

Understanding the magnetic, electronic and optical properties of Iron titanium Oxyphosphate $\text{Fe}_{0.5}\text{TiOPO}_4$ using DFT, GGA and GGA+U approaches

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Abstract : An investigation into the structural, electronic, magnetic and optical properties of oxyphosphate $\text{Fe}_{0.5}\text{TiOPO}_4$ was conducted using first-principles calculations based on density functional theory (DFT) with the Plane-Wave Self-Consistent Field (PWSCF). The results are used to discuss the quality of the generalized-gradient expansion GGA and GGA+U approximation for describing these atoms. We showed that the obtained symmetry lattice parameter agree well with the experimental results. The influence of iron element on the magnetic and electronic properties of oxyphosphate $\text{Fe}_{0.5}\text{TiOPO}_4$ is analyzed. The electronic structure calculations for monoclinic oxyphosphate $\text{Fe}_{0.5}\text{TiOPO}_4$ predict an energy-gap in both spin-up and spin-down. The partial density of states (PDOS) of $\text{Fe}_{0.5}\text{TiOPO}_4$ show that the oxygen 2p-derived states hybridize strongly with iron-3d at the conduction band when it's hybridize with titanium and iron at the valence band and the theoretical band gap energy is found to be $E_g = 0.62$ eV (GGA) and 2.2 eV (GGA+U).

Keywords: Self-consistent (DFT+U); Band structure; Magnetic material; Oxyphosphate $\text{Fe}_{0.5}\text{TiOPO}_4$; Electronic charge transfers; Electronic transitions.

1. Introduction

Theoretical and experimental research activities on crystalline magnetic materials have been increased over the past half-century mainly due to their unique and interesting structural, electronic and magnetic properties. Potassium titanium phosphate (KTiOPO_4) is one of inorganic phosphate materials that has attracted special attention in many applied and fundamental area of solid state physics and advanced materials science due to exotic electronic and magnetic properties.

Motivated by the attractive properties such as structural stability, high band gap energy and the high magnetic moment at Curie temperature (T_c), many oxyphosphate compound type $\text{M}_{0.5}\text{TiOPO}_4$ with M divalent atoms like (Mg^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , ...) have been done by our group [1-5] for identifying possible fundamental differences in their structural. For example Benmokhtar et al. [3] studied the magnetic and optical properties of oxyphosphate $\text{Cu}_{0.5}\text{TiOPO}_4$ and they found that the stable magnetic order it's antiferromagnetic with curie constant $C=0.52$ and the result of the optical absorption spectrum show two absorptions bands in ultraviolet region, the first one at 282 nm attributed to electronic charge transfers from O^{2-} (2p) to Ti^{4+} (3d), from O^{2-} (2p) to Cu^{2+} (3d), and the second one at 411 nm attributed to the Ti^{4+} (3d) to Cu^{2+} (3d) electronic charge transfers and three bands absorptions observed

in visible and infrared regions located at 791 nm, 977 nm, 1260 nm, correspond to the crystal field transitions between the full occupied states ${}^2\text{E}_g(\text{dx}_2\text{y}_2)$, ${}^2\text{B}_{2g}(\text{dxy})$ and ${}^2\text{A}_{1g}(\text{dz}^2)$ and the partially occupied level ${}^2\text{B}_{1g}(\text{dx}^2-\text{y}^2)$ of Cu^{2+} ion ($3d^9$) in octahedral site. The optical properties of $\text{Mg}_{0.5}\text{TiOPO}_4$ have been studies also by Benmokhtar et al [1] the optical absorption spectrum show a very strong absorption band at 368 nm attributed to the electronic charge transfer from O^{2-} (2p) to Ti^{4+} (3d) and the band gap energy was calculated to be E_g (eV) = 3.37 eV.

The results of the theoretical studies single crystals of Potassium titanium phosphate KTiOPO_4 by Ali Hussain Reshak and al. [6] show that the crystals have a direct band gap with (E_g (eV) = 3.37 eV). The electronic structure and magnetic properties of $\text{Cu}_{0.5}\text{TiOPO}_4$ have been study by Harbi and al. [7] using density functional theory (DFT) employing generalized gradient approximation (GGA) the result of calculation show that the antiferromagnetic state is more stable than the ferromagnetic in agreement with experimental one and the partial densities of states (PDOS) show that the band valence is formed by O-2p and Cu-3d states and the conduction band formed by Ti-3d state with gap energy $E_g=2.24$ eV and a spin polarization around the Fermi level appears due to the magnetic impurity. The structure and the optical properties of oxyphosphate $\text{Li}_{0.50}\text{Co}_{0.25}\text{TiO}(\text{PO}_4)$ also study using two approaches (GGA) and (EVGGA) by Ali Hussain Reshak and al. [8] the

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results of the band structure show a direct band gap energy of 3.0 states/Ry cell using (GGA), and 2.66 states/Ry cell using (EVGGA) and the density of states show that the valence band formed by Co-d and O₁-5p states, the group around Fermi energy consists of Co-d, Ti-s/p/d, P-s/p, and O₁-5s/p states. The conduction band is hybridization of Co-d, Ti-s/p/d, P-s/p, and O₁-5s/p states.

In the present paper, the electronic structure, magnetic and optical properties of oxyphosphate Fe_{0.5}TiOPO₄ have been investigated. The electronic structure information, ground states, band-gaps, and total and partial densities of states are calculated for the first time by using the generalized-gradient approximation in the framework of density functional theory (DFT and DFT+U). It is expected that the present study will help in understanding the mechanism responsible on these properties and also we present the results of UV-visible spectroscopy for this oxyphosphate in order to define the experimental band gap energy and the nature of the transition between the valence band and the conduction band (direct or indirect).

2. Computational method

The calculations of the present study are performed using density functional theory (DFT), with the Plane-Wave Self-Consistent Field (PWSCF) code implemented in Quantum-ESPRESSO package [9]. The generalized gradient approximation GGA and GGA+U [10,11] have been utilized to study the electronic structure and magnetic properties of the oxyphosphate Fe_{0.5}TiOPO₄.

Table 1

Calculated and experimental parameters for Fe_{0.5}TiOPO₄ compound.

	a(Å)	b (Å)	c(Å)	β(°)
Experimental	7.4039	7.3838	7.4083	120.366
Theoretical	7.2681	7.2382	7.4229	119.468
Stress tensor = -7.38kBar	forces= 0.0045mRy/au			

Table 2

Interatomic distances for Fe_{0.5}TiOPO₄ compound.

	Exp(Å)	Cal(Å)		Exp(Å)	Cal(Å)		Exp(Å)	Cal(Å)
Fe-O(1)	2.12	1.95	Ti-O(1)	1.73	1.78	P-O(2)	1.53	1.55
Fe-O(1')	2.12	1.95	Ti-O(1')	2.22	2.17	P-O(3)	1.52	1.54
Fe-O(2)	2.12	1.93	Ti-O(2)	2.07	2.06	P-O(4)	1.51	1.53
Fe-O(2)	2.12	1.93	Ti-O(3)	1.89	1.91	P-O(5)	1.50	1.52
Fe-O(5)	2.14	1.98	Ti-O(4)	1.90	1.92			
Fe-O(5)	2.14	1.98	Ti-O(5)	2.13	2.10			

As seen in Fig.1, from ref. [2], the 3D geometric crystal structure of the monoclinic formula unit of Fe_{0.5}TiOPO₄ in P₂/c symmetry can be described by a three-dimensional (3D) framework built up from [TiO₆], [FeO₆] octahedra and isolated [PO₄] tetrahedra. Titanium atoms are displaced from the center of the octahedron giving rise to an alternating long (2.22Å) and short (1.73) distances. The [TiO₆] octahedra shares the corners and forms infinite chains of -Ti-O-Ti-O- along c-

The self-consistency was achieved with (6×6×6) k-points in the Brillouin zone and the plane wave basis energy cutoff and charge cutoff are 50 Ry and 758 Ry respectively and calculations are considered to be converged when the total energy of the system is stable within 10⁻⁷ Ry. The electronic configurations of all atoms included in the compounds are Fe [Ar] 3d⁶, Ti [Ar] 3d²4s², P [Ne] 3s² 3p³, O [He] 2s²2p⁴. Here, the geometry optimization has been performed using Broyden-Fletcher-Goldfarb-Shanno algorithm (BFGS) algorithm implemented in the PWSCF code.

Optical properties: The optical spectrum of the oxyphosphate Fe_{0.5}TiOPO₄ has been recorded at 300 K using a double monochromator Cary 2400 spectrometer.

3. Results and discussion

3.1. Description of the structure

M_{0.5}TiOPO₄ (M= Mg²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, ...) crystallize in monoclinic system with space-group of (P₂/c; No. 14). The lattice constants (a, b, c and β) are approximately equal to (a ≈7.4Å, b≈7.3Å, c≈7.4Å and β≈120.3°). Tables 1-2 displays the lattice parameters, and the bond distances (Å) [2] for Fe_{0.5}TiOPO₄ compound at room temperature. These parameters are used for structural optimization. In fact, the optimized final structure is obtained when a threshold is reached under 0.1 mRy per atom for Hellman-Feynman forces and 0.5 kbar for stress tensor [12]. From the values given in Table1, the lattice parameters is found to be under estimated by 1.8% for a(Å), by 1.9% for b(Å) and by 0.2% for c(Å).

axis via oxygen atom O₁, linked by phosphate tetrahedra via oxygen atoms (O₂, O₃, O₄ and O₅). And each [TiO₆] shares the face with [FeO₆] octahedra, while each [FeO₆] octahedra share faces with two [TiO₆] octahedra and corners with four [PO₄] tetrahedra, The Phosphor atoms is found in [PO₄] tetrahedra site surrounded by four oxygen atoms O₂, O₃, O₄ and O₅, the Iron atoms are surrounded by six oxygen atoms 2O₁, 2O₂ and 2O₅ formed in [FeO₆] octahedra site, each octahedra is

isolated and sharing faces with two $[\text{TiO}_6]$ octahedra and corners with four $[\text{PO}_4]$ tetrahedra.

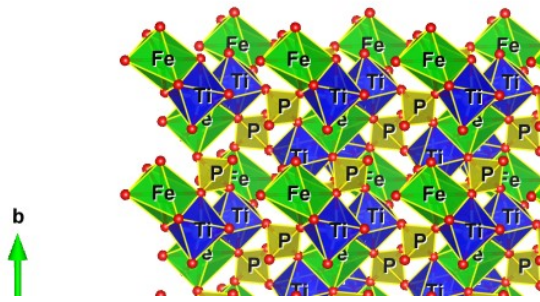


Fig.1. Structure of $\text{Fe}_{0.5}\text{TiOPO}_4$

3.2. Electronic structure and magnetic properties of $\text{Fe}_{0.5}\text{TiOPO}_4$

In order to define the stable magnetic structure of $\text{Fe}_{0.5}\text{TiOPO}_4$, we perform the total-energy calculations of different magnetic configurations, ferromagnetic (FM) and anti-ferromagnetic (AFM). After comparing the results of the calculation of total energies, we find that the AFM configuration is more stable than the FM configuration the results of the totals energies are summarized in the Table 3.

The total and partial densities of states of the ground states of $\text{Fe}_{0.5}\text{TiOPO}_4$ compound have been calculated using the (GGA) approaches its clear from the Fig.2 that the major contribution in the valence band from 0.95 eV to 6.62 eV, is due to the Ti-3d, O-2p and Fe-3d states, and the major contribution in the conduction band from 7.37 eV to 11.37 eV, is due to O-2p and Fe-3d and the energy of the band gap ($E_g = 0.62$ eV) this values is more lower than the experimental one

the (GGA) calculations were not good enough to describe the strong electron correlation systems such as transition metal oxides. The deficiency in first-principle calculation was corrected by using a strong-correlation correction to the (GGA), which is called the (GGA+U) method. This method yielding quite satisfying results for many strongly correlated systems, is considered to be a useful approach [13] using this method the band gap energy E_g has been improved with $U = 5\text{ eV}$ [14] (Fig.3) and shifted from 0.62 eV to 2.2 eV.

The theoretical partial and total spin magnetic moments have been calculated under the (GGA) and (GGA+U) methods and the results summarized in Table 3 the effective magnetic moment of Fe (3d) is $3.65\mu_B$ (GGA) while $3.77\mu_B$ (GGA+U), the total magnetic moments per unit cell are $0\mu_B$.

Table 3

The electronic and magnetic parameters of $\text{Fe}_{0.5}\text{TiOPO}_4$ couponed.

	$\text{Fe}_{0.5}\text{TiOPO}_4$
E_{AFM} (Ry)	-2076.1816
E_{FM} (Ry)	-2076.1810
U_{Fe} (eV)	5
Fermi Energy (GGA) (eV)	7.742
Fermi Energy (GGA+U) (eV)	7.47
E_g (GGA+U) (eV)	2.2
E_g (GGA) (eV)	0.62
m_{eff} (Fe) μ_B (GGA+U)	3.77
m_{eff} (Fe) μ_B (GGA)	3.65
m_{tot} μ_B	0

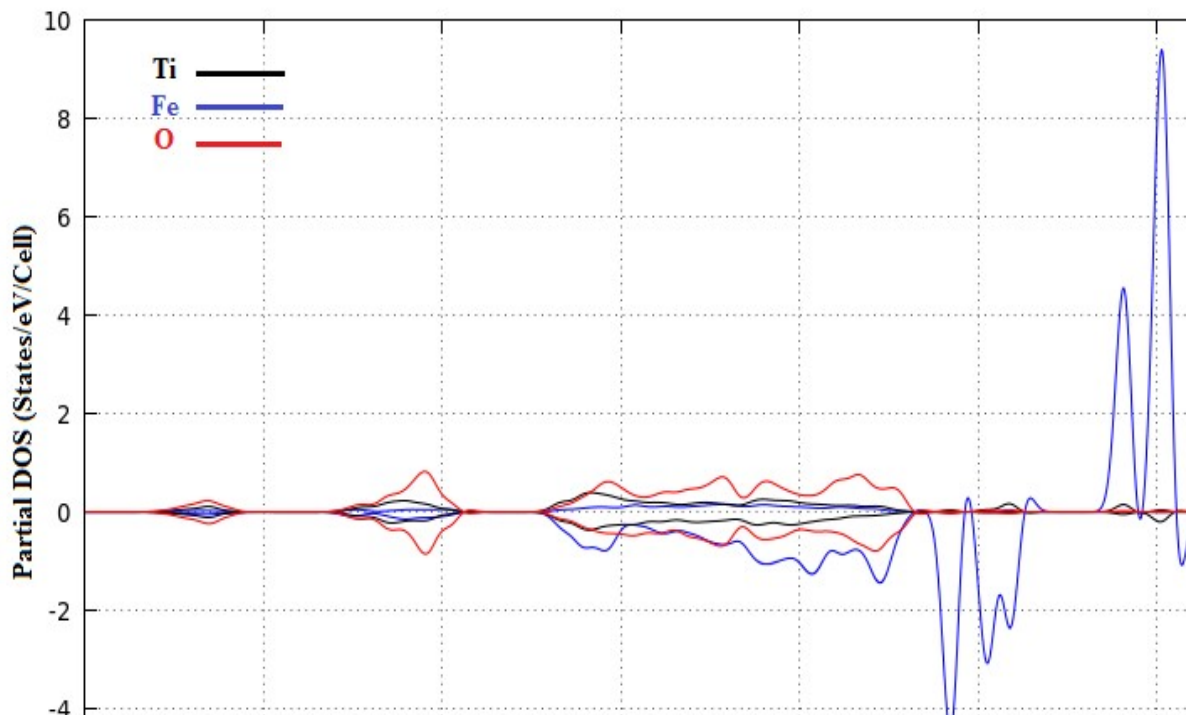


Fig.2. The partial density of states of $\text{Fe}_{0.5}\text{TiOPO}_4$ using (GGA) approximation.

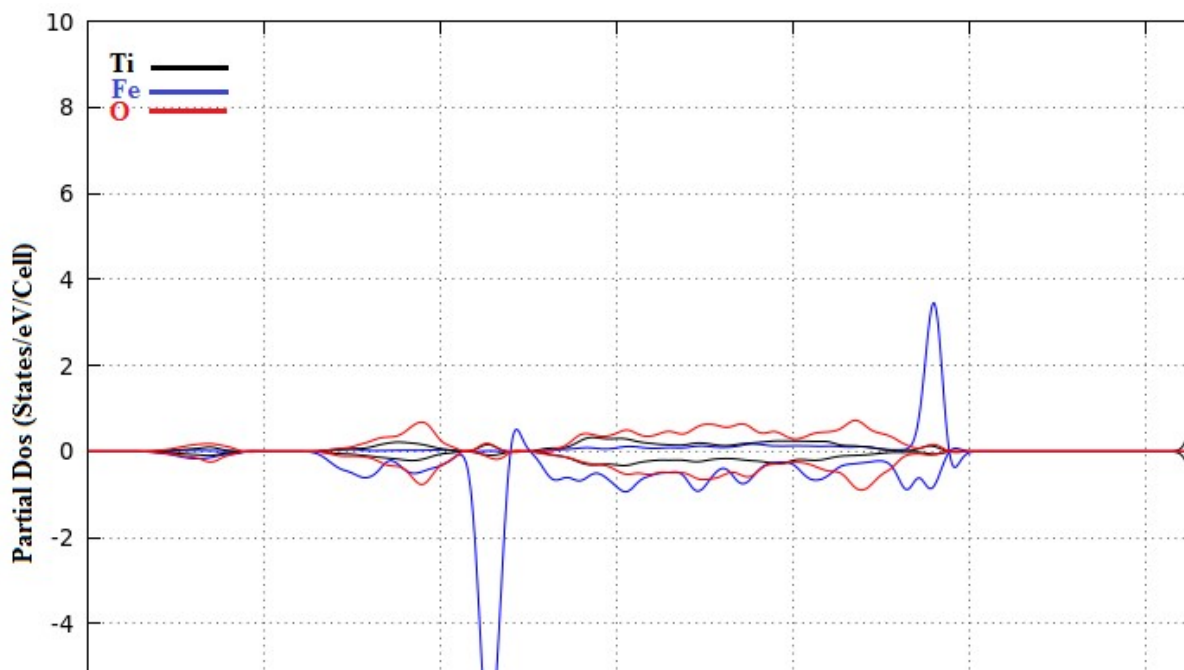


Fig.3. The partial density of states of $\text{Fe}_{0.5}\text{TiOPO}_4$ using (GGA+U) approximation.

3.3. Optical properties

The UV-Vis spectrum is very important because it provides the details related with the optical band. The absorbance spectrum shown in Fig.4 a sharp increase in absorption at wavelength near to the absorption edge 510 nm (≈ 2.45 eV) of the threshold wavelength for onset of absorption, the energy corresponding to this determines the band gap of the material. The inset of Fig.4 shows the $\text{Fe}_{0.5}\text{TiOPO}_4$ absorption coefficient α of around $4 \times 10^4 \text{ cm}^{-1}$ near to the absorption edge (510 nm). The UV-Vis absorption spectrum of $\text{Fe}_{0.5}\text{TiOPO}_4$ plotted in Fig.4 show a strong absorption band at 290 nm wavelength attributed to charge transfer between $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ and between $\text{O}^{2-} \rightarrow \text{Fe}^{2+}$ in $[\text{FeO}_6]$ and $[\text{TiO}_6]$ sites is similar to the isostructural oxyphosphate $\text{Cu}_{0.5}\text{TiO}(\text{PO}_4)$, and the second absorption band shown at

428 nm wavelength attributed to charge transfer between $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$ the same results found in [3]. The bands observed found at 910 nm and 1182 nm correspond to transitions between the orbital d levels $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$.

The Fig.5 shows that graph between $(\alpha h\nu)^2$ versus photon energy ($h\nu$) the extrapolation of the straight line to $(\alpha h\nu)^2 = 0$, give the value of band gap. The determination of optical band gap is obtained by Tauc's equation $\alpha h\nu = A(h\nu - E_g)^n$ [15,16]. Where, A is a constant, $h\nu$ is photon energy ($E = h\nu = 1242/\lambda$ (nm) in the units of eV), (α) the absorption coefficient, The value of n allowed to define the nature of transition for ($n = 1/2$ for direct allowed transition, $n = 3/2$ for direct forbidden transition, $n = 2$ for indirect allowed transition, and $n = 3$ for indirect forbidden transition) [16].

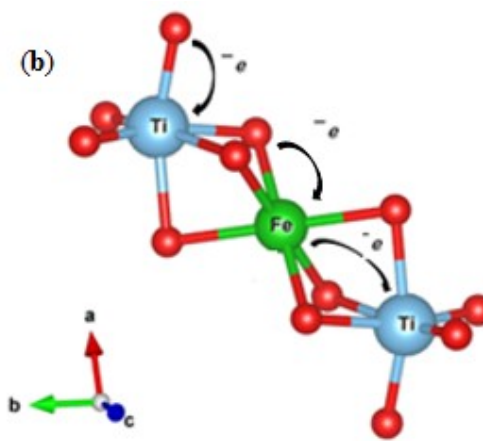
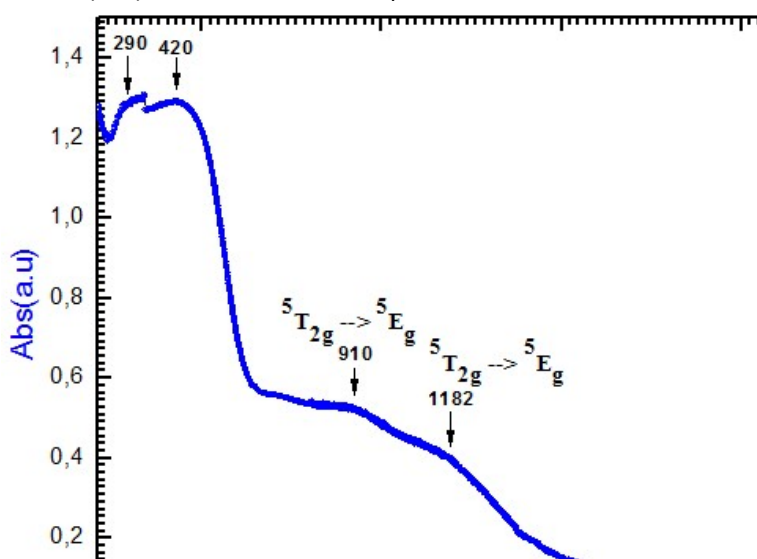


Fig.4. Absorption spectra $\text{Fe}_{0.5}\text{TiOPO}_4$ (a) and the electronic transfer between Fe, Ti and O atoms (b).

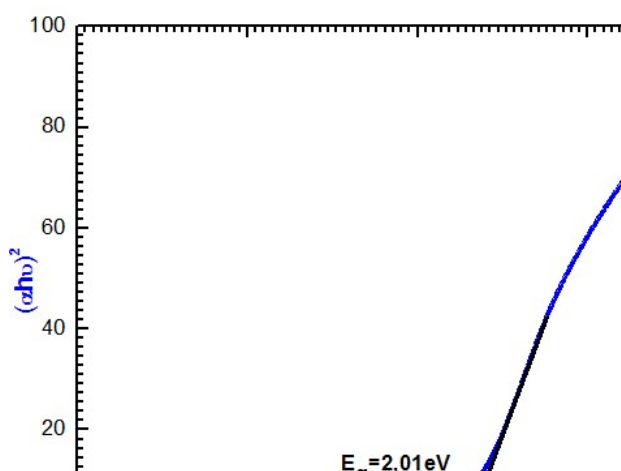


Fig.5. $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ curves of $\text{Fe}_{0.5}\text{TiOPO}_4$

The band gap energy was calculated to be $E_g = 2.01$ eV. This value is lower than that of TiO_2 rutile (24191 cm^{-1} , $E_g = 3.00$ eV) and of oxyphosphate of $\text{Mg}_{0.5}\text{TiOPO}_4$ (27175 cm^{-1} , $E_g = 3.37$ eV). The value of n can be defined from the linear part of the curve $\ln(\alpha h\nu) = \ln(K) + n \ln(h\nu - E_g)$ (Fig.6) the value of n was calculated to be $n = 0.423$ is close to 0.5 for a direct allowed transition.

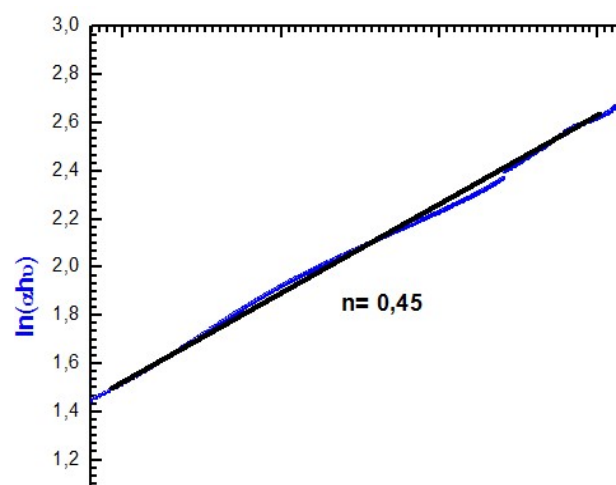


Fig.6. $\ln(\alpha h\nu - E_g)$ versus photon energy $\ln(\alpha h\nu)$ curves of $\text{Fe}_{0.5}\text{TiOPO}_4$

4. Conclusion

The structural, magnetic, electronic, and optical properties of the oxyphosphate phase $\text{Fe}_{0.5}\text{TiOPO}_4$ have been investigated by the first-principles calculations based on DFT with exchange correlation functional GGA and GGA+U ($U = 5.0$ eV). The calculated lattice parameter of this compound is in good agreement with the experimental finding. The calculated band gaps energy

are 0.62 eV (GGA) and 2.2 eV (GGA+U) and the effective moment was calculated to be $3.65 \mu_B$ (GGA) and $3.77 \mu_B$ (GGA+U). The first time study of optical properties such as absorption spectrum are determined and analyzed in detail. The experimental band gap energy was calculated using Tauc's equation $\alpha h\nu = A(h\nu - E_g)^n$ the results show a direct band gap $n = 0.45$ and the value of the band gap energy found to be $E_g = 2.01$ eV.

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