ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Structural Stability and Electronic Properties of Neutral, Anionic and Cationic Cesium Chloride Nanostructures – A DFT Study.

Nagarajan V and Chandiramouli R*

School of Electrical & Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur -613 401, India

ABSTRACT

The realistic nanostructures of CsCl such as CsCl buckyball, CsCl nanocube, CsCl nanocone and CsCl nanosheet are optimized and simulated successfully using B3LYP /LanL2DZ basic set. With the help of calculated energy and binding energies, stability of CsCl nanostructures are studied. Electronic properties of CsCl nanostructures are discussed using HOMO-LUMO, ionization potential and electron affinity. Dipole moment and point symmetry of CsCl nanostructures are also reported. The current work gives the information regarding improved electronic properties of CsCl nanostructures which is suitable for electrically conducting glasses and in optical spectrometers.

Keywords: nanostructures; cesium chloride; binding energy; electronic property; embedding energy

Corresponding author

ISSN: 0975-8585

INTRODUCTION

Cesium chloride (CsCl) finds its potential importance in engineering field due to its physical and chemical properties. CsCl as an impurity obtained from carnalite, kainite and mineral waters [1]. CsCl is a wide band gap material with a gap of 8.35 eV which weakly conducts electricity [2]. The conductivity of CsCl is ionic not electronic. CsCl plays a vital role in many application particularly in nuclear medicine and for treatment of cancer [3,4] by using CsCl radioisotopes ^{137}CsCl and ^{131}CsCl [5,6]. Other than medical application CsCl is used to prepare electrically conducting glasses [7], welding by activation of electrodes and mineral water manufacturing [8]. CsCl is highly transparent from UV to IR. CsCl can be used for prisms, cuvettes and as window material in optical spectrometers [9].

The inspiration behind this work is to recognise the optimized nanostructure of CsCl which leads to improved electronic properties and structural stability of CsCl nanostructures. These aspects can be fulfilled by density functional theory (DFT). DFT method is an efficient method to fine tune the electronics properties of nanostructures [10]. Different nanostructures of CsCl are simulated successfully and the results are reported.

COMPUTATIONAL METHODS

The CsCl nanostructures are optimized and simulated successfully by using NWChem package [11]. Right choice to optimize CsCl nanostructures is LanL2DZ basic set along with Becke's three- parameter hybrid functional (B3LYP)[12-16]. LanL2DZ basis set is applicable for the elements, Hf-Bi, H and Li-La which provides the accurate results with pseudo potential approximation [17]. Since the atomic number of Cs is fifty five and Cl is seventeen, LanL2DZ is a suitable basis set to optimize CsCl nanostructures. The electronic properties and structural stability can be computed by DFT which mainly relates to electron density functional. In the present work four different CsCl nanostructures are constructed and optimized successfully.

RESULTS AND DISCUSSION

The existing effort primarily focus on vibrational studies of CsCl nanostructures, electron affinity (EA), ionization potential (IP), embedding energy(EE), dipole moment (DM), binding energy (BE), HOMO-LOMO gap and calculated energy with all the three possible states such as neutral, anionic and cationic nanostructures. Four distinct CsCl nanostructures are CsCl buckyball, CsCl nanocube, CsCl nanocone and CsCl nanosheet are shown in Fig. 1(a)-1(d) respectively. CsCl buckyball consist of six Cs atoms and eight Cl atoms forming ball like structure. CsCl nanocone is the combination of eight Cs atoms and eight Cl atoms which resembles cone like structure. CsCl nanocube contains six Cs atoms and six Cl atoms form an extended cubic structure. CsCl nanosheet has eight Cs atom and Cl atom forms two dimension sheet.

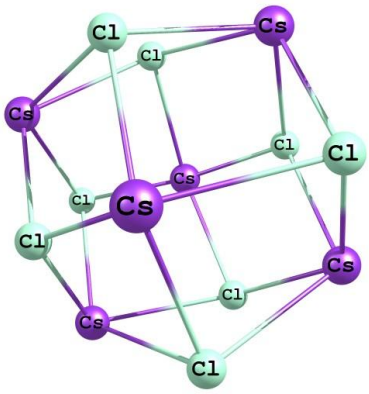
ISSN: 0975-8585

Table 1: Energy, Dipole moment and Point group of CsCl nanostructures

Nanostructures	Energy (Hartrees)	Dipole moment (Debye)	Point Group
Neutral Buckyball	-239.48	2.61	C_1
Cationic Buckyball	-239.24	1.43	C_1
Anionic Buckyball	-239.64	3.55	C_1
Neutral nanocube	-209.76	0.032	C_1
Cationic nanocube	-209.49	0.097	C_1
Anionic nanocube	-209.77	0.23	C_1
Neutral nanocone	-314.30	32.72	C_1
Cationic nanocone	-314.09	23.58	C_1
Anionic nanocone	-314.35	23.11	C_1
Neutral nanosheet	-279.64	0.0017	C_S
Cationic nanosheet	-279.40	0.0028	C_S
Anionic nanosheet	-279.67	0.0015	C_S

The stability of CsCl nanostructures can be studied using calculated energy as shown in Table-1. The energy of all the four different nanostructures is found in terms of three possible states neutral, anionic and cationic respectively. The energy of CsCl buckyball is found to be -239.48 Hartrees for neutral and not much difference are found in both anionic state and cationic state. CsCl neutral nanocube is calculated to be -209.76 Hartrees, -314.30 Hartrees is observed for CsCl neutral nanocone and neutral CsCl nanosheet has -279.64 Hartrees. By adding more number of atoms in nanostructures, the stability of CsCl nanostructures increases. Dipole moment of neutral buckyball is 2.61 Debye, 1.43 Debye for cationic and 3.55 Debye for anionic buckyball. DM are found to be low for both nanocube and nanosheet which is in the range of 0.0015 – 0.23 Debye, since atoms are well packed and charges are distributed uniformly inside the nanostructures. Regarding the DM of nanocone, it is observed to be high due to improper charge distribution. The point group of all the discussed nanostructures belongs to C_1 or C_S which represents asymmetry in the structure.

Fig.1(a). Structure of CsCl buckyball



ISSN: 0975-8585

Fig.1(b). Structure of CsCl nanocone

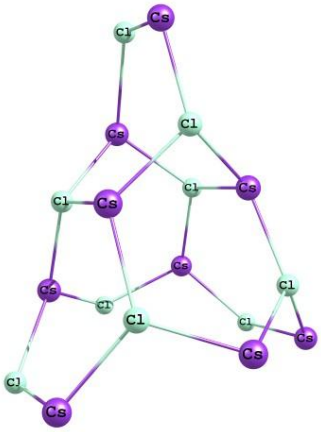


Fig.1(c). Structure of CsCl nanocube

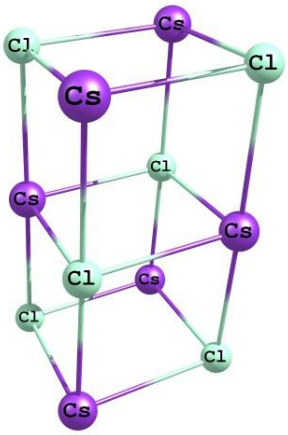
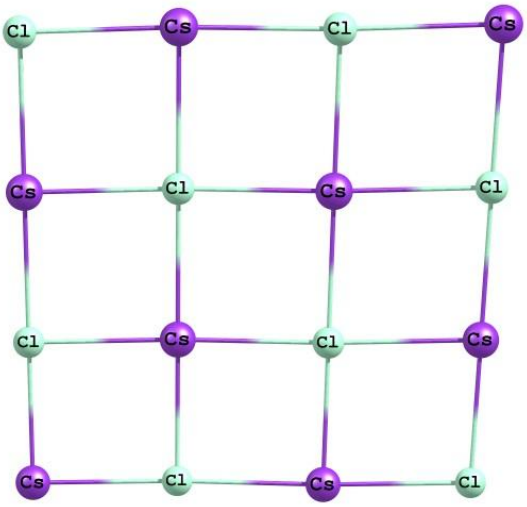


Fig.1(d). Structure of CsCl nanosheet



ISSN: 0975-8585

HOMO-LUMO gap of CsCl nanostructures

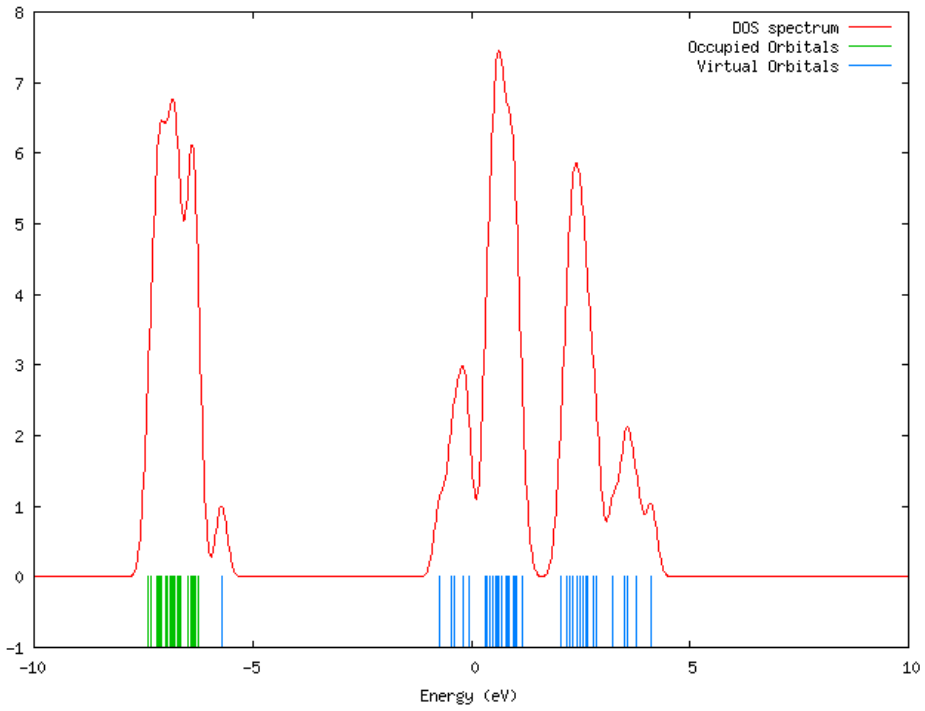
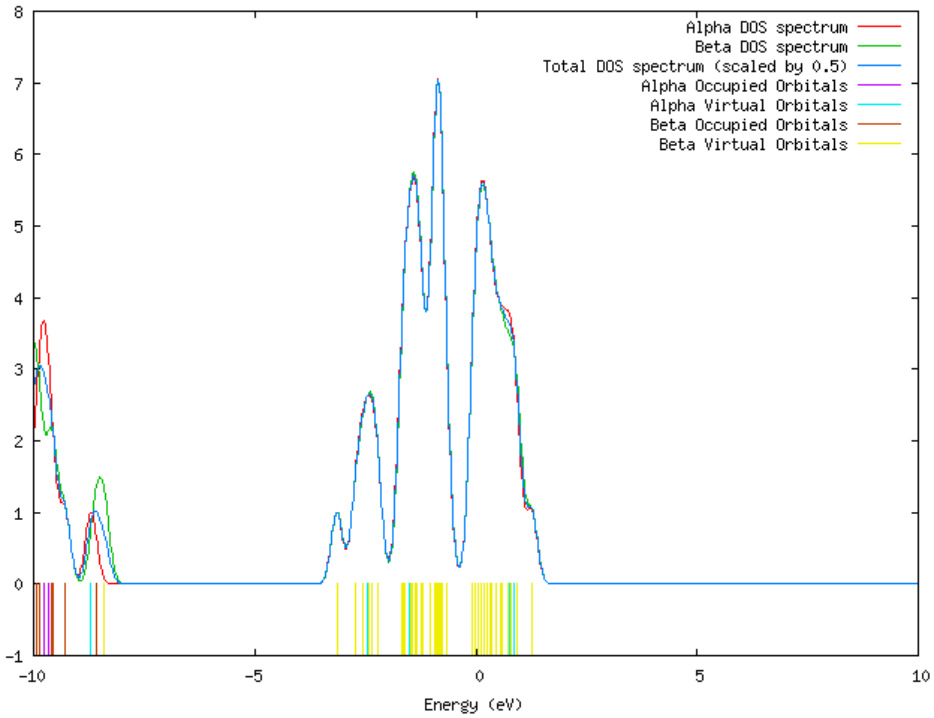
The electronic properties of CsCl nanostructures can be explained by lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [18, 19]. The alpha gap arise due to spin up electron and beta gap arise due to spin down electron. HOMO - LUMO gap of CsCl buckyball has low value in alpha neutral, alpha cationic, beta cationic and beta anionic structures of CsCl is in the range of 0.46 – 0.69 eV. When the gap is very narrow, it resembles near metallic nature and less energy is enough for transition of electron from valence band to conduction band. In contrast CsCl buckyball alpha anionic CsCl structure has high value of 4.03 eV. CsCl nanocube energy gap is low only in alpha anionic structure which is 0.36 eV and beta cationic structure has 0.52 eV. The other possible structures have high energy gap in the range of 2.05 – 6.18 eV. Moreover the same trend is found in both CsCl nanocone and CsCl nanosheet as shown in table 2. The localization charge of CsCl nanstructures are envisaged by density of states (DOS) spectrum. DOS spectrums are tabulated in Table-3.

Table 2: HOMO, LUMO and DOS Spectrum of InSb Nanostructures

Nano structures	HOMO	LUMO	E_g(eV) Alpha	HOMO	LUMO	E_g(eV) beta
Neutral Buckyball	-6.24	-5.71	0.53	-	-	-
Cationic Buckyball	-9.29	-8.7	0.59	-9.29	-8.6	0.69
Anionic Buckyball	-2.73	1.3	4.03	-2.4	-1.94	0.46
Neutral nanocube	-5.7	-0.84	4.86	-	-	--
Cationic nanocube	-9.44	-3.26	6.18	-9.21	-8.69	0.52
Anionic nanocube	0.32	0.68	0.36	-3.73	0.8	4.53
Neutral nanocone	-4.18	-2.13	2.05	-	-	
Cationic nanocone	-7.83	-3.67	4.16	-7.32	-7.05	0.27
Anionic nanocone	-0.22	0.29	0.51	-2.71	0.28	2.99
Neutral nanosheet	-4.71	-1.33	3.38	-	-	-
Cationic nanosheet	-8.36	-2.87	5.49	-8.04	-7.8	0.24
Anionic nanosheet	-0.13	0.03	0.16	-3.46	0.54	4

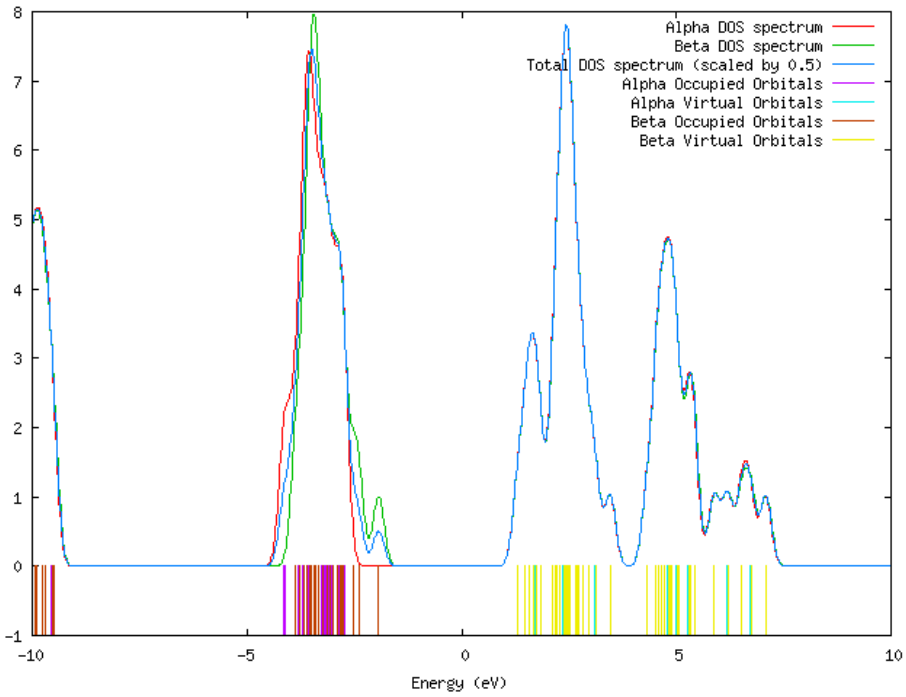
ISSN: 0975-8585

Table 3: HOMO, LUMO and DOS Spectrum of CsCl Nanostructures

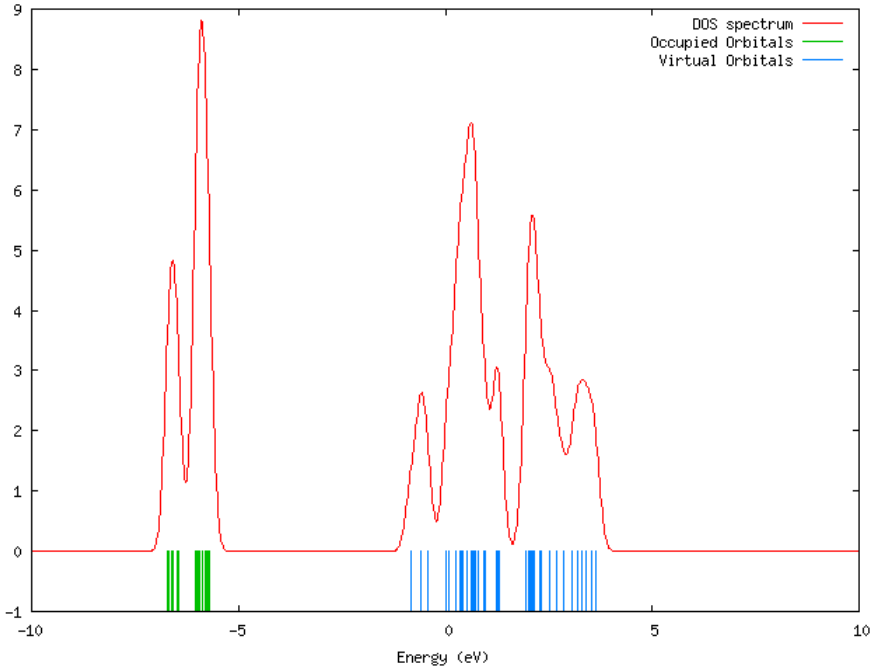
Nanostructures	HOMO, LUMO and DOS Spectrum
Neutral Buckyball	
Cationic Buckyball	

ISSN: 0975-8585

Anionic Buckyball

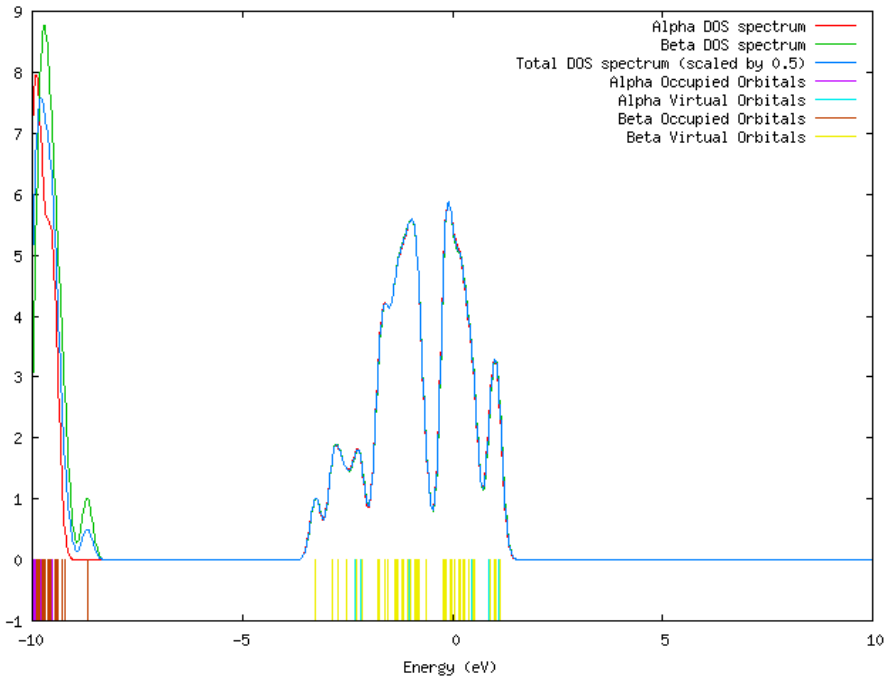


Neutral nanocube

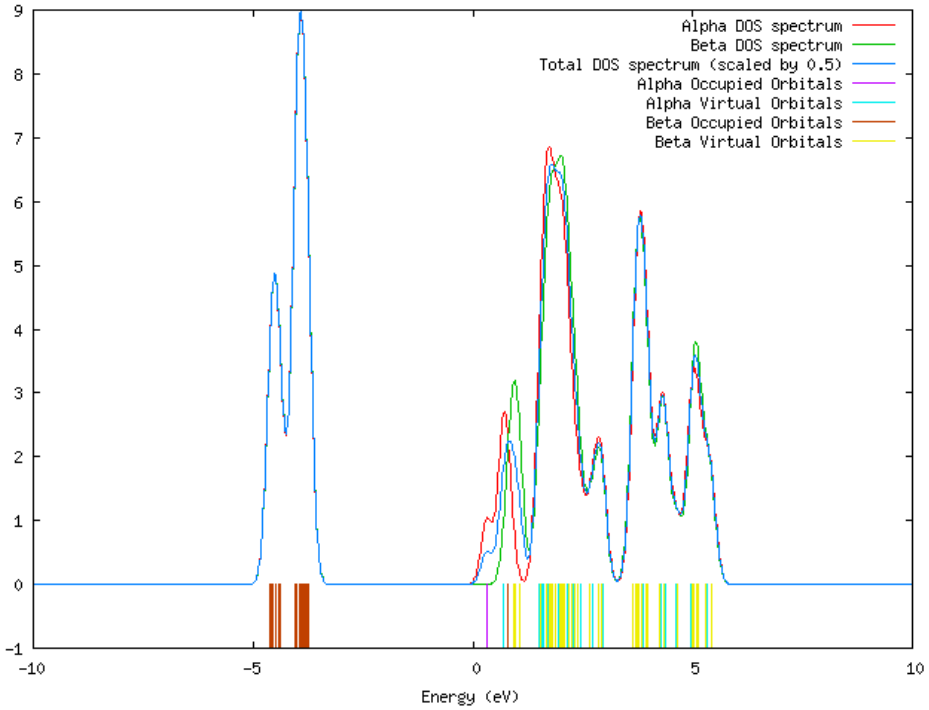


ISSN: 0975-8585

Cationic nanocube

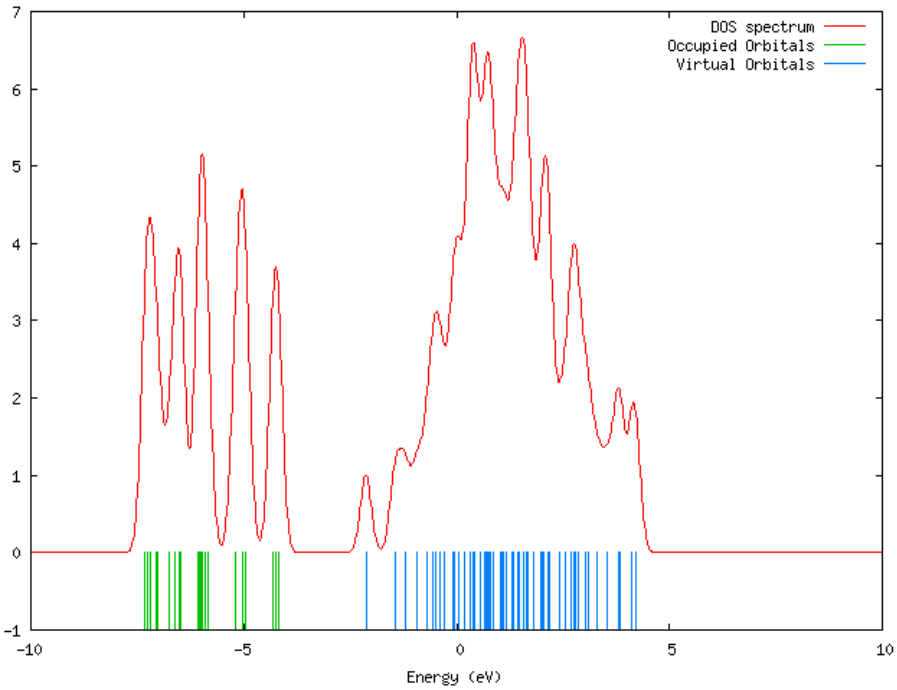


Anionic nanocube

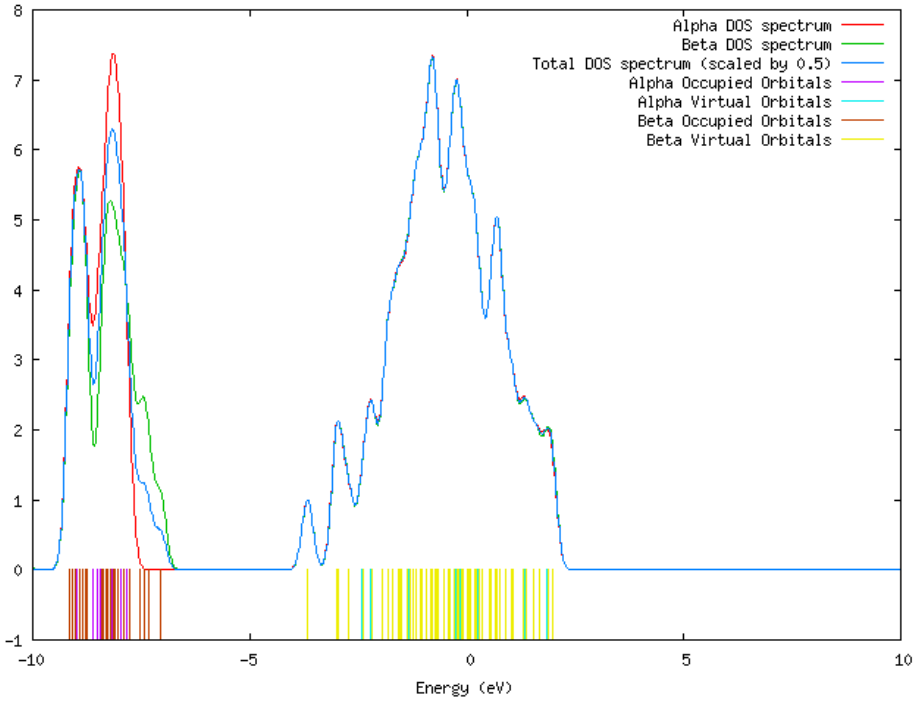


ISSN: 0975-8585

Neutral nanocone

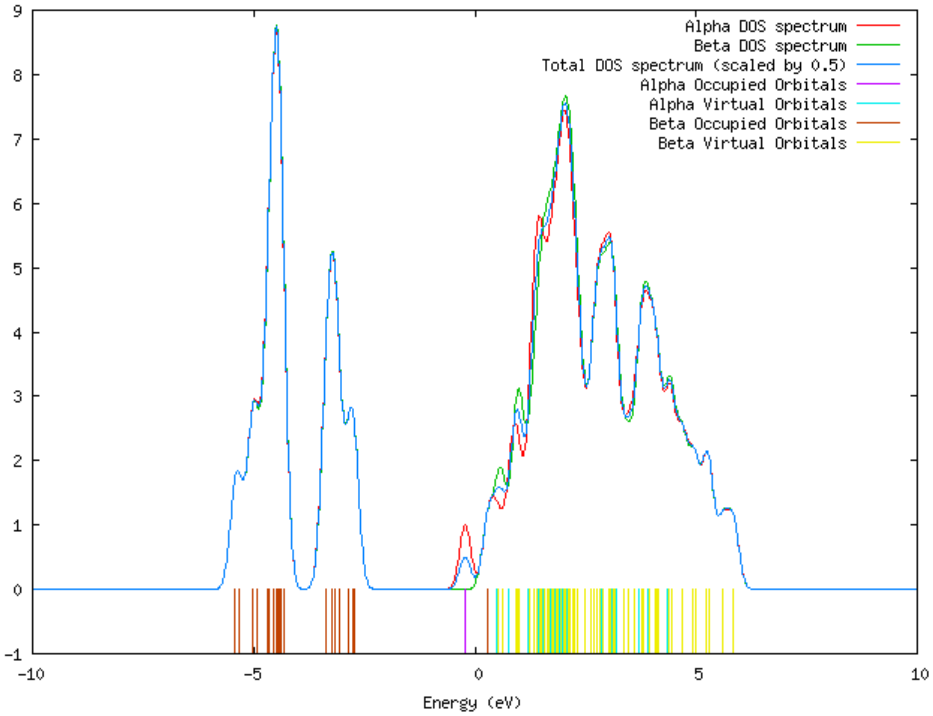


Cationic nanocone

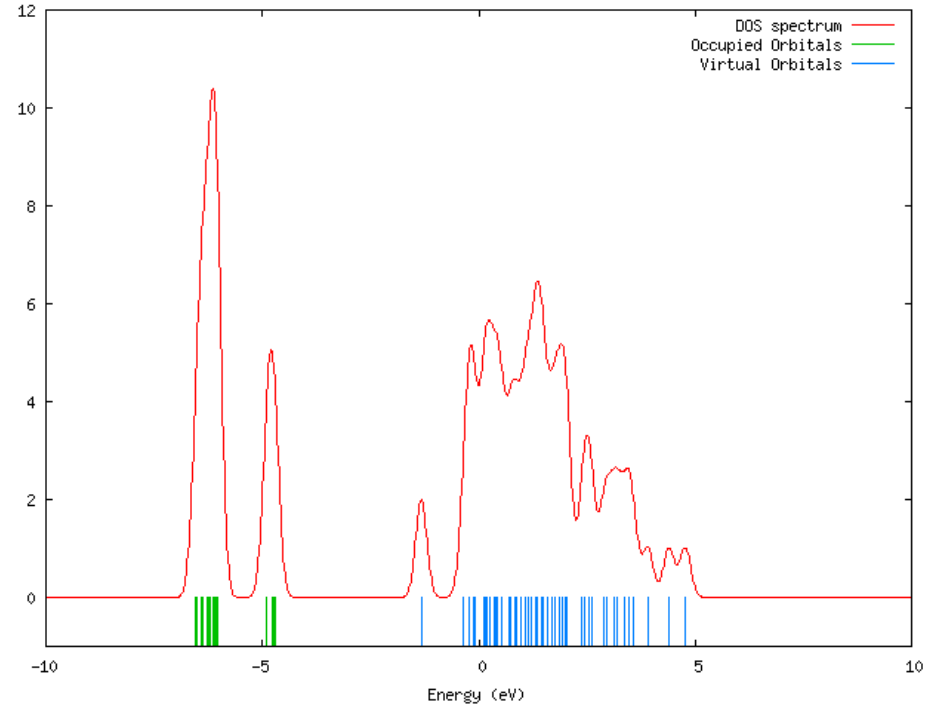


ISSN: 0975-8585

Anionic nanocone

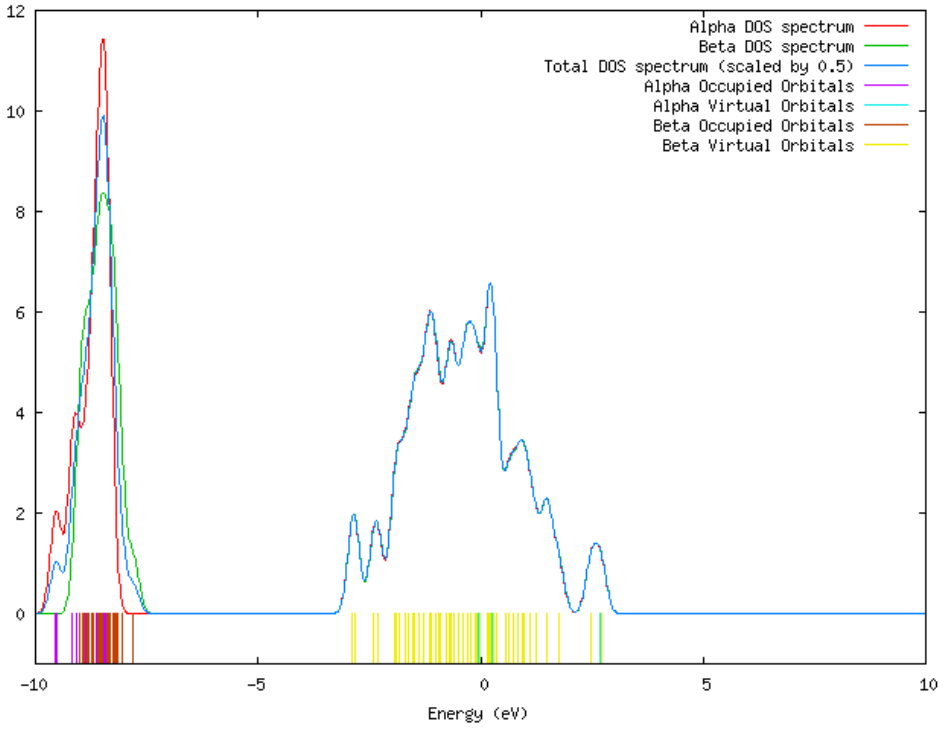


Neutral nanosheet

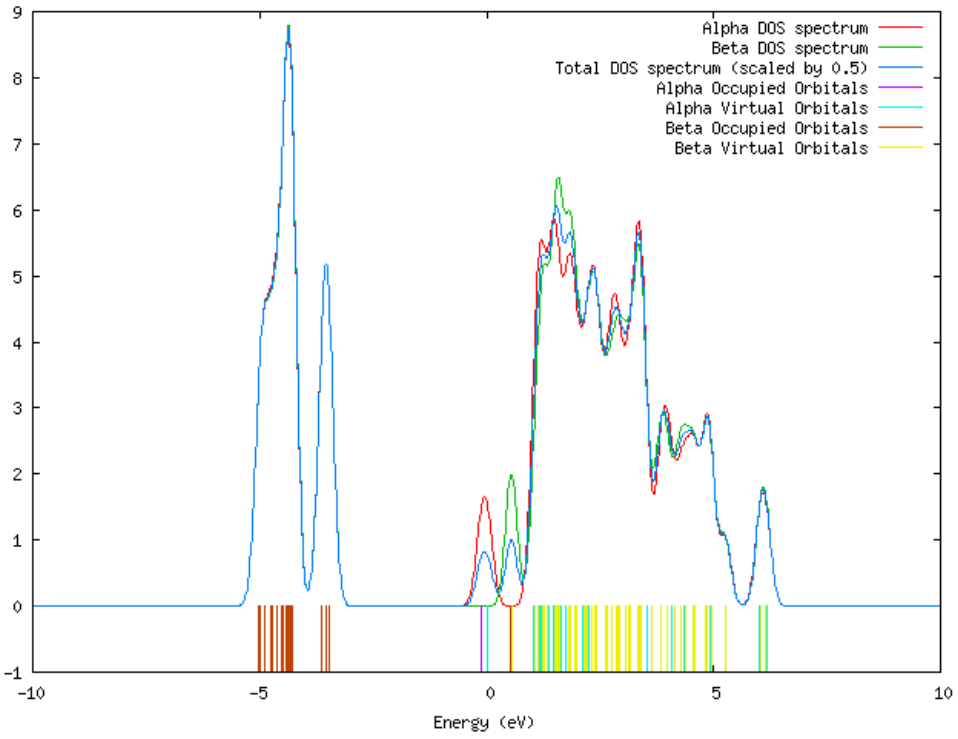


ISSN: 0975-8585

Cationic nanosheet



Anionic nanosheet

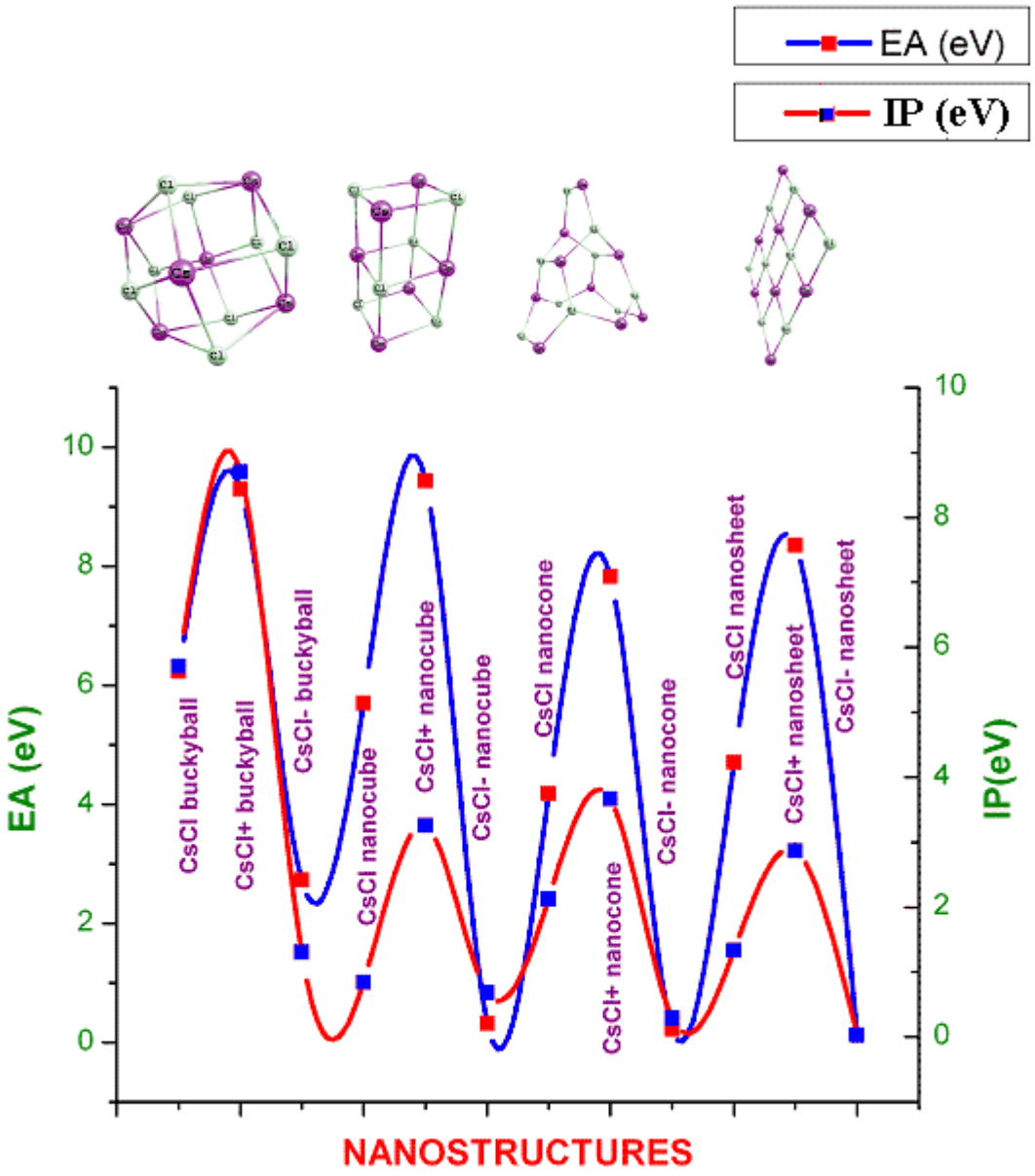


Ionization potential and Electron affinity of CsCl nanostructures

The electronic properties can also be discussed with ionization potential (IP) and electron affinity (EA). The change in the energy due to the addition of electron to nanostructures is called as EA and the energy required to remove the electron from nanostructure is termed as IP [20]. EA plays a vital role in both chemical sensors and in Plasma Physics. From the observation of Fig.2, it clearly noted that CsCl cationic

nanostructures has high value of EA and IP ranging from 7.05 – 9.44 eV and it is very much applicable to chemical sensors as well as in Plasma Physics. Neutral CsCl nanostructures have moderate value of EA and IP. In contrast anionic CsCl nanstructures has low value which is not suitable for above mentioned applications.

Fig.2. Ionization potential and Electron affinity of CsCl nanostructures



Binding energy and Embedding energy of CsCl nanostructures

The stability of CsCl nanostructures can also studied by binding energy [21-23]. Equation 1 illustrates the BE of CsCl nanostructures as follows

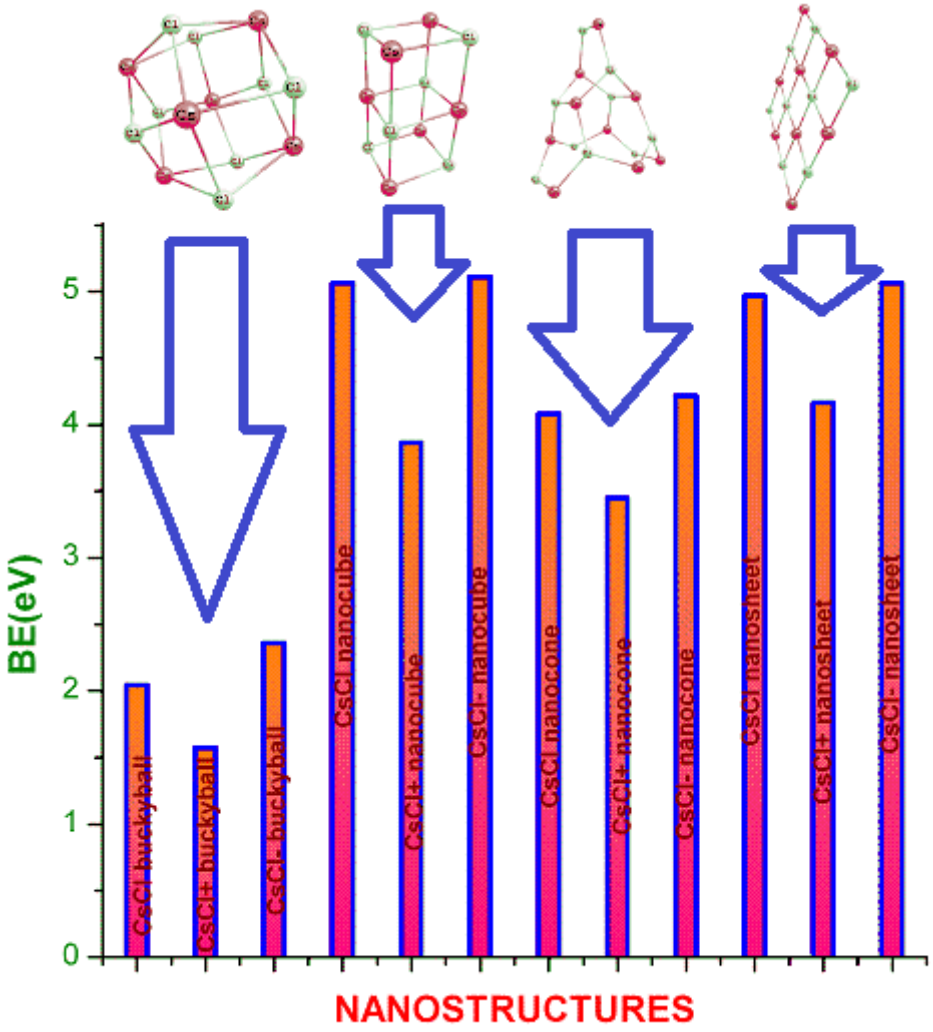
$$BE = [(n * E(Cs) + n * E(Cl) - n * E(CsCl)] / n \text{ ---------- (1)}$$

where the energy of Cs atom and Cl is denoted by E(Cs) and E(Cl) respectively. The combined energy of CsCl nanostructures is E(CsCl) and number of atoms in nanostructures is

ISSN: 0975-8585

denoted by n. CsCl anionic nanostructures has high value of BE which range from 2.36 – 5.10 eV, hence these nanostructures are more stable. CsCl neutral nanostructures has more or less same trend observed with CsCl anionic nanostructures as shown in the Fig.3.

Fig.3. Nanostructures size vs Binding Energy



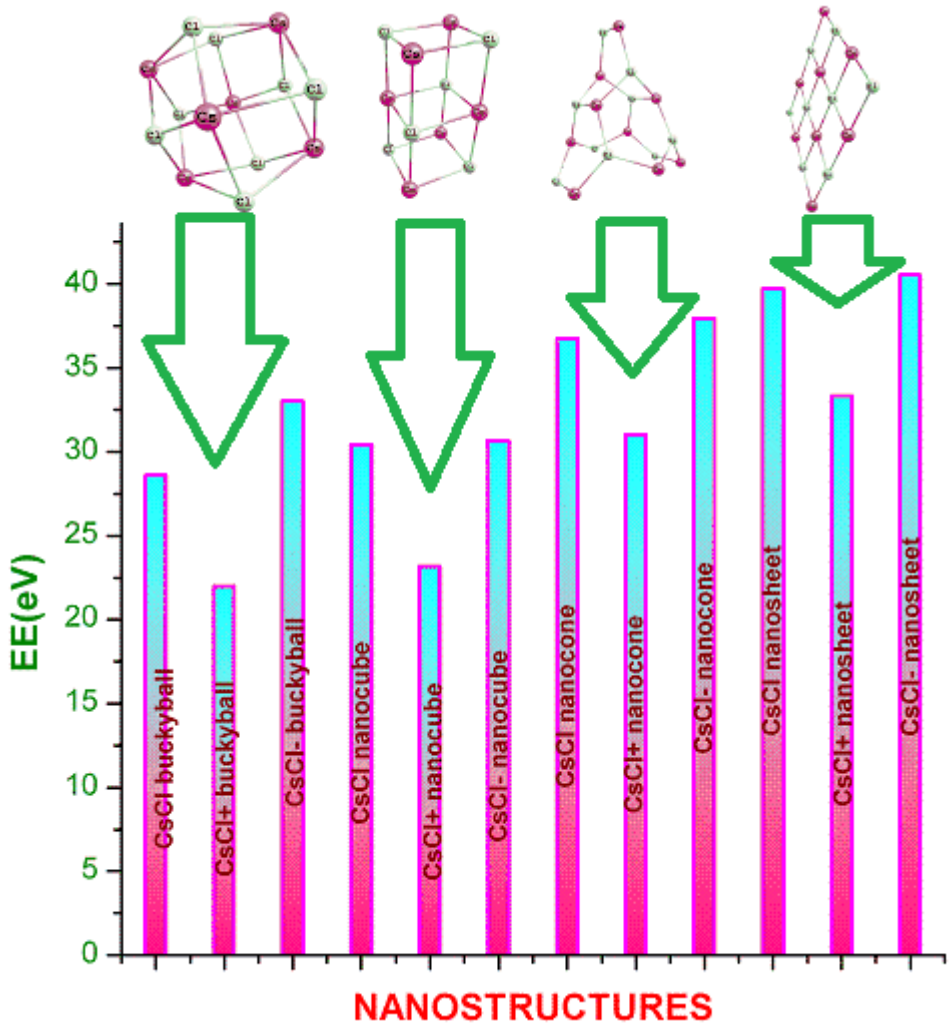
Embedding energy (EE) refers the possibility of substitution impurity in nanostructures. The EE of CsCl nanostructure is represented in equation 2 as follows,

$$EE = [(n * E(Cs) + n * E(Cl) - n * E(CsCl)] \text{ ---------- (2)}$$

CsCl cationic nanostructures have low value in the range from 21.95 – 33.32 eV which is most suitable to incorporate foreign atom with nanostructures. In contrast the remaining CsCl neutral and cationic nanostructure has high value which is not optimum to substitute impurities in nanostructures. EE of CsCl is shown in Fig.4.

ISSN: 0975-8585

Fig.4. Nanostructures size vs Embedding Energy



CONCLUSION

In conclusion by using DFT nanostructures of CsCl are optimized and simulated successfully along with LanL2DZ basic set / B3LYP. Stability of CsCl nanostructures are examined by using calculated energy and binding energy. With the use of IP, HOMO-LUMO gap and EA electronic properties are studied precisely. Dipole moment and point symmetry for four different CsCl nanostructures are reported. Incorporation of impurities in nanostructures is also reported in terms of embedding energy. The current work can be used to tailor the CsCl nanostructures which are most applicable to electrically conducting glasses and highly transparency prism.

REFERENCES

[1] Knunyants I. L. Moscow: Soviet Encyclopedia 1998; 5: 654–656.
[2] Lushchik A Feldbach E, Frorip A, Ibragimov K, Kuusmann I, Lushchik C. Journal of Physics: Condensed Matter 1994; 6 (12): 2357–2366.

[3] Carrea JR, Gleason G, Shaw J, Krontz B. American heart journal 1964; 68 (5): 627–636.
[4] McGeehan, John T. JAMA: the Journal of the American Medical Association 1968; 204 (7): 585.
[5] Alikbaeva LA, ED. New Handbook of chemical and process engineer (in Russian). St. Petersburg 2005 ISBN 5-98371-025-7.
[6] U.S. Geological Survey, 2010, Mineral commodity summaries 2010: U.S. Geological Survey, 193 p. ISBN 978–1–4113–2666–8.
[7] Tver'yanovich, Y. S. Glass Phys. Chem 1998;24: 446.
[8] Morris, Ch. G. Academic Press Dictionary of Science and Technology. San Diego: Academic Press 1992;395.
[9] Manfred Bick, Horst Prinz. Wiley-VCH, Weinheim 2002; 6A: 153–156.
[10] Sriram S, Chandiramouli R. Res Chem Intermed. 2013; DOI: 10.1007/s11164-013-1334-6.
[11] Valiev M, Bylaska E.J, Govind N ,Kowalski K , Straatsma T.P, Van Dama H.J.J, Wang D, Nieplocha J, Apra E , Windus T.L, deJong W.A. Computer Physics Communications 2010; 181: 1477–1489.
[12] Refat Mahfouz, Eida Al-Frag, Rafiq H, Siddiqui M, Waed Z, Al-kiali, Karama O. Arabian J. Chem. 2011; 4: 119-124.
[13] Droghetti A, Alfè D, Sanvito S. J. Chem. Phys. 2012; 137: 124303-124312.
[14] Mohammed Bouklah, Houria Harek, Rachid Touzani, Belkheir Hammouti, Yahia Harek. Arabian J. Chem. 2012;5: 163-166.
[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, de Jong Wibe A. J. Phys. Chem. 2008;112A: 508-521.
[16] Chandiramouli R. Res. J. Chem. Environ. 2013; 17: 64-73.
[17] Srinivasaraghavan R, Chandiramouli R, Jeyaprakash B.G, Seshadri S. Spectrochim. Acta, Part A. 2013;102: 242-249.
[18] Arivazhagan M, Jeyavijayan S. Spectrochim. Acta, Part A. 2011;79: 376-383.
[19] John Xavier R., Gobinath E. Spectrochim. Acta, Part A. 2012;97: 215-222.
[20] Chang-Guo Zhan, Nichols J.A, Dixon D.A. J. Phys. Chem. A. 2003;107: 4184- 4195.
[21] Sriram S, Chandiramouli R , Balamurugan D , Ravichandran K, Thayumanavan A. J. At. Mol. Sci. 2013;4(4): 336-348.
[22] Sriram S, Chandiramouli R. Eur. Phys. J. Plus. 2013; DOI 10.1140/epjp/i2013-13116-y.
[23] Sriram S, Chandiramouli R , Balamurugan D, Thayumanvan A. Eur. Phys. J. Appl. Phys. 2013;62: 30101.