Virtual screening of nitrogen-, phosphorous- and halide-containing materials as p-type transparent conductors

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Abstract

In this work, a high-throughput screening of binary and ternary pnictide- and halide-based compounds is performed to identify promising p-type transparent conductors. Our investigation profits from the emergence of open-access databases based on ab-initio results. The band gap, stability, hole effective mass, and p-type dopability are employed for the materials screening and the validity of these descriptors is discussed. Among the final candidates, BaSiN$_2$ is the most promising compound.

1. Introduction

Transparent conductors (TCs) are widely used in various applications such as touchscreens, liquid-crystal displays, light-emitting diodes, and solar cells [1–4]. While for technological applications both n-type and p-type TCs are required [5], most high-performance TCs are n-type oxide-based semiconductors. The performance of p-type transparent conducting oxides (TCOs) are hampered because of two main reasons: [6–8] (i) the major contribution to the valence band maximum (VBM) of TCOs is from localized O-2$p$ orbitals leading to the poor hole mobility and p-dopability. (ii) The small energy difference between the VBM and low-lying valence band states, due to degenerate O-2$p$ bands, resulting in intraband optical absorption and transparency degradation.

In 1997, Hosono and coworkers proposed the concept of the chemical modulation of the valence band (CMVB) for the Cu-based chemistry by discovering CuAlO$_2$ [6]. The authors observed a rise in the Cu-3$d$ energy level above the O-2$p$ level leading to the enhanced p-type performance. This led to the identification of delafossite-based compounds such as CuMO$_2$ (M = Al, In, B, Cr, Sc, Y, Ga) as p-type TCOs [9–12]. However, the majority of these compounds were hindered due to poor transparency or low p-type conductivity. Later, B$_6$O was identified as a promising p-type TCO in a high-throughput study, which showed the presence of s orbitals could also influence the band structure and enhance p-type conductivity [13].

The CMVB theory was further extended to chalcoxides leading to the synthesis and characterization of several layered p-type oxychalcogenide-based semiconductors, including LaCuOS and LaCuOSe [6]. However, LaCuOS shows poor conductivity, whereas LaCuOSe has a small band gap. Layered oxysulfide Sr$_2$Cu$_2$S$_2$O$_5$S$_2$ was found to be a promising p-type TC having a relatively wide band gap (3.1 eV) and good electrical conductivity compared to all other Cu-based compounds [14]. Extending the CMVB theory to chalcofluorides led to the discovery of layered p-type BaCuFCh (Ch = S, Se, and Te) [15] compounds, whose crystal structures are similar to LaCuOSe [16].

For the last decade, numerous research efforts were put forward to investigate oxychalcogenides, chalcofluorides, and oxychalcocfluorides to discover promising p-type TCs. Identifying promising p-type transparent materials with alternative chemistries and design rules still calls for more research efforts. Our previous works led to the identification of promising binary and ternary chalcogenides beyond Cu-based oxides [17, 18]. Recent high-throughput studies on nitride- and phosphide-based compounds have got attention owing to the stability and good hole conductivity of these compounds [19–22]. Yet, the virtual screening of N- and P-containing materials with different screening criteria might lead to the identification...
of new p-type TCs [23]. In addition, the constant growth of databases rationalizes repeating the screening of the same family of materials. Halides, on the other hand, did not receive much attention and are often considered in combination with chalcogenides. Hence, we have performed a computational high-throughput study to identify pnictide- and halide-based compounds for p-type TC applications. Our investigation profits from the emergence of free-access databases based on ab-initio results [24] allowing the consideration of thousands atomic structures. These large numbers of compounds cannot be examined experimentally. The list of compounds was drastically reduced by applying appropriate screening criteria. The outcome of our computational materials screening is a handful of compounds with requested properties that can be the subject of further investigations.

2. Methodology

2.1. Computational details
All calculations were carried out within the framework of density functional theory (DFT) [25] employing the projector augmented wave method [26, 27] as implemented in the Vienna ab initio software package (VASP) [28]. For our calculations, we used either the functional of Perdew, Burke, and Ernzerhof (PBE) [29] based on the generalized gradient approximation or the hybrid functional from Heyd, Scuseria, and Ernzerhof (HSE06) [30].

To determine the band gap values, we employed an atomate workflow with the following steps: (i) structure optimization with the PBE functional, (ii) calculation of the band gap at the hybrid level (HSE06) with a homogeneous k-point mesh [31] followed by (iii) the calculation of the HSE06 band gap with a denser homogeneous k-point mesh. The HSE06 band structures (in the Pymatgen [32] band structure format) were processed with the branch point routine of the matminer library [33] to calculate the branch point energy (BPE) which is defined as [34]

$$\frac{1}{2N_K} \sum_k \frac{1}{N_{VB}} \sum_i \varepsilon_i(k) + \frac{1}{N_{CB}} \sum_j \varepsilon_j(k).$$

The BPE is calculated as the average of the energy of the \(N_{VB}\) numbers of highest valence bands \(\varepsilon_i(k)\) plus the energy of the \(N_{CB}\) numbers of lowest conduction bands \(\varepsilon_j(k)\), which are evaluated at each k-point \((N_K)\) of the outer sum. We included two valence bands and one conduction band in the branch point calculations. The relative shift of the conduction band minimum (CBM) is defined as the CBM shift with respect to the BPE divided by the size of the band gap.

2.2. High-throughput screening
The Materials Project Database (MPDB) [24] was employed to screen binary and ternary compounds. The hole effective mass values were derived from the ab initio electronic transport database for inorganic materials provided by Ricci et al on the Dryad Digital Repository [35]. The values listed in this database were calculated based on Boltzmann transport theory as implemented in Boltztrap [36] and are, therefore, the eigenvalues of the conductivity effective mass tensor computed at 300 K and for a doping level of \(10^{18} \text{ cm}^{-3}\).

High-throughput calculations were performed with the atomate [31] workflow with the parameters defined in the Materials Project [37]. The screening criteria were based on the band gap, stability, and average hole effective mass of compounds. Our materials screening steps are as follows (see figure 1): we considered only the compounds that are thermodynamically stable. This means that they are the most stable phase with respect to all competing phases. In the next step, we eliminate all compounds with PBE band gaps smaller than 1.0 eV. After limiting the number of atoms per unit cell and excluding some elements (hydrogen, noble gases, toxic elements, etc), the average hole effective mass was considered. Our cutoff for average hole effective mass descriptor is 1.5 \(m_e\). In the next step, we calculated band gaps with hybrid functional (HSE06). If the compounds met all these criteria then defect calculations at the PBE level is performed. Intrinsic defects such as vacancies, antisites, and interstitial defects were studied to determine the p-type dopability in the next step. Materials that upheld intrinsic defects were further examined for doping with extrinsic atoms. It is noted that while the number of compounds to be considered decreases after each screening step, the computational cost increases. Nonetheless, virtual screening is still a rather effective method for narrowing down the search space compared to high-throughput experiments.

2.3. Defect chemistry
The optimized structures were used to calculate the formation energies for neutral and charged defects as implemented in the Python Charge Defects Toolkit (PyCDT) [38]. The formation energy of a defect \(X^q\) is calculated as
\[ \Delta E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] \pm \sum_i n_i \mu_i + qE_F + E_{\text{corr}}^q, \]  

(2)

where \( E_{\text{tot}}[\text{bulk}] \) is the total energy of the bulk, which is subtracted from the total energy of the cell with a defect (\( E_{\text{tot}}[X^q] \)). Therein, \( n_i \) indicates the number of atoms of species \( i \) that were added to/removed from the system. The grand-canonical approach was applied to determine the limits on chemical potentials \( \mu_i \) by analyzing competing phases retrieved from the MPDB \cite{38}. For binary compounds, this translates into two conditions: cation- or anion-rich conditions. In the case of ternary compounds, there are several regions depending on the complexity of the corresponding phase diagrams. For charged systems, \( i.e. q \neq 0 \), the energy of removing/adding electrons from/to the system was taken into account by the fourth term, where \( E_F \) is the position of the Fermi energy. The correction term for charged systems (\( E_{\text{corr}}^q \)) was employed (Freysoldt et al \cite{39} approach for isotropic systems or Kumagai et al \cite{40} approach for anisotropic systems) to correct the formation energies \cite{38}.

3. Results

3.1. Database screening

We applied our screening criteria to 133,691 compounds that exist in the MPDB (retrieved in Feb. 2019). We are interested in stable materials, therefore, we enforced the strict criterion of \( E_{\text{hull}} = 0 \) eV, which means the formation energies of compounds should lie on the convex hull. Furthermore, we only considered materials with less than 50 atoms in the primitive cell to allow an efficient HSE06 band gap screening. Compounds that contain rare earth elements (except scandium), period 7 elements, hydrogen, noble gases, arsenic, strontium, cadmium, cesium, hafnium, technetium, tantalum, mercury, and lead were eliminated from the list. In addition, we excluded compounds containing gold, which are known to have a strong spin–orbit interaction \cite{41}, since our screening procedure does not take the spin–orbit interaction into account. Based on these screening criteria, we found a total of 172 N-, 238 P-, and 559 halide-containing compounds.

The compounds were further screened based on the harmonic average of the hole effective mass available in the Dryad repository \cite{35}. In this step, 17 binary and 58 ternary pnictides found to have hole effective masses smaller than 1.5 \( m_\text{e} \). Since P is less electronegative than N, we expected more P-containing compounds to satisfy this criterion. In fact, 13 of the 17 binary compounds and 35 of the 58 ternary compounds are phosphide based. It should be mentioned that 1 binary compound and 3 ternary compounds contain both N and P atoms. Regarding halides, 14 binaries and 34 ternaries satisfy this criterion.

In the first step of the screening based on the band gap (see figure 1), only materials with PBE band gaps greater than 1.0 eV were considered. In the second step, we selected compounds with a HSE06 band gap larger than 3.0 eV. The size of the band gap often correlates with the difference in the electronegativity of the constituent elements. Thus, it is more likely to find wide band gap materials among compounds containing a low electronegative metal and a high electronegative non-metal element. Regarding ternary pnictides, the HSE06 band gap criterion results in the elimination of all phosphides. Phosphates and chalcophosphates dominate the remaining P-containing compounds. For 18 N-containing compounds that satisfy the HSE06 band gap criterion, 7 compounds have two anions, and 11 compounds have two cations. Both P- and N-containing compounds are dominated by main group elements, especially calcium and magnesium which are often encountered (for more details, see \cite{42}). Filtering out halides with the band gap criterion reduced the number of materials to 3 binary and 8 ternary halides of interest for further studies.
A wide band gap and high electrical conductivity are the primary requirements for a good p-type TCM. However, the possibility of enhancing the carrier concentration is not guaranteed for the compounds that satisfy the above-mentioned criteria. Hence, it is necessary to understand the defect chemistry of these compounds to identify the detrimental intrinsic defects and proper extrinsic dopants. The formation of anion vacancies is found to hinder the p-type performance in binary compounds [17]. In ternary compounds, in addition to anion vacancies, antisite and interstitial defects might also inhibit p-type performance [18]. In addition, nitrides are prone to the formation of \( \text{O}_N \) hole-killer defects [43–45]. In the following sections, we discuss the defect chemistry for binary and ternary compounds that satisfied previous screening criteria. We note in passing that the underestimation of the semiconductor band gaps by DFT calculations may sometimes make calculations of defects formation energies for certain compounds impossible. However, for our compounds, PBE band gaps are larger than 2 eV.

### 3.2. Binary compounds

The majority of binary pnictides that satisfy our screening criteria were found to be nitrides (see table 1). For binary nitrides, the defect formation energies were computed in the anion-rich region of the phase diagrams to hinder the formation of anion vacancies. Nevertheless, it was observed that \( \text{Vac}_N \) defects have lower formation energies compared to other intrinsic defects. All intrinsic defects, however, have relatively high formation energies (≥2 eV). For example, \( \text{Vac}_N \) has a formation energy larger than 3 eV in AlN and Si\(_N_4\), which results in a low concentration of \( \text{Vac}_N \) in these compounds. The high formation energy of intrinsic defects makes these compounds appropriate for doping. Hence, we calculated the formation energies of Zn, Mg, and Be point defects in AlN and the formation energies of Al, Ca, and Ga point defects in Si\(_N_4\). Regarding AlN, we observed a Fermi-level pinning caused by \( \text{Be}_{\text{Al}} \), whereas Mg\(_{\text{Al}}\) and Zn\(_{\text{Al}}\) defects were found to be acceptor defects enhancing the hole concentration (figure 2(a)) in a good agreement with the recent publication [46]. It has been recognized that oxygen is the main impurity that contaminates the AlN crystals [47]. Our results show that the presence of \( \text{O}_N \) defects results in the Fermi-level pinning above the VBM in agreement with previous DFT results [45]. In Si\(_N_4\), Al\(_{\text{Si}}\) and Ga\(_{\text{Si}}\) were found to be acceptor defects (figure 2(b)). Our results are consistent with the results of Lu et al for \( \beta \)-Si\(_N_4\) [48]. Similar to AlN, \( \text{O}_N \) defects result in the Fermi-level pinning in the gap of Si\(_N_4\). For BN, \( \text{N}_B \) defects that act as a deep donor defect have lower formation energy compared to other intrinsic defects (see figure S1 in the supplementary information (SI) (available online at https://stacks.iop.org/JPMATER/4/015004/mmedia)). Moreover, the formation energy of Be substitutional defects in BN is high. The defect chemistry of BN makes it an unfavorable p-type compound.

### Table 1

| Compound | MPDB ID | Space group | \( E^{\text{HSE}}_{\text{h}} \) (eV) | \( m^*_h \) (m\(_0\)) | CBM shift |
|----------|---------|-------------|----------------|-----------------|-----------|
| Si\(_N_4\) | mp-988 | P\(_6\)/m | 5.71 | 1.13 | 50.4% |
| AlN | mp-661 | P\(_6\)/mc | 5.42 | 1.03 | 42.7% |
| BN | mp-7991 | P\(_6\)/mmc | 5.41 | 0.94 | 54.6% |
| P\(_3\)N\(_4\) | mp-567 907 | C2/c | 4.97 | 1.08 | 50.4% |
| Be\(_2\)N\(_2\) | mp-18 337 | Ia\(_3\) | 4.56 | 1.17 | 36.9% |
| Be\(_2\)P | mp-28 395 | R\(_3\)/m | 3.23 | 0.84 | 48.9% |

### Table 2

| Compound | MPDB ID | Space group | \( E^{\text{HSE}}_{\text{h}} \) (eV) | \( m^*_h \) (m\(_0\)) | CBM shift |
|----------|---------|-------------|----------------|-----------------|-----------|
| BaCl\(_2\) | mp-568 662 | Fm\(_3\)/m | 6.71 | 1.43 | 47.7% |
| TICl | mp-569 639 | Fm\(_3\)/m | 3.60 | 0.57 | 52.8% |
| TiBr | mp-568 560 | Fm\(_3\)/m | 3.01 | 0.51 | 50.6% |
with Si, although there is a Fermi-level pinning close to the VBM due to the close formation energies of SiP and SiB defects close to the VBM.

We calculated the defect formation energies for BaCl$_2$, TlBr, and TlCl under anion-rich conditions. Our results show that TlCl and TlBr are intrinsic p-type semiconductors (figure S3 in the SI). However, we were not able to find a dopant for these compounds. On the other hand, K and Cs found to be good dopants to increase the hole concentration in BaCl$_2$ (see figure 2(d)).

### 3.3. Ternary compounds

Among 23 ternary pnictides, we found 11 nitrides, 3 nitridophosphates, 2 phosphates, 4 chalcophosphates, and 3 cyanamides. All ternary halides except Rb$_2$ZnI$_4$ contain two anions with.

#### 3.3.1. Halides

The intrinsic defects hinder the p-type dopability of the halides in our final list (table 3). For example, the vacancy of iodine in ScIO causes the Fermi-level pinning close to the VBM (figure S9 in the SI). Having two anions in these compounds makes it impossible to find a growth condition under which the formation of hole-killer defects are prevented.

#### 3.3.2. Nitrides

Among ternary nitrides (table 4), the hole-killer defects were found to be anion vacancies as well as cation antisites due to the presence of two cations with similar ionic radii and different charge states [19]. For Li$_3$GaN$_2$, LiMgN, Li$_3$ScN$_2$, ZnGeN$_2$, and MgGeN$_2$ the cation antisite defects were found to be hole-killer defects. Moreover, we were not able to find suitable dopants for LiMgN, ZnGeN$_2$, Li$_3$GaN$_2$, and Li$_3$ScN due to the relatively high defect formation energies of dopants leading to the Fermi-level pinning (corresponding figures are shown in the SI).

For ternary nitrides containing two cations with different ionic radii, we observed Vac$_N$ defects to be more detrimental compared to antisite defects. Hence, we calculated the formation energy of extrinsic defects under N-rich conditions. Nevertheless, we were not able to find a suitable dopant for CaGeN$_2$ and Ca$_3$Ga$_2$N$_4$ due to the Fermi-level pinning caused by anion vacancies. For Ca$_5$(SiN$_3$)$_2$, we identified Li$_{Ca}$ as a
potential dopant, but Li_{10a} defect acts as a hole-killer defect making this compound unfavorable. Several dopants for BaSiN₂ (figure 3(a)) were explored: Na_{10a}, K_{10a}, Rb_{10a}, and Al_{10a} were found to be acceptor defects making BaSiN₂ a promising compound. Similar to binary nitrides, the formation of Oₙ defects in BaSiN₂ results in the Fermi-level pinning.

In the case of MgBe₂N₂ and CaMg₂N₂, cation antisite defects were neutral owing to the equally charged cations. For MgBe₂N₂, the Fermi-level pinning was avoided for Na_{10p}, Li_{10p}, and Be defects under N-rich conditions (figure 3(b)). For CaMg₂N₂, we were able to identify Li_{10p} as a good dopant under N-rich conditions (figure 3(c)). While Oₙ defects are harmless in MgBe₂N₂, they caused a Fermi-level pinning in CaMg₂N₂.

### 3.3.3. Cyanamides and beryllium carbonitride

The cation antisites in Li$_3$CN$_2$ and CaCN$_2$ are less harmful than BeCN$_2$ (table 5). However, the formation of anion vacancies in Li$_3$CN$_2$ and CaCN$_2$ makes these compounds less favorable (see figures S21 and S22 in the SI). The formation of anion vacancies can be hindered by synthesizing under anion-rich conditions. However, under these conditions, the concentration of N$_c$ antisites, which are hole-killer defects, increases. Under these conditions, only cation substitutional doping seems reasonable. Nevertheless, we were not able to find a dopant for Li$_3$CN$_2$. Extrinsic defects in BeCN$_2$ and CaCN$_2$ had relatively high formation energies and resulted in the Fermi-level pinning making these compounds unfavorable.

### 3.3.4. Nitridophosphates

Among nitridophosphates (table 6), the hole-killer defects were found to be Vac$_N$ and Vac$_P$ in Ca$_3$PN$_3$ and Mg$_2$PN$_3$, respectively. However, Vac$_N$ has a high formation energy in Mg$_2$PN$_3$ (≥2 eV) under N-rich

| Compound          | MPDB ID  | Space group | $E_{\text{HSE}}^g$ (eV) | $\mu_m^a$ (m_e) | CBM shift |
|-------------------|----------|-------------|-------------------------|-----------------|-----------|
| BeCN$_2$          | mp-15703 | I42d        | 5.19                    | 0.76            | 34.5%     |
| Li$_3$CN$_2$      | mp-9610  | I4/mmmm     | 4.88                    | 1.34            | 37.2%     |
| CaCN$_2$          | mp-4124  | R3m         | 4.77                    | 1.04            | 45.3%     |
Figure 3. Defect chemistry of (a) BaSiN$_2$, (b) MgBe$_2$N$_2$, and (c) CaMg$_2$N$_2$ under N-rich conditions. Only defects with a low formation energy are shown.

Table 6. List of nitridophosphates sorted by their HSE06 band gap values.

| Compound | MPDB ID | Space group | $E_{\text{HSE}}$ (eV) | $m^*_h$ (m$_e$) | Shift CBM |
|----------|---------|-------------|------------------------|----------------|----------|
| LiPN$_2$ | mp-3524 | I4 2d       | 5.13                   | 1.37           | 35.8%    |
| Mg$_2$PN$_3$ | mp-3933 | Cmc2$_1$    | 4.88                   | 1.29           | 46.1%    |
| Ca$_2$PN$_3$ | mp-8977 | Cmce        | 3.87                   | 0.87           | 47.3%    |

conditions. Hence, formation energies for extrinsic dopants were calculated for this compound. The substitution of P with Si, Ge, and Ti was found to enhance the hole concentration in Mg$_2$PN$_3$ (figure 4(a)). Although Li$_3$Al$_4$ appeared to be a promising substitutional dopant for Mg$_2$PN$_3$, the p-dopability was found to be inhibited due to the formation of Li$_{\text{int}}$. Compared to Mg$_2$PN$_3$, the defect chemistry for Ca$_2$PN$_3$ is less favorable due to the formation of Ge$_P$ and Li$_{\text{int}}$ defects. Only Si was found to be a promising dopant (Si$_P$) (figure 4(b)). Further, O$_N$ defects have lower formation energy than other extrinsic defects in Ca$_2$PN$_3$ leading to the Fermi-level pinning close to the VBM. Regarding LiPN$_2$, the formation of detrimental intrinsic defects (Vac$_N$ and Li$_{\text{int}}$) implies the synthesis under N-rich and Li-poor conditions. However, no suitable
dopants were found due to the high formation energy of extrinsic defects and low formation energy of Li\textsubscript{int}, which resulted in the Fermi-level pinning (figure S23).

3.3.5. Phosphates and chalcophosphates

Phosphorus-based compounds that satisfy our screening criteria are either phosphates or chalcophosphates containing two anions (table 7). SbPO\textsubscript{4} and BiPO\textsubscript{4} failed the intrinsic defect criterion because of the facile formation of anion vacancies (figures S24 and S25). Among chalcophosphates, InPS\textsubscript{4} and MgPS\textsubscript{3} failed the intrinsic defects criterion due to the presence of hole-killer defects in all regions of the phase diagram (figure S26). The formation energies of intrinsic defects in MgPSe\textsubscript{3} were relatively high resulting in the low concentration of hole-killer defects. However, we could not identify any dopant for MgPSe\textsubscript{3} due to the high formation energies of extrinsic defects (figure S27). The intrinsic defects in Na\textsubscript{3}PS\textsubscript{4} were found to have low formation energy of extrinsic defects and low formation energy of Li\textsubscript{int}, which resulted in the Fermi-level pinning (figure S23).

Table 7. List of phosphates and chalcophosphates sorted by their HSE06 band gap values.

| Compound | MPDB ID | Space group | $E_{\text{K}}^{\text{HSE}}$ (eV) | $m^*_h$ ($m_e$) | CBM shift |
|----------|---------|-------------|-----------------|-----------------|------------|
| SbPO\textsubscript{4} | mp-3439 | P2\textsubscript{1}/m | 5.34 | 1.27 | 51.2% |
| BiPO\textsubscript{4} | mp-558 798 | P2\textsubscript{1}/m | 5.00 | 0.92 | 48.7% |
| MgPS\textsubscript{3} | mp-675 651 | C2/m | 3.90 | 1.13 | 48.6% |
| InPS\textsubscript{4} | mp-20 790 | I\textsuperscript{\textsubscript{4}} | 3.40 | 1.15 | 50.4% |
| Na\textsubscript{3}PS\textsubscript{4} | mp-28 782 | P\textsuperscript{\textsubscript{2}}\textsubscript{1}/c | 3.39 | 1.47 | 44.8% |
| MgPSe\textsubscript{3} | mp-30 943 | R\textsuperscript{\textsubscript{3}} | 2.98 | 0.94 | 49.2% |

Figure 4. (a) Defect chemistry of Mg\textsubscript{2}PN\textsubscript{3} under N-rich conditions. (b) Defect chemistry of Ca\textsubscript{2}PN\textsubscript{3} under N-rich conditions. Only defects with a low formation energy are shown.
concentrations under S-rich and Na-poor conditions. Under these conditions, substitutional Si$^P$ defects can enhance the hole concentration in Na$_3$PS$_4$ (see figure 5).

4. Discussion

To carry out efficient virtual materials screening over a large number of compounds, the descriptors employed as the screening criteria should be obtained by performing cost-efficient DFT calculations (if they are not available in databases). In our screening process, we calculated the HSE06 band gaps and defect chemistry of compounds that satisfy less computationally-expensive criteria. The list of compounds was reduced after we applied conservative cutoffs for stability and PBE band gap descriptors. The cutoff for the hole effective mass descriptor is 1.5 $m_e$, which seems a reasonable cutoff for p-type TCMs [23]. It should be mentioned that varying descriptors cutoffs might result in a different list of candidates [19–22]. In the following sections, we discuss the validity of our screening criteria.

4.1. Atomic structure and stability

In our approach, stable compounds lie on the convex hull, although in practice, the onset of instability can strongly depend upon kinetics. This conservative cutoff for stability is applied to make sure our results do not lead to false-positive predictions. It is noted that the convex hull data show the thermodynamical stability of compounds under equilibrium conditions. These data do not predict the phase transition and decomposition under ambient/acidic/basic conditions. For example, our results show that Mg(BeN)$_2$, Na$_3$PS$_4$, BaSiN$_2$, and CaMg$_2$N$_2$ are stable but sensitivity to moisture and air was reported for these compounds [49–51]. Furthermore, Ca$_3$PN$_3$ was reported to be more sensitive to hydrolysis than Mg$_3$PN$_3$, which is not attacked by air, moisture, acids, and bases under normal conditions [52]. For the rest of the suggested compounds, we did not find further information on their stability in the literature. We note in passing that the stability of a compound is not correlated with the feasibility of its synthesis [53].

Table 8. Final list of binary and ternary compounds. For each compound the HSE06 ($E^\text{HSE}_g$) and experimental band gaps ($E^\text{exp}_g$), harmonic mean hole effective mass ($m^*_h$), relative shift of the CBM, and suggested dopants are listed.

| Compound | $E^\text{HSE}_g$ (eV) | $E^\text{exp}_g$ (eV) | $m^*_h$ ($m_e$) | CBM shift | Dopants |
|----------|----------------------|----------------------|----------------|-----------|---------|
| Si$_3$N$_4$ | 5.71 | 5.2-5.5 | 1.13 | 50.4% | Si: Ga, Al |
| AlN | 5.42 | 6.2 | 1.03 | 42.7% | Al: Mg, Zn |
| B$_3$P | 3.23 | 3.35 | 0.84 | 48.9% | P: Ge |
| P$_3$N$_3$ | 4.97 | 5.87 | 1.08 | 50.4% | P: Si |
| BaCl$_2$ | 6.71 | – | 1.43 | 47.7% | Ba: K, Cs |
| MgBe$_2$N$_2$ | 5.36 | – | 1.33 | 48.9% | Mg: Li, Na Be: Li |
| Mg$_3$PN$_3$ | 4.88 | 5.0 | 1.29 | 46.1% | P: Si, Ge, Ti |
| BaSiN$_2$ | 3.99 | 4.1 | 0.90 | 52.4% | Ba: Na, K, Rb Si: Al |
| Ca$_3$PN$_3$ | 3.87 | – | 0.87 | 47.3% | P: Si, Ge |
| Na$_3$PS$_4$ | 3.39 | – | 1.47 | 44.8% | P: Si |
| CaMg$_2$N$_2$ | 3.05 | 3.25 | 1.36 | 36.2% | Mg: Li |

Figure 5. Defect chemistry of Na$_3$PS$_4$ under S-rich and Na-poor conditions. Only defects with a low formation energy are shown.
4.2. Bandgap and transparency

We considered bandgap values as the indicator of the transparency of compounds. To maintain an efficient screening procedure, the screening based on the bandgap descriptor is performed in two steps. That is, compounds are filtered out based on PBE band gap values available in the MPDB ($E_g > 1.0$ eV) and then a more accurate but time-consuming criterion, the HSE06 band gap, is applied ($E_g > 3.0$ eV). We note in passing that a cutoff of 1 eV for PBE band gap values might lead to false-negative predictions [23]. It has been shown that HSE06 functional underestimates the band gaps larger than 5 eV [54]. This is true for $P_3N_5$, where we calculated a band gap of 4.97 eV, whereas experimental results indicate a band gap of $5.87 \pm 0.2$ eV [55]. Similarly for AlN, the calculated band gaps (5.42 eV) is smaller than the experimentally measured band gap (6.2 eV) [56, 57]. It should be mentioned that our result for AlN is in good agreement with the previously calculated band gap of 5.48 eV [54].

Considering other wide band gap compounds, the band gap of $\beta$-$Si_3N_4$ (5.7 eV) is overestimated compared to the measured values (5.2 and 5.5 eV) [58, 59]. It is important to point out that the band gap of $\beta$-$Si_3N_4$ is very sensitive to the doping level [48]. The band gap of $B_3P$ (3.23 eV) is in a good agreement with the optically measured value of 3.35 eV [60]. Using the modified Becke-Johnson functional [61], a band gap of 6.1 eV was calculated for Mg(BeN)$_2$ which is larger than the band gap calculated in this work (5.36 eV). Our calculated band gaps for Mg$_2$P$_3N_5$ (4.88 eV) and BaSiN$_2$ (3.99 eV) are in good agreements with the measured values of 5.0 eV [62] and 4.1 eV [63]. The band gap of Na$_3$PS$_4$ calculated by Kang et al [64] using the screened exchange local density approximation (3.26 eV) is slightly smaller than the band gap calculated by HSE06 (3.39 eV). For CaMg$_2$N$_2$ we calculated a band gap of 3.05 eV which is in a reasonable agreement with the band gap measured by the diffuse IR reflectance spectroscopy (3.25 eV) [65]. To the best of our...
knowledge, no band gaps have been reported for CaPN$_3$. It is noted that the reflectance of the materials was not investigated in this work. For example, among our final candidates, ceramics made of AlN and Si$_3$N$_4$ are reflective [66–68].

4.3. Effective mass and conductivity
Computing mobility is a nontrivial task that makes the virtual materials screening computationally expensive. Therefore, the hole effective mass descriptor was used as an indicator for good conductivity. It is noted that the hole effective mass is independent of scattering mechanisms in solids. The hole effective mass can be calculated in two ways: either by calculating the curvature of a specific path in the reciprocal space or by Boltzmann transport theory. We obtained the effective mass values calculated with Boltztrap, which are available in the Dryad database. Our cutoff for this descriptor is 1.5 m$_e$, which seems reasonable for pnictides and halides [69]. For AlN and Si$_3$N$_4$ the effective masses calculated from Boltzmann transport theory are between the effective mass of the light and heavy holes calculated by curve fitting. For Si$_3$N$_4$, the hole effective masses of 0.85 and 2.9 were calculated [70], while the values of 0.94, 0.94, and 1.95 are obtained from the Dryad database. For AlN, the hole effective masses of 0.36 and 4.24 were measured experimentally [71], whereas 0.25 and 3.68 were calculated for light and heavy holes, respectively [72]. These numbers can be compared with 0.43, 3.58, and 3.58 calculated by Boltztrap. It should be noted that Na$_3$PS$_4$ is considered as a solid electrolyte in sodium batteries [73, 74] which means it is an ionic conductor.

4.4. Defect chemistry and dopability
The underestimation of the semiconductor band gaps by semi-local functionals like PBE may sometimes make calculations of defects formation energies impossible. The narrow gap may induce the defect level to be a resonance in the conduction or valence band. A possible remedy is to use functionals that can predict the band gap of semiconductors close to the experimental values. However, calculations with these functionals
are time-consuming and can make the virtual materials screening computationally expensive. Therefore, we have performed HSE06 defect calculations for the best candidate in our final list, namely BaSiN$_2$. Additionally, since none of our ternary halides are p-dopable, we considered a ternary halide (ZrBrN) with the band gap smaller than 3 eV to compare its defect chemistry computed with different functionals. The results are depicted in figure 6. While the defect chemistry of BaSiN$_2$ calculated with HSE06 shows the same trend as PBE results, the behavior of defects in ZrBrN is different from PBE results. That is, the Sc$_{Zr}$ defect which is a shallow acceptor in PBE calculated defect chemistry, becomes a deep defect with transition levels in the middle of the gap in HSE06 calculated results. It shows the importance of the approach employed to study the defect chemistry of semiconductors.

4.5. Branch point energy and dopability

The branch point energy is considered to be an indicator for the dopability of semiconductors [75], although it is an approximation based on bulk properties. It is shown that a good p-type dopability is correlated with a small relative shift of the VBM with respect to the BPE, which means a large relative shift of the CBM with respect to the BPE [75]. However, it is observed that known p-type conductors often exhibit relative CBM shifts between 50%–60% [23]. It has been suggested that the formation energy of the hydrogen (FEH) interstitial defect (with the Fermi level at the VBM) is a good descriptor for p-dopability [10]. An interstitial hydrogen transfers an electron to the VBM that corresponds to the Fermi level. Therefore, FEH correlates with the valence band position with respect to the vacuum. It has been shown that the BPE correlates very well with the interstitial hydrogen transition level [76]. Regarding our compounds (see figure 7), we observe relative CBM shifts between 35 % and 55 % for most of the compounds. Among the final ternary compounds, BaSiN$_2$ found to be the most promising compound with the relative CBM shift of 52 %.

5. Conclusion

A computational high-throughput study has been performed to identify wide band gap pnictide and halide semiconductors that show good p-type conductivity. Our screening criteria are based on stability, band gap, hole effective mass, and defect chemistry. The defect chemistry revealed that the majority of binary and ternary compounds suffer from intrinsic anion vacancy defects. Moreover, ternary compounds that contain cations with unequal charge states and similar ionic radii showed an unfavorable defect chemistry. Finding a suitable dopant turned out to be the major problem for the ternary compounds because of the high formation energies of extrinsic defects leading to the Fermi-level pinning. Our materials screening led to the identification of non-oxide binary and ternary compounds that are promising for p-type TC applications. Among the final candidates, BaSiN$_2$ is the most promising compound.

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