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Triclinic apatites

Tom Baikie, Patrick H. J. Mercier, Margaret M. Elcombe, Jean Y. Kim, Yvon Le Page, Lyndon D. Mitchell, T. J. White and Pamela S. Whitfield
Apatites commonly adopt P63/m hexagonal symmetry. More rarely, monoclinic chemical analogues have been recognized, including the biologically significant hydroxyapatite, Ca\(_{10}(\text{PO}_4)_6(\text{OH})_2\), but the driving force towards lower symmetry has not been systematically examined. A combination of diffraction observations and \textit{ab initio} calculations for Ca\(_{10}(\text{AsO}_4)_6\)F\(_2\) and Ca\(_{10}(\text{VO}_4)_6\)F\(_2\) show these materials are triclinic \(\text{P}\)\(_1\) apatites in which the As\(_4\) and VO\(_4\) tetrahedra tilt to relieve stress at the metal and metalloid sites to yield reasonable bond-valence sums. An analysis of the triclinic non-stoichiometric apatites La\(_{10-x}(\text{GeO}_4)_6\)O\(_3-x\).5\(_{\text{x}}\) and Ca\(_{10}(\text{PO}_4)_6(\text{OH})_2-x\text{O}_{\text{x}/2}\) confirms this scheme of tetrahedral rotations, while Cd\(_{10}(\text{PO}_4)_6\)F\(_2\) and Ca\(_{10}(\text{CrO}_4)_6\)F\(_2\) are predicted to be isostuctural. These distortions are in contrast to the better known \(\text{P}\)\(_{112}/\text{b}\) monoclinic dimorphs of chloroaapatite and hydroxyapatite, where the impetus for symmetry reduction is ordered anion (OH\(^-\) and Cl\(^-\)) displacements which are necessary to obtain acceptable bond lengths. These results are important for designing apatites with specific structural and crystal-chemical characteristics.

1. Introduction

Hydroxyapatite is a familiar biomaterial for bone replacement (Weiner & Wagner, 1998) and the apatite crystal family is of considerable importance in environmental remediation (Manecki et al., 2000) and catalysis (Eon et al., 2006), and as fertilisers (Bolland et al., 1995), electrolytes (Nakayama et al., 1995) and phosphors (Li et al., 2006). The structure of apatites, whose general formula can be written as \(A^2_{\text{large}}B_{\text{large}}(\text{BO}_4)_{\text{X}_2}\) \((A = \text{large cations}; \ B = \text{metalloids}; \ X = \text{anion and oxyanions})\) accommodates diverse chemistries with more than 74 discrete varieties now recognized (White et al., 2005). These disparate compositions are possible because of the inherent flexibility of an \(A^2_{\text{large}}(\text{BO}_4)_{\text{X}_2}\) framework that circumscribes one-dimensional tunnels, which expand or contract in response to the filling characteristics of the \(A^2_{\text{large}}X_2\) component (White & Dong, 2003). While the default symmetry for apatites is hexagonal \(P6_{\text{3}}/m\) only 57% of chemical end-members adopt this space group; a further 34% crystallize in hexagonal subgroups (\(P6_{\text{3}}, P6\) and \(P\bar{3}\)), with the balance monoclinic (White et al., 2005). Recently, two \(\text{P}\)\(_1\) apatites \([\text{La}_{10-x}(\text{GeO}_4)_6\text{O}_{3-x}.5_{\text{x}}], 9.66 < 10 - x < 9.75\) (León-Reina et al., 2003; Abram et al., 2005) and Ca\(_{10}(\text{PO}_4)_6(\text{OH})_2-x\text{O}_{\text{x}/2} (0.78 < x < 1.56)\) (Kriedl et al., 2001) have been reported, but no general conclusions concerning the origin of the triclinic distortions were drawn.

Although details pertaining to lower-symmetry apatites are sparse, their existence has long been recognized (Organova et al., 1994; Kriedler & Hummel, 1970; Banks & Jauanarajs, 1965). In an early stability field diagram, Kriedler & Hummel...
(1970) showed that the metal-substituted fluoroapatites \( \text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2 \), \( \text{Ca}_{10}(\text{VO}_4)_6\text{F}_2 \) and \( \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \) were distorted, as the ionic radius of the 10(As/VO/PO)\( ^{3+} \) component is large relative to the A\( ^{3+} \) cation. Banks & Jauanaraj (1965) observed a similar structural distortion in \( \text{Ca}_{10}(\text{CrO}_4)_6\text{F}_2 \). However, a rigorous examination of the modifications accompanying apatite symmetry changes has not been attempted because the structure is inherently difficult to visualize and an undistorted prototype, against which structural adjustments can be calibrated, did not exist. In a re-examination of this problem, we have shown (White et al., 2005; White & Dong, 2003) that apatites can be classified as zeolite-like microporous frameworks composed of face-sharing \( \text{A}^4\text{O}_6 \) trigonal prismatic columns that are corner-connected to the \( \text{BO}_4 \) tetrahedra (Fig. 1). The channels can adjust their size to suit the remaining \( \text{A}^4\text{X}_3 \) by converting the trigonal prisms to metaprism through rotation of the triangular faces over an angle \( \varphi \). In practice, \( 5 \leq \varphi \leq 25^\circ \) and the smaller the \( \text{A}^4\text{X}_3 \) portion relative to the \( \text{A}^4\text{X}_3(\text{BO}_4)_6 \) framework, the larger the metaprism twist angle. From the trigonal prismatic prototype, a geometrical parameterization of \( \text{P}6_{3}3\text{m} \) apatites has been developed that allows structural refinement from crystal chemical parameters in which polyhedral distortions conform to \textit{ab initio} minimum-energy solutions for apatites of different compositions (Mercier et al., 2005, 2006, 2007). To assess the distortions of metal-substituted fluoroapatites, an experimental and theoretical investigation was launched to examine the crystal structures of \( \text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2 \) and \( \text{Ca}_{10}(\text{VO}_4)_6\text{F}_2 \). In this report, electron, neutron and X-ray powder diffraction as well as \textit{ab initio} calculations were used to show that these compounds are isostructural triclinic \( \mathbf{P}1 \) apatites and that the reduction of symmetry from \( \text{P}6_{3}3\text{m} \) is caused by \( \text{BO}_4 \) tetrahedral tilting to obtain satisfactory bond-valence sums.

2. Experimental methods

\( \text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2 \) and \( \text{Ca}_{10}(\text{VO}_4)_6\text{F}_2 \) were synthesized in the solid-state through reaction of \( \text{CaO} \) (obtained by firing AR grade \( \text{CaCO}_3 \) at 1173 K), \( \text{As}_2\text{O}_3 \), \( \text{V}_2\text{O}_5 \) and \( \text{CaF}_2 \) mixed in stoichiometric proportions at 1073 K for 15 h. Grinding and re-firing were repeated until a single-phase product was obtained.

Neutron powder diffraction data were collected on the high-resolution powder diffractometer (HRPD) at the High Flux Australian Reactor (HIFAR) operated by the Australian Nuclear Science and Technology Organization (ANSTO). A neutron wavelength of 1.8845 \( \text{Å} \) was used from 0.029 to 150.079° 2\( \theta \) in 0.05° steps. Approximately 15 g of each apatite was loaded into a 12 mm diameter vanadium can that was rotated during data collection. Structure refinement was carried out from 10 to 150° 2\( \theta \) using the software \textit{TOPAS}, Version 3.0 (Bruker, 2005). A pseudo-Voigt peak shape corrected for asymmetry was used. The refined instrument parameters included four polynomial background coefficients, peak half widths \( U, V, W \) and an asymmetry parameter. The scattering lengths \( 0.470, 0.6580, 0.5805 \) and \( 0.5654 \times 10^{-12} \text{cm} \) were used for Ca, As, O and F, respectively. As vanadium is transparent to neutrons \((-0.0443 \times 10^{-12} \text{cm})\), its coordinates were determined \textit{via} X-ray powder diffraction.

X-ray powder data were collected with a Shimadzu LabX XRD-6000 diffractometer (Bragg–Brentano geometry) equipped with a Cu \( \text{K} \alpha \) X-ray tube operated at 40 kV and 40 mA. Samples were mounted in a top-loaded trough, which was not rotated during data collection. Under these conditions, the intensity of the strongest peak was 10 000–12 000 counts. Rietveld refinement of X-ray data was performed using the fundamental-parameters approach and a full axial divergence model (Cheary & Coelho, 1992, 1998). Refined specimen-dependent parameters included the zero error, a user-specified number of coefficients of a Chebyshev polynomial fitting the background and the ‘crystallite size’.

Selected-area electron diffraction patterns (SAED) were collected from powders ultrasonically dispersed in ethanol with several drops of suspension deposited onto a holey carbon-coated copper grid. A Jeol-2100 microscope operating at 200 kV and fitted with a double-tilt holder was used to locate the required orientations.

The modelling and \textit{ab initio} interface software environment \textit{Materials Toolkit}, Version 2.0 (Le Page & Rodgers, 2005), was used to prepare input files for \textit{ab initio} total-energy minimization calculations with \textit{VASP}4.6.3 (Kresse, 1993; Kresse & Hafner, 1993, 1994). The common execution parameters were: GGA PAW potentials (Kresse & Joubert, 1999); electronic convergence at \( 1 \times 10^{-3} \text{eV} \), convergence for forces of \( 1 \times 10^{-4} \text{eV Å}^{-1} \), Davidson-blocked iterative optimization of the wavefunction in combination with reciprocal-space projectors (Davidson, 1983); a Methfessel–Paxton (Methfessel & Paxton, 1999) smearing scheme of order 1 and width 0.2 eV.

![Figure 1](image)

Apatite prototype structure in which \( \text{A}^4\text{O}_6 \) trigonal prisms share faces along [001] and are corner-connected to \( \text{BO}_4 \) tetrahedra to form one-dimensional channels that are filled by \( \text{A}^{10} \) and \( X \) ions.
for energy corrections; a \(k\)-mesh dimension of \(2 \times 2 \times 3\) for reciprocal space integration (Monkhorst & Pack, 1976). Spin polarization corrections were not used. The calculations took about 5 d per triclinic structure on a single 3 GHz Athlon-64 PC running VASP 4.6.3 under Microsoft Windows using the execution scheme described above.

Secondary electron images (SEI) were collected using a Hitachi S-4800 Field Emission Scanning Electron Microscope. The instrument was fitted with two secondary detectors and composite images acquired at a working distance of 8 mm using a beam energy of 2 kV and 5 \(\mu\)A current. Typical SEI of \(\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2\) and \(\text{Ca}_{10}(\text{VO}_4)_6\text{F}_2\) confirmed the samples to be crystalline and homogeneous (see Figs. S1a and S1b of the supplementary data\(^1\)). An Oxford Inca EDS (energy-dispersive spectroscopy) system provided semi-quantitative elemental analyses consistent with the expected metal proportions.

3. Results and discussion

For \(\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2\) the \(a^*\) and \(c^*\) vectors in [010] selected-area electron diffraction patterns are clearly not orthogonal because the reciprocal lattice vectors from the reflection 302 to 302 are relatively shorter by \(\sim 1.5\%\) compared with 302 to 302 (Fig. 2a). This precludes the existence of a symmetry axis along \(c\) and a symmetry plane perpendicular to it, which proves the material to be triclinic (\(P\overline{1}\) or \(P1\)). In addition, the patterns show no superlattice reflections, which confirms the triclinic distortion is fundamentally different from the monoclinic type previously described in chloroapatite (Mackie et al., 1972; Bauer & Klee, 1993) and hydroxyapatite (Elliott et al., 1973; Suetugu & Tanaka, 2002) where a doubling of the \(b\) axis is characteristic.

Starting from the approximate cell constants obtained by electron diffraction and a \(P\overline{1}\) structural model using fractional coordinates adapted from fluorapatite (Sudarsanan et al., 1972), a satisfactory profile fit (Fig. S2a of the supplementary material), accurate unit-cell parameters and refined atomic positions could be extracted from the neutron diffraction profile by Rietveld refinement (see Table S1a of the supplementary material). Selected bond lengths are given in Table S2 of the supplementary material. Similar structural refinements in space groups \(P6_3/m\) and \(P112_1/m\) yielded agreement factors (\(R_{wp}\) and \(R_{Bragg}\) values) that were of inferior quality to those obtained using \(P\overline{1}\) (see Fig. S2a and Table S3 of the supplementary material). \textit{Ab initio} optimization of cell constants and

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\(1\) Supplementary data for this paper are available from the IUCr electronic archives (Reference: LM5005). Services for accessing these data are described at the back of the journal.
Table 1

<table>
<thead>
<tr>
<th>Tetrahedra</th>
<th>Along a (°)</th>
<th>Along b (°)</th>
<th>Along [110] (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-AP</td>
<td>12</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>V-AP</td>
<td>8.5</td>
<td>9.5</td>
<td>3</td>
</tr>
<tr>
<td>Oxy-HAP</td>
<td>14</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>La_{10-4}(GeO$_4$)O$_3$-1.5s*</td>
<td>18.5</td>
<td>13.5</td>
<td>3</td>
</tr>
</tbody>
</table>

References: (a) Alberius-Henning et al., 2001; (b) León-Reina et al. (2003).

atomic coordinates of Ca$_{10}$(AsO$_4$)$_2$F$_2$ through total energy minimization was performed assuming $P6_3/m$ and $P1$ symmetry. The lower energy of the triclinic model over the hexagonal one is consistent with the observed stability of the former and yields cell edges and angles together with fractional coordinates (Table S4) close to the refined values (Table S1a). Those results argue strongly in favour of the correctness of the $P1$ triclinic structure for Ca$_{10}$(AsO$_4$)$_2$F$_2$.

The non-perpendicularity of $a'$ and $c'$ is less obvious for Ca$_{10}$(VO$_4$)$_2$F$_2$ (Fig. 2) because the departure from the hexagonal metric is about half that of the arsenic material, but the vector $302^\circ$ is perceptibly longer than $302^\circ$. Cell data and composite structure results with Ca and O fractional coordinates from neutron diffraction and V positions from X-ray diffraction are shown in Table S1b and Fig. S2(b) of the supplementary material. Overall, these hybrid results for Ca$_{10}$(VO$_4$)$_2$F$_2$ are not as precise as those for Ca$_{10}$(AsO$_4$)$_2$F$_2$ and lead to approximations but not entirely convincing BVS (bond-valence sums). However, a superior triclinic structural model (Table S5 of the supplementary material) was built from the experimental coordinates for Ca$_{10}$(AsO$_4$)$_2$F$_2$ (Table S1a) and the cell data of Dong & White (2004) for the proposed monoclinic structure of Ca$_{10}$(VO$_4$)$_2$F$_2$. Here the oxygen coordinates were adjusted to allow for a 2% expansion of V–O bond lengths with respect to As–O bond lengths, with no change in the cation positions, rotations and bond angles of the BO$_4$ tetrahedra. This procedure gave accurate BVS of 1.972, 1.946 and 5.022 v.u. (valence units) for the $A^IV$, $A^VI$ and $B$ sites, respectively. This is a considerable improvement over the BVS from Mercier et al. (2007) for hexagonal Ca$_{10}$(V$_{5+}$P$_{1-4}$O$_{4}$)$_2$F$_2$ structures with compositions close to the V end-member, as well as the BVS calculated using the monoclinic structure of Ca$_{10}$(VO$_4$)$_2$F$_2$ (V-AP) reported in Dong & White (2004). The changes with respect to the experimental input atom coordinates that were observed upon ab initio optimization of this triclinic model were small and the cell angles agree with the refined cell data within 0.17° (Tables S6 with S5 of the supplementary material). The similarity of the axial ratios and angles ($a/b$, $c/b$, $a$, $b$, $c$), and the corresponding atom positions between experimental (Table S1a) and ab initio (Table S6) results for Ca$_{10}$(VO$_4$)$_2$F$_2$ compared with neutron (Table S1a) and ab initio (Table S4) results for Ca$_{10}$(AsO$_4$)$_2$F$_2$ confirms that these apatites have similar geometrical configurations, i.e. similar bond angles and polyhedral rotations.

Ca$_{10}$(PO$_4$)$_2$F$_2$ (F-AP) (Fig. 3a) and Ca$_{10}$(AsO$_4$)$_2$F$_2$ (As-AP; Fig. 3b) differ primarily in the rotations of the symmetry-independent tetrahedra in the triclinic As-AP (Table 1). Two pairs of tetrahedra directed along $a$ and $b$ rotate by similar angles of 12 and 11°, respectively, about the normal to one of their faces that was perpendicular to the (001) mirror in F-AP. The third pair of tetrahedra along [110] tilt by a modest 5° about their edges that lie on the mirror plane in F-AP (Table 1). Similar analyses of V-AP, oxy-hydroxyapatite (oxy-HAP; Alberius-Henning et al., 2001; Fig. 3c) with a 78% degree of dehydration, and triclinic La$_{10-4}$(GeO$_4$)$_2$O$_3$-1.5s (Leon-Reina et al., 2003; Table 1), revealed the same tetrahedral tilting scheme confirming that the materials are isomorphous. While ab initio modelling of the latter non-stoichiometric materials is not possible, calculations for Ca$_{10}$(PO$_4$)$_2$O (Table S7) and La$_{10-4}$(GeO$_4$)$_2$O$_3$ (Table S8), yield cell parameters and structural distortions not far removed from the experimental results for non-stoichiometric, stable materials.

In a separate study of the Ca$_{10}$(V$_{5+}$P$_{1-4}$O$_{4}$)$_2$F$_2$ compounds (Mercier et al., 2007), the origin of the symmetry reduction in the end-member Ca$_{10}$(VO$_4$)$_2$F$_2$ is clear: if $P6_3/m$ symmetry is retained, the BVS at the $A^IV$ calcium site decreases linearly with increasing vanadium content, with a large increase in BVS at the tetrahedral site as the phase transition is approached. Crystal chemical analysis shows that the combination of a small divalent cation at the $A$ sites and a large pentavalent metalloid at the $B$ site leads to extension stress at $A^IV$ (BVS < +2 v.u.) and compressive stress at $B$ (BVS > +5 v.u.). As V$_5^+$ and As$_5^+$ are both large tetrahedral pentavalent ions, it is concluded that the symmetry reduction in Ca$_{10}$(AsO$_4$)$_2$F$_2$ is also driven by the need to reduce considerable over-bonding at $B$. Bond-valence sums for calcium and arsenic sites for the refined triclinic phase show much-relieved stress with average values of 1.989, 1.949 and 5.124 v.u. at the putative $A^IV$, $A^VI$ and $B$ sites, respectively. This is well within BVS variability commonly observed in minerals and inorganic compounds (Brown & Allernatt, 1985).

Tetrahedral rotations seen in Figs. 3(h) and (c) achieve precisely the bond-valence regularization described above. The larger size of vanadium and arsenic with respect to phosphorus increases the distance between $A^IV$ metaprisms and enlarges the tunnel diameter. This leads to a gradual under-bonding at the $A^IV$ positions and over-bonding at the $B$ positions upon the addition of larger metalloids. In $P6_3/m$ the VO$_2$/AsO$_2$ tetrahedra are constrained to rotate around an axis parallel to $c$ that further separates the $A^IV$O$_6$ metaprisms in the $a$ plane increasing the diameter of the pores, and leads to a severe under-bonding of the $A^IV$ ions. This dilemma is overcome by lowering the symmetry. By removing a mirror plane, tetrahedra are free to rotate around an axis perpendicular to $c$, such that one O of the BO$_4$ unit moves towards Ca$^{10+}$ while another more strongly caps the Ca$^{10+}$ prism faces. This structural adjustment simultaneously results in a more acceptable BVS for the $A^IV$ and $A^VI$ sites, whilst establishing pentavalence at $B$. 

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Using similar arguments together with quantum mechanical energy minimization, it is predicted that the distorted apatites Cd_{10}(PO_{4})_{6}F_{2} (Kreidler & Hummel, 1970; Table S9) and Ca_{10}(CrO_{4})_{6}F_{2} (Banks & Jauanarajs, 1965; Table S10) will also adopt P\bar{1} symmetry.

Le Page & Rodgers (2005) attribute symmetry reduction in chloroapatite to the Cl atoms, on the basis that all other atoms which are polyhedra midway between trigonal prisms and octahedra.

Trigonal prisms have twisted their triangular faces to create metaprism, about axes as indicated by the arrows. Unlike the prototype (Fig. 1), the polyhedra twist their triangular faces to create metaprism, which are polyhedra midway between trigonal prisms and octahedra.

![Figure 3](image)

**Figure 3**
Polyhedral representation of (a) Ca_{10}(PO_{4})_{6}F_{2}, in which there is no tilting of the tetrahedra, (b) Ca_{10}(AsO_{4})_{6}F_{2}, and (c) Ca_{10}(PO_{4})_{6}(OH)_{2-X}O_{x}2 with x = 1.56, where the tetrahedra directed along a, b and [110] rotate about axes as indicated by the arrows. Unlike the prototype (Fig. 1), the trigonal prisms have twisted their triangular faces to create metaprism, which are polyhedra midway between trigonal prisms and octahedra.

conform to P6_{3}/m symmetry within 0.16 Å while the halide coordinates deviate by 0.43 Å. When chloro- and fluoroapatites are compared it is found that chlorine, being larger than fluorine, would have a BVS exceeding -1 v.u., if it was located at the 6 position on the mirror plane containing the Ca\textsuperscript{II} atom to which it is bonded. Consequently, Cl ions alternate occupy positions above and below the mirror plane, with inter-tunnel correlation along the b axis, transforming this mirror into a b-glide plane. This lowers the symmetry to monoclinic P11\textsubscript{2}1/b, doubles the b axis and causes slight tilting of BO\textsubscript{4} tetrahedra (Fig. S3a). Analysis of monoclinic hydroxyapatite (Elliott et al., 1973; Suetsugu & Tanaka, 2002) shows very similar structural adjustments (Fig S3b). Rather than adopting the P6\textsubscript{3} isomorphic subgroup of P6\textsubscript{3}/m that would accommodate ordered hydroxyl in a hexagonal space group, OH groups are seen to alternate above and below the Ca–Ca–Ca triangular units, which leads to displacements of the A\textsuperscript{III} ions away from the mirror plane in P6\textsubscript{3}/m and results in a tilting of the tetrahedra to accommodate these displacements. While the symmetry reduction to monoclinic in chloroapatite and hydroxyapatite is caused by ordered anion displacements to achieve chemically correct BVS at the anion (X) sites in the tunnels, the triclinic structures of the calcium arsenate and vanadate apatite arise to relieve stresses at metal (A) and metalloid (B) sites caused by the larger size of the A\textsuperscript{III}(BO\textsubscript{4})\textsubscript{6} framework relative to the A\textsuperscript{III}X\textsubscript{2} component.

**4. Conclusions**

In summary, electron diffraction has demonstrated that Ca_{10}(AsO_{4})_{6}F_{2} and Ca_{10}(VO_{4})_{6}F_{2} are the first reported examples of stoichiometric triclinic apatites. Neutron and X-ray diffraction substantiate this analysis and show that the rotation of the BO\textsubscript{4} tetrahedra lowers the symmetry from P6\textsubscript{3}/m to P1\textsubscript{1} while preserving topology and achieving more satisfactory BVS. Ab initio calculations provide further confirmation that the P1\textsubscript{1} structure is energetically favoured, reproduces the unit-cell distortions and provides optimized atomic coordinates close to the observed values. This distortion is required when the A\textsuperscript{III}(BO\textsubscript{4})_{6} framework is expanded with respect to the A\textsuperscript{III}X\textsubscript{2} channel contents. The origin of triclinic P1\textsubscript{1} symmetry is distinct from the phase change to P11\textsubscript{2}1/b monoclinic in hydroxy- and chloroapatite where the tunnel/channel framework nearly retains P6\textsubscript{3}/m symmetry, but is penetrated by an ordered arrangement of the X anions that cause A\textsuperscript{III} cationic displacements along c accompanied by slight tetrahedral tilting, leading to a non-maximal subgroup of the P6\textsubscript{3}/m parent. The ability to model the crystallographic distortions of apatites is of fundamental importance for tailoring chemical analogues with specific chemical and physical functionality.

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