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DFT Study of $CsCaF_3$: Eu

Murat AYCIBIN [1,♠], Bahattin ERDINC[1]

[1] *Department of Physics, Faculty of Sciences, Yuzuncu Yıl University 65080 Van, Turkey*

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ABSTRACT

In this article, we studied some changes on structural, optical and electronic properties of $CsCaF_3$ when it is doped with Eu atom. All properties of doped $CsCaF_3$ are calculated using the full potential linearized augmented plane wave to the density functional theory. The exchange-correlation potential is evaluated using generalized gradient approximation. This work presents comparison of undoped and doped with Eu atoms of $CsCaF_3$ compound. Moreover, we show that $CsCaF_3$:Eu has indirect band gap with the Generalized Gradient Approximation and doping makes energy band gap values decreases.

Key words: DFT, CsCaF3:Eu, Optical Properties, Semiconductor, Indirect band transition

1. INTRODUCTION

Perovskite ABX-type crystal is a large group. In these crystals, if X is halogen (X^-: Cl^-, Br^- , F^-, …), the cations A and **B** stands for K^+, Rb^+, Ca^+, … and Cs^{2+}, Sr^{2+}, Pb^{2+},…, respectively. If X^{-2} is oxide (X^-: O^{-2}), combination like A^+B^{5+}, $A^{2+}B^{4+}$, and $A^{3+}B^{3+}$ are possible where A^+: Na^+, Ca^+, …, B^{5+}: Nb^{5+}, Ta^{5+},…, A^{2+}: Cs^{2+}, Sr^{2+},…,B^{4+}: Tl^{4+}, Br^{4+}, …, A^{3+}: La^{3+}, Pr^{3+}, …, and B^{3+}: Al^{3+}, Ga^{3+};…. This group has been investigated intensively due to combination of their relatively simple crystal structure, easiness of preparations, doping with different impurity ions and variety of other properties of electrical, optical, magnetic etc. The compounds which adopt the fluoro-perovskite structures ABF_3 (A is alkali metal and B is the alkaline earth or transition metal) are very interesting materials due to their unique properties (ferroelectricity, semiconductivity and optical properties). Generally fluoride perovskite have wide band gaps and they are preferable materials for the lenses and transparent optical coating [1]. The cesium calcium fluoride ($CsCaF_3$) is one of these group members.

Belonging to perovskite-type structure, $CsCaF_3$ has attracted attentions of researchers due to the unique luminescence [2] and spectroscopic properties [1] as well as structure phase transition behaviors [3] when doped with some transition-metal ions.

Meziani and Belkhir used density functional theory (DFT) to calculate structural, electronic and elastic properties of $CsCaF_3$ compound [4]. Veeraiah et al. studied electronic structure and optical properties of $CsCaF_3$ compounds using full potential linearized augmented plane wave (FP-LAPW) plus orbitals method with generalized gradient approximation (GGA) in the framework of the DFT [5]. Murtaza et al. investigated and analyzed shift of indirect to direct band gap for series of $XCaF_3$ (X= K, Rb and Cs)[6]. Ghebouli et al. made theoretical prediction of physical properties of cubic $CsXF_3$ compounds under pressure effect [7]. Bespalov et al. studied Yb doped $CsCaF_3$ using electron paramagnetic resonance (EPR) and optical spectroscopy methods [8]. They studied paramagnetic center of Yb^{3+} ions. Barandiaran et al. Cr^{3+} investigated defects in $KMgF_3$, $KZnF_3$ and $CsCaF_3$ compounds [9]. Casas-Gonzalez et al. used ENDOR to measure Gd^{3+} center in $CsCaF_3$ [10]. Brik and Avram investigated fine structure of lasing $^4T_{2g}$ level in a $CsCaF_3$: V^{2+} compound [11]. Falin et al. used magnetic resonance and optical spectroscopy to study a trigonal Yb^{3+} paramagnetic center in $CsCaF_3$ single crystal [12]. They established the structural model of the complex and the empirical energy level scheme. The results of an electron-nuclear double resonance study of the cubic paramagnetic Yb^{3+} center in Cs_2NaYF_6 and $CsCaF_3$ single crystals are presented [13]. Wu et al. made theoretical study for obtaining g factors and ligand super

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*Corresponding author, e-mail: murataycibin@yyu.edu.tr hyperfine parameter $\acute{A}$ and $\acute{B}$ for Ni^{3+} in $KMgF_3$, $CsCaF_3$ and $RbCaF_3$ compounds [14]. Brik and Ma made hybrid density functional calculation of structural, elastic and electronic properties to analyze series of cubic perovskite $CsMF_3$ compounds (M= Ca, Cd, Hg, and Pb) [15]. Sommerdijk and Bril measured luminescence properties of Eu^{2+} doped $CsCaF_3$ and published results in a series of papers [16-18]. Uwe et all performed emission, excitation and life time measurement of Eu^{2+} doped $CsCaF_3$ to explain abnormal luminescence properties [2].

In this paper, we presented first-principles study of the structural, elastic and electronic properties of Eu doped $CsCaF_3$ compound using full potential linearized augmented plane wave (FP-LAPW) method with generalized gradient approximation (GGA) for the the exchange-correlation potential. This calculation will help to understand the optoelectronic and structural nature of this compound.

2. COMPUTATIONAL METHODS

When DFT is used to calculate physical properties of crystal, full potential linearized augmented plane wave (FP-LAPW) method with reasonable computational efficiency and high accuracy is one of the most powerful tool [19]. Kohn-sham equation of a many-electron system is solved using FP-LAPW method. We used WIEN2k [20] package to calculate physical properties of Eu doped $CsCaF_3$. In this method, wave function, charge density, and potential are expanded in spherical harmonic within non-overlapping muffin-tin spheres, and plane waves are used in the remaining interstitial region of the unit cell. In the code, the core and valance state were treated differently. Scalar Relativistic approach was used for valance state, while core states were treated within a multi-configuration relativistic Dirac-Fock approach. To calculate exchange-correlation energy, we used GGA correction of Perdew et al. [21]. Moreover, we did very careful step analysis to ensure convergence of total energy in the terms of the variation cutoff-energy variation. At the same time, we used appropriate set of k points to compute the total energy.

3. RESULTS AND DISCUSSION

3.1 Structure Property

The atomic electronic configuration used in our calculation was Cs : [Xe] $6s^1$; Ca : [Ar] $4s^2$; F : [He] $2s^2$ and Eu: [Xe] $6s^2$ $5d^1$ $4f^6$. In addition, the Eu 5s and 5p state were treated as valence-band states using local orbital extension of LAPW method [22]. Eu impurity has been studied by constructing supercell, and internal atomic coordinates calculated for the pure $CsCaF_3$ used as our initial coordinates where the Cs locates at the origin (0, 0, 0)a, the Ca is at the body center (1/2, 1/2, 1/2)a and the three Fluor atoms sit at the three face centers (0, 1/2, 1/2)a, (1/2, 0, 1/2)a, and (1/2, 1/2, 0)a. Fig.1a shows the crystal structure of the pure $CsCaF_3$ compound. Here substitutional defect are considered. The supercell is constituted by multiples of the lattice parameter a, b, and c like 2x2x2 for the $CsCaF_3$. With this construction, one of the Ca atom was replaced by Eu atom and we obtained $Cs_4Ca_3EuF_{12}$ compond (after this point, we use $CsCaF_3$:Eu for $Cs_4Ca_3EuF_{12}$) (Fig.1b). Then, in order to get minimum energy for the system, a fully relaxed calculation for all the atomic positions in the supercell was done, where the criterion for convergence was taken 0.0001 Ry/au. After doping progress, to get minimum energy of the system as function of the volume, we plotted volume versus energy graph (Fig. 2).To fitting data with the Burch-Murnaghan equation of state [23], we obtained bulk modulus, energy value and pressure derivative of the bulk module for $CsCaF_3$:Eu. They are given in Table 1. In addition, we also plot pressure versus volume graph to show that minimum energy value is obtained under zero pressure and lattice constant with increasing pressure gets minimum values (Fig. 3). The total energy was minimized for $CsCaF_3$:Eu using set of 100 k points in the irreducible Brillouin zone, equivalent to a 10x10x10 Monkhorst-Pack [24] grid in the unit cell, and value of 10 Ry for the cutoff energy was used.

As seen in Fig. 2, the minimum value of Energy, -55426.84 Ry, is corresponding to ground state volume value 1367.70 $(a.u)^3$.

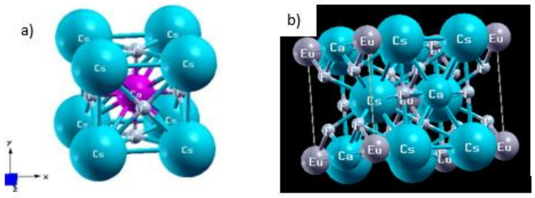

Figure 1 a) Atomic Structure of $CsCaF_3$ compound and

b) $CsCaF_3$:Eu obtained from Xcrysden

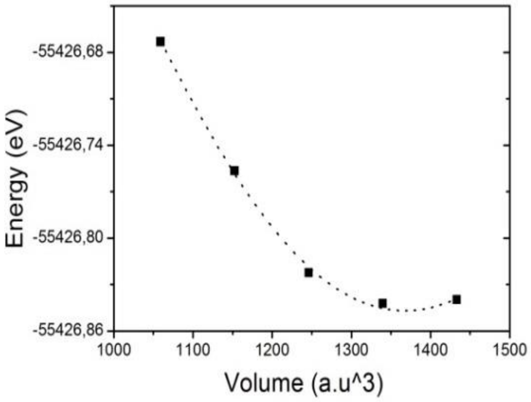

Figure 2 Dependence of total energy on unit cell volume for cubic $CsCaF_3$:Eu .

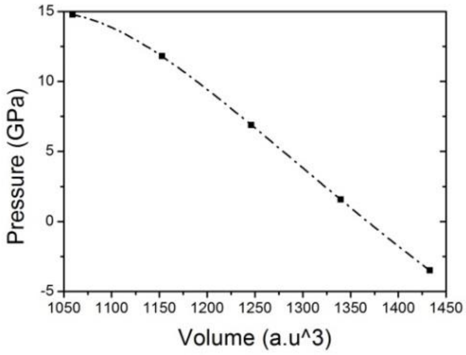

Figure 3 Dependence of pressure on unit cell volume for cubic $CsCaF_3$: Eu.

Table 1. Calculated ground state volume, lattice constant, bulk modulus, derivative of bulk modulus and ground state energy per unit cell of cubic $CsCaF_3$.

	Present work	Undoped Case
Volume $(a.u)^3$	1367.70	
Bulk Modulus (GPa)	75.62	51.77[a], 45.77[b], 45.63[c]
B'	0.1066	5.0[a], 4.62[b], 4.68[c]
E_0 (Ry)	-55426.847	-17538,398[a], -17541,5071[b],

[a] [6], [b] [5], [c] [7]

3.2 Electronic Properties

The calculated band structure for $CsCaF_3$: Eu is given in Fig. 4. In Fig. 4, Fermi energy level was set to origin and shown with dash line. It is obvious that, $CsCaF_3$:Eu has indirect transition and it has energy band gap 0.133 eV between top of the valence located in the **X** high symmetry point and bottom of the conduction band the **Γ** high symmetry point region of the BZ. Therefore, $CsCaF_3$: Eu can be classified as a semiconductor. Previous studies used different approximation namely generalized gradient approximation (GGA) [4,5], local density approximation (LDA) [5,7], generalized gradient approximation of Wu-Cohen [6] and generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE) [7] to calculate electronic band structure of undoped $CsCaF_3$ material. Babu et al. and Ghebouli et al. found that undoped $CsCaF_3$ material has indirect band gap, 6.9 and 7.25 eV respectively, between valence band maximum, at **W** high symmetry point, and conduction band minimum, at **Γ** high symmetry point [5]. On the other hand, Meziani et al. and Murtaza et al. showed that $CsCaF_3$ has direct band gap at **Γ** high symmetry point, 7.274 eV and 8.20 eV, respectively. All calculated values of electronic band gap of undoped $CsCaF_3$ is higher than electronic band gap of $CsCaF_3$: Eu. This shows that when we doped $CsCaF_3$ material with Eu atom, the electronic band gap values decreases as expected. Moreover, we also showed lower band of conduction state and upper band of valence state (Fig. 4c).

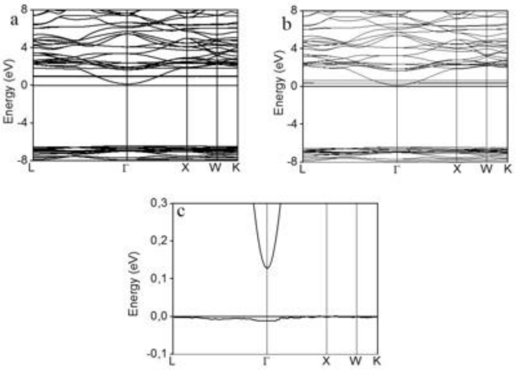

Figure 4 Energy band structure of Eu doped $CsCaF_3$ a) Spin up b) Spin down c) Lower part of conduction part and upper band of valence band

To further elucidate the nature of electronic band gap of materials, Total and partial density of state (DOS) is also given in Fig. 5.

DOS of $CsCaF_3$ without doped was analyzed in detailed and given in references [4-7]. They shown total and partial DOS of undoped $CsCaF_3$. According to their result, conduction band of $CsCaF_3$ is mixed by d state of Cs and d state of Ca atoms and valence band is constructed by p state of Cs and F atoms. In Fig. 5 c, d and e, we can easily see contribution of Cs, Ca and F atom to DOS. Our result confirmed their calculation. In addition, we also showed contribution of dopant Eu atom to DOS. One can see from Fig. 5f, the main contribution to band-gap-induced state comes from the Eu 4f orbitals. In electronic band structure, we observed additional state located around 0 eV regions where at Fermi energy level was set and shown with dot line. This state came from Eu atom.

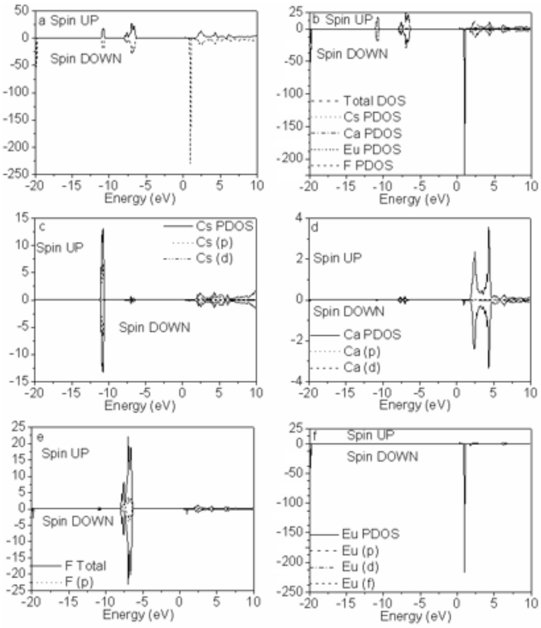

Figure 5 (a,b) Calculated DOS for $CsCaF_3$:Eu crystal, and (c) Partial contribution of Cs (d) Partial contribution of Ca (e) Partial contribution of F and (f) Partial contribution of Eu to DOS for both spin up and spin down cases

4. OPTICAL PROPERTIES

Due to the cubic symmetry of CsCaF$_3$: Eu, to calculate one dielectric component is sufficient. 0-40 eV photon energy range was chosen for optical response. The chosen range was sufficient to calculate optical response of CsCaF$_3$: Eu. The calculated real and imaginary parts of dielectric constant are given in Fig 6. As seen in Fig 6, the static values of real part of dielectric constant, ε_1 (0), is found 2.4, close to undoped case, for calculated lattice constant. In addition, ε_1 (ω) has negative values at the photon energy regions between 13.45-13.89 eV and 15.28-17.56 eV. The negative values of ε_1 (ω) means that the indecent electro-magnetic waves are entirely reflected and material shows metallic behavior. Behind the energy values of 35.75 eV, ε_1 (ω) gets closer to zero values that means there is no transition between states.

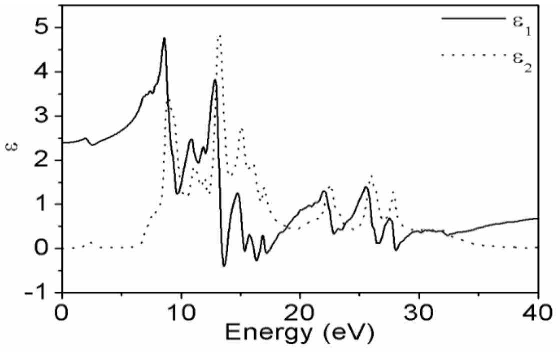

Figure 6 Real (ε_1) and imaginary (ε_2) parts of dielectric constant for CsCaF3:Eu

Analyzing imaginary part of dielectric constant, we can see that there is a peak starting around 0.13 eV where absorption was observed. To see peak more detailed, we realigned both x and y axes according to our needs (Fig. 7). If we analyzed pure CsCaF$_3$ material for dielectric constants, it can see that there is no transition until 6.5 eV or beyond depending on references [5-7]. Comparing our results with undoped case, we can say that this peak is due to dopant Eu atom and associated with f-d transition.

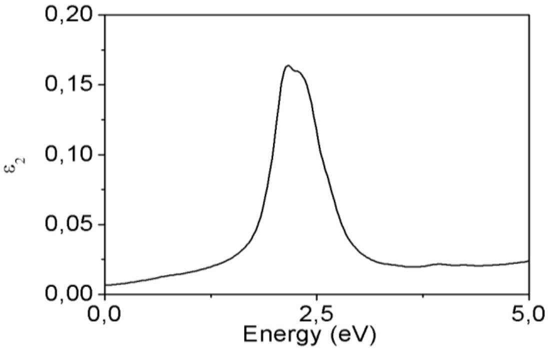

Figure 7 Enlarged imaginary (ε_2) parts of dielectric constant for CsCaF$_3$: Eu in the range of 0-5 eV

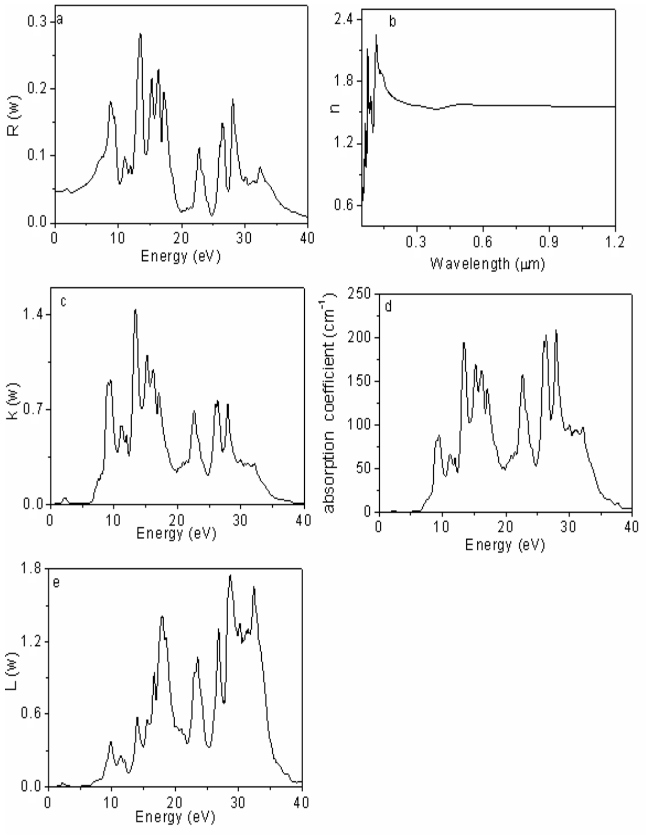

Figure 8 Optical constants for CsCaF$_3$: Eu

Fig. 8 a, b, c, d and e) show results for reflectivity R (ω), refractive index n (ω), extinction coefficient k (ω) and energy loss L (ω), respectively. The optical reflectivity, R(w), is given in Fig 8a. The zero-frequency reflectivity is 4.6 % which is close to undoped case. The maximum reflectivity value is almost 28 % at 13.43 eV where real part of dielectric constant goes below zero Fig. 6. The static refractive index n(0) shown in Fig 8b is obtained to have value 2.4. The refractive index is bigger than one due to interaction between photons, entering material, with electrons. The more photons slow down by the interaction, the greater refractive index will be. Hence, refractive index value of doped CsCaF$_3$ has bigger value than undoped case because $CsCaF_3$: Eu material has more electrons per unit cell.

The local minimum of extinction coefficient k(ω) plot in Fig. 8c corresponds to the zero of $\varepsilon_1(\omega)$. Detail analyzing extinction coefficient, similar trend with imaginary part of dielectric coefficient is observed. The absorption coefficient is shown in Fig. 8d and enlarge version Fig. 9. It starts around 0.13 eV and reaches the maximum value at 27.96 eV. The absorption range predicts the usefulness of compound for optoelectronic devices. The function L (ω) shown in Fig. 8e describes the energy loss of a fast electron traversing the material. The prominent peak in L(ω) spectra present the characteristic associated with plasma resonance and corresponding frequency is the so-called plasma frequency ω_p. As is seen from Fig.8e, sharp peaks are associated with plasma oscillation which correspond negative values of real part of dielectric constant. The peaks of the L(ω) calculated by Wien2k code are located at 28,72 eV, for energy loss.

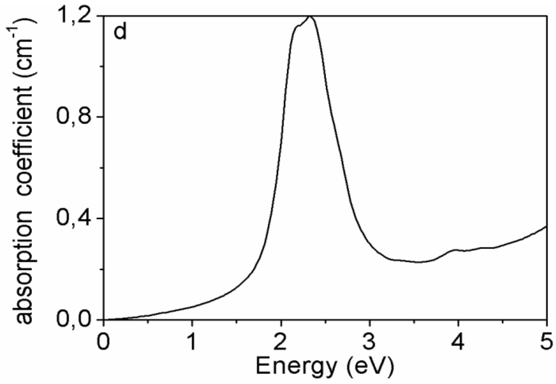

Figure-9 Enlarged absorption coefficient of CsCaF3:Eu

6. CONCLUSION

In this paper, we have investigated structural, electronic, and optical properties of $CsCaF_3$ when doped with Eu atoms. When we added dopant Eu atom in $CsCaF_3$ compounds, it is found that the energy band gap decreases 6.9 eV to 0.13 eV. İt also is found that $CsCaF_3$ compounds has indirect band with GGA. Comparing optical properties, it is seen that optical transitions start at low energy values when doping with Eu atoms.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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