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Optical Properties of the Tysonite Phase of LaF3 Compound in the Ground State by First Principles Calculations

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Abstract— ***LaF_3 compound have wide applications such as optical fibers and solid state lasers. So study of its optical properties is important. In this paper some important optical properties, Such as dielectric function, refractiive index, energy loss function and optical conductivity, in theoricaly have been studied. The calculations were performed in the frame work of density functional theory (DFT), using the full potentional linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA). Also, we used Kramers-Kronig transformations for obtaining optical constants.***

Index Terms- **LaF_3 crystal, Density Functional Theory, Optical properties, Optical fiber.**

I. INTRODUCTION

Lanthanides fluoride form a class of materials which have broad range of applications in optical fibers, multi-layer interference, electrodes, florescence lamp and radiation [1,2,3]. Among theses, LaF_3 is one of the most significant host materials which is extensively used for phosphoric purposes. LaF_3 has low energy and consequently quenching of excited states of La ions will be minimum [1,4]. Another applicable characteristic of LaF_3 is its ionic conductivity and super-ionic transitions. Due to this characteristic, LaF_3 can be used as a solid electrolyte which has potential application in battery industry. Besides, it can be applied as special ionic electrodes in detectors. It has a good moderate ionic conductivity even in room temperature [1,5,6]. Super-ionic transitions in LaF_3 exist well in LaF_3 compounds, and they have been studied by Brillouin and Raman spectroscopy [1,7]. Among the materials, injected compounds of Ce and Nb are of importance in for adjusted lasers in UV and UV vacuum domain [1,8,9]. Moreover, use of LaF_3 as an active region for solid state lasers has been investigated [10,11]. LaF_3 is a main candidate as a material with high available refractive index for multi-layer interference [12]. LaF_3 has a trigonal structure called Tysonite. Fluorine ions are located in three separate sub-lattices which are F1, F2 and F3 [13]. Motionless Lanthanum cations are situated on layers perpendicular to the axis c. F1 anions, which form layers between La planes, are very mobile [14,15]. So far, there has not been a theoretical research on optical properties of LaF_3. Most of theoretical researches concern its electronic and structural properties.

II. METHOD OF CALCULATION

We used WIEN2k code which is one of strong and most application codes for simulation of crystals [16,17]. In this study, calculations have been performed using the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method in the framework of Density Functional Theory (DFT). Generalized Gradient Approximation (GGA) has been used for exchange-correlation term. LaF_3 is crystallized in tetragonal, orthorhombic and cubic phases. However, it is in trigonal phase in environmental conditions. Space group of the compound in trigonal phase is $P\bar{3}C1$ and the numbers of its symmetries are 12 and there are 4 atoms inside unit cell. Figure 1 show the crystal structure of LaF_3. Muffin-Tin's radius of atoms was chosen as there is no overlapping between Muffin-Tin's spheres. Atomic positions and Muffin-Tin's radius are summarized in table 1. Separation energy between valance electrons and core electrons has been considered as -6Ryd. For this compound, $R_{MT} \times k_{max}$ and number of k-points in the first Brillouin zone has been chosen to be equal to 6 and 2000, respectively that R_{MT} and k_{Max} are the smallest radius of atoms and the maximum value of the reciprocal lattice vector respectively. The converge criterion of calculations have been

considered when the integrate charge difference between input and output charge is less than 0.0001.

Table 1. Atomic position and RMT of LaF_3 atoms [1]

Atom	Atomic position			RMT(a.u)
	x	y	z	
La	0.6597	0.000	0.2500	2.05
F1	0.3333	0.6667	0.1856	1.86
F2	0.3656	0.0535	0.0813	1.86
F3	0.0000	0.0000	0.2500	1.86

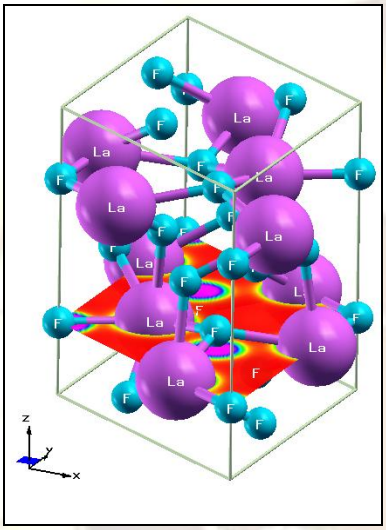


Fig 1. Crystal structure of LaF_3

III. RESULTS

We know that dielectric function indicate response of material to electro-magnetic waves. The dielectric function can be written as [18]:

$$\varepsilon(\omega)= \varepsilon_1(\omega)+i\varepsilon_2(\omega)$$

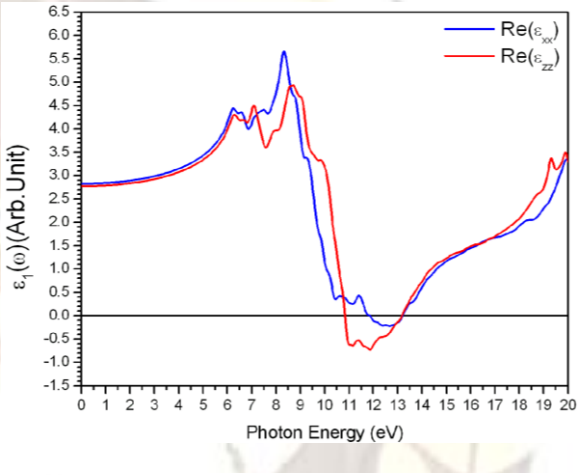
That, $\varepsilon_1(\omega)$, is real part and $\varepsilon_2(\omega)$, imaginary part of dielectric function.

Figure 2 and 3, show changes of real and imaginary part of dielectric function, in the x- and z-directions, in terms of incident photon energy that real part of dielectric function has been extracted from imaginary part of dielectric function by the Keramers-Kronig's transformations. As know, the imaginary and real part of dielectric function can be written as [19]:

$$Im\,\varepsilon_{ij}(\omega)=\frac{4\pi e^2}{m^2\omega^2}\sum_{c,v}\int dk < C_k|p_i|V_k >< V_k|p_j|C_k > \times\delta(\varepsilon_{ck}-\varepsilon_{vk}-\omega)$$

$$Re\,\varepsilon_{ij}(\omega)=\sigma_{ij}+\frac{2}{\pi}p\int_0^{\infty}\frac{\omega'\,Im\,\varepsilon_{ij}(\omega')}{\omega'^2-\omega^2}d\omega'$$

Where $|C_k>$ and $|V_k>$ are conduction and valence states of the electron in a given wave vector k. According Figure 2, there is no major difference between real part of dielectric function at x- and z-direction to 6 eV and main difference is happened at the range 6 eV to 13 eV, after this range, again, there is no important different. So, we can say this compound in low energy is nearly isotropic. When $\varepsilon_1(\omega) < 0$, electro-magnetic wave don't propagate[18], so, roots of $\varepsilon_1(\omega)$ indicate forbidden region for propagation. Roots of $\varepsilon_1(\omega)$ in x-direction are lied at energies 16.60 eV and 13.19 eV and in z-direction, at energies 10.82 eV and 13.17 eV. In other word, forbidden region in z-direction is more than x-direction. Also, according Figure 2, depth of $\varepsilon_1(\omega)$ inside negative value in z-direction is more than x-direction, so, we expect energy loss in z-direction be more than x-direction but width of peak of energy loss be less than x-direction.



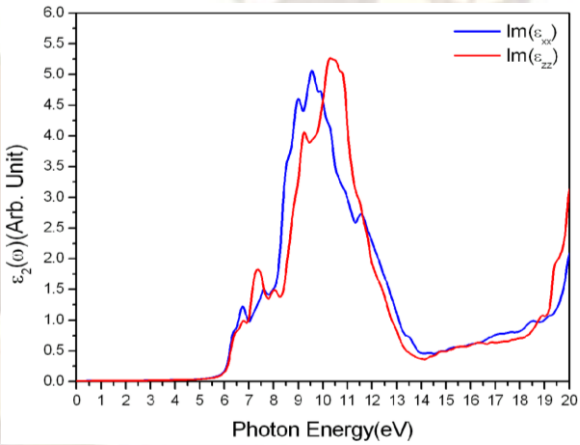


Fig 2. Real part of dielectric function of LaF_3 .
Fig 3. Imaginary part of dielectric function of LaF_3.

The roots of $\varepsilon_1(\omega)$ indicate plasma oscillations but it is not enough condition and we have to consider the energy loss function. Figure 4 show the energy loss function of LaF_3 compound in terms of photon energy. The clear peaks of energy loss function are happened at energies 13.28 eV and 13.29 eV in x- and z-direction, respectively. These peaks is good agreement with roots of $\varepsilon_1(\omega)$. Also, peak of energy

loss in z-direction is more than x-direction that it is adapted by our expectation.

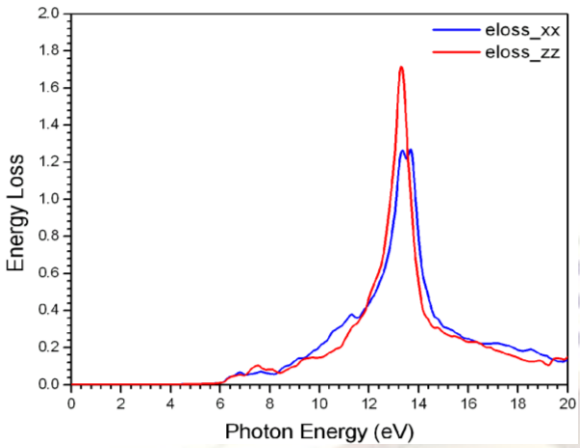


Fig 4. Energy Loss function of LaF_3.

In the optical applications such as optical fiber, we attempt to using materials which they have less refraction changes inside an energy range. Figure 5 show the refractive index of LaF_3 in terms of photon energy. According Figure 5, we can say LaF_3 have isotropic refractive index at the low energy and its birefractive value to 6 eV is small. The value of static refractive index and static dielectric function of LaF_3 and refractive index at the 0.6328 μm summarized in table 2. The result of refractive index at the 0.6328 μm is in good agreement with experimental results [20,21].

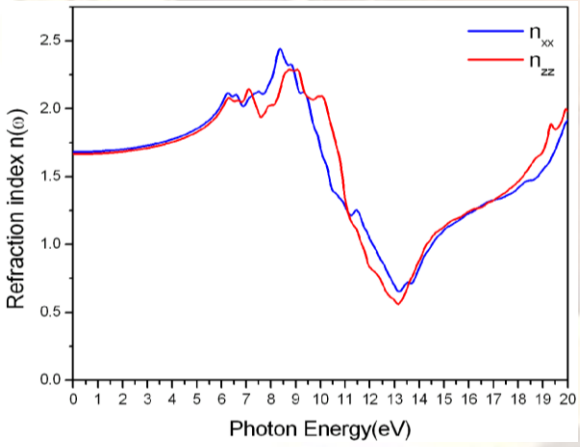


Fig. 5. Refractive index of LaF_3

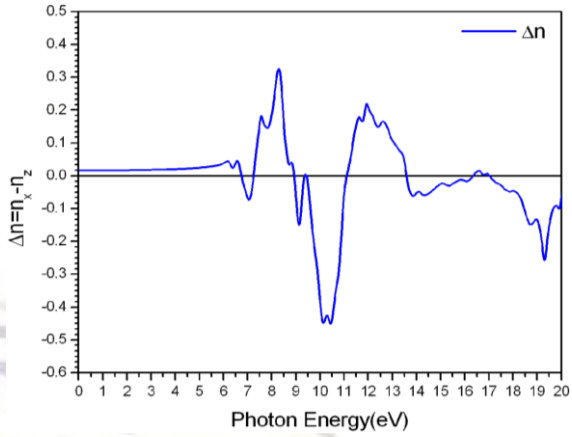


Fig 6. Difference between n_x and n_z.

Table2. Static refractive index and static dielectric function

Method	Static refraction		Refractive index at 0.6328 μm		Static dielectric function	
	n_{0x}	n_{0z}	n_x	n_z	ε_{0x}	ε_{0z}
GGA	1.68	1.67	1.699	1.681	2.83	2.77
Exp[20,21]	1.59**	1.58**	1.606	1.602	-	-

**Experimental values of static refractive index have been obtained by limit of Sellmiere's relation at high wave lengths.

In the visible region, the dispersion relation of refractive index in terms of wave length, λ, can be calculated by Sellmiere's relation [22] :

$$n^2(\lambda) = A + \frac{B\lambda^2}{\lambda^2 - C^2}$$

That A, B and C are Sellmiere's coefficients. The Sellmiere's coefficients have been obtained by evaluation of n^2 data in Sellmiere's relation. The results of evaluation summarized in table 3. By the dispersion relation we can indicate Group index of compound. The Group index is factor which determines group velocity of waves, in dielectric medium, to propagation velocity waves in free space. The Group index can be written [23]:

$$N_g(\lambda) = n(\lambda) - \lambda \frac{dn(\lambda)}{d\lambda}$$

The Group index is quantity which used in optical fiber for calculating dispersion because of Ng indicate group velocity of propagated optical pulse inside glass or transparent medium. According to figure 7, there is small difference between n_x and n_z, nevertheless difference at Ng is very small.

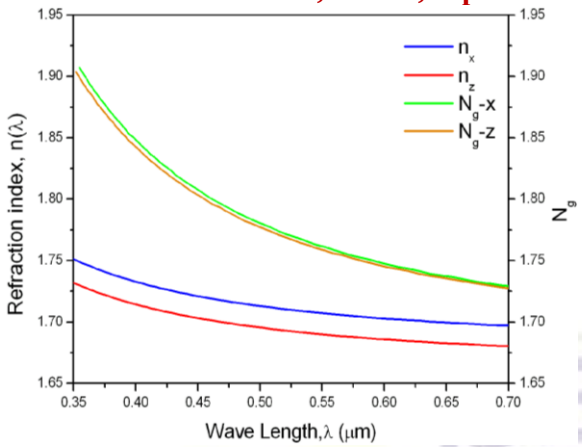


Fig 7. Group index of LaF_3 at the visible range

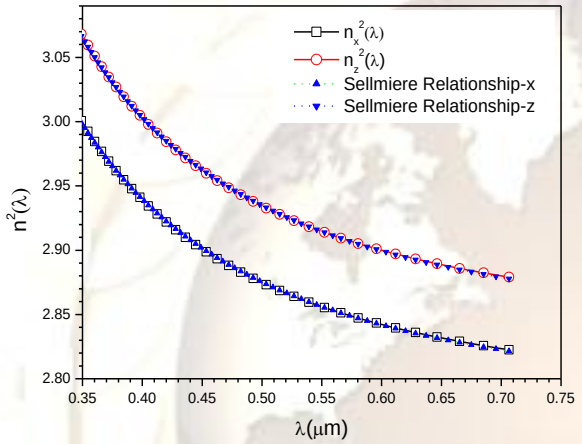


Fig 8. Sellmiere's relation for LaF_3 and Fitted data In the visible region.

Table 3. Calcualted and experimental Sellmiere's coefficients.

Method	Sellmiere's coefficients				
	A in x-and z-dir	B in x-dir	B in z-dir	C^2 (μm^2) in x-dir	C^2 (μm^2) in z-dir
GGA	1.000	1.824	1.770	0.119	0.118
Exp[20]	1.000	1.537	1.514	0.088	0.087

Other important optical property is optical conductivity. When a optical pulse incident on matter the electrons of occupied states under Fermi level exited to unoccupied states above the Fermi level, so, density of states under and above Fermi level are an effective factor for optical conductivity[24]. Figure 9 and Figure 10 show the optical conductivity and threshold of optical conductivity in terms of incident photon energy, respectively. The threshold of optical conductivity determine optical band gap of compound. According to Figure 7 threshold of optical conductivity in x- and z-direction nearly same and for x- and z-direction is begun about 6.4 eV which it is good agreement with 6.6 eV experimental band gap value of LaF_3. [20].

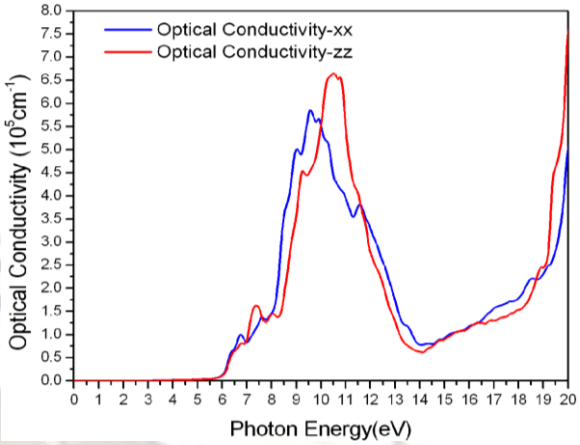


Fig 9. Optical conductivity of LaF_3.

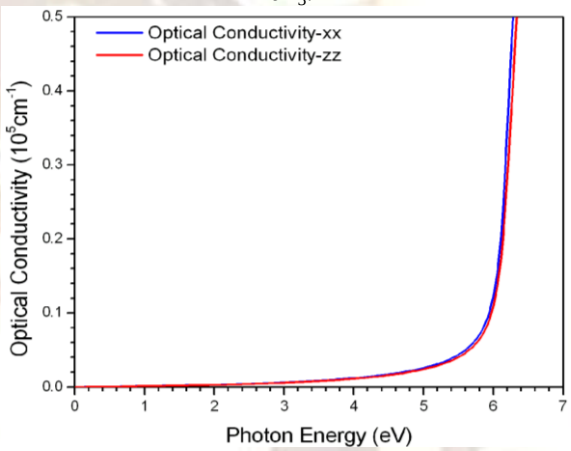


Fig 10. Threshold of optical conductivity of LaF_3.

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IV. CONCLUSION

In this paper, we exhibited that dielectric function and refractive index and other important optical properties of LaF_3 at the low energy nearly are isotropic. The forbidden region and depth of real part of dielectric function inside negative value in z-direction are more than x-direction that it is adapted with observation of the energy loss function and plasma oscillation. The calculated values of refractive index and optical band gap are in good agreement with reported values. The Sellmiere's relation at the visible range is calculated. The calculation of dispersion for refractive index demonstrates there is

very small difference between Ng in x- and z-directions.

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