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<td>Dong, Zhili; White, Timothy John</td>
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Calcium–lead fluoro-vanadinite apatites. I. Disequilibrium structures

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The synthetic vanadinites (Pb$_x$Ca$_{10-x}$)(VO$_4$)$_6$F$_{2x}$, $1 < x < 9$, adopt a $P6_3/m$ apatite structure with $a = 9.7590 (1)$ Å and $c = 7.0434 (3)$ Å. The partitioning of calcium and lead over the $A^I(4f)$ and $A^{II}(6h)$ positions is nonstoichiometric with lead preferentially entering the larger $A^{II}$ site. High-resolution electron microscopy showed that samples annealed for 10 h at 1073 K are in disequilibrium with calcium- and lead-rich microdomains coexisting at unit-cell scales. For (Pb$_5$Ca$_5$)(VO$_4$)$_6$F$_{2x}$, sintering in excess of 2 weeks is required for the metals to order macroscopically. As annealing progresses, $c/a$, the partitioning coefficient $k_{Pb}(A^I/A^{II})$ and the $A^I$O$_6$ metaprism twist angle ($\psi$) adjust cooperatively to enlarge the apatite channel, and thereby accommodate higher lead content. These results demonstrate that $\psi$ is a sensitive measure of disequilibrium and a useful device for monitoring changes in apatite topology as a function of composition.

1. Introduction

The apatite family is most often described by the general formula $[A^I_4][A^{II}_6]BO_4$X$_2$, although $[A_{10}]$$(BO_5)_n$X$_2$ and $[A_{10}]$$(BO_3)_n$X$_2$ derivatives are observed less commonly (White & Dong, 2003). All belong to maximal non-isomorphic subgroups of $P6_3/mcm$ (193). In $P6_3/m$ apatites the $A^I$ and $A^{II}$ cation acceptor sites accommodate large mono-, di- and trivalent ions, while B positions are filled by smaller 3+, 4+, 5+, 6+ and 7+ metals and metalloids. The $X$ anion site, which may be highly nonstoichiometric, is normally occupied by halides, oxygen or hydroxyl, and rarely by boron, copper or cyanamide (Ito et al., 1988; Carrillo-Cabrera & von Schnering, 1999; Habelitz et al., 1999). Apatites can be derived from regular anion nets and deviations from this ideal proves useful for systematizing composition and structure. In particular, the $A^I$O$_6$ metaprism twist angle ($\psi$) is a sensitive measure of A-cation ordering (White et al., 2004).

Apatite and several related minerals hold considerable promise for the stabilization and recycling of industrial waste and are already applied to the treatment of lead-contaminated soils and waters (Jeanjean et al., 1994; Zhang & Ryan, 1999; Ioannidis & Zouboulis, 2003). However, the apatites are a diverse group and systematic crystal chemistry studies for simplified (non-phosphate) systems relevant to waste immobilization remain sparse. Apatite-group minerals with potential environmental technology applications include the prototype Ca$_{10}$(PO$_4$)$_6$(OH,F) (Kim et al., 2000), pyromorphite Pb$_{10}$(PO$_4$)$_5$Cl$_2$ (Dai & Hughes, 1989), mimetite...
Pb\textsubscript{10}(AsO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2} (Calos & Kennard, 1990) and vanadinite Pb\textsubscript{10}(VO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2} (Dai & Hughes, 1989).

Because eco-apatites encompass a wide range of compositions, a holistic crystallochemical account of the systematic changes that occur as a function of composition and processing conditions is required. One approach is that of Elliott (1973), where the rather regular \ldots ABA \ldots hexagonal close-packing arrangement of BO\textsubscript{4} tetrahedra is emphasized with the interstices occupied to produce columns of larger A cations and X anions. On this basis, simple trigonometry allows the prediction that the a axis will dilate more rapidly than the c axis as larger ions are inserted. In a related, but different simplification, Dong & White (2004) considered the regular triangular network of oxygen as the key tessellation that through rotation could generate a range of distorted structures in response to variations in the average ionic radius of the cell contents. In this description the fundamental parameter was defined as the \textit{A}\textsuperscript{IV}O\textsubscript{6} metaprism twist angle (Fig. 1) that adopts values from 0 to 60° in response to changes in chemistry. Like the description of Elliott, this method rationalized the relative changes in cell parameters and additionally emphasized the one-dimensional tunnels and adaptable framework nature of apatites.

![Figure 1](https://example.com/figure1.png)

**Figure 1**
Polyhedral representations of idealized [\textit{A}\textsuperscript{III}][\textit{A}\textsuperscript{IV}]\textsubscript{1}BO\textsubscript{4}\textsubscript{4}X\textsubscript{2} apatites emphasizing the \textit{A}\textsuperscript{IV}O\textsubscript{6} trigonal prisms/metaprism (light shading) and BO\textsubscript{4} tetrahedra (dark shading). In this depiction [0001] channels are evident as the locations of \textit{A}\textsuperscript{IV} cations and X anions. To accommodate a necessary shortening of bond lengths as the relative crystal radius of channel atoms decrease, the \textit{A}\textsuperscript{IV}O\textsubscript{6} units may be twisted through an angle of \(\varphi\), the projected displacement between oxygen ligands. While in principle 0 < \(\varphi\) < 60°, for real apatites twist angles have not been observed to exceed 27°.

While the crystal structures of this family are well defined, eco-apatites are usually formed under conditions far from equilibrium and little detailed crystallographic data is available for such materials. To address this issue we have used X-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) to compare the crystallography of idealized wasteform vanadinites (Pb\textsubscript{10}Ca\textsubscript{10-x}VO\textsubscript{4}\textsubscript{6}F\textsubscript{2x}, 0 < x < 9, synthesized using short and long annealing times, to investigate the evolution of Pb/Ca-site partitioning over the \textit{A}\textsuperscript{IV} and \textit{A}\textsuperscript{II} positions. In the following paper (Dong & White, 2004) the changes in the \textit{A}\textsuperscript{IV}O\textsubscript{6} metaprism twist angle (\(\varphi\)) of equilibrated powders are systematized as a function of composition.

### 2. Experimental methods

Fluoro-vanadinites were synthesized by the solid-state reaction of freshly prepared CaO (obtained by decomposition of AR-grade CaCO\textsubscript{3} at 1127 K), PbO, V\textsubscript{2}O\textsubscript{5} and CaF\textsubscript{2}. The powders were mixed in stoichiometric proportions and fired at 1073 K in alumina boats at ambient atmosphere for 10 h. This firing temperature is just below the melting point of the lead endmember Pb\textsubscript{10}(VO\textsubscript{4})\textsubscript{6}F\textsubscript{2}. Ten compositions of ideal stoichiometry (Pb\textsubscript{10}Ca\textsubscript{10-x}(VO\textsubscript{4})\textsubscript{6}F\textsubscript{2x}, 0 < x < 9) were prepared. In the single case of (Pb\textsubscript{9}Ca\textsubscript{1}(VO\textsubscript{4})\textsubscript{6}F\textsubscript{2}, the annealing time was extended to 1, 2 and 7 weeks and samples retained at these intervals. During longer sintering no attempt was made to control fluoride loss through closed-system firing or fluorate overpacking, and 2F\textsuperscript{-} \leftrightarrow O\textsuperscript{2-} substitution was confirmed by semi-quantitative energy-dispersive X-ray analysis (EDX) and subsequent structure refinement.

Powder X-ray diffraction (XRD) patterns were collected using a Siemens D5005 X-ray diffractometer fitted with a Cu-tube operated at 40 kV and 40 mA. Divergence, anti-scatter, receiving and detector slits of

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**Table 1**
Revised cell parameters and \(k_{pw}\) for (Pb\textsubscript{3}Ca\textsubscript{10-x})(VO\textsubscript{4})\textsubscript{6}(F\textsubscript{1-x}O\textsubscript{x})\textsubscript{2} annealed for 10 h at 1073 K.

\(|x| x = 0: \text{Ca}_{10}(\text{VO}_{4})_{6}F_{2} \text{is strictly monoclinic, space group P}2_{1}/m, \text{with } a = 9.7112(2), b = 9.7082(2), c = 7.0159(3) \text{Å}, \gamma = 120.02(2)^{\circ}; \text{V} = 572.62 \text{Å}^{3}.\)

| \(a (\text{Å})\) | 9.7073 (4) | 9.7590 (1) | 9.8125 (1) | 9.8534 (1) | 9.9027 (1) | 9.9462 (1) | 9.9980 (1) | 10.0372 (1) | 10.0762 (1) | 10.1179 (1) |
| \(c (\text{Å})\) | 7.0153 (3) | 7.0843 (1) | 7.1079 (1) | 7.1084 (1) | 7.1455 (1) | 7.1983 (1) | 7.2502 (1) | 7.3039 (1) | 7.3585 (1) | 7.4021 (1) |
| \(V (\text{Å}^{3})\) | 572.5 (5) | 581.0 (1) | 590.2 (2) | 597.7 (2) | 606.8 (2) | 616.7 (2) | 627.6 (1) | 637.2 (2) | 647.0 (2) | 656.2 (2) |

\(N(Ca1)\) | 1 | 0.93 (3) | 0.83 (4) | 0.77 (5) | 0.71 (6) | 0.61 (6) | 0.55 (6) | 0.52 (7) | 0.37 (8) | 0.20 (8) |
\(N(Ca2)\) | 1 | 0.91 (3) | 0.76 (3) | 0.70 (4) | 0.62 (6) | 0.49 (6) | 0.31 (7) | 0.22 (8) | 0.18 (10) | 0.13 (8) |

\(k_{pw}(A^{IV}A^{II})\) | 0.54 | 0.47 | 0.51 | 0.51 | 0.52 | 0.43 | 0.41 | 0.51 | 0.61 |

\(\uparrow N(A^{IV}) = N(Ca1) + N(Pb1) = 1 \text{ and } N(A^{II}) = N(Ca2) + N(Pb2) = 1. \) \(\uparrow k_{pw}(A^{IV}A^{II}) = [2 - 2N(Ca1)]/[3 - 3N(Ca2)].\) For equal partitioning of Pb over \(A^{IV}\) and \(A^{II}\), \(k_{pw}\) would be 0.66 for all compositions.

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method as implemented in re®ned by Rietveld analysis using the fundamental parameter Pb10(VO4)6F2 or Ca10(VO4)6F2, the starting model for re®ne-
1998). In the absence of crystallographic data for Pb(VO4)6(F0.6O0.7); 2 weeks: (Pb4.78Ca5.22)(VO4)6(F0.6O0.7) 7 weeks: (Pb7.6Ca7.6)(VO4)6(F0.6O0.7) 7 weeks: (Pb7.6Ca7.6)(VO4)6(F0.6O0.7) ± [Pb6.8Ca5.2](Pb0.64Ca3.36)[Pb4.14Ca1.96] 2

The crystal structure of (Pb5Ca5)(VO4)6(F1 2 < 0.1 and 0.6 mm, respectively, were inserted. Soller slits in the incident and diffracted paths were used to limit the beam divergence to within 2.3°, and a post specimen mono-
Scans were collected from samples rotating around the holder axis at 30 r.p.m. over the angles 10–140° 2θ with a step size of 0.01° and counting time of 5 s per step. Under these conditions the gross intensity of the strongest peak was 2000–3000 counts. Prior to data collection, the fired agglomerates were mechanically ground to fine powders to minimize crystal size effects and mixed with approximately 25 wt.-% of standard silicon powder with a0 = 5.43088 Å (NIST 640c) to internally calibrate the zero shift.

For each data set, a four-coef®cient background polynomial, a zero error and a sample displacement were re®ned sequentially followed by unit-cell parameters, scale factor and peak shape. Isotropic temperature factors for calcium, lead and vanadium were re®ned, however, those for oxygen and ﬂuorine were set at 1 Å2. X-ray scattering factors for the charged species Ca2+, Pb2+, V5+, O2− and F− were used. Cation positions were re®ned ®rst, followed by the oxygen positions. To ensure reasonable bond lengths in the VO4 tetrahedra, fractional coordinates were constrained close to the V—O bond length of 1.735 Å (Shannon & Prewitt, 1970) using a penalty function. Calcium and lead occupancies were then released such that N(Ca) + N(Pb) = 1 was satis®ed for the A1

Figure 2
Unit-cell parameter trends after annealing for 10 h at 1073 K for (Pb2xCa10−2x)(VO4)6(F1−2xOx)2. Vergard’s Law is obeyed in independent compositional segments for a and c. Error bars are smaller than the graphing symbols (see Table 1).
Table 3
Selected bond distances (Å) in (Pb\textsubscript{x}Ca\textsubscript{10-x})(VO\textsubscript{4})\textsubscript{y}(F\textsubscript{1-2y}O\textsubscript{y})\textsubscript{2} as a function of sintering time.

<table>
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<th>Composition</th>
<th>10 h</th>
<th>1 week</th>
<th>2 weeks</th>
<th>7 weeks</th>
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<tr>
<td>A\textsuperscript{I}—O1 × 3</td>
<td>2.409 (14)</td>
<td>2.410 (15)</td>
<td>2.394 (14)</td>
<td>2.403 (14)</td>
</tr>
<tr>
<td>A\textsuperscript{I}—O2 × 3</td>
<td>2.612 (20)</td>
<td>2.616 (18)</td>
<td>2.601 (19)</td>
<td>2.605 (19)</td>
</tr>
<tr>
<td>Average</td>
<td>2.511</td>
<td>2.513</td>
<td>2.498</td>
<td>2.504</td>
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Table 4
Symmetry of apatite-family members.

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<th>Special projections</th>
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<td>P\textsubscript{6}i/m (176)</td>
<td>p6</td>
</tr>
<tr>
<td>P\textsubscript{6} (174)</td>
<td>p3</td>
</tr>
<tr>
<td>P\textsubscript{6}&lt;sub&gt;x&lt;/sub&gt; (173)</td>
<td>p6</td>
</tr>
<tr>
<td>P\textsubscript{5} (147)</td>
<td>p6</td>
</tr>
<tr>
<td>P\textsubscript{2}&lt;sub&gt;1&lt;/sub&gt;/m (11)</td>
<td>p2</td>
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and A\textsuperscript{II} cations – less than 100% occupancy was not considered. Patterns were analysed systematically from the calcium to lead end-members. In all refinements the apatite was treated as a single phase, although for Ca\textsubscript{10}(VO\textsubscript{4})\textsubscript{6}F\textsubscript{2} a trace of Ca\textsubscript{10}(VO\textsubscript{4})\textsubscript{2} was present.

For high-resolution transmission electron microscopy (HRTEM) powdered specimens were dispersed with ethanol in an ultrasonic bath for 5 min and a drop of suspension deposited onto a holey carbon-coated copper grid. Images were collected digitally using a JEM-3010 microscope (C\textsubscript{s} = 1.2 mm) operated at 300 kV and fitted with a low-background Gatan double tilt holder. Crystals were tilted to [2110] and [0001] zone axes. Simulated images were calculated by the multislice method (Stadelmann, 1987) using as a starting point the average structures determined by XRD refinement. A slice thickness of about 3 Å was used and the absorption coefficient fixed as 0.1. Other parameters included in the simulation process were objective aperture diameter ≃ 10 nm\textsuperscript{-1}, spread of focus ≃ 10 nm and beam semi-convergence≈ 0.8 mrad. Digital filtering and tests for local symmetry were carried out using Fourier filtering methods, as implemented in CRISP (Hovmöller, 1992).

3. Results

3.1. Variations with composition

The unit-cell constants and A-site partitioning coefficients for the vanadinites annealed for 10 h are collected in Table 1. As (Pb\textsubscript{x}Ca\textsubscript{10-x})(VO\textsubscript{4})\textsubscript{y}F\textsubscript{2} became progressively more plumbo-sous the lattice parameters dilate as the lead (effective ionic radii = 1.29 Å for VIII coordination) to calcium (1.12 Å) ratio increases (Shannon & Prewitt, 1970) (Fig. 2). Dilation of the a and c edges did not obey Vergard’s law over the entire compositional join, but were composed of two linear segments such that

\[ a = 9.7073 + 0.04693x \quad \text{for} \quad 0 < x < 6 \] (1a)

\[ a = 10.1579 - 0.04036(1 - x) \quad \text{for} \quad 7 < x < 10 \] (1b)

\[ c = 7.0153 + 0.03091x \quad \text{for} \quad 0 < x < 3 \] (2a)

\[ c = 7.4585 - 0.05205(1 - x) \quad \text{for} \quad 4 < x < 10 \] (2b)

Volume = 572.5 + 8.5282x \quad \text{for} \quad 0 < x < 3 \] (3a)

Volume = 667.05 - 10.045(1 - x) \quad \text{for} \quad 4 < x < 10. \] (3b)

In all cases the fit residuals \( R^2 > 0.99. \) The rate of change of the lattice parameters as a function of composition is controlled by the partitioning of lead and calcium, which in turn determines the rate of change of the metaprism twist angle (\( \psi \)) (Dong & White, 2004). As described below, the materials annealed for 10 h had not attained equilibrium, the partitioning coefficient for lead over the A\textsuperscript{I} and A\textsuperscript{II} sites did not vary systematically (Table 1), and HRTEM revealed substantial disorder at the unit-cell scale. While structure refinement from such powders represents an averaging of local structures, for all compositions \( k_{pb} \) was less than the expected value for equal partitioning over the large cation sites, indicating lead enrichment of the A\textsuperscript{II} position (Table 1). It should be noted that the correlations between cell constants and composition for these vanadinites in disequilibrium are quite distinct from those obtained for equilibrated material (see Fig. 2 in Dong & White, 2004).
3.2. Variations with annealing time

Annealing of Pb$_5$Ca$_5$(VO$_4$)$_6$F$_{2.8}$ at 1073 K for a cumulative total of 7 weeks resulted in a reduction in the $c/a$ ratio that advanced especially rapidly in the first 2 weeks (Fig. 3b), beyond which the cell parameters stabilized (Table 2). Relatively small changes from 2–7 weeks firing are most probably related to incipient vanadium reduction and/or loss of fluorine and lead. The trend in the axial ratio was tracked by $k_{Pb}$ and the metaprism twist angle $\varphi$. A significant redistribution of lead occurred with the $A^{III}$ site becoming substantially enriched (Fig. 3c). After 7 weeks $k_{Pb}(A^{II}/A^{III})$ was 0.17 compared with 0.52 for 10 h material. As the $A^{IV}O_6$ metaprism lost lead, the apatite channel expanded to accommodate

Figure 4
Polyhedral representations of (a) the ‘average structure’ of non-equilibrated $(Pb_{4.62}Ca_{5.38})(VO_4)_6F_2 \simeq [Pb_{1.56}Ca_{2.44}][Pb_{2.06}Ca_{3.44}](VO_4)_6F_2$ and (b) the equilibrated structure of $(Pb_{4.76}Ca_{5.64})(VO_4)_6(F_{0.6}O_{0.7}) \simeq [Pb_{1.56}Ca_{2.44}][Pb_{4.08}Ca_{1.92}](VO_4)_6(F_{0.6}O_{0.7})$ projected down [0001]. The $A^{IV}O_6$ metaprisms and $VO_4$ tetrahedra are emphasized to highlight the cooperative movements of these polyhedra. Not shown are three more distant O atoms that cap each (0001) metaprism face.

Figure 5
Calculated [0001] high-resolution electron microscope images for $(Pb_{4.62}Ca_{5.38})(VO_4)_6F_2$ with (a) $x = 0$, (b) $x = 5$ and (c) $x = 10$. Input crystal and atomic parameters were derived from refined X-ray diffraction data. Substantial contrast differences appear over the compositional range that can be recognized in experimental images.

Figure 6
[0001] high-resolution electron micrographs collected from $(Pb_{4.76}Ca_{5.64})(VO_4)_6(F_{0.6}O_{0.7})$ thin crystal wedges annealed for (a) 10 h and (b) 7 weeks. Inserts of the power transforms confirm the orientation. The upper image is poorly equilibrated with microdomains 2 nm in diameter arising from local variation in Ca/Pb content, as would be anticipated from the multislice simulations (see Fig. 5). Conversely, the equilibrated sample shows regular contrast changes in passing from the thin edge (left) to the thicker crystal (right).
additional lead with $\psi$ becoming more acute and ultimately reducing to $14.4^\circ$ from $22.0^\circ$ (Fig. 3a).

Throughout annealing the VO$_4$ tetrahedra were essentially invariant with an average V–O bond length of 1.71 Å, a figure somewhat smaller than the soft constraint value of 1.735 Å. The A$^{4+}$ metaprisms bonds contracted slightly and the A$^{4+}$O$_6$F polyhedron expanded as Pb/Ca partitioning was established (Table 3). The disposition of the A$^{4+}$O$_6$ and VO$_4$ polyhedra before and after annealing is illustrated in Fig. 4. In disequilibrium the metaprisms are substantially twisted, as the channels are rich in smaller calcium, which in turn drives apart the regular VO$_4$ tetrahedra. The refinements also suggest that some fluorine loss occurred, probably through replacement of $2F^{-} \rightarrow O^{2-}$, but this could not be examined in detail using the current data.

3.3. A$^{4+}$/A$^{11+}$ local disorder

The investigation of cation order–disorder in apatites by HRTEM is challenging on two counts. First, it is well known that for some compositions (especially the extensively studied hydroxyapatite HAp), etching and amorphization can proceed rapidly unless low electron fluxes and/or cooled specimen stages are used (e.g. Sato et al., 2002). However in a supplementary investigation, Dong et al. (2004) established that while vanadinite will undergo an electron-beam-induced transformation to perovskite via glaserite when subjected to intense or prolonged irradiation, the conditions used in the current experiments were relatively mild and would not have compromised the structure beyond partial loss of fluorine. Second, the structure of apatite is relatively complex and without the benefit of a short ($\lesssim 3\,\text{Å}$) crystallographic projection providing an unobscured view of homoatomic cation columns, intuitive interpretation of HRTEM images is impossible. For the specific case of lead substitution in HAp, calculations by Brés et al. (1986) suggested that microchemical ordering over the A$^{4+}$/A$^{11+}$ sites may be recognized in thicker crystals when viewed along [0001] with a 400 keV microscope. Our calculations of [0001] thickness defocus wedges for (Ca$_{10}$)(VO$_4$)$_6$F$_2$, (Pb$_{5}$Ca$_5$)(VO$_4$)$_6$F$_2$ and (Pb$_{10}$)(VO$_4$)$_6$F$_2$ also imply that unit-cell scale fluctuations in Ca/Pb...
ratio will be detectable as subtle changes in image contrast (Fig. 5). Basal plane micrographs collected from short-annealed non-equilibrated material displayed obviously mottled contrast ascribed to short-range compositional disorder (Fig. 6a). However, longer heat treatment yielded crystals with a regular progression of contrast from thinner to thicker regions (Fig. 6b).

3.4. Image processing

The subgroups adopted by apatites are summarized in Table 4 along with the plane symmetries for the [100] \equiv [2110] and [001] \equiv [0001] special projections (White & Dong, 2003). Using the methods of Hovmöller (1992) and Zou et al. (1996), Fourier processing of equilibrated (Pb,Ca)\(_4\)(VO\(_4\))\(_6\)(F\(_{1-x}\)O\(_x\))\(_2\), [0001] images yielded comparable figures of merit (\(R_{\text{amplitude}}\) and \(\varphi_{\text{clos}}\)) for \(p \leq 6\) (consistent with space groups \(P6_3/m\), \(P6_3\), \(P2_1/m\), and \(P3\)) ([0001] symmetries (Fig. 7a). A similar analysis of non-equilibrated (Pb,Ca)\(_4\)(VO\(_4\))\(_6\)(F\(_{1-x}\)O\(_x\))\(_2\) \([2110]\) images consistently gave equivalent results for \(p = 1\) and \(p = 2\) \(m\) (Fig. 7c). Therefore, either \(P6_3/m\) or \(P6_3\) are possible space groups for these apatites. Following normal crystallographic practice, the correspondence of the potential maps to the crystal structures are illustrated in Figs. 6(b) and (d).

Simulated [0001] and [2110] images of (Pb,Ca)\(_4\)(VO\(_4\))\(_6\)(F\(_{1-x}\)O\(_x\))\(_2\) and (Pb,Ca)\(_4\)(VO\(_4\))\(_6\)(F\(_{1-x}\)O\(_x\))\(_2\) were calculated from input data derived from Rietveld refinement. For equilibrated [0001] the relative intensities of the processed and simulated images agree well (Fig. 6a). For \(x = 0.5\) and with \(0.16 < k_{\text{Pb}} < 0.67\), the images are relatively insensitive to the \(k_{\text{Pb}}\) used and the potential maps cannot differentiate \(A\)-cation ordering quantitatively. On the other hand, for non-equilibrated samples the [120] of calculated and experimental intensities were quite dissimilar, although an extensive exercise in varying crystallographic and microscopic parameters was undertaken to obtain a more satisfactory match.

4. Discussion

The \(a\) and \(c\) cell constants varied linearly in compliance with Vergard’s Law over two compositional ranges 0 \(< x < \sim 3.5\) and \(\sim 3.5 < x < 10\) (Fig. 2). This behaviour suggests that while the materials were single phase over the entire compositional range, long annealing of compositions close to (Pb\(_3\),Ca\(_6\))(VO\(_4\))\(_6\)(F\(_{1-x}\)O\(_x\))\(_2\) may promote phase separation, which was subsequently confirmed (Dong & White, 2004). A reduction in slope of the cell parameters as a function of composition indicates that the rate of change of \(\varphi\) has changed due to different modes of channel filling. There was no correlation of \(k_{\text{Pb}}\) with lattice constants, as unit-cell scale disorder was ‘averaged’ during refinement in a manner not accommodated by the Rietveld model.

During long-term annealing, metaprism volume and \(\varphi\) decreased linearly as a function of the average \(A^+\) ionic radius (Fig. 9). For (Pb,Ca)\(_4\)(VO\(_4\))\(_6\)(F\(_{1-x}\)O\(_x\))\(_2\) vanadinite annealed from 10 h to 7 weeks, \(\varphi\) ranged from 22 ± 1 to 14 ± 2 such that the \(A^+\)–O bond lengths decreased slightly, with simultaneous lead enrichment of \(A^{11}\) leading to expansion of the tunnel cavity and an increase in the average bond length of the \(A^{11}\)O\(_4\)F polyhedra from 2.535 to 2.589 Å. Tunnel opening is accomplished through reduction in \(\varphi\), although the precise significance of the twist angles refined from the short annealed and heavily disordered vanadinite is not certain.

The kinetics for attaining equilibrium are quite slow and several weeks annealing near the melting point are required to stabilize \(k_{\text{Pb}}\) with disequilibrium yielding HRTEM images interpretable as microdomains of variable Ca/Pb content. Longer firing serves to steady partitioning, but vanadium reduction and/or loss of lead and fluorine may become significant over extended periods. While most compositions could be satisfactorily fitted to \(P6_3/m\) [the exception being \(P2_1/m\) Ca\(_{10}\)(VO\(_4\))\(_2\)F\(_2\)], the presence of local regions with lower symmetry in the poorly equilibrated vanadinite should not be ruled out, despite reasonable matching of the Fourier processed images with simulated images. In these materials the inability to match semi-quantitatively the contrast in [2110] processed images and simulations is consistent with differences of \(k_{\text{Pb}}\) at the unit-cell level. Careful inspection of the [120] processed image (Fig. 8b) shows that at short range the unit cell may be doubled along [0001].

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References