Cadmium and lithium doping in silver orthophosphate: An *ab initio* study

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Using hybrid functional calculations, we investigate the effects of defects and defect complexes related with Cd, Li, and N impurities on the atomic and electronic properties of Ag\(_3\)PO\(_4\). It was found that substitutional Cd on Ag lattice site (Cd\(_{\text{Ag}}\)) contributes to the \(n\)-type conductivity of Ag\(_3\)PO\(_4\). For substitutional Cd on P (or O) lattice site (Cd\(_{\text{P}}\) (or Cd\(_{\text{O}}\)), it is not expected that Cd will incorporate into the P (or O) site due to the strong covalent interactions in the PO\(_4\) structural units. The interstitial Cd (Cd\(_i\)) acts as a shallow donor, but its formation energy is relatively high compared with that of Cd\(_{\text{Ag}}\). For the (Cd\(_{\text{Ag}}\)-2N\(_{\text{O}}\)) complex, the formation of this inactive complex generates a fully occupied impurity band just above the valence band maximum of Ag\(_3\)PO\(_4\), which significantly reduces the acceptor transition energy level. But the formation energy of the (Cd\(_{\text{Ag}}\)-2N\(_{\text{O}}\)) complex is even higher than that of the corresponding single point defect NO. Unlike Li\(_{\text{P}}\) and Li\(_{\text{O}}\) which has relatively high formation energy, interstitial Li (Li\(_i\) or Li\(_i\) (s)) with an appreciable solubility is likely to be the \(n\)-type dopant under O-poor condition.

Owing to that fact that oxide semiconductor photocatalysts have promising applications in the development of renewable energy (e.g., converting solar energy into chemical fuels) and the treatment of environment pollution (e.g., degradation of pollutants), much attention has been paid to these materials over the past several decades\(^1\)-\(^3\). One of the most popular oxide semiconductors for this purpose, titanium dioxide (TiO\(_2\)), based on its high photocatalytic activity, resistance to photocorrosion, low cost and non-toxicity, has received intense research interest as a promising photocatalyst for water splitting and hydrogen production\(^4\)-\(^5\). However, 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%. Hence great efforts have been made to extend the photoabsorption of TiO\(_2\) to the visible light region\(^5\)-\(^7\). Recently, silver-based oxides semiconductors are reported to own high photocatalytic activation in the visible light region, such as Ag\(_3\)VO\(_4\)\(^8\), AgGaO\(_2\)\(^9\), AgSbO\(_3\)\(^10\). Especially, Ye *et al.*\(^11\) have found that Ag\(_2\)PO\(_4\) exhibits strong oxidation power leading to O\(_2\) production from water, and the quantum yield achieve up to nearly 90% under visible light. This is intriguing because most photocatalysts give much poorer quantum yields of ~20%\(^12\). Therefore, further studies\(^13\)-\(^17\) were carried out to understand the mechanism of its high water-oxidation activity. For example, Umezawa *et al.*\(^18\) revealed that the excellent photocatalytic performance of Ag\(_2\)PO\(_4\) is attributed to the Ag s-\(d\) hybridization without localized d states which results in the highly dispersive band structure of the CBM of Ag\(_2\)PO\(_4\). Although pure Ag\(_2\)PO\(_4\) achieves an extremely high quantum yield under visible light, it has been recently found that native point defects are unlikely responsible for the electrical conductivity\(^12\). However, photoelectrochemical cell needs two-electrode to convert light energy into electric energy, e.g., metal cathode and photoanode made of \(n\)-type semiconductor\(^16\),\(^19\). Therefore, we expect that external doping can further improve the photocatalytic activity of this novel photooxidation material.

The valence-band maximum (VBM) of Ag\(_3\)PO\(_4\) composes of mostly Ag 4d and O 2p states\(^20\). Oxygen is much more electronegative than the attempted nitrogen acceptor dopant, and the transition energy level of the N\(_2\) acceptor should be high. Indeed, the calculated transition level for single acceptor N\(_2\) is 0.4 eV above the VBM of Ag\(_3\)PO\(_4\). On the other hand, since the cohesive energy of N\(_2\) is large, the chemical potential of N\(_2\) is very low and the formation energy of N\(_2\) is very high\(^21\). To obtain net \(p\)-type Ag\(_3\)PO\(_4\), the low solubility of N monodoping is unlikely to generate sufficient number of holes to compensate the free electrons. Successful \(p\)-type doping requires a shallow delocalized acceptor level. But doping generally destroys the local symmetry, and the chemical

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mismatch between the host and dopant may result in deep defect levels in the band gap. The codoping method was originally proposed by Yamamoto and Katayama-Yoshida for carrier control in wide-band-gap semiconductors. Using codoping method one may be able to enhance the dopant solubility and lower the defect transition energy levels. However, further study found that although codoping could be useful in increasing dopant incorporation, the different wave function characters and symmetry of donor and acceptor levels may result in a too weak repulsion between these levels, and codoping will fail to reduce the defect transition energy levels.

In order to decrease the ionization energy of N acceptor in ZnO, Yan et al. proposed the impurity band model to explain the real codoping mechanism. The essence of this model is the rise of the VBM. According to the “doping pinning rule”, the lower the VBM of a semiconductor is, the higher the probability that the semiconductor cannot be doped p-type is. Moreover, Li et al. considered that the anion and cation kinetic p-d repulsion was one of the reasons why N_d defect level is deep in ZnO, if replacing Zn atom by isovalent Mg or Be atom containing no d orbital, the defect transition energy level of nX2N_X (X=Mg, Be, n=1, 2, 3, 4) should be lower than that of N_d in ZnO. But there is little studies on Li (without occupied d orbital) codoping in Ag₃PO₄, which will be addressed in this work.

In this present work, we used screened Coulomb potential hybrid DFT calculations to investigate the atomic structure and electronic properties of Cd, Li monodoping and (Cd, N), (Li, N) codoping in Ag₃PO₄. We calculate the formation energies and the transition energy levels of Cd₃Ag, Cd₅, Cd₆, Cd₇, Cd₈, the (Cd₃Ag-2NO) complex, Li₅, Li₆, Li₇, and the (Li₂Ag-N) complex, as well as the binding energies of all defect complexes. The results show that Cd₃Ag and Li (or Li(s)) may serve as possible sources of n-doping and (Cd, N), (Li, N) codoping in Ag₃PO₄, which will be addressed in ZnO. But there is little studies on Li (without occupied d orbital) codoping in Ag₃PO₄.

The likelihood of incorporating an impurity in Ag₃PO₄ is determined by its formation energy. In this paper, the formation energy of a charged defect is defined as the following:

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

where, \( \Delta E (\alpha, q) = E (\alpha, q) - E (\text{host}) + \sum nE (i) + qE_{\text{VBM}} (\text{host}) \)

A more detailed discussion of the formation energy is described elsewhere. When Ag₃PO₄ is grown under thermal equilibrium conditions, the chemical potentials of the constituent atoms, which is referenced to the values of their elemental forms, must satisfy the equilibrium condition:

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

where \( \Delta H_f (\text{Ag}_3\text{PO}_4) \) is the formation enthalpy of Ag₃PO₄. In addition, we must enforce the constraint such as \( 2 \mu_{\text{Ag}_3} + \mu_{\text{O}} < \Delta H_f (\text{Ag}_3\text{O}) \), to prevent the precipitation of Ag₂O during the growing process of Ag₃PO₄. Similar constraint must be applied to P₂O₅. To avoid the precipitation of constituent atoms, \( \mu_{\text{Ag}_3} + \mu_{\text{Li}} + \mu_{\text{O}} = \Delta H_f (\text{Li}_2\text{O}) = -5.96 \text{ eV} \), to satisfy other constraints to avoid the formation of impurities-related phases. Specifically, the chemical potential of Cd is constrained by \( \mu_{\text{Cd}} < -2.40 \text{ eV} \).

The binding energy of a complex defect represents energy changing from isolated dopants to a complex defect. To determine whether the binding of two dopants is energetically preferred (e.g., Cd₃Ag and NO), we calculate the binding energy \( E_b \) which is defined as:

\[ E_b = \Delta H_f (\text{Cd}_{3\text{Ag}}, q_1) + \Delta H_f (\text{NO}, q_2) - \Delta H_f (\text{Cd}_{3\text{Ag}} - \text{NO}, q_3) \]

where \( q_1, q_2 \) are the most stable charge states of Cd₃Ag and complex (Cd₃Ag-NO), respectively, at any given \( E_F \). A positive \( E_b \) indicates the reaction is exothermic and the defect pair tends to bind to each other when both are present in the system.

**Results and Discussion**

**Cd monodoping.** Cadmium sits to the right of Ag in the periodic table, having an atomic size very close to that of Ag which makes sure that negligible strain energy is introduced to the Ag₃PO₄ host. Thus, we expect Cd to preferentially occupy the Ag site in Ag₃PO₄, leading to relatively small relaxations and acting as a shallow donor. Indeed, in the neutral charge state (Cd₃Ag⁰), the neighboring O atoms relax inward, resulting in a Cd-O
bond length (2.21 Å) that is 6.8% shorter than the equilibrium Ag-O bond length (2.37 Å), while the Cd-Ag bond length (3.22 Å) becomes 7% longer than the equilibrium Ag-Ag bond length (3.01 Å). In the positive charge state (CdAg\(^+\)), the Cd-O bond length is 2.2 Å, and the Cd-Ag bond length is 3.23 Å. It is noteworthy that the Cd-O bond length is similar to the counterpart (2.35 Å) in CdO unit cell\(^42\).

As expected, CdAg is shallow donor, and the transition energy level of \(\varepsilon(0/+)\) is located at 0.01 eV below the CBM. The conductivity of a semiconductor depends not only on the transition levels of donor or acceptors, but also on their formation energies. The results of formation energy for the defects under consideration are listed in Table 1. Figure 1 shows the calculated formation energies of Cd Ag as a function of Fermi level under O-rich [Fig. 1(a)] and O-poor [Fig. 1(b)] conditions, respectively. Under O-poor growth condition [Fig. 1(b)], the formation energy of CdAg is much lower than that under O-rich condition, and becomes negative in the entire range of \(E_F\) value in the band gap. This is because the chemical potential of Cd is limited by the O chemical potential due to the limit of impurity-related phase CdO. Therefore, the highest possible \(\mu_{Cd}\) requires the lowest \(\mu_O\), i.e. O-poor condition. Our results suggest that \(n\)-type Ag\(_3\)PO\(_4\) is achievable by Cd-doping under O-poor condition.

When Cd dopant occupies the P lattice site, this defect behaves as a triple acceptor. The transition energy levels of \(\varepsilon(-/0)\), \(\varepsilon(2-/0)\) and \(\varepsilon(3-/0)\) are located at 0.13 eV, 0.27 eV and 0.25 eV above the VBM, respectively. In general, deep impurity-related levels typically represent localized electron distributions, and a change of occupancy usually results in change of structures\(^43\). Indeed, because of the large size mismatch between the Cd and P atoms,

Table 1. Calculated transition energy levels and binding energies \(E_b\) of the defect complexes, and defect formation energies with \(E_F = 0\) under O-rich and O-poor conditions in Ag\(_3\)PO\(_4\). All energies are in eV.

|       | \(\varepsilon(0/+\) | \(\varepsilon(0/2+/)\) | \(\varepsilon(0/3+/)\) | \(\varepsilon(0/4+/)\) | \(E_b\) | \(\Delta H_f\) (O-rich) | \(\Delta H_f\) (O-poor) |
|-------|---------------------|----------------------|----------------------|---------------------|--------|------------------------|------------------------|
| Cd    |                     |                      |                      |                     |        |                        |                        |
| Cd\(_{Ag}\) | 0.01                | -0.02                | -0.24                | 0.53                | 0.91   | 8.59                   | 5.21                   |
| Cd\(_{O}\) | 0.27                | 0.14                 |                      |                     |        | 4.74                   | 3.05                   |
| Cd\(_{Ag}(s)\) | 0.1                 | 0.01                 |                      |                     |        | 4.90                   | 3.21                   |
| Acceptor | \(\varepsilon(-/0)\) | \(\varepsilon(2-/0)\) | \(\varepsilon(3-/0)\) | \(\varepsilon(4-/0)\) | \(E_b\) | \(\Delta H_f\) (O-rich) | \(\Delta H_f\) (O-poor) |
| Cd    | 0.13                | 0.27                 | 0.25                 |                      | 7.89   | 10.42                  |                        |
| Cd\(_{Ag}(s)\) | 0.49              |                      |                      |                     | 0.51   | 8.80                   | 4.57                   |
| Cd\(_{Ag}(s)\) | 0.18              |                      |                      |                     | -0.08  |                        |                        |
| N\(_O\) | 0.46                |                      |                      |                     |        | 5.46                   | 3.77                   |
| V\(_Ag\) | 0.18                |                      |                      |                     |        | 0.46                   | 1.35                   |
| Li    |                     |                      |                      |                     |        |                        |                        |
| Li\(_O\) | 0.18                | 1.55                 | 2.0                  |                      | 5.90   | 3.37                   |                        |
| Li\(_{Ag}\) | -0.04              |                      |                      |                     |        | 2.22                   | 1.38                   |
| Li\(_{Ag}(s)\) | -0.15             |                      |                      |                     |        | 2.16                   | 1.32                   |
| Acceptor | \(\varepsilon(-/0)\) | \(\varepsilon(2-/0)\) | \(\varepsilon(3-/0)\) | \(\varepsilon(4-/0)\) | \(E_b\) | \(\Delta H_f\) (O-rich) | \(\Delta H_f\) (O-poor) |
| Li\(_P\) | 0.70                | 0.69                 | 0.85                 | 0.89                |        | 6.62                   | 10.0                   |
| Li\(_{Ag}\) | 0.54                |                      |                      |                     | -0.11  | 3.51                   | 1.82                   |
| Li\(_{Ag}(s)\) | -0.04              |                      |                      |                     |        | 0.04                   |                        |

Figure 1. The formation energies of possible Cd monodoped defects, Cd\(_{Ag}\), Cd\(_{P}\), Cd\(_{O}\), Cdi and Cdi\(_{Ag}(s)\), together with (Cd\(_{Ag}(s)\)-2NO) complex as a function of the Fermi energy under O-rich (a) and O-poor (b) conditions. Only the lowest formation energy states are shown.
the four oxygen neighbors of Cd lie at a distance of 2.20–2.21 Å, which are larger than the equilibrium P-O bond length of 1.56 Å for bulk Ag₃PO₄. As seen in Fig. 1, the formation energy of Cd₃ is quite high even under extreme O-rich condition. Moreover, recent studies, based on a revised molecular orbital diagram for Ag₃PO₄, have pointed out that the strong covalent interactions are formed in the tetrahedral PO₄ structural units¹⁴. It is therefore not expected that Cd will incorporate on the P site with an appreciable solubility.

Since oxygen atom can provide six electrons and cadmium can provide only two electrons, it is expected that Cd₃ acts as donor. Indeed, the calculated transition energy levels of ε(0/+), ε(0/2/+), ε(0/3+) and ε(0/4+) are located at −0.02 eV, −0.24 eV, 0.53 eV and 0.91 eV below the CBM, respectively. For Cd₄ in the 0, 1+, 2+, 3+ and 4+ charge states, the distances between Cd and the nearest-neighbor O atoms are 3.32, 3.05, 2.88, 2.86 and 2.84 Å, respectively. This dramatic lattice distortion can lead to higher formation energy. According to Fig. 1, Cd₃ has much lower formation energy under O poor condition than under O rich condition. But even under O poor condition, Cd₃ has a formation energy that is 1.91 eV higher than that of CdAg at the VBM, and so its contribution is less significant.

For interstitial Cd, we have studied two possible atomic configurations. One is the tetrahedral site coordinated by four O atoms (expressed as Cd₄), the other is the so-called split interstitial site which consists of two atoms on a single substitutional lattice site (expressed as Cd₄(s)), as shown in Fig. 2. For Cd₄(s), this configuration is 0.16 eV higher in energy than Cd₄ and the calculated transition energy levels of ε(0/+), ε(0/2/+), ε(0/3+) and ε(0/4+) are located at 0.27 eV and 0.14 eV below the CBM, which are 0.17 eV and 0.13 eV higher than that of Cd₃, respectively. Therefore, in the following discussion we consider only the Cd₄ configuration. In the neutral charge state, the distance between Cd and the nearest-neighbor O atom is 2.33 Å which is very close to the Cd-O bond length in CdO unit cell. In the 1+ and 2+ charge states, the Cd-O bond lengths are 2.29 and 2.26 Å, respectively. As shown in Fig. 1, the calculated formation energies of Cd₄ are −0.14 and −1.83 eV under O-rich and O-poor conditions at the VBM, respectively. It implies that O-poor condition would produce much more abundant numbers of Cd donors in comparison with O-rich condition. However, its formation energy is relatively high compared with that of CdAg under both O-rich and O-poor conditions, regardless of the Fermi level position. Our results indicate that Cd will not be a relevant configuration for Cadmium in Ag₃PO₄.

**Cd codoping.** The formation of the (Cd₄₋Nₐ₋) complex is a result of Coulomb binding between positively charged donor (Cd₄) and negatively charged acceptor (Nₐ₋). To see if the complex can form, we calculated the binding energy. We find that Cd₄ is likely to bind with Nₐ₋ to form the (Cd₄₋Nₐ₋) complex with a binding energy of 0.03 eV. The positive binding energy means that the complex is energetically favorable and can be seen as the passive complex. Obviously, the (Cd₄₋Nₐ₋) complex is dielectric and will not provide electron or hole in Ag₃PO₄. But it may affect the electrical properties by changing the electronic structure⁴¹. The values of E_b for this complex are shown in Fig. 3 as a function of the Fermi level. Figure 4 shows the calculated total DOS of Ag₃PO₄ with and without the (Cd₄₋Nₐ₋) complex in order to see the effect of passivation on relative shift of the VBM. As can be seen from Fig. 4, the formation of a passive (Cd₄₋Nₐ₋) complex does not change the basic electronic structure, but only generates an additional fully occupied impurity band with the energy width of 0.54 eV above the VBM of Ag₃PO₄. The distance between Cd and N in the complex is 2.14 Å. The bond length of Cd and its nearest-neighbor O atom is 2.18 Å, which is 8% shorter than the equilibrium Ag-O bond length. The Cd-Ag bond length (3.01 Å) becomes 2% longer than the equilibrium Ag-Ag bond length.

When a second N atom is added to a neighbor site of the passive (Cd₄₋Nₐ₋) complex (the configuration of Cd₄₋2Nₐ₋ complex is shown in Fig. 5), we find that the binding energy of (Cd₄₋2Nₐ₋) is 0.51 eV with respect to the (Cd₄₋Nₐ₋) complex and Nₐ₋. The positive binding energy means that the p-type complex is energetically stable and can form if more acceptors are doped into Ag₃PO₄. Based on the fact that the transition will occur between the N defect levels and the fully occupied impurity bands rather than the original valence band, we calculated the transition energy level ε(−/0) of (Cd₄₋2Nₐ₋) which is 0.49 eV above the VBM of Ag₃PO₄. And the value is

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Figure 2. Atomic geometry of the relaxed structures of the (a) Cd and (b) Cd(s) configurations in Ag₃PO₄.

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reduced to $-0.05$ eV from the impurity band of the passive (CdAg-NO) complex. Therefore, the transition level can be reduced dramatically. In the neutral charge state (CdAg-2NO)$^0$, the distances between Cd and N1, Cd and N2 atoms in the complex are 2.16 and 4.09 Å, respectively. The bond lengths of Cd-O and N1-P are 2.18 and 1.65 Å,

Figure 3. Binding energies $E_b$ of complex defects as a function of the Fermi level.

Figure 4. The calculated total DOS for pure Ag$_3$PO$_4$ and a supercell containing a (Cd$_{ag}$-N$_0$) complex.

Figure 5. Crystal structure of Ag$_3$PO$_4$ supercell with codoping of Cd$_{ag}$ and two N$_0$. The silver, pink, red, khaki and blue balls represent Ag, P, O, Cd and N atoms, respectively.
Li monodoping. Since Li and Ag are isovalent, Ag substituted by Li (LiAg) is electrically inactive and Li monodoping is not considered. Similar to CdP, LiP has rather high formation energies under both O-rich and O-poor conditions (as shown in Fig. 6) because of the strong covalent interaction in the PO₄ units, which indicates that the formation of LiP is energetically unfavorable. The calculated results are summarized in Table 1. In the neutral charge state, the four equivalent oxygen atoms move outward by 25% of the initial P-O bond length. For Li substituting O (LiO), the calculated formation energies of LiO are lower than LiP, mainly because of the small misfit of atomic radius. The distance between Li and the nearest-neighbor O atom is 1.9 Å in the neutral charge state, and this highly perturbed structure can be described as Li going to an interstitial site and leaving behind an O vacancy. The calculated transition energy levels ε(0/+) for LiO are located at 0.18 eV above the VBM, 0.15 eV above the VBM, and 0.11 eV above the VBM, respectively.

Although substitutional Li behaves as an acceptor, Li tends to occupy the interstitial site and loose its outmost electron to behave as a donor. This will lead to the self-compensation and limit its application as an efficient p-type dopant in ZnO. Therefore, we have also studied two possible atomic configurations for interstitial Li as shown in Fig. 7. The most stable configuration is the split interstitial doping and Li(s) is only 0.06 eV lower in energy than LiP. The calculated transition energy level ε(0/+)(LiP) is located at 0.18 eV above the VBM, respectively. Figure 6 shows the calculated defect formation energy as a function of the Fermi level under O-rich and O-poor conditions. From Fig. 6, it was found that Li impurity prefers interstitial sites over substitutional sites regardless of the Fermi level position. For example, the formation energy of Li (LiP) is 2.21 eV (2.38 eV) lower than that of LiO under O-poor condition. However, the formation energies of the positively charged interstitial Li (LiP) increase with the Fermi energy while the negatively charged complex (LiAg⁻-VAg) decreases with the Fermi energy and the (LiAg⁻-VAg) complex is not stable (see discussion later). Our analysis suggests that interstitial Li (LiP) is likely to be the n-type dopant under O-poor condition.

Li codoping. Because LiAg is electrically inactive and NO is a deep acceptor, the (LiAg⁻-NO) complex is an acceptor. The calculated transition energy level ε(−/0) for the complex is located at 0.54 eV above the VBM, deeper than the corresponding single N dopant (0.46 eV). It is because the radius of Li is very different from Ag. To make sure whether the complex can form, we have also calculated the binding energy. The calculated binding energy for the (LiAg⁻-NO) complex is negative (−0.11 eV), indicating that LiAg will not bind with NO in Ag₃PO₄.
This is likely because the Ag-N bond is stronger than the Li-N bond. According to our calculations, the Ag-N bond length (2.11 Å) is shorter than the Li-N bond length (4.61 Å). It should be that the stable $p$-type conductivity will not be achieved by the (LiAg$_{16}$-N$_{2}$) complex. We also calculated the transition energy level $\varepsilon (\pm 0)$ for the (LiAg$_{16}$-V$_{Ag}$) complex, which is located at 0.04 eV below the VBM. The binding energy of this complex is positive (0.04 eV), which implies that this complex is stable in Ag$_3$PO$_4$.

Conclusions

In summary, we have investigated the formation of isolated defects and defect complexes in Cd and Li monodoped, (Cd, N) and (Li, N) codoped Ag$_3$PO$_4$ by the hybrid functional calculations. It is found that Cd$_{Ag}$ contributes to the $n$-type conductivity of Ag$_3$PO$_4$ under O-poor conditions. For Cd$_{D}$ and Cd$_{O}$, both of the two configurations will not be the relevant configurations for Cd doping in Ag$_3$PO$_4$, on account of the strong covalent interactions in the tetrahedral PO$_4$ structural units. For interstitial Cd (Cd$_{I}$), the calculated formation energy is relatively high compared with that of Cd$_{Ag}$ donor. Our results demonstrate that Cd can bind to N atom to form a stable passive (Cd$_{Ag}$-N$_{2}$) complex. Although the transition energy level of the acceptor (Cd$_{Ag}$-2N$_{2}$) complex is reduced from 0.49 to $\approx 0.05$ eV when electrons are transited from the impurity band of the passive complex rather than the original valence band, the formation energy of the acceptor complex is high in comparison with the isolated N$_{2}$. Same as Cd$_{D}$ and Cd$_{O}$, Li$_{D}$ and Li$_{O}$ will not be the relevant configurations for Li doping in Ag$_3$PO$_4$. But interstitial Li (Li$_{I}$ or Li$_{i}(s)$) with suitable level and appreciable solubility is likely to be the $p$-type dopant under O-poor condition. For the (LiAg$_{16}$-NO) complex, the calculated binding energy is negative ($\approx -0.11$ eV) because the Ag-N bond is stronger than the Li-N bond. While, the (LiAg$_{16}$-V$_{Ag}$) complex is potentially to be the $p$-type dopant under O-rich condition.

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Author Contributions
Y.H. carried out the DFT calculations and prepared the manuscript. M.Y.L., T.M., Z.P.L., C.C. and Y.H. contributed the discussion and suggestions. All authors read the manuscript.

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