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Ab-initio calculations of structural, electronic, and optical properties of $Zn_3(VO_4)_2$

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The structural, electronic, and optical properties of $Zn_3(VO_4)_2$ are investigated using full potential linearized augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT). Various approaches are adopted to treat the exchange and correlation potential energy such as generalized gradient approximation (GGA), GGA+U, and the Tran–Blaha modified Becke–Johnson (TB-mBJ) potential. The calculated band gap of 3.424 eV by TB-mBJ is found to be close to the experimental result (3.3 eV). The optical anisotropy is analyzed through optical constants, such as dielectric function and absorption coefficient along parallel and perpendicular crystal orientations. The absorption coefficient reveals high absorption (1.5×10^6 cm^{-1}) of photons in the ultraviolet region.

Keywords: density functional theory, $Zn_3(VO_4)_2$, electronic structure, optical properties

PACS: 31.15.ej, 31.15.ae, 61.50.–f, 71.15.Mb **DOI:** 10.1088/1674-1056/27/3/033101

1. Introduction

Metal vanadates normally denoted as $M_3(VO_4)_2$ where M is a transition or alkaline earth metal, such as $Mg_3(VO_4)_2$, $Zn_3(VO_4)_2$, $Co_3(VO_4)_2$, and $Ni_3(VO_4)_2$, show interesting magnetic,[1] photocatalytic,[2] and light emission properties.[3,4] These compounds show orthorhombic crystal symmetry and lie in space group *Cmca*. $Zn_3(VO_4)_2$ is one example of ternary oxide phosphor due to its large band gap of about 3.25 eV.[5,6] It has three polymorphs: α-, β-, and γ-phases. Among them, α-$Zn_3(VO_4)_2$ is a stable phase at room temperature,[7] which has orthorhombic crystal structure with lattice parameters $a = 6.088$ Å, $b = 11.489$ Å, and $c = 8.280$ Å.[8]

Extensive experimental work has been conducted to investigate the structural and photonic properties of $Zn_3(VO_4)_2$,[4,8–14] but rarely is theoretical work done to study this novel material. Electronic and magnetic properties of other metal vanadates such as $Co_3(VO_4)_2$ and $Ni_3(VO_4)_2$ have been studied theoretically in the last decade,[1,15–18] but very few reports related to the electronic band structure of $Zn_3(VO_4)_2$ are found,[19–21] while the optical properties have not been reported until now to the best of our knowledge. The interesting photonic and photocatalytic properties of $Zn_3(VO_4)_2$ motivate us to study the electronic and optical properties of $Zn_3(VO_4)_2$ in detail.

In density functional theory (DFT), different basis functions, such as augmented plane wave (APW), projector augmented wave (PAW),[22,23] and full potential linearized augmented plane wave (FP-LAPW),[24,25] are chosen to solve the Kohn–Sham equation. The *ab-initio* calculations of the electronic structures of $Zn_3(VO_4)_2$ and $Mg_3(VO_4)_2$ have been performed using the PAW method under different exchange correlation potential functionals (GGA, GGA+U, TB-mBJ).[19] It was noted that the band gap of these materials depends strongly on the exchange correlation potential energy used for calculations. In the present study, the full potential linearized augmented plane wave (FP-LAPW) method with the same exchange correlation functionals is adopted to investigate the structural and electronic properties of $Zn_3(VO_4)_2$, and a comparison is made between PAW and LAPW methods. Moreover, the optical and photoluminescence properties of $Zn_3(VO_4)_2$ are also investigated.

2. Method of calculations

Calculations are carried out using GGA, GGA+U, and TB-mBJ approximations as the exchange correlation potential energy implemented in the Wien2k package.[26] In this study, Hubbard potentials U for Zn and V are taken as 4.7 eV and 3.25 eV, respectively. Normally, it is observed that the GGA approximation underestimates the band gap compared to the experimental band gap, which is its main disadvantage. To resolve this shortcoming, other methods such as GGA+U and TB-mBJ approximations are used. These approximations work well for the systems containing strongly correlated 3d, 4f, or 5f electron orbitals. Compared to GGA or GGA+U, the TB-mBJ approximation gives the band gap energy in close agreement with the experimental data.

For the crystal potential, the muffin-tin model is adopted

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in which the unit cell is divided into two regions: core and valence. The electron density lying inside the muffin-tin radius (R_{MT}) is treated as the core whereas outside is the valence. In the core states, the electronic wave functions are considered as atomic-like wave functions (spherical harmonics type), while in the valence states, the wave function is taken in the form of plane waves plus local orbitals (LO), therefore named as full potential LAPW. In comparison to the LAPW method, the PAW method assumes a pseudo potential in the core states and plane waves in the valence states. In the present study, the non-overlapping sphere of radius R_{MT} around each atom is chosen in a way that no charge leaks out from the core and the total energy convergence is ensured to the desired energy, ~0.0001 eV between the energy steps. The R_{MT} for Zn, V, and O atoms are taken as 1.62 a.u., 1.58 a.u., and 1.2 a.u., respectively. A mesh of $19 \times 19 \times 12$ k points for electronic and optical calculations is made with $R_{MT}k_{max} = 6$ (k_{max} is the cut-off for the plane wave in the interstitial region) for the convergence of the total energy. The magnitude of the largest vector in charge density Fourier expansion, G_{max}, is 12. The separation for the core and valence energy states is chosen as -7 Ry.

Table 1. Optimized positions of atoms in a unit cell.

Atom	Experiment[8]	PAW[19]	Optimized positions (FP-LAPW)
Zn(1)	0,0,0	0, 0, 0	0, 0, 0
Zn(2)	0.25, 0.1359, 0.25	0.25, 0.1373, 0.25	0.25, 0.1364, 0.25
V	0, 0.3780, 0.1228	0, 0.3785, 0.1203	0, 0.3779, 0.1199
O(1)	0, 0.249, 0.232	0, 0.2503, 0.2261	0, 0.2503, 0.2297
O(2)	0, 0.002, 0.245	0, 0.0006, 0.2444	0, 0.0003, 0.2450
O(3)	0.1186, 0.1186, 0.995	0.2735, 0.1176, 0.0012	0.2708, 0.1192, 0.9981

3. Results and discussion

3.1. Band structure and density of states

Before the calculations for the electronic structure and optical properties, we have optimized the Wyckoff positions of all atoms in the unit cell with a convergence criterion of 0.05 mRyd/Å. The optimized positions along with experimental[8] and reported theoretical[19] Wyckoff positions of different atoms are presented in Table 1. We have calculated the band structure and optical properties of $Zn_3(VO_4)_2$ using these optimized internal positions of the atoms.

Figure 1 shows the electron density contour for $Zn_3(VO_4)_2$ in 2D space. Polar covalent bonding is observed between Zn–O atoms and V–O atoms with higher electron density towards the O atom end, giving partial negative charge on the O atom and partial positive charge on the Zn and V atoms. This is because the O atom is more electronegative (3.44) than the Zn (1.65) and V (1.63) atoms. The calculated bond lengths of Zn(1)–O and Zn(2)–O are 2.14 Å (2.13 Å) and 2.09 Å (2.10 Å), respectively (experimental values[8] are given in the parenthesis for comparison). The V–O(2) bond length, i.e., the oxygen atom shared with three Zn^{2+}, is 1.79 Å (1.79 Å), longer than the V–O(1) and V–O(3) bond lengths of 1.72 Å (1.73 Å) and 1.70 Å (1.67 Å), because they share only two Zn^{+2} atoms.[8] No bonding is observed between Zn–V atoms while weak metallic bonding is observed between Zn–Zn atoms.

The bandgap of $Zn_3(VO_4)_2$ is calculated by using GGA, GGA+U, and TB-mBJ exchange correlation functionals as shown in Fig. 2. The bandgap of $Zn_3(VO_4)_2$ is indirect and has values of 2.703 eV, 3.094 eV, and 3.424 eV, respectively. A comparison of the bandgaps calculated by PAW[19] and FP-LAPW (present study) reveals that the bandgap calculated by the present method is improved by using all three exchange correlation functionals (Table 2). By using the TB-mBJ exchange correlation potential, the calculated bandgap is close to the experimental bandgap of 3.3 eV.[6]

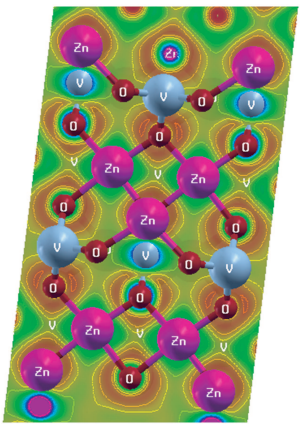


Fig. 1. (color online) Valence electron density in $Zn_3(VO_4)_2$.

The electronic distribution is well described by the total density of states of $Zn_3(VO_4)_2$ and the partial density of Zn, V, and O using GGA, GGA+U, and TB-mBJ exchange potentials (Fig. 3). Figure 3 indicates that the V-3d states make the major contribution to the conduction band whereas the O-2p and Zn-s states play minor roles in the conduction band. The lower part of the valence band is dominated by the Zn-3d states which are hybridized t_{2g} and e_g states as shown in

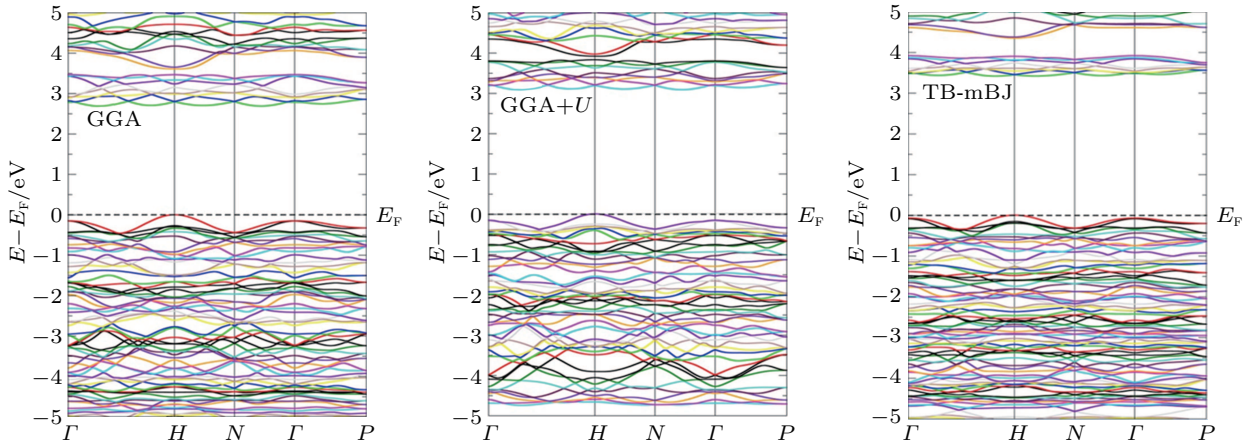


Fig. 2. (color online) Calculated band structures of $Zn_3(VO_4)_2$ by using (a) GGA, (b) GGA+U, and (c) TB-mBJ approximations.

Table 2. Calculated band gap and static dielectric function in x and z directions using GGA, GGA+U, and TB-mBJ approaches.

Method	Band gap/eV	PAW band gap/eV[19]	$\varepsilon_1(0)_{\parallel}$	$\varepsilon_1(0)_{\perp}$
GGA	2.703	2.620	5.179	5.018
GGA+U	3.094	2.790	4.764	4.583
TB-mBJ	3.424	3.279	3.744	3.611

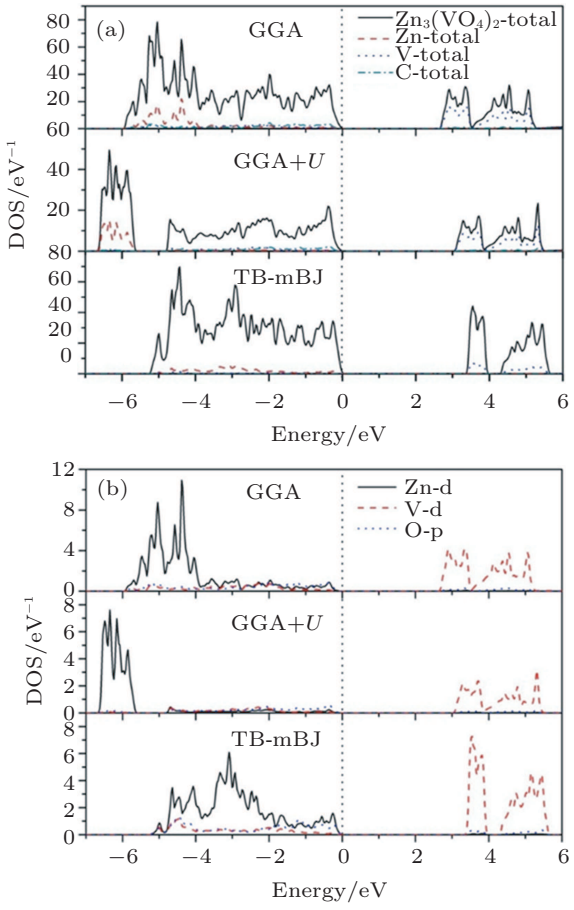


Fig. 3. (color online) Calculated (a) total and (b) partial density of states for $Zn_3(VO_4)_2$ using GGA, GGA+U, and TB-mBJ approximations.

Fig. 4. The upper part of the valence band is comprised of hybridized Zn-3d, V-3d, and O-2p states. Therefore, the electronic transition from all these valence states to the conduction band is possible, and in the materials containing vanadate group (VO_4), the electronic transition between O-2p and V-3d states is suggested.[27] The p–d hybridization in the valence band enhances the density of states and hence the mobility of the photo-induced holes, a characteristic of efficient photocatalytic and photoluminescent materials.[20] By using the GGA+U functional, the Zn-3d and V-3d states are shifted to the lower and upper energy levels respectively as compared to those by using the GGA functional, which causes broadening of the band gap. By using the TB-mBJ exchange potential, the V-3d and O-2p states are hybridized in the conduction band and shift to the higher energy, whereas the hybridized Zn-3d states with O-2p states participate in the whole region of the valence band. The shift of the V-3d states to higher energy increases the band gap to 3.424 eV, in comparison to 2.703 eV of GGA and 3.09 eV of GGA+U. The results agree well with the bandgap previously calculated by using the PAW method[19] as shown in Table 2.

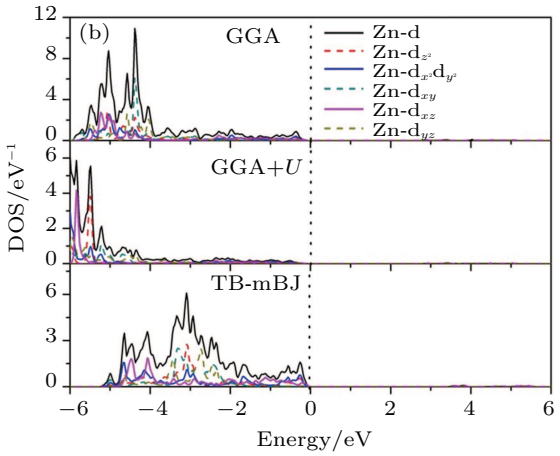


Fig. 4. (color online) Zn-3d partial density of states for $Zn_3(VO_4)_2$ using GGA, GGA+U, and TB-mBJ approximations.

3.2. Optical properties

The optical properties of $Zn_3(VO_4)_2$, i.e., dielectric function and absorption, are described in x and z crystal orienta-

tions with respect to the photon polarization direction. Being a property of the anisotropic crystal, the dielectric function shows slightly different behaviors in the prescribed directions (Table 2). The complex dielectric function of a material consists of two parts, real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$. The imaginary part of the dielectric function represents the absorption of photons, and consequently the electronic transition from the valence band to conduction band. The equation for calculation of $\varepsilon_2(\omega)$ is[28]

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2\omega^2}\sigma_{ij}\int \langle i|M|j\rangle^2 f_i(1-f_i)\delta(E_j - E_i - \omega)\mathrm{d}^3k, \tag{1}$$

where M denotes the dipole matrix, m is the free electron mass, i and j are used for the initial and the final states, respectively, f_i is the Fermi distribution function in the i-th state, E_i and E_j are the energy of free electron in the initial and the final states, respectively.

As $\varepsilon_2(\omega)$ is strongly connected to the electronic transitions, it can be investigated with the help of the electronic partial density of states as illustrated in Fig. 3. The real part of the dielectric function $\varepsilon_1(\omega)$ describes the dispersion of photons in the material. $\varepsilon_1(\omega)$ can be calculated from $\varepsilon_2(\omega)$ by using the Kramers–Kronig relation[28]

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi}\mathrm{P}\int_0^\infty \frac{\omega'\varepsilon_2(\omega')\mathrm{d}\omega'}{\omega'^2 - \omega^2}, \tag{2}$$

where P stands for the principal integral.

Real and imaginary dielectric functions of $Zn_3(VO_4)_2$ in two crystallographic directions x and z are studied by using GGA, GGA+U, and TB-mBJ approaches (Fig. 5). The threshold energy for $\varepsilon_2(\omega)$ is calculated as 2.952 eV, 3.333 eV, and 3.523 eV in x direction and 2.925 eV, 3.279 eV, and 3.551 eV in z crystallographic direction, respectively. It can be observed that the threshold energy for $\varepsilon_2(\omega)$ is in close agreement with the band gap energy which mainly originates from the electronic transition between the occupied O-2p energy levels and the unoccupied V-3d orbitals.[27]

The static dielectric function $\varepsilon_1(0)$ is an important parameter which is calculated at the zero frequency limit. It has a strong relationship with the bandgap energy as described by the Penn model[28]

$$\varepsilon_1(0) = 1 + \left(\frac{\hbar\omega}{E_\mathrm{g}}\right)^2. \tag{3}$$

This equation shows that $\varepsilon_1(0)$ changes inversely with the band gap energy E_g. The calculated $\varepsilon_1(0)$ in parallel and perpendicular directions of the incident electromagnetic wave with respect to the crystal orientations agree well with the Penn model as given in Table 2.

The absorption coefficient $\alpha(\omega)$ can be calculated directly with dielectric function $\varepsilon(\omega)$ by using the following relation:[28]

$$\alpha(\omega) = \sqrt{2}\omega[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)]^{1/2}. \tag{4}$$

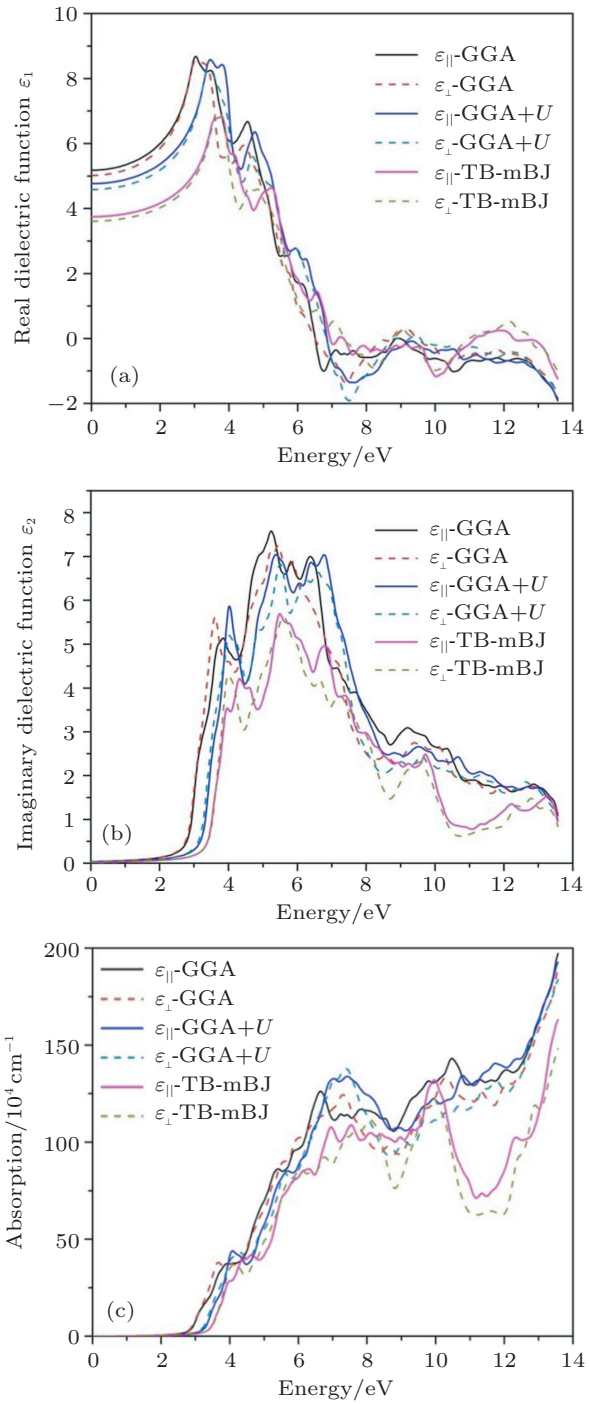


Fig. 5. (color online) (a) Real part and (b) imaginary part of the dielectric function, and (c) absorption coefficient versus energy using GGA, GGA+U, and TB-mBJ approximations.

The threshold energy of absorption for $Zn_3(VO_4)_2$ is calculated by using all mentioned approximations, which lies in the range 2.3–2.9 eV in x and z crystal orientations, respectively (Fig. 5(c)). The threshold energy of absorption is closely related to the optical band gap of the material. Above the threshold energy, the absorption coefficient gradually increases with a large value of $\sim 10^6$ cm^{-1}, which depicts the

strong absorption of photons in the ultraviolet (UV) region. It indicates that $Zn_3(VO_4)_2$ can easily be excited by UV light due to its broad absorption bands in the near UV region, and has the capability to emit visible light in the range of 400–700 nm.[4,13] Charge transition from the O-2p orbital to V-3d orbital in the vanadate (VO_4) group[27] provides luminescence and photocatalytic characteristics to this material.[20]

4. Conclusion

The structural, electronic, and optical properties of $Zn_3(VO_4)_2$ are calculated by using FP-LAPW method. GGA, GGA+U, and TB-mBJ approaches are used for the exchange correlation potential energy. The indirect bandgaps calculated by using these methods are 2.703 eV, 3.094 eV, and 3.424 eV, respectively. Among these methods, TB-mBJ gives the best results that match the theoretical and experimental studies. It is found that the V-3d states have a major contribution to the conduction band whereas hybridized Zn-3d and O-2p states participate in the valence band. The static dielectric function calculated by using these approximations is 5.179, 4.764, and 3.744, respectively. The absorption coefficient is very high ($\sim 10^6$ cm^{-1}) in the ultraviolet region, which implies that this material is suitable for exciting high-energy photons and can be utilized for photoluminescence and photo catalysis applications. Moreover, an optical anisotropy is observed for different crystal orientations.

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