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Electronic structures and optoelectronic properties of ATiOPO$_4$ ($A = H, Li, Na, K, Rb, Cs, Fr, NH$_4$, Ag) compounds and their applications in water splitting, CO$_2$ reduction, and photo-degradation

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Abstract

In this paper, we have presented a computational study on the crystal structures, electronic, and optical properties of the titanyl phosphate family (ATiOPO$_4$, where $A = H, Li, Na, K, Rb, Fr, NH_4$ and Ag). The lattice parameters and bandgaps were calculated with the Perdew-Burke-Ernzerhof (PBE), Revised Perdew-Burke-Ernzerhof (RPBE), Perdew Wang (PW91), Wu-Cohen (WC), and Perdew-Burke-Ernzerhof for solids (PBEsol) non-local functionals of the generalized gradient approximations (GAA). The PBEsol functional provided better results and closer to the experimental data of the ATiOPO$_4$ compounds; and thus, this method was used to analyze the band structures, density of states, and optical properties. A comparison between the optical properties (dielectric function, refractive index, absorption coefficient, reflectivity, electron energy loss spectrum, and photoconductivity) of ATiOPO$_4$ compounds were discussed. The potentials of valance band and conduction band edges were calculated and used to investigate the protentional applications of the ATiOPO$_4$ materials in water splitting, CO$_2$ reduction, and photo-degradation processes. The results obtained in our investigations show that many of the investigated ATiOPO$_4$ semiconductors could be used as effective photocatalysts in these photocatalytic reactions.

1. Introduction

Potassium titanyl phosphate KTiOPO$_4$ (KTP) family are one of the main materials for nonlinear optical applications. They possess outstanding physical properties, such as high nonlinearity [1], wide range of transmission wavelengths [2], high absorption coefficient [3], excellent chemical and thermal stabilities [4], and ion exchange characteristics [5]. More than hundred compounds belong to KTP family [6–8], about ninety in which the potassium, titanium, and phosphorus atoms were replaced or doped by other elements. The chemical formula of this family is ATiOXO$_4$, where A is K, Li, Na, K, Rb, Cs NH$_4$, and Ag; and X is P or As. The titanium atom is replaced by Nb, Zr, Hf, Ge, Sn, Sb, Ta, Fe, and Zn. The KTP family are generally synthesized by two methods: hydrothermal growth and flux growth [8]. These materials have piezoelectric and ferroelectric properties [9], and have high laser damage threshold [10]. Some of these compounds showed promising performance as sodium ion batteries (NIBs) [11] and lithium ion batteries (LIBs) anodes [12–16], as well as in sodium and potassium ion storage [17].

Lowther et al [18] have studied effects of Rb impurities on the structural and electronic properties of KTP by using ab initio calculations. Ghoohestani et al [19] have also investigated the structural, electronic, and optical properties of KTP, as well as the effects of Rb substitution. Reshak et al [20] have studied experimentally and theoretically the linear and nonlinear optical susceptibilities of KTP. Atuchin et al [21] have studied the relationship between crystal structure, electronic and nonlinear optical properties of the systems KTP and...
rubidium titanyl phosphate (RTP) by theoretical and experimental methods. The atomic geometry, electronic, and optical properties of oxygen and potassium vacancies in KTP have been studied within density functional theory (DFT) [22].

In this work, we employ first principle calculations to investigate the effect of changing A-site on the structural, band gap, and optical properties of ATIOPo₄ (ATP) family considering nine different cations (A = H, Li, Na, K, Rb, Cs, Fr, NH₄ and Ag). In general, all of them have orthorhombic structure but the known materials with crystal structures are NaTP, KTP, RbTiOPO₄, NH₄TiOPO₄ and AgTiOPO₄ (AgTP). For the first time, this work explores the opportunity of using these materials in the photocatalytic processes, such as CO₂ reduction, water splitting and photo-degradation. It is well known that titanate compounds are considered to be one of the most promising photocatalysts owing to their high photocatalytic activity, chemical stability, and inexpensiveness [23, 24]. They are widely employed in several photocatalysis processes, e.g., photodegradation, water splitting, and CO₂ reduction [24]. The enhancement of photocatalytic activity of titanate was induced by doping with phosphorus, and was attributed to the decrease in the recombination of electrons and holes, the narrowed band gap, and thermal stability [25]. The phosphate anion species bound to the titanate surface has promoted the photodegradation of organic pollutants and hydrogen production [26]. The fact that the phosphate species enhanced the photocatalytic reactions motivated us to investigate KTP family.

2. Computational methods

The ab-initio calculations were performed by the plane-wave basis with the pseudopotential methods in the framework of DFT, as implemented in the CASTEP code [27]. We used five different non-local functional generalized gradient approximations (GGA) [28]: Perdew-Burke-Emzerhof (PBE) [29], Revised Perdew-Burke-Emzerhof (RPBE) [30, 31], Perdew Wang (PW91) [32], Wu-Cohen (WC) [33] and Perdew-Burke-Emzerhof for solids (PBEsol) [34]. Each exchange-correlation (XC) functional was computed using two different kinetic-energy cut-offs: 340 eV and 750 eV at ultrasoft and norm conserving pseudopotentials [35], respectively. A 1 × 2 × 1 Monkhorst-Pack grid [36] was used. About the relaxation of the lattice parameters, we used the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method [37, 38]. The self-consistent field (SCF) tolerance was 1.0 × 10⁻⁵ (eV/atom). The total energy tolerance, maximum ionic Hellmann-Feynman force, and maximum ionic displacement tolerance were 2.0 × 10⁻⁶ (eV/atom), 0.006 (eV/Å) and 2.0 × 10⁻⁶ (Å), respectively. For the optical spectra calculations, a dense mesh of uniformly distributed k-points is required; hence, the Brillouin zone integration was performed using a 2 × 4 × 2 grid of Monkhorst-Pack points.

The HTP, LiTP, CsTP, FrTP, NH₄TP, and AgTP structures were constructed by a full substitution in those other optical properties, such as the refractive index, reflectivity, extinction coefficient, absorption coefficient, optical conductivity, and electron energy-loss spectrum, can be derived from ε₁(ω) and ε₂(ω). The optical properties were calculated along [100] direction and using polarized light.

3. Results and discussion

3.1. Structural properties

Table 1 reports the calculated lattice parameters for the NaTP, KTP, RbTP, NH₄TP, and AgTP using the investigated XC functionals, together with the experimental crystal parameters. While table 2 summarizes the predicted lattice parameters for the HTP, LiTP, CsTP and FrTP materials. It is clear from table 1 that the most XC functionals that exhibit better agreement with the experimental results were PBEsol and WC when pseudopotential treated with norm conserving method. The PBEsol functional is used to analysis and discuss the electronic and optical properties, since it introduces a sufficient and corrected data [39].

Figure 1 shows the optimized crystal structures of the studied ATP compounds using GGA/PBEsol/norm conserving method. The ATP crystals have orthorhombic structure with group number 33 and space group Pna21. The cell formula of the studied ATP materials is M₈T₈P₈O₄₀, the unit cell contains 64 atoms where A = H, Li, Na, K, Rb, Cs, Fr, NH₄ and Ag; and the unit cell of NH₄TP contains 96 atoms. All the ATP materials remain with the same crystal structure after optimizations.
Table 1. Comparison between the calculated and experimental lattice parameters of NaTP, KTP, RbTP, NH₄TP, and AgTP materials.

| ATP  | Functionals | a (Å) | b (Å) | c (Å) | V (Å³) |
|------|-------------|-------|-------|-------|--------|
| NaTP | PBE         | 12.81 | 6.38  | 10.72 | 876.95 |
|      | RPBE        | 12.91 | 6.42  | 10.83 | 899.12 |
|      | PW91        | 12.79 | 6.37  | 10.72 | 874.42 |
|      | WC          | 12.71 | 6.34  | 10.62 | 855.37 |
|      | PBEsol      | 12.70 | 6.33  | 10.61 | 853.57 |
|      | EXP [40]    | 12.55 | 6.25  | 10.55 | 829.2  |
| KTP  | PBE         | 12.98 | 6.48  | 10.71 | 906.80 |
|      | RPBE        | 13.14 | 6.55  | 10.83 | 932.32 |
|      | PW91        | 12.96 | 6.47  | 10.69 | 897.37 |
|      | WC          | 12.84 | 6.42  | 10.61 | 874.55 |
|      | PBEsol      | 12.83 | 6.41  | 10.60 | 873.03 |
|      | EXP [40]    | 12.82 | 6.41  | 10.61 | 871.89 |
|      | EXP [41]    | 12.82 | 6.40  | 10.58 | 868.20 |
| RbTP | PBE         | 13.15 | 6.58  | 10.68 | 924.84 |
|      | RPBE        | 13.31 | 6.67  | 10.78 | 957.73 |
|      | PW91        | 13.13 | 6.57  | 10.66 | 920.58 |
|      | WC          | 13.00 | 6.51  | 10.59 | 897.14 |
|      | PBEsol      | 12.99 | 6.50  | 10.58 | 895.63 |
|      | EXP [42]    | 12.97 | 6.49  | 10.56 | 888.89 |
|      | EXP [41, 43]| 12.97 | 6.49  | 10.56 | 890.7  |
| NH₄TP| PBE         | 13.04 | 6.67  | 10.65 | 926.90 |
|      | RPBE        | 13.01 | 7.40  | 10.42 | 1003.76|
|      | PW91        | 13.01 | 6.65  | 10.64 | 921.79 |
|      | WC          | 12.88 | 6.56  | 10.58 | 895.96 |
|      | PBEsol      | 12.88 | 6.56  | 10.59 | 894.13 |
|      | EXP [44]    | 12.91 | 6.49  | 10.59 | 888.18 |
| AgTP | PBE         | 12.67 | 6.36  | 10.82 | 872.70 |
|      | RPBE        | 12.82 | 6.41  | 11.00 | 903.33 |
|      | PW91        | 12.65 | 6.36  | 10.81 | 869.67 |
|      | WC          | 12.52 | 6.31  | 10.64 | 841.97 |
|      | PBEsol      | 12.52 | 6.30  | 10.63 | 841.49 |
|      | EXP [44]    | 12.52 | 6.26  | 10.53 | 825.95 |

Table 2. The predicted lattice parameters for HTTP, LTTP, CsTP, and FrTP materials.

| ATP  | Functionals | a (Å) | b (Å) | c (Å) | V (Å³) |
|------|-------------|-------|-------|-------|--------|
| HTP  | PBE         | 12.91 | 6.32  | 10.94 | 892.94 |
|      | RPBE        | 13.05 | 6.36  | 11.05 | 916.73 |
|      | PW91        | 12.89 | 6.31  | 10.92 | 889.33 |
|      | WC          | 12.74 | 6.28  | 10.84 | 867.47 |
|      | PBEsol      | 12.73 | 6.28  | 10.83 | 865.82 |
|      | EXP [45]    | 12.81 | 6.37  | 10.68 | 872.73 |
| LTTP | PBE         | 12.81 | 6.37  | 10.68 | 872.73 |
|      | RPBE        | 12.90 | 6.41  | 10.79 | 893.67 |
|      | PW91        | 12.81 | 6.37  | 10.66 | 869.55 |
|      | WC          | 12.73 | 6.33  | 10.57 | 852.38 |
|      | PBEsol      | 12.72 | 6.32  | 10.56 | 849.98 |
|      | EXP [44]    | 13.43 | 6.82  | 10.54 | 965.66 |
|      | RPBE        | 13.05 | 8.01  | 10.16 | 1062.80|
|      | PW91        | 13.4  | 6.82  | 10.53 | 961.98 |
|      | WC          | 12.21 | 6.67  | 10.53 | 928.62 |
|      | PBEsol      | 13.21 | 6.68  | 10.52 | 928.15 |
|      | EXP [44]    | 13.10 | 7.73  | 10.14 | 1027.98|
| CsTP | PBE         | 13.32 | 7.90  | 10.21 | 1074.67|
|      | RPBE        | 13.03 | 7.82  | 10.13 | 1031.61|
|      | PW91        | 13.29 | 6.74  | 10.52 | 942.81 |
|      | WC          | 13.30 | 6.74  | 10.52 | 943.34 |
|      | PBEsol      | 13.30 | 6.74  | 10.52 | 943.34 |

[1] M K Abdel-Sattar and M Taha 045901 Mater. Res. Express 7 (2020)
3.2. Electronic properties

The energy/band gaps ($E_g$) of the ATP compounds were calculated using PBE, RPBE, PW91, WC, and PBEsol with the ultrasoft and norm conserving pseudopotentials. KTP is the only material with a known bandgap ($E_g$); it has a direct bandgap at 3.2 eV and indirect one at 3.8 eV [2, 20, 45–48]. The best value in our results that closer to the experimental data was 3.22 eV using PBEsol with ultrasoft pseudopotential, and 3.35 eV using the same functional but when treated with norm conserving one. But in our next results we will use PBEsol treated with norm conserving pseudopotential since the high energy cut-off provides more accurate results for optical properties. The bandgap of KTP was calculated theoretically by Ghoohestani et al. [19] using WC, PBEsol and modified Becke-Johnson (mBJ). The $E_g$ of KTP with PBEsol was 3.29 eV [19] which is closer to our predicted value. The obtained bandgaps of the studied ATP materials are reported in table 3. The $E_g$ values obtained by the GGA/PBEsol with ultrasoft and norm conserving pseudopotentials method were plotted in figure 2. We observed that $E_g$ decreases with changing the cation in the order of NaTP > KTP > NH$_4$TP > RbTP > HTP > LiTP > CsTP > FrTP. The $E_g$ values for the NaTP, KTP, NH$_4$TP, RbTP, HTP, LiTP, CsTP, and FrTP were in the range of 3.14 – 3.41 eV. The AgTP has the lowest bandgap (2.36 eV) among these materials. Moreover, the bandgaps obtained by the norm conserving pseudopotential were greater than those of the ultrasoft one. The band structures of ATP compounds are presented in figure 3.

The properties of the ATP materials are related to the specific features of their atomic positions. The structure of ATP crystals has rigid 3-dimensional framework, in which the vertex-oxygen octahedra (TiO$_6$) is alternating with the phosphours-oxygen tetrahedra (PO$_4$). The TiO$_6$ octahedral have a distorted structure. The TiO$_6$ octahedra contain a long (Ti–O) and short (Ti=O) bond lengths. It was reported [49] that the nonlinear optical properties of ATP crystals were associated with alternation of these two bonds in the TiO$_6$ octahedral chain (table 4). The difference between (Ti–O) and (Ti=O) bond lengths leads to TiO$_6$ octahedra distortion. The bond lengths of (Ti–O) and (Ti=O) are reported in table 4, together with the octahedral distortion parameter ($\Theta$). This distortion parameter was determined by OctaDist program (https://octadist.github.io), which measures the deviation of the Ti center geometry from the perfect octahedron to trigonal prismatic. The higher the $\Theta$ value the more distorted the octahedron. It was reported that a larger distortion is generally

![Figure 1. The optimized crystal structures of ATP compounds using GGA/PBEsol method.](image-url)
increases the nonlinear optical property [48]. Nevertheless, Thomas et al [50] state that the octahedra distortion in the KTP family is a necessary but not the sole condition for high nonlinear optical properties. It can be seen from the $\Theta$ values that the NH$_4$TiOPO$_4$, AgTiOPO$_4$, NaTiOPO$_4$, and HTiOPO$_4$ are more distorted than the other ATP materials.

The electronic partial density of states (PDOS) of ATP materials using are plotted in figures 4 and 5. It can be seen that the fermi level ($E_F$) is near to the valence band ($VB$). The p-orbital showed a high DOS close to the $E_F$, which appears as a broad peak with a width of 8 eV belongs to the O-2p states [19, 51]. Three peaks within range of 14−21 eV for O-2s states were observed. As for the Ti atoms, they have two sharp peaks located at lower energies of about $-32.2$ eV for 3p states and $-55$ eV for 4s, indicating that these two states do not contribute in the bonding with O atoms. There is a small and broad peak near to the fermi level for 3d states. Thus, the top of the VB involves high O-2p states, Ti-3d states, and Ti-3p states. The bottom of the conduction band ($CB$) region consists of high DOS for 3d states of Ti atoms and low DOS for O-p states, respectively. As for the P atoms, they have two peaks for p states appeared in the VB at $-17$ eV and $-6$ eV, as well as a peak in the CB at $11$ eV.

The states for A-cation in each ATP compound have their own significant peaks (figure 4). H-1s states have three small peaks at $-5$ to $-8$ eV and another three small peaks at $-17$ to $-20$ eV. Li-2s states have very small peaks at $-7.7$ eV, $-18$ eV, and $-20$ eV. The Na-3s, K-4s, Rb-5s, and Cs-6s states showed sharp peaks at about $-40$, $-27$, $-22$, and $-19$ eV, respectively. The Na-2p, K-3p, Rb-4p, and Cs-5p states showed also sharp peaks at about $-22.5$, $-11$, $-8$, and $-5.8$ eV, respectively. The Cs-5p showed very small peak near to the bottom of the VB. As we moved from Na to Cs these two states are shifted toward $E_F$. The s and p states of these alkali metal displayed small broad peaks in the CBs. NH$_4$-2p states for N atom appear at $-6.4$ eV and peak H-1s states appear at the same value. The H-1s and N-2s states have sharp peak at $-16.5$ eV. Additionally, the NH$_4$-2s and NH$_4$-2p states have broad peak in the conduction band at $11$ eV. From the above discussion, it is

![Figure 2. The bandgaps (eV) results using GGA/PBEsol with ultrasoft (black) and norm conserving (red) pseudopotentials.](image)

| ATP     | PBE | RPBE | PW91 | WC  | PBEsol | PBE | RPBE | PW91 | WC  | PBEsol |
|---------|-----|------|------|-----|--------|-----|------|------|-----|--------|
| HTP     | 2.98| 2.83 | 2.98 | 3.13| 3.15   | 3.09| 2.94 | 3.11 | 3.26| 3.27   |
| LiTP    | 3.10| 3.02 | 3.08 | 3.11| 3.12   | 3.22| 3.15 | 3.23 | 3.26| 3.26   |
| NaTP    | 3.17| 3.10 | 3.18 | 3.27| 3.29   | 3.28| 3.18 | 3.29 | 3.39| 3.41   |
| KTP     | 3.11| 3.01 | 3.12 | 3.21| 3.22   | 3.22| 3.11 | 3.23 | 3.34| 3.35   |
| RbTP    | 3.06| 2.96 | 3.06 | 3.14| 3.16   | 3.19| 3.06 | 3.19 | 3.31| 3.32   |
| CsTP    | 2.92| 2.71 | 2.93 | 3.03| 3.04   | 2.96| 2.93 | 2.98 | 3.18| 3.19   |
| FrTP    | 2.90| 2.78 | 2.86 | 2.96| 2.98   | 3.09| 2.98 | 3.09 | 3.13| 3.14   |
| NH$_4$TP| 3.05| 3.06 | 3.06 | 3.16| 3.19   | 3.19| 3.17 | 3.19 | 3.29| 3.30   |
| AgTP    | 2.43| 2.53 | 2.42 | 2.34| 2.33   | 2.46| 2.58 | 2.46 | 2.40| 2.36   |
clear that the band structure of the ATP materials (where A = H, Li, Na, K, Rb, Cs, NH4) is weakly depend on the nature of the A-cation element, since their states are located far from the VB and CB edges. Fr-6p states have a high-DOS broad peak near $E_F$. The Fr-5d states have a small broad peak near the $E_F$, and a high-DOS broad located at the CB edge. The Fr-7s states have a sharp peak at $-20$ eV and small peak in the CB. In case of AgTP (figure 5), the PDOS show high peaks for both 4p and 4d states in valence band, since Ag atom is a transition metal. The PDOS AgTP has a sharp peak at $-50$ eV for Ag-4p states. The Ag-5s states have sharp peak located at $-81.4$ eV and small peak located near the CB edge.

3.3. Optical properties

Reflectivity describes how much light is reflected from the material in relation to an amount of light incident on the material. The reflection coefficient ($R$) can be obtained for the simple case of normal incidence onto a plane surface by matching both the electric and magnetic fields at the surface. Figure 6 represents the reflectivity
spectra of ATP materials as a function of photon energy ranging from 0.01 up to 75 eV. At photon energy equals 0.01 (infrared region), the reflectivity of KTP, LiTP, NaTP, RbTP, and NH$_4$TP are $\sim$0.1, while for FrTP, CsTP, AgTP, and HTP are, respectively, 0.51, 43, 0.38, and 0.33 and then decreases dramatically to $\sim$0.1 at photon energy $\sim$1.1 eV. The reflectivity of the ATP materials is more significant in the range of 1.2 eV to 30 eV. The reflectivity reached almost zero beyond 50 eV and in the range of 30-50 eV. It was found small reflectivity peak with a maximum of $\sim$0.05 in the range of photon energy 34 to 40 eV. Among the ATP materials, KTP showed the lowest reflectivity.

The absorption coefficient provides useful data when these materials are used in solar energy conversion to achieve optimum efficiency. Figure 7 shows the absorption coefficient spectra of ATP materials. In general, these compounds show strong absorption coefficient starting from 3 eV to 25 eV, in case of KTP the absorption of this region extended to 30 eV. The HTP, LiTP, KTP, NaTP, CsTP, NH$_4$TP, and AgTP displayed maximum absorption at 18 eV. Among these compounds, the KTP has the lowest absorption. The FrTP showed two maxima at 12 eV and 18 eV, while CsTP exhibited maximum absorption at 20 eV. The ATP materials showed good absorption in the range of 45 to 40 eV, with a maximum absorption at 36 eV. The HTP, AgTP, CsTP, and FrTP materials exhibited small peak in the IR region. Moreover, the AgTP showed small peak at $\sim$55 eV.

The refractive index $n(\omega)$ indicates the amount of light refracted or bent, when entering a material. The imaginary part $k(\omega)$ is called the extinction coefficient, which refers to the mass attenuation coefficient term and determines the amount of attenuation when the light propagates through the material. Figures 8(a)–(d) represents the refractive index (real part) and extinction coefficient (imaginary part) for the ATP materials. FrTP, AgTP, NH$_4$TP and CsTP exhibit high values of $n(\omega)$ and $k(\omega)$ in the infrared region and gradually decrease in the visible and ultraviolet region. The LiTP, NaTP, KTP, RbTP, and NH$_4$TP exhibited refractive index $\sim$1.9 at photon energy of 0.01. While the $n(\omega)$ values of FrTP, CsTP, AgTP, and HTP were 5.9, 4.7, 4.1, and 3.6, respectively.

The dielectric function illustrates how the electric field such as an oscillating light wave would do to material. The real part $\varepsilon_1(\omega)$ of the complex dielectric function, indicates the polarization of material caused by the propagating light, while imaginary part $\varepsilon_2(\omega)$ represents the amount of absorption in a material.

Figure 9 shows the predicted dielectric function, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, for the ATP compounds. In figure 9(a) one can notice that for most ATP compounds, $\varepsilon_1(\omega)$ is positive up to (17.5–18.5) eV and presents several peaks at (4, 7, 10, 12.5, 15 and 16.3) eV. However, FrTP and CsTP have positive up to 11.5 and 16 eV, respectively. On the other hand, KTP does not have negative values. The material displays dielectric behavior when $\varepsilon_1(\omega) > 0$ and metallic behavior when $\varepsilon_1(\omega) < 0$ above and below plasma frequency, respectively. The LiTP, NaTP, KTP, RTP,

![Figure 4. The PDOS of the ATP (A = H, Li, Na, K, Rb, Cs, Fr, and NH$_4$) materials using GGA/PBEsol/norm conserving.](image-url)
Figure 5. The PDOS of the AgTiOPO$_4$ using GGA/PBEsol/norm conserving.

Figure 6. The reflectivity of ATP compounds (a) as a function of energy (eV). For the sake of clarity, each data plot is extracted into separate plots (b).
and NH$_4$TP have dielectric constant of $\sim 3.7$ at photon energy of 0.01. While the $\varepsilon_1(\omega)$ values of FrTP, CsTP, AgTP, and HTP were 33.9, 21.4, 16.8, and 13.1, respectively.

The imaginary dielectric function is a significant quantity; it represents the several inter-band transitions between VB and CB. From the characteristic of the imaginary part $\varepsilon_2(\omega)$ shown in figures 9(c), (d), each compound has a first peak is due to the optical transition according to the value of band gap followed by four more peaks except for FrTP which showed only four total peaks\cite{19}. The major peak occurs around 4.0 eV for most of these compounds except for CsTP and FrTP which lies at 9 and 14 eV, respectively.

Figures 10(a)–(d) shows the optical conductivity spectra of ATP materials as a function of photon energy. The optical conductivity is the extension of electrical transport to high (optical) frequencies. It is a contact free quantitative measurement, mostly sensitive to charged responses\cite{52}. In general, the calculated optical conductivity for all ATP compounds has many maxima and minima within the energy range taken according to the energy band gap. However, RbTP, CsTP, FrTP and NH$_4$TP show higher optical conductivity peaks than the others.

Figure 11 represents the energy loss function as a function of photon energy. The electron energy loss function (L) is an important optical parameter. The function L describes the energy loss of fast electrons traversing the material. The peaks in L function are associated with the plasma resonance and the corresponding frequency is the so-called plasma frequency\cite{53}. This function has the usefulness of enveloping the full energy range, involving scattered elastically and non-scattered electrons, which excite the electrons of the valence inter-band transitions or atom’s outer shell\cite{54}. The maximum critical peaks are found at (21.97, 21.49, 22.4, 25.3, 23.82, 23.30, 22.40, 23.45 and 23.03 eV for HTP, LiTP, NaTP, KTP, RbTP, CsTP, FrTP, NH$_4$TP and AgTP, respectively. These points represent the lossless regions. CsTP and FrTP show the highest peaks than others, while KTP shows the lowest. However, HTP, LiTP and NaTP show a moderate peak compared to the others.

3.4. Photocatalytic processes
It is known that the valance and conduction band edges position is one of the important properties for semiconductors to be used as photocatalysts. It determines the thermodynamic limitation of the photochemical reaction carried out by photo-generated electrons and holes. In general, the reduction-oxidation potentials of reactants should be positioned between the conduction band and valance band edges position of the photocatalyst. If the water splitting is desired by the photocatalyst, then the conduction band edge of the photocatalyst must be more negative than the redox potential of H$^+$/H$_2$, and the valance band position has to be more positive than the redox potential of O$_2$/H$_2$O. Photocatalytic CO$_2$ conversion into renewable solar fuels such as CO, CH$_4$, HCOOH, HCHO, and CH$_3$OH is a promising technique to reduce the CO$_2$ emissions, solving the global warming problems, and produces ‘solar fuels’. For achieving the overall CO$_2$ reduction, the conduction band level of the photocatalyst must be more negative than the redox potentials of CO$_2$ and its...
reduced-products, and the valance band edge position must be more positive than water oxidation potential or other oxide species. If the photodegradation of an organic molecule is required by the photocatalyst, then its valence band edge position has to be positioned lower than oxidation potential of the organic molecule and the conduction band can react with O₂ forming an anion radical superoxide.

Based on the \( E_g \) values obtained from the GGA/PBEsol/norm-conserving method, the potentials of both valence band (\( E_{\text{VB}} \)) and conduction band (\( E_{\text{CB}} \)) edge positions were calculated by equations (1), (2) \[55, 56\].

\[
E_{\text{CB}} = \chi - E^e - \frac{1}{2}E_g \\
E_{\text{VB}} = E_{\text{CB}} + E_g
\]

where \( E^e \) is the energy of free electron on the hydrogen scale (4.44 ± 0.02 eV); and \( \chi \) is the Mulliken’s electronegativity of the semiconductor. Figure 12 displays a diagram of \( E_{\text{VB}} \) and \( E_{\text{CB}} \) of the investigated semiconductor, as well as potentials of useful reactions in some photocatalytic processes at normal hydrogen electrode (NHE) scale at pH = 0, such as CO₂ reduction, water splitting, and photo-degradation.
As shown in figure 12, the $E_{CB}$ values of LiTP, NaTP, KTP, RbTP, and CsTP are more negative than all potentials of all the reactions of CO$_2$ reduction; and their $E_{VB}$ values are more positive than the water oxidation reaction. Thus, these semiconductors can be used as photocatalysts in overall CO$_2$ reduction process. The $E_{CB}$ values of these materials are also more negative than the H$_2$ reduction; therefore, they can be used in overall water splitting process. Additionally, these semiconductors can be also used as photocatalysts in photodegradation, since their $E_{VB}$ values are more positive than ·OH/·OH, as well as H$_2$O/·OH (except for CsTP). The KTP, RbTP, and CsTP have $E_{CB}$ more negative than O$_2$/·O$_2$ reaction potential, which enhance the efficiency of photodegradation process. As for the HTP, NH$_4$TP, and AgTP semiconductors, they have high positive $E_{VB}$ values, in particular, HTP and NH$_4$TP, but their $E_{CB}$ values are positive. Thus, they cannot be used as photocatalysts for the previously mentioned photocatalytic processes. Nevertheless, type II junction photocatalysts would be fabricated by combining HTP or NH$_4$TP with one of the LiTP, NaTP, KTP, RbTP, and CsTP semiconductors.

Figure 9. Calculated spectra for the (a) real ($\epsilon_1(\omega)$) and (c) imaginary ($\epsilon_2(\omega)$) parts of the dielectric function for the ATP compounds. For the sake of clarity, each data plot of the $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are extracted into separate plots (b) and (d), respectively.
4. Conclusions

The purpose of this work was to investigate theoretically the crystal structures, electronic and optical properties of the ATP family ($A = H, Li, Na, K, Rb, Cs, Fr, NH_4, Ag$) using five different exchange-correlation functionals, GGA/PBE, RPBE, PW91, WC, and PBEsol, two pseudopotential functionals (ultrasoft and norm conserving). We ended up by using Perdew-Burke-Ernzerhof for solids (PBEsol) in measuring lattice parameters, energy bandgap and optical properties of the investigated materials. The computed energy gaps of KTP is close to the experimental value. We noticed that AgTP has a lower energy band gap (2.36 eV) than the others. We also investigated the applications of HTP, LiTP, NaTP, KTP, RbTP, CsTP, NH_4TP, and AgTP in different photocatalytic reactions. The results revealed that the LiTP, NaTP, KTP, RbTP, and CsTP semiconductors could be used as effective photocatalysts in these photocatalytic reactions.

**Figure 10.** Calculated real part (a) and imaginary part (d) of the optical conductivity (fs$^{-1}$) for the ATP compounds versus energy (eV). For the sake of clarity, each data plot of the real part and imaginary part are extracted into separate plots (b) and (d), respectively.
Figure 11. The energy loss function for all ATP compounds versus photon energy (eV). For the sake of clarity, each data plot is extracted into separate plots (b).

Figure 12. The $E_{\text{VB}}$ (black bar) and $E_{\text{CB}}$ (blue bar) of the HTP, LiTP, NaTP, KTP, RbTP, CsTP, NH$_4$TP, and AgTP semiconductors; together with the potentials of useful reactions in CO$_2$ reduction, water splitting, and photodegradation processes at normal hydrogen electrode (NHE) scale at pH = 0.

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