A computational approach to study the optoelectronic properties of F-BODIPY derivatives at the bulk level for photovoltaic applications

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Abstract

The Dipyrrin compounds are recognized as imminent and hi-tech organic semiconductor materials (OSMs) designed for photovoltaic applications owing to low-cost, flexible, and eco-friendly nature. In a latest study, several optoelectronic properties of conjugated F-BODIPY derivatives were studied by using the density functional theory (DFT) at (GGA/PBE) level. This analysis classifies Comp_1 (5,5-difluoro-1,3,7,9-tetramethyloctahydro-1H,5H-5l4-dipyrrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinine) as a direct band-gap semiconductor with a band-gap of 2.81 eV. The band-gap of Comp_2 (2-ethyl-5,5-difluoro-1,3,7,9-tetramethyloctahydro-1H,5H-5l4-dipyrrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinine) and Comp_3 (2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyloctahydro-1H,5H-5l4-dipyrrrolo[1,2-c:2′,1′-f][1,3,2]diazaborinine) are reduced by 1.25 and 1.09 eV, respectively in comparison with parent molecule Comp_1 owing to the influence of p-orbitals of all atoms in crystal structures. The reduction in energy and density of states (DOS) for these compounds in this study validated that band-gap could be improved to a required value for optoelectronic applications by derivatives modeling. Additionally, optoelectronic properties at the solid-state bulk level were also computed. Several features of interest at solid-state bulk level exposed the F-BODIPY derivatives as competent compounds for organic semiconductor devices applications.

1. Introduction

The small π-conjugated organic semiconductor materials (OSMs) are receiving astonishing responses from the scientific investigators currently, owing to the comparatively high stability, enriched fluorescence, rational bandgap and enhanced conductivity [1–3] which are crucial for sophisticated portable optoelectronic applications. The OSMs have become imperious by presenting distinctive functionalities and affluent uses in several high-tech fields such as photovoltaic device, light emitting diodes, thin film transistors, field effect transistors and third-order nonlinear optical application due to their prominent performance, cost-effective process, large area flexible devices, easy manufacturability and eco-friendly nature [4–11]. The direct bandgap OSMs have been of specific consideration, ever since these are proficient, quicker and trustworthy for modern optoelectronic applications [12–15] and establish many benefits above obsolete forms such as minor energy cost, and enhanced illumination capability [15–17].

OSMs using the 4,4-difluoro-4-boro-3a,4adiaza-s-indacene (F-BODIPY) [18–20] as basic skeleton accredited owing to high thermal reliability and adjustable fluorescence properties that marks F-BODIPYs essentially suitable basic chunk for OSMs. Recently F-BODIPY derivatives synthesized via a novel and enriched
scheme with Dipyrrins and Bis(dipyrrin)s and established as a decent OSMs by excellent fluorescence properties [1]. F-BODIPYs typically produced via Dipyrrin doping as its BF₃ complex by means of a reaction among BF₃·OEt₂ and NEt₃ [21, 22]. Though many F-BODIPY derivatives were reported in literature [23–25], where the capabilities for photovoltaic applications were described as well. In present investigation, the impact of ethyl group on the optoelectronic properties are explored at the solid-state (bulk) level when assigning ethyl group at positions X and Y in F-BODIPY derivatives 5,5-difluoro-1,3,7,9-tetramethyloctahydro-1H,5H-5l4-dipyrrolo[1, 2-c2',1'-f] [1–3] diazaborinine (Comp_1) leading to 2-ethyl-5,5-difluoro-1,3,7,9-tetramethyloctahydro-1H,5H-5l4-dipyrrolo[1,2-c2',1'-f] [1–3] diazaborinine (Comp_2) and 2,8-diethyl-5,5-difluoro-1,3,7,9-tetramethyloctahydro-1H,5H-5l4-dipyrrolo[1,2-c2',1'-f] [1–3] diazaborinine (Comp_3) derivative, respectively, see figure 1.

The optoelectronic properties of F-BODIPY derivatives were investigated by distinctive density functional theory (DFT) through (GGA/PBE) [26–28] level. An unchanging experimental data [1] is used to optimized these derivatives. The optoelectronic properties analytically assessed for F-BODIPY derivatives. Though numerous studies were available to examine the scopes of F-BODIPY derivatives for applications in leading-edge tools, the optoelectronic reaction of F-BODIPY derivatives in solid-state bulk level is still needed to probe. This work scrutinizes first-time optoelectronic properties at the solid-state bulk level for F-BODIPY derivatives.

2. Computational methodology

The experimental structures of Comp_1, Comp_2, and Comp_3 were copied into Materials Studio (MS) [29] for minimize of energy. The energies of crystals Comp_1, Comp_2, and Comp_3 minimized consuming same experimental lattice parameters of Comp_1 (a = 11.700 Å, b = 14.423 Å, c = 11.934 Å, α = γ = 90°, β = 38.56°) [1] with P2₁/c space group and monoclinic lattice type. In the same way for Comp_2 (a = 8.618 Å, b = 9.252 Å, c = 10.414 Å, α = 74.07°, β = 66.26° and γ = 84.45°) [1] with P-1 space group and triclinic lattice type, whereas Comp_3 (a = 9.369 Å, b = 12.21 Å, c = 8.635 Å, α = 104.02°, β = 114.14° and γ = 99.81°) [1] with P-1 space group and triclinic lattice type. The optoelectronic properties have been computing employing the CASTEP [30] as presented in MS [29]. The GGA/PBE [31] is utilized to deal with the exchange and correlation potential/ energy. The energies of Comp_1, Comp_2, and Comp_3 minimalized via cutoff energies of 380 eV.

The integration of Brillouin Zone (BZ) is done by adopting the Monkhorst-Pack special k-point approach [32]. The plane-wave expansion with optimized cutoff energy of 330 eV is used to automatically generates the Fast Fourier Transform (FFT) grid (54 × 72 × 54), (40 × 45 × 48) and (45 × 60 × 40) for Comp_1, Comp_2 and Comp_3, respectively. The reciprocal space and density mixing technique are utilized by choosing the Ultra-soft Pseudo-potential and electronic minimization method. The energy convergence is used by program’s fine to generate the k-point mesh for Monkhorst-Pack grid at (2 × 2 × 2) for Comp_1, Comp_2 and Comp_3, respectively. The energy of the three molecular crystals under study is minimized through the Broyden-Fletcher-Goldfarb-Shanno (BFGS) hessian updated scheme [33]. The following threshold has been

Figure 1. The schematic diagram of Comp_1, Comp_2, and Comp_3 structures with molecular labeling; however, the H atoms omitted for clarity.
Comp display the static Table 1 and 3.1. Optical properties 3. Results and discussion 

used for the converged structure as: the self-consistent field (SCF) converged tolerance is \(2.0 \times 10^{-6}\) eV/atom; the energy change tolerance is \(1.0 \times 10^{-5}\) eV/atom; the root mean square (RMS) force on atom tolerance is \(0.03\) eV Å; RMS displacement of atoms is 0.001 Å and RMS stress is 0.05 GPa. The optimized structures of Comp_1, Comp_2, and Comp_3 with minimized energy are shown in figures S1–S3 is available online at stacks.iop.org/MRX/6/125110/mmedia of supporting information, respectively.

3. Results and discussion

3.1. Optical properties

3.1.1. Dielectric function

Table 1 and figure 2 demonstrates real and imaginary dielectric functions \((\varepsilon_1\) and \(\varepsilon_2\)) of Comp_1, Comp_2, and Comp_3. The \(\varepsilon_1\) unveils high peaks in the small energy value among 1 to 3 eV as 4.48, 3.30, and 5.42 for Comp_1, Comp_2, and Comp_3, respectively. The Comp_1, Comp_2, and Comp_3 crystal structures displayed the static \(\varepsilon (\varepsilon (0))\) driven from the real part of dielectric function as 3.27, 2.66 and 4.01 in (010) direction, respectively. The \(\varepsilon (0), \varepsilon_1\) (max) and \(\varepsilon_2\) (max) has been summarized in table 1. The Comp_3 displayed larger \(\varepsilon (0)\) and \(\varepsilon_1\) follows by Comp_1 and Comp_2, which reveals that the polarizability is higher in Comp_3 among three studied compounds hence would be good to transport the electron through the crystal. The \(\varepsilon (0)\) at zero photon energy having excellent values disclosed the substantial aptitude for optical transitions of electron through the crystals of these compounds.

The (010) direction is dominating \(\varepsilon_2\) for all compounds, while Comp_3 (5.12) poses greater \(\varepsilon_2\) as compared to Comp_1 (3.9) and Comp_2 (2.5). The distribution of \(\varepsilon_2\) designate electron transitions (optical transitions) between valance bands and conduction bands as well as the transitions within the valance band from lower energy to higher energy states. The figure 2 indicates that the optical transitions in the \(F\)-BODIPY derivatives mainly occurs in the visible range of electromagnetic spectrum. The compounds Comp_1, Comp_2, and Comp_3 with these values of dielectric functions revealed that these compounds might be worthy for charge transport inside the crystals.

3.1.2. Conductivity

The real and imaginary parts of conductivity \((\sigma_1\) and \(\sigma_2\)) have been presented in figure 3. The \(\sigma_1\) is evaluated as 1.0, 0.87 and 1.22 in (010), (100) and (010) directions, respectively, for Comp_1, Comp_2, and Comp_3. The major curves were perceived between 1 to 8 eV for \(\sigma_1\) of Comp_1, Comp_2, and Comp_3 that collapse to lowest
power swiftly at 10 eV, though displaying some little peaks among 10 - 15 eV. The $\sigma_1$ for Comp_1, Comp_2, and Comp_3 presenting identical conductivity afterward 16 eV having nil strength. The unchanged spectra disclosed the decent chemical strength of F-BODIPY derivatives that were ultimately originating huge ability for electron transference in the crystal, illuminating improved charge transport in the F-BODIPY derivatives.

3.1.3. Refractive indexes and extinction co-efficient
Calculated highest refractive indexes ($n$) are 2.16, 1.84, and 2.38 for the studied compounds in (010) direction have been demonstrated in figure 4. The computed $n$ is clarifying that Comp_1, Comp_2, and Comp_3 would be superior to deflect a photon at minor energies. The Comp_1, Comp_2, and Comp_3 display decent $n$ at smallest energy between 0 to 3 eV, hitherto the spectra began tumbling after 5 eV and made unaffected spectra of same power afterward 7 eV. The figure 4 exposed that these compounds would be capable for generating decent yields at smaller energy responses of 3 eV.

3.1.4. Reflectivity and energy loss function
The reflectivity for Comp_1, Comp_2, and Comp_3 has been computed and presented in figure 5 to explore these compounds precisely. The Comp_1, Comp_2, and Comp_3 revealed higher reflectivity as 0.224, 0.148 and 0.314, respectively, that grows amongst 1 to 4 eV in the (010) direction, respectively. The Comp_1, Comp_2, and Comp_3 demonstrate peaks at lesser energy in reflectivity spectra, then starts to grasp identical heights successively after 9 eV as might be seen in figure 5. These values of reflectivity unveil that these compounds might be effective for OPV applications at lower energy. The energy loss function is a crucial feature that reveals the loss of electron energy when traveling within the compound [34–36]. The loss function for studied compounds is presented graphically via figure 5. The loss function is assessed as 2.10, 1.32, and 1.99 in (010) direction amongst 2 to 6 eV. The utmost values of loss function interrelated to the swift decay of reflectivity.

Figure 3. The real and imaginary parts ($\sigma_1$ and $\sigma_2$) of conductivity against photon energy of Comp_1 (left), Comp_2 (center) and Comp_3 (right). The black, red and blue lines represent the (100), (010) and (001) directions, respectively, whereas the solid and dotted lines corresponds to real and imaginary parts of conductivity, respectively.

Figure 4. The refractive index ($n$) / extinction coefficient ($k$) against photon energy of Comp_1 (left), Comp_2 (center) and Comp_3 (right). The black, red and blue lines represent the (100), (010) and (001) directions, respectively, whereas the solid and dotted lines represent the ‘n’ and ‘k’, respectively.
3.1.5. Absorption
We calculate the absorption wavelengths for Comp$_1$, Comp$_2$, and Comp$_3$ molecular crystals and displayed in figure 6. It is clear from figure 6 that Comp$_3$ exhibited the uppermost intensity for the absorption in comparison to Comp$_1$ and Comp$_2$. The Comp$_1$ revealed main peaks at 203, 212 and 202 nm, while displaying some major peaks with higher wavelengths at 502, 501 and 521 nm in (100), (010) and (001) directions, respectively. The most significant absorption for Comp$_2$ is at 202, 203 and 202 nm along (100), (010) and (001) directions, whereas the (100) and (010) directions showing the second peaks at 522, and 525 nm, respectively. Similarly, the Comp$_3$ displayed the maximum absorption peaks at 208, 241 and 203 nm in (100), (010) and (001) directions, respectively, while (010) direction displayed second major peak at 502 nm.

3.2. Electronic properties
The electronic properties are equally essential to estimate the charge transport capability of OSMs.

3.2.1. Density of states (DOS)
TDOS and PDOS have estimated for Comp$_1$, Comp$_2$, and Comp$_3$ crystals to distinguish electronic properties and displayed in figures 7 and 8. The contribution of carbon (C), nitrogen (N), flurin (F) and boron (B) atoms in the formation of PDOS has shown in figure 8 for Comp$_1$; whereas for Comp$_2$ and _3, the involvement from C, N, F and B atoms have shown in Figures S4 and S5 of supporting information. A careful inspection of figure 7 displays the impact of $s$- orbitals are leading in lowermost energy states; however, it is almost immaterial in high energy levels. Conversely, the input of $p$-orbitals is considerably excessive for higher energy states that are perhaps due to the valance electronic behavior of $p$-orbitals contributions. For Comp$_1$, $s$-orbitals denote the energy bands in the lower valance bands (VB) from $-7$ to $-3.5$ eV, though, no partaking in conduction bands (CB) clarifying the minor effect of $s$- orbitals in electro-optical properties. The $p$-orbitals control the TDOS along-with the PDOS in VB and CB. The TDOS displays the domination of $p$- orbitals adjacent the Fermi level of Comp$_1$. Similarly, the participation from $s$- and $p$-orbitals have been originated for the Comp$_2$ and Comp$_3$. The evaluation of electronic outline reveals that these compounds might be a consequent competitor for OPV applications having remarkable electro-optical properties.

3.2.2. Electronic band structure
The electronic band structure for studied compounds has been evaluated at GGA/PBE level of DFT in BZ at the symmetrical point as revealed in figure 9. The zoomed energy spectra of studied compounds can be found in figure 10 for a more precise idea of the bandgap. The TDOS and PDOS have been revealed in figures 7 and 8 for total energy states that expressed a vibrant involvement in the electro-optical properties of a OSMs. The electronic band structures of Comp$_1$, Comp$_2$, and Comp$_3$ adjacent to Fermi level are shown in figure 9 to...
Figure 6. The absorption spectra against wavelength of Comp_1 (top left), Comp_2 (center left) and Comp_3 (bottom left), while the absorption spectra against photon energy of Comp_1 (top right), Comp_2 (center right) and Comp_3 (bottom right). The black, red and blue lines represent the (100), (010) and (001) directions, respectively.

Figure 7. Total density of states (TDOS) and partial density of states (PDOS) against photon energy of Comp_1 (left), Comp_2 (center) and Comp_3 (right). The black and red lines represent the contributions from $s$-orbitals and $p$-orbitals, whereas blue lines represent the total density of states, respectively.
clarify bandgap explicitly. The figures 9 and 10 revealed that the valance band maxima (VBM) of Comp_1 produced at B- point in BZ, however conduction band minima (CBM) is too initiated at B- point, enlightening that Comp_1 unveils direct bandgap as 2.81 eV at B. The VBM of Comp_2 is generated at point E-point, whereas the CBM is at Y-point revealing the fact that Comp_2 unveiled an indirect bandgap of 1.56 eV from E to Y symmetrical point. Similarly, a careful analysis of Comp_3 band structure profile indicates that it has a direct bandgap of 1.78 eV at G symmetrical point as can be seen from figures 9 and 10.

4. Conclusions

Hence the analysis at the bulk level, we found the following fascinating findings in this study. The static dielectric functions at 0 eV with exceptional values revealed remarkable capability for electron transportation in the crystals of F-BODIPY derivatives. The imaginary dielectric function specifies the transmission of an electron from VB to CB. These outcomes verified that Comp_1, Comp_2, and Comp_3 may be superior for charge transport inside the crystals.

The unchanged spectra of conductivity disclosed the decent strength of Comp_1, Comp_2, and Comp_3 that ultimately originating enormous capability for conducting the electrons through the crystals. The calculated refractive indexes are enlightening that Comp_1, Comp_2, and Comp_3 might be worthy of refracting a photon at minor energy. The smaller reflectivity finds that F-BODIPY derivatives might be proficient compounds for OPV application.

Our evaluation demonstrates that F-BODIPY derivatives unveiled the bandgap of scale 2.81, 1.56, and 1.78 eV, respectively. The exploration of electronic configuration establishes that F-BODIPY derivatives having remarkable electro-optical properties might be a successive candidate for OPV application. These features at bulk level disclosed that F-BODIPY and its derivatives might be efficient materials and for multifunctional organic microelectronic applications.
Figure 9. The electronic band structure along with $Z\rightarrow G\rightarrow Y\rightarrow A\rightarrow B\rightarrow D\rightarrow E\rightarrow C$ for crystals of Comp$_1$ (top), Comp$_2$ (center) and Comp$_3$ (bottom) are schematically shown.
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Figure 10. The zoomed spectra for electronic band structure along the Z—G—Y—A—B—D—E—C direction of BZ for Comp_1 (top), Comp_2 (center) and Comp_3 (bottom) are schematically shown. The arrows displaying the nature of direct and indirect bandgap of Comp_1 (top), Comp_2 (center) and Comp_3 (bottom).
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References

[1] Lundrigan T et al 2012 An improved method for the synthesis of F-BODIPYs from dipyrins and bis (dipyrin) a Org. Lett. 14 2158–61
[2] Beh M H R, Douglas K I B, House K T E, Murphy A C, Sinclair J S T and Thompson A 2016 Robust synthesis of F- BODIPYs Organic & Biomolecular Chemistry 14 11473–9
[3] Smithen D A, Baker A E, Offman M, Crawford SM, Cameron T S and Thompson A 2012 Use of F-BODIPYs as a protection strategy for dipyrins: optimization of BE2 removal The Journal of Organic Chemistry 77 3439–53
[4] Kwon J, Takeda Y, Shiwaku R, Tokito S, Cho K and Jung S 2019 Three-dimensional monolithic integration in flexible printed organic transistors Nat. Commun. 10 54
[5] Lüssem B 2019 Beyond 100% doping efficiency Nature Materials 18 93–4
[6] Li M et al 2019 Performance optimization of dye-sensitized solar cells by gradient-ascent architecture of SiO2@Au@TiO2 microspheres embedded with Au nanoparticles Journal of Materials Science & Technology 35 604–9
[7] Lee J H et al 2019 Effect of crystallization modes in TIPS-pentacene/insulating polymer blends on the gas sensing properties of organic field-effect transistors Scientific Reports 9 21
[8] Li J et al 2019 Band-like crystallization in small-molecule thin films toward high mobility and ultrahigh detectivity phototransistor arrays Nat. Commun. 10 12
[9] Jia X, Fuentes-Hernandez C, Wang C-Y, Park Y and Kippelen B 2018 Stable organic thin-film transistors Science Advances 4 eaao1705
[10] He W and Ye C 2015 Flexible transparent conductive films on the basis of Ag Nanowires: design and applications: a review Journal of Materials Science & Technology 31 581–8
[11] Zhou JH, Wang Y X, Chen XT, Song Y L, Weng L H and You X Z 2002 Synthesis, structure and third-order nonlinear optical properties of a planar nickel complex with rigid quadridentate Schiff base derived from S-benzyl dithiocarbazate Chin. J. Inorg. Chem. 18 533–6
[12] Bang D et al 2014 Novel wide band-gap polymer utilizing fused hetero-aromatic unit for efficient polymer solar cells and field-effect transistors Polymer 55 6708–16
[13] Kroger M, Hamwi S, Meyer J, Riedl T, Kowalsky W and Kahn A 2009 P-type doping of organic wide band gap materials by transition metal oxides: a case-study on Molybdenum trioxide Org. Electron. 10 932–8
[14] Li W et al 2014 Wide band gap diketopyrrolopyrrole-based conjugated polymers incorporating biphenyl units applied in polymer solar cells Crystallization. 50 679–81
[15] Wang Q, Sun B and Azzi H 2014 Exciton–polaron-induced aggregation of wide-bandgap materials and its implication on the electroluminescence stability of phosphorescent organic light-emitting devices Adv. Funct. Mater. 24 2975–85
[16] Gidron O, Kadovan A, Sheynin Y, Bendiok M and Perepichka D F 2012 Towards “green” electronic materials. a-Oligofuranos as semiconductors Chem. Commun. 47 1976–8
[17] Gidron O et al 2013 Oligofuran-containing molecules for organic electronics Journal of Materials Chemistry C 1 4538–67
[18] Benstead M, Mehli G H and Boyle R W 2011 14, 4’-Diﬂuoro-4-bora-3a,4a-diaza-s-indacenes (BODIPYs) as components of novel light active materials Tetrahedron 20 3573–601
[19] Loubet A and Burgess K 2007 BODIPY dyes and their derivatives: syntheses and spectroscopic properties Chem. Rev. 107 4891–932
[20] Ziesler R, Ulrich G and Harriman A 2007 The chemistry of bipyrid: a new El Dorado for ﬂuorescence tools New J. Chem. 31 496–501
[21] Wood T E, Uddin MJ and Thompson A 2010 The synthesis and properties of dipyrins Handbook of Porphyrin Science (Volume 8) With Applications to Chemistry, Physics, Materials Science, Engineering and Biology (8) ed K M Kadish, K M Smith and R Guilard 8 (USA: World Scientific) 4 235–91 (https://www.worldscibooks.com/10.1142/7752-vol8#toc)
[22] Wood T E and Thompson A 2007 Advances in the chemistry of dipyrins and their complexes Chem. Rev. 107 1831–61
[23] Bura T et al 2012 High-performance solution-processed solar cells and ambipolar behavior in organic field-effect transistors with Thienyl-BODIPY scaffolds J. Am. Chem. Soc. 134 17404–7
[24] Crawford SM and Thompson A 2011 Investigations into the nucleophilic meso-substitution of F-BODIPYs and improvements to the synthesis of 4, 4'-difluoro-4-bora-3a, 4a-diaza-s-indacene Heterocycles 83 311–22
[25] Crawford SM and Thompson A 2010 Conversion of 4, 4'-Difluoro-4-bora-3a, 4a-diaza-s-indacenes (F-BODIPYs) to dipyrins with a microwave-promoted deprotection strategy Org. Lett. 12 1424–7
[26] Giese TJ and York DM 2010 Density-functional expansion methods: evaluation of LDA, GGA, and meta-GGA functionals and different integral approximations J. Chem. Phys. 133 244107
[27] Shapley W A and Chong DP 2001 PW86–PW91 density functional calculation of vertical ionization potentials: Some implications for present-day functional methods Int. J. Quantum Chem. 81 34–52
[28] Perdew JP, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865
[29] Materials Studio. 2013 Version 7.0 (San Diego, CA: Accelrys Software Inc.)
[30] Clark SK et al 2005 First principles methods using CASTEP Zeitschrift für Kristallographie- Crystalline Materials 220 567–70
[31] Perdew JP, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8
[32] Monkhorst H J and Pack J D 1976 Special points for Brillouin-zone integrations Physical Review B 138 5186–92
[33] Press WH, Teukolsky SA, Flannery BP and Greenwell Yanik E 1994 Numerical recipes in fortran–the art of scientiﬁc computing SIAM Rev. 36 149–149
[34] Fabricius G, y Blanca E P, Rodriguez P, Ayala A, De la Presa P and Garcia A L 1997 Electronic structure of cubic SrHfO3: ferroelectric stability and detailed comparison with SrTiO3 Phys. Rev. B 56 164
[35] Luo B, Wang X, Zhang Y and Xia Y 2012 First principles study of structural, electronic and optical properties of Pb doped SrHfO3 Mater. Chem. Phys. 133 857–62
[36] Liu H, Liu Z-T, Ren J and Liu Q-J 2017 Structural, electronic, mechanical, dielectric and optical properties of TiSiO4 first-principles study Solid State Commun. 251 43–9