. V. Nagarajan, V. Ganesan, R. Chandiramouli, *Int. J. Chem. Tech. Res.* **7**, 1835 (2015).
19. M.J. Frisch, G.W Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Bar-one, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J. Sonnen-berg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida,

T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A.J. Montgomery, J. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gmperts, R. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford, CT (2009).

20. A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
21. P.J. Hay, W.R. Wadt, *J. Chem. Phys.* **82**, 270 (1985).
22. N.M.O. Boyle, A.L. Tenderholt, K.M. Langner, *J. Comp. Chem.* **29**, 839 (2007).
23. R. Chandiramouli, V. Nagarajan, *Chem. Phys. Lett.* **665**, 22 (2016).
24. S. Sriram, R. Chandiramouli, D. Balamurugan, A. Thayumanvan, *Eur. Phys. J. Appl. Phys.* **62**, 30101 (2013).
25. V. Ganesan, V. Nagarajan, V. Saravanakannan, R. Chandiramouli, *Int. J. Chem. Tech. Res.* **6**(7), 3832 (2014).
26. V. Nagarajan, R. Chandiramouli, *J Inorg. Organomet. Polym.* **26**, 394 (2016).
27. V. Nagarajan, V. Saravanakannan, R. Chandiramouli, *Int. J. Chem. Tech. Res.* **6**(5), 2962 (2014).
28. V. Nagarajan, R. Chandiramouli, *Int. J. Chem. Tech. Res.* **6**(1), 21 (2014).
29. V. Nagarajan, R. Chandiramouli, *Appl. Surf. Sci.* **385**, 113 (2016).
30. V. Nagarajan, R. Chandiramouli, *Progress in Natural Science: Materials International* **26**, 129 (2016).
31. V. Nagarajan, R. Chandiramouli, *Int. J. Chem. Tech. Res.* **9**(4), 663 (2016).
32. V. Ganesan, V. Nagarajan, V. Saravanakannan, R. Chandiramouli, *Int. J. Chem. Tech. Res.* **6**(7), 3822 (2014).
33. S. Sriram, R. Chandiramouli, B.G. Jeyaprakash, *Struct. Chem.* **25**, 389 (2014).