

Electronic properties of highly-active Ag_3AsO_4 photocatalyst and its band gap modulation: An insight from hybrid-density functional calculations

(Supplementary Information)

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Charge distribution at the conduction band minimum

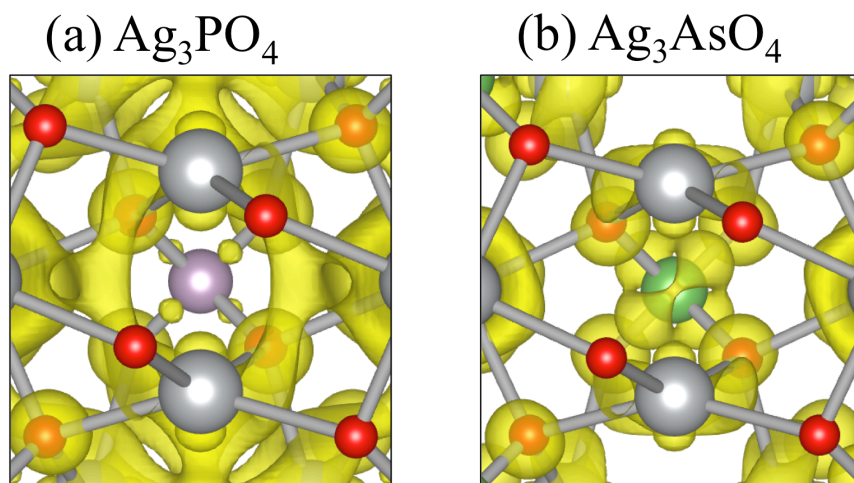


Fig S1. Charge distribution of the bottom of the conduction band minimum in (a) Ag_3PO_4 and (b) Ag_3AsO_4 . The isosurfaces are set to about 90% of the maximum of the respective charge densities.

Charge distribution at the valence band maximum

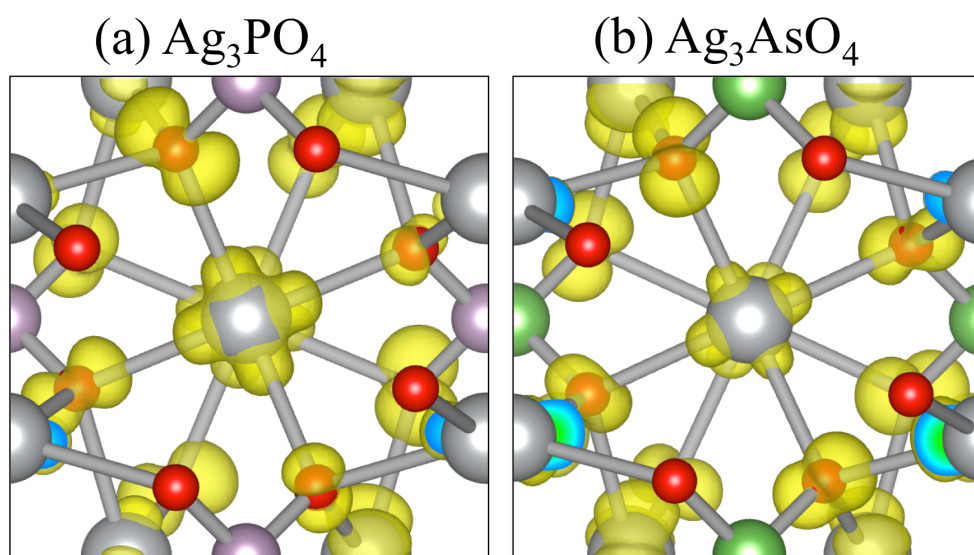


Fig S2. Charge distribution of the bottom of the valence band maximum in (a) Ag_3PO_4 and (b) Ag_3AsO_4 . The isosurfaces are set to about 90% of the maximum of the respective charge densities.

Mixing enthalpy and free energy of mixing of $\text{Ag}_3\text{As}_x\text{P}_{1-x}\text{O}_4$

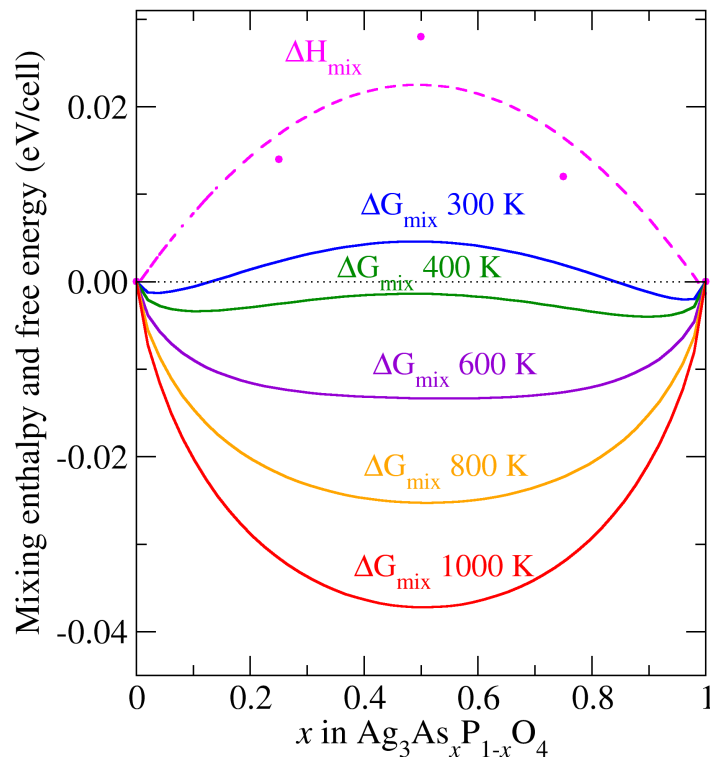


Fig S3. Enthalpy (ΔH_{mix}) and free energy (ΔG_{mix}) of mixing of $\text{Ag}_3\text{As}_x\text{P}_{1-x}\text{O}_4$ solid solutions as a function of composition. Only ΔG_{mix} for the temperatures of interest are included. The enthalpy of mixing of solid solution is small but positive, indicating the mixing is slightly exothermic process. The negative values of free energy of mixing indicate that the solid solutions are thermodynamically stable at all temperatures of interest.

To study the stability of the alloys $\text{Ag}_3\text{As}_x\text{P}_{1-x}\text{O}_4$, the enthalpies ΔH_{mix} and free energies ΔG_{mix} of mixing were calculated as a function of composition as:

$$\Delta H_{\text{mix}} = E(\text{Ag}_3\text{P}_{1-x}\text{As}_x\text{O}_4) - (1-x)E(\text{Ag}_3\text{PO}_4) - xE(\text{Ag}_3\text{AsO}_4), \quad (1)$$

and

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S \quad (2)$$

where T is the temperature in Kelvin and ΔS is the mixing entropy. The average entropy of each subsystem can be expressed as

$$\Delta S = -k_B \sum_{i=1}^N p_i \ln p_i, \quad (3)$$

where p_i is probabilities of subsystems i. In binary mixtures, the average mixing entropy per atom is given by 1

$$\Delta S = -k_B [(1-x) \ln(1-x) + x \ln x] \quad (4)$$

Here, we directly calculate ΔH_{mix} from density functional theory (DFT) for $x = 0.00, 0.25, 0.50$ and 1.00 using 16-atom and 32-atom cells. For simplicity, a 2nd degree polynomial function is used to represent ΔH_{mix} (dashed line in Fig.2) and ΔG_{mix} is numerically calculated from Eq. (2). ΔG_{mix} as a function of various temperatures are shown in Figure S3. Our results show that the free energy of mixing turns negative at temperatures greater than 400 K. These negative values of ΔG_{mix} indicate that the structures formed will be thermodynamically stable when the temperature is over 400 K. It should be noted that the actual temperature criteria can be deviated from our calculated results because the approximations we adopted. Nevertheless, the tendency of stability of solid solution should remain valid, i.e., higher temperatures are favored for solid solution formation.

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References

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