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Role of dopants in LiF:Mg,Cu, LiF:Mg,P and LiF:Mg,Cu,P detectors

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ABSTRACT

In this study, electronic structure of LiF crystal doped with Mg,Cu,P impurities was studied with WIEN2k code on the basis of FPLAPW+lo method. Results show that in Mg-doped LiF composition, an electronic trap was created with impurity concentration of 1.56% and 3.125%. In this condition, the electronic trap with increasing the percentage of the impurities up to 4.687% is annihilated. It was found, that by doping of Mg and Cu or P simultaneously, a hole-trap is created in valence band. It was realized that in LiF:Mg, Cu, LiF:Mg,P and LiF:Mg,Cu,P, Cu impurity and Li atom, have a key role in creation of levels which lead to create electronic and hole traps. Mg impurity and F atom, only have a role in creation of electronic traps. In addition, P impurity has a main role in creation of the electronic and hole traps in LiF:Mg,Cu,P. The activation energy of electronic and hole trap in LiF:Mg,Cu, LiF:Mg,P and LiF:Mg,Cu,P crystalline lattice were obtained as 0.3 and 5.5 eV, 0.92 and 3.4 eV and 0.75 and 3.1 eV, respectively.

1. Introduction

Lithium fluoride (LiF) dosimeters are the most applicable thermoluminescence (TL) dosimeter up to now. It was discovered and utilized as TL dosimeter by McKeever [1]. It was found that the TL intensity and sensitivity of LiF crystal are intensely modified by doping of impurity ions within a crystalline lattice. Lee et al. [2] found that TL emission in LiF depends on the type and amount of dopant as well as the preparation procedure and the optimized conditions. In fact, the existence of dopants in such phosphorus is the cause for enhancement of TL sensitivity and number of peaks observed in the shape of TL glow curves. Tang et al. [3] reported that the glow curve shape and the intensity of TL peaks clearly depend on the Mg concentration. McKeever based on the results of unchanged TL emission spectrum of LiF:Mg,Cu,P doped with either monovalent or divalent copper salts concluded that Cu does not play any role in the TL emission process and phosphorus is the main activator responsible for TL emission [2]. Bilski et al. [4,5] studied radiation-induced sensitivity loss of LiF:Mg,Ti and LiF:Mg, Cu,P over the dose range 1–5000 Gy and found that LiF:Mg,Cu,P is more resistant to radiation than LiF:Mg,Ti. While some researchers have found that Mg is the essential dopant and plays an important role in the TL emission process, there is no unanimity on the role of dopants on the TL response yet [2–7]. Also, recent studies have demonstrated that TL properties of material get modified by the physical shape of the TL material and its size as well as the impurities doped [7].

The purpose of this study is to:

(1) Simulate bandgap structure and activation energy of LiF:Mg,Cu and LiF:Mg, P and study the effects of the Mg, Cu and P impurities on the dosimety response.
(2) Simulate bandgap structure and activation energy of the above stated dopants and their effects on dosimetry response of LiF: Mg,Cu,P phosphorus using WIEN2K Code.
(3) Determination of the activation energy of electronic and hole traps and their effects on glow curve structure.

2. Computational method

All calculations presented in this work are based on density functional theory (DFT) [8] using the all electrons, full potential WIEN2K code [9]. The maximum angular momentum of the atomic orbital eletronic basis functions was set to lmax=10. The radii of the muffin-tin spheres were set to $R_{Li}=1.76$ a.u. $R_F=1.65$ a.u., $R_{Cu}=1.86$ a.u., $R_{Mg}=1.65$ a.u. and $R_P=1.76$ a.u. In order to achieve energy eigenvalues convergence, the wave functional in the interstitial region were expanded in terms of plane waves with a cut-off parameter of RMT × Kmax=8, where RMT denotes the smallest atomic sphere radius and Kmax largest k vector in the plane wave expansion. For the exchange-correlation energy functional, we used the generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) [10]. The Brillouin zone integration

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is performed within the Gamma-centered Monkhorst–Pack scheme [11] using $10 \times 10 \times 10$ *k*-points.

3. Results and discussion

3.1. Structural and electronic properties of pure LiF

A LiF crystal in the ground state has a cubic crystal structure with space group 225-Fm-3 m. Each unit cell of this combination has been made of one Li atom at the location (0,0,0) and one F atom in place (0.5, 0.5, 0.5). The lattice optimized parameter and bulk modulus are calculated using the Murnaghan equation [12,13]. The total energy–volume curves for LiF compound is shown in Fig. 1.

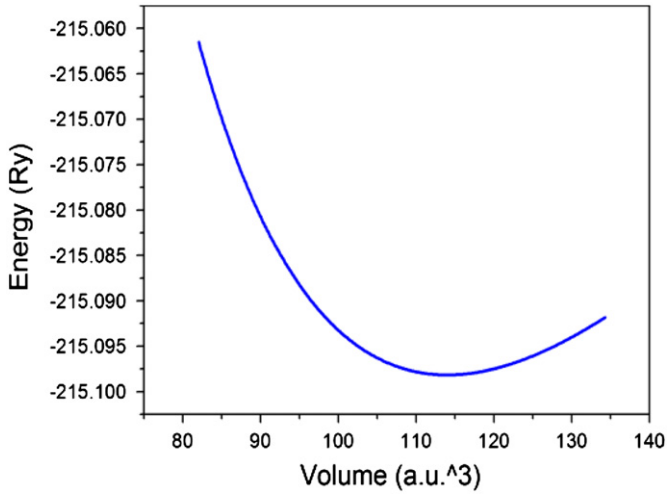

Fig. 1. The total energy–volume curves of LiF within GGA in the cubic structure.

The calculated lattice parameter of 4.05 Å obtained in this study has good agreement with experimental value of 4.03 Å [14]. Also, the calculated bulk modulus of 67.2 GPa obtained in this study matches relatively well with the experimental value of 62.03 GPa [14]. Fig. 2 shows electronic band structure and density of states (DOS) for the LiF. Obviously, this crystal has a direct band gap with a size of approximately 9 eV at the Γ point.

3.2. Electronic structure of LiF doped with Mg impurity

The structural properties of LiF crystal are simultaneously investigated by doping various concerntrations of Mg. A supercell of LiF crystal for substituting of Mg impurity with different contributions within its crystalline lattice that includes 32 F atoms and 32 Li atoms (a total of 64 atoms), have been considered. Mg impurity was replaced with Li atom in ratios of 1.56%, 3.125% and 4.687% for substituting one, two and three atoms, respectively. Table 1 shows the lattice parameter, bulk modulus and band gap energy of the electronic trap created for the substitution of Mg

Table 1
Calculation of the lattice parameter (Å), bulk modulus and activation energy of electronic trap for percentages of impurity Mg in LiF crystal.

Type	Lattice parameter (Å)	Bulk modulus (GPa)	Activation energy of electronic trap (eV)
Pure LiF	4.05	67.2	0
LiF:$Mg_{1.56\%}$	4.15	76.46	0.9
LiF:$Mg_{3.125\%}$	4.17	62.81	0.5
LiF:$Mg_{4.687\%}$	4.22	61.639	0

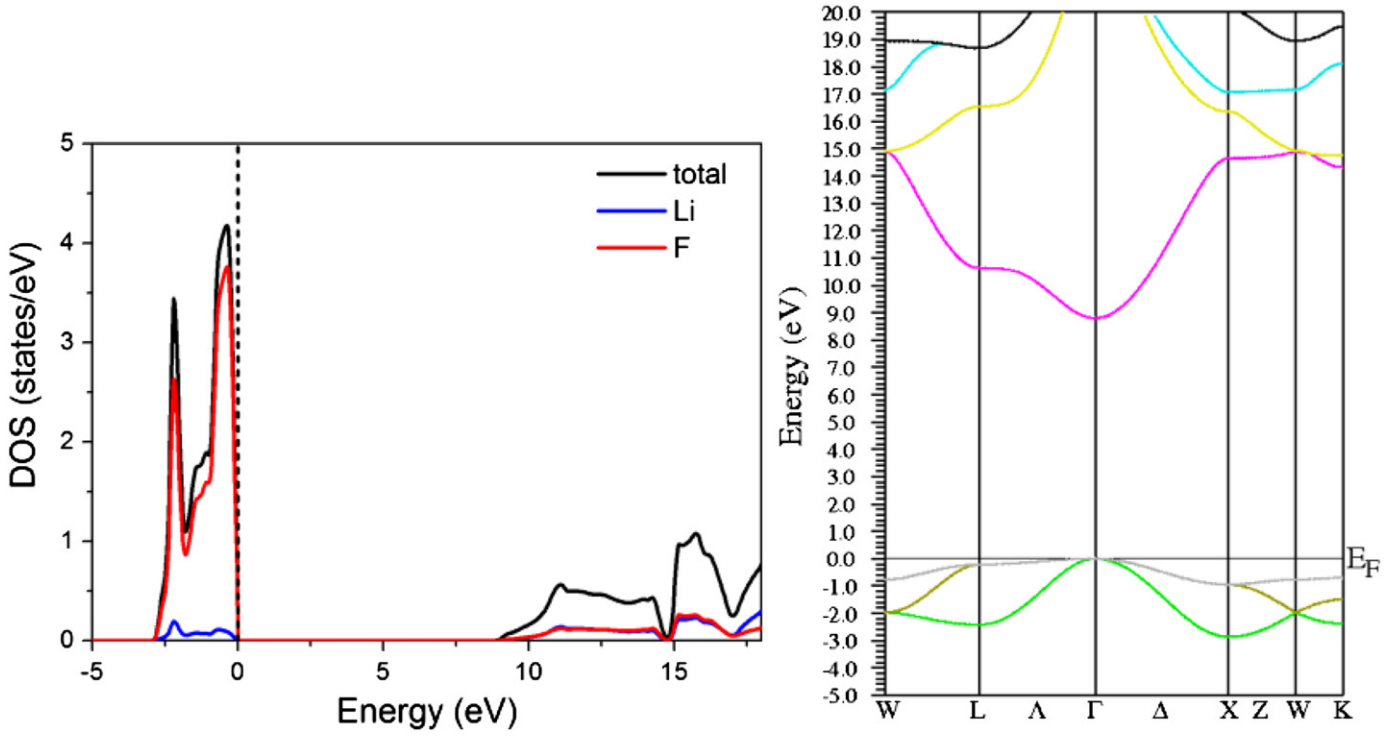

Fig. 2. Electronic band structure and density of states for pure LiF crystal.

impurity within LiF crystal with different ratios. As it is observed, because of the large atomic radius of Mg in compared to Li, the lattice parameter become bigger by increasing the percentage of Mg impurity. The bulk modulus of LiF doped Mg with 1.56% ratio is bigger than the pure LiF crystal's one, however the bulk modulus decreases by increasing Mg impurity percentage.

Fig. 3 shows the electronic band structure of LiF doped Mg with different ratios. As it is clear, in this state, there is one energy gap

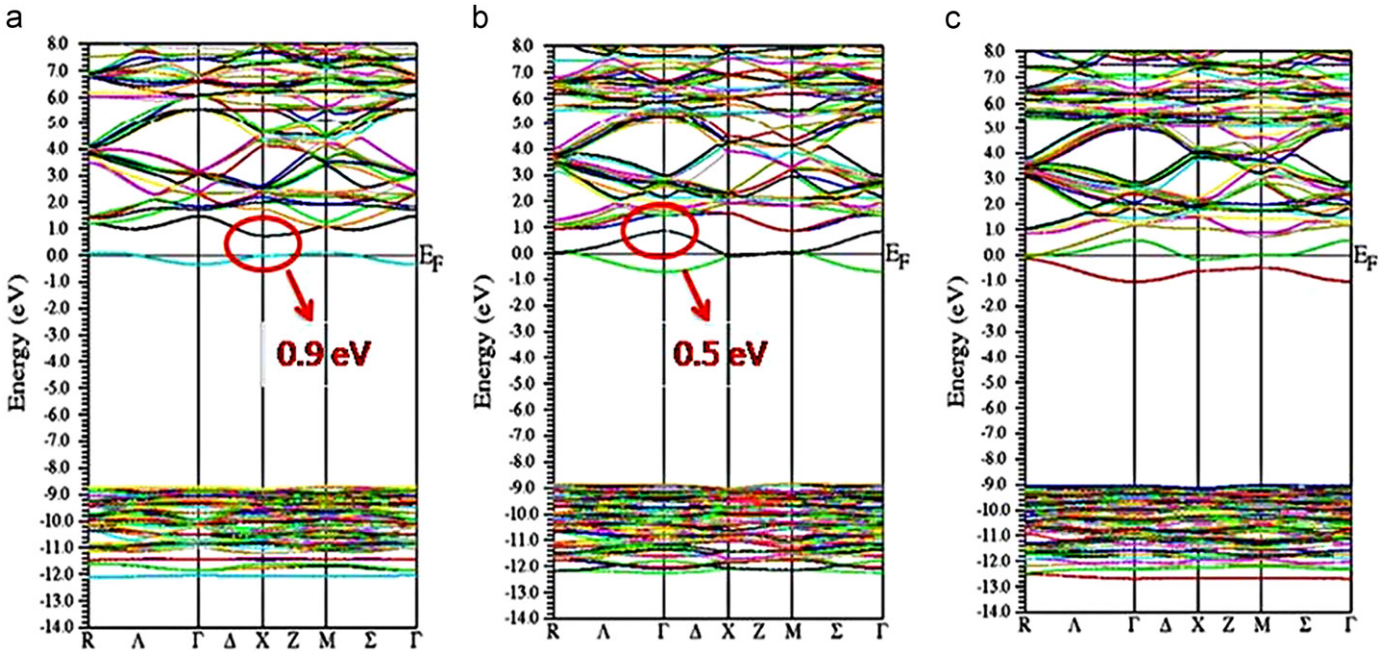

Fig. 3. Diagram of the band structure for LiF compound that the magnesium is replaced in it with ratio of: (a) 1.56%; (b) 3.125% and (c) 4.687%.

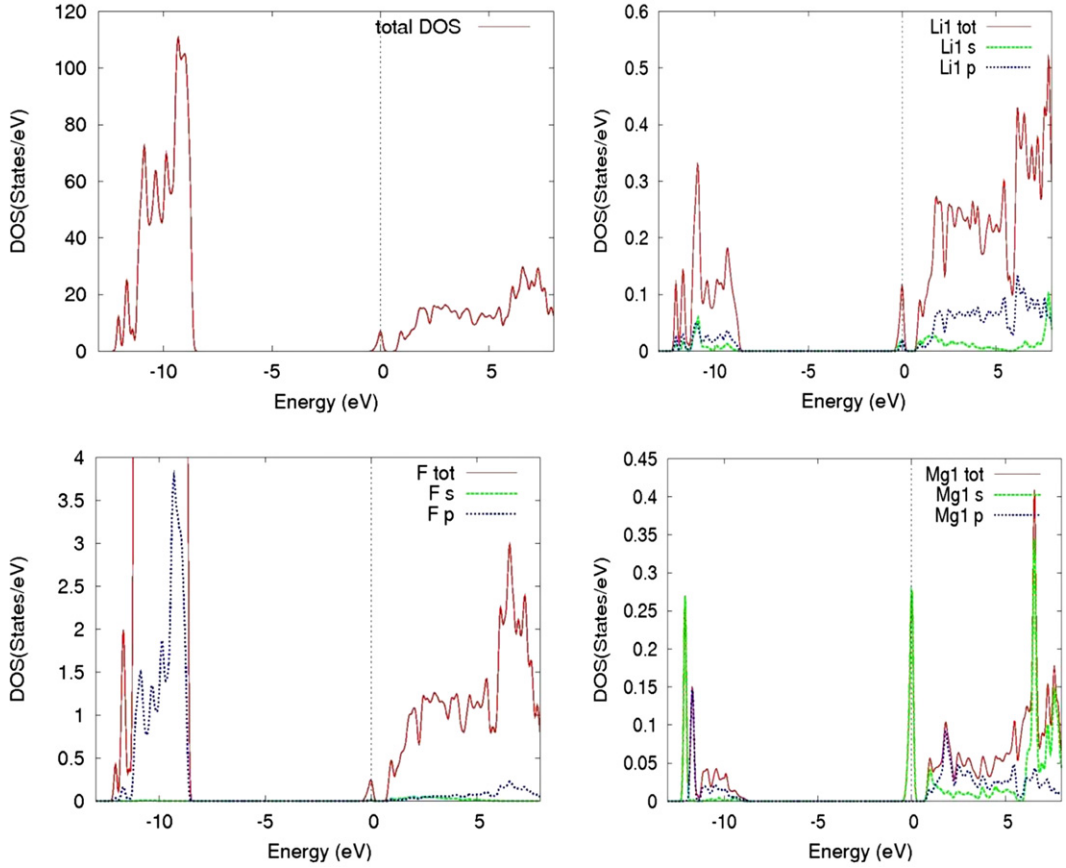

Fig. 4. Total and partial DOS for the Mg-doped LiF compound for concentration of 1.56%.

with energy of 9 eV between valence and conductance levels. Levels shift compared to its pure form is quite distinctive. Fermi surface in pure form was close to valences levels, while, here, the Fermi level is close to the conductance levels. Also, it was observed one electronic trap with activation energy of 0.9 and one with 0.5 eV for 1.56% at the X-point and 3.125% at Γ-point in conductivity bands, respectively. The electronic trap is annihilated by increasing the percentage of impurities (the ratio of 4.687%). For further evaluatation, the density of states (DOS) was calculated in 1.56% which has a bigger electronic trap. The DOS for this ratio has been shown in Fig. 4. By calculated partial DOS for Li atom, it is found that the s and p orbital eletronics of this atom play main role in creating levels and creating traps, consequently. The same result can be observed for F atom. But the situation for Mg impurity atom is slightly different. With observing density of partial states plotted for Mg impurity, it is found that s orbital electronic plays main role in creating of levels which cause to create traps.

3.3. Electronic structure of LiF doped with Mg, Cu and Mg, P impurities

The structural properties of LiF crystal are simultaneously investigated by doping couple atoms of Mg, Cu and Mg, P with a ratio of 1.56%. Mg impurity created the largest electronic trap due to substitution of Mg with a ratio of 1.56%. In this part, the substitution of Cu and P impurities with a ratio of 1.56% is investigated. For this purpose, in previous supercell one Li atom is replaced with one Mg impurity and the other replaced with Cu or P impurities. First the structural properties of these two compounds were studied. Using Murnaghan equation, optimized parameters for both structures were calculated. The bulk modulus for these structures is presented in Table 2. According to the table, the lattice parameters for these situations became bigger than the pure LiF crystals. The lattice parameters for the LiF:$Mg_{1.56\%}Cu_{1.56\%}$ and LiF:$Mg_{1.56\%}P_{1.56\%}$ compound are obtained as 4.17 and 4.2 Å, respectively. By substituting the atomic radius of Mg, Cu and P in LiF crystal, which are larger than Li atomic radius, lattice parameter increased. Also bulk modulus of LiF:$Mg_{1.56\%}Cu_{1.56\%}$ calculated as 67.356 GPa and its value has increased as 0.156 GPa compared to the pure LiF crystal. It means that crystal has become harder. However, the bulk modulus in this case compared to the sample which Mg impurity substituted, has reduced to 9.64 GPa. On the other hands, the crystal in this case has become softer. It is because of the covalent bonding and presence of copper impurities in the compound. The bulk modulus calculated for LiF:$Mg_{1.56\%}P_{1.56\%}$ is 59.30 GPa. This means that the crystal has become softer.

Table 2
The lattice parameters, bulk modulus and activation energy of electronic and hole traps for LiF:$Mg_{1.56\%}Cu_{1.56\%}$ and LiF:$Mg_{1.56\%}P_{1.56\%}$.

Type	Lattice parameter (Å)	Bulk modulus (GPa)	Activation energy of electronic trap (eV)	Activation energy of hole trap (eV)
LiF:$Mg_{1.56\%}Cu_{1.56\%}$	4.17	67.356	0.3	5.5
LiF:$Mg_{1.56\%}P_{1.56\%}$	4.2	59.30	0.92	3.4
LiF:$Mg_{1.56\%}Cu_{1.56\%}P_{1.56\%}$	4.19	63.2	0.75	3.1

The electronic properties of these compounds were studied. In Fig. 5(a) and (b) the band structure diagrams for LiF:$Mg_{1.56\%}Cu_{1.56\%}$ and LiF:$Mg_{1.56\%}P_{1.56\%}$ compounds have been shown. It is clear that activation energy of electronic trap in LiF:$Mg_{1.56\%}Cu_{1.56\%}$ is 0.3 eV. Also, levels are created within the energy gap lower than Fermi levels, due to the substitution of copper impurities. The distance between this levels and valence band is equal to 5.5 eV. This gap is leads to creation a hole-trap in valence band. By drawing the density of partial states for LiF:$Mg_{1.56\%}Cu_{1.56\%}$ in Fig. 6, it was found that in Li atom, s and p orbital eletronics have key roles in creation of electronic traps. Also, this atom is factor of the creation of levels lower than Fermi level which leads to hole-traps. F atom only has role in creation of electronic traps but it has no role in creation of hole-traps. But for Mg impurity according to Fig. 6, s orbital

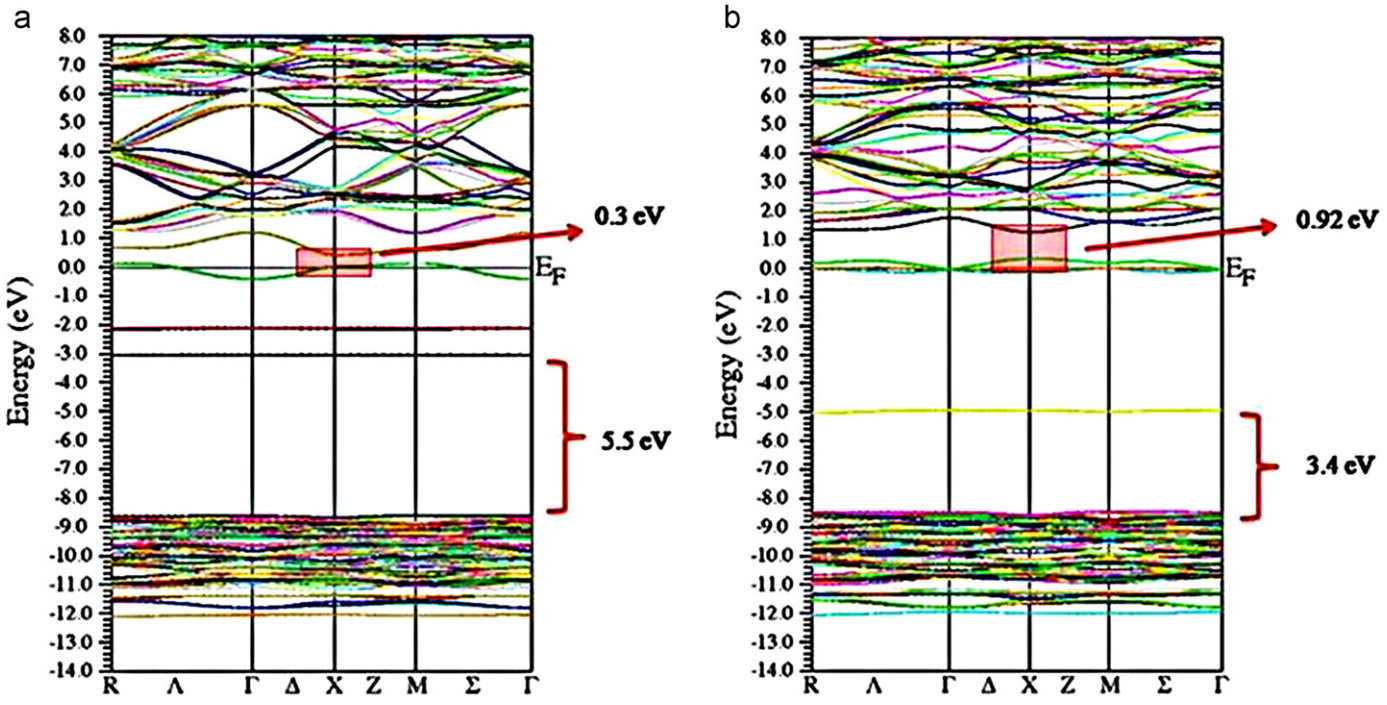

Fig. 5. Electronic band structure diagrams for compounds: (a) LiF:$Mg_{1.56\%}Cu_{1.56\%}$ and (b) LiF:$Mg_{1.56\%}P_{1.56\%}$.

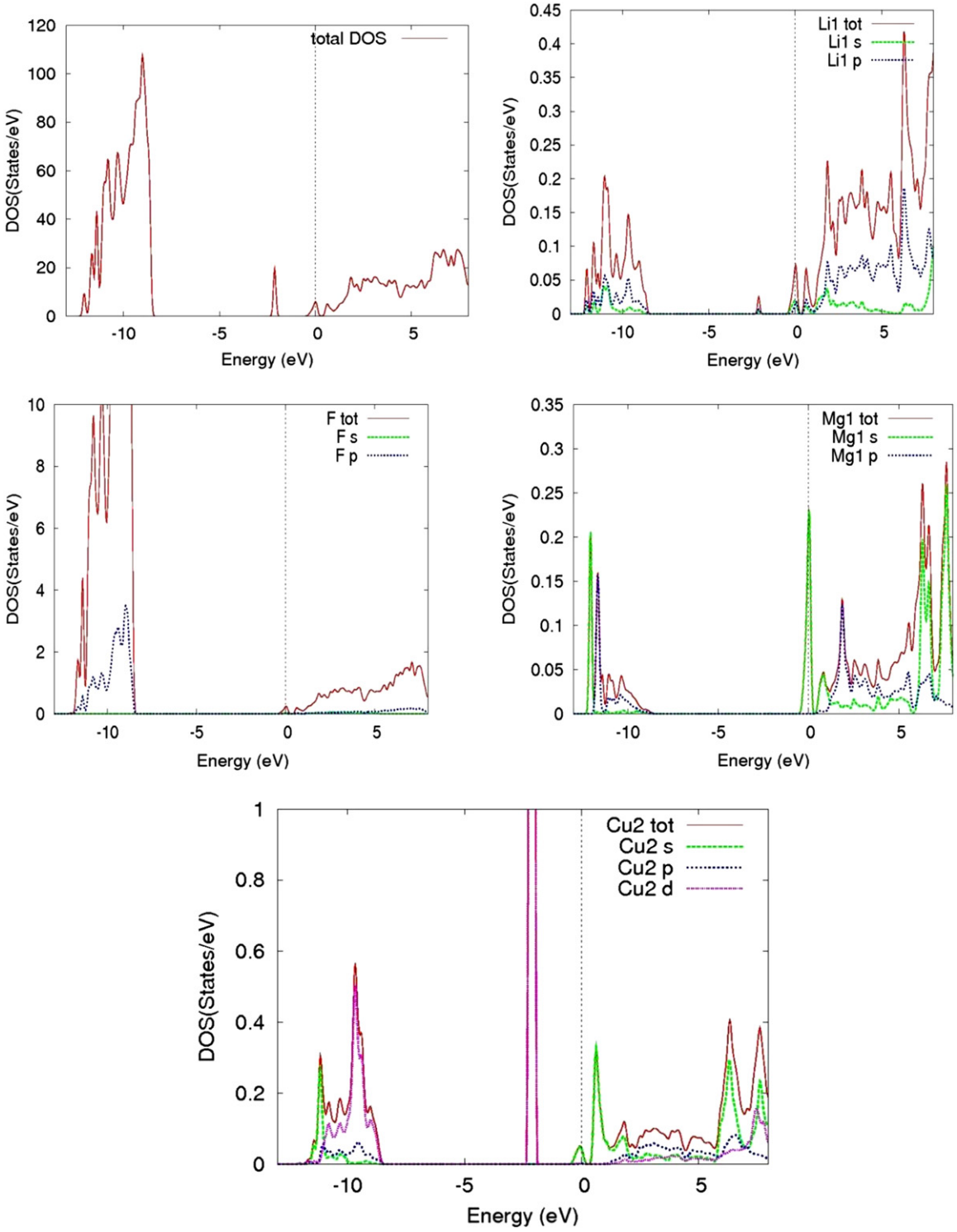

Fig. 6. Total and partial DOS for Mg- and Cu-doped LiF compound for concentration of 1.56%.

eletronic plays main role in creation of levels which have led to create traps. In Cu impurity, s orbital eletronic has role in creation of levels close to conduction band, while d orbital eletronic is a key factor in creation of levels within region of energy gap that lead to create hole-traps. The p orbital eletronic of Cu atom has no role in creation of these traps.

Fig. 5(b) shows electronic band structure diagram for LiF: $Mg_{1.56\%}P_{1.56\%}$. In this case, the activation energy of electronic and hole traps are 0.92 and 3.4 eV, respectively. In analogy with the combination LiF:$Mg_{1.56\%}Cu_{1.56\%}$, the hole trap is smaller while the electronic trap is larger. Total and partial DOS for the LiF:$Mg_{1.56\%}P_{1.56\%}$ compound have been shown in Fig. 7. It was

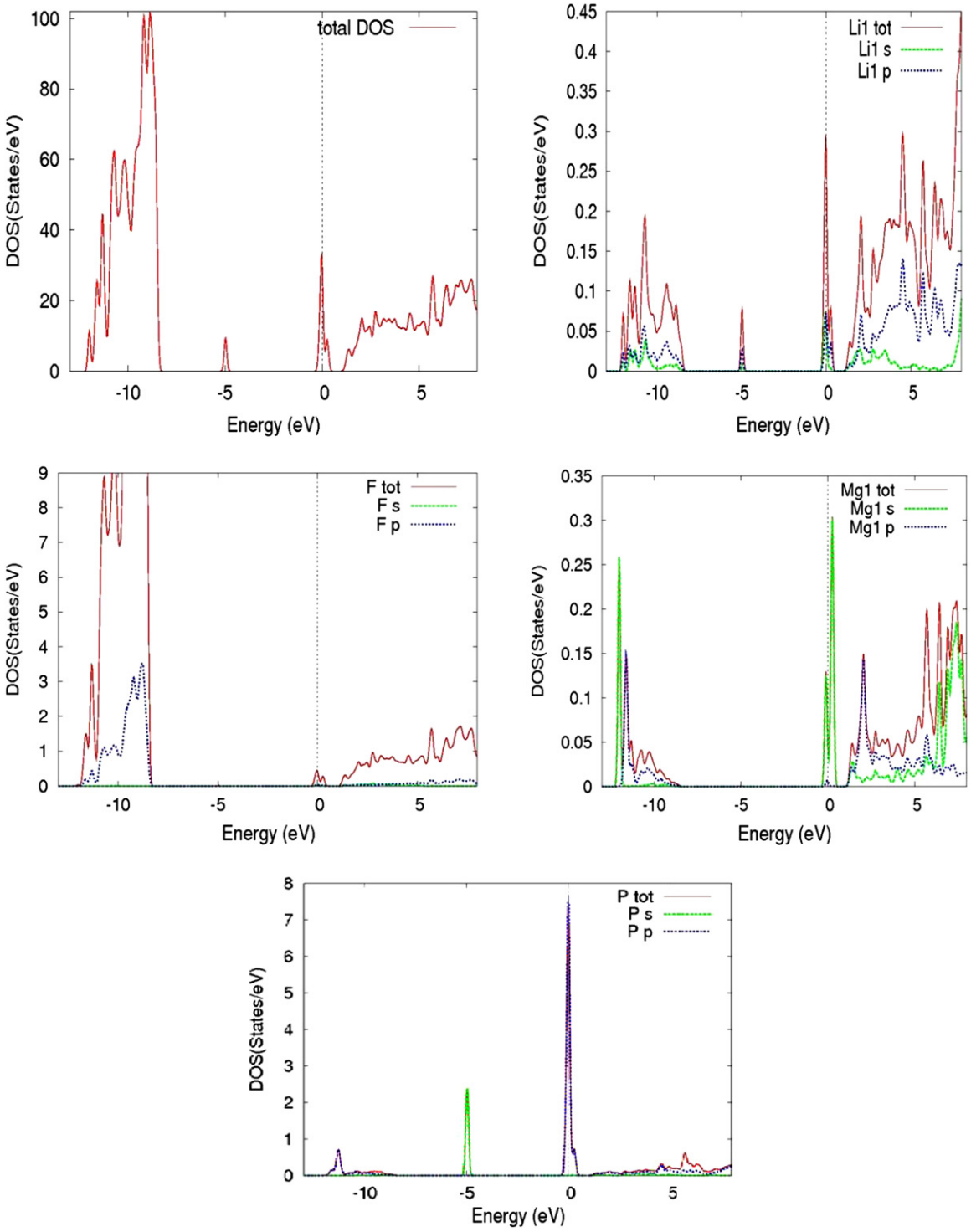

Fig. 7. Total and partial DOS for Mg- and P-doped LiF compound for concentration 1.56%.

found that the s and p orbital eletronics of this atom are very effective in creating levels which cause electronic traps. Also this atom plays role in creating low levels of Fermi level which leads to a hole-trap. F atom is involved in the creation of electronic traps. But according to Fig. 7 for Mg impurity, s orbital eletronic plays main role in creating levels leading to traps. For P impurity, s orbital eletronics are key factors in creating levels in energy gap region which lead to creation of hole-trap, while p orbital eletronic is main factor in creation of levels near the conduction bands which lead to the creation of electronic traps.

The electron charge density of plane (001) has been shown in Fig. 8(a) and (b), for LiF:$Mg_{1.56\%}Cu_{1.56\%}$ and LiF:$Mg_{1.56\%}P_{1.56\%}$ compounds, respectively. According to Fig. 8, LiF crystal has ionic bonding which has been established between an alkali metal (Li) and a halogen (F). Type of bond is not changed with substitution of Mg in LiF crystal; it means that established link between Mg and F

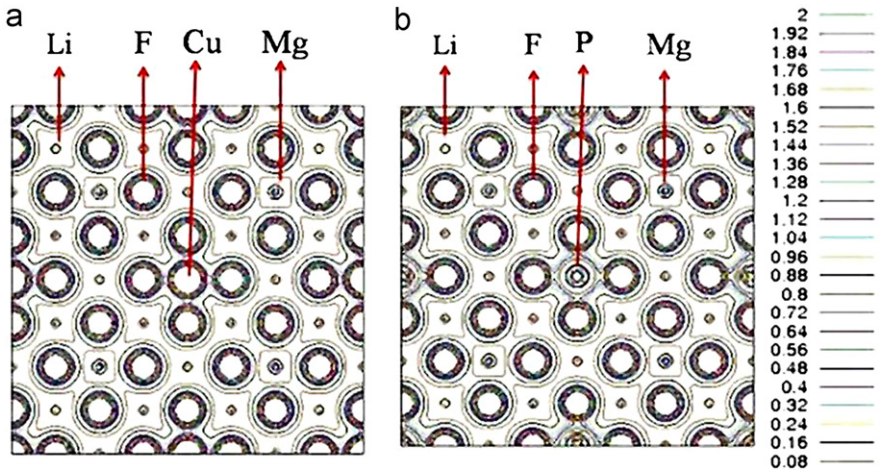

Fig. 8. Electron charge density contour plots for the compounds LiF:$Mg_{1.56\%}Cu_{1.56\%}$ and LiF:$Mg_{1.56\%}P_{1.56\%}$.

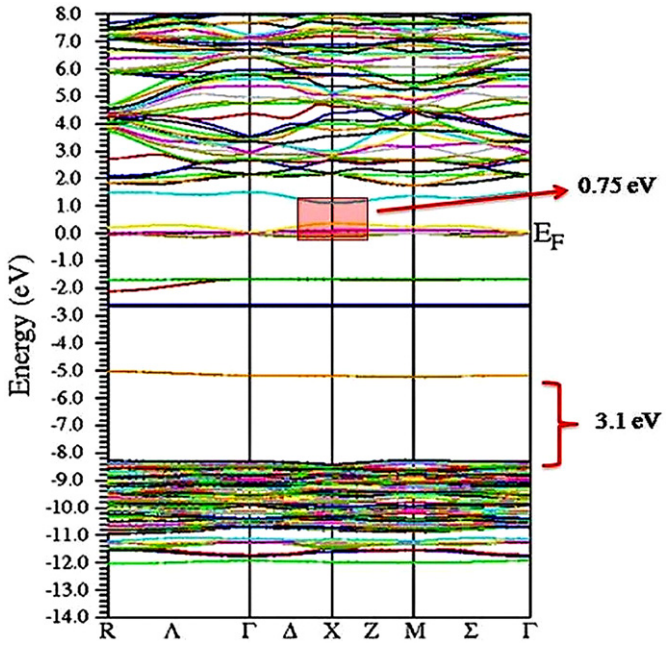

Fig. 9. Electronic band structure for the LiF crystal, that magnesium, copper and phosphorus are replaced in it by ratios of 1.56%.

is ionic type. Obviously, the additional charge in valence band of the Mg leads to electronic density. However, the bonding changes from ionic to covalent for Cu and P impurities as it is clear from Fig. 8.

3.4. Doping of Mg, Cu and P impurity in LiF

The structural properties of LiF crystal are simultaneously investigated by doping three atoms of Mg, Cu and P with a ratio of 1.56%. In this case, the lattice parameter is equal to 4.19 Å and the calculated bulk modulus is 63.2 GPa. This means that the bulk modulus has decreased due to the substitution of Mg and Cu impurities with a ratio of 1.56% which makes the crystal softer. But the bulk modulus has increased due to substitution of Mg and P impurities with a ratio of 1.56% which makes the crystal harder. Fig. 9 shows the electronic band structure of LiF with Mg, Cu and P impurities with a ratio of 1.56%. In this case, the electronic and hole trap activation energies are 0.75 and 3.1 eV respectively.

The total and partial DOS for Li atom are shown in Fig. 10. It was found that s and p orbital elecctronics of Li atom play a role in the creation of activation energy levels which lead to creation of electronic traps. Also, this atom can create activation energy levels lower than Fermi level which leads to creation hole traps. F atoms while playing a role in the creation of electronic traps has no role in creating hole traps. But for Mg impurity by considering partial DOS, it was found that s orbital electronic of this atom has a main role in creating activation levels which lead to electronic traps. Mg impurity like F atom has no role in creating hole traps. For Cu impurity, s orbital electronics cause creation of activation energy levels close to the conductance band while d orbital electronics of this atom are the main factor in the creation of levels within the energy gap that lead to the creation of hole traps. The p orbital electronics of Cu impurity have no role in creation of these traps. For P impurity, the s orbital electronic is the main factor in creation of levels in the region of energy gap that lead to creation of hole traps.

4. Conclusion

We have investigated, that the lattice parameter for pure LiF crystal is equal to 4.05 Å which has a good agreement with the experimental value 4.03. For Mg-doped LiF composition, Mg impurity similar to F atom has no role in creating hole-trap. With observing the density of the partial states which has plotted for Mg impurity, s orbital eletronic plays main role in creating of levels which cause to create traps. The largest electronic trap has been created with 1.56% Mg impurity based on our results. The lattice parameters were obtained as 4.17 and 4.2 Å for the LiF:$Mg_{1.56\%}Cu_{1.56\%}$ and LiF:$Mg_{1.56\%}P_{1.56\%}$ compounds, respectively. In addition, the calculated bulk modulus is 67.356 GPa for LiF:$Mg_{1.56\%}Cu_{1.56\%}$. This value increased to 0.156 GPa in comparison with pure LiF crystal. Presence of copper impurity in this compound, leads to harder crystal. In conclusion, In LiF:Mg,Cu,P each of three dopants appears to play a crucial role in presence of each other. In this study, the dosimetric peak in LiF is a strong function of the activation energy of Mg trap. The activation energy of Mg was optimized in LiF:Mg and main dosimetric peak observed. In presence of the second dopant in the LiF:Mg,Cu system, Cu in combination with Mg is responsible for the luminescence and the

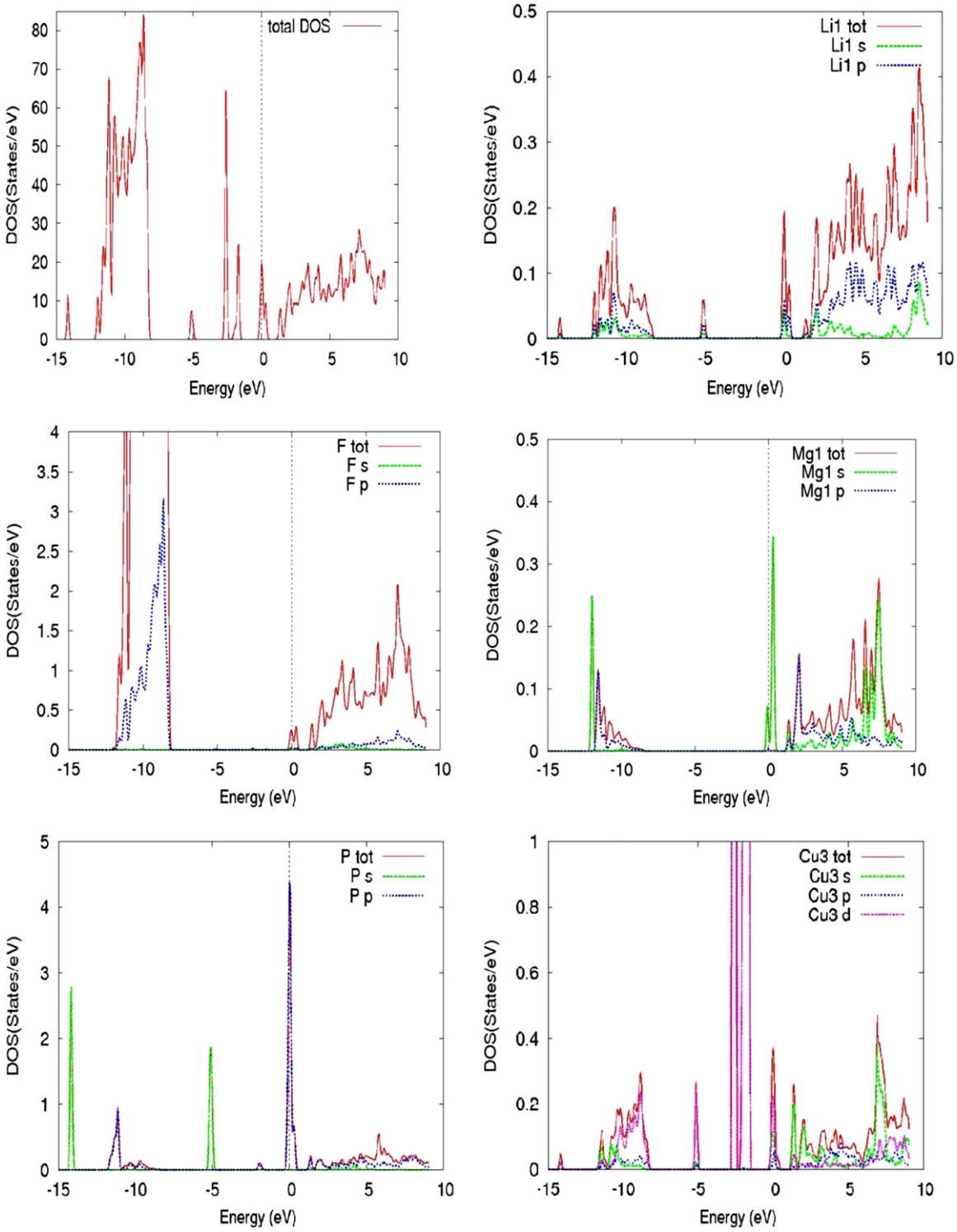

Fig. 10. Total and partial DOS for Mg-, Cu- and P-doped LiF compound for concentration of 1.56%.

presence of the third dopants in LiF:Mg,Cu,P only influences the TL sensitivity.

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