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Thermal expansion of fluorapophyllite $\text{KCa}_4[\text{Si}_8\text{O}_{20}]\text{F}\cdot 8\text{H}_2\text{O}$ in the 323–473 K range from X-ray powder diffraction data

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Abstract

Thermal expansion of fluorapophyllite $\text{KCa}_4[\text{Si}_8\text{O}_{20}]\text{F}\cdot 8\text{H}_2\text{O}$ has been analysed in the 323–473 K thermal range by laboratory parallel-beam transmission X-ray powder diffraction. Thermal expansion is markedly anisotropic as indicated by $\bar{\alpha}_a$ of $2.205(13) \cdot 10^{-5}$ and $\bar{\alpha}_c$ of $4.98(15) \cdot 10^{-6}$. Very minor variations of relevant bond distances are observed during heating. Anisotropy of thermal expansion has been attributed to the fact that the mean plane passing through Ca, O(4), K has a prevalent component along the (001).

Key words: High-Temperature X-ray powder diffraction; Rietveld method; apophyllite; thermal expansion.

Introduction

Fluorapophyllite, ideally $\text{KCa}_4[\text{Si}_8\text{O}_{20}]\text{F}\cdot 8\text{H}_2\text{O}$, is an hydrous silicate belonging to the apophyllite group, constituting one end member of the fluorapophyllite-hydroxyapophyllite solid solution series. Fluorapophyllite is tetragonal, space group $P4/mnc$, $Z = 2$, $a = 8.963 \text{ \AA}$, $c = 15.804 \text{ \AA}$. Its structure, first determined by Taylor and Náray-Szabo (1931) and subsequently refined by Colville et al. (1971) and Prince (1971), consists of $\text{Si}_2\text{O}_5^{2-}$ layers stacked along the [001] direction, centered

at $z = 1/4$ and $3/4$ (Figure 1). Silicates sheets are arranged in 4 and 8-membered rings with apical oxygen atoms forming groups of four elements alternatively pointing up or down the c -axis, thus forming a puckered structure. Each layer is linked to the ones above and below through the oxygen atoms coordinated by K^+ and Ca^{2+} and through hydrogen bonding. No significant structural variations have been observed with changing composition along the whole F-OH series (Rouse et al., 1978; Marriner et al., 1990). However, cell parameters may be safely used to establish the

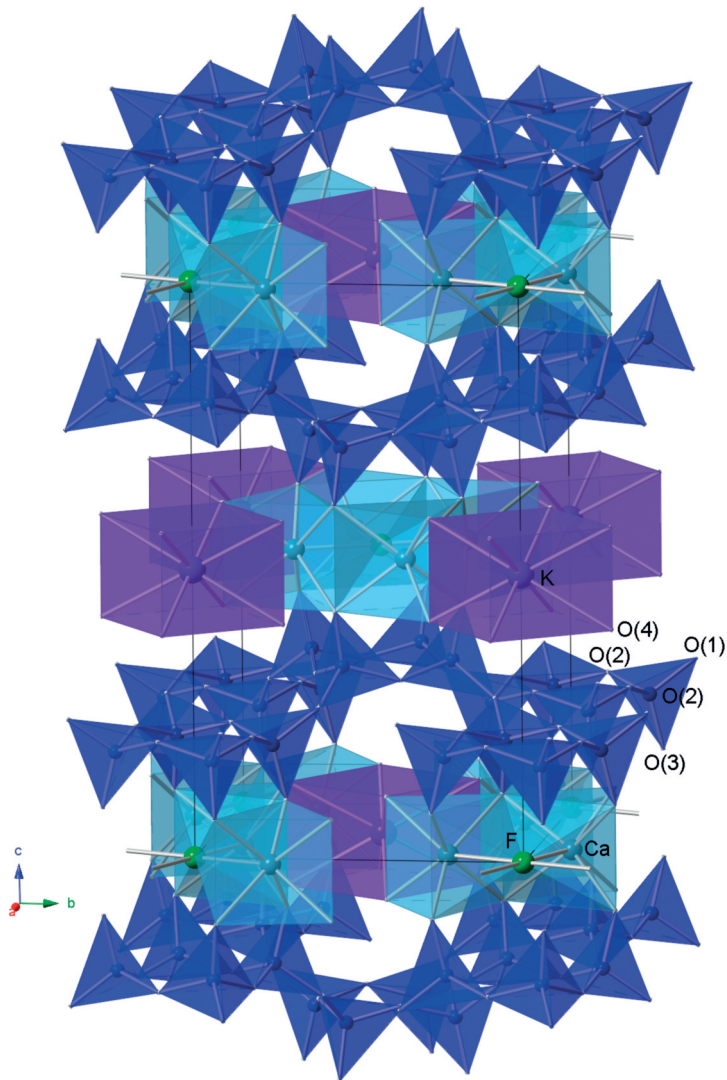


Figure 1. Polyhedral representation of the structure of fluorapophyllite. Hydrogen atoms removed for clarity.

proportion of the $F \leftrightarrow OH$ substitution (Marriner et al., 1990). Apophyllite behaviour in thermally-induced dehydration has been intensively investigated, although a quite unclear understanding about the number of reaction step

and the proportion of water loss currently persists. However, in most of the literature a two-step dehydration process is reported (Aumento, 1965; Ståhl et al., 1987; Marriner et al., 1990; Włodyka et al., 2004) consisting in a first water loss (at ca.

600-620 K) that causes minor structural distortion (a water molecules reordering on the mirror plane at $z = 0$ is only observed) followed by further water loss (at ca. 715-725 K) that makes the structure collapse into a non diffracting amorphous phase. In fact, the latter has unambiguously been observed as the final result of the discontinuous dehydration process (e.g. Aumento, 1965; Ståhl et al., 1987; Marriner et al., 1990).

Aumento (1965) has reported a peculiar dependence from temperature of the cell parameters of hydroxyapophyllite. In detail, while the a -parameter continuously increases, the c -parameter was found to decrease as the first dehydration step is approached, then increasing on further heating. Chao (1971) justified such behaviour stating that since the silicate framework puckers to accommodate the water molecules, their partial loss leads the tetrahedral rings to relax laterally, thus making the a -parameter expand and the c -parameter reduce.

As the RT c -parameter of hydroxyapophyllite reported by Aumento (1965) is significantly smaller (15.62 Å) than 15.89 Å reported by Marriner et al. (1990), further work would be desirable to disclose the thermal behaviour of the members of the apophyllite group. In this work we focused on investigating the thermal behaviour of fluorapophyllite in the temperature range of 323-473 K by in-situ X-ray powder diffraction (XRPD). The value of the high-temperature limit was set to avoid significant dehydration of the mineral (Włodyka et al., 2004). Diffraction patterns were measured in transmission mode on a sample prepared as capillary mount. Such experimental set-up

produces high-quality diffraction data, nearly at the same level of synchrotron radiation beamlines (Ballirano, 2011). The choice of this analytical technique is justified by the fact that more accurate cell parameters may be obtained as compared to single-crystal X-ray diffraction, as well as exploiting its excellent thermal stability and limited thermal gradient onto the capillary.

Experimental

A single-crystal of fluorapophyllite from Pune District (Poonah District), Maharashtra State, India, was picked up from the matrix and crushed in an agate mortar. The reference chemical formula for Pune fluorapophyllite is $K_{0.93}Na_{0.09}Ca_{4.03}[Al_{0.03}Si_{7.97}O_{20.06}]F_{1.03} \cdot 7.75H_2O$ as recalculated, on the basis of 8 (Al+Si), from the chemical data of Frost and Xi (2012). The powder was loaded in a 0.7 mm diameter SiO_2 -glass capillary that was glued to a 1.2 mm diameter Al_2O_3 tube using a high-purity alumina ceramic. Data were collected on a parallel-beam Bruker AXS D8 Advance diffractometer operating in transmission θ - θ geometry using Cu $K\alpha$ radiation. It is fitted with diffracted-beam radial Soller slits and a 1-D position sensitive detector VÅNTEC-1 set to a $6^\circ 2\theta$ aperture and a prototype of capillary heating chamber (Ballirano and Melis, 2007). Diffraction data were collected in the angular range 8 - $145^\circ 2\theta$ with a step-size of $0.022^\circ 2\theta$, and 5s of counting time. Thermal behaviour of fluorapophyllite was investigated in the 323-473 K temperature range at steps of 25 K. A magnified view of the

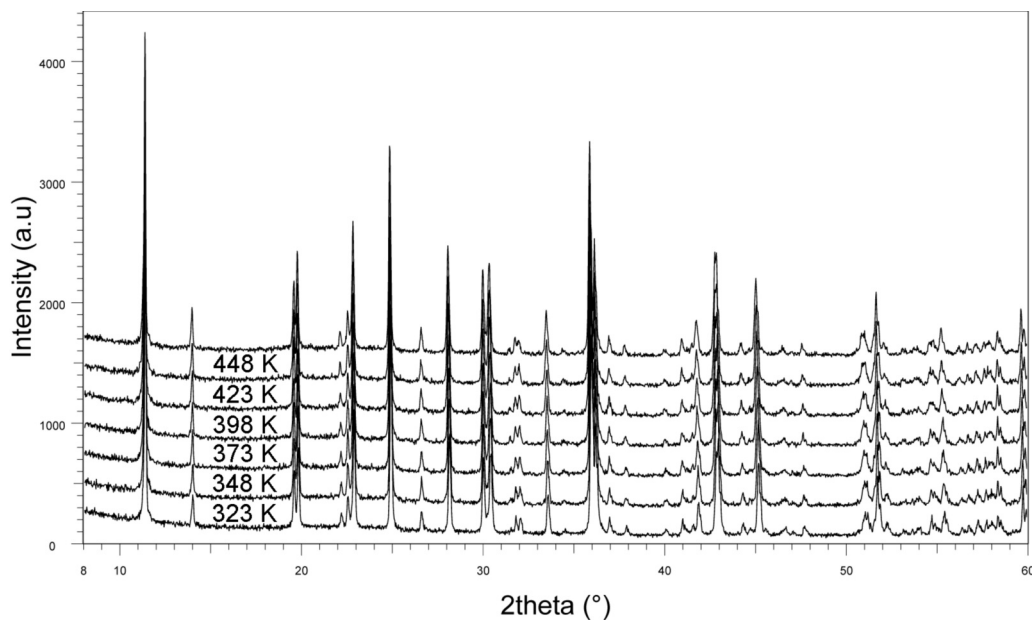


Figure 2. Magnified view of the full data set. Diffraction patterns are displaced vertically for clarity.

complete data set is reported in Figure 2. Diffraction data were evaluated by the Rietveld method using TOPAS v. 4.2 (Bruker AXS, 2009) operating in launch-mode. This program implements the Fundamental Parameters Approach FPA (Cheary and Coelho, 1992). According to Delhez et al. (1993), peak broadening was assumed to follow a Lorentzian (size) and a Gaussian (strain) behaviour. Absorption was refined at 323 K, following the approach devised by Ballirano and Maras (2006 a,b). Preferred orientation was modelled using spherical harmonics (Järvinen, 1993). A first series of refinements was carried out allowing optimization of spherical harmonics terms (five refinable parameters up to the 6th order) that were found to be significantly constant

throughout the analysed thermal range. Selection of the number of parameters was performed according to Ballirano (2003). The final structural data set was obtained keeping the spherical harmonics terms fixed to the corresponding averaged values ($y_{20} = -0.109$; $y_{40} = -0.252$; $y_{44p} = -0.076$; $y_{60} = 0.003$; $y_{64p} = -0.075$). Starting structural data were those of Ståhl et al. (1987). In order to reduce correlation isotropic displacement parameter of the oxygen atoms were constrained to be equal in magnitude. Besides, fractional coordinates of hydrogen atoms were kept fixed to the reference values. A structure refined at a certain temperature was used as input for the subsequent one. An example of Rietveld plots for the refinement of the data collected at $T = 323$ K is

shown in Figure 3. Conventional agreement indices obtained for the various refinements are listed in Table 1.

Discussion

The dependence from temperature of the cell parameters and volume of fluorapophyllite is reported in Table 2 and in Figure 4 and Figure 5, respectively. The linear and volume thermal expansion coefficients have been calculated applying the approach proposed by Fei (1995) and following the procedure described by Ballirano (2012) using a T_r of 323 K. Results of

the fitting procedure are reported in Table 3. Thermal expansion is markedly anisotropic as indicated by $\bar{\alpha}_a$ of $2.205(13) \cdot 10^{-5}$ and $\bar{\alpha}_c$ of $4.98(15) \cdot 10^{-6}$. Therefore, the a -parameter is softer than the c -parameter against heating. Nevertheless, present results are in disagreement with those reported by Aumento (1965) for hydroxyapophyllite. In fact, the thermal behaviour of the cell parameters of fluorapophyllite, despite of being anisotropic, results in an expansion of both a - and c -parameter differently from the expansion of the a - and the contraction of the c -parameter indicated by reference data. Accordingly, two

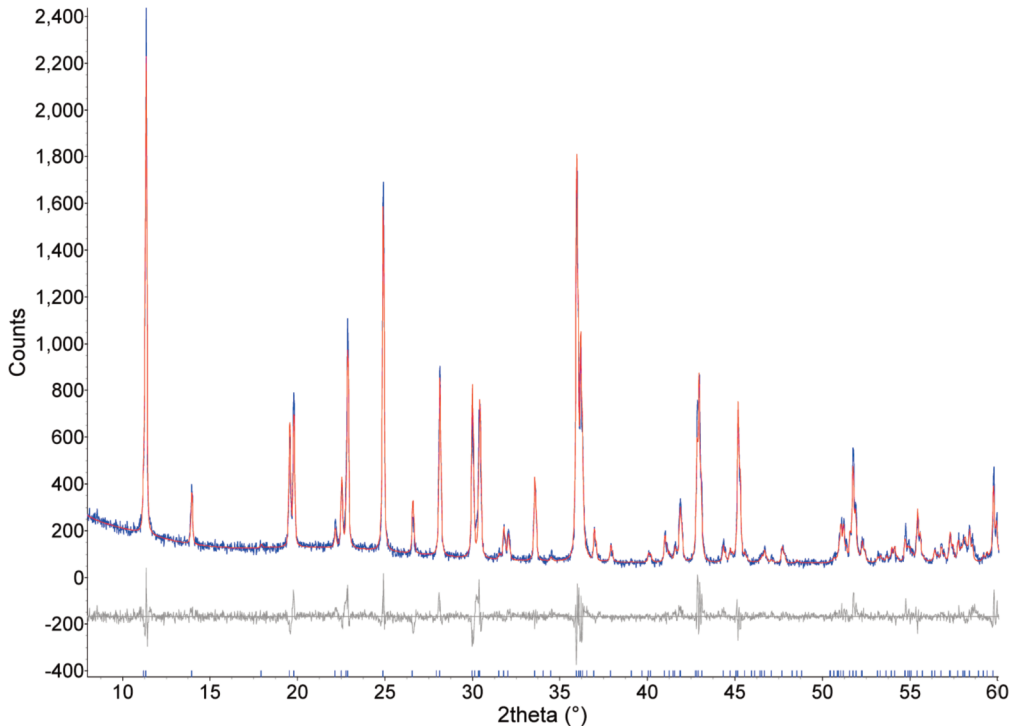


Figure 3. Example of Rietveld plots for the refinement at 323 K. Blue: experimental; red: calculated; gray: difference. Vertical bars refer to the position of calculated Bragg reflections.

Table 1. Conventional agreement indices as obtained from the refinements of the data collected in the 323-473 K thermal range. Agreement indices as defined in Young (1993).

	323 K	348 K	373 K	398 K	423 K	448 K	473 K
Rwp	12.02	12.12	11.93	11.92	11.67	11.80	11.95
Rp	9.27	9.33	9.24	9.28	9.11	9.22	9.28
χ^2	1.38	1.40	1.38	1.38	1.35	1.36	1.38
DWd	1.15	1.14	1.11	1.16	1.17	1.20	1.18
R _{Bragg}	4.47	4.78	4.89	4.69	4.71	4.65	4.79

Table 2. Dependence of cell parameters and volume of fluorapophyllite from T.

	<i>a</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
323 K	8.97051(15)	15.7893(4)	1270.56(5)
348 K	8.97571(14)	15.7917(4)	1272.23(5)
373 K	8.98056(14)	15.7938(4)	1273.78(5)
398 K	8.98567(15)	15.7957(4)	1275.38(5)
423 K	8.99061(14)	15.7973(4)	1276.92(5)
448 K	8.99489(15)	15.7994(4)	1278.30(5)
473 K	8.99998(16)	15.8001(4)	1279.80(5)

hypotheses may be invoked to explain the disagreement: a) different thermal behaviour of hydroxyapophyllite and fluorapophyllite; b) unreliable X-ray data of Aumento (1965). The very small RT *c*-parameter of hydroxyapophyllite reported by Aumento (1965) let to lean toward the second hypothesis.

Structure modifications of fluorapophyllite as a function of temperature are extremely small, coherently with the findings of Ståhl et al. (1987). In fact, those authors reported that only minimal variations in relevant bond distances, generally < 0.01 Å, were observed by comparing the structural data obtained at 295 and 373 K. The

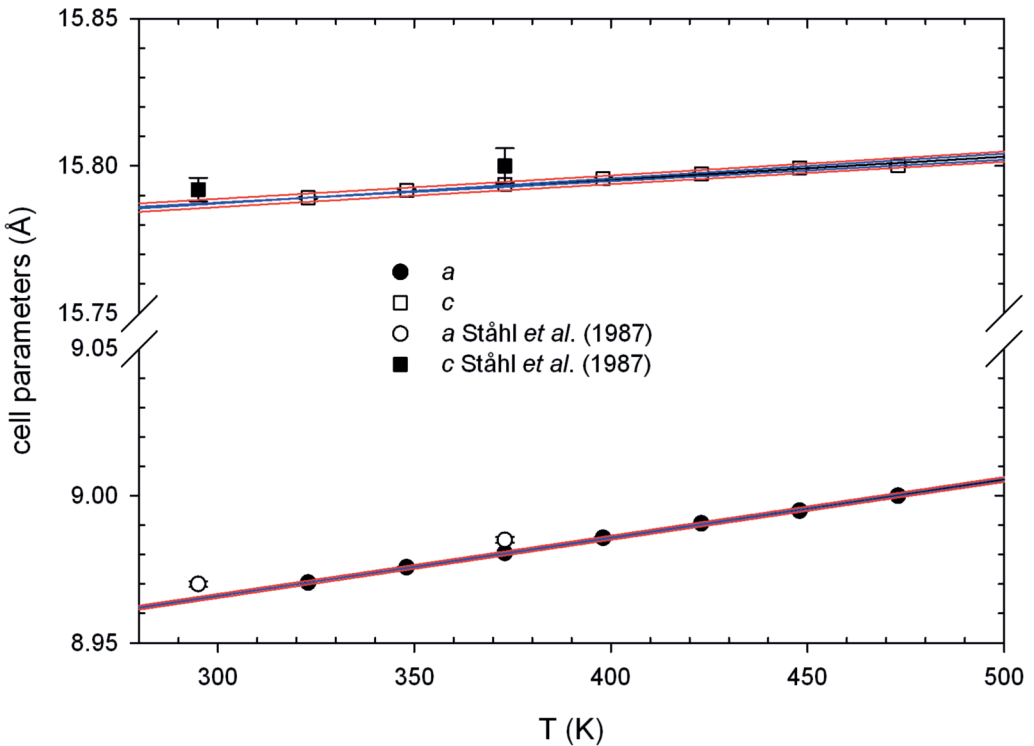


Figure 4. Dependence from temperature of the cell parameters of fluorapophyllite. Error bars are smaller than used symbols. Reference data of Ståhl *et al.* (1987) are reported for comparison purposes. Regression equations $a = a_{Tr}[1 + \bar{\alpha}_a(Tr-T)]$ and $c = c_{Tr}[1 + \bar{\alpha}_c(Tr-T)]$ are plotted as well as the corresponding 95% confidence (blue) and 95% prediction (red) bands.

evolution of the relevant bond distances in the 323–473 K thermal range is reported in Table 4 and graphically displayed in Figure 6. No clear regular trend has been observed, the distances oscillating around the average value. As can be seen the agreement with respect to reference data is remarkable. The largest difference is observed for the K–O(4) bond distance and it is due to the slight displacement of O(4), i.e. the oxygen atom of the water molecule, possibly arising from the driving effect occurring because of the well known different location of the hydrogen atoms

from X-ray and neutron diffraction techniques. Besides, it is worth noting that the largest data dispersion of the present series of refinements is typical of the bond distances involving O(4), in particular Ca–O(4). This is probably due to a minor lengthening of such distance as temperature is raised, as observed by Ståhl *et al.* (1987). At $T = 473$ K a test was performed to investigate the possible occurrence of partial dehydration using as starting model that of Ståhl (1993). However, due to large estimated standard deviations of both fractional coordinates and site

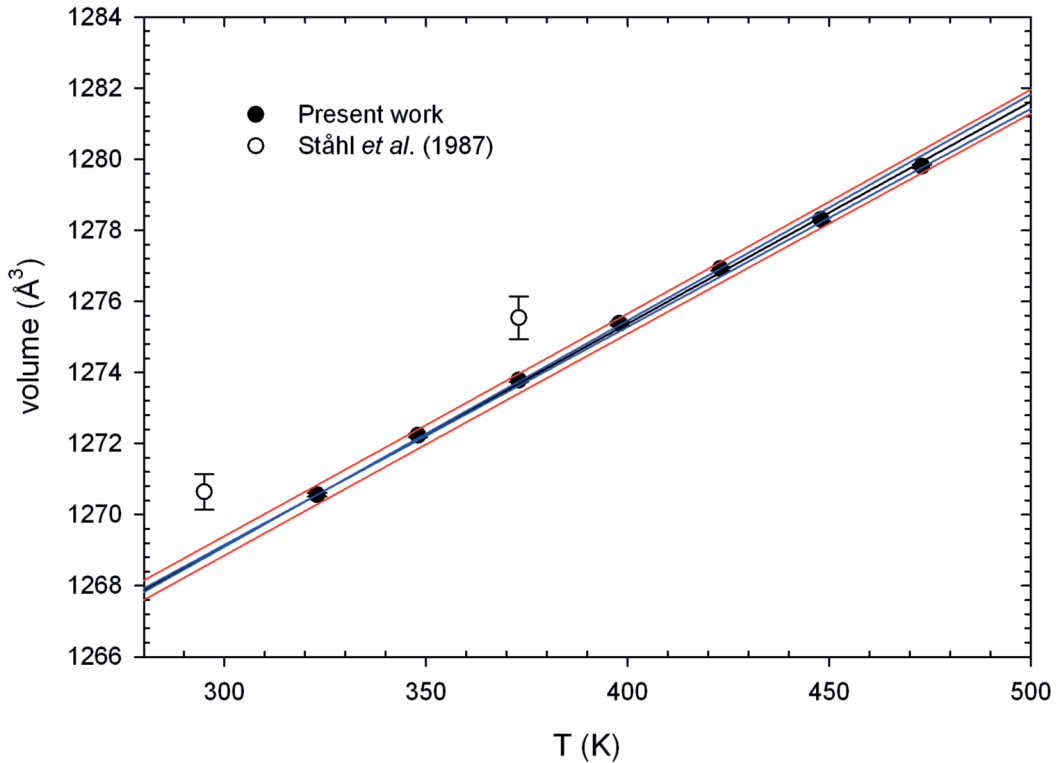


Figure 5. Dependence from temperature of the volume of fluorapophyllite. Reference data of Ståhl et al. (1987) are reported for comparison purposes. Regression equation $V = V_{Tr}[1 + \bar{\alpha}_T(Tr-T)]$ is plotted as well as the corresponding 95% confidence (blue) and 95% prediction (red) bands.

occupancy of the extra oxygen atom, possibly occurring because of correlation between displacement parameters and site occupancy, we cannot consider those results as fully reliable. It is worth noting that relevant bond distances obtained through the refinement of the two models differ of less than 1σ .

In order to try to understand the reason of the relatively marked anisotropy of its thermal expansion it is necessary to describe the structure of fluorapophyllite in more detail (Figure 1). The structure consists of alternating puckered layers

of four-members rings of Si-O₄ tetrahedra, and layers built-up by trigonal-prisms CaO₆ capped by a further F⁻ anion and square-prisms K(H₂O)₈. A relatively weak hydrogen-bond O(4)-H(1)...O(3) contributes to fasten the layers together. Connectivity between adjacent layers is assured by the O(3) oxygen atoms of the SiO₄ tetrahedra. Besides, lateral corner-sharing connection between CaFO₆ and K(H₂O)₈ is provided by O(4) oxygen atoms of the water molecules. The remaining, stronger, O(4)-H(2)...O(2) hydrogen bond helps stabilizing the

Table 3. Linear and volume thermal expansion coefficient of fluorapophyllite. a_{Tr} , c_{Tr} , and V_{Tr} are the a -parameter, c -parameter, and volume at reference temperature $Tr = 323$ K. R^2 = determination coefficient.

a -parameter	R^2	0.9993
	$\alpha a(x 10^{-6})$	22.05(13)
	a_{Tr}	8.97051(14)
c -parameter	R^2	0.9792
	$\alpha c(x 10^{-6})$	4.98(15)
	c_{Tr}	15.7893(4)
V	R^2	0.9989
	$\alpha V(x 10^{-6})$	49.2(4)
	V_{Tr}	1270.56(5)

Table 4. Relevant bond distances (Å) of fluorapophyllite as a function of T. Reference data of Ståhl et al. (1987) are reported for comparison.

	Present work							Ståhl et al. (1987)	
	323 K	348 K	373 K	398 K	423 K	448 K	473 K	295 K	373 K
Ca-O(3)x2	2.379(7)	2.378(7)	2.371(7)	2.374(7)	2.358(7)	2.370(7)	2.367(7)	2.3929(11)	2.3919(13)
Ca-O(3)x2	2.380(7)	2.383(7)	2.383(7)	2.390(7)	2.402(7)	2.396(7)	2.402(7)	2.3979(11)	2.3981(13)
Ca-O(4)x2	2.510(8)	2.497(8)	2.484(8)	2.501(8)	2.491(8)	2.487(8)	2.519(8)	2.4854(12)	2.4969(15)
Ca-F	2.413(3)	2.415(3)	2.420(3)	2.415(3)	2.419(3)	2.422(3)	2.420(3)	2.4221(11)	2.4187(13)
F-O(3)x8	2.901(7)	2.900(7)	2.892(7)	2.899(7)	2.897(6)	2.899(6)	2.904(7)	2.9293(7)	2.9304(9)
K-O(4)x8	2.990(7)	2.997(7)	3.014(7)	3.012(7)	3.022(7)	3.010(7)	2.997(7)	2.9657(9)	2.9699(12)
Si-O(1)	1.644(5)	1.635(4)	1.637(4)	1.639(4)	1.637(4)	1.636(4)	1.636(5)	1.6200(9)	1.6198(11)
Si-O(2)	1.629(8)	1.644(8)	1.640(8)	1.630(8)	1.644(8)	1.645(8)	1.635(8)	1.6290(11)	1.6279(12)
Si-O(2)	1.651(8)	1.644(8)	1.647(8)	1.658(8)	1.632(8)	1.634(8)	1.641(8)	1.6320(11)	1.6338(12)
Si-O(3)	1.592(6)	1.588(6)	1.592(5)	1.584(5)	1.591(5)	1.588(5)	1.588(6)	1.5875(10)	1.5871(13)
<Si-O>	1.629	1.628	1.629	1.628	1.626	1.626	1.625	1.617	1.617

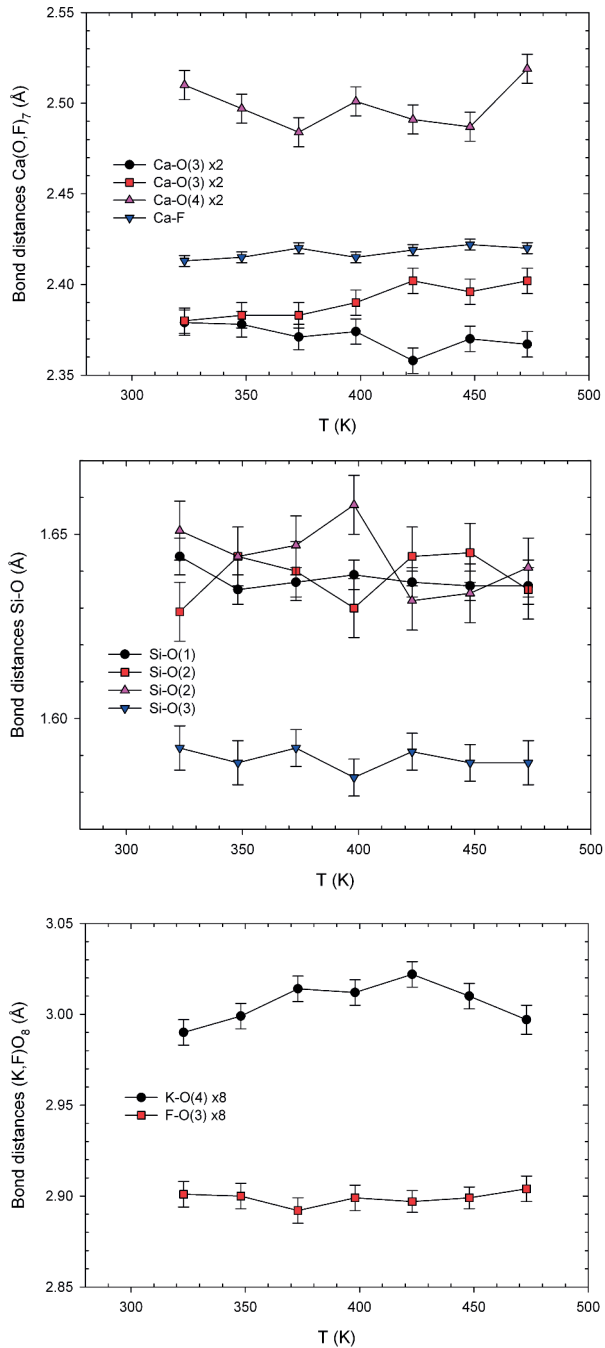


Figure 6. Dependence from temperature of the relevant bond distances of fluorapophyllite: a) Ca(O,F)₇ polyhedron; b) SiO₄ tetrahedron; c) KO₈ and FO₈ polyhedra.

layer. Due to the virtual non-expandibility of the SiO₄ tetrahedra only the CaFO₆ and K(H₂O)₈ polyhedra may contribute to the expansion process. Ståhl et al. (1987) reported the occurrence of minor increasing of Ca²⁺ and K⁺ to water molecules bond distances. Therefore, the fact that the mean plane passing through Ca,O(4),K has a prevalent component along the (001) plane justifies the larger expansion coefficient $\bar{\alpha}_a$ as compared to $\bar{\alpha}_c$.

Conclusions

The response to heating of fluorapophyllite in the 323-473 K range results in extremely small structural variations, consisting in minor deviations from the average values of the relevant bond distances. Thermal expansion of fluorapophyllite turns out to be markedly anisotropic, as shown by the linear thermal expansion coefficients $\bar{\alpha}_a = 2.205(13) \cdot 10^{-5}$ and $\bar{\alpha}_c = 4.98(15) \cdot 10^{-6}$. Such behaviour is different with respect to that reported by Aumento (1965) for hydroxyapophyllite. The difference has been attributed to a low quality of the reference X-ray diffraction data. The anisotropy might be reliably linked to the prevalent component along (001) of the mean plane passing through Ca,O(4),K, since only the CaFO₆ and K(H₂O)₈ polyhedra may contribute to the expansion process, owing to the stiffness of the SiO₄ tetrahedra.

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