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Least-squares thermal expansion tensor of vanadate and arsenate triclinic apatites derived from laboratory X-ray powder diffraction cell data

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Cell data for triclinic end-member $\text{Ca}_{10}(\text{VO}_4)_6\text{F}_2$ and $\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2$ apatites were measured in the temperature range from 303 to 773 K. Reversible phase transitions at, respectively, 453 and 583 K are shown and attributed to mobility of contact surfaces for triclinic twins within a mosaic block at about the transition temperature. The simple method developed here is based on 12 separate linear regressions. The first six regressions are on observations for individual lattice parameters a , b , c , α , β or γ . The last six are on linear data sets, each involving a single expansion coefficient α_{11} , α_{22} , α_{33} , α_{12} , α_{13} or α_{23} . Singular-value decomposition of the least-squares thermal expansion tensors obtained below the transition temperatures shows that both materials actually contract considerably along $[2\bar{1}4]$ upon heating. Expansion in the plane perpendicular to this direction differs somewhat for the two materials. In contrast, the expansion above the transition temperature is barely anisotropic in both materials. The ability to measure thermal expansion tensors for triclinic materials with decent accuracy from routine powder data is demonstrated. This possibility extends the applications of the powder method because some samples may not be readily available in single-crystal form.

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1. Introduction

Triclinic apatites have recently been shown by Baikie *et al.* (2007) to be a new structure type where topologically similar rotations of tetrahedral groups present in arsenate and vanadate apatites are also present in several other apatites from the literature. They are also predicted to exist for a number of other apatite compositions. Such rotations of tetrahedra are shown to be needed to accommodate a misfit between the size of the tetrahedral and octahedral ions in the hexagonal apatite structure type. It is then reasonable to anticipate changes to those rotations under the cell stretching caused by thermal expansion. In other words, we expect somewhat unusual thermal expansion behavior in those materials. We have accordingly collected powder diffraction cell data as a function of temperature for vanadate and arsenate triclinic apatites in 10 K steps from 303 to 773 K, and analyzed them for thermal expansion coefficients. As we were initially unaware of post-1973 literature on the topic of strains and thermal expansion (Schlenker *et al.*, 1975, 1978; Haussühl, 1983; Jessen & Küppers, 1991; Catti, 1992; Paufler & Weber, 1999), we did not find such an analysis for triclinic materials in the literature. We accordingly devised one that we report below. In spite of previous detailed algebraic work by, for example, Jessen & Küppers (1991) and Paufler & Weber (1999) on the least-squares extraction of thermal expansion

coefficients for triclinic crystals, we hope that the simplicity of our geometric approach will be of sufficient interest to readers. It shows that thermal expansion in the general case is an easily accessible physical property for X-ray powder diffractometers equipped with adjustable heating or cooling. This is an important fact about a key property of materials that may have been partially obscured by the complexity of previous exact algebraic work. In the process, we also discovered phase transitions in the vanadate and arsenate apatites.

2. Extraction of the thermal expansion tensor from powder data

2.1. Theory

Standard physics textbooks define the thermal expansion coefficient α of isotropic matter through $\Delta L/L = \alpha \Delta T$, where $\Delta L/L$ is the linear strain and ΔT is the temperature change. Similarly, standard crystal-physics textbooks, such as Nye (1957) and Wooster (1973), define the thermal expansion tensor α through $\epsilon = \alpha \Delta T$, where ϵ is a homogeneous strain caused by a temperature change ΔT in a crystalline material. This definition shows that α is a symmetrical rank-2 tensor because strains are defined to be symmetrical rank-2 tensors. According to tensor algebra and notation, a vector with Cartesian components a_j at temperature T then has compo-

nents $a'_i = a_i + \alpha_{ij}a_j\Delta T$ at temperature $T + \Delta T$. This allows, for example, the recalculation of cell data or of the shape of the unit cube in §2.1.1 at all temperatures from their dimensions and orientation at temperature T and the thermal expansion tensor.

2.1.1. A ruler-and-protractor way to measure coefficients of α . Fig. 1 illustrates a straightforward way to measure the coefficients of tensor α at a given temperature T_0 . We first machine a cube of crystalline matter with unit edges along the Cartesian reference axes of the material at temperature T_0 . To a first-degree approximation, we can express the thickness Θ_i between the pair of parallel faces approximately perpendicular to edge i at temperature $T_0 + \Delta T$ as $\Theta_i(T_0 + \Delta T) \simeq 1 + \alpha_{ii}\Delta T$. Neglecting second-order terms, we can also relate the dihedral angle θ_{jk} between the faces j and k of the cube at temperature $T_0 + \Delta T$ to coefficients α_{jk} and α_{kj} through $\cos\theta_{jk} \simeq (\alpha_{jk} + \alpha_{kj})\Delta T$.

As α_{jk} and α_{kj} are equal because α is symmetrical, measurement of the thickness Θ_i and of the dihedral angle θ_{jk} then gives

$$\alpha_{ii} \simeq [\Theta_i(T_0 + \Delta T) - 1]/\Delta T, \quad (1)$$

and

$$\alpha_{jk} = \alpha_{kj} \simeq (\cos\theta_{jk})/(2\Delta T). \quad (2)$$

The approximate relations [equations (1) and (2)] above are geometrically obvious. We also derive them analytically in Appendix A.

Figure 1

Top: a unit cube machined along the IRE axes at temperature T . Bottom: the same cube, but deformed at temperature $T + \Delta T$. The thickness Θ_i is measured along the normal to face i . The dihedral angle θ_{jk} can be measured with a protractor at the edge between face j and face k . It is also the angle between the normal to plane j and that to plane k .

2.1.2. A corresponding way to calculate α from cell data.

At temperature T_0 , the normal to face i of the cube limited by edges j and k is then a unit vector with fractional components $\mathbf{h}_i$ in the reciprocal crystallographic reference system. As the number of atomic planes constituting the cube is not altered by thermal expansion, it follows that the reciprocal components of $\mathbf{h}_i$ are not altered either by dimensional changes brought about by temperature changes.

Those indices $\mathbf{h}_i$ can be calculated as follows. Matrix $\mathbf{D}$ relates direct-space *column* vectors $\mathbf{X}$ referred to the Cartesian axes, and the crystallographic components of corresponding direct-space *column* vectors $\mathbf{u}$ through $\mathbf{X} = \mathbf{D}\cdot\mathbf{u}$. Similarly, Cartesian reciprocal *row* vectors $\mathbf{Y}$ and reciprocal crystallographic *row* vectors $\mathbf{h}$ are accordingly related through $\mathbf{Y} = \mathbf{D}^{-1}\cdot\mathbf{h}$. As $\mathbf{Y}$ is the identity matrix $\mathbf{I}$ for the faces of the Cartesian unit cube at temperature T_0 , it follows that the reciprocal vectors $\mathbf{h}$ representing the faces of the cube at temperature T_0 are the *rows* of $\mathbf{D}$ because $\mathbf{D}^{-1}\cdot\mathbf{D} = \mathbf{I}$. We can accordingly follow the evolution *versus* T of the reciprocal Cartesian vectors representing the faces of the cube as that of the *rows* of $\mathbf{Y} = \mathbf{D}^{-1}(T)\cdot\mathbf{D}(T_0)$. The numerical expression for matrix $\mathbf{D}$ derives directly from the measured cell data $\mathbf{C}(T)$ and the actual selection of Cartesian axes.

Having determined $\mathbf{h}_i$ at temperature T_0 , the above ideal experiment of monitoring the thicknesses Θ_i and dihedral angles of a cube can then be duplicated by calculations from just the knowledge of the cell data $\mathbf{C}(T)$ over a range of temperature about T_0 . The corresponding calculations are

$$\Theta_i(T) = 1/|\mathbf{Y}_i|(T), \quad (3)$$

$$\cos[\mathbf{Y}_j(T) \wedge \mathbf{Y}_k(T)] = [\mathbf{Y}_j(T)\cdot\mathbf{Y}_k(T)]/[\|\mathbf{Y}_j(T)\|\|\mathbf{Y}_k(T)\|], \quad (4)$$

where $\mathbf{Y}_i$, $\mathbf{Y}_j$ and $\mathbf{Y}_k$ are Cartesian vectors corresponding to crystallographic $\mathbf{h}_i$, $\mathbf{h}_j$ and $\mathbf{h}_k$ mutually perpendicular reciprocal unit vectors at T_0 derived from the cell geometry at temperature T_0 . Entering those values from equations (3) and (4) in the formulas (1) and (2) for α_{ii} and α_{jk} gives equations (5) and (6),

$$\alpha_{ii}\Delta T \simeq [1/|\mathbf{Y}_i(T_0 + \Delta T)|] - 1, \quad (5)$$

$$\alpha_{jk}\Delta T \simeq -\{[\mathbf{Y}_j(T_0 + \Delta T)\cdot\mathbf{Y}_k(T_0 + \Delta T)]/[\|\mathbf{Y}_j(T_0 + \Delta T)\|\|\mathbf{Y}_k(T_0 + \Delta T)\|]\}/2. \quad (6)$$

As observations (5) and (6) involve a single variable (one expansion coefficient) each, the whole problem is then amenable to individual linear regression on each of the six independent thermal expansion coefficients α_{11} , α_{22} , α_{33} , α_{23} , α_{13} and α_{12} .

2.2. Implementation

2.2.1. Least-squares cell data at temperature T_0 . We start by finding the least-squares solution to the problem of cell data at temperature T_0 and its temperature dependence. This is obtained by individual linear regression for each of the six cell parameters $a, \dots, \gamma$ in the temperature range about T_0 . From this information, we produce the cell $\mathbf{\Gamma}(T_0)$ that

represents the least-squares fit at T_0 for the experimental cell data $\mathbf{C}(T)$. We then calculate matrix $\mathbf{D}(T_0)$ from the least-squares cell $\mathbf{\Gamma}(T_0)$ by, for example, applying the IRE rules (Brainerd, 1949) for triclinic symmetry. In the triclinic case, the axes XYZ of the right-handed IRE reference system are selected with X along crystallographic $\mathbf{a}^*$, and Z along $\mathbf{c}$. The corresponding IRE expression for matrix $\mathbf{D}$ can be found at many places in the literature, for example, as equation (1) of Schlenker *et al.* (1978). Other selections of Cartesian axes can be useful for specific purposes.

2.2.2. Least-squares extraction of α and standard uncertainties. We can follow the evolution *versus* T of the reciprocal Cartesian vectors representing the faces of the cube as that of the rows of $\mathbf{Y} = \mathbf{D}^{-1}(T) \cdot \mathbf{D}(T_0)$. Using equations (5) and (6), each cell observation at temperature $T_0 + \Delta T$ then produces six experimental values of $\alpha_{ij}\Delta T$, one for each independent coefficient α_{ij} . Performing individual linear regressions on these data sets gives least-squares solutions for α_{ij} as well as standard uncertainties on corresponding values.

2.2.3. Principal directions and principal values for the tensor. Diagonalization of α by singular-value decomposition (SVD) gives the principal values as well as the direction cosines $\mathbf{X}$ for the principal axes of α in the IRE reference system. The direct-space crystallographic indices $\mathbf{u}$ of Cartesian directions $\mathbf{X}$ can then be found by left-multiplication of $\mathbf{X} = \mathbf{D} \cdot \mathbf{u}$ by $\mathbf{D}^{-1}$, giving $\mathbf{D}^{-1} \cdot \mathbf{X} = \mathbf{u}$, hence $\mathbf{u}$.

3. Experimental

Sample synthesis was previously reported by Baikie *et al.* (2007). The data collection was carried out using a Bruker D8 Advance, equipped with a Cu tube and a Vantec PSD with radial Soller slits to reduce the background at low angles. A divergence slit of 0.2° was used for all the experiments to avoid beam-overspill at low angles. As the goniometer circle was 500 mm, the Vantec window was set for 10° .

The temperature stage used was an Anton-Paar HTK1200 chamber, which has been fitted with a stepper motor (Anton-Paar) to enable automatic correction for temperature-dependent displacement of the stage. The height reference point for room temperature (297 K) was determined using the peak position of the 111 reflection of SRM640c silicon.

The calibration of stage displacement with temperature was carried out using SRM674a corundum and a high crystallinity quartz in two separate experiments between 303 and 1273 K. Other than at 303 K, the data were collected at 323 K and 373–1273 K in 100 K steps. The sample displacement was refined in *TOPAS* (Bruker, 2005) during a Pawley (1981) refinement of the unit cells.

In addition to the controlled-temperature experiment, a data set was collected at room temperature prior to the start of the experiment. The data presented here were collected between 8 and $90^\circ 2\theta$ using a 0.0142° step and an effective count time of 0.5 s between 303 and 773 K in 10 K steps. The programmed ramp rate used was 0.1 K s^{-1} . However, the temperature controller slows to 0.01 K s^{-1} within 10 K of the set temperature, so the actual ramp rate was significantly

slower than 0.1 K s^{-1} . A dwell time of 5 min was added during the data collection for the sample to equilibrate.

Pattern decomposition of low-symmetry cells has been shown to be potentially problematic *versus* Rietveld refinement simply because of the high density of *hkl* reflections (Peterson, 2005). Unlike Rietveld refinement, there is no indication of the relative intensities of the different reflections, leading to possible mis-identification of reflections with significant intensity *versus* those with little or no intensities. This could obviously induce error into the cell refinement. The apatites in this study are triclinic and, despite the unit cells being smaller than the tricalcium silicate analyzed by Peterson (2005), are still likely to be prone to problems in pattern decomposition.

Data analysis was carried out using a beta version dated 23 January 2007 of *TOPAS 4*. A methodology was employed to try and prevent such mis-assignment of *hkl* peak intensities. Initially, the room-temperature data were refined using a Rietveld refinement with the crystal structures previously published by Baikie *et al.* (2007). The fundamental parameter instrument broadening for linear PSDs incorporated into *TOPAS 4* was used, which appeared to fit the data quite satisfactorily without any additional corrections for axial divergence. Parameters refined included cell parameters, Lorentzian size broadening and Gaussian microstrain broadening, together with sample displacement. The zero point error was not refined as it had previously been determined to be negligible on system alignment. No attempt was made to refine atomic positions.

The refinement was then exported to an *hkl* phase in *TOPAS* terminology, which preserves the peak positions and intensities. The default 'delete hkl on refinement' option was unchecked to keep the peak intensities from the Rietveld refinement as the starting point. After refining this cell to the room-temperature data using a Pawley (1981) fit, the final decomposition result in terms of cell parameters, size parameter, microstrain parameter, peak positions and peak intensities were exported to a *TOPAS* 'inp' file. This 'inp' file was then imported for the analysis of the 303 K data. Once again, the default 'delete hkl on refinement' option was unchecked, the sample displacement from the previous refinement was entered and fixed, and the cell parameters were fixed. The Pawley fit was then run in order to fit the background with a fifth-order Chebychev polynomial, before refining the cell parameters and sample displacement. This process was continued iteratively until all of the data sets were analyzed.

4. Results

Experimental data for the arsenate apatite are shown in Figs. 2 and 3. Fig. 2 shows data for the whole temperature range but for a limited 2θ range. The three-dimensional plot visually shows the triclinic-to-hexagonal phase transition, which appears to progress as a second-order phase transition. Fig. 3, however, shows data for the full 2θ range for the triclinic structure at 303 K before heating, the metrically hexagonal

Figure 2
Three-dimensional plot showing the progression of the triclinic to hexagonal phase transition with temperature for $\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2$.

Figure 3
Plot showing the diffraction patterns of $\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2$ at 303, 773 K and 303 K on cooling. The 773 K plot has been displaced vertically by 10000 counts and the cooled 303 K plot by 35000 counts.

phase at 773 K, and then at 303 K after cooling. The triclinic distortion in the arsenate apatite at 303 K is very obvious in Fig. 2. The vanadate apatite behaves in a very similar fashion, although the room-temperature triclinic distortion is not as large.

The metrically hexagonal nature of the high-temperature phases can be seen in Fig. 4. The fit to the data with the metrically hexagonal cell is almost identical to the triclinic $P\bar{1}$, although the latter has over five times the number of reflections in which to fit the peaks. Differences in the fits may partially arise as a result of small peak shifts induced by the slight difference in refined sample displacement between the triclinic and hexagonal cells.

Figs. 5 and 6 report in graphic form the evolution of the six cell parameters, the cell volume, the column-length and the

Figure 4
Difference plots for Pawley fits to $\text{Ca}_{10}(\text{VO}_4)_6\text{F}_2$ at 773 K using (a) $P6_3/m$ and (b) $P\bar{1}$ cells.

microstrain in the material *versus* temperature for, respectively, the vanadate and the arsenate materials. The corresponding data have been deposited as supplementary tables S1(a) and S1(b).¹

The above data were analyzed as follows. The essentially linear sections between 303 and 393 K for vanadate and 303 and 573 K for arsenate below the transition temperature, respectively, gave the thermal expansion tensors in the IRE reference system that are shown in Tables 1(a) and 1(b), together with their principal values. Lattice vectors lying approximately along the principal axes of α are also indicated in this table. Similarly, the linear sections between 523 and 773 K for vanadate, as well as 643 and 773 K for arsenate, are shown in Tables 2(a) and 2(b). If we assume that the arsenate and vanadate materials are hexagonal above the transition temperature, a fact that should be more firmly established through additional study of the phase transitions, we obtain the constrained results in Tables 2(c) and 2(d).

¹ Supplementary data are available from the IUCr electronic archives (reference: DB5031). Services for accessing these data are described at the back of the journal.

Table 1

Least-squares thermal expansion tensor α in IRE axes below transition temperature for (a) vanadate and (b) arsenate apatite.

(a) Triclinic vanadate apatite at 343 K, data from 303 to 393 K.

$$\begin{bmatrix} 301(15) & 83(8) & -220(9) \\ 83(8) & 236(16) & 223(23) \\ -220(9) & 223(23) & 46(6) \end{bmatrix} \times 10^{-7} \text{ K}^{-1}.$$

Principal values are

$$(443 \quad 346 \quad -207) \times 10^{-7} \text{ K}^{-1},$$

respectively, and approximately along $[10\bar{1}]$, $[241]$ and $[2\bar{1}4]$. See Fig. 5.

(b) Triclinic arsenate apatite at 388 K, data from 303 to 473 K.

$$\begin{bmatrix} 371(9) & 119(7) & -239(15) \\ 119(7) & 150(11) & 140(6) \\ -239(15) & 140(6) & 68(5) \end{bmatrix} \times 10^{-7} \text{ K}^{-1}.$$

Principal values are

$$(507 \quad 248 \quad -166) \times 10^{-7} \text{ K}^{-1},$$

respectively, and approximately along $[85\bar{5}]$, $[165]$ and $[2\bar{1}4]$. See Fig. 6.

5. Discussion

This study demonstrates the quality of cell data that can be obtained nowadays with in-lab X-ray instrumentation. Cell data recalculated at each temperature from least-squares cell data at temperature T_0 and least-squares thermal expansion coefficients extracted here reproduce the experimental data within very few standard uncertainties for each cell parameter. This demonstrates that the standard uncertainties printed by the instrument for refined cell data are then realistic estimates of uncertainties and not optimistic assessments of precision for cell parameters.

It is remarkable that, for both vanadate and arsenate apatites, the direction with greatest contraction upon heating is approximately along $[2\bar{1}4]$ shown in Fig. 7. In contrast, the directions with greatest expansion differ in both materials. There is little doubt that the observed contraction has to do with the cell shear that accompanies the rotations of tetrahedral groups upon transformation to the triclinic phase. Quantum calculations model quite well this cell shear at 0 K (Baikie *et al.*, 2007), but this phenomenon baffles our crystal-chemical intuition. We have accordingly not been able to rationalize the reason why maximum contraction is along this direction. However, this observation reinforces the claim that the two materials are isostructural.

Cell data evolution as a function of temperature is usually visualized with graphs of cell edges and cell angles. We feel that the analysis presented here in terms of thermal expansion tensor coefficients is considerably more informative than such graphs. Firstly, this analysis carries a measure of the precision in the data in the form of standard uncertainties on each coefficient. This analysis also leads to a more global representation of the expansion of the material. There is very little in Figs. 5 and 6 to suggest to the reader that the material

Table 2

Results above transition temperature for (a, c) vanadate and (b, d) arsenate apatite.

(a) Triclinic vanadate apatite at 343 K, data from 303 to 393 K.

$$\begin{bmatrix} 130(5) & -9(4) & 2(6) \\ -9(4) & 135(7) & 5(4) \\ 2(6) & 5(4) & 125(3) \end{bmatrix} \times 10^{-7} \text{ K}^{-1}.$$

The material is barely anisotropic within this temperature range.

(b) Arsenate apatite at 708 K, triclinic data between 643 and 773 K.

$$\begin{bmatrix} 98(28) & -11(8) & -6(5) \\ -11(8) & 103(23) & 13(5) \\ -6(5) & 13(5) & 125(9) \end{bmatrix} \times 10^{-7} \text{ K}^{-1}.$$

The thermal expansion results are imprecise because the cell data are somewhat noisy.

(c) Vanadate apatite at 648 K, 'hexagonal' data between 523 and 773 K. If we assume that the material is hexagonal in the temperature range 523–773 K, the corresponding thermal expansion tensor would be

$$\begin{bmatrix} 140(2) & 0 & 0 \\ 0 & 140(2) & 0 \\ 0 & 0 & 125(2) \end{bmatrix} \times 10^{-7} \text{ K}^{-1}.$$

(d) Arsenate apatite at 708 K, 'hexagonal' data between 643 and 773 K. If we assume that the material is hexagonal in the temperature range 643–773 K, the corresponding thermal expansion tensor would be

$$\begin{bmatrix} 128(3) & 0 & 0 \\ 0 & 128(3) & 0 \\ 0 & 0 & 131(3) \end{bmatrix} \times 10^{-7} \text{ K}^{-1}.$$

The lower noise in cell data results in greater precision on thermal expansion.

actually contracts considerably along $[2\bar{1}4]$. Even without the diagonalization by SVD, the existence of contraction along a principal direction is obvious on the numerical expression of α in Tables 1(a) and 1(b), because the determinant of α is negative. Changes of Cartesian reference system for a rank-2 tensor do not alter its determinant, and therefore, when reduced to diagonal representation, one of the diagonal values will necessarily be negative.

The cell transformations observed here are reversible as clearly shown in Fig. 3. The column length, shown in graph (e) in Figs. 5 and 6, is also seen to increase at the transition while the microstrain shown in graph (f) decreases. Both effects are very clear effects with considerable magnitude. Put together, those three observations are consistent with the following explanation. At synthesis temperature, the material is probably hexagonal, with fairly large mosaic blocks constituting single-crystal coherent regions. Below the transition temperature, two or several triclinic domains can appear in a single mosaic block, causing the apparent decrease of the domain size. Those triclinic domains are static twins occupying a single mosaic block. The crystallite size is then that of a single crystal in the twin. At about the transition temperature, the contact surface between the individuals in the twin becomes mobile. Above the transition temperature, the

structure within the mosaic block then becomes averaged, making the whole mosaic block appear like a single crystal. This causes the apparent increase in the block dimension, the

Figure 5

Plots of the refined parameters: (a) a lattice parameter (Å), (b) b lattice parameter (Å), (c) c lattice parameter (Å), (d) α (°), (e) β (°), (f) γ (°), (g) cell volume (Å³), (h) column length (nm) and (i) microstrain for $\text{Ca}_{10}(\text{VO}_4)_6\text{F}_2$.

Figure 6

Plots of the refined parameters: (a) a lattice parameter (Å), (b) b lattice parameter (Å), (c) c lattice parameter (Å), (d) α (°), (e) β (°), (f) γ (°), (g) cell volume (Å³), (h) column length (nm) and (i) microstrain for $\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2$.

decrease in strain at the transition upon heating and the reversibility of the transition. The number of constituent twin individuals in a mosaic block derives from the ratio of column length above and below the transition temperature. This number turns out to be close to the cube root of 2 for both vanadate and arsenate, thus pointing to a dominant splitting of high-temperature domains into two sub-domain components.

It should be noted that, contrary to recent work by, for example, Schlenker *et al.* (1978), Jessen & Küppers (1991) or Paufler & Weber (1999), our approach is not algebraically bolted to a specific reference system from step one. The reference system here only appears in the matrix **D** of face normals. This is most convenient especially in the case of phase transitions like here, where the use of different Cartesian systems imposed by the IRE rules for different symmetries might obscure rather than clarify issues. It should be noted that neither of the two triclinic cells used here are conventional. They have been selected that way to reflect both the hexagonal pseudosymmetry and the orientation of the common structural pattern of rotations for the tetrahedral groups. Use of those unconventional reference systems is rewarded through exposure of a same direction with

Figure 7

The principal value of thermal expansion that is approximately along $[2\bar{1}4]$ is negative below the transition temperature. (a) The vanadate apatite accordingly contracts by nearly 0.5% along this direction between 303 and 473 K. This lattice vector starts expanding again above 503 K. (b) The arsenate apatite contracts by a similar amount, but more gradually.

maximum contraction. This physical observation reinforces the claim from neutron and electron diffraction (Baikie *et al.*, 2007) that the two materials are isostructural. Sticking too rigidly to a given set of conventions in calculations might have obscured this important fact.

Schlenker *et al.* (1978) print an exact algebraic derivation of strain from cell data for four formalism variants called linear Lagrangian, linear Eulerian, finite Lagrangian and finite Eulerian. The various formalism variants boil down to the same thing for infinitesimal strains as higher-order difference terms between them vanish. The higher-order terms neglected here in the derivation of equations (1) and (2) (Appendix A) also vanish for infinitesimal strains. Results from all those calculations, including ours, will then tend toward the same value as strain magnitudes in the calculation will decrease. Smaller and smaller strain magnitudes will gradually be made possible by development and use of better equipment. The actual numerical values extracted are probably more dependent on details of the way the experimental data are processed than on the formalism actually used. In view of the facts that the average strain magnitude used in this analysis is less than 5×10^{-4} , while the best statistical precision claimed in the results is about 3%, values that would be extracted by the different methods could then hardly differ by more than a fraction of the standard uncertainty.

6. Conclusions

We have developed here a simple approach for the extraction of the coefficients of the thermal expansion tensor α of triclinic materials from precise cell data obtained with laboratory X-ray powder diffraction. The principal axes can then be derived by SVD analysis of α . Rather than extracting the thermal expansion tensor α in triclinic crystals through solving a 6×6 (or larger) system of normal equations, the least-squares method developed here extracts the coefficients in twelve separate linear regressions, the first six on individual lattice parameters ($a, b, c, \alpha, \beta, \gamma$), and the last six on linear data sets yielding the individual expansion coefficients ($\alpha_{11}, \alpha_{22}, \alpha_{33}, \alpha_{12}, \alpha_{13}, \alpha_{23}$). The method is general for all symmetries, but it is most helpful for triclinic and monoclinic symmetries where the principal axes of expansion are not all imposed by symmetry. In the case of vanadate and arsenate fluorapatites, the present study has disclosed two reversible phase transformations at, respectively, 453 and 583 K, with two linear regions for cell-data dependence, one above and one below the transition for both materials. We rationalize the low-temperature phase as triclinic twins within mosaic blocks and the phase transition as due to mobility of their contact surface under the action of temperature, in agreement with unusual observations for the column length and the micro-strain. SVD analysis has disclosed contraction of both materials approximately along $[2\bar{1}4]$, a fact that was not obvious from the customary cell-data *versus* temperature plots. This physical observation reinforces the claim from diffraction that the two materials are isostructural.

APPENDIX A

Derivation of approximate relations (1) and (2) in §2.1.1

Applying tensor relationship $a'_i = a_i + \alpha_{ij}a_j\Delta T$ to vectors $\mathbf{V1}(T) = (1, 0, 0)$, $\mathbf{V2}(T) = (0, 1, 0)$, $\mathbf{V3}(T) = (0, 0, 1)$ along cube edges at temperature T , they, respectively, become

$$\mathbf{V1}(T + \Delta T) = (1 + \alpha_{11}\Delta T, \alpha_{21}\Delta T, \alpha_{31}\Delta T), \quad (7)$$

$$\mathbf{V2}(T + \Delta T) = (\alpha_{12}\Delta T, 1 + \alpha_{22}\Delta T, \alpha_{32}\Delta T), \quad (8)$$

$$\mathbf{V3}(T + \Delta T) = (\alpha_{13}\Delta T, \alpha_{23}\Delta T, 1 + \alpha_{33}\Delta T). \quad (9)$$

The normal to face 1 in Fig. 1(b) is along $\mathbf{V2} \times \mathbf{V3}$ with components

$$\begin{aligned} \mathbf{V2}(T + \Delta T) \times \mathbf{V3}(T + \Delta T) \\ = [(1 + \alpha_{22}\Delta T)(1 + \alpha_{33}\Delta T) - \alpha_{23}\Delta T\alpha_{32}\Delta T, \\ \alpha_{32}\Delta T\alpha_{13}\Delta T - \alpha_{12}\Delta T(1 + \alpha_{33}\Delta T), \\ \alpha_{12}\Delta T\alpha_{23}\Delta T - (1 + \alpha_{22}\Delta T)\alpha_{13}\Delta T]. \end{aligned} \quad (10)$$

Designating by ‘ $\dots$ ’ higher-order terms in ΔT that we do not spell out, this simplifies to

$$(1 + \alpha_{22}\Delta T + \alpha_{33}\Delta T + \dots, -\alpha_{12}\Delta T + \dots, -\alpha_{13}\Delta T + \dots). \quad (11)$$

The square of its length is then

$$\begin{aligned} L1^2 &= [1 + (\alpha_{22} + \alpha_{33}\Delta T)]^2 + (\alpha_{12}\Delta T)^2 + (\alpha_{13}\Delta T)^2 + \dots \\ &= 1 + 2(\alpha_{22} + \alpha_{33})\Delta T + \dots \end{aligned} \quad (12)$$

From the Taylor series expansion for the square root of $(1 + u)$, we deduce

$$L1 = 1 + (\alpha_{22} + \alpha_{33})\Delta T + \dots \quad (13)$$

The thickness between faces 1 is then the projection of $\mathbf{V1}(T + \Delta T)$ onto the direction of $\mathbf{V2}(T + \Delta T) \times \mathbf{V3}(T + \Delta T)$. This is expressed as the dot product with a unit vector along this direction, namely

$$\begin{aligned} \Theta_1 &= [(1 + \alpha_{11}\Delta T)(1 + \alpha_{22}\Delta T + \alpha_{33}\Delta T + \dots) \\ &\quad - \alpha_{21}\Delta T(\alpha_{12}\Delta T + \dots) - \alpha_{31}\Delta T(\alpha_{13}\Delta T + \dots)] \\ &\quad / [1 + (\alpha_{22} + \alpha_{33})\Delta T + \dots] \\ &= \{(1 + \alpha_{11}\Delta T)[1 + (\alpha_{22} + \alpha_{33})\Delta T + \dots] + \dots\} \\ &\quad / [1 + (\alpha_{22} + \alpha_{33})\Delta T + \dots]. \end{aligned} \quad (14)$$

Neglecting the higher-order terms in the simplification by $[1 + (\alpha_{22} + \alpha_{33})\Delta T + \dots]$, we now obtain an approximation for Θ_1 ,

$$\Theta_1 \simeq 1 + \alpha_{11}\Delta T, \quad (15)$$

from which we derive the approximate relation

$$\alpha_{11} \simeq (\Theta_1 - 1)/\Delta T. \quad (1)$$

The dot product of the normals to face 1 and face 2 is the cosine of the angles between them,

$$\begin{aligned} \cos(D12) &= \{[\mathbf{V2}(T + \Delta T) \times \mathbf{V3}(T + \Delta T)] \cdot [\mathbf{V3}(T + \Delta T) \\ &\quad \times \mathbf{V1}(T + \Delta T)]\} / (L1L2). \end{aligned} \quad (16)$$

By circular permutation we derive

$$\mathbf{V}3(T + \Delta T) \times \mathbf{V}1(T + \Delta T) = (-\alpha_{21}\Delta T + \dots, \\ 1 + \alpha_{33}\Delta T + \alpha_{11}\Delta T + \dots, -\alpha_{23}\Delta T + \dots), \quad (17)$$

and

$$L2 = 1 + (\alpha_{33} + \alpha_{11})\Delta T + \dots, \quad (18)$$

from which we obtain

$$\cos(D12) = -[(1 + \alpha_{22}\Delta T + \alpha_{33}\Delta T + \dots)(\alpha_{21}\Delta T + \dots) \\ + (1 + \alpha_{33}\Delta T + \alpha_{11}\Delta T + \dots)(\alpha_{12}\Delta T + \dots) \\ - (\alpha_{13}\Delta T + \dots)(\alpha_{23}\Delta T + \dots)]/(L1L2) \\ = -[(\alpha_{12} + \alpha_{21})\Delta T + \dots]/(1 + \dots). \quad (19)$$

Taking into account the equality $\alpha_{12} = \alpha_{21}$, we obtain the approximate relation

$$\alpha_{12} \simeq -\cos(D12)/(2\Delta T). \quad (20)$$

Because the angle between the normals and the external dihedral angle θ that is measured with a protractor add up to 180° , their cosines are opposite. We accordingly obtain the relation

$$\alpha_{12} \simeq \cos \theta/(2\Delta T). \quad (2)$$

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