Synthesis, Crystal Structure, Ca²⁺ and Proton Conduction Pathways of New Triphosphate Ca_{0.5}FeHP₃O₁₀

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A new calcium iron phosphate Ca_{0.5}FeHP₃O₁₀ was synthesized under hydrothermal conditions at 453K and studied by single-crystal X-ray diffraction at room temperature. It crystallized in monoclinic space group *C*2/c with lattice parameters a = 12.102(3) Å, b = 8.459(2) Å, c = 9.387(3) Å, $\beta = 112.21(2)$ °, V = 889.7(4) Å³ and Z = 4. The final agreement factors are $R(F^2) = 0.027$ and $wR(F^2) = 0.073$. The anionic framework of the title compound consists of FeO₆ octahedra linked by hydrogentriphosphate HP₃O₁₀ anions to form a three-dimensional framework containing tunnels parallel to *c*-axis where Ca²⁺ cations are located. The structural model was validated by bond valence sum (BVS), distortion indices (DI) and charge distribution (CD) methods. Ca²⁺ and H⁺ pathways migration simulation was studied by BVSE model.

Keywords: Iron phosphate, Synthesis, X-ray diffraction, Single crystal, Crystal structure, Bond valence analysis, Pathways simulation, Ionic conductor.

1. INTRODUCTION

Recently, many research activities have focused on the investigation of new iron phosphates. Open-framework materials have been extensively studied, owing to their potential applications in many domains such as catalysis [1], ionic conductivity [2], electrochemistry [3-4], etc.

In this work we are interested in new member of triphosphates compounds. According to the literature, six different structure types are known for the hydrogen triphosphates with the general formula

 $A^{I}M^{III}HP_{3}O_{10}$ (A is a monovalent cation, M: is a trivalent metal). These types comprise one triclinic type, four monoclinic types and one orthorhombic type, and these will now be discussed.

In the first system (triclinic), five compounds crystallize in the space group *P*-1: KMnHP₃O₁₀ [5], RbPrHP₃O₁₀ [6], (NH₄)BiHP₃O₁₀ [7], KSmHP₃O₁₀ [8] and (NH₄)SmHP₃O₁₀ [8] (structure determined and refined from X-ray powder diffraction).

In the second system (monoclinic), there are four different crystal systems. Two primitive lattices are represented by (NH₄)AlHP₃O₁₀, *P*2/a [9], and CsGaHP₃O₁₀, *P*2/n [10]. The two others type is nonisomorphous C-centered monoclinic cells. In the space group *C*2/c (β form), there are five compounds, CsVHP₃O₁₀ [11], (NH₄)FeHP₃O₁₀ [12], RbMnHP₃O₁₀ [13], KMnHP₃O₁₀ [14] and CsInHP₃O₁₀ (structure determined and refined from X-ray powder diffraction) [15]. The last monoclinic type is noncentrosymmetric, (space group *C*2). It was described by CsGaHP₃O₁₀ [16] and CsMnHP₃O₁₀ [17].

Finally, only CsGaHP₃O₁₀ [18], crystallizes in the orthorhombic system (space group *P*ca2₁).

 $AMnHP_3O_{10}$ showed interesting open frame works [6-8, 16] leading to remarkable mobility of A^+ and H^+ cations [5]. In addition to monovalent cations, multivalent cations in general showed interesting ionic conductivity by providing high capacity, due to the divalency of the carrier charge [19]. Recently, calcium batteries have received attention. Earth abundance [20], small ionic size of Ca²⁺ (1.00 Å) and low intercalant ion charge density (0.49 e/Å³) of calcium made calcium compounds attractive candidates for ionic batteries [21-22]. Herein we describe the synthesis and structural determination and validation of a new triphosphate Ca_{0.5}FeHP₃O₁₀. We also report the bond valence sum of Ca²⁺ and H⁺ migration paths simulation of the title compound.

2. EXPERIMENTAL

2.1. Synthesis

Light pink single crystals of $Ca_{0.5}FeHP_3O_{10}$ (I), were prepared hydrothermally from a mixture of CaCO₃, Fe(NO₃).9H₂O and H₃PO₄ in the molar ratio Ca:Fe:P = 1:1:4 in aqueous solution. The reaction mixture was filled into a Teflon–lined autoclave and heated under autogenous pressure at a 180 °C temperature for fifteen days, light pink and colourless single crystals were obtained. They have been identified as $Ca_{0.5}FeHP_3O_{10}$ and orthorhombic CaHPO₄ by using single crystal diffraction analyses. The reaction product was separated from the excess flux by successive washing with boiling water.

2.2. Single crystal X-ray diffraction

Light pink crystals were selected under an optical microscope equipped with a polarized light attachment and mounted on glass fibres for the structure determination and refinement. The data collections were carried out at room temperature using a four-circle Enraf-Nonius CAD-4 diffractometer [23-24] and equipped with a graphite monochromatic Mo K_{α} radiation ($\lambda = 0.71073$ Å) (ω -2 θ scan). The reflections were corrected for Lorentz and polarization effects and secondary extinction [25]. The

absorption correction was reached by psi-scan [26]. The crystal structure was solved by direct methods and refined against F^2 in the space group *C*2/c using SHELX97 computer programs [25] included in the WingX software package [27]. Iron, phosphate, and calcium atoms were first positioned and then oxygen atoms were located by successive Fourier difference synthesis. The agreement factors *R* and *wR* converged to 0.027 and 0.073, respectively, considering 845 independent reflections (*I*>2 σ (*I*)).

The crystallographic data for the title compound is summarized in Table 1. The atomic coordinates, isotropic thermal factors and atomic fractional occupancies are listed in table 2. Bond distances are summarized in Table 3. The structure figures were drawn with diamond 2.1 given by Crystal Impact [28].

| Crystal data | | | | |
|--|---|--|--|--|
| Empirical formula | Ca _{0.5} FeHP ₃ O ₁₀ | | | |
| Crystal system; Space group | Monoclinic, C2/c | | | |
| Unit cell dimensions | a=12.102(3) Å, b =8.459(2) Å, c =9.387(3) Å, β =112.21(2) ° | | | |
| Volume; Z | 889.7(4) Å ³ ; 4 | | | |
| Formula weight; ρ_{cal} | 329.81gmol ⁻¹ ; 2.462 g·cm ⁻³ | | | |
| Crystal sharp; color | Prism; light pink | | | |
| Crystal size | 0.28×0.21×0.18 mm | | | |
| Absorption coefficient (μ) | 2.56 mm ⁻¹ | | | |
| Data col | lection | | | |
| Diffractometer | Enraf-Nonius CAD-4 | | | |
| Wavelength; Temperature | $\lambda_{Mo K\alpha} = 0.71073 \text{ Å}; 298(2) \text{ K}$ | | | |
| Theta range of data collection | $3.0^{\circ} < \theta < 27.1^{\circ}$ | | | |
| Limiting indices h, k, l | $\text{-15}{\leq}h{\leq}15;-1{\leq}k{\leq}10;\text{-12}{\leq}l{\leq}12$ | | | |
| Scan mode | ω/2θ | | | |
| Absorption correction; T_{\min} ; T_{\max} ψ scan; 0.534; 0.656 | | | | |
| Standards; frequency (min); decay (%) | 2; 120; 1 | | | |
| Reflections collected | 1956 | | | |
| Independent reflections | 957 [$R_{int} = 0.032$] | | | |
| Number of reflections [$I \ge 2\sigma(I)$] | 845 | | | |
| Refinement | | | | |
| Refinement method | Full-matrix least-squares on F ² | | | |
| Reflections; parameters | 957;73 | | | |
| Final R indices $[I > 2\sigma(I)]$ R(F ²)=0.027; wR(F ²)=0.073 | | | | |
| $\Delta \rho \max ; \Delta \rho \min (e Å^{-3})$ 0.44; -0.64 | | | | |
| Goodness-of-Fit on F ² | 1.08 | | | |

Table 1. Crystal data and structure refinement for Ca_{0.5}FeHP₃O₁₀.

| Atom | wyck | x | у | z | Ueq [*] , Å ² | Occ. (<1) |
|------|------|-------------|-------------|-------------|-----------------------------------|------------------|
| Fe1 | 4c | 0.25 | 0.25 | 0 | 0.0071 (2) | |
| P1 | 8f | 0.20973 (6) | 0.06671 (8) | 0.29424 (8) | 0.0085 (2) | |
| P2 | 4e | 0 | 0.8754 (1) | 0.25 | 0.0084 (2) | |
| 01 | 8f | 0.2587 (2) | 0.1143 (3) | 0.1759 (2) | 0.0168 (5) | |
| 02 | 8f | 0.2877 (2) | 0.0575 (2) | 0.9026 (2) | 0.0131 (4) | |
| 03 | 8f | -0.0738 (2) | 0.7825 (3) | 0.1099 (2) | 0.0124 (4) | |
| 04 | 8f | 0.1791 (2) | 0.2047 (3) | 0.3759 (2) | 0.0216 (5) | |
| 05 | 8f | 0.0817 (2) | -0.0127 (3) | 0.1966 (2) | 0.0147 (4) | |
| Ca1 | 4e | 0 | 0.443 (1) | 0.25 | 0.079 (2)* | 0.30 |
| Ca2 | 8f | 0.0004 (12) | 0.438 (2) | 0.184 (2) | 0.070* | 0.10 |
| H1 | 4d | 0.25 | 0.25 | 0.5 | 0.11 (4)* | |

Tables 2. Atomic coordinates and equivalent displacement parameters ($Å^2$) for Ca_{0.5}FeHP₃O₁₀.

*Ueq is defined as one-third of the trace of the orthogonalized Uij tensor.

Table 3. Interatomic distances (Å) in the structure for $Ca_{0.5}FeHP_3O_{10}$.

| P1 tetrahedron | | P2 te | trahedron | |
|---|-----------|------------------------|-----------|--|
| P101 | 1.498 (2) | P2—O3 | 1.502 (2) | |
| P1—O4 | 1.517 (2) | P2—O3 ^{vii} | 1.502 (5) | |
| P1—O2 ^{vi} | 1.518 (2) | P2—O5 | 1.581 (2) | |
| P1—O5 | 1.618 (2) | P2—O5 ^{vii} | 1.581 (2) | |
| | Fe1 oct | ahedron | | |
| Fe1—O1 ⁱ | 1.981 (2) | Fe1—O2 ⁱⁱⁱ | 2.003 (2) | |
| Fe1—O1 | 1.981 (2) | Fe1—O3 ^{iv} | 2.006 (2) | |
| Fe1—O2 ⁱⁱ | 2.003 (2) | Fe1—O3 ^v | 2.006 (2) | |
| | Ca1 po | lyhedron | | |
| Ca1—O4 | 2.869 (7) | Ca1 ^{ix} —O1 | 2.878 (7) | |
| Ca1—O4 ^{vii} | 2.869 (7) | Cal—O3 | 2.878 (7) | |
| Ca1—O1 ^{xvi} | 3.094 (5) | Ca1—O ²ⁱⁱⁱ | 3.02 (1) | |
| Ca1—O1 ^{xv} | 3.094 (5) | Ca1—O2 ^{xx} | 3.02 (1) | |
| | Ca2 po | lyhedron | | |
| Ca2 ⁱⁱⁱ —O2 | 2.97 (1) | Ca2—O4 ^{vii} | 2.83 (2) | |
| Ca2 ^{xiv} —O3 | 3.06 (2) | Ca2 ^{vii} —O4 | 2.83 (2) | |
| Ca2—O3 ^{xix} | 3.06 (2) | Ca2—O4 | 2.98(2) | |
| Ca2 ^{viii} —O1 | 3.09 (1) | Ca2—O2 ^{xx} | 3.08 (1) | |
| Ca2 ^{xii} —O2 | 3.08 (1) | Ca2—O1 ^{xv} | 3.09 (1) | |
| Symmetry codes: (i) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$; (ii) x, y, $z-1$; (iii) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$; (iv) | | | | |
| $x + \frac{1}{2}, y + \frac{1}{2}, z; (v) -x, -y, -z; (vi) x, -y, z - \frac{1}{2}; (vii) -x, y, \frac{1}{2} -z; (viii) \frac{1}{2} -x,$ | | | | |
| $y - \frac{1}{2}, \frac{1}{2} - z;$ (ix) $x + \frac{1}{2}, y - \frac{1}{2}, z;$ (x) $x, -y, z + \frac{1}{2};$ (xi) $x, y, z + 1;$ (xii) $x + \frac{1}{2}, y - \frac{1}{2},$ | | | | |
| $z+1$; (xiii) $x-\frac{1}{2}$, $y-\frac{1}{2}$, z ; (xiv) x , $y-1$, z ; (xv) $\frac{1}{2}-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$; (xvi) $x-\frac{1}{2}$, | | | | |
| $y+\frac{1}{2}$, z; (xvii) x, $1-y$, $z+\frac{1}{2}$; (xviii) $-x$, $-y+1$, $-z$; (xix) x, $y+1$, z; (xx) $x-\frac{1}{2}$, | | | | |
| $y + \frac{1}{2}, z - 1.$ | | | | |

2.3. Crystal structure validation tools

Charge Distribution analysis (CHARDI) [29] and Bond Valence Sum (BVS) methods [30] were used to validate the structural model. Both calculations were performed using CHARDI2015 [31] and SoftBV [32] programs. The dispersion factor of the cation charges (σ_{cat} =0.7) determined by CHARDI method confirms the structure in particular the distribution of M1 (Ca1/Ca2) site. BVS analysis shows that the calculated valences V(i) are in agreement with the oxidation numbers [33] (Tab.4).

| Cation | q(i).sof(i) | Q(i) | d(ij>r) | CN(i) | ECoN(i) |
|--|--------------------|------|---------|-------|---------|
| Ca1 | 0.6 | 0.59 | 3.089 | 8 | 8.41 |
| Ca2 | 0.2 | 0.20 | 3.037 | 8 | 7.53 |
| P1 | 5.00 | 5.00 | 1.529 | 4 | 3.88 |
| P2 | 5.00 | 5.05 | 1.535 | 4 | 3.91 |
| Fe1 | 3.00 | 2.97 | 1.996 | 6 | 5.99 |
| H1 1.00 0.99 1.218 2 2.00 | | | | | |
| Notes: $q(i) = formal oxidation number; sof(i) = site occupation factor; d(ij>r)= weighted average distance; CNs = coordination number for d(Ca-O)_{max} = 3,40\text{Å});; ECoN(i)= number of effective coordination; \sigma = dispersion factor on cationic charges measuring the deviation of the computed charges (O) with respect to the formal oxidation numbers: \sigma cat = [\Sigma_i(\alpha_i-\Omega_i)^2/N-1]^{1/2} = 0.007$ | | | | | |

Table 4. CHARDI and BVS analysis of cation polyhedra in Ca_{0.5}FeHP₃O₁₀.

2.4. Pathway transport modelling

The cations motion in the anionic framework was first studied by Daniel Mazza [34] via a progressed Pauling BVS model [35] which was reformulated by Brown & Altermatt [36] with the following empirical relationship for an individual bond-valence s_{A-X} :

$$S_{A-X} = \exp\left(\frac{R_0 - R_{A-X}}{b}\right) \quad (1)$$

Where R_{A-X} = distance between counter-ions A and X; R_0 and b= fitted constants, R_0 = length of a bond of unit valence.

The interactions between cations A and anions X were expressed in arbitrary "valence units". However, they have been recently related to an absolute energy scale by expressing the bond valence as a Morse-type potential [37-38]. In this approach, the ionic transport pathway are identified as regions of low site energy E(A):

$$E(A) = D_0 \left[\sum_{i=1}^{N} \left(\frac{s_{A-X_i} - s_{min,A-X_i}}{s_{min,A-X_i}} \right)^2 - N \right] + E_{Coulomb}(A - B) \quad (2)$$

Where $E_{Coulomb}$ term describes the electrostatic interactions of A cation with the anionic framework.

The Bond Valence Site Energy (BVSE) calculations were performed by SoftBV program using Ca^{2+} and H⁺ as test ions and 0.1 Å resolution grids [39]. The BVSE isosurfaces were visualized using the VESTA 3 program [40].

3. RESULTS AND DISCUSSION

3.1. Structure description and comparison with other triphosphate materials

Crystal structure of Ca_{0.5}FeHP₃O₁₀ (**I**) is isotopic to CsVHP₃O₁₀ [11] and (NH₄)FeHP₃O₁₀ [12]. It crystallizes in C2/c space group. The asymmetric unit of (**I**) (Fig. 1) contains one FeO₆ octahedron, two phosphates tetrahedra P1O₄ and P2O₄ groups connected by corners and a hydrogen atom. The neutrality is assured by calcium ions Ca1 and Ca2 sharing the same site.



Figure 2. The asymmetric unit with atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) ½ -x, ½ -y, -z; (ii) x, y, -1+z; (iii) ½ -x, ½-y, 1-z; (iv) ½+x, ½+y, z; (v) -x, -y, -z; (vi) x, -y, -½ +z; (vii) -x, y, ½ -z]



Figure 2. Polyhedral representation of the structure showing tunnels parallel to c-axis, where Ca²⁺ cations reside.

The structure consists of FeO_6 octahedra and hydrogen tripolyphosphate HP_3O_{10} anions sharing oxygen atoms to form a three-dimensional open framework. All atoms are located in general positions except Fe1, P2, Ca1 and H1 atoms. The central phosphorus atoms P2 are located on a binary axis, and show a tetrahedral environment. These tetrahedra share two corners with two other tetrahedron via oxygen O5 and O5^{vii} to form P₃O₁₀ group (Fig. 2).

 P_3O_{10} groups are usually compared through P–P distances, P–O–P and P–P–P angles, and for (I) these values are 2.905(7) Å, 130.44(15)° and 112.28(2)° respectively and are typical of a P_3O_{10} group, as shown by comparison with isotopic compounds (Tab. 5).

| Formula | S.G | P-P (Å) | P–O–P (°) | P-P-P (°) | Ref. |
|--|--------------|----------------|------------------|------------------|------|
| KMn(HP ₃ O ₁₀) | | 2.741-2.991 | 135.12 144.83 | 101.56 | [5] |
| RbPr(HP ₃ O ₁₀) | | 2.882 -2.982 | 126.81 136.94 | 85.04 | [6] |
| (NH ₄)Bi(HP ₃ O ₁₀) | <i>P</i> -1 | 2.878- 2.977 | 126.34 137.51 | 84.52 | [7] |
| KSm(HP ₃ O ₁₀) | | 2.876-2.974 | | 84.34 | [8] |
| (NH4)Sm(HP3O10) | | 2.855 - 2.997 | 136.01 129.66 | 85.31 | [8] |
| (NH ₄)Al(HP ₃ O ₁₀) | <i>P</i> 2/a | 2.919 | - | 127.69 | [9] |
| CsGa(HP ₃ O ₁₀) | <i>P</i> 2/n | 2.935-2.935 | 144.28 | 128.40 | [10] |
| $CsV(HP_3O_{10})$ | | 2.882 | 128.33 | 111.57 | [11] |
| $(NH_4)Fe(HP_3O_{10})$ | C2/a | 2.897 | 130.47 | 112.19 | [12] |
| $Ca_{0.5}Fe(HP_3O_{10})$ | C 2/C | 2.905 | 130.44 | 112.28 | * |
| $RbMn(HP_3O_{10})$ | | 2.942 | 131.59 | 112.77 | [13] |
| CsGa(HP ₃ O ₁₀) | \sim | 2.882 | 127.77 | 111.89 | [16] |
| $CsMn(HP_3O_{10})$ | C2 | 2.894 | 129.29 | 113.16 | [17] |
| CsGa(HP ₃ O ₁₀) | $Pca2_1$ | 2.938-2.943 | 134.99 134.53 | 127.70 | [18] |

Table 5. Geometry of the tripolyphosphate anions

* This work

The two crystallographically distinct phosphate atoms of the triphosphate group P_3O_{10} show a slightly distorted tetrahedral coordination with effective coordination numbers which are ECoN(P1) = 3.875, ECoN(P2) = 3.907 and the distortion index does not exceed 3% (Tab. 6). The average distances for P1O₄ and P2O₄ are $\langle P1-O \rangle = 1.538$ Å and $\langle P2-O \rangle = 1.542$ Å respectively (Fig.3).



Figure 3. Projections of phosphate tetrahedra (a) showing tetrahedra distortions, (b) showing P1-O and P2-O distances.

The Fe–O bond distances within octahedron range from 1.981(2) to 2.006(2) Å (Fig.4). The effective coordination number ECoN(Fe1) = 5.993 and the distortion indices DIs (Tab. 6) show that the Fe1 octahedron is almost regular.



Figure 4. Projections of iron octahedron (a) showing regular iron octahedron, (b) showing Fe1-O distances.

Table 6. Distortion parameters ECoN and DI for the coordination polyhedra around Fe and P in (I)

| | P1 | P2 | Fe1 | |
|--|-------|-------|-------|--|
| ECON | 3.875 | 3.907 | 5.993 | |
| DI_d | 0.026 | 0.026 | 0.005 | |
| DIa | 0.034 | 0.031 | 0.029 | |
| DIo | 0.012 | 0.015 | 0.020 | |
| $DI_d = \sum_{i=1}^{n_1} (d_i - d_m) / n_1 d_m$; $DI_a = \sum_{i=1}^{n_2} (a_i - a_m) / n_2 a_m$ and $DI_o = 0$ | | | | |
| $\sum_{i=1}^{n_2} (o_i - o_m) / n_2 o_m.$ | | | | |
| <i>d</i> , <i>a</i> and <i>o</i> signify Fe/P-O bond distance. O-Fe/P-O angle and O-O edge within the relevant | | | | |
| polyhedron; index <i>i</i> indicates individual values, index <i>m</i> the mean value for the polyhedron. | | | | |
| <i>n1</i> and <i>n2</i> are 4 and 6 for the arsenate tetrahedral; 6 and 12 for the iron octahedral. | | | | |

Strong symmetric O...H...O hydrogen bonding, which was found in many hydrogen phosphates, links the triphosphate anions into chains [25] (Fig.5).



Figure 5. Projection of $[HP_3O_{10}^{4-}]^n$ along *c* direction

The hydrogen atom occupied a center of symmetry between two O4 atoms. However, the high thermal factor in the 2K neutron refinement, corresponding to a root-mean-square displacement of 0.18 Å, shows that a static or dynamic disorder of hydrogen appears near the mean position.



Figure 6. octahedral environments; (a) FeO₆ octahedron in (I) ,(b) GaO₆ octahedron in CsGa HP₃O₁₀



Figure 7. Projection of CsGaHP₃O₁₀ structure; (a) along [001] direction, (b) along [110] direction

This result is in agreement with the low BVS value of H⁺. Such symmetric O...H...O hydrogen bonding has been detected in CaHPO₄ at room temperature [26] to be transformed into long and short O-H bonds at 145 K [27]. However, it has not been possible to determine if the same H ordering occurs at low temperatures in this study due to the low resolution of the neutron data.

According to the previous crystal studies of $A^{(I)}M^{III}HP_3O_{10}$ compounds, all materials of this family, apart from those which crystallize in *C*2 and *C*2/c space groups, adopt two-dimensional anionic structures where cations occupy inter-layer spaces. The structure is one-dimensional with channels directed along *c* axis where monovalent cations are located [5-18]. The difference between the studied structure and the *C*2 triphosphate is due to the absence of the inversion center which leads to a different octahedron environment from that of the studied compound (I). For example, in CsGaHP₃O₁₀, four P₃O₁₀ groups and one iron octahedra are sharing corners: two adjacent corners are linked with two P₃O₁₀ groups and the other two groups are fixed by bidentate links (Fig.6). This arrangement leads to a three-dimensional framework revealing two types of tunnels according to *c* direction where Cs⁺ reside (Fig.7).

3.2. Pathways transport simulation proposed from bond valence analysis

3.2.1. Calcium pathways transport simulation by BVSE

The bond valence simulation energy (BVSE) was widely used to simulate monovalent alkali cations conduction pathways in the crystal bulk [41-43]. However, there was an only attempt of bivalent alkali cations Ca^{2+} [21] and Mg^{2+} [44] migration BVS mapping.

BVSE showed that calcium ion migration pathways are one dimensional allowed only by tunnels parallel to *c* direction. In fact, Tunnels minimum width (4.856 Å) along *c* direction is higher than the geometrical size sum of oxygen and calcium diameters 4.8 Å corresponding to $2 \times (r_{Ca2+}+r_{O2-}) = 2 \times (1+1.40)$ (Fig. 8).



Figure 8. Dimension sections of tunnels along c axis of (I)

As shown in figure 4 the migration is assured by conventional calcium crystallographic sites and one type of interstitial sites i1 with an energy minimum site 0.003 eV. The structure is characterized by

4 saddles for Ca^{2+} migration. However, the ion meets only three saddles; the lowest saddle S1 with a 0.072 eV energy located at 1.654 Å from Ca^{2+} site and the highest saddle S4 located at 3.547 Å with 0.143 eV energy (Fig. 9). The energy migration barrier required to cross the unit cell along *c* direction is E_{mig} = 0.140 eV (Fig. 10). This value was determined by the difference between the potential energy of the site and the saddle point of the pathway [44].

Although Ca^{2+} path is only one-dimensional, the barrier energy of Ca^{2+} migration is noticeably low compared to monovalent alkali cation materials [45-46].



Figure 9. 1D migration pathways of calcium cations along *c*- axis





3.2.2. Proton pathways transport simulation by BVSE

Proton migration was observed in several materials like Cs_3H (SeO₄)₂, Rb₃H (SeO₄)₂, KH₂PO₄ and CsH₂PO₄ [47-48]. BVSE model was successfully employed to simulate proton migration model in Fe²⁺Fe³⁺_{3.2}(Mn^{2+,}Zn)_{0.8}(PO₄)₃(OH)_{4.2}(HOH)_{0.8} [49].

As shown in figure 6, H^+ ions are generally distributed over hydrogen crystallographic sites and 7 types of interstitial sites. Energy interstitial sites vary from 0.565 eV to 0.689 eV (Fig.11).



Figure 11. Isosurfaces corresponding to constant potential determined by the BVSE model for H⁺ proton; (a) E_{min}=0.565 eV (showing only the lowest energy interstitial sites (i1)), (b) E_{min}=0.689 eV (showing all energy interstitial sites)

The highest energy barrier E_{mig} for proton migration from an interstitial site to another is 0.765 eV. However larger barrier energy between i5 and H⁺ sites causes the higher activation energy of about $E_a = 0.957$ eV. The first migration of proton from a crystallographic site to an interstitial site requires an energy equal to $E_{mig} = 0.883$ eV which is higher than the energy required for proton migration from an interstitial site to another.



Figure 12. 3D energy profile of H⁺ pathways estimated from the BVSE model ($E_{mig} = 0.883$)

This can be explained by that the strong symmetric O...H...O hydrogen bonding imposes higher energy for the proton migration but does not inhibited its migration. This structure is characterized by 31 saddles; the highest one S31 is located at 0.889, 0.406, 0.885 with a threshold energy 1.443 eV. However, only 20 paths with a maximum energy barrier $E_{mig} = 0.957$ eV are possible leading to a threedimensional migration of the proton (Tab.7) (Fig. 12). This value was also observed in promising lithium and sodium battery materials [50].

| Site 1 | saddle | Site 2 | Barrier (eV) |
|--------|--------|--------|--------------|
| i6 | s2 | i5 | 0.027 |
| i7 | s3 | i2 | 0.121 |
| i6 | s4 | i7 | 0.046 |
| i4 | s5 | i2 | 0.154 |
| i3 | s6 | i2 | 0.190 |
| i1 | s7 | i3 | 0.236 |
| i4 | s8 | i7 | 0.168 |
| i5 | s9 | i4 | 0.168 |
| i6 | s10 | i3 | 0.231 |
| i1 | s12 | i1 | 0.307 |
| i1 | s13 | i1 | 0.319 |
| i5 | s17 | H1 | 0.893 |
| i3 | s18 | i1 | 0.328 |
| i2 | s19 | H1 | 0.908 |
| H1 | s20 | i5 | 0.957 |
| i4 | s21 | i1 | 0.426 |
| i5 | s22 | i3 | 0.481 |
| i4 | s24 | i3 | 0.680 |
| i7 | s25 | i3 | 0.762 |
| i4 | s26 | i6 | 0.765 |

Table 7. Possible migration paths of the proton

4. CONCLUSION

New triphosphate Ca_{0.5}FeHP₃O₁₀ was synthesized by hydrothermal method. The crystal structure was determined by X-ray diffraction and confirmed by BVS and CHARDI methods. The new compound's structure is characterized by a three-dimensional open framework and by large tunnels along *c* direction hosting calcium ions. Migration pathways simulations of Ca²⁺ and H⁺ were used in order to model the ionic migration of cations in the structure. BVSE model showed one dimensional Ca²⁺ migration along *c* direction with low migration energy E_{mig} =0.140 eV. However, it indicated a three-dimensional migration of the proton with higher migration energy E_{mig} = 0.957 eV.

This study suggests a new type of a promising conductive material by offering an estimation of Ca^{2+} and H^+ migration in the structure. The ionic conduction provided by both cations can be validated by experimental measurements in subsequent works.

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