# Investigation of the electronic and optical properties of fluoride crystals for laser applications

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## INTRODUCTION

Fluoride crystals have long been recognized as excellent short-wavelength solid-state laser host materials in the vacuum ultraviolet (VUV) and ultraviolet (UV) regions especially when doped with trivalent rare-earth ions such as cerium ($Ce^{3+}$) and neodymium ($Nd^{3+}$) [1-4]. When used as laser materials, knowing the optical and electronic properties of the laser active crystal is important to determine energy transfer mechanisms that either inhibit or enhance laser emission. However, theoretical and experimental investigations of these properties are limited. For example, previous calculations have underestimated the band gap energy of fluoride crystals while experiments have not implemented different conditions such as varying pressure or temperature [5]. Moreover, the optical properties of fluoride crystals such as absorption coefficient, refractive index, or transmission under high pressure are not investigated both theoretically and experimentally. In order to achieve efficient laser systems and photonic applications, theoretical studies with better approximation are important to understand the material's salient features and to aid the crystal's growth and development. This project studied the electronic and optical properties of lithium yttrium fluoride ($LiYF_4$). Through numerical calculations, we determined this crystal's prospects as a VUV laser host material.

## METHODOLOGY

The numerical calculations used are based on density functional theory (DFT) using Perdew-Burke-Ernzerhof (PBE) hybrid functionals. The calculations employ plane-wave basis sets and projector-augmented wave (PAW) pseudopotentials as implemented within the Vienna Ab initio Simulation Package (VASP). The exchange-correlation interactions are described by the generalized gradient approximation (GGA) with (PBE0) hybrid functional [6-8]. The plane-wave basis cutoff is 500 eV.

The crystal unit cell volume is initially optimized using the Murnaghan equation of state to fit the curve of the total energy as a function of volume [9]. The lattice constants are then obtained from the optimized volumes to compute for the electronic band structures and optical properties of the fluoride crystal. For the band structure and density of states (DOS) diagrams, the k-points are chosen following the first Brillouin zone [10]. All valence band maxima of the resulting diagrams are also shifted to zero. For the optical properties, the complex dielectric function was first obtained. The refractive index, absorption coefficient, and optical transmittance were derived from the complex dielectric function. In the calculations, the excitonic effect is ignored, while the local field effect is considered.

## RESULTS AND DISCUSSIONS

Figure 1 shows the electronic structure of $LiYF_4$. Both the valence band maximum and the conduction band minimum are situated at the $\Gamma$ point. It has a direct band gap energy of 11.09 eV.
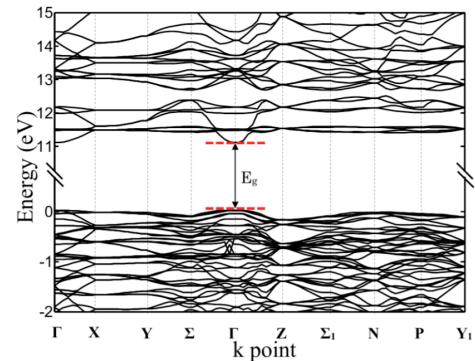


Fig. 1. Simulated electronic band structure of the $LiYF_4$ crystal at equilibrium. $LiYF_4$ has a direct band gap of 11.09 eV at the $\Gamma$ point.

The total and partial densities of states (DOS) of the $LiYF_4$ crystal are shown in Fig. 2. Three bands can be observed from the total DOS in the range of – 25 to 16 eV. The bands from – 22.62 to – 17.64 eV are due to the F 2s and Y 4p orbitals. On the other hand, the valence band from – 3.46 to 0 eV is mainly derived from the F 2p orbital, while the conduction band from 10.70 to 16 eV is mainly derived from the Y 4d orbital. The Li 2s orbital has minor contributions to both valence and conduction bands. The direct band gap of $LiYF_4$ originates from the transition from F 2p of the valence band maximum to Y 4d of the conduction band minimum.
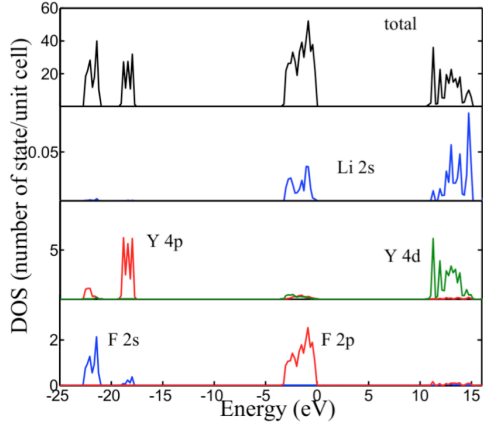
Fig. 2 Total and partial DOS of the LiYF$_4$ crystal at equilibrium. With a minor contribution from Li 2s, the valence and conduction bands of LiYF$_4$ are mainly derived from F 2p and Y 4d, respectively.
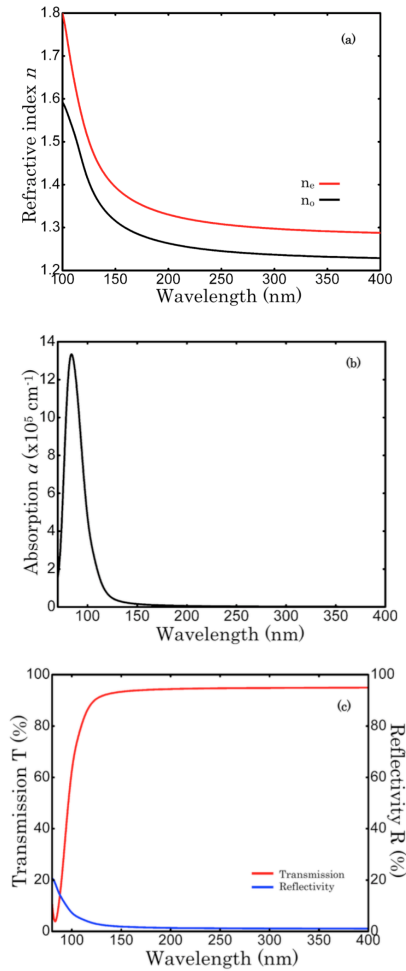


Fig. 3 (a) Refractive index, (b) absorption coefficient, and (c) transmission and reflectivity of the LiYF$_4$ crystal. LiYF$_4$ has a maximum refractive index of 1.60, an absorption edge at 121 nm, and high transparency up to the visible region.

The refractive index, absorption coefficient, reflectivity, and transmittance of the LiYF$_4$ crystal are shown in Fig. 3. Its refractive index has similar ordinary

($n_o$) and extra-ordinary ($n_e$) components. The calculated refractive indices confirm that YLiF$_4$ is a positive birefringent crystal where the extra-ordinary refractive index $n_e$ is greater than the ordinary refractive index $n_o$. The maximum refractive indices are 1.6 and 1.8 for ordinary and extra-ordinary components, respectively. These occur at 100 nm. The ordinary and extra-ordinary refractive indices become constant at 1.22 and 1.30, respectively, for wavelengths longer than 400 nm. Our calculations differ by around 13 % compared with the experimental refractive index for wavelengths ranging from 225 to 2600 nm (0.48 to 5.51 eV) [11]. The difference could be due to the temperature of the sample during the experiment as the refractive index decreases significantly with temperature [12]. Our calculations are done at 0 K, while the experiments were done at liquid nitrogen temperature (77 K) [11]. LiYF$_4$ has an absorption band in the VUV region from 100 to 200 nm. We will perform future experiments to confirm these absorption bands. LiYF$_4$ is highly transparent down to the VUV region with an absorption edge around 121 nm.

**CONCLUSIONS**

The electronic band structure and optical properties of a perfect LiYF$_4$ crystal were calculated based on DFT using PBE0 hybrid functional. This crystal was found to have a 289.31-Å$^3$ crystal volume and 75.04-GPa bulk modulus, which are all close to the reported experimental values. LiYF$_4$ was also determined to have an 11.09-eV direct band gap originating from the F 2p to Y 4d transition. Experimental investigations based on the present results are expected in the near future.

**ACKNOWLEGEMENT**

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