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SHIFT OF BAND GAP FROM DIRECT TO INDIRECT AND OPTICAL RESPONSE OF LiF UNDER PRESSURE

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We hereby are reporting the transition pressure at which lithium fluoride (LiF) compound transforms from direct band gap to indirect band gap insulator on the basis of FP-LAPW calculations. The fundamental band gap of LiF compound suffers direct to indirect transition at a pressure of 70 GPa. The study of the pressure effect on the optical properties e.g. dielectric function, reflectivity, refractive index and optical conductivity of LiF in the pressure between 0–100 GPa, shows that this pressure range is very critical for LiF compound as there are significant changes in the optical properties of this compound.

Keywords: Lithium fluoride; DFT; hydrostatic pressure; band structure; optical properties.

PACS Number(s): 78.20.-e

1. Introduction

Lithium fluoride (LiF) is chemically stable and optically transparent insulator.[1] Its large band gap (14.0 eV) and ionic crystal structure produces its unique high ultraviolet transmissivity. Under shock compression, LiF is found to remain transparent

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up to a pressure of 200 GPa[2−4] while when ramp compressed it is found to be transparent up to a pressure of 4000 GPa which is the highest pressure reported up to which any transparent insulator have been observed.[5] The ability to remain transparent at higher pressure makes it possible to measure the properties of different materials in a wide range pressures using LiF windows. LiF with rock salt crystal structure has been previously studied both theoretically and experimentally,[2−10] while there have been extensive studies on nonmetal to metal transition, equation of state and optical properties of LiF in high pressure ranges (> 100 GPa)[2,11,12] there is a lack of knowledge of electronic and optical properties of LiF in low pressure range (< 100 GPa). It is well known that LiF in rock salt crystal structure and in ground state is a direct band gap material.[6,7,10] In a recent theoretical study, it was shown that LiF transform from direct to indirect band gap insulator when the pressure increased from 0 to 300 GPa.[6] But exact transition pressure is still not reported. This study will show that the pressure range (< 100 GPa) is very critical for direct to indirect band gap transition.

In this work, the exact transition pressure at which LiF transforms from direct band gap to indirect band gap insulator is reported for the first time by first principle calculations. Furthermore, optical properties e.g. dielectric function, conductivity and reflectivity are also studied in the pressure range between 0–100 GPa. We have also compared our results with recent experimental and theoretical studies on LiF compound.

2. Computational Details

In the present density functional calculations, FP-LAPW method with Wu–Cohen generalized gradient approximation (GGA)[13] and modified Beck Johnson (mBJ),[14] as implemented in the Wien2k code,[15] are used to solve Kohn–Sham equation[16] for LiF compound. In the full potential scheme wave function, potential and charge density are expanded into two different basis. The wave function is expanded in spherical harmonics in the atomic spheres while outside the spheres (interstitial region) it is expanded in plane wave basis. The potential is also expanded in the same manner:

$$V(r) = \begin{cases} \sum\limits_{lm} V_{lm}(r) Y_{lm}(r) & \text{(1a)} \\ \sum\limits_{k} V_K e^{ikr} & \text{(1b)} \end{cases}$$

where Eq. (1a) is for inside and Eq. (1b) for outside the atomic sphere. Inside the sphere maximum value of l for the wave function expansion is $l_{\max} = 10$. The muffin-tin radii (R_{MT}) = 1.6 a.u. is chosen for both Li and F atoms. For wave function in the interstitial region, the plane wave cut-off value of $K_{\max} = 7/R_{\mathrm{MT}}$ is chosen. For the k-space integration in the irreducible Brillouin zone (IBZ), modified tetrahedron method[17] with 35 k-points was used in the full Brilluion zone (BZ) to

calculate structural properties. A uniformly distributed mesh of k-points (500 k-points for electronic and 3000 for optical properties) were used in the full BZ to ensure the convergence.

3. Results and Discussion

The binary LiF crystallizes in the face centered cubic structure with space group Fm-3m (#225) and its unit cell contains one molecule. The Li atom is positioned at the corners of the unit cell $(0, 0, 0)$ while F atom at the center of the cell $(1/2, 1/2, 1/2)$. Important structural parameters of LiF are calculated using the volume optimization. In the volume optimization process, unit cell energy of LiF is varied with the variation of the unit cell volume. The configuration with minimum energy is the ground state of the system (as shown in Fig. 1(a)). The volume
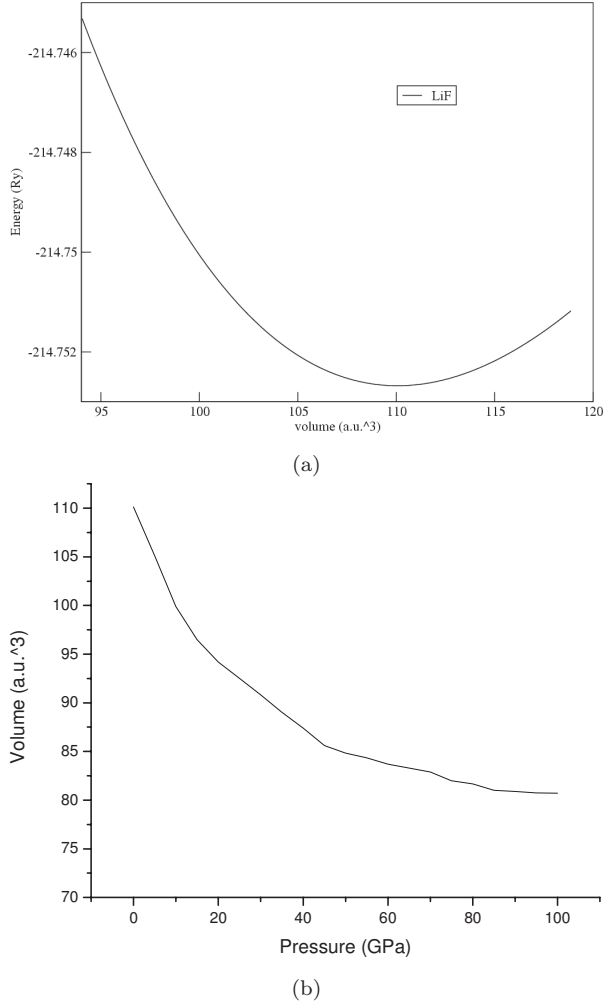

(a)

(b)

Fig. 1.   (a) Unit cell energy as a function of volume. (b) Unit cell volume as a function of pressure.

Table 1. Calculated structural parameters along with experimental and other theoretical calculations.

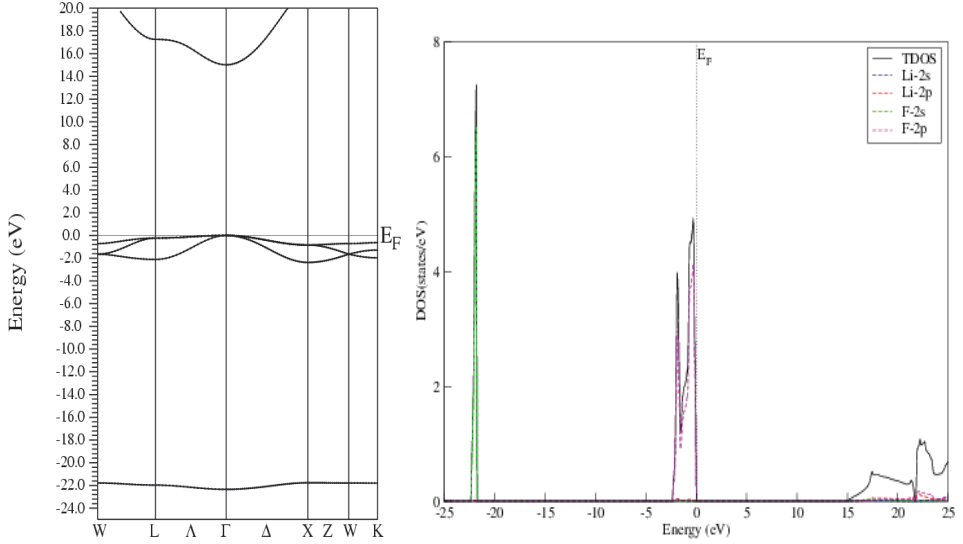|	α_0 (Å)	B_0 (GPa)	B^p	E_0 (Ry)
This work	4.02	70.37	5	214.75
Experimental	4.01 (Ref. 18)	69.9 (Ref. 18)		
Other works	3.88 (Ref. 19), 4.05 (Ref. 20)	95 (Ref. 19), 78.3 (Ref. 20)		

Fig. 2. (Color online) Calculated band structure and density of states of LiF compound at zero pressure.

corresponding to this minimum energy is the optimized volume. Using this volume the lattice parameter is obtained. The lattice constant, α_0 (Å) and other parameters like bulk modulus, B_0 (GPa), pressure derivative of the bulk modulus, B^P and the ground state total unit cell energy, E_0 (Ry), were obtained and presented in Table 1, alongwith the available experimental and other calculations. From the table it can be seen that the calculated α_0 (Å) and B_0 (GPa) at zero pressure are in close agreement to the experimental results compared to the previous calculations. Unit cell volume as a function of pressure is also plotted in Fig. 1. It is seen that the volume decreases with increase in the pressure.

The calculated band structure along high symmetry directions in the Brillouin zone and density of states (DOS) at 0 pressure is shown in Fig. 2. It is shown that LiF compound is a direct (Γ–Γ) band gap insulator (15.2 eV) at zero pressure, in excellent agreement with experimental data[21] (14.5 eV). The indirect band gap (Γ–L) is 17.4 eV at 0 pressure. The DOS shows that the valence band (below Fermi level) is composed of F-$2p$ state and the conduction band is formed by the
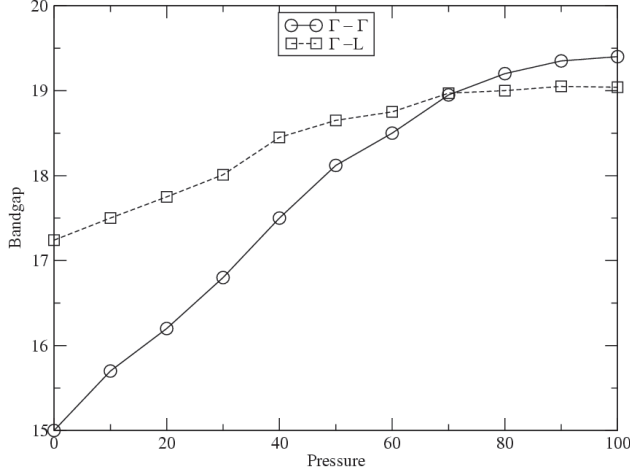
Fig. 3.   Variation of Γ–Γ and Γ–L band gaps with pressure.

hybridization of "s" and "p" states of both "Li" and "F" atoms in agreement with the previously reported DOS for LiF.[6,7] The bands around −22 eV is mainly occupied by F-2s state.

Figure 3 accounts for variation of both Γ–Γ and Γ–L band gaps with pressure in range between 0–100 GPa. It can be found that both Γ–Γ and Γ–L band gaps increased with the increase in pressure. It may be understood in terms of madelung potential.[22,23] With the increase in pressure, the attractive potential of anions on electrons increases due to denser packing of cations under pressure. As madelung potential is more effective for localized states than delocalized states, the valence band which is more localized for LiF compared to conduction band suffers larger downward energy shift with the decreasing of unit cell volume compared to conduction band. Thus, band gap increases. Moreover within the conduction band more localized, s-states of anions responsible for lowering of the conduction band at Γ symmetry point suffer larger energy perturbation compared to less localized cation's s-states responsible for indirect Γ–L band gap. Consequent upon with the increase of pressure Γ–Γ band gap increases at a faster rate than Γ–L band gap. As a result Γ–Γ curve with a steeper slope crosses Γ–L curve, which has relatively smoother slope and this cross-over occurs at a pressure of 70 GPa (Fig. 2). This is the transition pressure as the material has been transformed from direct band gap to indirect band gap insulator. This is a striking feature of pressure application which changes the electronic behavior of the material completely.

We now discuss the influence of pressure on the frequency dependent optical properties of LiF compound in the pressure range between 0–100 GPa with intervals of 20 GPa by using optical code by Claudia *et al.*[24] as implemented in Wien2k.[15] The optical parameters, refractive index, reflectivity and optical conductivity are

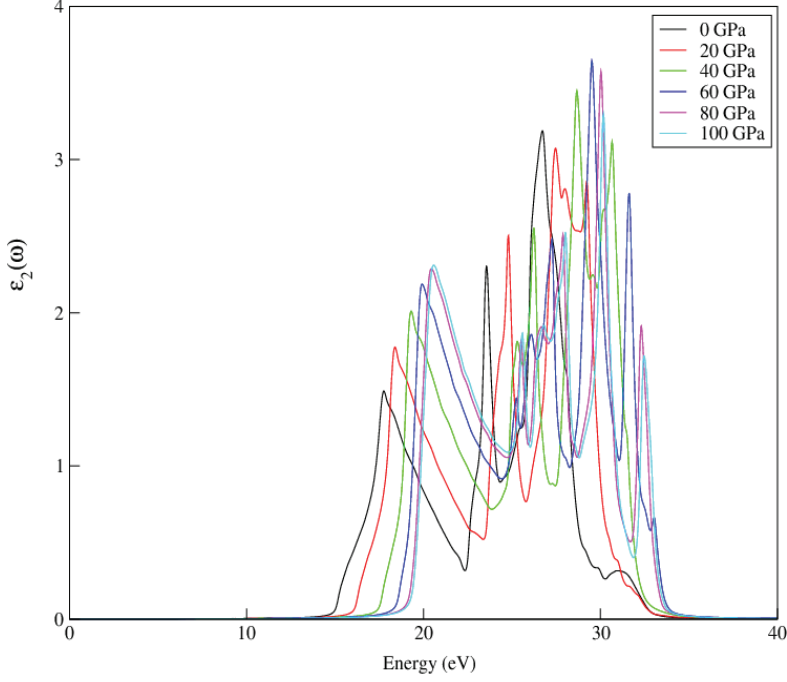*A. Sajid, G. Murtaza & A. H. Reshak*

Fig. 4. (Color online) Pressure induced variation in the imaginary part of frequency dependent dielectric function.

calculated by using following relations, respectively:

$$n(\omega) = \frac{1}{\sqrt{2}} [\{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2\}^{1/2} + \varepsilon_1(\omega)]^{1/2}, \tag{2}$$

$$R(\omega) = \left| \frac{\tilde{n} - 1}{\tilde{n} + 1} \right| = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \tag{3}$$

$$\sigma(\omega) = \frac{2W_{cv}\hbar\omega}{\mathbf{E}_0^2}. \tag{4}$$

Behavior of the imaginary part $\varepsilon_2(\omega)$ of frequency dependent dielectric function with pressure variation is shown in Fig. 4. As a remarkable finding, the high peaks which are observed in $\varepsilon_2(\omega)$ spectrum at the energies 17.8 eV, 23.5 eV and 26.8 eV at zero pressure, are shifted to higher energy with increase in pressure. The shift of the peaks from lower to higher energy is attributed to the fact that increase in pressure lead to increase in the value of the band gap. We should emphasize that the intensity of peaks increases as the pressure increases gradually above zero till 70 GPa. The highest peak seen in spectrum at zero pressure (26.8 eV) gets its maximum intensity between 60–70 GPa. This high intensity is ascribed to transition from direct to indirect band gap. At 70 GPa and beyond, the intensities of all peaks start to decrease.
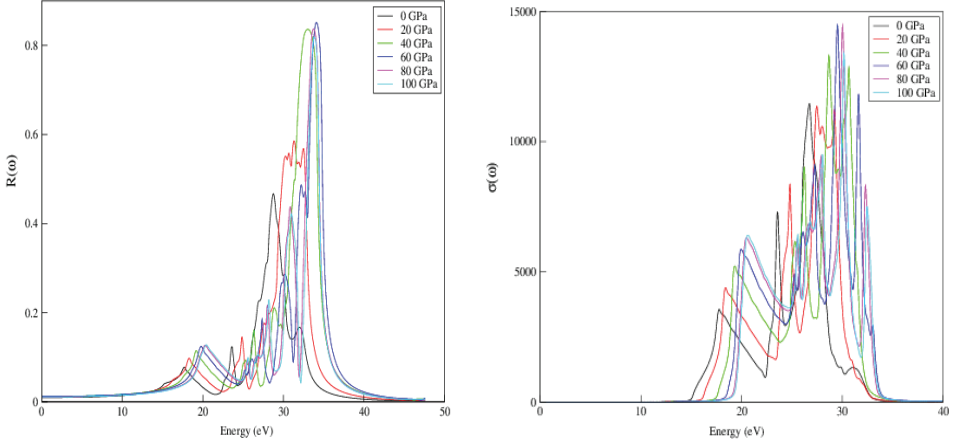
Fig. 5. (Color online) Response of frequency dependent reflectivity and optical conductivity of LiF compound.

Frequency dependent reflectivity spectrum of LiF compound is shown in Fig. 5. It is seen that onset of reflectivity shifts to higher energy with increase of pressure. The reflectivity spectrum at 0 GPa contains a major peak which shows that the reflectivity reaches about 50% at 28 eV. This result is consistent with recent FP-LAPW based calculations[6] giving a reflectivity of 40% at energy of 22 eV. Moreover, Sun *et al.*[6] reported that reflectivity decreases from its maximum value as the pressure increases from 0 to 300 GPa. But on resolving the pressure range of 0–100 GPa in the steps of 20 GPa, it can be seen that reflectivity reaches even 80% at an energy of 34 eV at a pressure between 60–70 GPa. It can be concluded that the pressure range 60–70 GPa is very critical for LiF compound. In this pressure range, LiF compound becomes highly reflecting and can be used as a ultraviolet reflecting mirror.[25] The spectra of optical conductivity shows the same behavior, while maximum optical conductivity of 1400 Ω^{-1} cm^{-1} is at 70 GPa.

The refractive index of LiF compound at different pressures is also plotted against energy as shown in Fig. 6. It is noted from the figure that the threshold point for refraction at 13 eV at zero pressure shifts to high energy as pressure is increased to 100 GPa. Moreover, the peaks seen in the spectrum also shift to high energy by increasing pressure. Our calculated zero frequency refractive index at zero pressure i.e. $n(0) = 1.215$, is in excellent agreement with the earlier experimental observation[26] ($n(0) = 1.21$). Also the zero frequency refractive index increases with the increase of pressure which is in agreement to the experimental results of Balzaretti and Jordnada.[27]

4. Conclusion

From this study, it is predicted that the pressure range 0–100 GPa is very critical for LiF compound as in this pressure range LiF suffers changes in its electronic

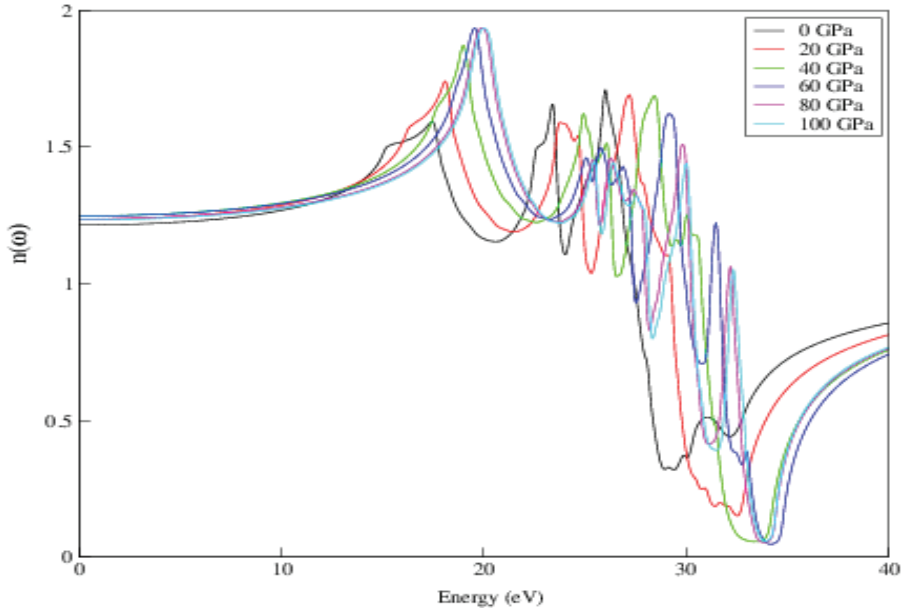*A. Sajid, G. Murtaza & A. H. Reshak*

Fig. 6. (Color online) Variation of refractive index with pressure.

and optical properties. The band gap of LiF is found to be transformed from direct to indirect one at a pressure of about 70 GPa. Reflectivity spectrum of LiF shows reflectivity up to 80% for high ultraviolet energy in the pressure range of 60–70 GPa. Our calculated zero frequency refractive index at zero pressure is found to be in close agreement with earlier experimental studies. Also the LiF compound is found to show maximum refraction to high ultraviolet energy in pressure range of 60–70 GPa.

Acknowledgments

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