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Optical properties of orthovanadates, and periodates studied from first principles theory

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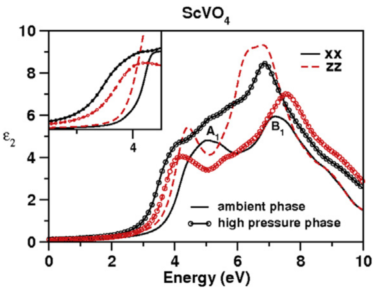
HIGHLIGHTS

- Orthovanadates, periodates are insulators.
- Band gap decreases with decrease in the cation size, and also moving to high pressure phase.
- Orthovanadates are better host scintillators than periodates.
- Orthovanadates can be better used as host scintillators in the high pressure phase.

GRAPHICAL ABSTRACT



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ABSTRACT

Detailed ab-initio studies on electronic structure and optical properties have been carried out for orthovanadates, and periodate compounds, $ScVO_4$, YVO_4, $LuVO_4$, and $NaIO_4$, KIO_4, $RbIO_4$, $CsIO_4$ based on the Full potential linearized augmented plane wave method within the frame work of Density Functional Theory using Tran and Blaha modified Becke–Johnson potential (TB-mBJ). We have compared the optical properties of orthovanadates with periodates, and also with its high pressure phase. The main difference observed in moving from orthovanadates to periodates is the increase in band gap, and bands turn out to be less dispersive. By considering all these facts, we predict orthovanadates to be better scintillators than periodates, which is well explained from the band structure, and optical properties calculations. In addition, we also compared the optical properties of orthovanadates at ambient, and high pressure and we observed a decrease in the band gap of orthovanadates, increase in valence band width at high pressure when compared to ambient phase. Tuning the band gap, which is an important criteria for scintillators, can be observed in orthovanadates by decreasing the cation size, and also by moving to the high pressure scheelite phase. High pressure phase of orthovanadates might be more favourable as the zircon to scheelite transition is irreversible, and the transition pressure is also less around 8 GPa.

1. Introduction

ABO_4 type ternary oxide compounds are important because of their wide range of applications as laser host compounds, catalyst, polarizer, phosphors, scintillators, field emission display, nuclear-waste storage medium, optical isolators, circulators, beam displacers, oxidizers etc. [1]. The main goal of this paper is to explore these ABO_4 type scintillator host compounds, which mainly focusses on orthovanadates, and periodates. Most of the orthovanadates crystallize in tetragonal zircon-type structure consisting of isolated VO_4 tetrahedra surrounding the A atom forming AO_8

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dodecahedra [2]. With the increase in the radius of the cation, these compounds crystallize in monazite structure rather than zircon. The zircon type structure is preferred over monazite structure because of the increased radiative transitions. These are good host compounds which emit colours with the addition of suitable dopant's. Among them, YVO_4 is one of the widely used optical material as it possess small radii and can emit variety of colours with doping [3]. Zuocai et al. [4] synthesised, studied the structural, elastic, lattice dynamical properties of both the phases of YVO_4 [5,6], and reported the dynamical stability of these two phases, where scheelite is more optically isotropic than zircon structure. At high pressure, these orthovanadates undergo phase transition from scheelite to further low symmetric monoclinic phase. Spectroscopic properties of $LuVO_4$ under high pressure have been studied and phase transitions are reported from zircon → scheelite → monoclinic structures at 8 GPa, 16 GPa respectively [7]. The electronic structure of zircon-type orthovanadates under pressure was investigated and it was reported that cation substitution influence the electronic states [8]. Red shift of the vanadate band gap observed with the cation substitution, further results in decrease of the band gap as observed with the Bi doping in these orthovanadates [9,10]. Errandonea et al. [2] studied the transition pressure of ABO_4 orthovanadates, and found it to be in the range of 7–8 GPa independent of cation size, and also observed two transitions i) zircon → scheelite ii) scheelite → monazite but in the case of $ScVO_4$ only first transition is observed, whereas in the case of $EuVO_4$, $LuVO_4$, both the transitions are observed. First transition i.e. from zircon to scheelite is an irreversible process, while the second (scheelite to monazite) one is reversible. Irreversible transition from zircon to scheelite is also observed by other groups [11,6]. It is well known that across the phase transition, electronic structure and optical properties changes quite significantly as seen for example in $TbVO_4$, $DyVO_4$, where the transmission changes from colourless to yellow, and also absorption edge decreases [12]. Similarly in YVO_4 absorption edge shift from 3.87 to 2.77 eV at 7.5 GPa indicating the importance of these properties [13].

In addition, we have also studied XIO_4 compounds ($X = $ Na, K, Rb, and Cs), which are good oxidizing agents. Perchlorates are used in pyrotechnics, but they are targeted for elimination because of environmental and health issues, and these can be replaced by the periodates which are less toxic. Periodates can also be used in explosives, which contain a mixer of fuels and oxidizer's. Secondary explosives generally have oxygen deficiency, which restrict the heat release. Addition of oxidizing agents in proper proportions to these explosives increases the combustion of explosives, resulting in large amount of energy release. These compounds decompose at high temperature and produce oxygen making them to act as good oxidizing agents. Periodates replaces perchlorates with less toxicity, and more thermodynamic stability [14,15]. These can also be used as nano energetic gas detectors, for gas generation, as conduction salts [16], and also find illumination application. $RbIO_4$ show pressure induced phase transition at 5.3 GPa, 7.2 GPa, where the former is the transition from scheelite to pseudoscheelite, while latter denotes the transition from pseudoscheelite to wolframite. At 7.2 GPa, it will change the colour to brownish black. Transition pressure from pseudoscheelite to wolframite phase increases with increasing ionic radius. At still higher pressure around 18.3 GPa, it further transform to still dense complex structure [17]. KIO_4 also undergo a phase transition at 6.5 GPa which is completed at 9.8 GPa [18]. Pressure induced phase transitions were observed in $CsIO_4$ at 1.5, 4.5, and 6.2 GPa. Transition at 1.5 GPa involve tilting of IO_4 tetrahedral unit, while at 4.5 GPa, 6.5 GPa transitions take place from pseudosheelite to wolframite, and wolframite to lower symmetric complex denser structure respectively. Temperature induced phase transition is also observed in $CsIO_4$ at around 423 K, where it transforms from orthorhombic to tetragonal scheelite phase [19]. These composites are very sensitive to the external impact or friction.

There are numerous experimental and theoretical studies available on the structural phase transition under pressure on these compounds [2,3,5,7,11,17–23], but there are only very few studies available regarding the optical properties. The optical properties calculations are important for scintillators in order to optimize their performance and also to develop new scintillaing materials. Here we are interested in studying, and comparing the optical properties of orthovanadates with periodates and also with its high pressure phase based on the electronic structure. In the case of periodates, calculations were performed only at ambient phase due to lack of structural information regarding the high pressure phase. To the best of our knowledge, no experimental or theoretical studies are available on the electronic structure and optical properties of periodates.

2. Computational details

All electron Density Functional Theory calculations have been performed in order to study the electronic structure and optical properties of orthovanadates, periodates using the Full potential linearized augmented plane wave method (FP-LAPW) implemented in wien2K code [24,25]. FP-LAPW is an accurate method to calculate the optical properties. In this method, each atom is surrounded by the muffin tin sphere, and the unit cell of the crystal is partitioned into atomic sphere region, and interstitial region. Atomic sphere region is expanded in terms of spherical harmonics up to $l_{max} = 10$, as atomic like wave function, while the interstitial region can be expanded through the plane wave basis with wave vector cut-off of K_{max}. We have used the R_{MT} K_{max} value to be 9, where R_{MT} is the smallest muffin tin radii, K_{max} is the plane wave cut-off. All the calculations were carried out at the corresponding experimental lattice constant with relaxed internal atomic positions by using the Perdew-Burke-Ernzerhof generalized gradient approximation [26] for exchange-correlation functional at ambient as well as at high pressures. Tetrahedron method is used to integrate the Brillouine zone. We have checked for the k-point convergence and 13 × 13 × 5 k-mesh with 147 k-points in Irreducible Brillouin zone (IBZ) is used for $CsIO_4$, 10 × 10 × 10 k-mesh with 102 k-points, 144 k-points in the IBZ for zircon and scheelite structure respectively. It is well known that band gap values calculated using the standard exchange-correlation functionals is usually underestimated compared with that of experimental band gap. So in the present calculations, we have used Tran and Blaha modified Becke–Johnson potential (TB-mBJ) [27,28], which is computationally less expensive compared to GW calculations and give comparable experimental band gap values. The calculated optical spectra depends strongly on the BZ sampling, so we increased the k-mesh for the optical properties calculations to 17 × 16 × 6 with 324 k-points in the IBZ for $CsIO_4$, 17 × 17 × 17 k-mesh with 405 k-points, 657 k-points in IBZ for zircon and scheelite phases of all the compounds respectively.

3. Results and discussions

3.1. Crystal structure

Orthovanadates crystallize in zircon-type tetragonal structure at ambient phase with space group $I4_1/amd$, and at high pressure, distortions lead to scheelite type tetragonal structures with space group $I4_1/a$. Lattice parameters of these compounds increases with increase in the cation size in the following sequence

$ScVO_4 < LuVO_4 < YVO_4$ [29]. Both the phases consists of VO_4 tetrahedra and AO_8 dodecahedra, but they differ by the way these polyhedra are connected, and the cation (M(Sc, Y, and Lu)) is in the S_4 symmetry in scheelite phase, D_{2d} in zircon phase. Among the periodates $NaIO_4$ [35], KIO_4, and $RbIO_4$ [36] crystallize in the scheelite crystal structure, while $CsIO_4$ [36] crystallizes in orthorhombic crystal structure.

3.2. *Orthovanadates*

Transition from zircon to scheelite phase may be due to the symmetry change, increase in bond lengths, electron localization, and these will be reflected in the band structure calculations with the reduction in band gap. A similar change i.e. reduction in the band gap is observed in the $PbWO_4$ near the phase transition [30]. We have performed the electronic structure calculations and the corresponding band structure at ambient and high pressure along the high symmetry directions are shown in Fig. 1. From the band structure plots, we can see that the bands are dispersive, which indicate the high mobility of carriers leading to better transport of carriers towards the activators, which enable them to be good host compounds. These compounds are insulators, and the calculated band gap values are shown in Table 1 at ambient as well as at high pressure phase along with the available experimental and other theoretical values, and our calculated values are in good agreement with these values. Band gap values are increasing from $ScVO_4$ to $LuVO_4$ at ambient phase. A similar trend is observed for $ScPO_4$, YPO_4, and $LuPO_4$ [32]. The band gap values are similar for YVO_4, $LuVO_4$ because of their similar cation size. At high pressure phase, these values increases from $ScVO_4$ to YVO_4 followed by a decrease in $LuVO_4$. The band gap follows the trend of cation size i.e. with the increasing cation size, band gap also increases. Bonding nature of these compounds are studied from the electron charge density difference plots as shown in Fig. 10(a), (b) at ambient and high pressure phase along (0 1 0) directions respectively. The plots clearly indicate the covalent nature of V–O bond, the ionic nature of

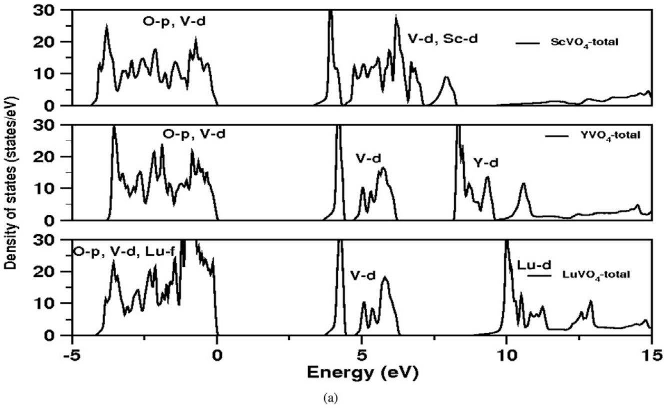
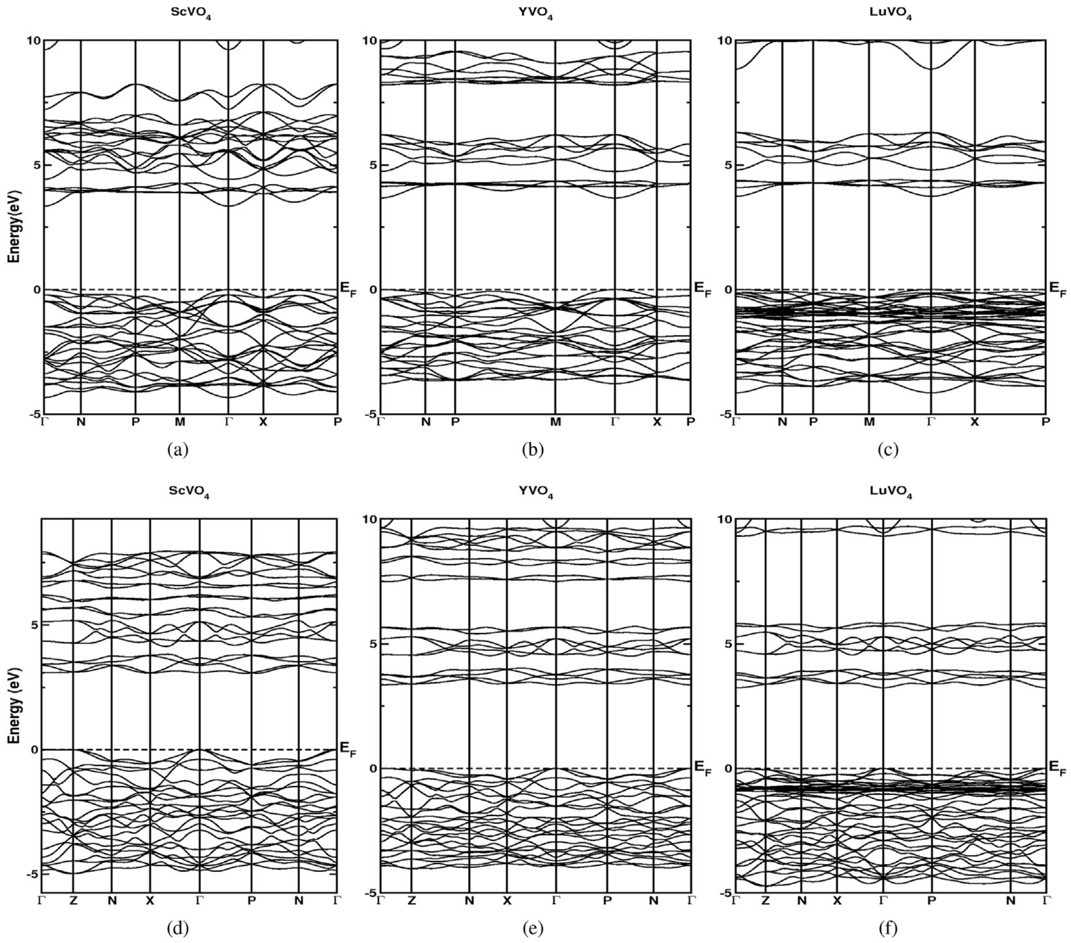


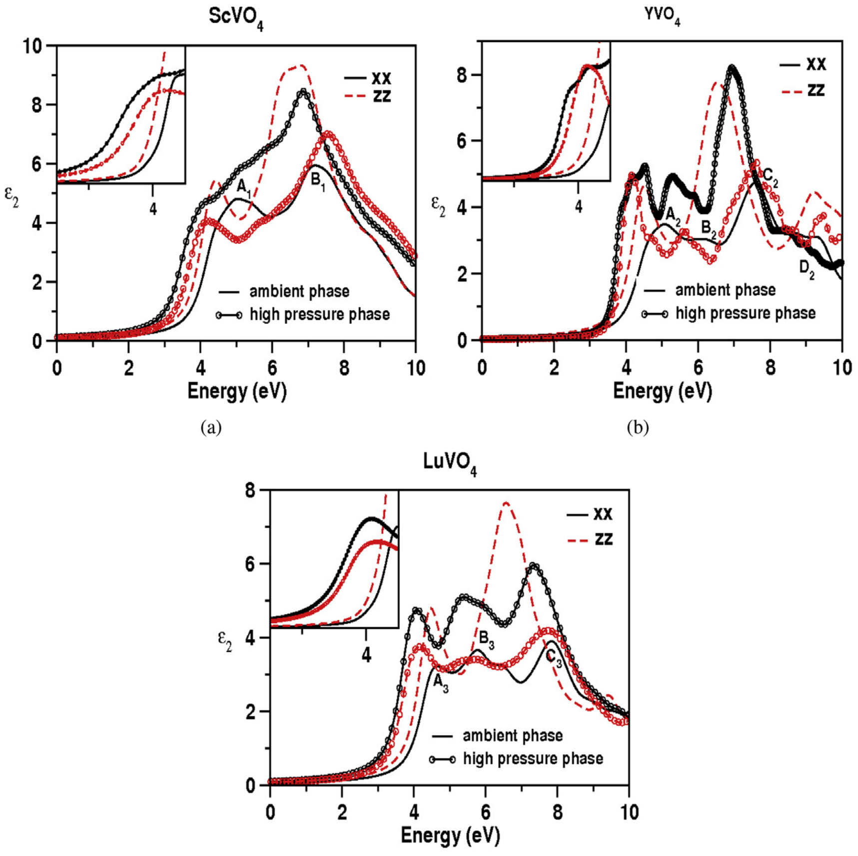
Fig. 2. Density of states of $ScVO_4$, YVO_4, and $LuVO_4$ at ambient using TB-mBJ functional.



(a) (b) (c)

(d) (e) (f)

Fig. 1. Calculated band structure of $ScVO_4$, YVO_4, and $LuVO_4$, (a), (b), (c) at ambient, (d), (e), (f) at high pressure phase respectively using TB-mBJ functional.



(a)

(b)

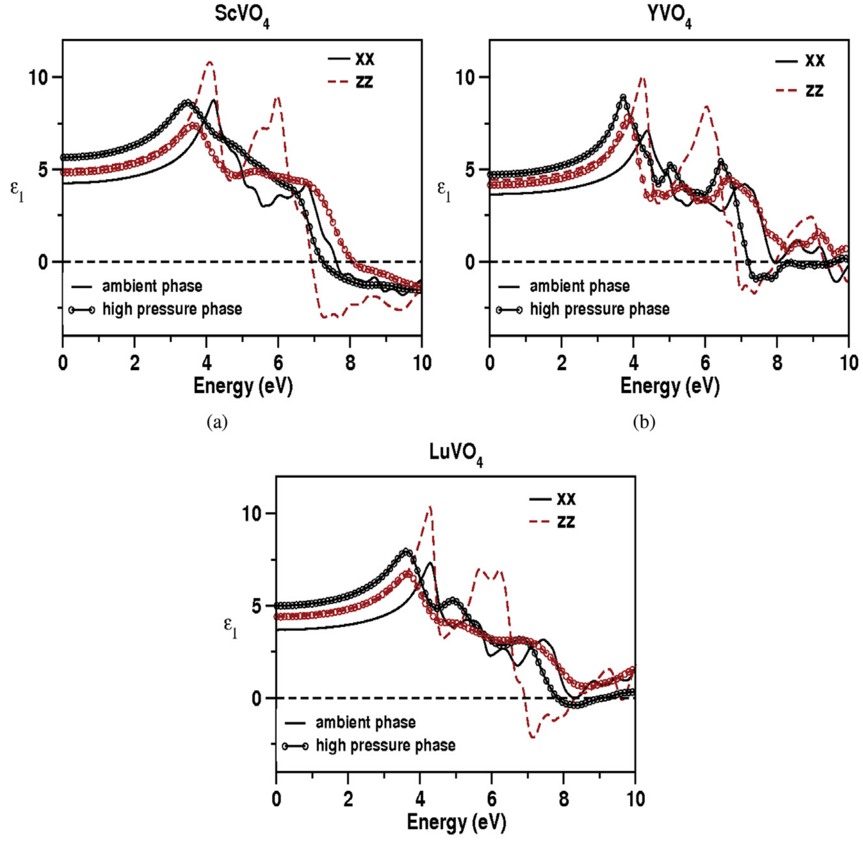
(c)

Fig. 3. Calculated imaginary part of dielectric function of (a) $ScVO_4$, (b) YVO_4, and (c) $LuVO_4$ at ambient and at high pressure phase. Inset shows the spectra to shift to lower energy regions moving from ambient to high pressure phase.

Sc—O bond. This is also observed from the bond lengths, where the bond length of V—O is shorter than the M—O(M—Sc, Y, and Lu) bond length indicating covalent nature of V—O, ionic nature of M—O bonds, and similar results were also observed by Zhang et al. [33].

From the band structure calculations, it is clear that all the orthovanadates are insulators with direct band gap, where the valence band maximum, and conduction band minimum occurs at the Γ point except for $ScVO_4$ in the high pressure phase where it is an indirect band gap insulator. The width of the valence band decreases from Sc to Y followed by an increase in Lu for both the phases i.e. valence band width increase with decrease in the cation size. The Density of States (DOS) of these orthovanadates are shown in Fig. 2. The major contribution to the valence bands are from O-p, V-d states with less hybridization of O-s states, and additional Lu-f states are present in the case of $LuVO_4$. Valence band width of these compounds are 4.4, 5.0, 3.8, 4.0, 4.2, and 4.8 respectively for $ScVO_4$, YVO_4, and $LuVO_4$ at ambient and high pressure, which is found to decrease with increase in the cation size. Conduction band is of V-d, M-d (M = Sc, Y, Lu) states, with the lower part of the conduction band being dominated by V-d states, and the upper part of conduction band by M(Sc, Y, Lu)-d states. The energy difference between the lower and upper conduction bands increases from Sc to Lu in both the phases. It is interesting to note that the valence band width increases, band gap decreases from zircon to scheelite phase indicating the increase in the number electron—hole pairs available for scintillation from ambient to high pressure scheelite phase.

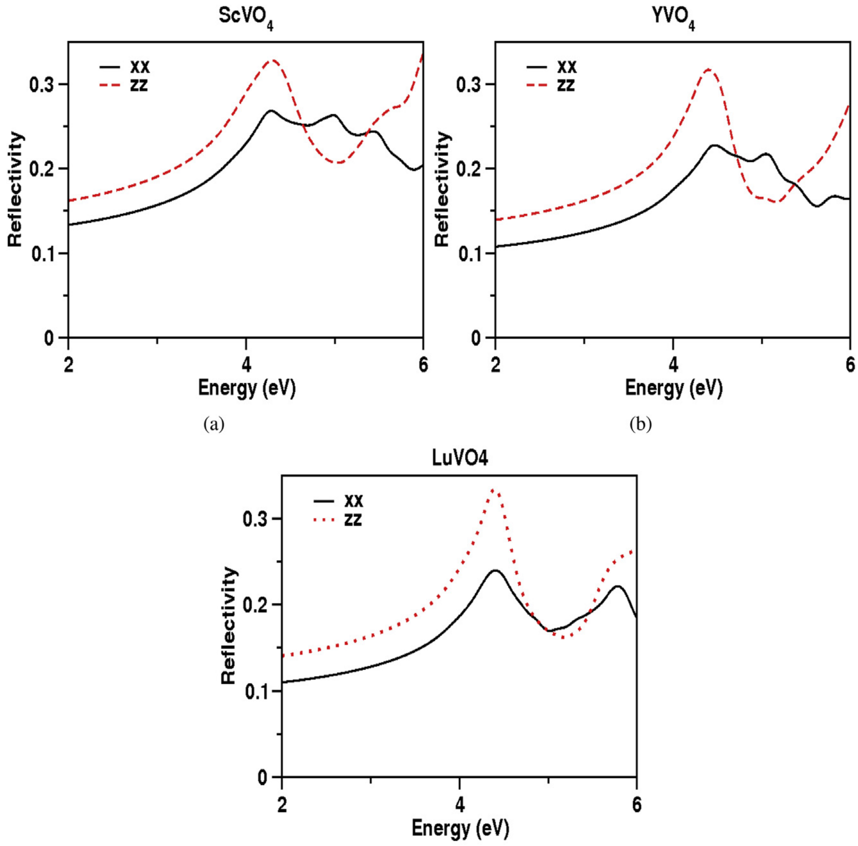
The presently studied orthovanadates are good scintillating host materials, and we attempt to explain the optical properties. In general, a change in the absorption spectra at high pressure indicates the phase transition of the compounds [12]. The response of the system to the electro-magnetic radiation can be well explained by using the absorptive part ε_2 and the dispersive part ε_1 of the complex dielectric function $\varepsilon(\omega)$. The ε_2 is calculated by summing the inter-band transitions from occupied valence band to unoccupied conduction band states. The calculated imaginary part of dielectric function as a function of photon energy is shown in Fig. 3 with TB-mBJ functional at ambient, and high pressure. We observe the spectra to shift to high energy regions moving from $ScVO_4$ to $LuVO_4$ at ambient phases, whereas at high pressure, a shift to higher energy with increase in the cation size is observed. Experimentally XianTao Wei et al. [9] also observed red shift in the spectra with decrease in the cation size. The lower energy part of spectra is due to transition of electrons from O-p states to V-d states in both the phases. In the case of $ScVO_4$ the peaks A_1, B_1 are due to transition of electrons from O-p states to V-d, Sc-d states respectively. The peaks in YVO_4 A_2, B_2, C_2 are due to the transition of electrons from O-p to V-d states and D_2 is from O-p to Y-d states. In the case of $LuVO_4$ the peaks A_3, B_3, and C_3 are due to transition from O-p, Lu-f states to V-d, the higher energy peaks arises mainly from the transition of O-p states to Lu-d states. The spectra is different for all the compounds because of the presence of different cations. This observed difference may be mainly due to the shifting of M-d(M-Sc, Y, Lu) states to higher energy region, and also due to increase in the energy difference between upper and lower conduction band states in moving from $ScVo_4$ to $LuVO_4$. Red shift in spectra is clearly observed in moving from ambient to high pressure, and is shown in inset in Fig. 3, which is because of the decrease in the band gap from ambient to high pressure phase.



(a) (b)

(c)

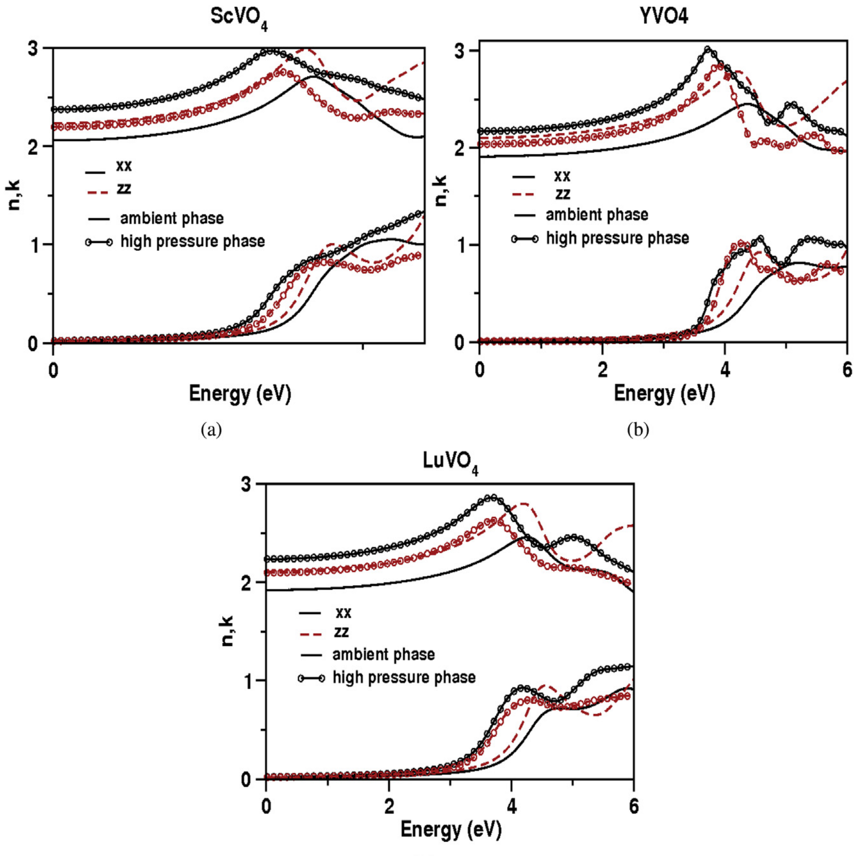
Fig. 4. Calculated real part of dielectric function of (a) $ScVO_4$, (b) YVO_4, and (c) $LuVO_4$ using TB-mBJ functional at ambient and at high pressure phase.



(a) (b)

(c)

Fig. 5. Reflectivity spectra of (a) $ScVO_4$ (b) YVO_4, and (c) $LuVO_4$ using TB-mBJ functional at ambient.



(a) (b)

(c)

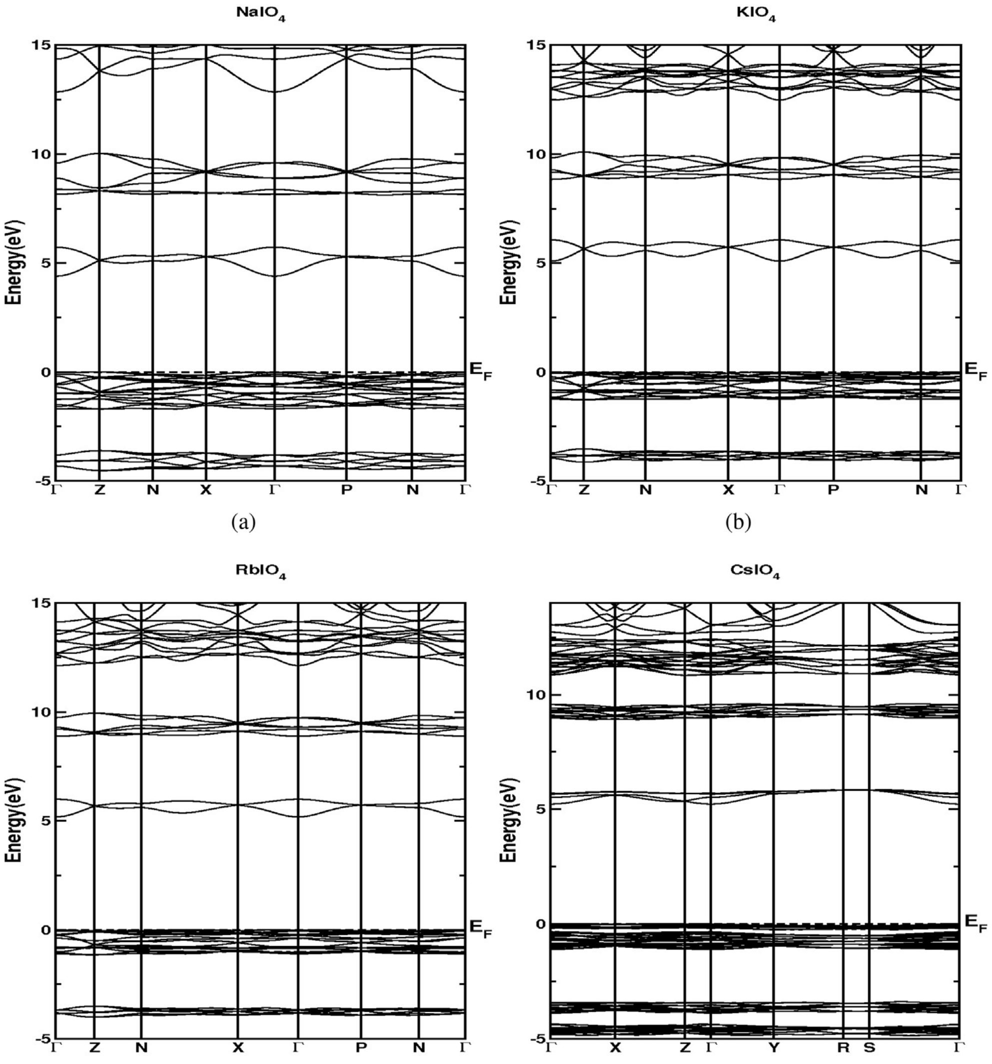
Fig. 6. Refractive index of (a) $ScVO_4$ (b) YVO_4, and (c) $LuVO_4$ at ambient and at high pressure phase indicating the optical anisotropy of these compounds.

As a next step, the real part of dielectric function is calculated from the imaginary part using the Kramers–Kronig relations, and the corresponding figures are shown in Fig. 4. The important quantity in ε_1 is the electronic part of static dielectric function $\varepsilon_1(0)$. These values are 4.23(5.00), 3.64(4.41), 3.68(4.44), and 5.64(4.82), 4.69(4.13), 5.0(4.39) for $ScVO_4$, YVO_4, and $LuVO_4$ respectively at ambient and high pressure along xx(zz) directions respectively. These values increases with energy, reaches maximum, then decrease and become negative at certain energy range where incident photons are completely attenuated. The maximum values of ε_1 for $ScVO_4$, YVO_4, and $LuVO_4$ at ambient, high pressure phase along xx(zz) directions are 8.7(10.7), 7.0(10.0), 7.2(10.2), and 8.5(7.3), 8.9(7.8), 7.9(6.6) respectively. Panchal et al. [8] calculated the reflectivity, absorption co-efficients for YVO_4, $LuVO_4$ experimentally, and observed a broad hump with maximum at 3.8 eV, sharp maximum at 4.4 eV followed by a minimum at 4.6 eV, where the first peak corresponds to the direct transition. A similar trend is observed in the calculated reflectance spectra of the present compounds also (shown in Fig. 5) except for a broad hump around 3.8 eV. From the figure, we can see that the reflectance spectra increases reaches maximum value then decreases, and the energies corresponding to maximum and minimum value for $ScVO_4$, YVO_4, and $LuVO_4$ are 4.28(4.3), 4.6(5.0), 4.4(4.4), 4.8(5.1), and 4.4(4.4), 5.0(5.1) eV respectively along xx(zz) directions.

Further, refractive index values are calculated with TB-mBJ functional and the corresponding figures are shown in Fig. 6 for both the phases. From the figures, it is clearly seen that the studied compounds are optically anisotropic. The static refractive index values are 2.05(2.22), 1.90(2.10), and 1.92(2.1) for $ScVO_4$, YVO_4, and $LuVO_4$ along xx(zz) directions respectively. These values at high pressure phase are 2.35(2.18), 2.15(2.03), and 2.21(2.07) for $ScVO_4$, YVO_4, $LuVO_4$ along the xx(zz) direction respectively. The refractive index initially increase with energy reaches maximum value then decreases similar to real part of dielectric function, and these are related to each other by the relation $n(0) = \sqrt{\varepsilon_1(0)}$. Huang [4] reported the refractive index values for YVO_4 to be 1.973, 2.181 along xx, zz directions at ambient, while in scheelite phase, these values are 2.276, 2.185 along xx, zz directions respectively, which are in comparison with our calculated refractive index values. From the imaginary part of dielectric function, it is clear that the spectra start at energies near to the visible region around 3–4 eV, which might lead to the emission in the visible region enabling these compounds to act as good scintillators. Experimentally, it was observed that orthovanadates show characteristic emission based on the type of cation M (Y, Sc, Lu) in MVO_4, where YVO_4 show blue emission, $ScVO_4$ show blue-green emission [34]. So we might expect from our theoretical results also that the orthovanadates might scintillate in the visible region.

3.3. Periodates

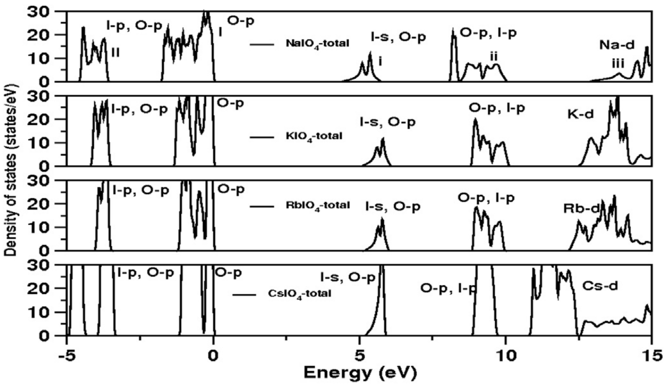
The band structures of these periodates are shown in Fig. 7 using the TB-mBJ functional. From the band structure it is clearly seen that these compounds are insulators with indirect band gap and the corresponding band gaps are given in Table 2 with GGA, TB-mBJ functionals. There are no experimental or theoretical data available for these compounds to compare our results. Valence band of XIO_4(X = Na, K, Rb, and Cs) are narrow and less dispersive similar to $XClO_4$(X = Na, K, Rb, and Cs) [37]. From the band structure of periodates, it is clearly seen that valence band states are less



(a) (b)

(c) (d)

Fig. 7. Calculated band structure of (a) $NaIO_4$ (b) KIO_4 (c) $RbIO_4$, and (d) $CsIO_4$ using TB-mBJ functional.



(a)

Fig. 8. Total density of states of XIO_4(X = Na, K, Rb, and Cs).

dispersive which leads to decrease in the mobility of charge carriers resulting in the reduced transport of carriers towards emission centres compared to orthovanadates. As a result, we can expect the scintillation to be lesser in the case of periodates compared to orthovanadates, which restrict these compounds to be good host compounds compared to orthovanadates. But these are good oxidizer's, because they decompose and give oxygen. The calculated total density of states of periodates are shown in Fig. 8. The results indicate that conduction bands are essentially dominated by i)I-s, O-p, ii)O-p, I-p, and iii)X-d(X = Na, K, Rb, and Cs) states, while moving from conduction band minimum to high energy regions. Similarly valence bands are dominated by I)O-p, II)I-p, O-p states as we move from valence band maximum to lower energy region. The valence band of periodates split into small bands, with less hybridization between them, whereas in the case of orthovanadates there is a broad band because of the hybridization of V-d, and O-p states. These compounds decompose and give oxygen, which is useful to be added to the explosives because of their oxygen deficiency. Similar to orthovanadates, we also studied the bonding nature of periodates based on charge density difference plots as shown in Fig. 10(c) indicating covalent nature of I—O bond, and ionic nature of Na—O bond. This is also observed from the bond lengths, where I—O bond length is lesser than the X—O(X = Na, K, Rb, and Cs) bond length.

The calculated imaginary part of dielectric function is shown in Fig. 9(a). The threshold energy (the energy at which spectra starts

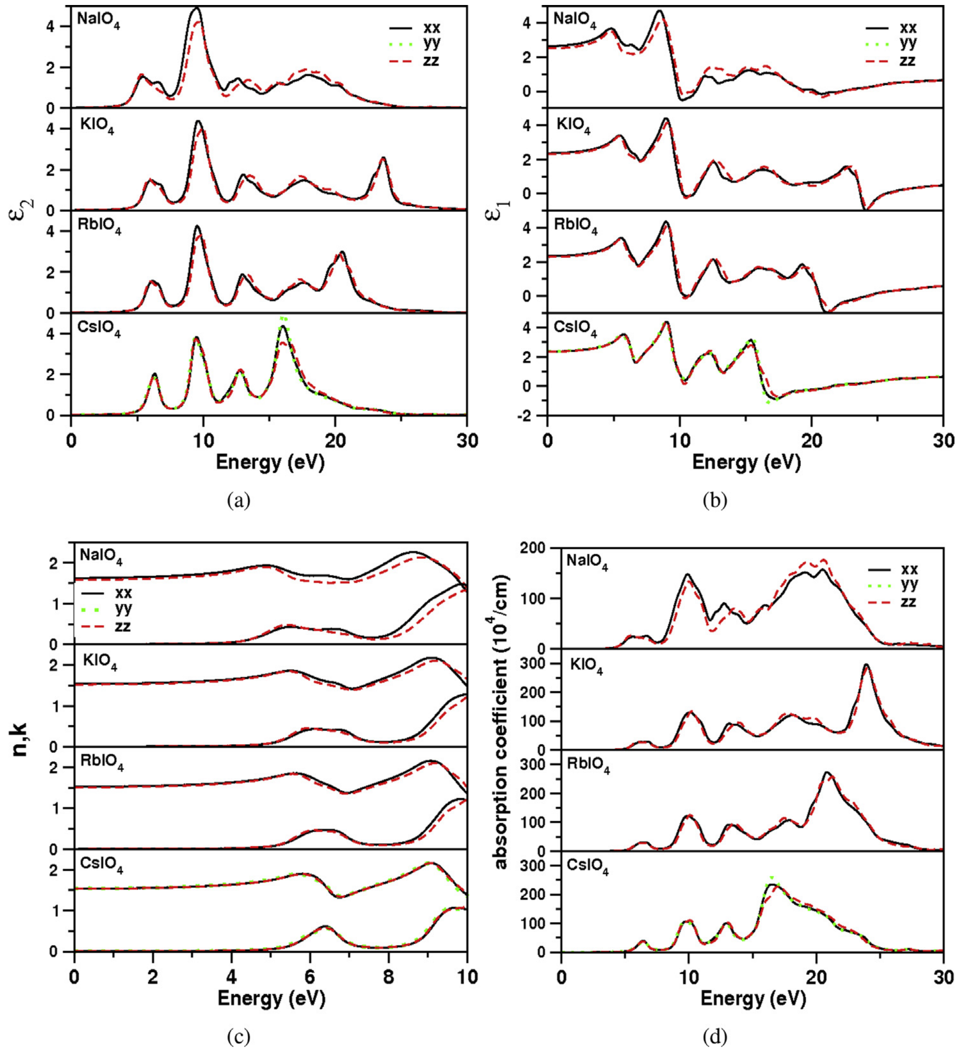
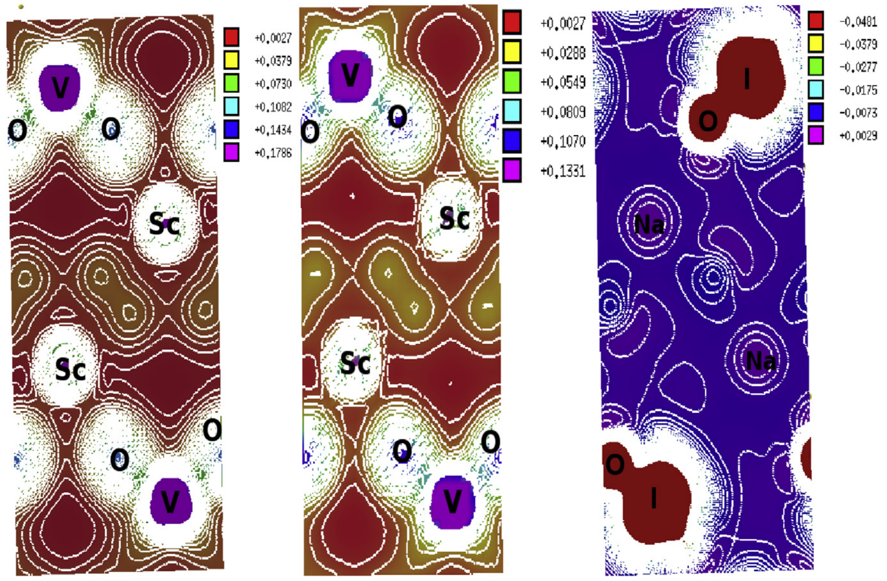


Fig. 9. Calculated optical properties of XIO_4 (X = Na, K, Rb, and Cs compounds (a) imaginary part of dielectric function (b) real part of dielectric function (c) refractive index (d) absorption coefficient using TB-mBJ functional.

raising) for these compounds is 3.9, 4.6, 4.8, and 5.1 eV for $NaIO_4$, KIO_4, $RbIO_4$, and $CsIO_4$ respectively, which gives the energy value at which direct optical transition between highest valence and lowest conduction bands occurs. The spectra is shifted to high energy regions with the increase in the cation size because of the increase in the band gap of these compounds from $NaIO_4$ to $CsIO_4$. We observe the imaginary part of dielectric function of all the compounds to be almost similar for all the compounds, except for the shifting of band gap to higher energy regions. The static dielectric constant values are 2.64(2.49), 2.37(2.31), 2.32(2.28), and 2.36(2.38, 2.35) for $NaIO_4$, KIO_4, $RbIO_4$, along xx(zz) direction, and for $CsIO_4$ along xx(yy, zz) direction respectively as shown in Fig. 9(b). Static refractive index values of these compounds are 1.62(1.58), 1.54(1.52), 1.52(1.51), and 1.536(1.54, 1.535) for XIO_4 (X = Na, K, and Rb) along xx(zz) directions, for $CsIO_4$ along xx (yy, zz) directions respectively (shown in Fig. 9(c)). The lower energy part of the dielectric function is due to transition of electrons from O-p states to I-s states, which is quite similar in all the studied XIO_4 (X = Na, K, Rb, ans Cs) compounds. Calculated absorption spectra of these compounds are shown in Fig. 9(d), which shows the spectra to start around 4–5 eV, which is in the ultra-violet region and the lower energy spectra remain almost unchanged as we move from Na to Cs, as their contribution is pronounced only in the higher energy region of the conduction bands.

3.4. Comparison of orthovanadates, periodates

Here we are interested in comparing the optical properties of orthovanadates, and periodates, together with germanates from our previous calculations. There is no phase transition in germanates, whereas orthovanadates, periodates undergo phase transition. Due to lack of experimental parameters we have studied the high pressure phase of only orthovanadates. In general, from all the ABO_4 compounds studied here, it is found that the band gap values of these compounds increases, valence band width decreases with the increase in the cation size for all the compounds. Among the three series studied, imaginary part of dielectric spectra of orthovanadates are near to visible range, whereas the absorption spectra of periodates, germanates starts far from the visible range around 4–6 eV. In the case of germanates, we doped Ti in $ZrGeO_4$ in our previous calculations [38] resulting in availability of the states in the band gap of the host compounds eventually reducing the band gap of these compounds. We observed no significant change in the imaginary part of dielectric function (Fig. 9(a)) in the case of periodates, especially in the lower energy region, whereas significant



(a) (b) (c)

Fig. 10. Charge density difference plots of $ScVO_4$ at (a) ambient, (b) high pressure phase, and (c) $NaIO_4$ along (0 1 0) direction.

Table 1
Calculated band gap (in eV) values of $ScVO_4$, YVO_4, and $LuVO_4$ compounds using GGA and TB-mBJ functionals at ambient, high pressure phase along with the available experimental, and other theoretical values.

Method	$ScVO_4$	YVO_4	$LuVO_4$
Ambient phase			
GGA	2.58	2.89	2.90
TB-mBJ	3.34	3.67	3.74
Other	2.57[a], 2.43[b], 2.48[c], 2.58[d]	2.79[b], 2.80[c], 3.60[e]	2.86[b], 2.76[c]
Exp		3.79, 3.78[b]	3.79, 3.76, 3.87[b]
High pressure phase			
GGA	2.39	2.71	2.53
TB-mBJ	3.06	3.35	3.23
Others	2.35[d]		

[a] Ref. [3].
[b] Ref. [8].
[c] Ref. [9].
[d] Ref. [20].
[e] Ref. [31].

change is observed in the case of orthovandates (Fig. 3) with the change in the cation. This may be due to the absence of cation states in the low energy region in the periodates. Fig. 11 clearly shows the absence of Na states in the lower conduction band, whereas Sc states contribute significantly to conduction band. The valence bands states are less dispersive in case of periodates, which might lead to lesser mobility of carriers. In the case of orthovanadates, bands are dispersive leading to more carrier transport making them better host scintilltors than periodates. One more supporting factor is that the valence band width of the orthovanadates are more, and the band gap is lesser than the periodates leading to more number of carriers available in orthovanadates than periodates. In addition to this, we also compared the optical properties of orthovanadates at ambient, and high pressure. We observed a decrease in the band gap, increase in the valence band width in the high pressure phase which may further lead to an increase in the number of electron–hole pairs. Other factor observed is the red shift of the spectra from ambient to high pressure. Red shift of the spectra is observed in the following two cases i) with the decrease in the cation size ii) moving to high pressure phase. The high pressure phase may be more favourable for scintillation as the spectra is near to visible range enabling the emission in the visible region. Moreover, the transition from zircon to scheelite phase is irreversible, and transition pressure is less around 7–8 GPa. From the electronic structure and optical properties, it prompts us to state that orthovanadates are better candidates for scintillation, and high pressure phase is more favourable for scintillation than the ambient.

Table 2
Calculated band gap values of XIO_4 (X = Na, K, Rb, and Cs) compounds, in eV using GGA and TB-mBJ functionals using WIEN2k.

	$NaIO_4$	KIO_4	$RbIO_4$	$CsIO_4$
GGA	2.12	2.86	2.98	3.16
TB-mBJ	4.40	5.09	5.18	5.22

4. Conclusions

In conclusion, we have studied the electronic structure and optical properties of host MVO_4 (M = Sc, Y, and Lu), and XIO_4 (X = Na, K, Rb, and Cs) compounds within the frame work of the density functional theory calculations using the wien2K code.

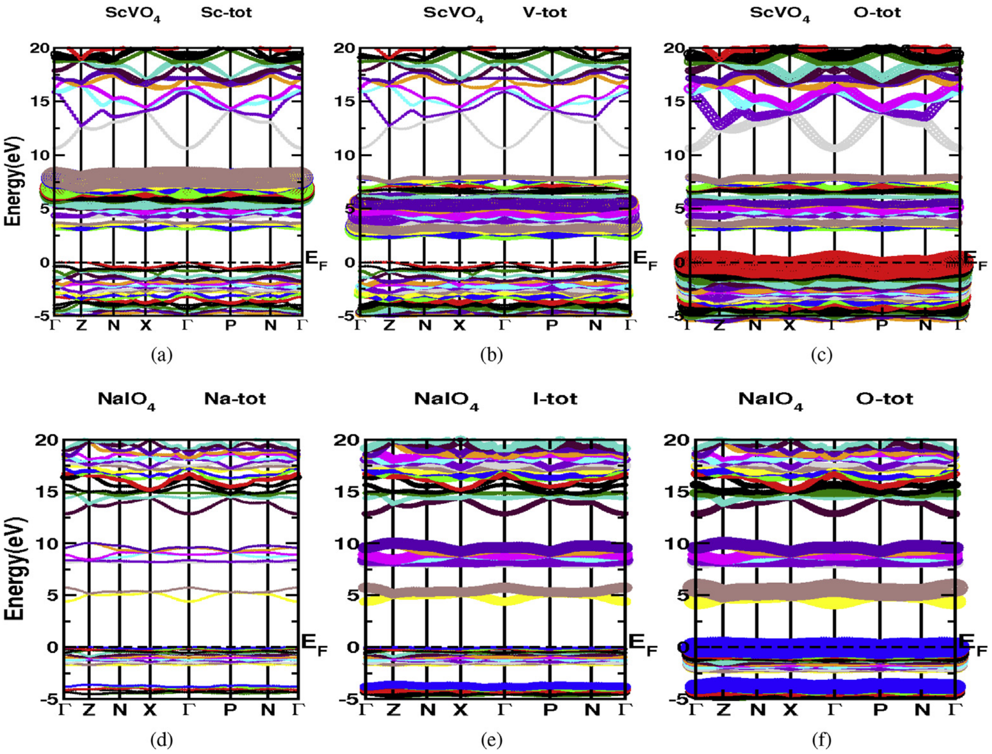


Fig. 11. Calculated site projected band structure of $ScVO_4$ (a,b,c), $NaIO_4$(d,e,f).

i) We observe the investigated compounds to be insulators with orthovanadates possessing direct band gap except for $ScVO_4$ at high pressure phase, where it is an indirect band gap insulator, and periodates possess indirect band gap. The band gap decreases with decrease in the cation size and also moving from ambient phase to high pressure phase.
ii) The band gap values increase, and the valence band width decreases in moving from orthovanadates to periodates leading to good scintillation in orthovanadates than periodates.
iii) We observe the absorption spectra of orthovanadates to be near the visible range (around 3–4 eV), which might favour the emission spectra to be in the visible range.
iv) We also observed red shift in absorption spectra of orthovanadates in the following two cases: one is with decrease in the cation size, while the other is by moving to the high pressure phase. These compounds may be best used as scintillators in high pressure phase, because of the decrease in the band gap, and the transition from zircon to scheelite is an irreversible process with the transition pressure around 7–8 GPa.

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References

[1] D. Errandonea, F.J. Manjón, Prog. Mater. Sci. 53 (2008) 711.
[2] D. Errandonea, R. Lacomba-Perales, J. Ruiz-Fuertes, A. Segura, S.N. Achary, A.K. Tyagi, Phys. Rev. B 79 (2009) 184104.
[3] H. Cong, H. Zhang, B. Yao, W. Yu, X. Zhao, J. Wang, G. Zhang, Cryst. Growth Des. 10 (2010) 4389.
[4] Z. Huang, L. Zhang, W. Pan, J. Alloys Comp 580 (2013) 544.
[5] F.J. Manjón, P. Rodríguez-Hernández, A. Muñoz, A.H. Romero, D. Errandonea, K. Syassen, Phys. Rev. B 81 (2010) 075202.
[6] X. Wang, I. Loa, K. Syassen, M. Hanfland, B. Ferrand, Phys. Rev. B 70 (2004) 064109.
[7] Rekha Rao, A.B. Garg, T. Sakuntala, S.N. Achary, A.K. Tyagi, J. Solid State Chem. 182 (2009) 1879.
[8] V. Panchal, D. Errandonea, A. Segura, P. Rodríguez-Hernandez, A. Muiñoz, S. Lopez-Moreno, M. Bettinelli, J. Appl. Phys. 110 (2011) 043723.
[9] X. Wei, J. Wen, S. Li, S. Huang, J. Cheng, Y. Chen, C. Duan, M. Yin, Appl. Phys. Lett. 104 (2014) 181904.
[10] F. Kang, X. Yang, M. Peng, L. Wondraczek, Z. Ma, Q. Zhang, J. Qiu, J. Phys. Chem. C 118 (2014) 7515.
[11] V. Panchal, F.J. Manjón, D. Errandonea, P. Rodriguez-Hernandez, J. López-Solano, Phys. Rev. B 83 (2011) 064111.
[12] S.J. Duclos, A. Jayaraman, G.P. Espinosa, A.S. Cooper, R.G. Maines Sr., J. Phys. Chem. Solids 50 (1989) 769.
[13] A. Jayaraman, G.A. Kourouklis, G.P. Espinosa, A.S. Cooper, L.G. Van Uitert, J. Phys. Chem. Solids 48 (1987) 755.
[14] J.D. Moretti, J.J. Sabatini, G. Chen, Angew. Chem. Int. Ed. 51 (2012) 6981.
[15] G. Jian, J. Feng, R.J. Jacob, G.C. Egan, M.R. Zachariah, Angew. Chem. Int. Ed. 52 (2013) 9743.
[16] Ch.V. Subba Reddy, Quan-YaO. Zhu, Li-Qiang Mai, Wen chen, J. Appl. Electrochem. 36 (2006) 1051.
[17] N. Chandrabhas, A.K. Sood, Phys. Rev. B 51 (1995) 8795.
[18] T.A. Al Dhahir, H.L. Bhat, P.S. Narayanan, A. Jayaraman, J. Raman Spectrosc. 22 (1991) 567.
[19] N. Chandrabhas, D. Victor, S. Muthu, A.K. Sood, H.L. Bhat, A. Jayaraman, J. Phys. Chem. Solids 53 (1992) 959.
[20] Shu-Fang Sheng, Phys. B 426 (2013) 20.
[21] L. Sun, X. Zhao, Y. Li, P. Li, H. Sun, X. Cheng, W. Fan, J. Appl. Phys. 108 (2010) 093519.
[22] J. López-Solano, P. Rodríguez-Hernández, A. Muñoz, High Press. Res. Int. J. 29 (4) (2009) 582.
[23] T.A. AL-Dhahir, A.K. Sood, H.L. Bhat, Solid State Commun. 70 (1989) 863.
[24] P. Blaha, K. Schwarz, P. Sorantin, S.B. Tricky, Comput. Phys. Commun. 59 (1990) 399.
[25] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2K, an Augmented Plane Wave Plus Local Orbitals Programe for Calculating Crystal Properties, Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001.
[26] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[27] D.J. Singh, Phys. Rev. B 82 (2010) 205102.
[28] D. Koller, F. Tran, P. Blaha, Phys. Rev. B 83 (2011) 195134.

[29] B.C. Chakoumakos, M.M. Abraham, L.A. Boatner, J. Solid State Chem. 109 (1994) 197.

[30] D. Errandonea, D. Martínez-García, R. Lacomba-Perales, J. Ruiz-Fuertes, A. Segura, Appl. Phys. Lett. 89 (2006) 091913.

[31] H.A. Rahnamaye Aliabad, Z. Parvizi, Comput. Mater. Sci. 93 (2014) 125.

[32] D.J. Singh, G.E. Jellison Jr., L.A. Boatner, Phys. Rev. B 74 (2006) 155126.

[33] J. Zhang, J. Wang, H. Zhang, C. Wang, H. Cong, L. Deng, J. Appl. Phys. 102 (2007) 023516.

[34] G. Blasse, A. Bril, J. Chem. Phys. 50 (1969) 2974.

[35] A. Kálmán, D.W.J. Cruickshank, Acta Cryst. B26 (1970) 1782.

[36] R. Hoppe, D. Fischer, J. Schneider, Z. Anorg, Allg. Chem. 625 (1999) 1135.

[37] Yu.N. Zhuravlev, A.S. Poplavnoi, Russ. Phys. J. 39 (1996) 952.

[38] G. Shwetha, V. Kanchana, K. Ramesh Babu, G. Vaitheeswaran, M.C. Valsakumar, J. Phys. Chem. C 118 (2014) 4325.