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RESEARCH ARTICLE

Electronic and Elastic Properties of $CsCaF_3$ Doped with Vanadium

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ABSTRACT

In this paper, we applied Density Functional Theory to see effect of doped vanadium (V) element on physical properties of $CsCaF_3$ compound by Wien2k software. Perdew-Burke-Ernzerhof General Gradient approximation was used for exchange-correlation energy. We observed that when $CsCaF_3$ compound doped with Vanadium, value of energy band gap gets smaller around 1eV as expected. In addition, we calculated and interpreted how the density of states was formed by atoms. Moreover, the compound has indirect band transition and it is classified as a semiconductor. Furthermore, calculated elastic constant verify mechanic stability conditions for cubic structure. Moreover, anisotropy factor is bigger than unity means material is anisotropic.

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1. Introduction

Luminescent materials, also called phosphors, are described as light emitting materials after absorbing energy. These kinds of materials include one host and one intentionally doped impurity (Figure 1) (Ronda, 2008). The doped atom is chosen according to desired emission wavelength. Due to luminescence efficiency, doping concentration is generally very low. Luminescence is obtained with either optical or electrical excitation. Most of the time, doped impurity called activator is responsible from luminescence. Activator atom is chosen from either lanthanides or transition atoms. In case when the intensity of emission of doping atom is not strong enough, the second atom called sensitizer is also doped in the host compound. Sensitizer absorbs energy at first and then transmits absorbed energy to activator atom.

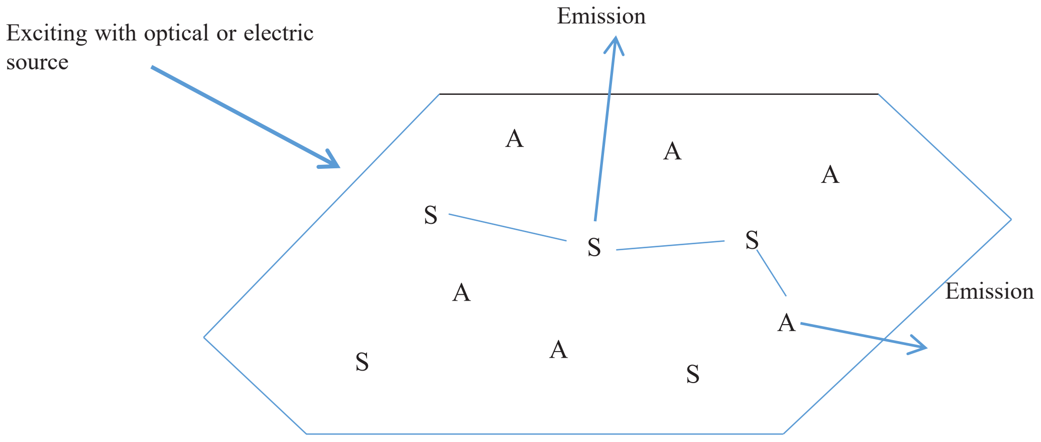

Figure 1. Example structure of the luminescent material (While A represents activator atom, S represents sensitizer atom)

Some fluoro-perovskite materials, XYF_3 (X= K, Cs, Rb and Y= Mg, Ca), doped with transition metals have unique properties, such as tunable laser, electron phonon interaction, phase transition behavior, ferroelectrics, high-temperature superconductivity and ionic conductivity (Hu et al., 2009; Ma and Brik, 2012). Therefore, they have applications in technological areas.

In this paper, we are interested in $CsCaF_3$ compound doped with V^{2+}. In literature, most of the studies are experimental studies. There are a few theoretical studies. At the near infrared region, Brauch and Dürr doped $CsCaF_3$ compound with V element and showed probability of using active element of a compound for tunable laser (Brauch and Durr, 1985). Brik and Avram performed theoretical calculations to compute the fine structure of the lansing $^4T_{2g}$ level in $CsCaF_3$: V^{2+} crystal (Avram et al., 2004). Moreover, they continued the theoretical analysis of the first excited state $^4T_{2g}$ level in $CsCaF_3$:V^{2+} crystal considering Janh-Teller Effect to determine electronic state (Avram et al., 2005).

In this paper, we used density functional theory to investigate effect of the doped element on physical properties of $CsCaF_3$ compound doped. This theoretical investigation will give opportunity for researchers to understand the compound more deeply.

2. Materials and Methods

Density Functional Theory (DFT) is a powerful approximation to determine physical properties of materials (Dreizler, 1990). To solve the Kohn-Sham equation for many-body particle, we chose full potential linear augmented plane wave method (FP-LAPW). We used Wien2k, detail of method can be found in reference (Blaha et al., 2001), to calculate physical properties of compound. Before starting the calculation, we obtained 2x2x2 supercell and replaced one of Ca atoms with V atom in the unit cell (Figure 2) in aim to look for influences of doped element on physical properties of compound. Initially, we used atomic coordinate of $CsCaF_3$ compound to obtain supercell. In undoped $CsCaF_3$, Cs is located at (½, ½, ½)a , Ca is to be found (0, 0, 0)a and 3 F atoms are located at (½,½, 0)a, (0, ½,½,)a and (½,0, ½)a position and space group of compound is 62 (Pnma) (Meziani and Belkhir, 2012). To get a more accurate result in the calculation, step analysis was performed carefully to get convergence of the total energy in terms of cutoff-energy variation. An appropriate set of k points was used to calculate total energy.

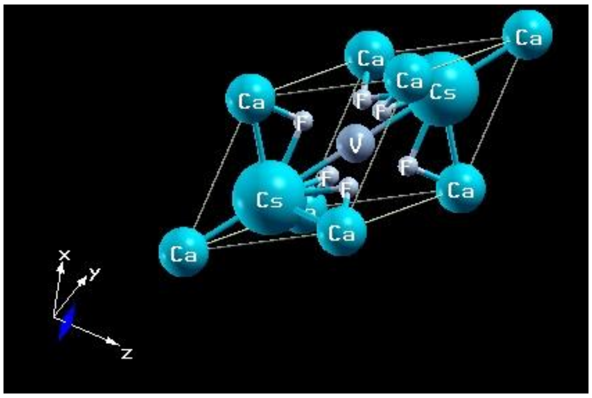

Figure 2. Unit cell of $CsCaF_3$: V compound

3. Result and Discussion

Initially, Cs: [Xe] $6s^1$; Ca: [Ar] $4s^2$ and; F: [He] $2s^2$ and V: [Ar] $4s^2$ $3d^3$ were taken as an electronic configuration. We have to optimize the lattice constant to obtain minimum energy value. For this aim, we plotted volume versus energy (Figure 3). Using Birch-Murnaghan state equation, we extracted Bulk modulus, derivation of Bulk modulus and lattice constant of compounds from plot (Figure 3). All obtained theoretical values were inserted into Table 1. After this point, the rest of the calculations were carried out with obtaining the theoretical lattice constant. In addition, we also draw pressure versus volume plot (Figure 4). As seen from Figure 4, zero pressure, meaning no force on compound, corresponded to the most stable energy value.

Table 1. Structural properties of $CsCaF_3$: V compound

Bulk modulus (GPa)	Derivation of bulk modulus (GPa)	Energy (Ry)	Volume (a.u)^3	Lattice constant
55.93	4.88	-35620	1192.06	8.9068 Å

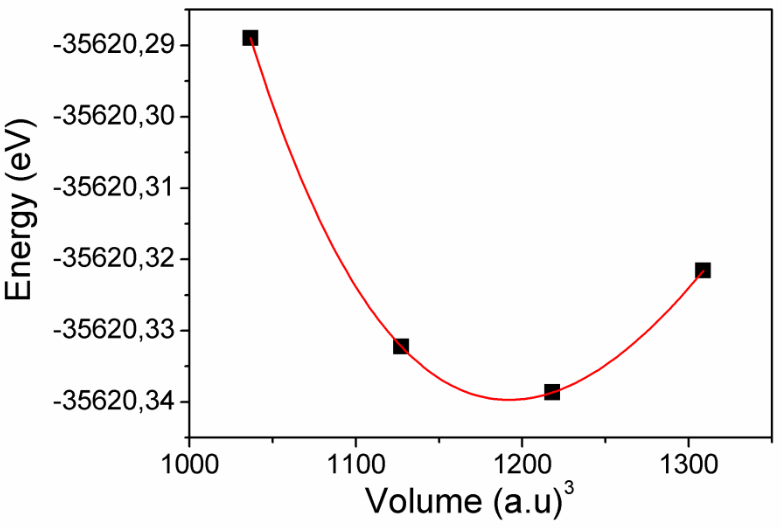

Figure 3. Graph of volume versus energy

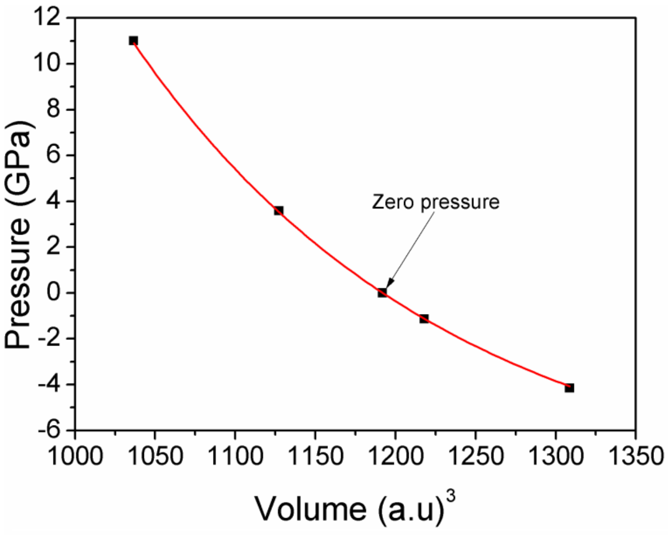

Figure 4. Graph of volume versus pressure

We plotted electronic band structure of cubic $CsCaF_3$:V through W-L-Γ-X-W and K high symmetry points (Figure 5). In this graph, we could not able to identify characteristic of compound. Therefore, we enlarged y axis to see the point at where the transition occurs from the valence band to the conduction band and to classify compound according to its forbidden energy gap value (Figure 6). As seen from Figure 6, an indirect transition was observed from W high symmetry point to X symmetry points. The indirect transition means when transition happens, it involves not only a photon, but also a phonon for momentum conversation. The forbidden band gap between the top of the valence band to the bottom of the conduction band is 0.837 eV. As a result, the compound is classified as a semiconductor.

The energy band gap of undoped $CsCaF_3$ was studied previously (Babu et al., 2012; Ghebouli et al., 2012; Meziani and Belkhir, 2012; Murtaza et al., 2013). Depending on chosen method, it was calculated between 6.2 eV and 8.2 eV. If the compound is doped with the impurity atom, its forbidden energy band gap decreases as expected. The separation between valence band to conduction band of $CsCaF_3$ doped with Eu atom (Aycibin and Erdinc, 2015) was calculated as 0.133 eV. The forbidden band gap of CsCaF3: V^{2+} was obtained 0.837 eV. In both cases, above statement was still valid. Moreover, comparing both doped case, $CsCaF_3$: Eu^{2+} has narrower energy band gap than $CsCaF_3$: V^{2+} compound. This is related with atomic radius. When atomic radius increases, the energy band gap decreases. In addition, the transition starts at either W high symmetry points or Γ symmetry points and finishes Γ high symmetry point (Babu et al., 2012; Ghebouli et al., 2012). When the compound was doped with Vanadium element, the indirect transition starts at W high symmetry points and it finishes at X symmetry points. This means when we doped compound with V element, electronic structure of the compound has been changed.

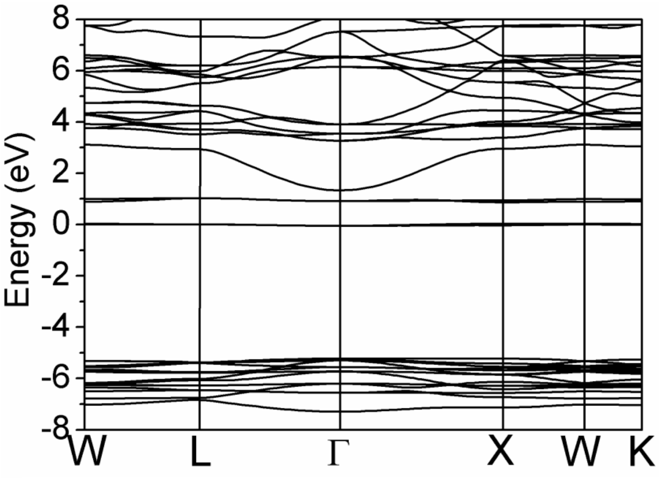

Figure 5. Electronic band structure of $CsCaF_3$:V compound

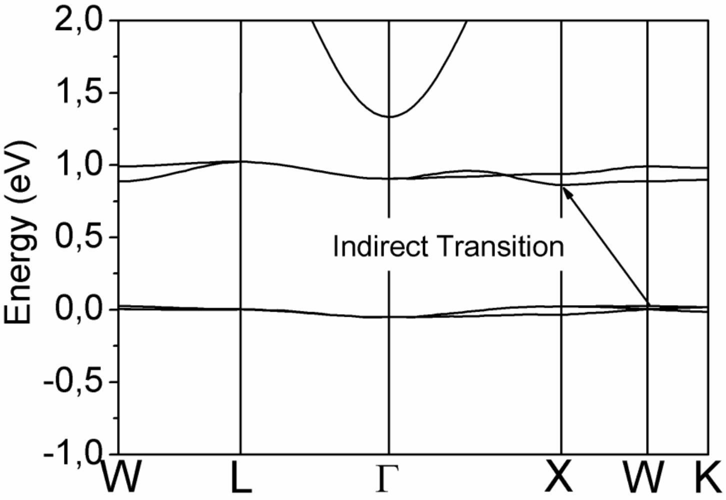

Figure 6. Electronic band structure of $CsCaF_3$:V compound while y axis was enlarged

To understand the electronic band structure, we also calculated and plotted density of state (DOS) and partial density of state (PDOS) showed which state was constructed by individual atom's orbit (Figure 7 and 8). From Figure 7, while Cs atom just contributed to the conduction band, Ca, V and F atoms contributed both to the valence and the conduction band.

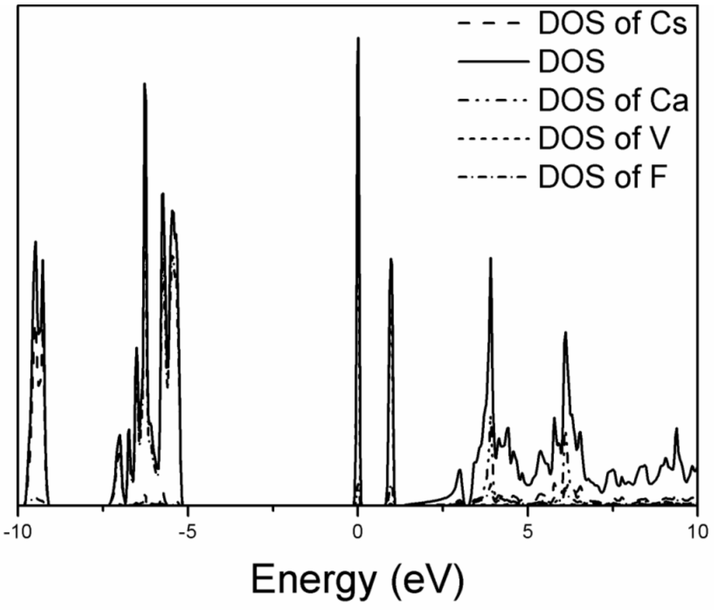

Figure 7. Graph of density of state

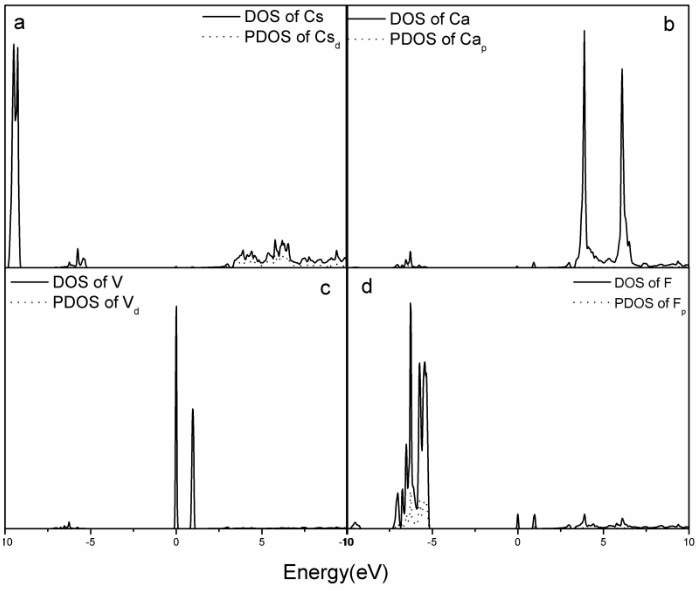

Figure 8. Partial DOS of elements

We also draw Figure-8 to show partial contribution of all atoms' orbital. In Figure 8a, we plotted DOS of Cs atom. It is obvious that while Cs atom contributed conduction and core region, the contribution of Cs atom at conduction region come from d orbital. p orbital of Ca atom contributed at the core region of compound (Figure 8b). The DOS contribution source of V atom is d orbital (Figure 8c). Finally, the F atom contributed not only core region, but also conduction band. In detail, the contribution to the core region comes from p orbital of F atom.

Finally, we will talk about the elastic properties of solid. The elastic properties are important properties providing information of structural stability, anisotropic character of materials. There are three independent elastic constants for cubic system, namely C_{11}, C_{12} and C_{44}. To compute them, the cubic unit cell is deformed using appropriate strain tensor. In this paper, we have used method developed and implemented in the Wien2k package by Jamal (Jamal, 2012). This program calculates all elastic constants and its dependents according to three different methods, namely Voigt, Reuss and Hill.

All obtained results were summarized in Table 2. We also enumerate mechanical stability conditions. C_{ij} elastic constants are positive in cubic crystal (Grimvall, 1999). Also, they should satisfy following formulas:

$$(C_{11} - C_{12}) > 0 \tag{1}$$

$$(C_{11} + 2C_{12}) > 0 \tag{2}$$

$$C_{44} > 0 \tag{3}$$

Table 2. Elastic constant, C_{ij}, of $CsCaF_3$: V compound

C_{11}	C_{12}	C_{44}
74.750	26.422	25.199

As seen from Table-2, elastic constants of $CsCaF_3$: V compound are positive and verify mechanic stability condition.

In addition, Bulk modulus, B, should satisfy $C_{12} < B < C_{11}$. Moreover, Young modulus, E, Poisson ratio, ν and Anisotropy factor, A, are also obtained from Jamal's program. If anisotropy factor of material is bigger or smaller than unity, the material is classified as an anisotropic material. Otherwise, it is an isotropic material. For materials ductility and brittleness, there is one criteria, namely B/G ratio. Pugh' criteria (Pugh, 1954) determine whether material is ductile or brittle depending on B/G ratio. If this ratio is bigger than 1.75 that material is ductile, otherwise it is brittle. To find this value, we have to calculate shear modulus, G. Shear modulus is given by following relation:

$$G = \frac{1}{10}(C_{11} - C_{12} + 3C_{44}) + \frac{5C_{44}(C_{11} - C_{12})}{8C_{44} + 6(C_{11} - C_{12})} \tag{4}$$

After finding the shear modulus, we can get B/G ratio. All calculated and obtained results were inserted in Table 3.

Table 3. Calculated elastic constant and Bulk Modulus, B, Anisotropy factor, A, Shear Modulus, G, Young's Modulus E, Poisson's ratio υ and B/G ratio of $CsCaF_3$: V compound

	B (GPa)	A	G	E	$\boldsymbol{\upsilon}$	$\boldsymbol{B/G}$
VOIGT	42.531		24.784	62.258	0.256	1.72
REUSS	42.531		24.774	62.237	0.256	1.716
HILL	42.531	1.043	24.779	62.248	0.256	1.716

From Table 3, Bulk modulus value calculated from elastic constant was obtained as 42.531 in GPa. This value is closer to the value obtained from volume-energy graph. This result shows that our calculation is correct. Also, the anisotropy factor of the compound was bigger than 1. That means the material is anisotropic. In addition, B/G ratio is less than 1.75. After Vanadium doped into compound, material is still brittle compared with the undoped case (Meziani and Belkhir, 2012).

4. Conclusion

In this paper, we investigated how physical properties of $CsCaF_3$ compound changed when doped with Vanadium element. After the doping process, it is found that forbidden energy band gap reduces to 0.835 eV as expected and the material is now classified as a semiconductor. It has the indirect transition from W high symmetry point to X high symmetry point and electronic structure has been changed after doping Vanadium compared with previous studies (Babu et al., 2012; Ghebouli et al., 2012; Meziani and Belkhir, 2012). Moreover, we also show which orbital of atom contributes at compound energy state.

We also calculated elastic properties of $CsCaF_3$: V compound. It is seen that this compound has mechanic stable condition. Anisotropy factor is different than unity so the material is anisotropic.

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