

Article

Defect Chemistry in $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$

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Abstract: Zinc-ion batteries have attracted great interest for their low cost, safety, and high energy density. Recently, $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ has been reported to be a promising cathode material for zinc-ion batteries. The defect chemistry, diffusion of Zn-ions, and solution of dopants are examined by advanced simulation techniques. The simulation results show that the most favorable intrinsic defect is the Zn-V anti-site. A zig-zag pattern of long-range Zn^{2+} diffusion is observed and the activation energy of 1.88 eV indicates that the ionic conductivity of this material is low. The most promising isovalent dopants on the Zn site are Ca^{2+} and Fe^{2+} . Although the solution of Ga^{3+} , Sc^{3+} , In^{3+} , Y^{3+} , Gd^{3+} , and La^{3+} on the V site is exoergic, the most promising is In^{3+} . Different reaction routes for the formation of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ are considered and the most thermodynamically favorable reaction consists of binary oxides (ZnO , V_2O_3 , and P_2O_5) as reactants.

Keywords: $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$; defects; diffusion; dopants; solution energy

1. Introduction

The battery is a promising sustainable energy source for both mobile and stationary applications [1–3]. Among various rechargeable batteries, lithium-ion batteries (LIBs) have been utilized for many years in many energy storage devices such as laptops, mobile phones, and e-bikes [4–9]. Although LIBs have achieved excellent progress, factors such as limited lithium resources, safety, and cost have led to finding other monovalent ion batteries consisting of Na^+ and K^+ ions [10–13] and multivalent ion batteries based on Mg^{2+} , Ca^{2+} , and Zn^{2+} ions [14–19].

Zinc ion batteries (ZIBs) have received extensive attention owing to their high volumetric energy density, low redox potential, low cost, safety, and high abundance [20–26]. In order to improve energy efficiency, there is a necessity to find new materials that can be used to construct key components of ZIBs (i.e., anodes, cathodes, and electrolytes).

The cathode is an important part of ZIBs hosting Zn^{2+} ions. The most promising cathode material that has attracted many researchers is MnO_2 due to its crystal structure and different oxidation states of Mn [27,28]. Other cathode materials studied so far include vanadium oxides [29], Prussian blue analogs [30], spinel-structured oxides [31], and organic materials [32].

Phosphate-based materials have attracted great attention for constructing cathodes due to their structural rigidity provided via strong $[\text{PO}_4]^{3-}$ units and high operating voltages [33]. NASICON-type phosphate materials (e.g., $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$) [34,35], fluorophosphates (e.g., $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$) [36], olivine-structure-based phosphates (e.g., LiFePO_4) [37], and layered phosphates (e.g., VOPO_4) [38] are expected to be candidate cathode materials for ZIBs. Recently, a vanadium-based phosphate material, $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ [39], was reported to be a candidate cathode material for ZIBs owing to its high stability and specific capacity. The performance of this material depends also on the diffusivity of Zn^{2+} ions in this material, and such diffusion relies on the defects. Although defects and diffusion properties of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ are experimentally challenging, computational modeling techniques can provide valuable information about the most thermodynamically stable defect processes, diffusion pathways and their activation energies, and solution of dopants.



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In a recent classical simulation study of spinel- ZnCo_2O_4 [40], it was reported that the Co-Zn anti-site is the most stable defect type and that Zn^{2+} ion diffusion is three-dimensional with an activation energy of 0.70 eV.

In this study, we used the computational modeling technique based on the classical pair-wise potentials to examine the defect, diffusion, and dopant properties of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$. Many oxide materials have been modeled using this methodology and the calculated properties agree with those measured in the experiments [41–45]. The electronic structures of the most stable dopants were analyzed using density functional theory (DFT) simulations.

2. Computational Methods

Defect simulations were employed using a classical simulation code GULP (Generalized Utility Lattice Program) [46]. In this simulation technique, interactions between ions in the lattice are described using long-range Coulombic and short-range electron–electron repulsion (Pauli) and attractive dispersion (van der Waals) forces. Short-range interactions were modeled using Buckingham potentials (see Table 1) [47,48]. Both lattice constants and ionic positions were relaxed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [49]. Point defect modeling was carried out by a method proposed by the Mott–Littleton method [50]. Vacancy-mediated diffusion of Zn^{2+} ions was modeled considering seven interstitial positions between two Zn atomic positions in a local hop. The energy difference was between the maximum energy and the energy of the Zn vacancy. Our simulation techniques assumed that all ions were spherical and fully charged. There was an overestimation of the defect energies but the trend’s consistency was retained.

Table 1. Buckingham potential parameters used in the classical simulations of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ [47,48]. Two-body ($\Phi_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6$), where A , ρ , and C are parameters reproducing the experimental data. The values of Y and K are shell charges and spring constants, respectively.

Interaction	A/eV	$\rho/\text{\AA}$	$C/\text{eV}\cdot\text{\AA}^6$	Y/e	$K/\text{eV}\cdot\text{\AA}^{-2}$
$\text{Zn}^{2+} - \text{O}^{2-}$	499.6	0.3595	0.00	2.00	99,999
$\text{V}^{3+} - \text{O}^{2-}$	1410.82	0.3117	16.00	2.04	196.3
$\text{P}^{5+} - \text{O}^{2-}$	897.2648	0.3577	0.00	5.000	99,999
$\text{O} - \text{O}^{2-}$	22,764.30	0.1490	27.89	−2.80	74.92

DFT simulations were employed to examine the electronic structures of the most favorable doped configurations. The plane-wave DFT simulation code VASP (Vienna Ab initio Simulation Package) [51] was used. In all cases, a plane wave basis set consisting of a cut-off of 500 eV, projected augmented wave (PAW) pseudopotentials [52], and a $4 \times 4 \times 4$ Monkhorst–Pack [53] k-point mesh were used. The PBE-GGA (Perdew, Burke, and Ernzerhof-generalized gradient approximation) [54] was used to describe the exchange–correlation energy. Full geometry optimization was performed using the conjugate gradient algorithm [55] with a force tolerance of 0.001 eV/Å. The Bader charge analysis [56] was used to estimate the effective charges on the atoms in the relaxed configurations.

3. Results and Discussion

3.1. Crystal Structure of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$

$\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ is three-dimensional with a triclinic space group of $P\bar{1}$. Its experimental lattice constants were reported to be $a = 6.349$ Å, $b = 7.869$ Å, $c = 9.324$ Å, $\alpha = 105.32^\circ$, $\beta = 108.66^\circ$, and $\gamma = 101.23^\circ$ [57]. In this complex structure, phosphorous and vanadium form tetrahedral units and octahedral units with nearest-neighbor oxygen atoms (see Figure 1a). These two units share their corners and form networks in the crystal. This complex structure was energy-minimized completely to determine the equilibrium lattice constants. The calculated values were in good agreement with the values reported in the experiment showing the efficacy of potential parameters and pseudopotentials (see Table 2).

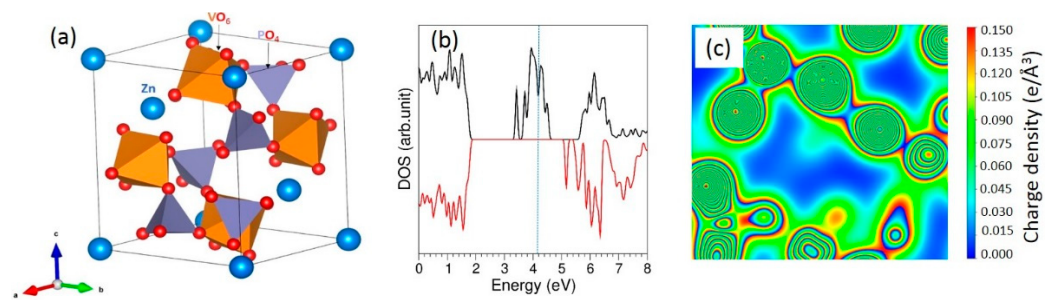


Figure 1. (a) Crystal structure of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$, (b) total DOS plot, and (c) charge density plot showing the bonding nature in $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$. The vertical blue dotted lines correspond to the Fermi energy level.

Table 2. Calculated and experimental parameters of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$.

Parameter	Calculated		Experiment [57]	Δ (%)	
	Classical	DFT		Classical	DFT
a (Å)	6.172	6.393	6.349	2.79	0.69
b (Å)	7.960	7.975	7.869	1.16	1.35
c (Å)	9.208	9.391	9.324	1.24	0.78
α (°)	105.43	105.45	105.32	0.10	0.12
β (°)	108.31	107.20	108.66	0.33	1.34
γ (°)	102.35	101.97	101.23	1.11	0.73

The calculated total DOS plot shows that the $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ exhibits a metallic characteristic (see Figure 1b), which is one of the essential conditions for a cathode material. Figure 1c shows the charge density plot showing the ion–ion interaction in the $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$.

Bader charges calculated on the atoms in the bulk $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ are reported in Table 3. Based on the formula of the $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$, ionic charges on the Zn, V, P, and O are +2.00, +3.00, +5.00, and −2.00, respectively. Although the Bader charges of Zn, V, and O are not closer to the values of the full ionic charge model, the bulk $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ can still be considered as ionic material.

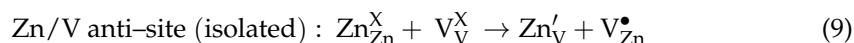
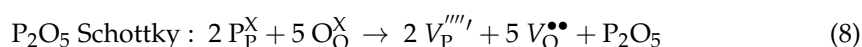
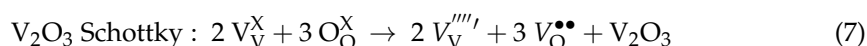
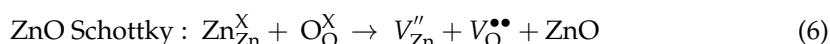
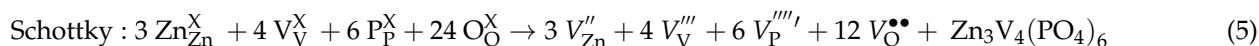
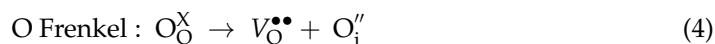
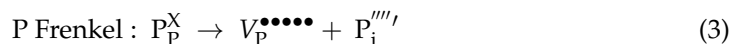
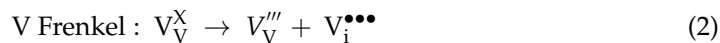
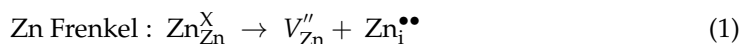
Table 3. Calculated Bader charges on the atoms in bulk $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$.

Atom	Bader Charge (e)
Zn	+1.43
V	+2.10
P	+5.00
O	−1.78

3.2. Intrinsic Defect Properties

Here, we calculated the Frenkel, Schottky, and anti-site defect formation energy processes. These defects are crucial as they determine the properties of materials. As point defect (vacancy and interstitial) energies are necessary to calculate the defect process energies, vacancy and interstitial formation energies were first calculated. The defect processes are written using Kröger–Vink notations [58]. In a Schottky defect process, vacancies are introduced in the lattice. A Frenkel defect consists of a vacancy–interstitial pair. The concentration of these two defect processes is temperature-dependent. In general, the concentration of these defects will increase with increasing temperature. The Frenkel defect process controls the ionic conductivity of a material as explained in a previous experimental study on AgI [59]. An enhancement in the electronic conductivity was explained in

the presence of Schottky defects in LaFeO_3 [60]. Point defect energies were combined to calculate Frenkel, Schottky, and anti-site defect formation energies.



In Figure 2, calculated defect energies are reported. The Zn-V anti-site cluster exhibits the lowest defect formation energy. In this defect process, a small amount of Zn^{2+} ions will be on the V site and vice versa. The defect formation energy difference between the anti-site (isolated) and anti-site (cluster) is defined as the binding energy (-0.18 eV). Exoergic binding shows that isolated defects (Zn_{V}' and $\text{V}_{\text{Zn}}^{\bullet}$) will aggregate as soon as the isolated defects are present in this material. This defect has been determined in a variety of oxide materials both experimentally and theoretically [61–65]. The influence of the cation anti-site defect has been discussed in an experimental study on LiFePO_4 [66]. The electrochemical performance of LiNiPO_4 upon the Li-Ni anti-site defect has been discussed by Kempaiah et al. [67]. The cycled structure of $\text{Li}_2\text{FeSiO}_4$ exhibited Li-Fe ion mixing and the Li-ion diffusion pathways and activation energies were different to those found in its as-prepared structure [68]. In a recent study, defect and diffusion properties of spinel- ZnCo_2O_4 were examined using classical simulation [40]. It was found that the Zn-Co anti-site cluster is the lowest-energy defect with a binding energy of -0.14 eV.

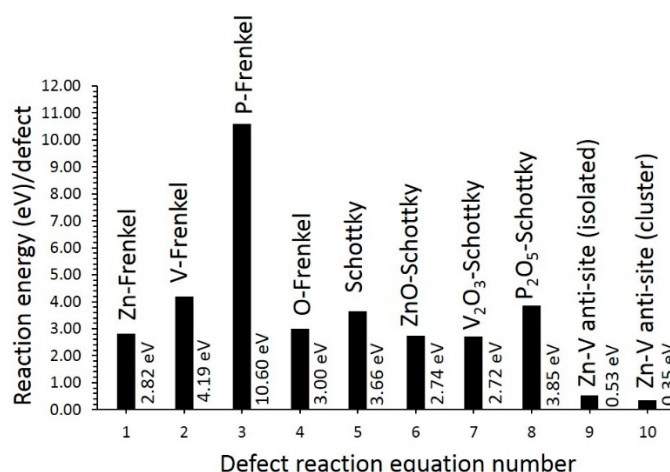


Figure 2. Energies of defects for different defect processes in $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$.

Partial Schottky (ZnO and V_2O_3) and Zn Frenkel defect energies are closer to each other. The Zn Frenkel is an important defect energy process as it can govern the vacancy-assisted Zn-ion migration in this material. This defect energy is 2.82 eV, much lower than that calculated in ZnCo_2O_4 . The O Frenkel has a defect energy of 3.00 eV. This is

higher only by ~ 0.30 eV than that calculated in the partial Schottky or Zn Frenkel. Other Schottky or Frenkel defects are higher-defect-energy processes and do not form under normal temperatures. In particular, the P Frenkel has the highest defect energy of 10.60 eV.

3.3. Diffusion of Zn^{2+} Ions

The understanding of Zn^{2+} ion diffusion is important as it determines the overall performance of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$. Here, we used classical simulation techniques to calculate the energies of activation of local Zn hops and construct diffusion pathways with long range. In a previous classical simulation study [69], it was reported that Li^+ ion migration in LiFePO_4 is one-dimensional with a curve that was later confirmed in a neutron diffraction study [70].

Five local Zn hops were found. In the first hop (A), Zn diffuses in the bc plane having an activation energy of 1.05 eV (see Figure 3). A jump distance of 3.98 Å and its activation energy 1.88 eV were calculated in the second hop. Both activation energies are quite high and, therefore, the diffusion of Zn^{2+} would be slow. Table 4 lists the activation energies of each hopping distance. In particular, longer hop distances (>4.00 Å) have higher activation energies (>3 eV). This means that Zn^{2+} ions would diffuse very slowly via those hops. The slow diffusivity of Zn^{2+} can be due to several reasons including the high positive charge of 2+, long Zn hop distance, and the crystal structure. Morkhova et al. [71] recently employed DFT simulations to calculate activation energies of some Zn^{2+} ion conductors. The most promising structures were found to be spinel compounds with the chemical formula of ZnM_2O_4 ($\text{M} = \text{Fe}, \text{Co}, \text{Cr}, \text{and V}$) and their activation energies ranged between 0.54 eV and 0.68 eV. In the crystal structure of $\text{Zn}_3\text{S}_2\text{O}_9$, the activation energy of Zn^{2+} is high (1.55 eV), although this compound consists of three Zn^{2+} ions per formula unit. In a previous classical simulation study of spinel- ZnCo_2O_4 , it was reported that the Zn^{2+} ions migrate in a linear pathway having an activation energy of 0.71 eV [40].

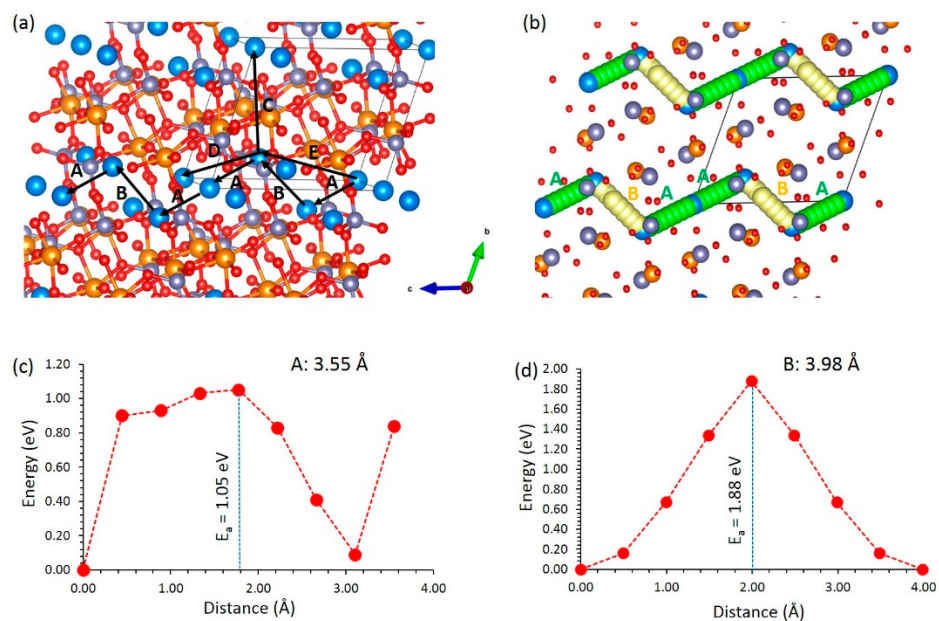


Figure 3. (a) Local Zn hops considered, (b) the most possible long-range diffusion pathway consisting of local hops A and B, (c) energy profile diagram showing the activation energy of the local hop A, and (d) similar diagram plotted for the local hop B.

Table 4. Calculated activation energies of different Zn hops.

Hop	Distance (Å)	Activation Energy (eV)
A	3.55	1.05
B	3.98	1.88
C	5.87	3.48
D	5.94	3.62
E	6.24	3.80

An improvement of Zn^{2+} ion diffusion can be made by preparing materials at the nanoscale, lowering the Zn-Zn separation. The polymerization intercalation method has also been applied to enhance the rate of diffusion of Zn^{2+} ions [72]. In this method, the electrostatic interaction between Zn^{2+} and O^{2-} ions is weakened to overcome the sluggish diffusion of Zn^{2+} ions. A combined experimental and DFT study of ZnCo_2O_4 showed that the oxygen vacancy formation can improve the Zn^{2+} ion diffusion by enlarging channels [73]. A facile hydrothermal method was applied to prepare a composite consisting of $\text{Zn}_x\text{V}_2\text{O}_5$ and graphene oxide to form a stabilized structure and enhance the diffusion of Zn^{2+} ions [74].

3.4. Solution of Dopants

Substitutional doping of elements is an important process to modify the properties of a material [75]. The ionic conductivity of zirconia was enhanced by the doping of yttria [76]. Such an enhancement was shown to associate with the point defects controlling the oxygen diffusion at grain boundaries. Ru doping on the Fe site reduced the Li-Li hop distances and enhanced the Li-ion diffusion in LiFePO_4 [77]. Here, we considered alkali earth (Mg, Ca, Sr, and Ba), divalent transition metal (Co, Mn, Fe, and Ni), and trivalent (Al, Ga, Gd, In, Sc, Y, and La) dopants to predict candidate dopants that can be tried experimentally. Appropriate lattice energies of dopant oxides and charge-compensating defects were introduced to construct defect reaction equations. Table 5 reports the potential parameters used for dopant oxides in this study.

Table 5. Interatomic potential parameters used for dopants in the atomistic simulations of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$. Two-body ($\Phi_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6$).

Interaction	A (eV)	ρ (Å)	C (eV·Å ⁶)	Y (e)	K (eV·Å ⁻²)
$\text{Mg}^+ - \text{O}^{2-}$	946.627	0.31813	0.000	2.000	99,999
$\text{Ca}^{2+} - \text{O}^{2-}$	1090.40	0.3372	0.000	1.260	34.00
$\text{Sr}^{2+} - \text{O}^{2-}$	776.84	0.35867	0.000	1.526	11.406
$\text{Ba}^{2+} - \text{O}^{2-}$	931.79	0.3949	0.000	1.460	14.78
$\text{Ni}^{2+} - \text{O}^{2-}$	683.5	0.3332	0.000	2.000	8.77
$\text{Co}^{2+} - \text{O}^{2-}$	696.3	0.3362	0.000	2.000	10.74
$\text{Fe}^{2+} - \text{O}^{2-}$	1207.6	0.3084	0.000	2.000	99,999
$\text{Mn}^{2+} - \text{O}^{2-}$	715.80	0.3464	0.000	3.000	81.20
$\text{Al}^{3+} - \text{O}^{2-}$	1725.20	0.28971	0.000	3.000	99,999
$\text{Ga}^{3+} - \text{O}^{2-}$	2901.12	0.2742	0.000	3.000	99,999
$\text{Sc}^{3+} - \text{O}^{2-}$	1575.85	0.3211	0.000	3.000	99,999

Table 5. Cont.

Interaction	A (eV)	ρ (Å)	C (eV·Å ⁶)	Y (e)	K (eV·Å ⁻²)
In ³⁺ – O ^{2–}	1495.65	0.3327	4.33	3.000	99,999
Y ³⁺ – O ^{2–}	1766.40	0.33849	19.43	3.000	99,999
Gd ³⁺ – O ^{2–}	1885.75	0.3399	20.34	3.000	99,999
La ³⁺ – O ^{2–}	2088.79	0.3460	23.25	3.000	99,999

First, alkali earth dopants (R = Mg, Ca, Sr, and Ba) were substitutionally doped on the Zn site. The following equation explains the doping process.



Solution energies are reported in Figure 4a. The Ca²⁺ is found to be the most favorable dopant. A negative solution energy (−0.16 eV) is calculated for this dopant. The solution energy calculated for the Mg²⁺ is also negative but lower by 0.05 eV than that calculated for the Ca²⁺. These dopants are favored partly due to their ionic radii (Mg²⁺: 0.89 Å and Ca²⁺: 1.12 Å) closely matching with the ionic radius of Zn²⁺ (0.88 Å). The solution of Sr²⁺ is endoergic with the solution energy of 0.41 eV. The Ba²⁺ exhibits a high positive solution energy of 1.73 eV, meaning that this dopant can be doped only at high temperatures. The total DOS plot shows that the Ca-doped Zn₃V₄(PO₄)₆ is still metallic (see Figure 4b). The states of the Ca lie in the deeper level of the valence band (see Figure 4c).

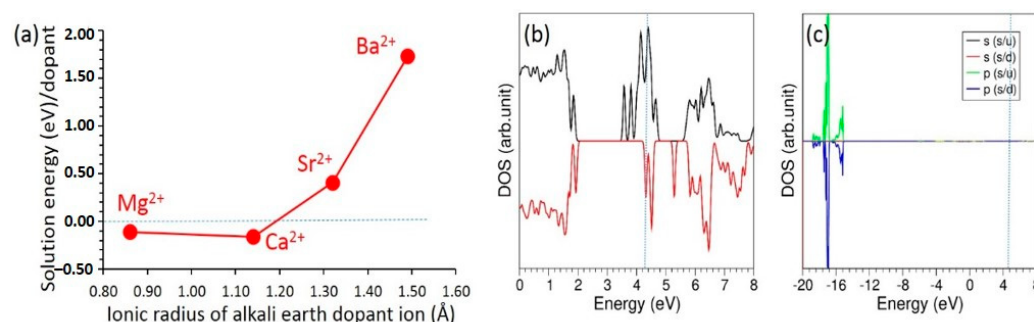


Figure 4. (a) Solution energies of alkali earth dopants on the Zn site, (b) total DOS plot of Ca-substituted Zn₃V₄(PO₄)₆, and (c) DOS plot associated with the Ca.

Next, divalent transition metal ions (Ni²⁺, Co²⁺, Fe²⁺, and Mn²⁺) were considered on the Zn site. The most promising dopant is Fe²⁺ and its solution energy is −1.30 eV (see Figure 5a). The negative solution energy indicates that the Fe²⁺ on the Zn site is thermodynamically stable. The second most favorable dopant is Mn²⁺. The solution energy for this dopant is negative (−0.08 eV), meaning that this dopant is also promising. Both Ni²⁺ and Co²⁺ exhibit positive solution energies. The most unfavorable dopant is Ni²⁺. The metallic characteristic of Zn₃V₄(PO₄)₆ is retained upon Fe-doping (see Figure 5b). The states in the Fermi energy level are significantly affected by the d-states of Fe (see Figure 5c).

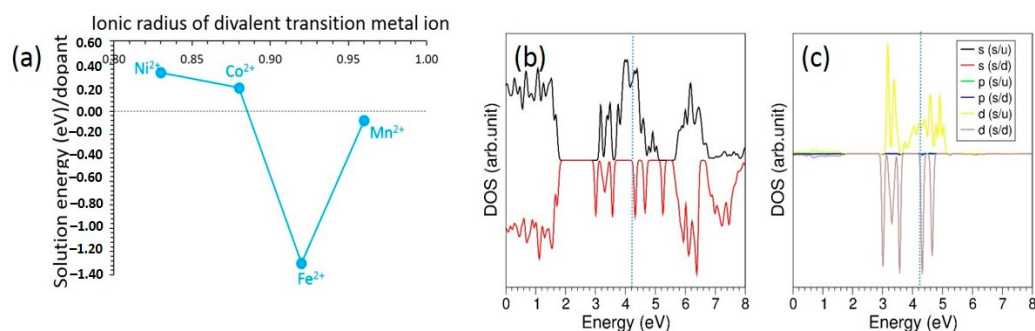
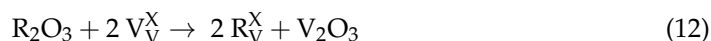


Figure 5. (a) Energies of solution calculated for transition metal dopants on the Zn site, (b) total DOS plot of Fe-substituted Zn₃V₄(PO₄)₆, and (c) DOS plot associated with the Fe.

Next, trivalent dopants were substituted on the V site. This doping process, as other processes mentioned above, requires no charge-compensating defects as defined by the following equation.



The solution energies reported in Figure 6a indicate that most of the dopants except Al³⁺ exhibit an exoergic solution. The most promising dopant of In³⁺ has the solution energy of −1.10 eV. The least promising dopant of Al³⁺ exhibits an endothermic solution energy of 0.30 eV. There is an increase in solution energy with increasing ionic radius from Al³⁺ to In³⁺. Then, there is a gradual drop in the solution energy up to Ga³⁺. The solution energy of La³⁺ becomes more negative than that calculated for Gd³⁺.

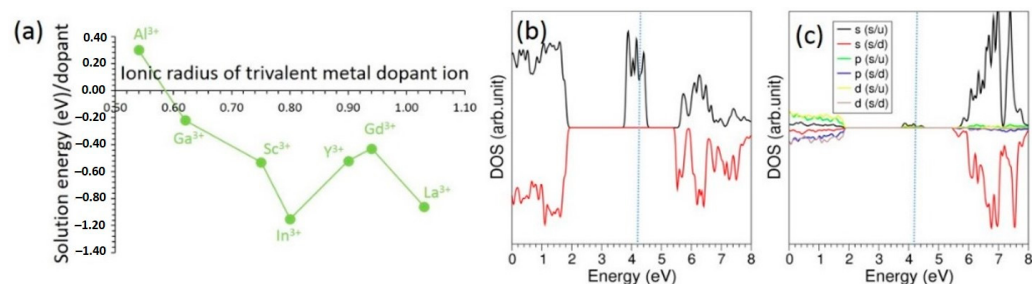


Figure 6. (a) Solution energies of trivalent dopants on the V site, (b) total DOS plot of In-substituted Zn₃V₄(PO₄)₆, and (c) DOS plot associated with the In.

The total DOS plot shows that In-doped Zn₃V₄(PO₄)₆ is metallic (see Figure 6b) and the states occupied at the Fermi energy level are a mixture of s, p, and d states of In (see Figure 6c).

A deformation charge density plot associated with the most favorable dopants interacting the lattice structure is provided in Figure 7.

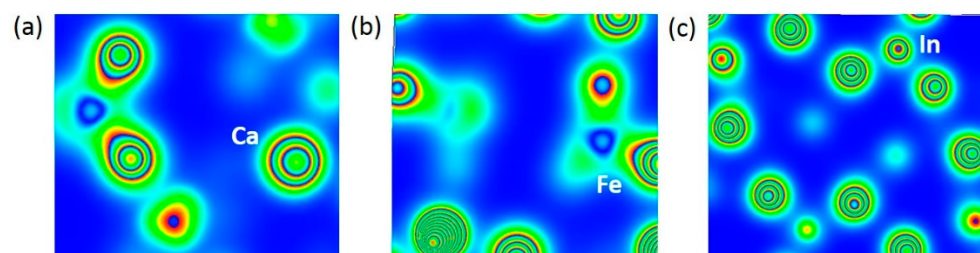


Figure 7. Charge density plots associated with the most favorable dopants: (a) Ca²⁺, and (b) Fe³⁺ and (c) In³⁺.

3.5. Synthetic Routes for the Formation of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$

The synthesis of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ was carried out using a high-temperature roasting method. In this complex method, $\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$, NH_4VO_3 , and $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ are used as starting materials [39]. Here, we consider some chemical reactions and calculate the formation energies by optimizing different oxides containing Zn, V, and P. In all cases, the formation of one mole of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ is considered and the reaction energies are exothermic (see Table 6). This means all five routes are theoretically feasible. In the first reaction, the reaction liberates energy (-6.27 eV) in the form of heat. In this reaction route, binary oxides are taken as reactants. The second reaction has two binary oxides and one ternary oxide. The inclusion of a ternary oxide results in a lower reaction energy of -3.12 eV. In the third reaction, a ternary oxide consisting of Zn, P, and O ($\text{Zn}_2\text{P}_2\text{O}_7$) is considered as a reactant. This reaction is still exothermic and its reaction energy is lower than those of reactions 2 and 3. In the least feasible reaction, a ternary oxide consisting of high Zn content ($\text{Zn}_3(\text{PO}_4)_2$) is used. This reaction is exothermic with a reaction energy of -0.29 eV. Although all the reaction energies are thermodynamically exothermic, the availability, abundance, cost of materials, and ease of experiments should also be considered. In addition, kinetic feasibility is also important as the start of the reaction depends on the activation energy. The kinetic barrier can be dealt with by using appropriate catalysts.

Table 6. Different reaction routes for the synthesis of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$.

Reaction Number	Reaction	Reaction Energy (eV)
1	$3 \text{ZnO} + 2 \text{V}_2\text{O}_3 + 3 \text{P}_2\text{O}_5 \rightarrow \text{Zn}_3\text{V}_4(\text{PO}_4)_6$	-6.27
2	$3 \text{ZnO} + 4 \text{VPO}_4 + \text{P}_2\text{O}_5 \rightarrow \text{Zn}_3\text{V}_4(\text{PO}_4)_6$	-3.12
3	$1.5 \text{Zn}_2(\text{P}_2\text{O}_7) + 2 \text{V}_2\text{O}_3 + 1.5 \text{P}_2\text{O}_5 \rightarrow \text{Zn}_3\text{V}_4(\text{PO}_4)_6$	-2.30
4	$3 \text{ZnO} + \text{V}_4(\text{P}_2\text{O}_7)_3 \rightarrow \text{Zn}_3\text{V}_4(\text{PO}_4)_6$	-1.72
5	$3 \text{Zn}(\text{PO}_3)_2 + 2 \text{V}_2\text{O}_3 \rightarrow \text{Zn}_3\text{V}_4(\text{PO}_4)_6$	-1.10
6	$\text{Zn}_3(\text{PO}_4)_2 + 4 \text{VPO}_4 \rightarrow \text{Zn}_3\text{V}_4(\text{PO}_4)_6$	-0.29

4. Conclusions

In conclusion, we have studied the nature of defects, migration of Zn^{2+} ions, a solution of isovalent dopants, and the thermodynamic stability of different reaction routes for the synthesis of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ using computational modeling techniques. The Zn-V anti-site is the most energetically favorable defect process. The diffusion of Zn^{2+} ions is low in this material. The Ca^{2+} and Fe^{2+} ions are the most promising dopant ions on the Zn site, while the V site prefers the In^{3+} dopant ion. The formation of $\text{Zn}_3\text{V}_4(\text{PO}_4)_6$ is favored by the reaction between binary oxides (ZnO , V_2O_3 , and P_2O_5).

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