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Research Paper

First-Principles Calculations Of Structural, Electronic And Elastic Properties Of Tysonite Lanthanum Fluoride (Laf_3)

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ABSTRACT: *The structural, electronic and elastic properties of tysonite Lanthanum fluoride (LaF_3) have been studied using Density Functional Theory. The lattice constants were calculated and then the values fitted into the energy volume relation using the Birch-Murnaghan third order equation of state. Lattice parameter in this calculations are as follows; a = 7.245Å, c = 7.388Å and c/a = 1.02Å against 7.128Å, 7.329Å and 1.028Å of CASTEP. A band gap of 7.78eV was obtained in comparison to the 9.0eV of experiment and this is because DFT-GGA/LDA is known to underestimate band gaps. The results for elastic constants for the directions C_{11} = 170.1, C_{12} = 76.26, C_{13} = 58.69, C_{14} = -1.66, C_{33} = 208.08 and C_{44} = 33.90. Compared to other theoretical and experimental values, these results are in good agreement.*
KEYWORDS: *Structural properties, Tysonite LaF_3, band gap, Elastic constants*

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I. INTRODUCTION

Lanthanum fluoride (LaF_3) belongs to low triflouride of lanthanides which displays transparency to visible light due to wide band gap and possess the property of low non-radiative emission due to low phonon energies [1].]. LaF_3 is a highly refractive layer material and highly transparent and is commonly used for deep ultra-violet (UV) and vacuum UV applications [2]. LaF_3 has been reported as having one of the highest known ionic conductivities and super-ionic transitions which can be employed as a solid electrolyte in battery industry [3].It has an anomalously high heat capacity (above 900 K), suitable for high temperature electrodes. Other applications include fluorescent lamps, fiber optics, and radiation applications [2]. It is with this broad range of applications that LaF_3 has been widely studied in the recent years.

LaF_3 crystallizes in three major structures tetragonal *14/mmm*, orthorhombic *Cmma* and tysonite *P3C1* [4]. However it is the tysonite structure that is stable at room temperatures and thus suitable for application at ambient conditions. Different experiments have thus led to different crystal structures of LaF_3. In the X-ray diffraction in a diamond anvil cell [4] for instance, it is reported that the tysonite structure of LaF_3 undergoes a structure phase transition at about 20 GPa to orthorhombic phase. The orthorhombic phase belongs to the space group *Cmma* with eight formulas in a unit cell. Winkler *et al*. [5] using computational method found that the previous reported high-pressure phase was tetragonal, which belongs to the space group *I4/mmm* having two formula units per cell. It has been found that the tetragonal phase is more stable than other phases above 25 GPa [5].The tysonite LaF_3 phase belongs to *P3C1*space group with twelve numbers of symmetries and four atoms inside unit cell.

Modak et al [6], carried out the analysis of the structural stability of LaF_3 under pressure using WIEN2K package .These was done on the basis of the total energy calculations on the tysonite, orthorhombic and tetragonal phases at different compressions. It was predicted that the tysonite structure transits to orthorhombic phase at ~ 25 GPa [6].

In recent years first-principles calculations based on the density-functional theory have become an important tool for the accurate study of the crystalline and electronic structures and mechanical properties of solids [7].This work focus on the study of LaF_3 which belongs to special class of superionic materials often used as a solid electrolyte in battery industry, but still their properties such mechanical, electronic and structural are

not yet studied exhaustively. In the present study, we report on an investigation of the structural, band structure characteristics and thermal properties of tysonite LaF_3 using the first principles calculations based on density functional theory and the results are discussed in comparison with the available experimental data and other theoretical results.

II. METHODOLOGY

Structural and Electronic Properties

All calculations were done within the Density Functional Theory as implemented in the QUANTUM ESPRESSO computer code [8] .The exchange and correlation energy was treated within the generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) [9]. This functional was picked because of computational efficiency and no adjustable parameter was required. The crystal structures were relaxed at 0 K with ambient pressure and plane wave basis set was truncated at 60 Ry.The Brillouin zone integration was carried out at 7 x 7 x 7 k-point mesh. The results obtained were then fitted in the Birch-Murnghan Equation of State (E.O.S) for the post processing. To plot the band structure of LaF3, the high symmetry points used were Γ-M-K-Γ-A-L-H-A/L-M/K-H. The density of states (DOS) and band structure characteristics of tysonite LaF_3 were also studied**.**

Elastic Constants

The elastic constants majorly define the mechanical and dynamical characteristics, especially the stability and the stiffness of a material [10]. These parameters may be used as means of probing the inter-atomic forces. Although LaF_3 belongs to tysonite structure, its mechanical properties were calculated within the hexagonal phase group of crystals [11] .With five independent elastic constants, C_{11} , C_{12} , C_{13} , C_{14} , C_{33} , and C_{44} .

The theoretical elastic constants were calculated from the energy variation by applying small strains to the equilibrium lattice configuration. The elastic energy of a solid under strain is given by

$$\Delta E = \frac{V}{2}\sum_{i=1}^{6}\sum_{j=1}^{6} C_{ij}\, e_i e_j \qquad (2)$$

where V is the volume of the undistorted lattice cell, ΔE is the energy increment from the strain with vector e= (e_1 e_2 e_3 e_4 e_5 e_6) and C is the matrix of the elastic constant. For the hexagonal phase, its primitive vectors are defined by

$$(a_1\ a_2\ a_3\ ) = (\frac{\sqrt{3}a}{2}\ \frac{1a}{2}\ 0\ \frac{-\sqrt{3}a}{2}\ \frac{1a}{2}\ 0\ 0\ 0\ c\ ) \qquad (3)$$

where *a* and *c* are lattice parameters

We applied the strain $e = (\delta, \delta, 0,0,0,0)$ to calculate C_{11} +C_{12}:

$$\frac{\Delta E}{V} = (c_{11} + c_{12})\delta^2 \qquad (4)$$

$C_{11} - C_{12}$ was then calculated using the strain $e = (0,0,0,0,0, \delta)$:

$$\frac{\Delta E}{V} = \frac{1}{4}(c_{11} - c_{12})\delta^2 \qquad (5)$$

C_{33} was then obtained using the strain$e = (0,0, \delta, 0,0,0)$:

$$\frac{\Delta E}{V} = \frac{1}{2}C_{33}\delta^2 \qquad (6)$$

C_{44} was then obtained using the strain$e = (0,0,0, \delta, \delta, 0)$:

$$\frac{\Delta E}{V} = C_{44}\delta^2 \qquad (7)$$

Under the condition of hydrostatic pressure,$e = (\delta, \delta, \delta, 0,0,0)$, the bulk modulus is calculated by:

$$B = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + \frac{C_{33}}{2})$$

$$\frac{\Delta E}{V} = \frac{9}{2}B\delta^2 \qquad (8)$$

Hence C_{13} is determined.

Appropriate averaging procedures can be used to obtain isotropic elastic constants such as the bulk, shear and Young modulus. The common three widely used averaging approaches are the Voigt approach which assumes a uniform strain [12]. While the Reuss procedure validates the case of uniform stress [13].The combination of the two approaches results to Voigt and Reuss Moduli which are expressed in terms of the stiffness constant. The bulk and shear modulus in the Voigt approach are:

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$B_V = \frac{1}{9}[(C_{11,} + C_{22,} + C_{33,}) + 2(C_{12} + C_{13} + C_{23,})]$ (9a)

$G_V = \frac{1}{15}[(C_{11,} + C_{22,} + C_{33,}) - (C_{12} + C_{13} + C_{23,}) + 3(C_{44} + C_{55} + C_{66})]$ (9b)

In the Voigt-Reuss-Hill (VRH) approximation [14], the B and G of the polycrystalline material are approximated as arithmetic mean of the Voigt and Reuss limits:

$B_{VRH} = \frac{1}{2}(B_V + B_R)$, (10a)

$G_{VRH} = \frac{1}{2}(G_V + G_R)$ (10b)

The Young modulus (E) and Poisson ratio (σ) can then be obtained in connection with bulk modulus and shear modulus.

III. RESULTS AND DISCUSSION

Structural Properties

The structure of Laf_3 as obtained by Quantum espresso calculations at ground state is as shown in figure 1.The calculated lattice constants are listed in table 1.

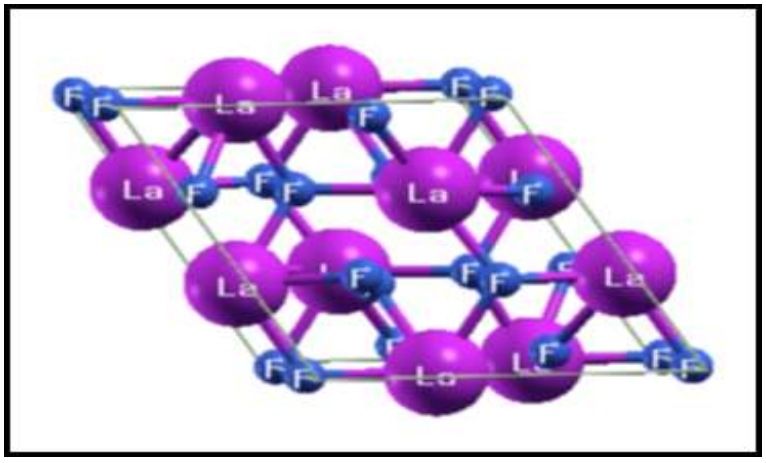

Fig 1: Tysonite *P3C1* LaF_3

Table 1: The calculated lattice parameter, Bulk modulus B_0 the first pressure derivative of the Bulk Modulus for LaF_3

	a_0 (Å)	c_0(Å)	c_0/a_0	V_0(Å^3)	B_0(GPa)	B'_0
Present work	7.245	7.388	1.02	327.14	114.44	4.25
CASTEP [15]	7.128	7.329	1.028	322.48	114.26	3.96
WIEN2K [7]	7.260	7.427	1.023	339.01	97.27	-
EXPT [4]	7.191	7.357	1.023	329.46	104.9	4.5(6)

From the results it is noted that there is a very close relation between calculated and experimental values with the smallest deviations in lattice parameters. The results obtained in this study compare favorably well with other calculated values obtained at ground state.

Electronic Properties

The band structure and the density of states are presented in figure 2 and 3 respectively.
The band gap is shown in table 2 below with a comparison with other studies.

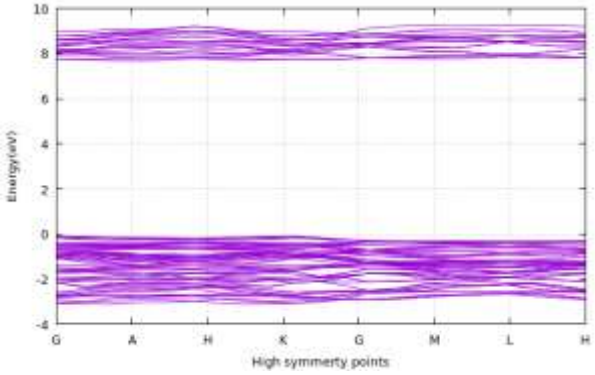

Figure 2: Band structure

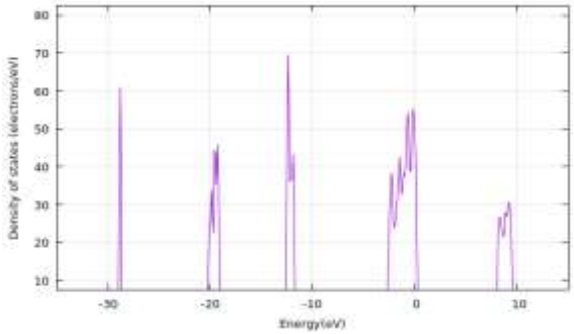

Figure 3: Density of states

Table 2: Band gaps for tysonite LaF_3

	CASTEP (LDA)	WEIN2K	EXPT	GGA
Direct band gap (eV)	7.74eV	6.0	9.7	7.78(eV)
Ref	[15]	[6]	[17]	This work

The gap above the highest occupied energy level and the lowest unoccupied energy level corresponds to the difference in the valence band maximum and conduction band minimum. The band structure indicates that the tysonite phase of LaF_3 is a strong insulator having a direct band gap of 7.78eV compared to experimental value of 9.0 eV.

Elastic Properties

The elastic constants of solids are important parameters that can provide useful information about mechanical and dynamic characteristics such as stability and stiffness of a material. The calculated elastic constants for LaF_3 at ground state are displayed in table 3.

Table 3: The calculated elastic constants C_{ij} (GPa) and Debye temperature Θ_D for tysonite at ground state

	C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}	Θ_D (K)
This work	170.10	76.26	58.69	-1.66	208.07	33.90	383.74
USPEX[14]	176	84	66	-	205	36B	-
CASTEP [15]	194.33	90.54	60.2	-1.64	240.27	34.28	399.14
EXPT[18]	180±1	88±4	59±5	-	222±1	34±2	382

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Apart from approximations factors, the results obtained are closer to both experimental and other theoretical methods. To obtain these elastic constant, there are several other constants used and this normally causes the noted deviations. It is worth noting that the experimental values are less than the calculated values in both Quantum Espresso and CASTEP. But the C_{14} obtained is comparable to the results obtained by CASTEP approach [15].

The tysonite structure is mechanical stable at 0 GPa according to the elastic constants test [16]:

$$C_{11} > 0, C_{33} > 0, C_{44} > 0, (C_{11} - C_{12}) > 0,$$

$$[(C_{11} - C_{12})C_{11} - 2C_{14}^2] > 0,$$

$$[(C_{11} + C_{12})C_{33} - 2C_{13}^2] > 0 \qquad (10)$$

IV. CONCULUSION

We have studied the structural, electronic and elastic properties of tysonite LaF_3 by use of generalized gradient approximation. The obtained results on the lattice constant a = 7.245Å, c = 7.388Å and c/a = 1.02Å against 7.128Å, 7.329Å and 1.028Å of CASTEP,which are in agreement with experimental and other theoretical results. The calculated Bulk Modulus (B) from the third order Birch-Murnaghan equation of state is 114.44 GPa comparable to experimentally obtained value of 110.4 GPa. From the calculated band gap, it is evident that LaF_3 has a wide band gap of 7.78eV.

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REFERENCES

[1]. F. Wang, X.G. Liu, Chem. Soc. Rev. 38 (2009) 976.
[2]. Y. Taki and K. Muramatsu,Hetero-epitaxial growth and optical properties of LaF_3 on CaF2,Thin Solid Films(2002) 420-421 30-3
[3]. V.V.Sinitsyn,O.Lips,A.F.Privalov,F.Fujara,I.V.Murin,J.Phys.Chem.Solids 64 (2003)1201
[4]. W.A.Crichton,P.Bouvier,B.Winkler and A.Grzechnik,Dalton Trans.39(2010) 4302
[5]. B. Winkler,K. Knorr,V.Milman,J.Alloys Compd.349(2003)111
[6]. P. Modak, A.K .Verma, S .Ghosh and G.P.Das,Phys.Chem.Solids 70 (2009)922
[7]. Fischetti, M., & Vandenberghe, W. G. . Advanced Physics of Electron Transport in Semiconductors andNanostructures. Springer, (2016) 5(3), 47-53.
[8]. N.Baroni,N.Amrane,S. Gironcoli, P.Giannozzi http://www.quantumespresso.org
[9]. K. Burke, J. P. Perdew, and M. Ernzerhof, Phys. Rev. Letters, (1996) 77 pp. 3865–3868
[10]. P.W.O Nyawere, N.W. Makau and G.O. Amolo. *Ab initio* calculations of electronic and mechanical properties of orthorhombic phase of BaF_2. *Physica B* (2014) 434
[11]. G.V.Sin'ko, N.A.Smirnow ,Ab initio calculations of elastic constants and thermodynamic properties of bcc,fcc and hcp Alcrystalsunderpressure.J.phys.Condens.Matter (2002)14,6989-7005.
[12]. W.Voigt, Lehrbuch der Kristallphysik, Teubner, Leipzig (1928)
[13]. A.Recuss and Z.Angew, Math.Mech.9, 49(1929)
[14]. R.Hill, Proc.Soc.Lond.A **65**,349(1952)
[15]. ZLv,C.Cheng,Y. Cheng,X.Chen and G Ji *Comput.Mater.Sci.***89** 57 (2014)
[16]. A.Belzner, H.Schulz, G.Heger, Z.Kristallogr.209 (1994) 239.
[17]. B.D Sahoo, K.D.Joshi and S.C Gupta Ab intio study on pressure induced structural sequence in LaF_3 up to 2 Mbar. Applied Physics Division (2017).

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