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STRUCTURAL AND ELASTIC PROPERTIES OF BaFCl

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ABSTRACT

The structural and elastic properties of polycrystalline tetragonal BaFCl have been calculated by *ab initio* first-principles calculations. The linear combination of atomic orbitals method within the density functional theory framework has been used. LDA, GGA (PBEsol), SOGGA and hybrid of HF and DFT, i.e. B3LYP schemes of CRYSTAL09 code were used for this study. Elastic constants, bulk modulus (B), shear modulus (G), Young's modulus (E) and elastic anisotropies of BaFCl have been computed. The results showed that these compounds have large elastic isotropy incompressibility and small elastic anisotropy in shear. The computed data is in well agreement with earlier reported values.

Key words: Band structural calculations, Matlockite compounds, Density functional theory, Second order elastic constants.

INTRODUCTION

Density functional theory (DFT)[1-3] is a successful theory used in condensed matter physics, chemistry, biophysics and nanosciences to probe the ground state properties of solids and molecules. It uses the density of the valence electrons as a fundamental variable to calculate the ground state energies and related properties. Elastic constants determination is essential to understand the macroscopic mechanical properties of matter. Elastic constants provide insight into the nature of binding forces between the atoms since they are represented by the derivatives of the internal energy. They also determine the response of the crystal to external forces, as characterized by bulk modulus, shear modulus, Young's modulus, and Poisson's ratio. The bulk modulus is related to the hardness of material. Shear modulus is a measurement of resistance to reversible deformations upon shear stress. Young's modulus is used to estimate the stiffness of materials and Poisson's ratio is defined as the ratio between diatropic strain and longitudinal strain.

For a long time, the BaFX (X = Br, Cl, I) have been a subject of thorough experimental and theoretical investigations[4-12] with respect to a variety of potential applications such as room temperature hole burning, radiation detection and pressure sensors[13,14]. These alkaline-earth fluoro-halides, crystallize in the matlockitestructure[15,16], are ionic insulators with the excess two electrons of the metal atom being transferred to the halide anions, which have a deficit of a single electron. When activated with divalent impurity, like Eu^{2+}, these compounds are used as X-ray phosphors for medical imaging via photostimulated luminescence processes (PSL)[17-19]. They also find application as *in situ* pressure gauges for experiments with diamond anvil cells at high temperatures[20,21].

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Computational method

In the present work, the local density approximation (LDA), generalized gradient approximation (GGA), second order GGA (SOGGA) and hybridization of HF and DFT, so called B3LYP approaches as embodied in CRYSTAL09 package[22] of Torino group, Italy have been used. In case of the DFT-LDA computation, the exchange potential of VBH[23] and the correlation potentials of VWN[24] have been adopted while for the DFT-GGA, the exchange and correlation potentials as prescribed by Perdew et al.[25] were implemented. The SOGGA theory has also been employed, as this functional approximates structural properties of solids accurately. The measurement of the elastic properties using the SOGGA functional has not been reported previously. It is named SOGGA because a second order density gradient expansion on the exchange enhancement factor is performed.

$$F(x) = 1 + \mu s^2 + \ldots \; (s \rightarrow 0) \qquad \ldots(1)$$

This functional was developed to improve the lattice constants in solids. For SOGGA, the exchange function of Zhag and Truhlar[26] and correlation potentials of Perdew et al.[27] were considered. In the B3LYP, the exchange correlation density functional energy involves the Becke's gradient correction[28] to the exchange and correlation functionals using prescription of Lee–Yang–Parr[29]. To compute the structural and elastic properties of BaFCl, Gaussian basis sets for Ba, F, and Cl from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets have been used. To obtain the elastic constants for the tetragonal BaFCl, the change of total energy with lattice deformation was evaluated by the theory of Perger et al.[30] In matlockite structure, the F ions occupy the Wyckoff positions 2*a* but the Ba and Cl atoms are at the positions 2*c*, which depend on the internal parameters *u* and *v*.

RESULTS AND DISCUSSION

As the first step, the equilibrium structural parameters were calculated: atomic positions andlattice constants (*a* and *c*) using DFT-LDA and GGA (PBEsol), SOGGA and B3LYP schemes. The obtained results are presented in Table 1 and are in reasonable agreement with the available experiments[8,9]. It can be seen that the calculated lattice constant, *a* in this work is slightly larger than the experimental value, whereas the value of *c* is showing a reverse trend. Also, the fractional coordinates and interatomic distances of all ions in a unit cell match well with earlier reported studies.

Table 1: Theoretical and experimental structural parameters and interatomic distances of BaFCl

Structural parameters (in Å)	Present study				LDA[8]	GGA[8]	B3LYP[8]	Expt.[9]
	LDA	PBEsol	SOGGA	B3LYP				
a	4.453	4.443	4.438	4.430	4.336	4.465	4.494	4.394
c	7.030	7.062	7.081	7.105	7.062	7.286	7.416	7.225
u	0.1961	0.2004	0.1997	0.2022	0.2082	0.2068	0.2035	0.2049
v	0.6580	0.6559	0.6575	0.6512	0.6522	0.6488	0.6469	0.6472
Ba-F	2.619	2.634	2.635	2.6410	2.620	2.693	2.708	2.649
Ba-Cl	3.247	3.217	3.230	3.1905	3.135	3.221	3.288	3.196
F-F	3.149	3.142	3.106	3.1012	3.066	3.157	3.178	3.106
F-Cl	3.277	3.292	3.289	3.2226	3.276	3.396	3.450	3.365
Cl-Cl	3.854	3.837	3.820	3.7748	3.744	3.830	3.853	3.765

The elastic constants (EC), C_{ij} determine the stiffness of a crystal against an externally applied strain. According to Hook's law, the dependence of crystal energy is quadratic on the strain for small deformations. The tetragonal crystals are characterized by six independent elastic constants: C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, and C_{66}. The present results are collated in Table 2 with previous reported data[8,10,11]. The second order elastic constants were determined by means of linear fitting of the stress–strain curves obtained from first principles calculations[31,32].

In tetragonal systems, $C_{11} = C_{22} \neq C_{33}$, and the difference between them is a measure of the anisotropic properties of mechanical moduli in the stacking plane and in the perpendicular [001] direction. From Table 2, it is clear that the values of C_{11} and C_{66} are slightly larger than those of C_{33} and C_{44}, respectively, which infer that the intra-layer chemical bonds are stronger than those between the layers.

Table 2: Elastic constants of BaFCl (in GPa) using various theories of LCAO scheme

		C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
Present study	LDA	80.16	67.59	17.30	26.01	13.07	33.04
	PBEsol	87.59	68.02	20.20	29.40	14.49	33.69
	SOGGA	89.01	60.86	22.43	31.12	13.82	32.26
	B3LYP	97.42	86.09	19.64	30.98	21.37	39.45
Previous theoretical studies	LDA[8]	101.8	88.7	27.0	35.6	30.7	46.4
	GGA[8]	82.8	73.0	20.8	32.4	18.0	31.6
	B3LYP[8]	72.3	61.6	18.4	24.5	23.4	33.5
	Shell model[10]	90.8	60.0	24.3	33.2	26.7	41.6
Previous experimental studies	11	74.3	65.8	21.1	33.0	23.8	25.0
	12	75.9	65.7	20.38	23.8	28.2	31.9

From the values of the elastic constants, one can check the intrinsic mechanical stability of the structure, the condition for mechanical stability of tetragonal crystals is usually characterized by the following conditions[33]:

$$C_{11} > 0;\ C_{33} > 0;\ C_{44} > 0;\ C_{66} > 0;\ (C_{11} - C_{12}) > 0;\ (C_{11} + C_{33} - 2C_{13}) > 0;$$

$$\{2(C_{11} + C_{12}) + C_{33} + 4C_{13}\} > 0 \qquad \ldots(2)$$

As observed from Table 2, the calculated elastic constants satisfy these criteria, showing that the compound studied is intrinsically stable.

In Table 3, the isotropic value of shear and bulk moduli (in GPa) are presented using the approximations of Voigt[34], Reuss[35], and Hill[36] (denoted by V, R, and H subscripts), respectively. In Voigt method, a uniform strain is assumed and the bulk (B) and shear moduli (G) are given as functions of the ECs whereas in Reuss method, one assumes a uniform stress and gives B and G as function of the ECs. The average of the Voigt and the Reuss bounds are considered to be the best theoretical polycrystalline elastic modulus. These are given by –

$$B_H = (B_V + B_R) / 2 \qquad \ldots(3)$$

$$G_H = (G_V + G_R) / 2 \quad \text{…(4)}$$

According to Pugh[37], B_H/G_H can give insight to the plastic properties of metals, i.e., the metal exhibits ductility when its value of B_H/G_H is greater than 1.75, otherwise brittleness. As another elastic parameter of metals, Poisson's ratio, ν is consistent with B_H/G_H, i.e., ductile materials usually possess large ν (> 0.26). So, our results show ductile nature of BaFCl as $B_H/G_H > 1.75$ and $\nu > 0.26$ (from Table 3).

Table 3: Isotropic value of shear and bulk moduli, Young's modulus (*Y*, in GPa), poisson's ratio (*ν*), Lamé's coefficients (λ and μ, in GPa) and elastic anisotropy indices are presented

Present calculations		LDA	PBEsol	SOGGA	B3LYP
Shear modulus B	B_V	42.91	45.22	43.95	53.49
	B_R	42.79	45.22	43.73	53.42
	B_H	42.85	45.22	43.84	53.45
Bulk modulus G	G_V	22.04	24.71	25.90	26.10
	G_R	20.30	22.89	23.69	24.33
	G_H	21.17	23.80	24.80	25.21
B_H/G_H		2.326	2.208	2.005	2.425
Young's modulus Y		54.52	60.75	62.59	65.36
Poisson's ratio ν		0.29	0.28	0.26	0.30
Lamé's coefficients	λ	28.74	29.35	27.31	36.65
	μ	21.17	23.80	24.80	25.21
Elastic anisotropy indices	A_U	0.43	0.40	0.47	0.36
	A_{comp}	0.15	0.00	0.25	0.07
	A_{shear}	4.12	3.83	4.45	3.51

In addition, the Young's modulus (Y), Poisson's ratio (ν), Lamé's coefficients (λ and μ) and elastic anisotropy indices (EA) are computed using DFT-LDA and GGA (PBEsol), SOGGA and B3LYP schemes for the first time. The polycrystalline Young's modulus and the Poisson's ratio are computed from the Hill's values using the relationships,

$$Y = 9 \cdot B_H \cdot G_H / (3 \cdot B_H + G_H) \quad \text{…(5)}$$

Poisson's ratio ν measures the stability of a crystal against shear.

$$\nu = (3 \cdot B_H - 2 \cdot G_H) / 2 \cdot (3 \cdot B_H + G_H) \quad \text{…(6)}$$

The value of Poisson's ratio (ν) for covalent materials is small, nearly 0.1, but for ionic materials, it has a typical value of 0.25. In present case of BaFCl, its value lies between 0.26-0.30, which shows a strong ionic intra-atomic bonding.

Lame's coefficients are given by

$$\mu = Y / (1 + \nu)$$

and $$\lambda = \nu Y / (1+\nu)(1-2\cdot\nu) \quad \ldots(7)$$

Another interesting property is EA, which is related to different bonding character in different crystallographic directions, and correlates with the possibility to induce microcracks in materials. The following relations are used to calculate:

$$A_U = 5\cdot(G_V/G_R) + (B_V/B_R) - 6 \quad \ldots(8)$$

$$A_{comp} = (B_V - B_R) / (B_V + B_R) \quad \ldots(9)$$

$$A_{shear} = (G_V - G_R) / (G_V + G_R) \quad \ldots(10)$$

Equation (8) presents universal anisotropy index A_U; for isotropiccrystals $A_U = 0$ and deviations of A_U from zero define the extent of EA[38]. The values of A_U, A_{comp}, and A_{shear} point to considerable EA for this tetragonal phase.A_{comp},and A_{shear}helps us to estimate elastic anisotropy in compressibility andshear[39], respectively. Azero value corresponds to complete elastic isotropy while a value of 100% means the maximum elastic anisotropy. The computed valuesofA_{comp}, and $A_{shear}$for BaFCl shows large elastic isotropy in compression and slight elastic anisotropy in shear.

CONCLUSION

In this paper, the structural and elastic properties of tetragonal BaFCl have been studied using linear combination of atomic orbitals method within the density functional theory framework. LDA, GGA-PBEsol, SOGGA and hybrid of HF and DFT, i.e. B3LYP schemes of CRYSTAL09 code have been used for this study.

Computed lattice constants, structural internal parameters are in marginally good agreement with previously reported data. It was observed that BaFCl is mechanically stable, and the parameter limiting themechanical stability of this material is the shear modulus G. The obtained values show that $B_H > G_H$, which indicates that BaFBr is a ductile material. Also the value of Poisson's ratio is around 0.3 which indicates a strong ionic intra-atomic banding.

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