

High-Throughput Design of Non-oxide p-Type Transparent Conducting Materials: Data Mining, Search Strategy, and Identification of Boron Phosphide

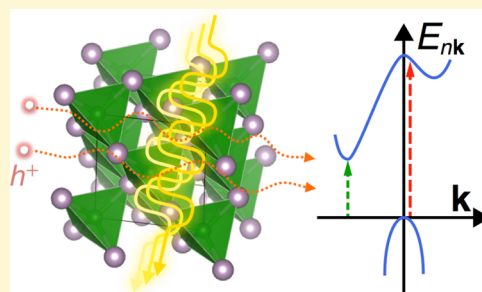
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Supporting Information

ABSTRACT: High-performance p-type transparent conducting materials (TCMs) are needed in a wide range of applications ranging from solar cells to transparent electronics. p-type TCMs require a large band gap (for transparency), low hole effective mass (for high mobility), and hole dopability. It has been demonstrated that oxides have inherent limitations in terms of hole effective masses making them difficult to use as a high-performance p-type TCM. In this work, we use a high-throughput computational approach to identify novel, non-oxide, p-type TCMs. By data mining a large computational data set (more than 30,000 compounds), we demonstrate that non-oxide materials can lead to much lower hole effective masses but to the detriment of smaller gaps and lower transparencies. We propose a strategy to overcome this fundamental correlation between low effective mass and small band gap by exploiting the weak absorption for indirect optical transitions. We apply this strategy to phosphides and identify zinc blende boron phosphide (BP) as a very promising candidate. Follow-up computational studies on defects formation indicate that BP can also be doped p-type and potentially n-type as well. Our work demonstrates how high-throughput computational design can lead to identification of materials with exceptional properties, and we propose a strategy to open the design of TCMs to non-oxide materials.



INTRODUCTION

Materials combining transparency, high conductivity, and/or carrier mobility are needed in a wide range of applications ranging from solar cells to transparent electronics.^{1–4} A typical approach to design transparent conducting materials (TCMs) is to use wide band gap compounds (to favor transparency) and dope them with a large amount of mobile carriers. Oxides are by far the most widely explored chemistry for TCMs with transparent conducting oxides (TCOs) forming a large field of materials science. One of the main challenges remaining in the field is to develop p-type TCOs (and more generally TCMs).⁵ Indeed, while n-type TCOs are ubiquitous and widely used in current devices,⁶ p-type materials are lagging behind as their materials properties, especially carrier mobility, are not yet sufficient. The lack of high-performance p-type TCMs impedes the development of new devices (e.g., transparent transistors) and motivates intense research efforts toward their discovery and development.

While oxides have been the main focus of the work on TCMs, the typical oxygen-based character of their valence band leads to large effective masses and low hole mobility.^{7,8} Strategies have been proposed both theoretically and experimentally to mitigate this issue,^{9–11} but it remains that oxides might not be the most convenient chemistry to develop high-performance p-type TCMs. Alternatives to oxides have

only been mildly studied in work on fluorides,¹² sulfides,^{13,14} oxianions,¹⁵ or germanides.¹⁶

We have recently developed a high-throughput computational strategy to quickly discover potential high-performance p-type TCOs.^{8,17,18} Our approach relies on a large database of density functional theory (DFT) computed data to select materials with adequate properties followed by more in-depth studies with advanced ab initio techniques for the most promising materials. In this work, we extend our approach to non-oxide materials. By data mining of a large computational data set, we demonstrate that non-oxide materials can lead to much higher p-type mobility (i.e., low hole effective masses) but to the detriment of smaller gaps and lower transparencies. We propose a strategy to overcome this fundamental correlation between low effective mass and small band gap by exploiting the weak absorption for indirect optical transitions. We apply this strategy to phosphides and identify zinc blende boron phosphide (BP) as a very promising candidate with an optimal band structure for a p-type TCM. Follow-up

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computational studies on defects formation indicate that BP could be doped p-type and potentially n-type as well. Our approach demonstrates how high-throughput computational design can lead to identification of materials with exceptional properties, and we present a strategy to open the TCMs design landscape to non-oxide materials.

METHODS

High-Throughput Computational Data. All DFT high-throughput computations were performed using VASP with the generalized-gradient approximation (GGA)¹⁹ within the PAW formalism.²⁰ Relaxed structures were obtained from the Materials Project database.²¹ A subsequent static and non-self-consistent band structure computation was performed using Fireworks.²² Effective masses were obtained using the BoltzTraP software and its interface within pymatgen.^{23,24} More details on the methodology can be obtained from refs 8 and 25. The effective mass is a tensor. In this work, we always use the highest of the three eigenvalues of this tensor, as it constitutes the worst-case scenario for transport. This ensures that all materials will lead to high mobility in all crystallographic directions. TCMs are usually grown as polycrystalline films, and we want to enforce that the mobility will be high whatever the grain orientations.

The full data set contains in total 39659 compounds. A publication of the effective mass data set is under preparation for a future publication. The statistics on oxides, nitrides, phosphides, and sulfides were obtained only on materials provided originally from the Inorganic Crystal Structure Database (ICSD). Only monoanionic compounds (i.e., containing one type of anion) were included in the analysis. We also excluded materials with very small DFT band gaps (<0.3 eV). Oxidation states were obtained from the ICSD. This data set contains 3787 oxides, 817 sulfides, 332 nitrides, and 171 phosphides.

GW Computations. The G_0W_0 calculations were performed using the ABINIT software package^{26,27} employing norm-conserving pseudopotentials generated using ONCVSP.²⁸ The calculations have been performed within the abipy/pymatgen framework. An automatic workflow that takes care of linking the individual steps of the GW calculations and convergence testing was used.²⁹

Defects Computations. All defect computations were performed using VASP with the HSE06 screened hybrid functional within the PAW formalism. The screening length was maintained at 0.2 Å while the fraction of exact exchange was set to 32%, leading to a slight overestimation of the indirect band gap (2.26 eV). All calculations adopted a 216-atom supercell with a plane-wave cutoff of 400 eV and a $2 \times 2 \times 2$ Monkhorst Pack k -point sampling. Defect formation energies and the associated charge state–transition levels were calculated as detailed in ref 30. Corrections for charged defects in a finite-size supercell were performed according to the method from Freysoldt et al.³¹ and adopted a static dielectric constant of $9.2\epsilon_0$ for BP.

RESULTS

Transparent Low Hole Effective Mass Materials beyond Oxides.

A low hole effective mass is a necessary condition for a high-mobility p-type conductor, but it is fundamentally difficult to design low hole effective mass oxides due to their localized oxygen p character. We study the opportunity for non-oxide TCMs in alternative chemistry such as sulfides, nitrides, and phosphides using a large database of effective masses for more than 30000 compounds. This database is built on the materials present in the Materials Project database³² and originating mainly from the Inorganic Crystal Structure Database (ICSD). Figure 1a shows a violin plot comparing the hole effective mass distribution among different chemistries. The oxides show by far the highest hole effective masses and the least opportunities for high hole mobility materials. Sulfides perform significantly better than oxides, but phosphides are clearly of the greatest interest with a

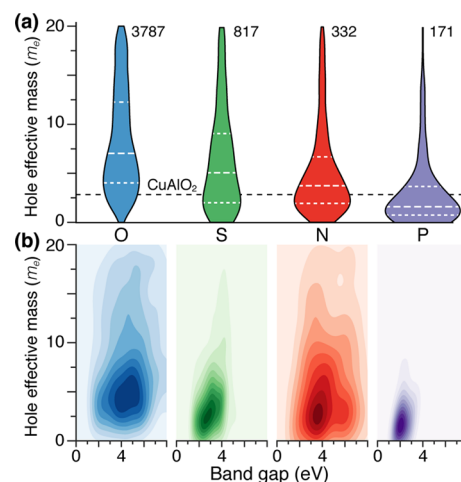


Figure 1. (a) Violin plot of the hole effective mass for four chemistries: oxides (O), sulfides (S), nitrides (N), and phosphides (P). The dashed white lines indicate median and quartiles. The hole effective mass of the typical p-type TCO CuAlO_2 is also indicated. (b) Hole effective mass vs empirically corrected DFT band gap for the four different chemistries. All masses are scaled relative to the electron mass (m_e). The number of investigated compounds is indicated at the top for each chemistry.

majority of them showing effective masses lower than state-of-the-art p-type oxides such CuAlO_2 .

A low hole effective mass is not the only requirement for an efficient p-type TCM. Transparency in the visible and therefore a large band gap is also required. In Figure 1b we present the distribution of hole effective masses but plotted as a function of an empirically corrected DFT band gap.³³ The three chemistries (nitrides, sulfides, and phosphides) leading to lower hole effective masses also lead to smaller band gaps that imply fundamentally more absorbing materials. Phosphides that are very appealing in terms of hole effective masses have band gaps around 2 eV on average and are much less likely to be transparent than oxides. Interestingly, the correlation between effective mass and band gap observed here on a large database of compounds emerges already from simple band structures models. In kp theory, the band structure energies in $k = 0$ are deducted from the $k = 0$ (Γ) energies through perturbation theory. This simple model leads to a linear relationship between the gap energy in Γ and the effective mass.³⁴ From this analysis, we could conclude that while offering more opportunities for low hole effective mass materials, the smaller band gaps for non-oxide materials make them less attractive as TCMs.

We present here a strategy that can overcome this fundamental correlation between transparency and effective mass. Large differences between optical and electronic band gaps can be present in certain materials. This is especially the case for materials with an indirect gap as indirect optical transitions are much weaker at room temperature due to the required involvement of phonon processes. Therefore, a material having a small, fundamental *indirect* gap could still be transparent if its *direct* gap is much larger than 3 eV. This is the mechanism at play in other TCMs such as SnO .³⁵ Our search strategy to detect non-oxide p-type TCMs is therefore to look for materials with low hole effective mass and a large *direct* gap despite a possibly small *indirect* gap. Figure 2a summarizes the trend between band gap and effective mass and our strategy to overcome it.

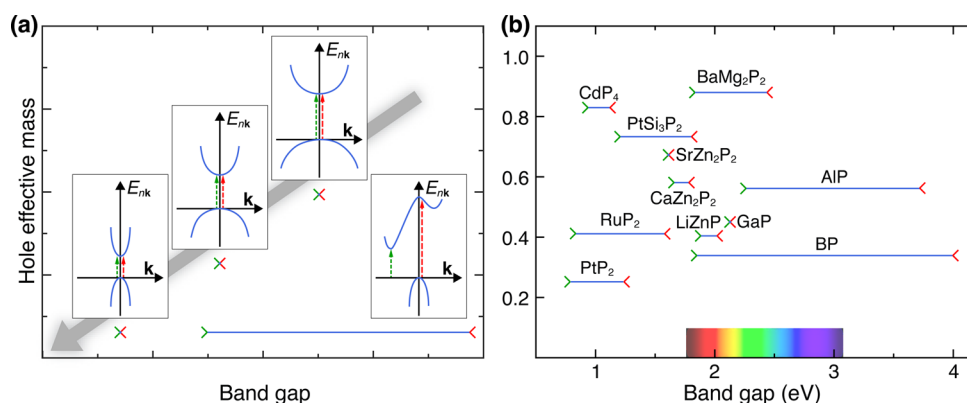


Figure 2. (a) Summary of the trend between effective mass and band gap and strategy to bypass it through the search for materials with large direct band gaps (but small indirect gaps). (b) Hole effective mass vs band gap computed by G_0W_0 : the green marker on the left of the bar is the indirect (fundamental) gap; the red marker indicates the direct gap.

Phosphides Computational Screening and Identification of Boron Phosphide.

Since phosphides lead to the lowest hole effective mass materials (see Figure 1a), we decided to focus on this chemistry. Interestingly, a very recent report investigated potential Cu-based phosphide TCMs. Their optical band gap were, as expected for most phosphides, relatively low (around 2 eV) leading to important absorption in the visible.³⁶ We selected phosphides in our database with hole effective masses from DFT lower than one electron mass. To obtain more accurate band structures, we used the G_0W_0 technique for these 12 selected compounds. We present the G_0W_0 computed band gaps and hole effective masses in Figure 2b. The red marker indicates the direct (optical) band gap while the left extremity of the bar (green marker) indicates the indirect (electronic) band gap. All these phosphides present a small (<2.5 eV) fundamental band gap as expected from their low effective masses. However, for some of them, this fundamental gap is indirect and the direct gap is much larger than 3 eV. Both AIP and BP present this characteristic, but BP shows a much lower hole effective mass ($0.35 m_e$) and is the most promising material identified by our high-throughput computational approach. The zinc blende crystal structure of BP and its band structure are shown in Figure 3. Boron phosphide combines extremely low hole effective mass compared to current leading p-type TCOs (such as $\sim 1-2 m_e$ for $CuAlO_2$ or SnO) with a very large direct band gap (4 eV). Additionally the “second gap” below the valence band minimum is extremely

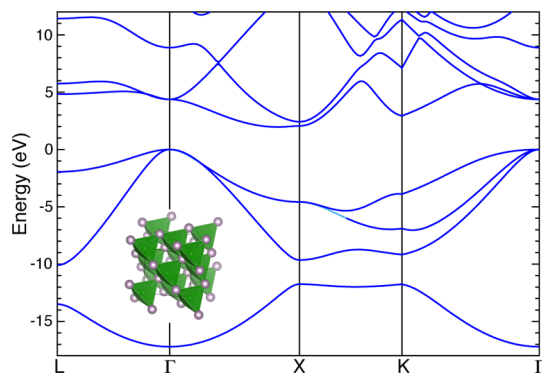


Figure 3. HSE band structure for boron phosphide (BP). Inset is the crystal structure of BP.

large in BP (>4 eV) which prevents any secondary direct absorption if the material is highly doped.³⁷

It is also of interest to understand the underlying structural and chemical reasons why boron phosphide emerges from our search. Among the 12 phosphides with effective mass lower than one, we found four zinc blende structures (GaP, AIP, BP, and LiZnP). What makes BP exceptional is the very large difference between its direct and indirect band gap (2 eV). In the series for the isoivalent compounds MP with $M = B, Al, Ga,$ and In , all compounds show favorable low hole effective masses (see Supporting Information Table S1) due to the similar character of their valence band (M-p/P-p). The major difference between these compounds comes from the direct or indirect character of their band gap. The heavier elements Ga and In show a direct transition unsuitable for transparency while the B and Al present an indirect transition (see Figures S1–S4). A detailed analysis of the character of the band structure indicates that this difference is related to a change in the nature of the conduction band at the Γ point (see Figures S1–S4). Figure 4 compares the band structure along the Γ –X direction for BP and GaP to illustrate this change. M-p/P-p and M-s/P-s bands are respectively in red and green. Both GaP and BP have a valence band formed by a bonding M-p/P-p state leading to low hole effective masses. Their conduction bands

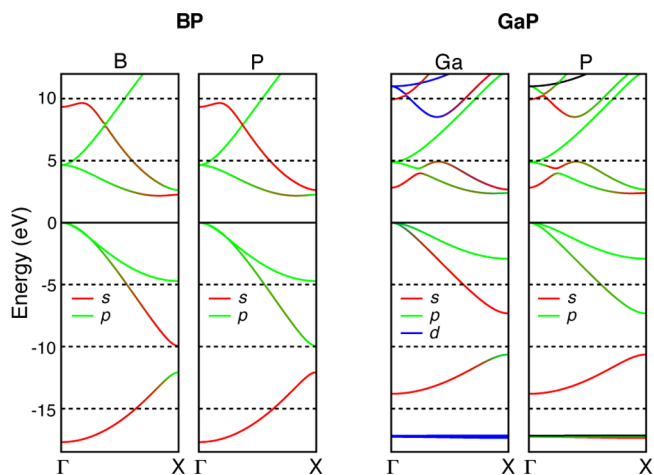


Figure 4. HSE band structure for BP and GaP projected on cationic (Ga and B) and anionic sites (P). Color indicates the orbitals (s, p, or d).

are similar at the X point with several states of M-p/P-p and M-s/P-s character close in energy. The major difference between GaP and BP is the character of the conduction band at the Γ point. For GaP, it consists of an antibonding Ga-s/P-s state (in red in Figure 4). In the case of BP, the antibonding B-s/P-s state is much higher in energy leading to the conduction band in Γ being a B-p/P-p antibonding state (in green in Figure 4). Hence, the transition at the Γ point is between B-p/P-p bonding and antibonding states leading to a larger direct gap. This switch from indirect to direct transition in MP with M in the B, Al, Ga, and In series appears gradually (see Figures S1–S4) and originates from a much larger overlap between M-s and P-p states for boron than the other column III elements.³⁸

While BP presents an almost perfect band structure for a p-type TCM, it is important to make sure that it is possible to sufficiently dope it p-type. We used hybrid functionals in the Heyd–Scuseria–Ernzeroff (HSE) approach to study intrinsic and extrinsic defects in BP (see Methods). Figure 6a shows the computed defect formation energy for intrinsic defects in the B-rich region of the phase diagram (all conditions are given in Figure S5). A concern for many p-type TCOs is the presence of intrinsic hole-killers (e.g., anionic vacancies) that will prevent any p-type doping attempt.^{7,39,40} This hole-killing process will appear through low energy donor defects. B-rich BP shows no hole-killing defects with the lowest energy hole-killer P on a B site (P_B) showing a very high formation energy. This demonstrates the possibility for this material to be significantly p-doped if grown in a B-rich region. However, no intrinsic shallow acceptor is present with the lowest acceptor B on P site (B_P) being a deep defect, which cannot provide many carriers. We also computationally evaluated the potential for extrinsic doping using a series of potential dopants: Mg, Be, C, and Si. The results are presented in Figure 5b and Figure S6. Be

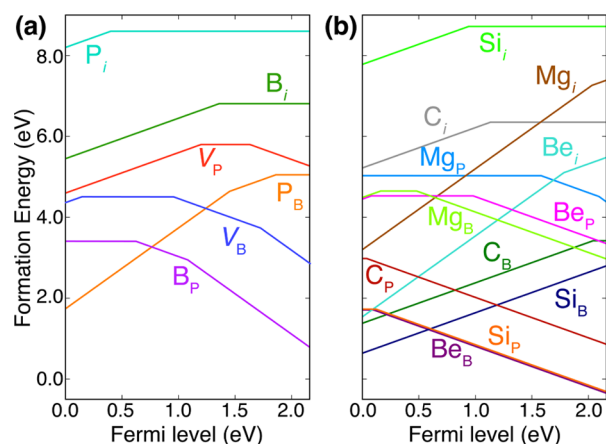


Figure 5. (a) Intrinsic defect formation energy vs Fermi level for BP in Boron-rich region. X_Y indicates Y on an X site. V relates to vacancy. (b) Extrinsic defect formation energy vs Fermi level for BP in boron-rich region.

(substituting for B) and C (substituting for P) both form very shallow acceptors. Carbon shows some compensation from C_B , but Be does not present any compensation and appears to be the most promising p-type dopant. Our computational work conclusively indicates that p-type doping could be achievable in BP. Interestingly, it presents also potential for n-type doping. In P-rich regions, no electron-killer is present (see Supporting Information) while silicon on the boron site (Si_B) is a clear

shallow donor that could lead to high electron concentration. Such transparent bipolar materials are even more sought for as they would offer the possibility to obtain p- and n-doped lattice matched semiconductors.^{41,42} It is not surprising that our strategy to search for materials with a small fundamental gap but large direct gap can lead to bipolar doping. It is known that smaller gap materials favor large dopability in both regimes, and this has been used to rationalize SnO's bipolar behavior.^{35,43}

Previous Experimental Results. Boron phosphide was relatively well studied during the 1970s but has not been the subject of strong research efforts since then. We can only conjecture as to why BP-based semiconductors have not matured technologically, but it likely has to do with the relative difficulty in growing high-quality single crystals combined with the dominance of III–V semiconductors or other alternatives for commercial device-level applications.⁴⁴ The challenges with reliable sample preparation are magnified by the complex behavior of unintentional dopants such as Si and C seen in Figure 5b, common impurities that can influence the electrical conductivity of BP in drastically different ways depending on the growth conditions. This makes control of the properties of BP difficult without the sufficient knowledge and understanding that has lagged behind other III–V semiconductors. Nevertheless, these earlier reports can be used to evaluate our computed data. Iwami et al. measured an indirect band gap of 1.96 (room temperature) to 2.03 eV (77 K) in excellent agreement with our GW results.⁴⁵ The authors report absorption coefficients between 50 and 1400 cm^{-1} in the range from 2 to 2.6 eV. A low absorption coefficient (lower than 1000 cm^{-1}) is also reported by Stone and Hill.⁴⁶ This is in agreement with transmission measurements of around 10% on a 25 mm film that would account for an absorption coefficient around 1000 cm^{-1} .⁴⁷ These experimental results confirm that while there is absorption between 2 and 3 eV, the indirect nature of the absorption makes it very weak. A typical film of 200 nm will absorb only 2% of the visible light. Such an absorption coefficient is close to the one of SnO, which is practically transparent.³⁵

Electrical properties have also been reported in the literature. While the results vary with process and growth conditions, the material is reported to be p-type in several instances with hole concentrations varying from $5 \times 10^{19} \text{ cm}^{-3}$, $5 \times 10^{18} \text{ cm}^{-3}$, to 10^{16} cm^{-3} .^{3,45,46,44,48} Hole mobilities were measured from 8 $\text{cm}^2/(\text{V s})$,⁴⁵ and 20–30 $\text{cm}^2/(\text{V s})$,^{46,44} to 350 $\text{cm}^2/(\text{V s})$.⁴⁸ These mobilities are extremely high for p-type transparent materials with the typical p-type oxides showing mobilities around 1–10 $\text{cm}^2/(\text{V s})$.⁵ The highest conductivity for BP was reported by Shohno et al. at 2800 $\Omega^{-1} \text{ cm}^{-1}$.⁴⁸ This conductivity is significantly higher than the best p-type conductivities reported in TCMs and approaches conductivities in optimized n-type TCOs (around $10^4 \Omega^{-1} \text{ cm}^{-1}$).¹ All these experimental results confirm our computational findings that boron phosphide is an exceptional material in terms of transparency, favorable defects, and low hole effective mass.

CONCLUSION AND OUTLOOK

Many efforts are directed toward the discovery and development of new p-type transparent conducting materials for various kinds of devices and applications. Computationally driven materials design has an important role to play in this challenging process. Targeting the identification of non-oxide p-type TCMs, we data mined a database of thousands of materials obtained from high-throughput ab initio computa-

tions. Our analysis indicated that non-oxide chemistries such as nitrides, sulfides, and phosphides indeed offer much more opportunities for low hole effective mass materials. However, we also found that these alternative chemistries lead to lower band gap materials, which would compromise transparency. To bypass this fundamental correlation between effective mass and band gap, we proposed to search for materials with a small indirect, fundamental gap but a large direct band gap. We demonstrated this design principle on phosphides and used a series of advanced ab initio techniques to identify phosphides with adequate band gap, hole effective mass, and defect behavior. Boron phosphide emerged from this search as a very promising candidate with exceptional properties. While experimental research, in agreement with our computational study, had been conducted previously on BP, its potential as a high-mobility p-type transparent material had never been realized. Our work strongly motivates a reinvestigation of this fascinating compound and future experimental research in its growth, characterization, and device integration. On a more general note, we also demonstrated how decoupling electronic and optical properties by using the difference between direct and indirect absorption could lead to a new generation of p-type TCMs. This design approach will be certainly useful for future materials screening in other chemical spaces.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.6b04663](https://doi.org/10.1021/acs.chemmater.6b04663).

Computed effective mass and projected band structure data for MP (M = B, Al, Ga, and In) in the zinc blende structure, and BP defect computations in both B-rich and P-rich conditions (PDF)

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Notes

The authors declare no competing financial interest.

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