Chapter 180
Calculation of Elastic Properties of Titanium Fluoride Compounds—A DFT Study

R. Mariyal Jebasty and R. Vidya

Abstract In the development of strong tooth filling material one needs to understand the connection between microstructure of the material and its mechanical strength. At present, titanium fluoride has been recognized as dental material because of its compatibility in oral environment. Especially TiF_4 has gained more attention in dental fillings due to its anticaries activity. In order to elucidate its medical applications, we studied the physical properties of TiF_n (n = 2, 3 & 4) using Density Functional Theory (DFT) where Ti takes up different oxidation states for different concentrations of fluorine. Here we present the electronic structure and mechanical characteristics of TiF_n.

180.1 Introduction

Dentistry employs numerous restorative materials. Picking the most suitable restorative material with properties similar to those of natural tooth structure that can withstand the adverse conditions of the oral environment is the principal goal [1]. The essential properties of a tooth-filling material are mechanical strength, corrosion resistant, non-toxicity and compatible with oral environment. Amalgam is a touted dental filling material for its mechanical strength despite being toxic because of its cost-effectiveness. Though usage of amalgam is banned in many countries it is still used in countries like India because of low cost. The alternative restoratives such as composites, gold, and glass ionomer composite (GIC) are attractive but their cost is high. Moreover GIC fails due to its low mechanical stability. Hence the choice falls on a new material which has good mechanical strength, corrosion resistant and toxic-free. TiF derivatives are promising in this perspective as they also prevent dental caries [2]. Titanium can form as binary, ternary and quaternary fluorides [3]. Using Density Functional Theory calculations elastic properties of materials can reliably be predicted if one takes into account the

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structural relaxations along with gradient corrections in the calculations [4]. The present study is initiated to understand the change in mechanical properties with respect to the various valence states of titanium ions with fluoride ions. As a preliminary work we evaluated the mechanical stability of TiF_4 using Born elastic stability criteria [5].

180.2 Computational Methods

The elastic constants are calculated within the framework of Density Functional theory (DFT) using the stress-strain relationship implemented in Vienna Ab initio Simulation Package (VASP) with projected augmented plane-wave (PAW). Perdew-Burke-Ernzerhof (PBE) [7]—generalized gradient approximation (GGA) were used to treat the exchange-correlation effect. Before performing calculations to obtain elastic constants, the structural stability of these compounds was analyzed using complete structural optimizations by minimizing the stress and force in the crystal structures with the tolerance factor for force is nearly zero (meV/atom). More precise DFT parameters were set in order to get the accurate elastic constants. For convergence criteria of electronic relaxation we choose energy difference of 10^{-5} eV and the irreducible brillouin zone was sampled by $8 \times 8 \times 8$ grid points. The plane wave basis set with energy cut-off 550 eV was used. Successively, ionic relaxations are applied to the lattice vectors and the resulting stress tensor is calculated from DFT. Resulting 6×6 stiffness (elastic) tensor was obtained from linear elasticity (Hooke's Law), connecting stress and strain [6].

180.3 Results and Discussions

180.3.1 Structural Description

TiF_2, TiF_3, and TiF_4 take up cubic, rhombohedral, and orthorhombic lattice type, respectively. TiF_2 can be synthesized with fluorite structure (MnF_2—space group *Fm-3 m*) at high pressure. TiF_3 crystallizes in cubic structure at room temperature while it can also have the RhO_3 type structure like other trifluorides at high temperature with space group (*R-3c*). In this study we have taken the rhombohedral crystal lattice which has metal ion (Ti^{3+}) at the octahedral void site. Among the chosen compounds, the only system which crystallizes at ambient condition is TiF_4, with the structural environment of corner sharing octahedral described by the space group *Pnma*. TiF_4 contains 60 atoms in its primitive cell. The optimized structural parameters are given in Table 180.1. It shows that the equilibrium structural parameters are in good agreement with the experimental lattice parameters. The optimized crystal structures are shown in Fig. 180.1. Especially TiF_4 has highly distorted octahedron with five different bond length values for Ti–F bonds in the orthorhombic structure.

Table 180.1 Structural parameters of TiF_2, TiF_3, and TiF_4

Compounds	Lattice parameter (Å)	
	Experiment	Theory
TiF_2	$a = b = c = 5.1555$ $\alpha = \beta = \gamma = 90°$	$a = b = c = 5.1304$ $\alpha = \beta = \gamma = 90°$
TiF_3	$a = b = 4.7670$; $c = 13.9900$ $\alpha = \beta = 90°= 120°$	$a = b = 5.5709$; $c = 13.6541$ $\alpha = \beta = 90° = 120°$
TiF_4	$a = 22.8110$; $b = 3.8480$; $c = 9.5680$ $\alpha = \beta = \gamma = 90°$	$a = 23.5987$; $b = 3.9170$; $c = 9.8908$ $\alpha = \beta = \gamma = 90°$

180.3.2 Electronic Properties

The total and partial density of states have been plotted to reveal the available electronic states. A detailed analysis says that the valence band maximum of all compounds is due to the Fluorine *p*-orbital, whilst the *d*-orbital of titanium plays the dominant role in the conduction band minimum. It is clearly seen in Fig. 180.2a that no states are available at the valence band region of Ti atom, and Fluorine states alone contribute to the valence bands. In addition, the electronic states are crossing the Fermi level, indicating the metallic nature of TiF_2. Similarly, non-negligible states cross the fermi level of TiF_3 indicating its metallic character which may also cause galvanic current while used as filling material.

In contrast to TiF_2 and TiF_3, TiF_4 has large bandgap of nearly 4 eV (Fig. 180.2c) between VBM and CBM. Owing to its electrical resistivity resulting from such insulating character, TiF_4 can be considered as a suitable material for dental fillings. Also there is a degeneracy of states Ti-*d* and F-*p* states between −3 eV to 1 eV. This hybridization of Ti-*d* electrons with F-*p* electrons shows covalent nature of Ti–F bond over the ionic nature. This increased covalent character of bond can give rise to stronger bonds between Ti and F in TiF_4 compared to TiF_2 and TiF_3.

180.3.3 Mechanical Stability

We have seen in previous section that among the three compounds, TiF_4 is considered for dental filling applications. Hence we calculated the elastic tensor (stiffness) coefficients for six different finite distortions of TiF_4 using the theoretically optimized crystal structure. As orthorhombic structure contains nine independent elastic constants, nine different strains are generally needed to determine the elastic constants as described by Ravindran et al. [4]. However VASP–PAW code only uses the six finite distortions [6]. The strain values of magnitude $\delta = \{-0.01, -0.005, +0.005, +0.01\}$ was used to calculate the stress tensor. The

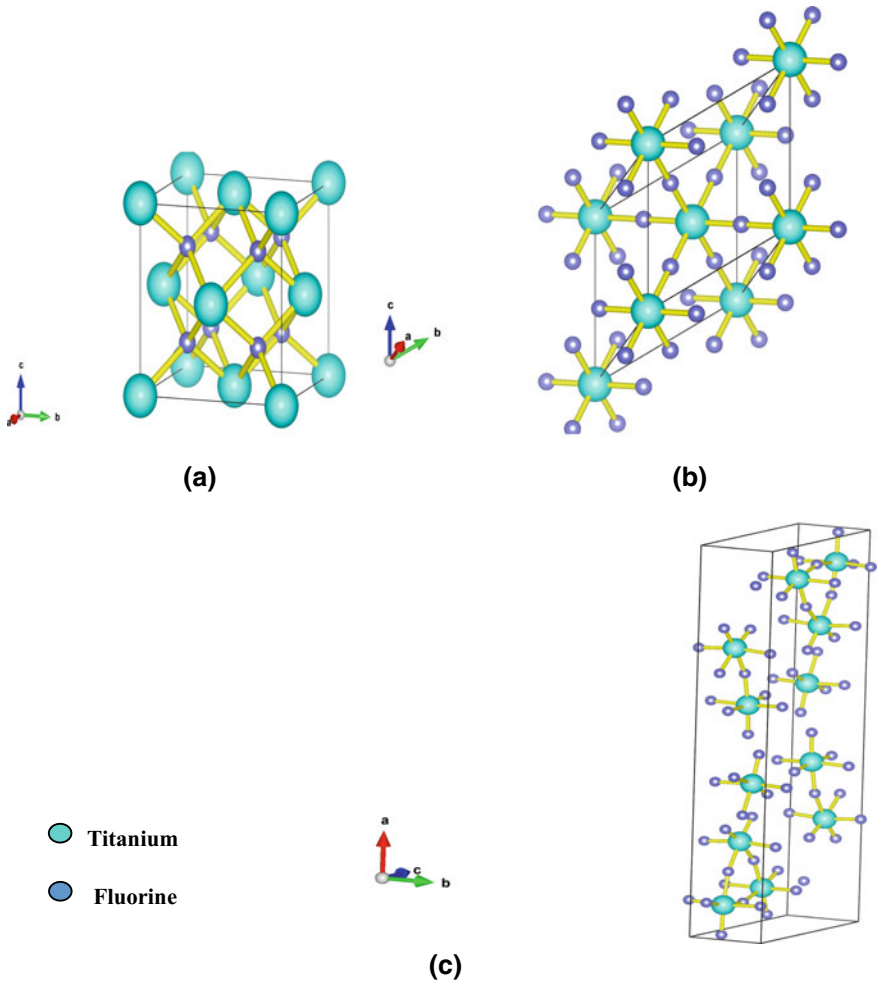

Fig. 180.1 Crystal structure of **a** TiF_2 **b** TiF_3 and **c** TiF_4 along standard orientation

elastic constants obtained from our calculation are given by 6×6 matrix. The values of these components are important because they provide the microscopic interpretation of stress in a crystal. The nine independent elastic constants for the orthorhombic crystal (TiF_4) are C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13} and C_{23} (voigt notation).

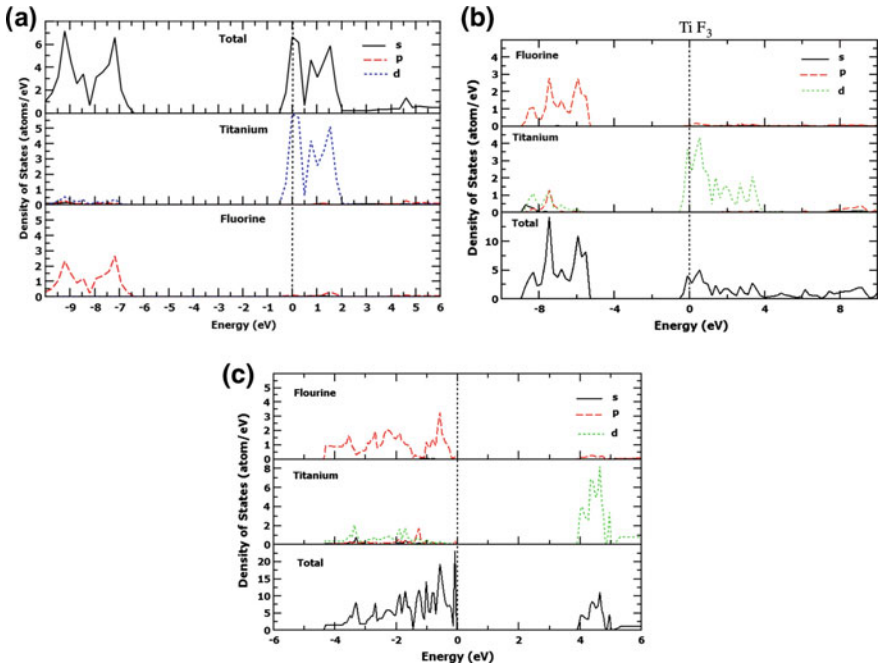

Fig. 180.2 Density of states plot of **a** TiF_2, **b** TiF_3, and **c** TiF_4

180.3.4 Total Elastic Moduli in GPa (Stiffness Tensor Matrix) C_{ij}

$$\begin{pmatrix} 33.555 & 5.230 & 7.394 & -0.0 & -0.0 & 0.0 \\ \mathbf{5.230} & 249.817 & 1.840 & -0.0 & -0.0 & 0.0 \\ 7.394 & 1.840 & 34.189 & -0.0 & 0.0 & 0.0 \\ -0.0 & -0.0 & -0.0 & 6.166 & -0.0 & -0.0 \\ -0.0 & -0.0 & -0.0 & -0.0 & 4.693 & 0.0 \\ -0.0 & 0.0 & 0.0 & -0.0 & 0.0 & 10.874 \end{pmatrix}$$

The normal strain leads to three 3×3 deformation matrices D_1, D_2, and D_3 whose linear responses are the elastic constants C_{11}, C_{22} and C_{33}, respectively. The remaining components are obtained by the shear strain and combination of other constants causing the other deformation matrices D_4, D_5 and D_6. Among all elastic constants of TiF_4, C_{22} exhibits higher value along *b*-axis, indicating that the more resistance to deformation of TiF_4. We have also calculated the Born stability parameter for all three compounds, from which we found that all TiF variants exhibit mechanical stability.

180.4 Conclusion

We have found that among the three halides TiF_2, TiF_3 and TiF_4 the desirable physical property and the mechanical stability for dental fillings is found only in TiF_4. The increased fluoride content may also play a role in preventing the tooth caries. In addition, TiF_4 exhibits the covalent nature of Ti–F bond which strengthens the material. Also the stress along *b*-axis reveals the anisotropic nature of TiF_4, turning our attention towards the shape and orientation of the filler material. This property plays a major role while the material comes into clinical usage.

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Appendix

A bench mark has been made for our calculation with elastic constants of Si for verifying our results and the error percentage was obtained as shown in the below table. An open-source online application ELATE has been used to extract elastic properties from elastic tensors [8].

Elastic constants (GPa)				Error (%)	
	Experiment	Theory			
		k-point (4 × 4 × 4)	k-point (8 × 8 × 8)	k-point (4 × 4 × 4)	k-point (8 × 8 × 8)
C_{11}	165.64	143.978	145.729	12.69	12.02
C_{12}	63.94	62.065	59.562	2.93	6.84
C_{44}	79.51	64.236	72.480	19.21	8.84
Bulk modulus *K*	97.84	89.37	88.285	8.65	9.76
Young's modulus E	165.72	136.76	148.19	17.71	10.57
Shear modulus G	68.046	54.924	60.721	19.28	10.76
Poisson's ratio *v*	0.218	0.245	0.220	−12.38	0

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