**Electronic structure studies of oxyphosphate Cu0.5TiOPO4**

1. **Harbi1\*, Y .Aharbil1, M. Ait Haddouch1, H. Labrim2, A.** **Benyoussef3,**

**M. jahid4, M. Moutaabbid1 S. Belaaouad1 and S. Benmokhtar1**

1Laboratoire de Chimie Physique des Matériaux LCPM, Faculté des Sciences Ben M’Sik, Université Hassan II de Casablanca, B.P 7955 Sidi Othman, Maroc

2Centre National de l’Energie, des Sciences et des Techniques Nucléaires, Rabat, Morocco

Laboratoire de Magne´tisme et de Physique des Hautes Energies (associe´ au CNRST) De´partement de physique, B.P. 1014, Faculte´ des sciences, Rabat, Morocco

3 Laboratoire de Magne´tisme et de Physique des Hautes Energies (associe´ au CNRST) De´partement de physique, B.P. 1014, Faculte´ des sciences, Rabat, Morocco  
3INANOTECH (Institute of Nanomaterials and Nanotechnology), Rabat, Morocco

4Univ Hassan 1 er, Laboratoire des Sciences des Matériaux, des Milieux et de la Modélisation (LS3M), 25000, Khouribga, Morocco

**Abstract**

The electronic structure and magnetic properties of Cu0.5TiOPO4 have been calculated 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 and the partial densities of states (PDOS) results show that the valence band is formed by O-2p and Cu-3d states and the conduction band formed by Ti-3d state with gap energy Eg=2.24 eV and spin polarization around the Fermi level appears due to the magnetic impurity.

Keywords: self-consistent (DFT), Cu0.5TiOPO4, Density of states, Magnetic property, magnetic impurity.

**Introduction**

The oxyphosphate materials MTiOPO4 (M = Na, K, Rb, Cs, Tl, Ag) are well known nonlinear optical materials of technological importance [1-4]. It has been shown that the same type of structure can be obtained by replacing TiIV ions by M = Zr, Sn, Nb, Ta or Sb, and/or PV atoms by B = As, Si or Ge atoms [5,6]. It is also possible to replace MI cations by MII (MII = Mg, Ni, Co, Fe, Zn, Cu ions) [7–9]. The oxyphosphate material (KTiOPO4; KTP) has shown many optical properties for several nonlinear-optical applications, high thermal stability, high optical damage and high nonlinear-optical coefficients. In recent study, Benmokhtar et al. studied the magnetic and optical proprieties of oxyphosphate Cu0.5TiOPO4 and they had mentioned that the compound is paramagnetic in the whole temperature range from 4 K to 340 K. with C = 0.52, curie constant. The optical absorption spectrum showed a strong absorption band observed in ultraviolet region at 282 nm and attributed to electronic charge transfers from O2- (2p) to Ti4+ (3d), from O2-(2p) to Cu2+ (3d), and at 411 nm is attributed to the Ti4+ (3d) to Cu2+ (3d) electronic charge transfers, three bands observed at 791 nm, 977 nm, 1260 nm, correspond to electronic transitions between Cu2+ (3d) orbital. Also theoretical studies using first principles density functional calculation approach have been done in the order to understand the electronic structure of Li0.50Co0.25TiO(PO4) the results of the partial density of states (PDOS) using GGA and EVGGA show that from -2.0 eV up to Fermi energy is 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 last group from Fermi energy and above is hybridization of Co-d, Ti-s/p/d, P-s/p, and O1-5s/p states [10]. The band structure have been study for KTiOPO4 (KTP) the results show that the compound present a direct band gap at Г the center of the BZ with band gap energy E= 3.1 eV which is in excellent agreement with experimentally measured (3.2 eV) [11] and the same results obtained in [11].

In this research, we deal with the electronic structure studies of Cu0.5TiOPO4 compound in order to explain and understand the mechanism responsible on magnetic properties for this reason we propose a description of the structure Cu0.5TiOPO4 compound and we are going to present the calculated parameters (unit cell, atomic position and bond distances) in the first section, we discuss our calculation results in the second section, In the last section we sum up our important results obtained

## **Method of calculations**

## The calculation are performed using the spin polarized density functional theory, with the Plane-Wave Self-Consistent Field (PWSCF) code implemented in Quantum-ESPRESSO package [12]. The generalized gradient approximation GGA [13,14] have been utilized to study the electronic structure and magnetic properties of oxyphosphat Cu0.5TiOPO4. The number of k points was chosen to be 6×6×6 have been checked for convergence test. The plan wave energy cut-off and kinetic energy cut-off are 50 Ry and 758Ry respectively for the both oxyphosphats, the Self-consistent calculations are considered to be converged when the total energy of the system is stable within 10-6 Ry. The electronic configurations of all atoms included in the two compounds are Cu [Ar] 3d104s1,Ti [Ar] 3d24s2, P  [Ne] 3s2 3p3 , O [He] 2s22p4. Here, we are going to use the unite cell parameters and the atomic position obtained by using the VC-Relax method.

## **Results and discussion**

The crystal structure of the oxyphosphate has been determined in monoclinic system P21/c space group, the compound atoms are placed at Wyckoff positions the Cu occupy the site 2a (0, 0, 0), the other atoms occupy the site 4e (x, y, z). The unite cell parameters, the selects bond lengths and the atomic coordinates for Cu0.5 TiOPO4 are shown in Tables (1–3)

## Table 1.Crystal parameters for Cu0.5TiOPO4

|  |  |  |  |
| --- | --- | --- | --- |
| Cu**0.5** TiOPO4 | | | |
|  | Exp Cal | |  |
| Crystal Structure  Space group  Lattice parameters  a  b  c  β | | Monoclinic Monoclinic  P21/c P21/c  7.5612 7.5595  7.385 7.0234  7.4874 7.3922  122.25 122.089 | |

## 

## Table 2.Bond distances (A˚) for Cu0.5TiOPO4

|  |  |  |
| --- | --- | --- |
|  | Cu0.5 TiOPO4 | |
| Cu-O(1)  Cu-O(1’)  Cu-O(2)  Cu-O(2)  Cu-O(5)  Cu-O(5)  Ti-O(1)  Ti-O(1’)  Ti-O(2)  Ti-O(3)  Ti-O(4)  Ti-O(5)  P-O(2)  P-O(3)  P-O(4)  P-O(5) | Exp | Cal |
| 1.979  1.979  2.290  2.290  1.970  1.970  1.722  2.308  2.013  1.895  1.909  2.099  1.535  1.522  1.529  1.549 | 1.9877  1.9877  2.3655  2.3655  1.9835  1.9835  1.7706  2.1786  2.0128  1.8907  1.9087  2.1014  1.5376  1.5321  1.5376  1.5526 |

## Table 3.atomic coordinates and equivalent isotropic displacement parameters (A˚) for Cu0.5 TiOPO4

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Atom** | **site** | **x** | **y** | **z** |
| Cu(exp)  Cu(cal) | 2a | 0  0 | 0  0 | 0  0 |
| Ti(exp)  Ti(cal) | 4e | 0.73519  0.7327 | 0.21943  0.2192 | 0.53513  0.5295 |
| P(exp)  P(cal) | 4e | 0.24896  0.2519 | 0.13120  0.1362 | 0.74781  0.7497 |
| O1(exp)  O1(cal) | 4e | 0.7696  0.7677 | 0.1511  0.1590 | 0.7724  0.7791 |
| O2(exp)  O2(cal) | 4e | 0.7568  0.7372 | 0.0017  0.0085 | 0.0935  0.0822 |
| O3(exp)  O3(cal) | 4e | 0.4410  0.4388 | 0.2579  0.2724 | 0.8556  0.8473 |
| O4(exp)  O4(cal) | 4e | 0.2440  0.2402 | 0.0189  0.0264 | 0.5709  0.5637 |
| O5(exp)  O5(cal) | 4e | 0.0544  0.0545 | 0.2392  0.2378 | 0.1546  0.1662 |

## **Description of the structure**

The structure can be described as a 3-dimensional network of [TiO6], [CuO6] octahedra and [PO4] tetrahedra (figure 1).

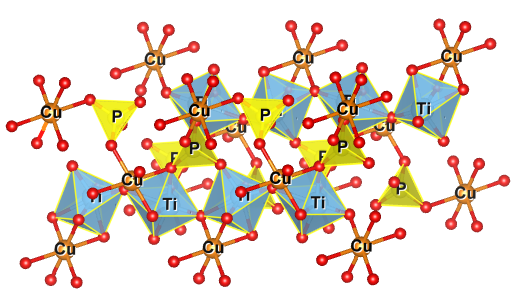


Fig.1.Structure of Cu0. 5TiOPO4

The [TiO6] octahedra shares the corners and forms infinite chains of –Ti-O-Ti-O- along c-axis, linked by phosphate tetrahedra via oxygen atoms (O2, O3, O4 and O5). Two successive [TiO6] octahedra of the same chains are linked via oxygen atom O1 which does not belong to the [PO4] tetrahedron. And each [TiO6] shares the face with [CuO6] octahedra, while each [CuO6] octahedra share faces with two [TiO6] octahedra and corners with four [PO4] tetrahedra figure 1, The Phosphor atoms is found in [PO4] tetrahedra site surrounded by four oxygen atoms O2, O3, O4 and O5 ,the Cu atoms are surrounded by six oxygen atoms 2O1, 2O2 and 2O5 formed in [CuO6] octahedra site, each octahedra is isolated and sharing faces with two [TiO6] octahedra and corners with four [PO4] tetrahedra, the distances between Cu-Oi with i=1,2,3 are 1.9877, 2.3655,1.9835A° respectively we observe four short distances between Cu-Oi i=1,3 and two long distance between Cu-Oi with i=2 is typical of the Jahn–Teller effect.

## **Structural properties of Cu0.5TiOPO4**

The magnetic and properties of Cu0.5TiOPO4 have been investigated by studying the total and partial densities of states using GGA approximation, since the structure of Cu0.5TiOPO4 have two Cu atom positions at (Cu1:(0, 0, 0) and Cu2:(0, 1/2, 1/2)), two possible modes of coupling between Cu atoms are suggests (ferromagnetic or antiferromagnetic), two types of calculations have been done; the first we propose that the Cu atoms are ferromagnetic coupling Figure (2) and the seconds suggestion we also propose the Cu atoms are antiferromagnetic coupling Figure (3) the total energy for the two cases are presented in the table(4) below. The difference between the both energies (∆E=EAF-EF) indicates that the antiferromagnetic coupling is more stable than the ferromagnetic one.

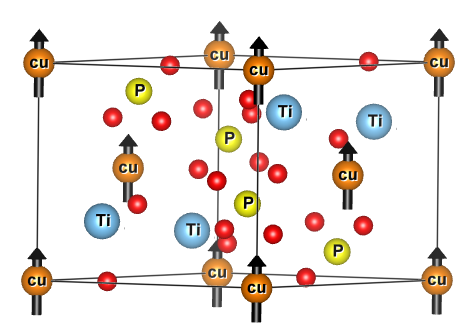
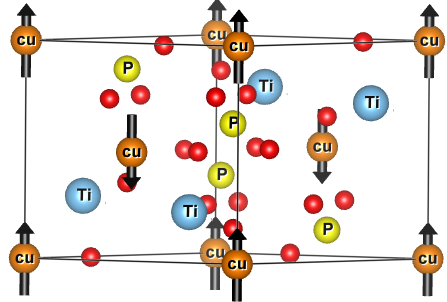


Fig.2.ferromagnetic coupling Fig.3.antiferromagnetic coupling

It is obvious that the partial density of states for Cu0.5TiOPO4 Figures (8-9) that the valence band, it location from -5.74 eV to -0.83 eV is mainly formed by O-2p and Cu-3d states and the conduction band divided in two parties the first region between 1.66 eV to 2.945 eV and the second part between 3.32 eV to 5.54 eV for the both regions we found that the major contribution is due to the Ti-3d state. Further it is clearly seen that spin polarization around the Fermi level appears due to the magnetic impurity in the both Figures (4-5) the same impurity obtained in [15,16]

In figure (4) the minority-spin impurity states are completely empty but the majority-spin ones are partially full at the Fermi level a strong hybridization appear between Cu-3d and O-2p states and the spin polarization for Cu-3d and O-2p are ferromagnetic coupling the same observation in minority-spin at the Fermi level in Figure (5), we infer from the both figures that the spin polarization for Cu-3d are antiferromagnetic coupling.

The total magnetic of Cu0.5TiOPO4 is null and the local magnetic moments of Cu and Oi with i=1-5 atoms are around 0.5612 μB, 0.0892 μB, 0.0111 μB, 0.0046 μB, 0.0003 μB and 0.0785 μB respectively. The values of band gap energy is about 2.24 eV obtained by using GGA approximation we observe a diminution of energy gap compared to 3.25eV for Mg0.5TiOPO4 the variation in the gap energy is due to the coulomb correlation interaction between cation Cu2+ and anion O-2 and the Jahn–Teller effect.

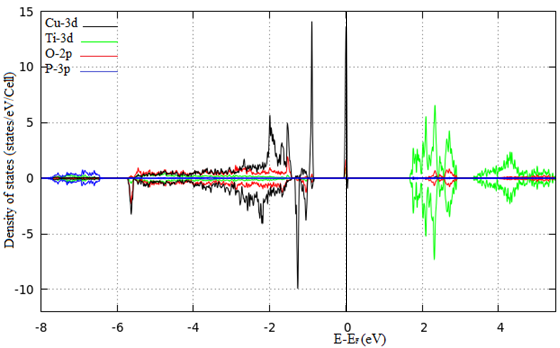


Fig.4.Partial density of states of Cu0.5TiOPO4

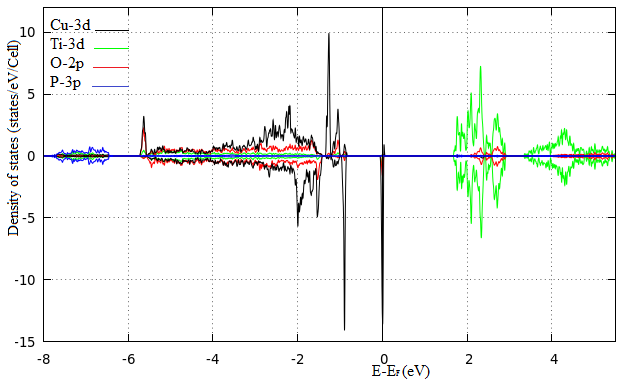


Fig.5.Partial density of states of Cu0.5TiOPO4

## Table 4.The calculated gap energy, the total energy and Fermi energy of Cu0.5TiOPO4

|  |  |  |  |
| --- | --- | --- | --- |
|  | Eg(eV) | Etot(Ryd) | Ef(eV) |
| ferromagnetic coupling  antiferromagnetic coupling | 2.47  2.24 | -2766.05630096  -2788.05654564 | 6.9377  6.8883 |

# **Conclusion**

In the present work we have studied the electronic and magnetic properties of Cu0.5TiOPO4 within using density functional theory with the Plane-Wave Self-Consistent Field (PWSCF) code. The calculated structure parameters is found to be in good agreement with experiment data. The electronic structure study for Cu0.5TiOPO4 indicate a strong hybridization between Cu-3d and O-2p electrons at the Fermi level and the spin polarization for Cu-3d are antiferromagnetic coupling with total spin magnetic moment of (m = 0 μB/f.u.) and the calculated band gap is about 2.24 eV using GGA approximation.

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