Effect of \( \text{Mn}^{2+} \) substitution on the structure, properties and HER activity of cadmium phosphochlorides†

Anand Roy, Anjali Singh, S. Assa Aravindh, Swaraj Servottam, Umesh V. Waghmare and C. N. R. Rao 

Cadmium phosphochlorides, \( \text{Cd}_4\text{P}_2\text{Cl}_3 \) and \( \text{Cd}_7\text{P}_4\text{Cl}_6 \), possess cadmium atoms differently bonded to chlorine and phosphorus ligands. A combined experimental and theoretical study has been carried out to examine the effect of manganese substitution in place of cadmium in these compounds. Experimentally it is found that manganese prefers the \( \text{Cd}_7\text{P}_4\text{Cl}_6 \) phase over \( \text{Cd}_4\text{P}_2\text{Cl}_3 \). First-principles calculations reveal, stabilization of \( \text{Cd}_7\text{P}_4\text{Cl}_6 \) upon Mn-substitution with a significant reduction in the formation energy when \( \text{Mn}^{2+} \) is substituted at \( \text{Cd} \)-sites coordinated octahedrally by Cl-ligands. Substitution of \( \text{Mn}^{2+} \) at two different \( \text{Cd} \)-sites in these compounds not only alters their formation energy differently but also causes a notable change in the electronic structures. In contrast to n-type conductivity in pristine \( \text{Cd}_4\text{P}_2\text{Cl}_3 \), \( \text{Mn}^{2+} \) substituted \( \text{Cd}_{7-y}\text{Mn}_y\text{P}_4\text{Cl}_6 \) analogues exhibit p-type conductivity with a remarkable enhancement in the photochemical HER activity and stability of the system. Photochemical properties of pristine and substituted compounds are explained by studying the nature of charge carriers and their dynamics.

Introduction

Cadmium phosphochlorides constitute a series of II–V–VII ternary semiconductors with novel bonding of P and Cl atoms with Cd-centres.\(^1\)\(^-\)\(^2\) Accordingly, besides different structural features, cadmium phosphochlorides also exhibit interesting electronic band structures and photophysical properties. We have shown recently how the variation in the Cl/Cd and P/Cd ratios in these compounds alter the optical band gaps and electronic features, cadmium phosphochlorides also exhibit interesting electronic band structures and photophysical properties. We considered it interesting to examine the effect of manganese substitution in place of cadmium in these compounds. Experimentally it is found that manganese prefers the \( \text{Cd}_7\text{P}_4\text{Cl}_6 \) phase over \( \text{Cd}_4\text{P}_2\text{Cl}_3 \). First-principles calculations reveal, stabilization of \( \text{Cd}_7\text{P}_4\text{Cl}_6 \) upon Mn-substitution with a significant reduction in the formation energy when \( \text{Mn}^{2+} \) is substituted at \( \text{Cd} \)-sites coordinated octahedrally by Cl-ligands. Substitution of \( \text{Mn}^{2+} \) at two different \( \text{Cd} \)-sites in these compounds not only alters their formation energy differently but also causes a notable change in the electronic structures. In contrast to n-type conductivity in pristine \( \text{Cd}_4\text{P}_2\text{Cl}_3 \), \( \text{Mn}^{2+} \) substituted \( \text{Cd}_{7-y}\text{Mn}_y\text{P}_4\text{Cl}_6 \) analogues exhibit p-type conductivity with a remarkable enhancement in the photochemical HER activity and stability of the system. Photochemical properties of pristine and substituted compounds are explained by studying the nature of charge carriers and their dynamics.

† Electronic supplementary information (ESI) available: EDAX and XPS spectra, UV/vis. absorption spectra, Tauc plots, PXRD of compounds before and after photochemical reactions, Hall measurement, apparent quantum yield calculations. See DOI: 10.1039/c9ra10711h
Substitution of Mn$^{2+}$ at the two different Cd-sites in Cd$_7$P$_4$Cl$_6$ not only affects the formation energy differently but also changes the electronic band structures in a contrasting manner. The photochemical hydrogen evolution reaction (HER) activity of p-type Cd$_{7-x}$Mn$_x$P$_4$Cl$_6$ is vastly superior to that of the pristine material wherein Cd$_{5.8}$Mn$_{1.2}$P$_4$Cl$_6$ shows an apparent quantum yield (AQY) of 47.6%. The influence of nature of charge carriers and their mechanism of action in pristine and Mn$^{2+}$ substituted analogues have been studied.

Results and discussion

Experimental results

Powder X-ray diffraction (PXRD) patterns of cadmium phosphochlorides with different extent of manganese substitution are shown in Fig. 1. In the absence of MnCl$_2$ in the precursor mixture, we obtain the thermodynamically stable Cd$_4$P$_2$Cl$_3$ with the cubic structure (Pa3). The presence of even small proportion of MnCl$_2$ in the precursor mixture ($X_{Mn^{2+}} = 0.04$ with respect to Cd$^{2+}$) affects the formation of Cd$_4$P$_2$Cl$_3$ and gives rise to Cd$_7$P$_4$Cl$_6$ (cubic, Pa3) (~12%) along with Cd$_4$P$_2$Cl$_3$ (~88%) (Fig. 1a). Increase in the proportion of MnCl$_2$ ($X_{Mn^{2+}} = 0.08$) results in an increase in the Cd$_7$P$_4$Cl$_6$ in the mixture from 12 to 20%. Thus, above $X_{Mn^{2+}}$ of 0.08 a greenish-yellow (major product) and an orange-yellow (minor product) compound, corresponding to pure Cd$_7$P$_4$Cl$_6$ and mainly Cd$_4$P$_2$Cl$_3$ are formed respectively (Fig. 1a and b). Furthermore, an increase in the MnCl$_2$ content ($X_{Mn^{2+}} \geq 0.15$) results in the exclusive formation of pure Cd$_7$P$_4$Cl$_6$ with only a trace of Cd$_4$P$_2$Cl$_3$ (Fig. 1b). Comparative PXRD patterns (using zero background sample holder) of pristine Cd$_7$P$_4$Cl$_6$ and Mn-substituted Cd$_{5.8}$Mn$_{1.2}$P$_4$Cl$_6$ in the selective 2θ region is shown in Fig. 1c. A right shift (towards higher 2θ) in the diffraction peaks of Cd$_{5.8}$Mn$_{1.2}$P$_4$Cl$_6$ is observed with respect to the pristine compound, indicating a decrease in the lattice parameter of the system as a result of substitution. The Rietveld refinement of Cd$_{5.8}$Mn$_{1.2}$P$_4$Cl$_6$ indeed revealed a reduction in the lattice parameter ($a = 11.926\ \text{Å}$) with respect to the pristine Cd$_7$P$_4$Cl$_6$ ($a = 11.940\ \text{Å}$) which can be attributed to the smaller size of Mn$^{2+}$ ions (Fig. 1d).

In order to estimate the manganese concentration in substituted compounds, we have carried out ICP-OES measurements. Samples were thoroughly washed in H$_2$O–C$_2$H$_5$OH (1 : 3 volume ratio) mixture to remove the unreacted

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Fig. 1 PXRD patterns of mixed phase cadmium phosphochlorides (a), and Cd$_{7-x}$Mn$_x$P$_4$Cl$_6$ compounds with different extents of Mn$^{2+}$ substitution (b), comparison of major diffraction patterns of pristine Cd$_4$P$_2$Cl$_3$ and Mn-substituted Cd$_{5.8}$Mn$_{1.2}$P$_4$Cl$_6$ (c), Rietveld refinement (pattern matching) pattern of Cd$_{5.8}$Mn$_{1.2}$P$_4$Cl$_6$ (d) (note: in (a), * and • represent Cd$_4$P$_2$Cl$_3$, and Cd$_7$P$_4$Cl$_6$ phases respectively).
Mn-salt present on the surface. The substitution of manganese is more favoured in Cd-P$_2$Cl$_6$ compare to Cd$_2$P$_2$Cl$_6$. Substitution of $\geq$12% manganese in Cd$_7$Mn$_{1.5}$P$_4$Cl$_6$ in place of cadmium causes it to crystallize in pure form free from other compositions. We have obtained Cd$_7$Mn$_{1.5}$P$_4$Cl$_6$ with y = 0.9–1.5, giving rise to the compositions, Cd$_6$Mn$_{0.5}$P$_4$Cl$_6$, Cd$_5$Mn$_{1.25}$P$_4$Cl$_6$, and Cd$_5.5$Mn$_{1.5}$P$_4$Cl$_6$ (Fig. 2a). The EDAX spectrum of Cd$_5.8$Mn$_{1.2}$P$_4$Cl$_6$ showed signals corresponding to Cd, Mn, P, and Cl throughout the sample, indicating uniform substitution of manganese (Fig. S1a†). An XPS scan of Cd$_5.8$Mn$_{1.2}$P$_4$Cl$_6$ revealed signals corresponding to Cd, Mn, P, and Cl (Fig. S1b†). High-resolution XPS-core level spectra of Cd and Mn (Fig. S1c and d†) show energy differences of 6.8 and 11.2 eV between 3d$_{3/2}$ and 3d$_{1/2}$ (in the case of Cd) and 2p$_{3/2}$ and 2p$_{1/2}$ (in the case of Mn) respectively, characteristic of Cd$^{2+}$ and Mn$^{2+}$ states. Phosphorus atoms in Cd$_2$P$_2$Cl$_6$ form P-P dumbbells, wherein each P atom in dumbbell is bonded to 3 Cd atoms (P$_2$Cd$_6$ unit). The P–P bounded P atom possess a charge of (P$_2$)$^{2-}$ and electronic features. Resulting compounds Cd$_6$Mn$_{0.25}$P$_4$Cl$_6$ and Cd$_1$Mn$_{0.125}$P$_2$Cl$_3$ amount to 3.6% and 3.1% Mn substitution in Cd$_2$P$_2$Cl$_6$ and Cd$_2$P$_2$Cl$_3$ respectively. An important difference between Cd$_2$P$_2$Cl$_6$ and Cd$_2$P$_2$Cl$_3$ is octahedral coordination of two kinds of Cd1 and Cd2 atoms.\(^{1,10}\) In Cd$_2$P$_2$Cl$_3$, (a) Cd1 is distorted octahedrally coordinated by 2 P and 2 Cl atoms, Cd–P bond length is 2.48 Å and a Cd–Cl bond length is 2.76 Å while the other three Cl atoms giving Cd–Cl bond lengths of 3.03 Å, 3.08 Å and 3.28 Å, and (b) Cd2 is octahedrally coordinated with 6 Cl atoms with bond lengths of 2.69 Å. In Cd$_2$P$_2$Cl$_6$, (a) Cd1 is coordinated by 1 P and 3 Cl atoms with Cd–P and Cd–Cl bond lengths of 2.50 Å and 2.64 Å respectively, and (b) Cd2 is coordinated by 2 P and 2 Cl atoms with Cd–P (Cd–P2) and Cd–Cl (Cd–Cl2) bond lengths of 2.49 Å (2.51 Å) and 2.85 Å (2.74 Å) respectively.\(^1\) We relaxed their structures internally upon Mn substitution until forces on each atom are less than 0.02 eV Å$^{-1}$. In Cd$_{6.75}$Mn$_{0.25}$P$_4$Cl$_6$, (a) with Mn$^{2+}$ substituted at the Cd1 site (Mn$_{Cd1}$) (Fig. 3a), Mn–P, Mn–Cl1, Mn–Cl2, Mn–Cl3 and Mn–Cl4 bond lengths are 2.47 Å, 2.42 Å, 2.50 Å, 3.50 Å and 3.69 Å (Fig. 3a and b) and (b) with Mn$^{2+}$ substituted at Cd2 site (Mn$_{Cd2}$), Mn–Cl bond length is 2.58 Å (Fig. 3c and d). In computational results

In order to understand the consequences of the substitution of manganese on the structural and electronic properties of cadmium phosphochlorides, we have carried out first-principles calculations. We have considered configurations with substitution of an Mn atom at two inequivalent Cd-sites in Cd$_2$P$_2$Cl$_6$ and Cd$_2$P$_2$Cl$_3$ to determine its effect on the structure and electronic features. Resulting compounds Cd$_6$Mn$_{0.25}$P$_4$Cl$_6$ and Cd$_1$Mn$_{0.125}$P$_2$Cl$_3$ amount to 3.6% and 3.1% Mn substitution in Cd$_2$P$_2$Cl$_6$ and Cd$_2$P$_2$Cl$_3$ respectively. An important difference between Cd$_2$P$_2$Cl$_6$ and Cd$_2$P$_2$Cl$_3$ is octahedral versus tetrahedral coordination of two kinds of Cd1 and Cd2 atoms.\(^{1,10}\) In Cd$_2$P$_2$Cl$_6$, (a) Cd1 is distorted octahedrally coordinated by 2 P and 4 Cl atoms, Cd–P bond length is 2.48 Å and a Cd–Cl bond length is 2.76 Å while the other three Cl atoms giving Cd–Cl bond lengths of 3.03 Å, 3.08 Å and 3.28 Å, and (b) Cd2 is octahedrally coordinated with 6 Cl atoms with bond lengths of 2.69 Å. In Cd$_2$P$_2$Cl$_3$, (a) Cd1 is coordinated by 1 P and 3 Cl atoms with Cd–P and Cd–Cl bond lengths of 2.50 Å and 2.64 Å respectively, and (b) Cd2 is coordinated by 2 P and 2 Cl atoms with Cd–P (Cd–P2) and Cd–Cl (Cd–Cl2) bond lengths of 2.49 Å (2.51 Å) and 2.85 Å (2.74 Å) respectively.\(^1\) We relaxed their structures internally upon Mn substitution until forces on each atom are less than 0.02 eV Å$^{-1}$. In Cd$_{6.75}$Mn$_{0.25}$P$_4$Cl$_6$, (a) with Mn$^{2+}$ substituted at the Cd1 site (Mn$_{Cd1}$) (Fig. 3a), Mn–P, Mn–Cl1, Mn–Cl2, Mn–Cl3 and Mn–Cl4 bond lengths are 2.47 Å, 2.42 Å, 2.50 Å, 3.50 Å and 3.69 Å (Fig. 3a and b) and (b) with Mn$^{2+}$ substituted at Cd2 site (Mn$_{Cd2}$), Mn–Cl bond length is 2.58 Å (Fig. 3c and d) in the absorbance mode employing Kubelka–Munk equation (Fig. S3a†). A small blue-shift (0.03 to 0.07 eV) occurs in the absorption spectra of Mn-substituted compounds compared to the pristine Cd$_2$P$_2$Cl$_6$ (band gap $\sim$ 2.62 eV; $\lambda_{edge}$ $\sim$ 472.30 nm). Tauc plots show linear behaviour between $(a$hv)$^{1/2}$ vs. $hv$ for $n = 1/2$, indicating direct band gap in the compounds (Fig. S3b†).
Cd\textsubscript{3.875}Mn\textsubscript{0.125}P\textsubscript{2}Cl\textsubscript{3}, (a) Mn–Cd and Mn–Cl bond lengths are 2.42 \textsubscript{A} and 2.44 \textsubscript{A} (Fig. 4a and b) and (b) Mn–Cd\textsubscript{2}, Mn–P\textsubscript{1} (Mn–P\textsubscript{2}) and Mn–Cl\textsubscript{1} (Mn–Cl\textsubscript{2}) bond lengths are 2.43 \textsubscript{A} (2.45 \textsubscript{A}) and 2.44 \textsubscript{A} (2.47 \textsubscript{A}) (Fig. 4c and d). Clearly, there is a significant reduction in metal–X bond length with Mn\textsuperscript{2+} substitution, as expected from their ionic radii.

Fig. 3 Crystal structure of Mn substituted Cd\textsubscript{7}P\textsubscript{4}Cl\textsubscript{6} at Cd1 site (a), Mn is octahedrally (distorted) coordinated with 2 P and 4 Cl atoms (b), and at Cd2 site (c) where Mn is octahedrally coordinated with Cl atoms (d).

Fig. 4 Crystal structure of Cd\textsubscript{4}P\textsubscript{2}Cl\textsubscript{3} with Mn substituted at Cd1 site (a), where Mn is tetrahedrally bonded with 1 P and 3 Cl atoms (b), and at Cd2 site (c), where Mn is tetrahedrally coordinated with 2 P and 2Cl atoms (d).
We estimate the formation energy \( E_f \) of Mn\(^{2+} \) substitution in Cd\(_7\)P\(_4\)Cl\(_6\) and Cd\(_4\)P\(_2\)Cl\(_3\) to find out the favourable site for Mn substitution,

\[
E_f = E_{\text{Mn-Cd1/Cd2}} - E_B = E_{\text{Mn}} + E_{\text{Cd}}
\]

where \( E_{\text{Mn-Cd1/Cd2}} \) and \( E_B \) are the energies of Mn-substituted and pure Cd\(_7\)P\(_4\)Cl\(_6\) or Cd\(_4\)P\(_2\)Cl\(_3\) phases. \( E_{\text{Mn}} \) and \( E_{\text{Cd}} \) are the energies of isolated Mn and Cd atoms. The difference in total energies for nonmagnetic and magnetic calculations show that the magnetic configuration is more stable than the non-magnetic one, highlighting the importance of considering spin polarization in the ground state of the system (Table 1). We find that Mn\(^{2+} \) substitution is more favourable in Cd\(_7\)P\(_4\)Cl\(_6\) than in Cd\(_4\)P\(_2\)Cl\(_3\) (Table 1). In Cd\(_7\)P\(_4\)Cl\(_6\), Mn\(^{2+} \) substitution at Cd2-site is energetically more favourable than that at Cd1-site and in Cd\(_4\)P\(_2\)Cl\(_3\), Mn\(^{2+} \) substitution is more favoured at Cd1-site than that at Cd2-site. Interesting to note that in both the compounds, Mn\(^{2+} \) prefers to occupy the site, which has a greater number of tightly bounded Cl-ligands. To explore the possibility of occurrence of Mn atom at the interstitial site, we introduced Mn atoms at the interstitial sites in Cd\(_7\)P\(_4\)Cl\(_6\) and Cd\(_4\)P\(_2\)Cl\(_3\), with coordinates \((0.5, 0.5, 0.5)\) and \((0.48, 0.88, 0.93)\) in Cd\(_7\)P\(_4\)Cl\(_6\) and Cd\(_4\)P\(_2\)Cl\(_3\) respectively (Table 1). From their energetics, we find that Mn\(^{2+} \) substitution occurs preferentially at Cd-sites, not in the interstitial sites of these compounds (Table 1). Such preferential substitution of Cd\(^{2+} \) by Mn\(^{2+} \) maintains the neutrality in Mn-substituted compounds.

We now examine the electronic structures of Mn\(^{2+} \) substituted Cd\(_7\)P\(_4\)Cl\(_6\) and Cd\(_4\)P\(_2\)Cl\(_3\) compounds and compare them with those of the pristine forms to understand the effects of substitution. Cd\(_{6.75}\)Mn\(_{0.25}\)P\(_4\)Cl\(_6\) (MnCd1) is a direct (at G-point) band gap semiconductor with a gap of 1.4 eV (Fig. 5b). The band gap of Cd\(_7\)P\(_4\)Cl\(_6\) (MnCd1) reduces by 0.4 eV upon Mn\(^{2+} \) substitution at Cd1 site. The states at valence band maximum (VBM) and conduction band minimum (CBM) are spin split, with VBM constituted of spin-up states whereas CBM is constituted of spin-down states. The VBM is mainly contributed by spin-up states of P 3p orbitals whereas CBM is constituted of spin-down states of Mn-3d orbitals (Fig. 6a). Noting that Cd\(_{6.75}\)Mn\(_{0.25}\)P\(_4\)Cl\(_6\) (MnCd1) is the lowest energy configuration, we find that Mn\(^{2+} \) substitution occurs preferentially at Cd-sites, not in the interstitial sites of these compounds (Table 1). Such preferential substitution of Cd\(^{2+} \) by Mn\(^{2+} \) maintains the neutrality in Mn-substituted compounds.

Table 1 Comparison of formation energies of Mn substitution Cd\(_7\)P\(_4\)Cl\(_6\) and Cd\(_4\)P\(_2\)Cl\(_3\) to Cd\(_7\)P\(_4\)Cl\(_6\) and Cd\(_4\)P\(_2\)Cl\(_3\) with Mn substitution at Cd1 and Cd2 sites. Note that in MnCd\(_7\)P\(_4\)Cl\(_6\) and MnCd\(_4\)P\(_2\)Cl\(_3\), Mn is at the interstitial site.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_f ) (eV)</th>
<th>( \Delta E(E_{\text{mag}} - E_{\text{non-mag}}) ) (eV)</th>
<th>Magnetic moment (( \mu_B ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(<em>{6.75})Mn(</em>{0.25})P(_4)Cl(_6) (MnCd1)</td>
<td>-6.59</td>
<td>-2.20</td>
<td>4.43</td>
</tr>
<tr>
<td>Cd(<em>{6.75})Mn(</em>{0.25})P(_4)Cl(_6) (MnCd2)</td>
<td>-7.10</td>
<td>-2.20</td>
<td>4.61</td>
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<tr>
<td>Cd(<em>{1.875})Mn(</em>{0.125})P(_4)Cl(_6) (MnCd1)</td>
<td>-6.77</td>
<td>-2.67</td>
<td>4.47</td>
</tr>
<tr>
<td>Cd(<em>{1.875})Mn(</em>{0.125})P(_4)Cl(_6) (MnCd2)</td>
<td>-6.67</td>
<td>-2.24</td>
<td>4.40</td>
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<tr>
<td>MnCd(_7)P(_4)Cl(_6)</td>
<td>-3.12</td>
<td>-2.28</td>
<td>4.50</td>
</tr>
<tr>
<td>MnCd(_4)P(_2)Cl(_3)</td>
<td>-5.04</td>
<td>-1.58</td>
<td>3.58</td>
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</table>

Fig. 5 Electronic structure of pristine Cd\(_7\)P\(_4\)Cl\(_6\) (a), Mn\(^{2+} \) substituted Cd\(_7\)P\(_4\)Cl\(_6\) at Cd1 site (b), Mn\(^{2+} \) substituted Cd\(_7\)P\(_4\)Cl\(_6\) Cd2 site (c), pristine Cd\(_4\)P\(_2\)Cl\(_3\) (d), Mn\(^{2+} \) substituted Cd\(_4\)P\(_2\)Cl\(_3\) at Cd1 site (e) and Mn\(^{2+} \) substituted Cd\(_4\)P\(_2\)Cl\(_3\) at Cd2 site (f).
find from its electronic structure that it is a direct (at Γ-point) gap semiconductor with a band gap of 1.8 eV, without any notable change in the gap with respect to pristine Cd7P4Cl6 (Fig. 5c). In contrast to Cd6.75Mn0.25P4Cl6(MnCd1), we do not find spin split states at VBM and CBM. The VBM is mainly contributed by spin-up and spin-down states of P 3p and Cl 3p orbitals whereas CBM is constituted of spin-down states of Mn 3d orbitals (Fig. 6b). Cd3.875Mn0.125P2Cl3(MnCd1) and Cd3.875–
Mn0.125P2Cl3(MnCd2) are direct (at Γ-point) gap semiconductor with a band gap of 1.3 and 1.0 eV respectively (Fig. 5e and f). Mn2+ substitution in Cd3P2Cl3 at Cd2 site affects its band gap notably. From the projected density of states, VBM of Cd3.875–
Mn0.125P2Cl3(MnCd1) is mainly contributed by spin-up states of P 3p and Mn 3d orbitals, and CBM is constituted of spin-down states of Mn 3d and 5s Cd orbitals (Fig. 6d). We find spin split states at VBM and CBM of those configurations which have Mn2+ coordinated with a greater number of P atoms, e.g., Mn2+ is octahedrally coordinated with 4 Cl and 2 P in Cd6.75–
Mn0.25P2Cl3(MnCd1) whereas, in Cd6.75Mn0.25P3Cl4(MnCd2), Mn is octahedrally coordinated with 6 Cl atoms (no P atoms). Similarly, Mn2+ is tetrahedrally coordinated with 3 Cl, and 1 P in Cd3.875Mn0.125P2Cl3(MnCd1) and Mn2+ is tetrahedrally coordinated with 2 P and 2 Cl in Cd3.875Mn1.25P2Cl3(MnCd2). Splitting of spin-up and spin-down bands arises due to broken inversion and crystal field symmetry in the system. Cd6.75–
Mn0.25P2Cl3(MnCd1) exhibits spin-split states at VBM and CBM as Mn2+ is bonded to 4 Cl and 2 P atoms, forming a distorted octahedra with broken inversion symmetry (Fig. 3a). In contrast, we do not find spin split states in Cd6.75Mn0.25P4Cl6(MnCd1) since Mn2+ is bonded to 6 Cl atoms forming symmetric octahedra maintaining inversion symmetry (Fig. 3d). Similarly, Mn2+ is at the center of proper and distorted tetrahedra in Cd3.875Mn0.125P2Cl3(MnCd1) and Cd3.875Mn0.125P2Cl3(MnCd2) respectively (Fig. 4b and d). Both these compounds exhibit spin-

![Fig. 6](https://example.com/fig6.png)

**Fig. 6** Projected density of states of Cd6.75Mn0.25P4Cl6(MnCd1) (a), Cd6.75Mn0.25P4Cl6(MnCd2) (b), Cd3.875Mn0.125P2Cl3(MnCd1) (c) and Cd3.875–

Mn0.125P2Cl3(MnCd2) (d). Magenta color shaded area shows Mn 3d orbitals.

<table>
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<th>Compound</th>
<th>Vacancy configuration</th>
<th>$E_f$ (eV/vacancy)</th>
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<td>Cd7P4Cl6</td>
<td>I (2 P)</td>
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</tr>
<tr>
<td>Cd7P4Cl6</td>
<td>II (2 Cl)</td>
<td>4.65</td>
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<td>Cd6.75Mn0.25P4Cl6(MnCd2)</td>
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<td>7.73</td>
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<tr>
<td>Cd6.75Mn0.25P3Cl4(MnCd2)</td>
<td>II (2 Cl)</td>
<td>4.84</td>
</tr>
<tr>
<td>Cd3.875Mn0.125P2Cl3(MnCd2)</td>
<td>III (Cl–Cl)</td>
<td>4.48</td>
</tr>
<tr>
<td>Cd3.875Mn0.125P2Cl3(MnCd2)</td>
<td>IV (Cl–P1)</td>
<td>7.16</td>
</tr>
<tr>
<td>Cd3.875Mn0.125P2Cl3(MnCd2)</td>
<td>V (Cl–P2)</td>
<td>7.00</td>
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Table 2 Comparison of defect formation energies of pristine Cd7P4Cl6 and Mn-substituted Cd7P4Cl6 with different vacancy configuration

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split states at VBM and CBM; the magnitude of splitting is weak in Cd$_{3.875}$Mn$_{0.125}$P$_2$Cl$_3$(MnCd1) as the P atom is along the principal axis and 3-fold symmetry is maintained by 3 Cl atoms bonded to Mn. In Cd$_{3.875}$Mn$_{0.125}$P$_2$Cl$_3$(MnCd2), Mn$^{2+}$ is bonded to 2 P and 2 Cl atoms, leading to broken 3-fold symmetry and stronger spin splitting of energy bands. Hence, Cd$_{3.875}$Mn$_{0.125}$P$_2$Cl$_3$(MnCd2) and Cd$_{6.75}$Mn$_{0.25}$P$_4$Cl$_6$(MnCd1) show spin-split states at VBM and CBM. From the spin-resolved projected electronic density of states (DOS) (Fig. 6) of Mn$^{2+}$ substituted Cd$_7$P$_4$Cl$_6$ and Cd$_4$P$_2$Cl$_3$ compounds, it is evident that there is a strong coupling between the Mn 3d orbitals and P 3p and Cl 3p orbitals of the host semiconductor.

Our estimates of magnetic moments of Mn-doped Cd$_7$P$_4$Cl$_6$ and Cd$_4$P$_2$Cl$_3$ are tabulated in Table 1. We find that 3d orbitals of Mn are occupied as (d$_{xy}$)$^1$(d$_{yz}$)$^1$(d$_{zx}$)$^1$(d$_{x^2-y^2}$)$^1$, resulting in an electronic configuration with $S = 5.0$ $\mu_B$. However, hybridizing interaction of 3d states of Mn with 3p states of Cl and P atoms results in partial cancellation of the magnetic moment $\mu = 5 - \delta$, resulting in effective local magnetic moments 4.61 $\mu_B$ in Cd$_{6.75}$Mn$_{0.25}$P$_4$Cl$_6$(MnCd2). Cd$_{6.75}$Mn$_{0.25}$P$_4$Cl$_6$(MnCd3) has a higher magnetic moment than that of Mn-substituted Cd$_7$P$_4$Cl$_6$ and Cd$_4$P$_2$Cl$_3$ compounds.

Halogen vacancies are inherently present in cadmium phosphochlorides compounds. The exact composition of Cd$_{2-x}$Mn$_x$P$_4$Cl$_6$ compounds by EDAX and XPS measurements reveal some amount of Cl and P vacancies in these compounds. We simulated Cl and P vacancies in energetically most favourable Mn$^{2+}$ substituted (at Cd2 site) Cd$_7$P$_4$Cl$_6$, considering 5 inequivalent configurations of vacancy pairs. In the configuration I, we removed a pair of P atoms from the crystal, each of which is bonded with three Cd1 atoms. Two Cl atoms are removed from octahedral coordination of Mn atom in configuration II, whereas one atom is removed from 6 Cl atoms bonded with Mn, and another Cl is extracted from octahedrally

![diagram](image_url)

**Fig. 7** Electronic structure and spin-resolved polarized projected density of states of Cd$_{6.75}$Mn$_{0.25}$P$_4$Cl$_6$(MnCd2) with Cl vacancy (a and b) and Cd$_{6.75}$Mn$_{0.25}$P$_4$Cl$_6$(MnCd3) with Cl–P2 vacancies (c and d). Note that defect peaks are marked by the red arrow in the projected density of states.
coordinated Cd2 atom in configuration III. Configurations IV and V have mixed pairs of Cl and P vacancies, in both cases, Cl atom is taken from octahedrally coordinated Mn atom, and P is removed from P1–P2 pair, such that the distance of Cl vacancy from P1 and P2 atoms is 5.33 Å and 3.85 Å respectively. We simulate pure Cl and P vacancy pairs in pristine Cd2P3Cl6, in the configuration I, we remove a P pair from crystal and remove 2 Cl atoms from octahedrally coordinated Cd2 atom in configuration II. From the formation energies of vacancies (Table 2), we conclude that it is relatively easy to introduce a Cl vacancy than a P vacancy in pristine as well as Mn substituted Cd2P3Cl6 compound. Secondly, it is easier to introduce P vacancy in Mn-substituted Cd2P3Cl6 compound than in the pristine one. Cl vacancies are easier to be introduced in Mn substituted Cd2P3Cl6 compound than in the pristine one when Cl atom is removed each from octahedrally coordinated Mn and Cd2 atoms rather than introducing both the vacancies at octahedrally coordinated Mn or Cd2 atom. We present the electronic structure of the configurations III and V as configuration III has the lowest defect formation energy, and configuration V has lower $E_f$ than of I and IV configurations and understands the combined effect of Cl and P vacancies. In the electronic structure, we find that Cl and P vacancy pairs make Cd$_{6.75}$Mn$_{0.25}$P$_4$Cl$_6$ an indirect (Γ–R) band gap semiconductor with gaps of 1.68 eV and 1.14 eV for III and V configurations (Fig. 7a and c). Associated with Cl vacancy, we identify a new defect band on the bottom of the CBM (Fig. 7a), which is also seen in the density of states (Fig. 7b). The peak has contributions mainly from minority spin states of Cl-3p and Cd-5s orbitals. The introduction of P and Cl vacancies leads to defect bands just above the VBM and below the CBM (Fig. 7c), as evident in the density of states (Fig. 7d). Spin-up and spin-down states at VBM and CBM here are mainly contributed by P 3p, Cd 5s, and Cd 5p orbitals.

**Photochemical studies**

In view of the correct band edge alignments in cadmium phosphochlorides with respect to the water redox potential and their notably superior photochemical HER performance with respect to the state-of-art photocatalyst materials such as CdS and TiO$_2$, we have examined the effect of Mn$^{2+}$ substitution on the photochemical hydrogen evolution reaction properties of these compounds.\(^1\) Fig. 8a, shows visible-light-induced H$_2$ evolution activity of (a) bare form of Cd$_7$Mn$_{y}$P$_4$Cl$_6$ compounds (b) comparative H$_2$ evolution activity of Cd$_{6.8}$Mn$_{1.2}$P$_4$Cl$_6$, pristine Cd$_2$P$_3$Cl$_6$ and Cd$_2$P$_3$Cl$_6$ in the presence of 1 wt% of Pt co-catalyst. Cyclic HER activity of (c) Cd$_2$P$_3$Cl$_6$ and (d) Cd$_{6.8}$Mn$_{1.2}$P$_4$Cl$_6$ in the presence of Pt co-catalyst. All the photochemical HER studied were done under visible-light irradiation in the presence of 0.18 and 0.24 M Na$_2$S–Na$_2$SO$_3$ sacrificial electron donor.

![Fig. 8](https://example.com/fig8.png)

Fig. 8 Time course of H$_2$ evolution activity of (a) bare form of Cd$_7$Mn$_{y}$P$_4$Cl$_6$ compounds (b) comparative H$_2$ evolution activity of Cd$_{6.8}$Mn$_{1.2}$P$_4$Cl$_6$, pristine Cd$_2$P$_3$Cl$_6$ and Cd$_2$P$_3$Cl$_6$ in the presence of 1 wt% of Pt co-catalyst. Cyclic HER activity of (c) Cd$_2$P$_3$Cl$_6$ and (d) Cd$_{6.8}$Mn$_{1.2}$P$_4$Cl$_6$ in the presence of Pt co-catalyst. All the photochemical HER studied were done under visible-light irradiation in the presence of 0.18 and 0.24 M Na$_2$S–Na$_2$SO$_3$ sacrificial electron donor.

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generation from Mn\textsuperscript{2+} substituted Cd\textsubscript{7-y}Mn\textsubscript{y}P\textsubscript{4}Cl\textsubscript{6} compounds (y = 0.9 to 1.5), without any co-catalyst. All the compositions exhibit robust HER activity, an increase in the Mn\textsuperscript{2+} content enhancing the HER activity. On account of the remarkable HER performance of these photocatalysts, we have examined their activity in the presence of Pt nanocrystals (1 wt%) as a co-catalyst. In the presence of Pt nanocrystals, Cd\textsubscript{5.8}Mn\textsubscript{1.2}P\textsubscript{4}Cl\textsubscript{6} exhibits HER activity of 9.9 mmol h\textsuperscript{-1} g\textsuperscript{-1}, whereas Cd\textsubscript{4}P\textsubscript{2}Cl\textsubscript{3} obtained at the same temperature in the absence of Mn\textsuperscript{2+} ions, exhibits the HER activity of only 1.70 mmol h\textsuperscript{-1} g\textsuperscript{-1}. Cd\textsubscript{7}P\textsubscript{4}Cl\textsubscript{6} with identical structural and absorption features as their Mn-substituted analogues (Cd\textsubscript{7-y}Mn\textsubscript{y}P\textsubscript{4}Cl\textsubscript{6}) exhibits a HER activity of 4.07 mmol h\textsuperscript{-1} g\textsuperscript{-1} (Fig. 8b). Table S1\textsuperscript{†} presents the comparison of HER activity of these compounds with the state-of-art semiconductor photocatalyst materials. The apparent quantum yield (AQY) of Cd\textsubscript{5.8}Mn\textsubscript{1.2}P\textsubscript{4}Cl\textsubscript{6} is 47.6%, significantly superior to that of the pristine analogues (Cd\textsubscript{4}P\textsubscript{2}Cl\textsubscript{3} = 8.1% and Cd\textsubscript{7}P\textsubscript{4}Cl\textsubscript{6} = 19.5% for the AQY calculation and photon flux, please see the ESI Fig. S7\textsuperscript{†}). Thus, substitution of Mn\textsuperscript{2+} in place of Cd\textsuperscript{2+} in cadmium phosphochlorides significantly enhances their photocatalytic activity.

In order to understand the enhancement in the photocatalytic HER activity, we have studied photogenerated charge carrier dynamics of these compounds using photoelectrochemical measurements. The open-circuit potential of the photoelectrodes demonstrates the process of charge carrier generation and recombination in materials.\textsuperscript{12,13} Pristine Cd\textsubscript{7}P\textsubscript{4}Cl\textsubscript{6} exhibits a cathodic shift in the potential upon light
irradiation, indicating n-type conductivity, similar to the earlier report (Fig. 9a).\textsuperscript{14} In contrast to the cathodic shift of the pristine compound, the manganese substituted analogue (Cd\textsubscript{5.8}Mn\textsubscript{1.2}P\textsubscript{4}Cl\textsubscript{6}) exhibits anodic shift, indicating p-type conductivity (Fig. 9b). In order to verify the nature of conduction in these compounds, Hall measurements were carried out at room temperature on the rectangular pallet of samples. Unlike the negative Hall coefficient of pristine Cd\textsubscript{7}P\textsubscript{4}Cl\textsubscript{6} (n-type conductivity) (Fig. 9c), Cd\textsubscript{5.8}Mn\textsubscript{1.2}P\textsubscript{4}Cl\textsubscript{6} exhibited positive Hall coefficient due to p-type conductivity (Fig. 9d). The variation of Hall voltage with the applied positive and negative magnetic field is given in ESI (Fig. S6\textsuperscript{†}).

The origin of the change in conductivity upon Mn-substitution can be understood by the electronic structure of compounds (Fig. 6). The electronic states at the CBM are dominated by 3d states of Mn. Their narrow bandwidth indicates their localized nature and hence, a large effective mass and lower mobility of the electron carriers. In contrast, the states in the VBM are dominated by p-orbital of Cl and P strongly hybridized with 3d orbitals of Mn, producing notable dispersion of bands giving a low effective mass and high mobility of hole carriers. Hence, holes contribute more significantly to conduction than electrons upon Mn-substitution in these compounds causing a change in n to p-type behaviour. We note that the overall p-type conduction in Mn-substituted compounds is weaker than the n-type conduction of the pristine ones.

Since the photocatalytic activity of semiconductor materials is prone to the nature of charge carriers, we have examined the effect of the change in the type of majority carriers on the photocatalytic properties.\textsuperscript{14} It is known that when an extrinsic semiconductor comes in contact with an electrolyte bending of bands occurs at the surface to equilibrate the Fermi level.\textsuperscript{15} An n-type semiconductor with the Fermi level near CBM undergoes upward band bending in contact with the electrolyte, resulting in electron migration towards the bulk of the semiconductor and hole migration towards the interface.\textsuperscript{14} This causes a decrease in the hot electron concentration at the interface and negatively impacts the HER (Fig. 10). In contrast, a p-type semiconductor with the Fermi level close to the VBM undergoes a downward band bending in the contact of the electrolyte. Such bending of the band helps in the separation of electron and holes at the surface wherein the holes are thrown to the bulk of semiconductor and electron are pushed to the space charge region, resulting in the enrichment of photogenerated electron population in the space charge region (semiconductor–H\textsubscript{2}O interface) (Fig. 10).\textsuperscript{14} A greater population of hot electrons at the interface (space charge region) positively impacts the reduction of H\textsubscript{2}O into H\textsubscript{2}. These observations lead support to our finding that p-type Cd\textsubscript{5.8}Mn\textsubscript{1.2}P\textsubscript{4}Cl\textsubscript{6} exhibits superior photochemical HER performance than their pristine n-type analogues.

**Conclusions**

In summary, we find that the substitution of manganese in Cd\textsubscript{7-x}Mn\textsubscript{x}P\textsubscript{4}Cl\textsubscript{6} is more favoured than Cd\textsubscript{4-x}Mn\textsubscript{x}P\textsubscript{4}Cl\textsubscript{6}, causing the former to appear at higher temperatures than the pristine material. Mn-substitution in the pristine n-type Cd\textsubscript{7}P\textsubscript{4}Cl\textsubscript{6} transforms it into a p-type material, as exemplified by Cd\textsubscript{5.8}Mn\textsubscript{1.2}P\textsubscript{4}Cl\textsubscript{6}. Such a change in the type of conductivity remarkably influences the HER properties. Theoretical calculations indicate a significant reduction in the formation energy of Mn-substituted Cd\textsubscript{7}P\textsubscript{4}Cl\textsubscript{6}. In both the compounds, the substituitional site is more favored than the interstitial site. The electronic structure of Cd\textsubscript{7-x}Mn\textsubscript{x}P\textsubscript{4}Cl\textsubscript{6} (Mn\textsubscript{cad}) does not undergo a notable change. In contrast, Cd\textsubscript{7-x}Mn\textsubscript{x}P\textsubscript{4}Cl\textsubscript{6} (Mn\textsubscript{cad} and Mn\textsubscript{cad}) exhibit spin-split states at the VBM and CBM of the configuration in which Mn\textsuperscript{2+} is coordinated with a larger number of P atoms. Halogen vacancies are more readily introduced in Mn\textsuperscript{2+} substituted Cd\textsubscript{7}P\textsubscript{4}Cl\textsubscript{6} when Cl vacancies are introduced at octahedrally coordinated...
Mn and Cd2 atoms rather than at sites localized at Mn atoms. Cl and P vacancy pairs give rise to an indirect band gap in Mn-substituted Cd3P2Cl4.

**Experimental**

**Synthesis**

In a typical synthesis, Cd3P2 (1.10 mmol), CdCl2 (1.99 mmol), red-P (0.89 mmol), and different amounts of MnCl2 were weighed inside a glove-box and ground homogenously. This homogenous precursor was transferred in a quartz tube (I. D. = 10 mm, O. D. = 12 mm) and sealed under vacuum. The sealed quartz tube was annealed at 500 °C for 24 h, followed by the cooling of the tube to room temperature with a rate of 2.5° min⁻¹. The reaction yielded a polycrystalline powder sample of two different colors (depending on the concentration of MnCl2 taken) in the form of the lump, which was carefully separated and ground in the form of fine powder. Pristine Cd3P2Cl4 was synthesized under similar condition in the absence of MnCl2 precursor. Pristine Cd3P2Cl4 was synthesized using a homogenous mixture obtained by the grinding of stoichiometric ratio of Cd-powder, red-P, and CdCl3 and annealing under sealed tube at 450 °C for 72 h.

**Characterization**

Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Diffraction system using a Cu Kα source (λ = 0.1541 nm). UV-vis absorption spectra were collected with PerkinElmer Model Lambda 900 spectrometer. Energy dispersive spectroscopy (EDS) and elemental mapping analysis were carried out with an EDAX genesis instrument attached to the SEM instrument. X-ray photoelectron spectra (XPS) were recorded with an Omicron nanotechnology spectrometer using Al-Kα (1486.6 eV) X-ray source. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was carried out using a PerkinElmer Optima 7000 DV machine. Electron paramagnetic resonance spectra were obtained at room temperature at an operating frequency of 9.5 GHz using Bruker D8 Advance-EPR-spectrometer.

**Photocatalytic H2O splitting**

The photocatalytic reactions were carried out at ambient conditions using home-made cylindrical quartz cells with headspace for gas collection, closed by high-quality septa. In a typical procedure, semiconductor photocatalyst samples were dispersed in a 0.1 M NaOH aqueous solution (50 mL), and a calculated amount of H2PtCl6 solution was added (equivalent to 1 wt% of Pt). The reaction solution was purged with Ar-gas for 15–20 minutes, and UV-light was switched on for 1 h tophoto-deposit the Pt nanoparticles on the semiconductor. After the photo-deposition reaction, the cell was removed from the light irradiation, and septa were taken out to add a sacrificial electron donor Na2S and Na2SO3 dissolved in 25 mL distilled water in order to make a total volume of 75 mL with Na2S and Na2SO3 concentrations of 0.18 M and 0.24 M respectively. The solution was further purged with Ar-gas for 15–20 minutes and irradiated with visible light (λ > 395 nm) using a Xe-lamp (400 W) (New-Port).

**Photoelectrochemical measurements**

Photoelectrochemical measurements were carried out on a CHI 1760E electrochemical work station (CH instrument Inc.) in a conventional three-electrode set-up. Spin-coated samples on FTO served as the working electrode, with a platinum wire as the counter electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode. The working electrode was prepared by spin coating. First, the catalyst slurry was prepared by ultrasonication 20–25 mg of photocatalyst in 50 μL Nafion (5.0 wt%, Sigma Aldrich) and 250 μL of ethanol mixture. Fluorine-doped tin oxide (FTO) (2 × 1 cm² pieces) which was used as the substrate was cleaned and dried at 100 °C. An area of 1 cm² of the substrate was masked by scotch tape, and spin coating (750 rpm, 60 seconds) was performed on the exposed area using 15 μL of slurry each time. The electrode films were then dried under vacuum at 100 °C for 1 hour, and a Cu wire connection was made with the help of Ag-paste. The portion of the electrode, except the photocatalyst part, was electronically sealed by transparent epoxy coating and left overnight. A 0.5 M Na2SO4 aqueous solution was used as the electrolyte. A 300 W Xenon lamp, with a calibrated intensity of 100 mW cm⁻² was used as the light source.

**Computational methods**

We have carried out first-principles calculations within density functional theory (DFT) employing VASP¹⁷,¹⁸ software package, treating the spin-dependent exchange–correlation energy with a generalized gradient approximation given by a functional parameterized by the Perdew–Burke–Ernzerhof (PBE).¹⁹ We used projected augmented wave wave—a method to describe the interaction between the valence electrons and ionic cores. Valence electron configurations used in the PAW potentials of Cd, Mn, Cl and P, are 4d¹⁰ 5s², 3d⁵ 4s², 3s² 3p⁵ and 3s² 3p³ respectively. We used a kinetic energy cut-off of 400 eV to truncate the plane wave basis for representing Kohn–Sham wave functions and a uniform mesh of 4 × 4 × 4 k-points to sample integrations over Brillouin zone (BZ). We iteratively relaxed the structures to minimize energy until Hellmann–Feynman force acting on each atom is less than 0.02 eV Å⁻¹.

Self-consistency in the Kohn–Sham solution was achieved with a convergence tolerance of 10⁻⁴ eV. In calculations of the density of states, we used electronic spectra obtained on the PAW potentials of Cd, Mn, Cl and P, are 4d¹⁰ 5s², 3d⁵ 4s², 3s² 3p⁵ and 3s² 3p³ respectively. We used a kinetic energy cut-off of 400 eV to truncate the plane wave basis for representing Kohn–Sham wave functions and a uniform mesh of 16 × 16 × 16 k-points in the BZ. We focus here on the structure and electronic properties of two compounds: Mn-substituted Cd3P2Cl4 and Cd3P2Cl4. We replaced one Cd-atom in the unit cell of cadmium phosphochlorides with an Mn atom to model Mn-substituted. Cadmium phosphochlorides, and simulated them with the spin-dependent DFT.

**Conflicts of interest**

Authors declare no conflict of interest.
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