Effects of dopants Ti and Al on the band gap of liF nanoparticles

H. Sadeghi, M.R. Jalali, S. Mohammadi, M. Kavosh Tehrani

***Abstract*— Base on the importance of dosimetry of high energy irradiations, Thermo-Luminescence(TL) measurement devices, and increase in the importance of nanoparticles in this area the present work have been made to deal with the characteristics of band gap of LiF, LiF:Al, and LiF:Ti nanoparticles by Density Function Theory (DFT) method. Here, using DTF theory with the help of Espresso® software, the nanoparticles Li_9F_9, $Li_{18}F_{18}$, $Li_{32}F_{32}$, Li_8F_9Al, $Li_{17}F_{18}Al$, $Li_{31}F_{32}Al$, Li_8F_9Ti, $Li_{17}F_{18}Ti$, and $Li_{31}F_{32}Ti$ have been simulated and their density of states energy have been calculated. With regard to the decrease in band gap in LiF:Al, LiF:Ti, and a sharp decrease in band gap to almost zero, the results show that these nanoparticles can be used in making thermo-luminescence measurement devices.**

***Index Terms*: Thermo-luminescence; nanoparticles; impurity concentration; defect sites; dosimetery; DFT calculations.**

I. INTRODUCTION

A general method for estimating the amount of dose received during irradiation of high energy radiations is to use a thermo-luminescence dosimeter. There are a variety of thermo-luminescence measurement devices,the most famous of which are: LiF:Mg,Ti (TLD-100), $CaSO_4$:Dy, LiF:Mg, Cu,P (TLD-700) and so on [1, 2]. In order to improve the detectors' performance, usually different materials are added to the crystal as impurities [3-6]. In low doses, the main problem in estimating the amount of dose is nose, whereas in high doses, the main problem is the saturation of thermo-luminescence signals.

Recently, the importances of nanoparticles in the area of thermo-luminescence have increased [7]. Considering to the literature a method to solve the above-mentioned problem is to use the nanostructure of these materials. $CaSO_4$:Dy phosphor, has been developed by Yamashita et. al. [8], and in many places, has been used as a dosimeter to measure the amount of high energy radiations like γ. In addition, $CaSO_4$:Dy nanoparticles have been used for TL[9]. On the other hand this nanoparticle is not "tissue equivalent" (energy independent). Another material, which has been used as TLD, is nano-rod with a diameter of 30-40nm and a length of 0.3-0.5 μm of LiF: Mg, Cu, and P [10], which are tissue equivalent. These nano-rod are highly sensitive and are not saturated in doses higher than 10 KGy. Moreover, $K_2Ca_2(SO_4)_3$:Eu nano-crystals have been produced and employed in TLD by conventional solid state diffusion method [11-12]. This material has a good sensitivity for γ-ray irradiation. The sensitivity of $K_2Ca_2(SO_4)_3$:Eu,Tb phosphor is around 0.33 times of that of TLD-700H, but around 15 times more than that of LiF-TLD-100 [13].

Concerning the importance of nanoparticles in TLD, the fact that TLD-100 is one of the important, common TLD devices and importance of electronic structure properties of defects, and dopants in LiF nanoparticles [14], decided to study on the physical characteristics of LiF:Mg, LiF:Al and LiF:Ti nanoparticles. Therefore, using DTF theory,have dealt with the study of band gap of these nanoparticles in various dimensions.

II. COMPUTATIONAL METHODS

Quantum mechanical calculations were conducted using Quantum ESPRESSO open source under Linux OS [15].The DFT with the local density approximation exchange-correlation functional and plane wave basis sets were applied on electronic structures using 3.4 GHz core and 8 gigabytes of RAM which was sufficient in this research. The conjugate-gradient diagonalization method which is typically slower in computer processing, but uses less memory and seldom fails has been used in these calculations. The pseudo potential of pbe-n-van with convergence threshold has been used for self consistency of energy. In these calculations, we used the Gygi-Baldereschi option which is the most appropriate for cubic and quasi-cubic supper cell structures [16,17]. The structures of quantum dots Li_9F_9, $Li_{18}F_{18}$, $Li_{32}F_{32}$, Li_8F_9Al, $Li_{17}F_{18}Al$, $Li_{31}F_{32}Al$, Li_8F_9Ti, $Li_{17}F_{18}Ti$, and $Li_{31}F_{32}Ti$ have been made and optimized. The cut-off kinetic energy to change density and potential were 80 Ry and 300 Ry respectively. Geometry relaxations were performed with the criterion that ionic forces are less than 0.001 eV. The unit cell consists of total atoms and also includes a vacuum space having a length of 12 angstrom. Use of the larger supercell with numerous atoms allows more subtle and longer range variation in conformation. After the optimization of nanoparticle structures, a survey and comparison of various curves of density of states of nanoparticle structures has been made.

III. RESULT AND DISCUSSION

According to the Fig. 1, a band gap sized 5.0eV is noticed in Li_9F_9 structure. By replacing a Li atom with an Al atom, in

Manuscript received May 14, 2014.

H. Sadeghi, Department of physics, Malek-ashtar university of technology , shahin-shahr, Iran,

M.R. Jalali,, Department of physics, University of payamenoor, Isfahan, Iran.

S. Mohammadi, Department of physics, University of payamenoor, Mashhad, Iran .

M. Kavosh Tehrani, Department of physics, Malek-ashtar university of technology, Isfahan, Iran.

the first place, Fermi energy level is increased from -4.54eV to -0.43eV (see Figure 1). The reason can be the existence of two non-bonding electrons in Al atom. These two extra electrons have caused an increase in the Fermi energy and the creation of two energy bands between the band gaps. It is noticed that one of these two extra bands is one in region of -2.1eV and the other is in region of -0.2eV. However the conductance band moves to a lower position, which causes the energy gap to be almost omitted by creating extra electrons resulting from the replacement of Li with Al. A similar process is created for the state in which a Ti atom is replaced with a Li atom in Li_9F_9 nanoparticle which illustrated on Fig. 2. For the Li_8F_9Al and Li_8F_9Ti nanoparticles, this gap is completely omitted.

Based on the Figure 3, in $Li_{18}F_{18}$ structure, the band gap is equal to 4.8eV and the Fermi energy level is close to the valance band. By replacing a Li atom with an Al atom, the structure of conductance bands moves towards lower energies. Fermi energy is also increased from -4.36eV to -0.1eV. The movement of Fermi energy towards higher energies causes Fermi energy to pass through conductance band resulting in the energy gap to reach zero. Figure 4 presented that, a similar process is created when an Al atom is replaced with a Ti atom. However, in this state, the band gap has been totally removed.

The calculations made and the results obtained which presented in the Figure 5, in $Li_{32}F_{32}$ nanostructure, the band gap is 5.8eV and Fermi balance is close to the valance band. By replacing a Li atom with an Al atom in this structure, the valance band moves towards higher energies. Meanwhile, Fermi energy is increased from -5.57eV to 0.28eV. The result of this process is a decrease of 0.04eV in the band gap. A similar process is created when Al is replaced with Ti. However, in this state, the band gap, too, is completely removed.

Base on the results obtained in this study, it can be concluded that pure LiF nanoparticles are not suitable for application in TLD detector because of the existence of some electron volts band gaps; however, in the event of doping, this nanoparticle with Ti and Al can be used as TLD detector because of its very low band gap.

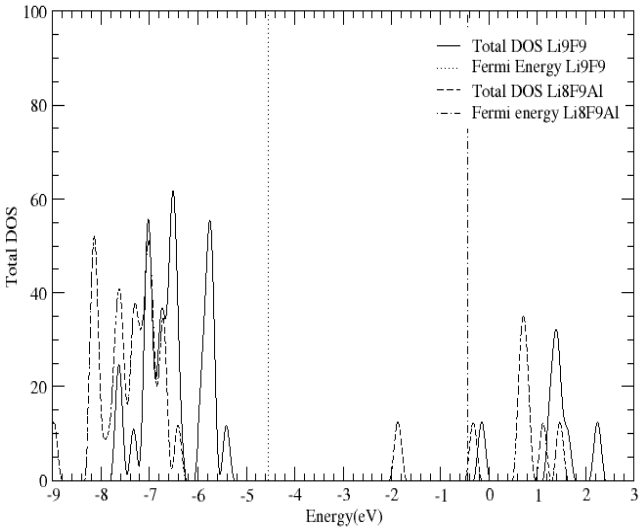

Fig. 1: Density of states and Fermi energy for Li_9F_9 and Li_8F_9Al

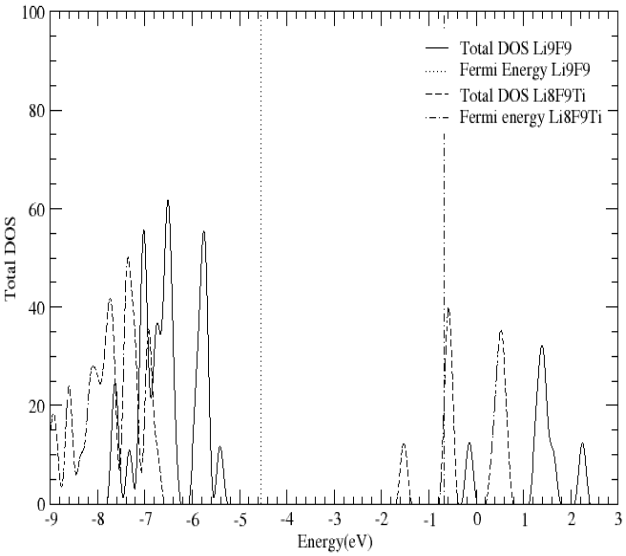

Fig. 2: Density of states and Fermi energy for Li_9F_9 and Li_8F_9Ti

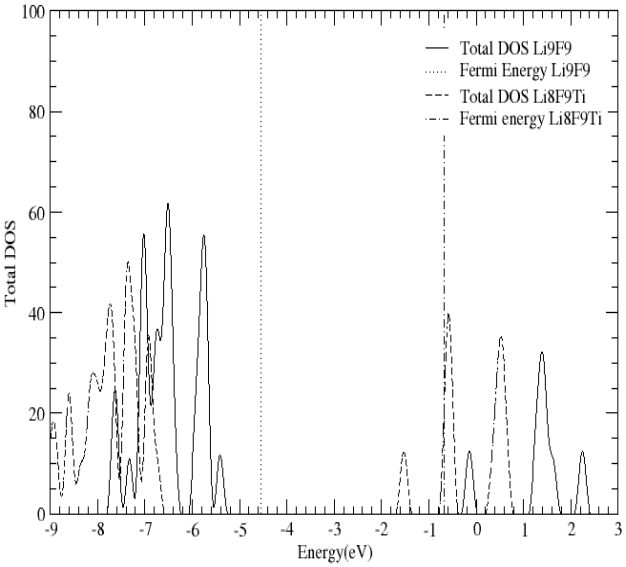

Fig 3: Density of states and Fermi energy for $Li_{18}F_{18}$ and $Li_{17}F_{18}Al$

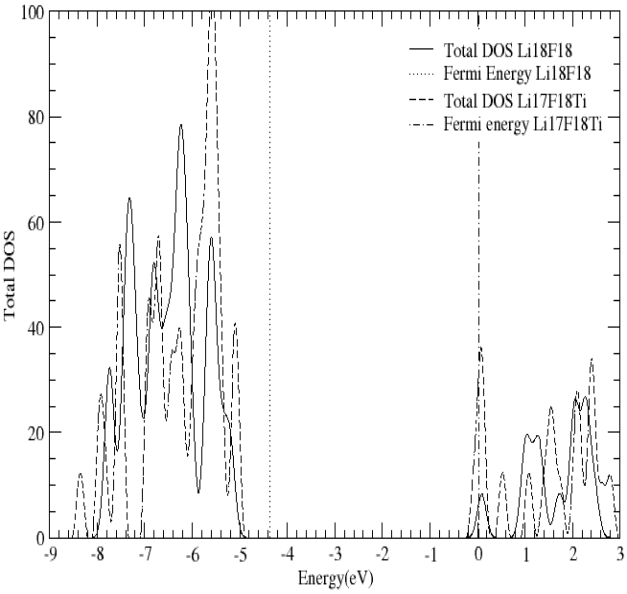

Fig 4: Density of states and Fermi energy for $Li_{18}F_{18}$ and $Li_{17}F_{18}Ti$

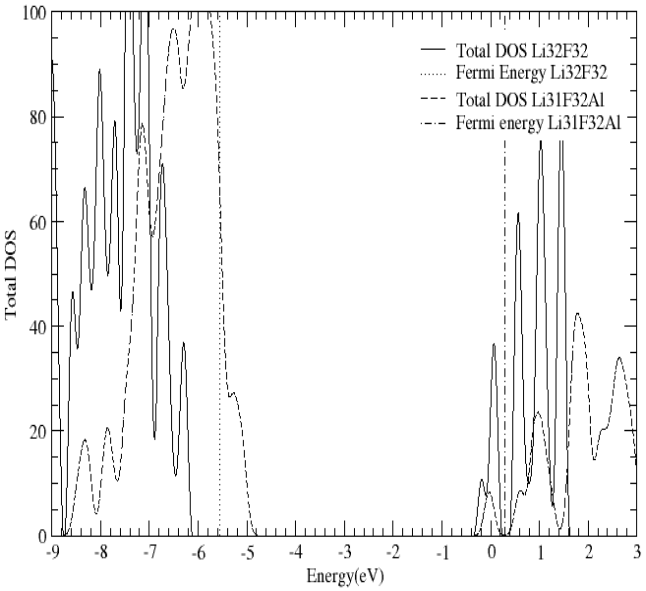

Fig 5: Density of states and Fermi energy for $Li_{32}F_{32}$ and $Li_{31}F_{32}Al$

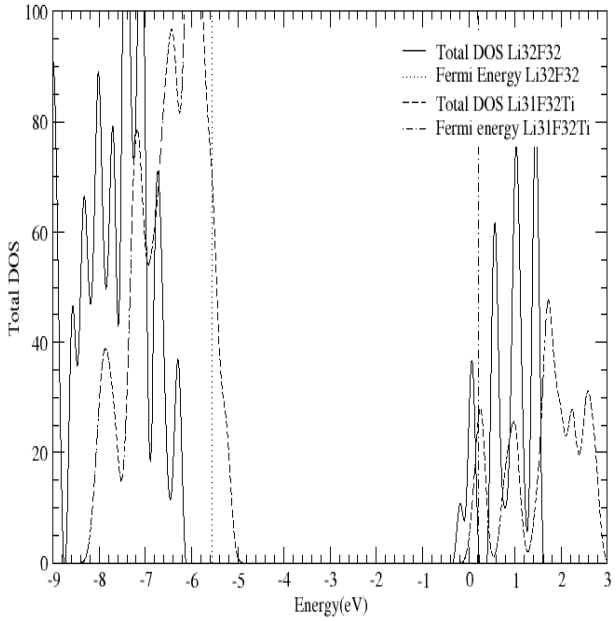

Fig 6: Density of states and Fermi energy for $Li_{32}F_{32}$ and $Li_{31}F_{32}Ti$

REFERENCES

[1] P.J. Fox, R.A. Akber, J.R. Prescott, J. Phys. D 21 (1988) 189.
[2] A.M. Noh, Y.M. Amin, R.H. Mahat, D.A. Bradley, Radiat. Phys. Chem. 61 (2001) 497.
[3] U. Madhusoodanan, M.T. Jose, A. Tomita, W. Hoffmann, A.R. Lakshmanan, J. Lumin. 82 (1999) 221.
[4] A.R. Lakshmanan, M.T. Jose, V. Ponnusamy, K.P.R. Vivek, J. Phys. D 35 (2002) 386.
[5] S.S. Shinde, B.S. Dhabekar, T.K. Gundu Rao, B.C. Bhatt, J. Phys. D 34 (2001) 2683.
[6] J.L. Kima, J.I. Leea, S.Y. Changa, K.S. Chungb, H.S. Choeb, Radiat. Meas. 38 (2004) 435.
[7] F. Nikanjam, R.S. Mamoory, N.R. Noori, "Optimization parameters in synthesis of LiF nanopowders via sol-gel method, NANO: Brief Reports and Reviews 6 (2011) 575-581.
[8] Yamashita, T., Nada, N., Ohishi, H., Kitamura, S., Health Phys. 21 (1971) 295.
[9] N. Salah, P.D. Sahare, S.P. Lochab, P. Kumar, Radiat. Meas. 41(2006) 40.
[10] N. Salah, P.D. Sahare, A.A. Rupasov, Journal of Luminescence 124 (2007) 357–364.
[11] P.D. Sahare, S.V. Moharil, Radiat. Eff. Defects Solids 114 (1990) 167.
[12] Salah, N., Lochab, S.P., Ranjan, R., Kanjilal, D., Habib, S.S., Aleynikov, V.E., Rupasov, A.A., J. Appl. Phys. 102 (2007) 64904.
[13] N. Salah, Radiation Physics and Chemistry 80 (2011) 1–10.
[14] H. Sadeghi, M. R. Jalali, S. Mohammadi, M. Kavosh Tehrani, J. Basic. Appl. Sci. Res., 3(5) (2013) 806-814.
[15] P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009).
[16] F. Gygi, A. Baldereschi, "Self-consistent Hartree-Fock and screened-exchange calculations in solids", Phys. Rev. B 34 (1986) 4405–4408.
[17] H. Sadeghi, M. R. Jalali, S. Mohammadi, M. Kavosh Tehrani, H. Jahanbakhsh., Indian J Physics (April 2014) 88(4); 375-379.