A first-principles study on structural stability and electronic properties of LiF nanostructures

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Abstract: The realistic structures of pure cubic LiF nanostructures, chlorine, sodium and potassium substituted cubic LiF nanostructures are simulated and optimized successfully using density functional theory with B3LYP/LanL2DZ basis set. The structural stability of cubic LiF nanostructures is discussed in terms of chemical hardness, formation energy and chemical potential. The dipole moment and point symmetry group of pure and impurity substituted cubic LiF nanostructures are also reported. The electronic properties of cubic LiF nanostructures are studied with the help of ionization potential, HOMO – LUMO gap and electron affinity. The present work will provide the information to tailor cubic LiF nanostructures by substituting suitable impurities and to enhance the structural stability and electronic properties which have its potential application in phosphors and radiation detectors.

Keywords: lithium fluoride, nanostructure, chemical hardness, chemical potential, HOMO-LUMO.

Introduction

Lithium fluoride (LiF) finds its potential importance as phosphor which is used as color center in Lasers, integrated optics and radiation detectors. LiF are used to detect beta rays, gamma rays and neutrons. LiF is also used in organic light-emitting diodes and polymer light emitting diodes. LiF as color centers are reported by many researchers [1-5]. LiF possess highest ultra-violet transmission, this property makes LiF to be used in UV transmission windows. LiF substituted with proper impurities is on focus for detecting ionizing radiations with thermo luminescence property. The synthesis of LiF with substitution impurities has been first reported by Nakajima et al [6]. Thereafter, many reported work on LiF is in the synthesis and characterization [7-16]. The energy gap of LiF is reported to be around 14.1 – 14.5 eV [17]. The experimental band gap of LiF is reported as 14.2 eV [18]. The motivation behind this work is to optimize the structural stability and to enhance the electronic properties of LiF nanostructures with substitution impurity. Density functional theory (DFT) is an efficient method to fine-tune the structural stability and electronic properties of LiF nanostructures [19-22]. In the present work, the structural stability and electronic properties of LiF nanostructures are studied with the substitution of chlorine, sodium and potassium impurity and the results are reported.

Computational methods

The pure, Cl, Na and K substituted LiF nanostructures in the form of cube are optimized and simulated precisely with the help of Gaussian 09 package [23]. The atomic number of lithium and fluoride is three and nine respectively. In the present work, various dopant atoms are substituted in pure LiF nanostructure and optimized. LiF nanostructures are optimized with Becke's three-parameter hybrid functional (B3LYP) along with suitable LanL2DZ basis set [24-26]. Meanwhile, the selection of basis set is most important for optimizing the LiF nanostructures. LanL2Dz basis set is promising basis set for optimizing LiF nanostructures with

pseudopotential approximation [27]. The density of states spectrum (DOS) of LiF nanostructures are drawn using Gauss Sum 3.0 package [28].

Results and Discussion

The present work is primarily focused on dipole moment (DM) , ionization potential (IP), chemical hardness (CH), electron affinity (EA), formation energy, vibrational studies and HOMO – LUMO gap of LiF nanostructures incorporating substitution impurities such as chlorine, sodium, potassium and defect structured LiF nanostructure. Figure 1 (a) represent pure cubic LiF nanostructure. Figure 1 (b) – Figure 1 (d) represents Cl, Na and K substituted cubic LiF nanostructures respectively. The defect structured cubic LiF nanostructure is shown in Figure 1 (e). The pure cubic LiF nanostructure consists of nine Li atoms and nine F atoms to form three dimensional cubic structures. Cl substituted cubic LiF nanostructure contains two Cl atoms, seven F atoms and nine Li atoms, Cl atoms are substituted in place of F atoms. Na substituted cubic LiF nanostructure has two Na atoms, seven Li atoms and nine F atoms. In K substituted cubic LiF nanostructure two Li atoms are replaced with two K atoms, the nanostructure has seven Li atoms and nine F atoms. Defect structured cubic LiF nanostructure have eight F atoms and eight Li atoms, one F atom and one Li atoms are removed to maintain stoichiometry.
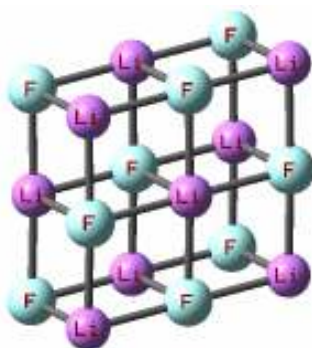

Figure.1 (a) Structure of pure cubic LiF nanostructure

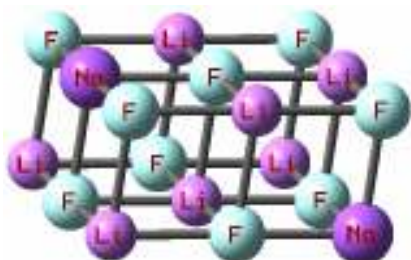**Figure.1 (b) Structure of Cl substituted cubic LiF nanostructure**

Figure.1 (c) Structure of Na substituted cubic LiF nanostructure
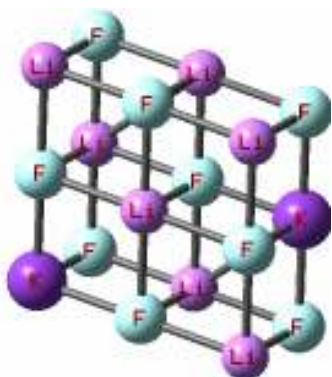
Figure.1 (d) Structure of K substituted cubic LiF nanostructure

Figure.1 (e) Defect structured LiF nanostructure

The structural stability of pure, Cl, Na and K substituted LiF nanostructures can be calculated using the formation energy as shown in equation 1,

$$E_{form} = E \text{ (LiF nanostructure)} – xE(Li) – yE(F) – zE(dopant) \qquad (1)$$

where E (LiF nanostructure) represents the total energy of LiF nanostructure, E(Li), E(F) and E(dopant) represents the corresponding energy of isolated Li, F and dopant atoms namely Cl, Na and K. Moreover, x, y and z represents the total number of Li, F and dopant atoms respectively. The formation energy, dipole moment and point group of pure, Cl, Na and K substituted LiF nanostructures are tabulated in Table 1. The formation energy of pure, Cl, Na and K incorporated LiF nanostructures are -71.26, -60.11, -66.37 and -51.41 eV respectively. The formation energy of defect structured LiF is -57.12 eV. From the observation of formation energy, it is revealed that the structural stability of LiF nanostructures decreases owing to incorporation of dopant atoms such as Cl, Na and K. Since, the formation energy of Cl, Na and K substituted LiF nanostructures have low value when compared to pure form of LiF nanostructure. Obviously, defect structured LiF nanostructure also has low stability in structure due to removal of one Li and one F atom from the regular arrangement of atoms. The DM refers the distribution of charge in LiF nanostructure. The charge distribution is not uniform in the case of defect structured LiF nanostructure, since the value of DM is very high in the order of 19.64 Debye. The other realistic structure of LiF has almost same value of DM in the range of 7.39 – 7.75 Debye. This can be argued that the arrangement of atoms and the charge distribution is almost uniform for all other optimized LiF nanostructures. There is no drastic variation in DM is noticed with substitution impurities. For all the structure the point symmetry is found to be C_1. This point symmetry has only one symmetry operation, identity operation E. The other symmetry operations such as rotation, reflection of a mirror plane are not possible.
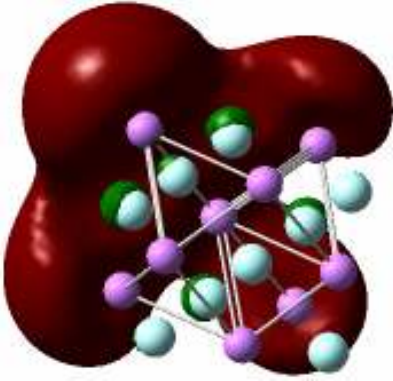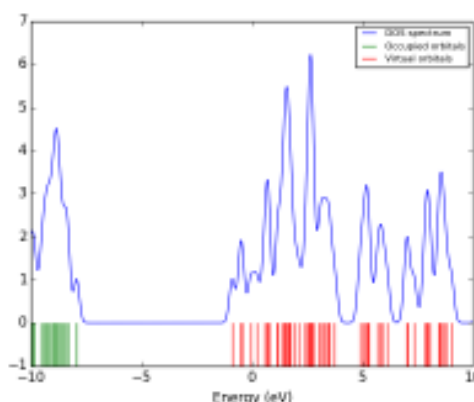
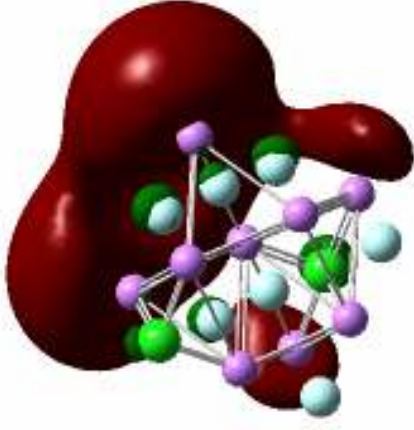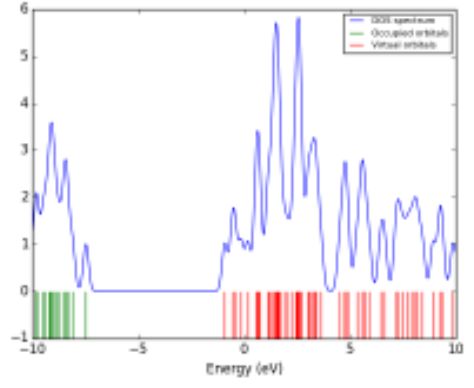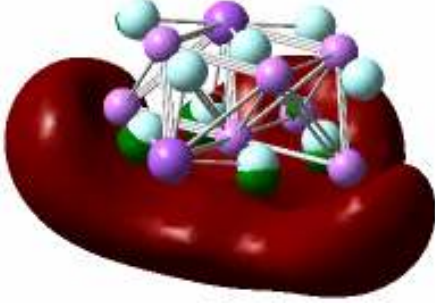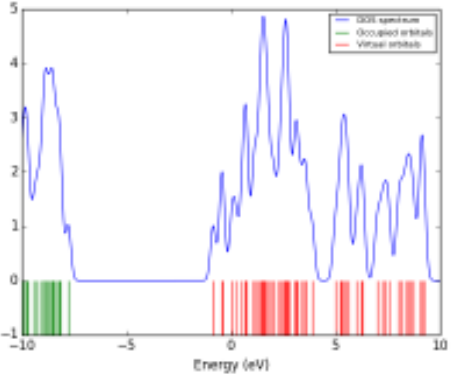**Table.1 Formation energy, point symmetry and dipole moment of LiF nanostructures**
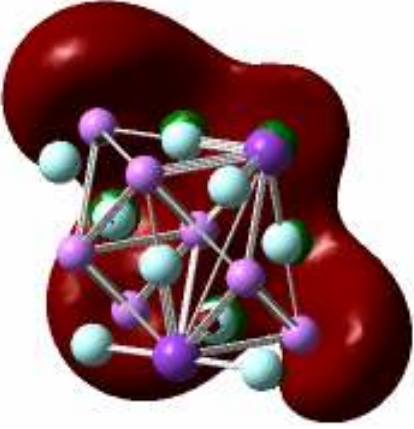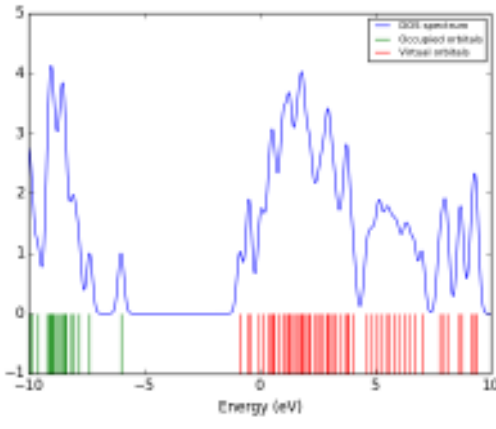
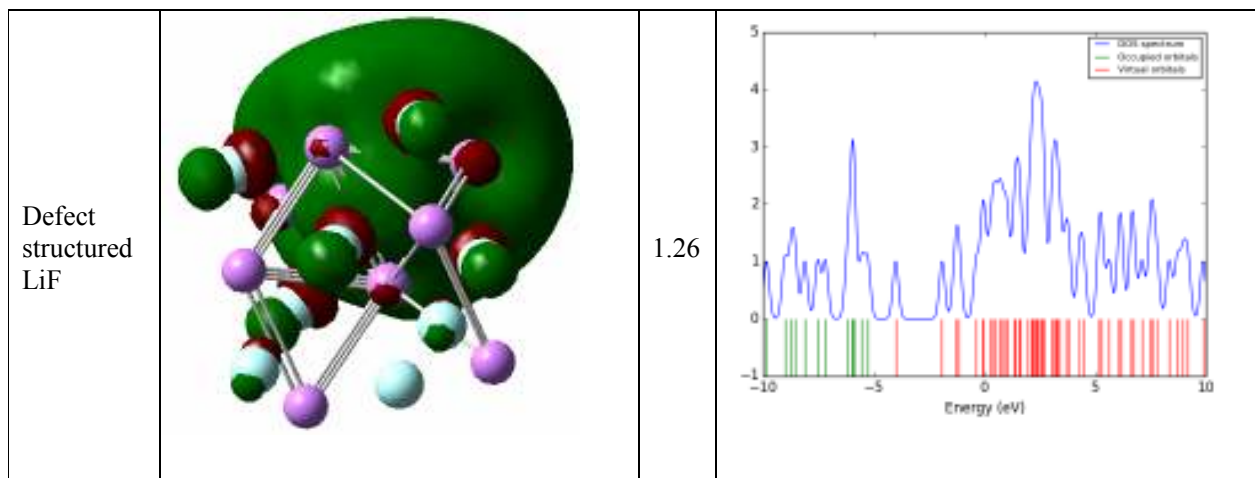| Nanostructures	Formation energy (eV)	Dipole moment (Debye)	Point Group
Pure cubic LiF	-71.264	7.66	C_1
Cl substituted cubic LiF	-60.112	7.39	C_1
Na substituted cubic LiF	-66.368	7.75	C_1
K substituted cubic LiF	-51.408	7.68	C_1
Defect structured LiF	-57.12	19.64	C_1

Density of states and HOMO-LUMO gap of LiF nanostructures

The electronic properties of cubic LiF nanostructures can be discussed in terms of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [29-32]. The HOMO – LUMO gap value for pure cubic LiF nanostructure is 7.04 eV. This infers the wide band gap, the electrons in the HOMO level requires more energy to move towards LUMO level. Moreover, the HOMO-LUMO gap can be tailored with the help of proper substitution impurities. In this work, all the three impurities such as Cl, Na and K are incorporated to fine-tune the band gap of LiF nanostructures. The energy gap value for Cl, Na and K substituted cubic LiF nanostructures is 6.55, 6.92 and 5.14 eV respectively. Moreover, the substitution of K in LiF nanostructures decreases the band gap drastically. Defect structured LiF nanostructure has the energy gap of 1.26 eV, the creation of defect in the structure at a particular site have the influence in tuning the band gap. The drastic decrease in the band gap value to 1.26 eV makes LiF nanostructure to transit from wide band gap to narrow band gap, but in defect structure the structural stability decreases. However, the position of the defect also plays a major role in decreasing the band gap. Table 2 shows density of states (DOS) spectrum and visualization of HOMO – LUMO gap. From the HOMO-LUMO visualization it can be clearly observed that due to wide band gap, the electron cloud in the virtual orbital (red color) is seen for all the substitution impurities, in contrast, due to the decrease in the band gap, the occupied orbital (green color) is seen for defect structured LiF nanostructure. Interestingly, on observing the DOS spectrum, the density of charge is more in the virtual orbital than occupied orbital for pure and impurity substituted LiF nanostructures. This can be clearly compared with the HOMO-LUMO visualization with DOS spectrum. However, for defect structured LiF nanostructure, the band gap decreases and peak maximum are noticed both in occupied and virtual orbital. The electronic properties have a much influence with substitution impurity and defect in the structure.

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

Nano Structures	HOMO – LUMO Visualization HOMO LUMO	E_g (eV)	HOMO, LUMO and DOS Spectrum
Pure cubic LiF		7.04	

R. Chandiramouli *et al* /Int.J. ChemTech Res. 2015,8(4),pp 1991-2001.

1995

Cl substituted cubic LiF		6.55	
Na substituted cubic LiF		6.92	
K substituted cubic LiF		5.14	

| Defect structured LiF | | 1.26 | |

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

The electronic properties of LiF nanostructures can also be discussed using Ionization potential (IP) and Electron affinity (EA) [33-36]. The graphical representation of IP and EA for cubic LiF nanostructures as shown in Figure 2. The energy required to remove the electron from LiF nanostructures are referred as IP. The amount of energy released due to addition of electron in LiF nanostructures is known as EA. The IP value for pure cubic LiF nanostructure is 7.93 eV. It reveals that more energy is required to remove electron from LiF nanostructures. The addition of Cl, Na and K impurities results in decrease in IP for LiF nanostructures. The corresponding IP value for Cl, Na and K substituted cubic LiF nanostructure is 7.46, 7.77 and 5.99 eV respectively. The EA is almost same for impurity substituted LiF nanostructures, in contrast, for defect structured LiF nanostructure EA value increases to 4 eV. EA play an important role in plasma physics, chemical sensors and in phosphor materials. The ranges of EA is observed in the order of 0.85 – 0.91 eV for impurity substitution LiF nanostructures. This indicates that less energy is released due to addition of electrons in impurity LiF nanostructures.
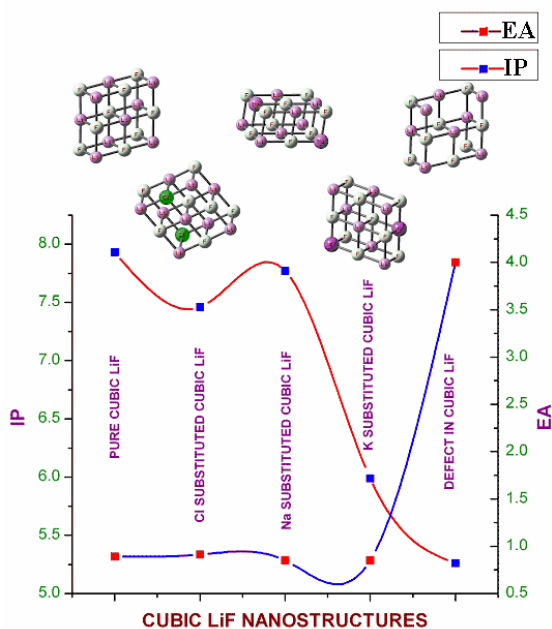

Figure.2 IP and EA of cubic LiF nanostructures (IP and EA in eV)

Chemical potential (CP) and chemical hardness (CH) are mainly related with IP and EA. Another way to discuss structural stability of LiF nanostructures is CH and CP [37-40]. The chemical hardness is given by is

$\eta = (IP-EA)/2$ and chemical potential is expressed as $\mu = -(IP+EA)/2$ respectively as shown in Table 3. There is not much variation observed in CP and the value ranges from 3.42 to 4.63 eV. It is nothing but potential energy which is absorbed or released due to the chemical reaction and it is represented by electronegativity. The negative of electronegativity is known as chemical hardness. The low value of chemical hardness is observed for defect structure. Precisely CP and CH can be calculated by the method of effective fragment potential.

Table.3 Chemical potential and chemical hardness of LiF nanostructures

Nanostructures	Chemical potential (eV)	Chemical hardness (eV)
Pure cubic LiF	-4.41	3.52
Cl substituted cubic LiF	-4.18	3.27
Na substituted cubic LiF	-4.31	3.46
K substituted cubic LiF	-3.42	2.57
Defect structured LiF	-4.63	0.63

Vibrational studies of LiF nanostructures

Vibrational studies are most important entity to study the stability of LiF nanostructures. The optimized LiF cubic nanostructures are said to be more stable if the imaginary frequency are not found for the nanostructure [41]. Table 4 depicts the vibrational frequency and infrared (IR) intensity of LiF nanostructures. The pure cubic LiF nanostructure has the vibrational frequency at 587.46 and 559.72 cm^{-1} with corresponding IR intensity of 606.13 and 493.62 km/mole. The prominent IR intensity of Cl substituted cubic LiF nanostructure is 296.31 and 279.56 km/mole for the vibrational frequency of 518.52 and 563.35 cm^{-1} respectively. Na substituted cubic LiF nanostructure has the vibrational frequency at 564.24 and 556.52 cm^{-1} which corresponds to IR intensity of 327.22 and 311.57 km/mole. For K substituted cubic LiF nanostructure IR intensity is observed at 408.85 and 320.43 km/mole with vibrational frequency of 522.04 and 561.97 cm^{-1} respectively. The IR intensity of defect structured LiF nanostructure is 352.86 and 227.56 km/mole which are associated for vibrational frequency at 541.67 and 522.35 cm^{-1} respectively. Molecular stretching vibrational modes are observed for all LiF nanostructures. Figure. 3 (a) – (e) represents the IR spectrum of pure, Cl, Na, K and defect structured LiF nanostructure respectively.

Table.4 Vibrational Frequency and IR Intensity of LiF nanostructures

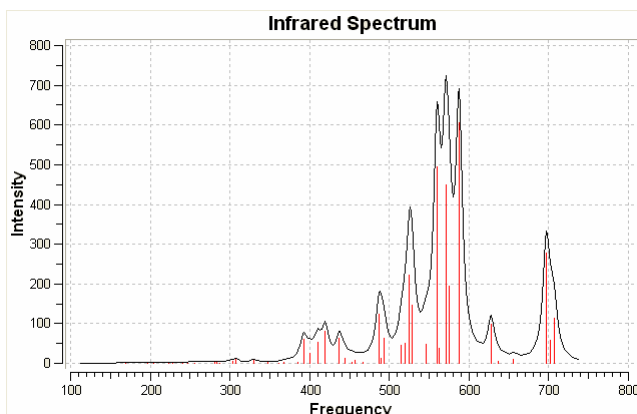| Nanostructures	Frequency (cm^{-1})		IR intensity (km/mole)	
Pure cubic LiF	587.46	559.72	606.13	493.62
Cl substituted cubic LiF	518.52	563.35	296.31	279.56
Na substituted cubic LiF	564.24	556.52	327.22	311.57
K substituted cubic LiF	522.04	561.97	408.85	320.43
Defect structured LiF	541.67	522.35	352.86	227.56

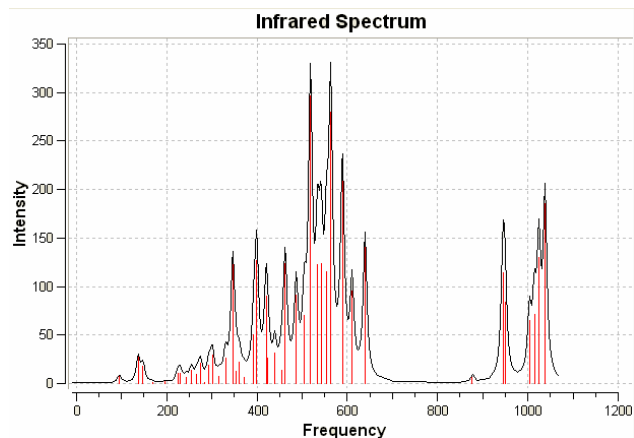

Figure.3 (a) Pure cubic LiF nanostructure

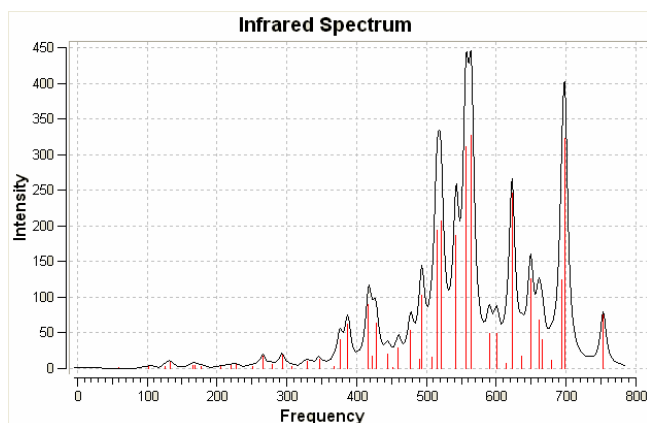**Figure.3 (b) Cl substituted cubic LiF nanostructure**

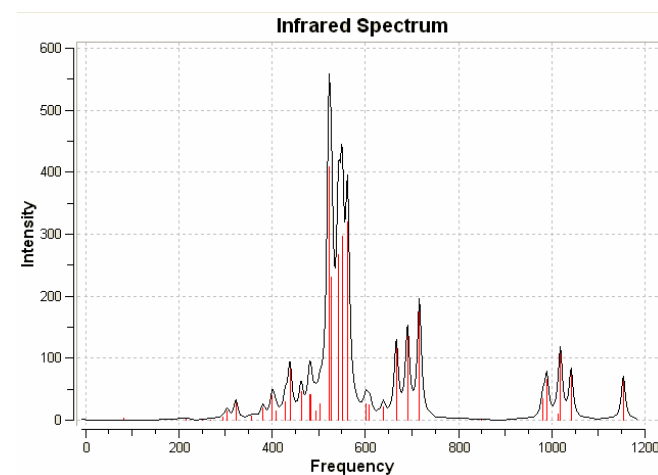**Figure.3 (c) Na substituted cubic LiF nanostructure**

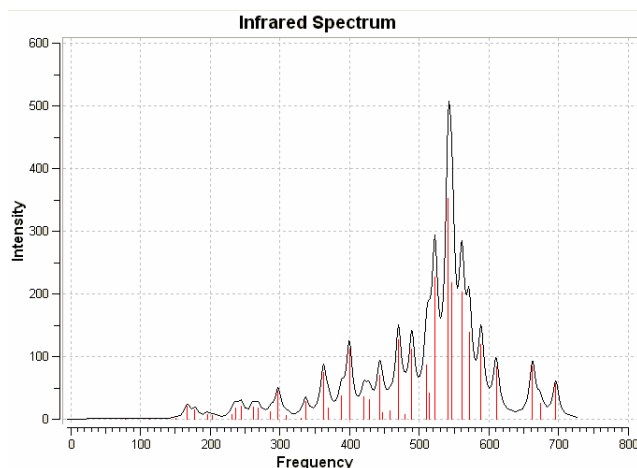**Figure.3 (d) K substituted cubic LiF nanostructure**

Figure.3 (e) Defect structured LiF nanostructure

Conclusion

Using density functional theory, pure, Cl, Na and K substituted cubic LiF nanostructures are simulated and optimized successfully by the help of B3LYP/LanL2DZ basis set. The structural stability of cubic LiF nanostructures is characterized by formation energy, chemical hardness and chemical potential. Dipole moment and point symmetry group of all optimized cubic LiF nanostructures are discussed and reported. Observation of electronic properties of all possible cubic LiF nanostructures are analyzed by HOMO – LUMO gap, electron affinity, density of states and ionization potential. In this work, optimized cubic LiF nanostructures are tailored with the help of substitution of Cl, Na and K impurities. The structural stability and electronic properties of cubic LiF nanostructures can be fine-tuned which is used as phosphor, integrated optics and radiation detectors.

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