The electronic properties of impurities (N, C, F, Cl, and S) in Ag$_3$PO$_4$: A hybrid functional method study

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The transition energies and formation energies of N, C, F, Cl, and S as substitutional dopants in Ag$_3$PO$_4$ are studied using first-principles calculations based on the hybrid Hartree-Fock density functional, which correctly reproduces the band gap and thus provides the accurate defect states. Our results show that NO and CO act as deep acceptors, FO, ClO, and SP act as shallow donors. NO and CO have high formation energies under O-poor condition therefore they are not suitable for $p$-type doping Ag$_3$PO$_4$. Though FO, ClO, and SP have shallow transition energies, they have high formation energies, thus FO, ClO, and SP may be compensated by the intrinsic defects (such as Ag vacancy) and they are not possible lead to $n$-type conductivity in Ag$_3$PO$_4$.

Since Honda and Fujishima first discovered the photocatalytic water splitting into H$_2$ and O$_2$\textsuperscript{1}, the photocatalysis of water splitting has become an active research field and a potential way to solve the severe environmental crisis and energy shortage issues\textsuperscript{2,3}. TiO$_2$ is the earliest photocatalyst used in water splitting, the intrinsic wide band gap of pure TiO$_2$ (~3.2 eV for anatase and ~3.0 eV for rutile) confines its photon absorption to the ultraviolet (UV) region, severely limiting solar energy utilization to ~5%\textsuperscript{4}. Metal oxides are considered as potential candidates for photoelectrochemical (PEC) water splitting because of their resistance to oxidation and possible stability in aqueous solutions\textsuperscript{5}.

Recently, Ye et al. reported that cubic structure semiconductor Ag$_3$PO$_4$, which exhibits strong oxidation power leading to O$_2$ production from water, and its quantum yield achieve up to nearly 90% under visible light\textsuperscript{6}. This is intriguing because most photocatalysts give much poorer quantum yields of ~20%\textsuperscript{7}. Theoretical studies have also been performed to understand their origin\textsuperscript{2-11}. Reunchan and Umezawa suggest that native point defects are unlikely to be responsible for an intrinsic conductivity of Ag$_3$PO$_4$, which an $n$-type character was observed in the previous report, but Ag$_3$PO$_4$ could feasibly be doped in $n$-type fashion\textsuperscript{7}.

First-principles density functional theory (DFT) calculations have been commonly used to study the electronic properties of point defects insulators and semiconductors. The local density approximation (LDA)\textsuperscript{12} or the generalized gradient approximation (GGA)\textsuperscript{13} functional are typically employed to describe the exchange-correlation energy within DFT. A major shortcoming of LDA and GGA calculations is the large uncertainty in the position of defect levels (and hence also formation energies) due to the severe underestimation of the semiconductor band gap. Heyd et al. recently proposed hybrid Hartree-Fock (HF) density functional\textsuperscript{14}, the hybrid functional has been used to accurately reproduce the band gap of insulators and semiconductors, therefore, the use of the hybrid functional is rationalized for the description of defect physics\textsuperscript{15-18}.

In this paper, we perform first-principles calculations based on the hybrid HF density functional to investigate the influence of N, C, F, Cl, and S impurities on the electronic properties of Ag$_3$PO$_4$. Because
interstitials of these impurities usually have large formation energies, we will only consider substitutional defects. The paper is organized as follow: Details of the calculations are provided in Sec. II. The electronic properties of each impurity are described in Sec. III. Finally, Sec. IV summarizes the results.

**Methodology**

The density functional calculations were performed in the Vienna *ab initio* simulation package (VASP)\(^{19,20}\). Interaction between the valence and core electrons was described using the projector augmented wave (PAW) approach\(^ {21}\). A plane-wave basis set was used to expand the wave functions up to a kinetic energy cutoff value of 300 eV.

We used the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06)\(^ {14,22}\), which adopts a screened Coulomb potential. Hence, greatly improving the description of structural properties and band structures, including band gaps. Both of these aspects are particularly important for defects. The HSE exchange is derived from the PBE0 (Perdew-Burke-Ernzerhof (PBE) functional containing 25% exact exchange)\(^ {23}\) exchange by range separation and then by elimination of counteracting long-range contributions as\(^ {4}\).

\[
E_{x}^{HSE} = aE_{x}^{HFSR}(\omega) + (1 - a)E_{x}^{PRESR}(\omega) + E_{x}^{PRESR}(\omega)
\]

Where \(a\) is the mixing coefficient and \(\omega\) is the range-separation parameter. A consistent screening parameter of \(\omega = 0.2 \text{Å}^{-1}\) is used for the semilocal PBE exchange as well as for the screened nonlocal exchange as suggested for the HSE06 functional\(^ {24}\). We find that a proportion of 33% HF exchange with 67% PBE exchange produces accurate values for lattice constants and the band gap in Ag_3PO_4.

We used a 128-atom supercell constructed by \(2 \times 2 \times 2\) replication of the cubic Ag_3PO_4 unit cell (space group \(P \bar{4} 3 n\)), which ensures sufficient spatial separation between the periodic images of the impurities. Various dopings of Ag_3PO_4 have been modeled by substitution of S at P or Y (Y = N, C, F, Cl) at O sites. For geometry optimizations and electronic structure calculations, the Brillouin zone was sampled with a \(2 \times 2 \times 2\) mesh of Monkhorst-Pack special \(k\)-points\(^ {25}\). Both the atomic positions and cell parameters were optimized until residual forces were below 0.01 eV/Å.

**Formation energies and transition levels.** To determine the defect formation energies and defect transition energy levels, we follow the procedure in Ref. 26. The defect formation energy \(\Delta H_f(\alpha, q)\) as a function of the electron Fermi energy \(E_F\) as well as the atomic chemical potentials \(\mu_i\) is as follows:

\[
\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + \sum n_i \mu_i + qE_F
\]

Where

\[
\Delta E(\alpha, q) = E(\alpha, q) - E(\text{host}) + \sum n_i E(i) + q\varepsilon_{\text{VBM}}(\text{host})
\]

\(E(\alpha, q)\) is the total energy for the studied supercell containing defect \(\alpha\) in charge state \(q\) and \(E(\text{host})\) is the total energy of the same supercell without the defect. \(n_i\) indicates the number of atoms of type \(i\) (host atoms or impurity atoms) that have been added to \((n_i < 0)\) or removed from \((n_i > 0)\) the supercell, and \(q\) is the number of electrons transferred from the supercell to the reservoirs in forming the defect cell.

\(E_F\) is the electron Fermi level referenced to the valence-band maximum (VBM) of host, \(\varepsilon_{\text{VBM}}(\text{host})\), and varies from the valence-band maximum to the conduction-band minimum (CBM). \(\mu_i\) is the chemical potential of constituent \(i\) referenced to its elemental solid or gas with energy \(E(i)\).

The defect transition energy level \(\varepsilon_{\alpha}(q/q') = E_F\) in Eq. (1), at which the formation energy \(\Delta H_f(\alpha, q)\) of defect \(\alpha\) in charge state \(q\) is equal to that of another charge \(q'\) of the same defect, i.e.,

\[
\frac{\varepsilon_{\alpha}(q/q')}{q} = \frac{\Delta E(\alpha, q) - \Delta E(\alpha, q')}{q - q'}\]

In this paper, we used a hybrid scheme to combine the advantages of both special \(k\)-point and \(\Gamma\)-point-only approaches\(^ {12}\). In this scheme, for acceptor level \((q < 0)\), the transition energy level with respect to VBM is given by:

\[
\varepsilon(0/q) = [\varepsilon_{\text{VBM}}^\Gamma(0) - \varepsilon_{\text{VBM}}(\text{host})] + [E(\alpha, q) - [E(\alpha, 0) - q\varepsilon_{\text{VBM}}^\Gamma(0)]]/( - q)
\]

For donor level \((q > 0)\), the ionization energy referenced to the CBM is given by:

\[
\varepsilon_{\text{CBM}}^\Gamma(\text{host}) - \varepsilon(0/q) = [\varepsilon_{\text{CBM}}(\text{host}) - \varepsilon_{\text{CBM}}^\Gamma(0)] + [E(\alpha, q) - [E(\alpha, 0) - q\varepsilon_{\text{CBM}}^\Gamma(0)]]/q
\]

Where \(\varepsilon_{\text{VBM}}^\Gamma(0)\) and \(\varepsilon_{\text{CBM}}^\Gamma(0)\) are the defect levels at the special \(k\)-points (averaged) and at the \(\Gamma\)-point, respectively, \(\varepsilon_{\text{VBM}}(\text{host})\) and \(\varepsilon_{\text{CBM}}(\text{host})\) are the VBM and CBM energies, respectively, of the host at the \(\Gamma\)-point; and \(\varepsilon_{\text{CBM}}^\Gamma(\text{host})\) is the calculated bandgap at the \(\Gamma\)-point. The formation energy of a charged defect is then given by

\[
\Delta H_f(\alpha, q) = \Delta H_f(\alpha, 0) - q\varepsilon(0/q) + qE_F
\]
Where \( \Delta H_f(\alpha, 0) \) is the formation energy of the charge-neutral defect. More details of calculation methods for formation energies and transition energies of defects are described elsewhere\(^{30}\).

**Chemical potentials.** Under thermal equilibrium growth conditions, the steady production of host material, \( \text{Ag}_3\text{PO}_4 \), should satisfy the following equation:

\[
3\mu_{\text{Ag}} + \mu_p + 4\mu_{\text{O}} = \Delta H_f(\text{Ag}_3\text{PO}_4) = -10.46\text{eV}
\]  

(6)

where \( \mu_{\text{Ag}} \), \( \mu_p \), and \( \mu_{\text{O}} \) are the chemical potentials of Ag, P, and O source, respectively, and \( \Delta H_f \) is the formation energy for \( \text{Ag}_3\text{PO}_4 \) per formula. In order to avoid the precipitation of the host elements, the chemical potential \( \mu_i \) must be bound by

\[
\mu_i < 0
\]

(7)

To avoid the formation of secondary phases (such as \( \text{Ag}_6\text{O} \) and \( \text{P}_2\text{O}_5 \)), \( \mu_{\text{Ag}} \), \( \mu_p \), and \( \mu_{\text{O}} \) must satisfy further constrains:

\[
2\mu_{\text{Ag}} + \mu_{\text{O}} < \Delta H_f(\text{Ag}_6\text{O}) = -0.32\text{eV}
\]

(8)

\[
2\mu_p + 5\mu_{\text{O}} < \Delta H_f(\text{P}_2\text{O}_5) = -15.86\text{eV}
\]

(9)

Considering Eqs. (6)–(9), the accessible ranges for \( \mu_{\text{Ag}} \), \( \mu_p \), and \( \mu_{\text{O}} \) are limited and are presented as the shaded area in Fig. 1. As shown in Eqs. (5), the calculated formation energies of charged defects depend sensitively on the selected values for \( \mu_{\text{Ag}} \), \( \mu_p \), and \( \mu_{\text{O}} \) and the Fermi-level positions. Here, the calculated values at two representative chemical potential points are labeled as O-rich and O-poor in Fig. 1. The exact value of chemical potentials at points O-rich condition and O-poor condition are \((-0.84, -7.93, 0)\) and \((0, -3.71, -1.69)\) for \( \mu_{\text{Ag}} \), \( \mu_p \), and \( \mu_{\text{O}} \), respectively.

For impurity doping, the chemical potentials of impurities also need to satisfy other constraints to avoid the formation of impurity-related phases, for example

\[
\mu_{\text{Ag}} + \mu_{\text{Cl}} < \Delta H_f(\text{AgCl})
\]

(10)

\[
\mu_{\text{S}} + 2\mu_{\text{Ag}} + 4\mu_{\text{O}} < \Delta H_f(\text{Ag}_2\text{SO}_4)
\]

(11)

\[
\mu_{\text{C}} + 2\mu_{\text{O}} < \Delta H_f(\text{CO}_2)
\]

(12)

\[
\mu_{\text{Ag}} + \mu_{\text{F}} < \Delta H_f(\text{AgF})
\]

(13)

The formation enthalpies of the AgCl, Ag$_2$SO$_4$, AgF, and CO$_2$ compounds obtained using the present HSE06 functional are listed in Table 1. The formation enthalpies obtained with the present HSE06 functional calculations are agreement with the experimental values.

**Results and Discussion**

**Bulk properties.** We first present the results for the structural and electronic properties of defect-free bulk \( \text{Ag}_3\text{PO}_4 \). The crystal structure of \( \text{Ag}_3\text{PO}_4 \) has a cubic structure with space group \( P\bar{T}3n \), its basic structural unit is constructed by \( \text{PO}_4 \) tetrahedron and \( \text{AgO}_4 \) tetrahedron. The interaction between phosphorus and oxygen is mainly by covalent bond, while the interaction between silver and oxygen is formed
mainly by ionic bond\(^8\). The optimized cell parameters are \(a = b = c = 6.02\,\text{Å}\), and excellent agreement with the experimental values of \(a = b = c = 6.00\,\text{Å}\)\(^8\). The P-O, Ag-O, and Ag-Ag bond lengths are calculated to be 1.56 \(\text{Å}\) (experimental value \(^{11}\): 1.56 \(\text{Å}\)), 2.37 \(\text{Å}\) (experimental value \(^{11}\): 2.36 \(\text{Å}\)), 3.01 \(\text{Å}\) (experimental value \(^{11}\): 3.00 \(\text{Å}\)), respectively. The calculated indirect band gap (M\(-\Gamma\)) is 2.33 \(\text{eV}\), and the direct gap at \(\Gamma\) is 2.45 \(\text{eV}\), in excellent agreement with the experimental value of 2.36 \(\text{eV}\) and 2.43 \(\text{eV}\)\(^6\), respectively.

### Table 1. The formation enthalpies (in eV) of Ag\(_2\)O, P\(_2\)O\(_5\), AgCl, Ag\(_2\)SO\(_4\), AgF, and CO\(_2\) molecules calculated from the HSE06 hybrid functional. The experimental values are also listed for comparison.

| Compound         | HSE06   | Experiment |
|------------------|---------|------------|
| \(\Delta H_f\) (Ag\(_2\)O) | −0.32   | −0.32\(^{31}\) |
| \(\Delta H_f\) (P\(_2\)O\(_5\)) | −15.86  | −15.60\(^{32}\) |
| \(\Delta H_f\) (AgCl)      | −1.20   | −1.32\(^{31}\) |
| \(\Delta H_f\) (Ag\(_2\)SO\(_4\)) | −7.06   | −7.42\(^{31}\) |
| \(\Delta H_f\) (AgF)       | −2.03   | −2.13\(^{31}\) |
| \(\Delta H_f\) (CO\(_2\))  | −3.82   | −4.08\(^{31}\) |

**Figure 2.** Thermodynamic transition levels for N, C, F, Cl and S impurities in Ag\(_3\)PO\(_4\) (Unit: eV).

**Nitrogen.** The electronic properties of substitutional N at O sites (N\(_O\)) has been confirmed by several reports\(^4,5,33\). The conductivity of a semiconductor depends not only on the thermodynamic transition levels of donor and acceptors, but also on their formation energies. The thermodynamic transition level corresponds to the intersection of the formation energies for the different charge states. Formation energy as a function of Fermi level for N\(_O\) in the O-rich and O-poor limit are shown in Fig. 3. When the Fermi level is low, the neutral charge state (N\(_O^0\)) is energetically preferable, as the Fermi level rises, above the Fermi level of 0.46 eV, the negative charge state (N\(_O^{-1}\)) becomes more favorable. The thermodynamic transition level of \(\varepsilon (-/0)\) is located at 0.46 eV above VBM. To obtain further details, the squared wave function \(|\psi|_\Gamma^2\) of the neutral defect state at \(\Gamma\) point is visualized in Fig. 4(a). The neutral defect state is highly confined around the N atom, which suggests that N\(_O^0\) induces a localized defect state.

The N 2p orbital energy is 1.9 eV higher than the O 2p orbital energy, this imply that upon N substitution on O, the N 2p will create a partially filled impurity state at the Fermi level\(^{15}\). Thus, we examined the total density of states and projected density of states of N\(_O^0\) (not shown). The neutral defect state has the main contribution from s orbitals and d orbitals of Ag, p orbitals of N and O, minor contribution from p orbitals of P. We also analyzed the local lattice relaxations around N\(_O^0\) and N\(_O^{-1}\). In the neutral state, the neighboring Ag atoms relax inward, resulting in a N-Ag bond length (2.11 Å) that is 11% shorter than the equilibrium O-Ag bond length, while the N-P bond length (1.65 Å) become 6% longer.
than the equilibrium O-P bond length. In the negative state, the N-Ag bond length is 2.11 Å, while the N-P bond length 1.64 Å.

Figure 3 shows that the formation energy of NO\(^0\) is more stable than NO\(^{−1}\) under O-poor condition but still relatively high even the Fermi level is near the conduction band. The high formation energy of the NO indicates that the N-doped Ag\(_3\)PO\(_4\) system using an N\(_2\) source may not readily produce p-type conductivity, which is consistent with the N-doped ZnO system\(^{36}\).

Carbon. As carbon atom has four valence electrons which is two electrons less than oxygen atom, the substitution of C on O site (CO) will act as a double acceptor. The 2\(p\) orbital energy of carbon is 3.8 eV higher than the O 2\(p\) orbital\(^{35}\). Consequently, CO has two distinct transition levels in the band gap: a \(\epsilon(−/0)\) transition at 1.54 eV above the VBM and a \(\epsilon(2+/0)\) transition at 1.39 eV above the VBM as shown in Fig. 2. This implies that CO in Ag\(_3\)PO\(_4\) is a negative-U system. A defect often has a negative \(U\) if the atomic position of the defect depends sensitively on its charge state\(^{37}\), \(U\) refers to the additional energy upon charging of the defect with an additional electron\(^{38}\). In the neutral charge state (CO\(^0\)), the three Ag nearest neighbors relax inward by 13% (of the equilibrium O-Ag bond length) while one nearest P atom slightly relaxes outward by about 13% (of the equilibrium O-P bond length).

Figure 4(b) plots the squared wave function of the neutral CO defect level. One can see that the squared wave function is localized around C atom, consistent with the deep level feature. The neutral defect state has \(p\) orbitals of C and O, \(s\) orbitals and \(d\) orbitals of Ag contribute primarily, \(p\) orbitals of P contribute in a small part. The formation energies of CO in the neutral, \(-1\), and \(-2\) charge states as a function of the Fermi level are shown in Fig. 5. Even the formation energies of CO under O-poor condition is significantly lower than under O-rich condition but still relatively high, therefore C is not suitable for p-type doping Ag\(_3\)PO\(_4\).

Fluorine. Shifting the Fermi level towards the conduction band, or in other words \(n\)-type conditions, likely enhance the photocatalytic activities in Ag\(_3\)PO\(_4\).\(^7\) In contrast to the NO\(^0\) and CO\(^0\), the substitutional F at O site (FO) exhibits distinct characteristics. Unlike the NO\(^0\) and CO\(^0\), where the defect states are highly localized at impurities, the defect state induced by FO is spatially distributed away from F as the delocalized state [see Fig. 4(c)]. The defect state has main contribution from \(s\) and \(d\) orbitals of Ag followed by \(s\) orbitals of F, O, and P. For FO\(^0\), the three nearest neighbor Ag atoms relax outward by 17%, while for FO\(^{+1}\) the relaxation are outward by 18% of the equilibrium Ag-O bond length.

The formation energy of FO in different charge states as a function of the Fermi level is shown in Fig. 6. When the Fermi level is low, the positive charge state (FO\(^{+1}\)) is energetically preferable, as the
Fermi level rises, the formation energy approaches that of the neutral charge state ($F_{O}^{0}$), above the Fermi level of 2.41 eV, the neutral charge state becomes more favorable. The thermodynamic transition level of $\epsilon_{(0/+)}$ is located 2.41 eV above the VBM (0.04 eV below the CBM). Though the Fermi level drops to the VBM the formation energy of $F_{O}$ becomes very small for the favorable growth condition (O-poor

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Figure 4. Spatial distribution of the squared wave functions $|\psi_{e}|^2$ of the neutral defect states created by (a) NO, (b) CO, (c) FO, (d) ClO, (e) SP, where the isosurface values are 0.05, 0.05, 0.005, 0.005, 0.005 e/Å³, respectively. The silver, pink, red balls represent Ag, P, O atoms, respectively.

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Figure 5. Calculated formation energies for C substituting on the O site as a function of Fermi level at O-rich and O-poor conditions.

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Fermi level rises, the formation energy approaches that of the neutral charge state ($F_{O}^{0}$), above the Fermi level of 2.41 eV, the neutral charge state becomes more favorable. The thermodynamic transition level of $\epsilon_{(0/+)}$ is located 2.41 eV above the VBM (0.04 eV below the CBM). Though the Fermi level drops to the VBM the formation energy of $F_{O}$ becomes very small for the favorable growth condition (O-poor
condition), but when the Fermi level is near the CBM, the formation energy of F$_0$ is still relatively high, thus, F$_0$ may be compensated by Ag vacancy and it is not possible lead to n-type conductivity in Ag$_3$PO$_4$.

**Chlorine.** Chlorine atom is a famous n-type dopant$^{37,39}$. The formation energy of substitutional Cl (Cl$_0$) against the Fermi level is shown in Fig. 7 for the two extreme cases. For Cl$_0$, no transition level is find in the gap (a $\varepsilon(0/\pm)$ transition at 0.14 eV above the CBM) and the $\pm 1$ charge state is energetically favorable for the whole range of the Fermi level. The extra electron from Cl$_0$ occupies a conduction-band-like state, i.e., an extended state that is only slightly perturbed by the presence of the impurity$^{33}$. Therefore, Cl$_0$ is a shallow donor.

We have plotted the squared wave function of the neutral defect state at the $\Gamma$ point in Fig. 4(d). It is seen that the squared wave function associated with the donor level distributed not only around Cl atom, but also around O atoms and Ag atoms away from the Cl atom, indicating a delocalized feature, which is consistent with the result that Cl$_0$ is a shallow donor. The defect state has main contribution from $s$ and $d$ orbitals of Ag followed by $s$ and $p$ orbitals of Cl, O, and P. The formation energy of Cl$_0$ is relatively high even under O-poor condition, therefore chlorine is not suitable for n-type doping Ag$_3$PO$_4$.

**Sulfur.** Sulfur is a possible candidate for n-type doping when substituted for P$^7$. In the case of the S substituting on the P site, the transition level $\varepsilon(0/\pm)$ is located at 2.37 eV (0.08 eV below the CBM). The defect state is spatially away from S$_0$ [Fig. 4(e)], which is consistent with the result that S$_0$ is a shallow donor. The defect state has main contribution from $s$ and $d$ orbitals of Ag followed by $s$ orbitals of S, O, and P. It is also clearly from the shape of wave function that $s$ and $d$ orbitals are the main contributor to the defect state.

Sulfur is surrounded by four O atoms, for S$_0$ these four nearest neighbor O atoms relax inward by 4% of the equilibrium P-O bond length. Formation energies of S$_0$ in its various charge state are shown in Fig. 8. We note, S$_0$ has lower formation energy than F$_0$ and Cl$_0$ for both O-rich and O-poor conditions. When the Fermi level near the VBM, S$_0$ is stable in the $+1$ charge state. In n-type Ag$_3$PO$_4$, where the Fermi level is near the CBM, S$_0$ is stable in the neutral charge state, but the formation energies in the n-type regime are high under O-poor condition for this sulfur is not suitable candidate for n-type doping Ag$_3$PO$_4$.

Figure 6. Calculated formation energies for F substituting on the O site as a function of Fermi level at O-rich and O-poor conditions.
Figure 7. Calculated formation energies for Cl substituting on the O site as a function of Fermi level at O-rich and O-poor conditions.

Figure 8. Calculated formation energies for S substituting on the P site as a function of Fermi level at O-rich and O-poor conditions.
Conclusion

Using hybrid density functional calculations we have investigated the electrical properties of \(N\), \(C\), \(F\), and \(S\) impurities in \(\text{Ag}_3\text{PO}_4\). We found that \(\text{NO}\) and \(\text{CO}\) act as deep acceptors, \(\text{FO}\), \(\text{ClO}\), and \(\text{SP}\) act as shallow donors. \(\text{N}_2\) and \(\text{C}_2\) have high formation energies even under most equilibrium condition (O-poor condition) therefore they are not suitable for \(p\)-type doping \(\text{Ag}_3\text{PO}_4\). Though \(\text{FO}\), \(\text{ClO}\), and \(\text{SP}\) have shallow transition energies, they have high formation energies, thus \(\text{FO}\), \(\text{ClO}\), and \(\text{SP}\) may be compensated by \(\text{Ag}\) vacancy and they are not possible lead to \(n\)-type conductivity in \(\text{Ag}_3\text{PO}_4\).

References

1. Fujishima, A. & Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature (London) 238, 37 (1972).
2. Lai, K., Zhu, Y., Dai, Y. & Huang, B. Intrinsic defect in \(\text{BiVO}_4\): A density functional theory study. J. Appl. Phys. 112, 043706 (2012).
3. Wang, D. F., Zou, Z. G. & Ye, J. H. Photocatalytic Water Splitting with the Cr-Doped \(\text{Ba}_2\text{In}_2\text{O}_5/\text{In}_2\text{O}_3\) Composite Oxide Semiconductors. Chem. Mater. 17, 3255 (2005).
4. Celik, V. & Mete, E. Range-separated hybrid exchange-correlation functional analyses of anatase \(\text{TiO}_2\) doped with \(\text{W}, \text{N}, \text{S}/\text{W}\), or \(\text{W}/\text{S}\). Phys. Rev. B 86, 205112 (2012).
5. Yin, W. J. et al. Doping properties of monoclinic \(\text{BiVO}_4\) studied by first-principles density-functional theory. Phys. Rev. B 83, 155102 (2011).
6. Yi, Z. et al. An orthophosphate semiconductor with photooxidation properties under visible-light irradiation. Nat. Mater. 9, 559 (2010).
7. Reunchan, P. & Umezawa, N. Native defects and hydrogen impurities in \(\text{Ag}_3\text{PO}_4\). Phys. Rev. B 87, 245205 (2013).
8. Liu, J. J. et al. Electronic structure and optical properties of \(\text{Ag}_3\text{PO}_4\) photocatalyst calculated by hybrid density functional method. Appl. Phys. Lett. 99, 191903 (2011).
9. Ma, X. et al. Origin of photocatalytic activation of silver orthophosphate from first-principles. J. Phys. Chem. C 115, 4680 (2011).
10. Ma, Z., Yi, Z., Sun, J. & Wu, K. Electronic and Photocatalytic Properties of \(\text{Ag}_3\text{PO}_4\) (C = O, S; Se): A Systemic Hybrid DFT Study. J. Phys. Chem. C 116, 25074 (2012).
11. Umezawa, N., Shuxin, O. & Ye, J. Theoretical study of high photocatalytic performance of \(\text{Ag}_3\text{PO}_4\). Phys. Rev. B 83, 035202 (2011).
12. Ceperley, D. M. & Alder, B. J. Ground State of the Electron Gas by a Stochastic Method. Phys. Rev. Lett. 45, 566 (1980).
13. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77, 3865 (1996).
14. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. J. Chem. Phys. 124, 219906 (2006).
15. Shimada, T., Ueda, T., Wang, J. & Kitamura, T. Hybrid Hartree-Fock density functional study of charged point defects in ferroelectric \(\text{PbTiO}_3\). Phys. Rev. B 87, 174111 (2013).
16. Lyons, J. L., Janotti, A. & Van de Walle, C. G. Effects of carbon on the electrical and optical properties of \(\text{InN}, \text{GaN}, \text{AlN}\). Phys. Rev. B 89, 035204 (2014).
17. Chen, S., Narang, P., Atwater, H. A. & Wang, L.-W. Phase Stability and Defect Physics of a Ternary \(\text{ZnSnN}_2\) Semiconductor: First Principles Insights. Adv. Mater. 26, 311 (2014).
18. Choi, M., Janotti, A. & Van de Walle, C. G. Native point defects in \(\text{LaAlO}_3\): A hybrid functional study. Phys. Rev. B 88, 214117 (2013).
19. Kresse, G. & Furthmüller, J. Efficient iterative schemes for \(\text{ab initio}\) total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169 (1996).
20. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758 (1999).
21. Blochl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953 (1994).
22. Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 140, A1133 (1965).
23. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77, 3865 (1996); 78, 1396 (1997).
24. Krukau, A. V., Vydrov, O. A., Izmaylov, A. F. & Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. J. Chem. Phys. 125, 224106 (2006).
25. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. Phys. Rev. B 13, 5188 (1976).
26. Wei, S.-H. Comput. Overcoming the doping bottleneck in semiconductors. Comput. Mater. Sci. 30, 337 (2004).
27. Baraff, G. A. & Schluter, M. Electronic Structure, Total Energies, and Abundances of the Elementary Point Defects in GaAs. Phys. Rev. Lett. 55, 1327 (1985).
28. Zhang, S. B. & Northrup, J. E. Chemical potential dependence of defect formation energies in GaAs: Application to Ga self-diffusion. Phys. Rev. Lett. 67, 2339 (1991).
29. Laks, D. B. et al. Native defects and self-compensation in ZnSe. Phys. Rev. B 45, 10965 (1992).
30. Yan, Y. & Wei, S.-H. Doping asymmetry in wide-bandgap semiconductors: Origins and solutions. Phys. Stat. Sol. (b) 245, 641 (2008).
31. David R. Lide, ed., CRC Handbook of Chemistry and Physics, 90th Edition (Internet Version 2010), CRC Press/Taylor and Francis, Boca Raton, FL (2010).
32. Jung, In-Ho & Hudon, P. Thermodynamic Assessment of \(\text{P}_2\text{O}_5\), J. Am. Ceram. Soc. 95, 3665 (2012).
33. Varley, J. B., Janotti, A. & Van de Walle, C. G. Group-V impurities in \(\text{SnO}_2\) from first-principles calculations. Phys. Rev. B 81, 245216 (2010).
34. Momma, K. & Izumi, F. VESTA: a three-dimensional visualization system for electronic and structural analysis. J. Appl. Crystallogr. 41, 653 (2008).
35. Wang, B. C. et al. Band gap engineering in \(\text{BiNbO}_4\) for visible-light photocatalysis. Appl. Phys. Lett. 100, 182102 (2012).
36. Duan, X. M., Stampfl, C., Bilek, M. M. M. & Mackenzie, D. R. Codoping of aluminum and gallium with nitrogen in \(\text{ZnO}\): A comparative first-principles investigation. Phys. Rev. B 79, 235208 (2009).
37. Wei, Su-Huai & Zhang, S. B. Chemical trends of defect formation and doping limit in II-VI semiconductors: The case of \(\text{CdTe}\). Phys. Rev. B 66, 155211 (2002).
38. Grundmann, M. The Physics of Semiconductors, 2nd ed. (Springer, Berlin, 2010).
39. Varley, J. B., Weber, J. R., Janotti, A. & Van de Walle, C. G. Oxygen vacancies and donor impurities in \(\beta\)-\(\text{Ga}_2\text{O}_3\). Appl. Phys. Lett. 97, 142106 (2010).
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Author Contributions
Yang Huang carried out the DFT calculations and prepared the manuscript. T.M., Q.C., C.C. and Y.H. contributed the discussion and suggestions. All authors read the manuscript.

Additional Information
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