

Ab-initio study on the electronic structures of LiLuF₄ crystal containing F and F₂ color centers

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ABSTRACT

The electronic structures of LiLuF₄ crystals containing F and F₂ color center with the lattice structure optimized are studied based on the density functional theory (DFT). The lattice is optimized by using ABINIT package. The calculations by using DV-X α indicate that both the F and F₂ centers create donor electronic density peak within the forbidden band of the perfect crystal. The electronic transition energies from the donor level to the bottom of the conduction band are 3.95 and 2.39 eV, corresponding to the 315 and 520 nm absorption bands, respectively. It is concluded that the 315 and 520 nm absorption bands are originated from the F center and F₂ centers, respectively in LiLuF₄ crystal.

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1. Introduction

Recently, LiLuF₄ (LLF) has been chosen for solid-state laser and scintillated applications [1,2]. Like LiYF₄ and LiGdF₄ etc., LLF is a scheelite structure ionic crystal. The usefulness of fluoride crystal-line materials as the active media in solid state lasers [3] and scintillator is well established. Most theoretical studies on laser crystals concentrated primarily on the spectroscopy of the environment of a given host material, developed in the framework of the ligand field theory [4–6]. The atomic multiple levels were typically calculated with crystal-field parameters fixed by experimental data, while the physical properties of the host itself were frequently ignored. The electronic structure and color centers in many laser crystals have not been extensively studied.

The study on the color center in the crystal may help us to understand the relevance of degradation processes due to external radiation and the microscopic mechanism. LiLuF₄ single crystal

was grown by Czochralski technology under CF₄ atmosphere in the laboratory [7] and would certainly contain some intrinsic defects. Those defects would cause additional absorption and dramatically affect the scintillation property of the crystal. It is necessary to understand the nature of the point defects contained and their effects on the crystal.

2. Computational model and method

2.1. Computational model

The as-grown LLF crystal in laboratory has the scheelite lattice structure having the space group C_{4h}^6 (I4₁/a) with the unit cell parameters $a = b = 5.15$ Å, $c = 10.47$ Å [8], respectively. The crystal-line cluster of LLF has each Li⁺ been surrounded by four F⁻ forming a distorted tetrahedron and each Lu³⁺ been eightfold coordinated by F⁻ in the form of octahedron made up of elongated and compressed tetrahedron, as shown in Fig. 1.

It is important to choose the appropriate cluster to calculate the crystal electronic structure using the cluster-embedding

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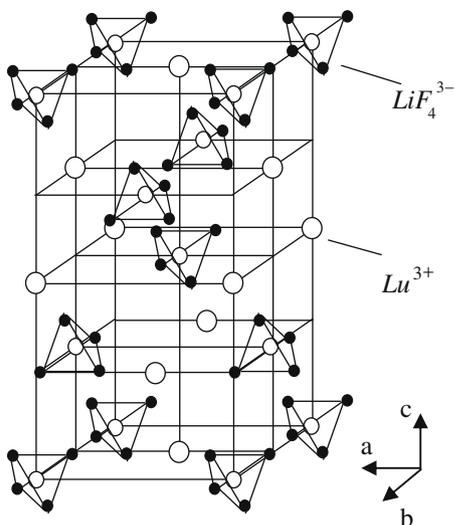


Fig. 1. Structure of LiLuF₄ Crystal.

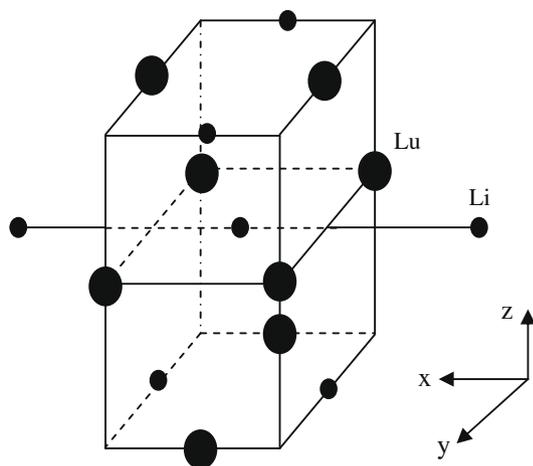


Fig. 2. Structure of Selected cluster.

calculation method. In this paper, the calculation cluster chosen consists of 8 Lu, 7 Li and 28 F centered at Li⁺ having the chemical

formula of [Li₇Lu₈F₂₈]³⁺ as shown in Fig. 2. And the central tetrahedron LiF₄ is put inside the cluster as a whole as shown in Fig. 3.

In this paper, the electronic structures of perfect LLF, LLF containing F center and LLF containing F₂ center are simulated, respectively. Where F center demonstrates a fluorine ion vacancy traps an electron and F₂ center demonstrates the aggregations of two F centers.

The boundary conditions for the clusters are described by the embedding cluster scheme [9]. The potentials of the external crystal ions surrounding the cluster are simulated by Madelung potentials. Pseudo-potentials are used for the cluster ions to avoid false charge transfer from the clusters to the external “host” [10,11].

2.2. Computational method

It is necessary to optimize the lattice structure before calculating the electronic structures of the crystal since the existence of fluorine vacancy V_F⁺ would cause lattice distortion. The ABINIT package [12] based on pseudo-potentials and plane waves was employed for geometry relaxation. The local density approximation (LDA) was employed for the exchange–correlation. The minimizations of conjugate-gradient energy was used, the force acting on ions were less than 1.0 × 10⁻⁴ eV/Å and the energy difference between two consecutive cycles was less than 1.0 × 10⁻¹⁰ Hartree. The maximal permitted scaling of the lattice parameters is 1.05 when the cell shape and dimension is varied. The optimized results are listed in Table 1. It can be seen from Table 1 that the distortion of the structure of the LiLuF₄ is obvious and will significantly affect the electronic structures of LiLuF₄ crystal.

In LLF fluorine ion occupying different lattice site would have different environment and exhibits different physical properties. It is necessary to determine the detail position of the fluorine vacancy to calculate the electronic structures of LLF containing either F or F₂ center. The most probable site the fluorine vacancy may occupy should have the total energy of the crystal being the lowest after the crystal structure optimized.

In LLF there are four fluorine ion sites just distributed on the four corners of the LiF₄ tetrahedron labeled as 1, 2, 3 and 4, as shown in Fig. 3.

The total energies of the cluster when the fluorine ion vacancy occupying site 1, 2, 3 and 4 are calculated, respectively, and are listed in Table 2. It can be seen from Table 2 that F center may most probably be created on site 4. Tables 1 and 3 represents the total energy of the crystal containing F₂ center having the two fluorine ion vacancies on different sites. It can be seen from Table 3 that

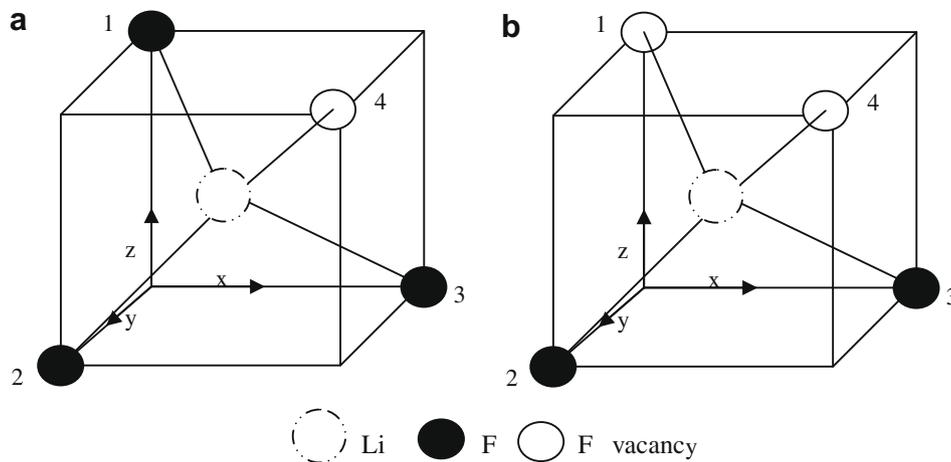


Fig. 3. (a) A fluorine vacancy in LiF₄ tetrahedron. (b) Two fluorine vacancies in LiF₄.

Table 1

The distances between ions before and after optimization.

System	Lattice constants (nm)	[LiF ₃]-V _F Li-F(V _F -Li) (nm)	[LiF ₃]-V _F V _F -F (nm)	V _F -Lu(nm)
<i>F center</i>				
Pre-optimized	$a = b = 0.515$ $c = 1.047$	0.2183	0.3172 0.3094	0.2423
Optimized	$a = 0.5674$ $b = 0.5780$ $c = 1.1110$	0.21434 0.21378 0.21382 0.22074(V _F)	0.30742 0.30464 0.30367	0.27367
<i>M center</i>				
Pre-optimized	$a = b = 0.515$ $c = 1.047$	0.2183	0.3172 0.3094	0.2423 0.2436
Optimized	$a = 0.5704$ $b = 0.5724$ $c = 1.1408$	0.21056 0.19864 0.22142(V _F) 0.22264(V _F)	0.30161 0.30254 0.37847(V _F -V _F)	0.27643 0.27873

Table 2

The total energy of cluster containing one fluorine vacancy.

Vacancy	Energy (Ha)	Vacancy	Energy (Ha)
1	-727.73598	3	-727.135236
2	-727.43472	4	-728.169099

Table 3

The total energy of cluster containing two fluorine vacancies (1–4 is the labels to the vacancies).

Vacancy	Energy (Ha)	Vacancy	Energy (Ha)
1,2	-722.70063	2, 3	-722.53464
1, 3	-722.71178	2, 4	-722.69774
1, 4	-722.71286	3, 4	-722.68517

the two fluorine ion vacancies in F₂ center may most probably be created in site 1 and 4, respectively.

The molecular-cluster model with the framework of the fully relativistic self-consistent Dirac–Slater theory, using a numerically discrete variational (DV-X α) method, is adopted to study the electronic structure in LLF. The program is written by Ellis [13]. The criterion of numerical convergence is that the maximal energy error per atom is smaller than 0.00001 eV. The number of points calculated is 24,000 in our calculation. This method is effective and easier to calculate the electronic structure in solids. It can save large computation time and keep high precision simultaneously.

The original basis sets are composed of free ionic and atomic orbitals. These basis sets are optimized in an iterative process according to the occupation of molecular orbitals, until the difference between two terms in the Hamiltonian goes to the minimum. The initial basis sets and the funnel potential well parameters are chosen for the calculation listed in Table 4. V₀ denotes the depth of atom potential well; R₁ and R₂ show the bottom radius of atoms and the cutoff radius. These parameters give the funnel potential information for the atomic orbitals.

Table 4

Initial basis sets and the funnel potential well parameters (FPWPs).

Ions	Frozen core	Orbits for basis functions	Funnel potential well parameters (arb. units)		
			V ₀ /eV	R ₁ /nm	R ₂ /nm
Li ⁰		1s, 2s, 2p	-2.5	0.20	0.70
Lu ³⁺	1s–5s	4p, 4d, 5s	-4.0	0.20	0.30
F ⁻	1s	2s, 2p, 3s	-4.0	0.25	0.40
H		1s, 2s, 2p	-2.5	0.20	0.40
H ₂		1s, 2s, 2p	-3.0	0.25	0.75

Considering the relaxation effect produced by the electronic transition in the crystal, we use the transition state method [14] to calculate the excitation energy. Ionization energy E_{ion} is the negative value of the orbit energy that is achieved by taking out half an electron from the primary its orbit,

$$E_{\text{ion}} = E(n_i - 1, n_j + 1) - E(n_i, n_j) \cong - \left. \frac{\partial E}{\partial n_i} \right|_{n_i = \frac{1}{2}} = -\varepsilon_{iT} \quad (1)$$

Similarly, excitation energy is also achieved by taking out half an electron from i orbit while putting half an electron into j orbit, thus the excitation energy can be expressed as the energy difference between i orbit and j orbit,

$$E_{i \rightarrow j} = E(n_i - 1, n_j + 1) - E(n_i, n_j) = \varepsilon_{jT} - \varepsilon_{iT} \quad (2)$$

(the “T” means “transition state” for short.; ε_i means the level of energy for No. i orbit, and the n_i means electron’s number of No. i orbit.)

The electronic wave functions in the calculation are chosen as a set of atomic orbital Li 1s, Li 2s, Li 2p, Lu 5p, Lu 5d, Lu 6s, F 2s, F 2p and F 3s for the normal lattice ions, respectively. Since the F center is a fluorine vacancy trapping one electron, so the F center is simulated by a hydrogen atom. While the F₂ center is the aggregation of two F centers therefore can be simulated by two hydrogen atoms [15]. And the electronic states of F and F₂ are chosen as the 1s, 2s and 2p orbital wave function of one and two hydrogen atoms, respectively. The simulation parameters are listed in Table 4.

3. Results and discussion

The calculated total densities of states (TDOS) and partial densities of states (PDOS) for the perfect LLF with the cluster (Li₇-Lu₈F₂₈)³⁺ is shown in Fig. 4.

It can be easily seen by comparing TDOS with PDOS that the top of the valence band is mainly attributed to F 2p states accompanied with some Li 2s states, while the bottom of the conduction band is

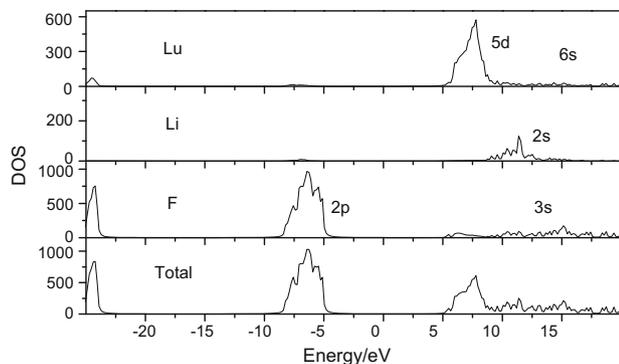


Fig. 4. Total and partial density of states for the perfect LiLuF_4 crystal.

mainly composed of Li 2s and Lu 5d states. The energy gap is 10.53 eV.

From the Figs. 4 and 5, we can see that the forbidden band of defect crystals are narrower than that of the perfect crystals. Since the fluorine vacancies in the F and F_2 centers lack the core of ion, the electronic negative need to be compensated by the surrounding negative ions. This makes the energy level of the Lu 5d and F 2p descend in the Fig. 4 and much lower in the Fig. 5.

The calculated TDOS and PDOS of LLF crystal with the cluster $(\text{Li}_7\text{Lu}_8\text{F}_{27}\text{H})^{3+}$ containing F color center on the foundation of the calculation of perfect LLF are shown in Fig. 5. It can be clearly seen from Fig. 4 that the construction of the valence band and the conduction band are similar to that of the perfect crystal. The main difference between perfect crystal and defect crystal is a new electronic state peak appearing within the forbidden band. The calculation indicated that the new electronic state peak appeared within the forbidden band is the H 1s state, or say the ground state of the F center. So this small peak appeared in the forbidden band is the characteristic state peak of the F center of the defect crystal containing F center. The energy difference between this 1s state of F center to the bottom of the conduction band is 3.95 eV corresponding to the 315 nm absorption band.

The TDOS and PDOS of LLF containing F_2 color center are also calculated by using the cluster $(\text{Li}_7\text{Lu}_8\text{F}_{26}\text{H}_2)^{3+}$, as shown in Fig. 6. As compared with Fig. 5, the 1s state of F_2 appears in the forbidden band of the perfect crystal. The only difference is that the F_2 center contained crystal has two small electronic states peaks having higher energy appeared within the forbidden band. The separation of the two peaks is very small to about 0.2 eV. The two peaks appear to result from two electrons trapped at two different vacancy sites. The energy difference between this 1s state of F_2 center to the bottom of the conduction band is 2.39 eV corresponding to the 520 nm absorption band.

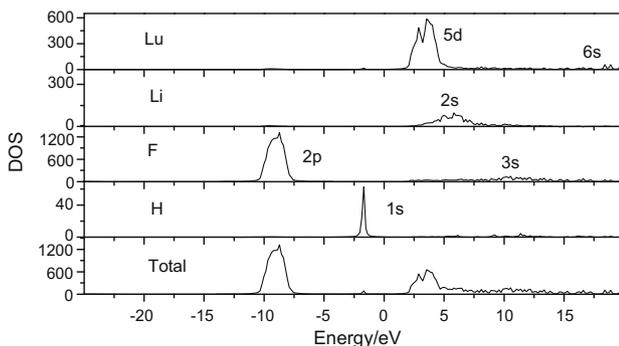


Fig. 5. Total and partial density of states of LiLuF_4 containing F color center.

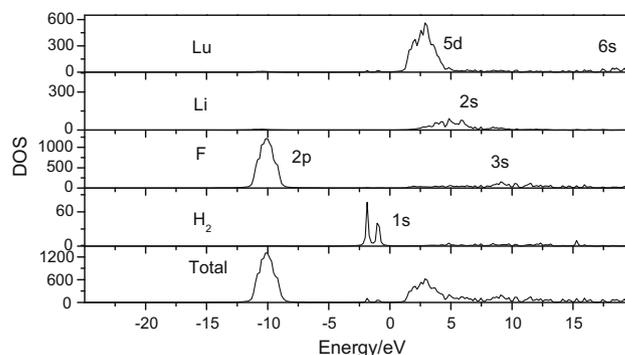


Fig. 6. Total and partial density of states of LiLuF_4 containing F_2 color center.

In the paper, the electron structures of LiLuF_4 crystals containing F and F_2 color centers are calculated by DV- X^α method. It can be seen from the calculated results (Figs. 5 and 6) that the transition for F (1s) \rightarrow Lu 5d and F_2 (1s) \rightarrow Lu 5d are possible. The transition energy calculated by using transition states are 3.95 and 2.39 eV, which correspond to the 315 and 520 nm bands.

4. Conclusions

The electronic structures of the perfect LLF crystal and the defect crystal containing F and F_2 center have been studied by using the relativistic self-consistent discrete variational embedded cluster method. Slawomir et al. described γ -ray induced radiation damage in the undoped LLF single crystals using optical absorption measurements in the UV/VIS/NIR spectral regions [8]. The irradiated crystal exhibits five absorption spectrum peaks at 240, 315, 380, 520 and 600 nm. Our calculation predicates that the 315 and 520 nm absorption bands originate from the F and F_2 color centers in LiLuF_4 crystals, which coincides with the experimental result. The two bands around 240 and 380 nm correspond probably to perturbed Vk centers [16]. The induced absorption band at 600 nm may be of N_2 type center as 550 nm band in LiF or generally coming from higher order F centre aggregates.

It is concluded that F and F_2 centers have donor energy levels in the forbidden bands of the perfect crystal. The electronic transition energies from the donor level to the bottom of the conduction band are 3.95 and 2.39 eV, corresponding to the 315 and 520 nm absorption bands respectively. This coincides with the experimental result well. The 315 and 520 nm absorption bands are originated from F and F_2 centers in LLF crystal [8]. In LiLuF_4 , and in other laser crystals, one would eventually like to understand the roles of defects and the effect of ion-ion interaction based on a more realistic first-principles approach. Therefore, we expect fundamental studies in the fluoride laser crystals will be an active area of research in years to come.

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