



In situ high-temperature behaviour of fluor-elbaite: breakdown conditions and products

Beatrice Celata¹ · Paolo Ballirano¹ · Giovanni B. Andreozzi¹ · Ferdinando Bosi¹

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Abstract

The thermal behaviour of a fluor-elbaite from Minas Gerais (Brazil) was investigated at room pressure through in situ high-temperature X-ray powder diffraction (HT-XRPD), until the breakdown conditions were reached. The variations of fluor-elbaite structural parameters (unit-cell parameters and mean bond distances) were monitored together with site occupancies, and two main internal reactions were identified: the thermally-induced Fe oxidation process counterbalanced by (OH)⁻ deprotonation, which starts at 500 °C (773 K), followed by a partial intracrystalline Fe–Al exchange between the octahedrally-coordinated Y and Z sites. The fluor-elbaite breakdown reaction occurs between 850 °C (1123 K) and 900 °C (1173 K). The breakdown products were identified at room temperature by XRPD and the breakdown reaction can be described by the following reaction: tourmaline → B-bearing mullite + hematite + spinel + B-poor (Na, Li, H₂O)-bearing glass. Boromullite itself was not observed in the final heating products, and the B-bearing mullite from the breakdown reaction exhibited unit-cell parameters $a = 7.5382(2)$ Å, $b = 7.6749(2)$ Å, $c = 2.8385(1)$ Å, $V = 164.22(1)$ Å³ (space group *Pbam*) consistent with an approximate Al_{8.5}B_{1.5}Si₂O₁₉ composition.

Keywords Fluor-elbaite · HT-XRPD · Thermal expansion · Iron oxidation · Deprotonation · Intracrystalline cations exchange · Structural breakdown

Introduction

Tourmaline is one of the most fascinating and colourful accessory mineral occurring in a variety of geological environments, from diagenetic stages to granulite facies grade (e.g., Henry and Dutrow 1996; Dutrow and Henry 2011; Bosi et al. 2018a, 2019a; Andreozzi et al. 2020).

Tourmaline is a cyclosilicate rich in B with a very complex composition represented by the general chemical formula: XY₃Z₆T₆O₁₈(BO₃)₃V₃W, where X = Na⁺, K⁺, Ca²⁺, □ (= vacancy); Y = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mg²⁺, Fe²⁺, Mn²⁺, Li⁺; Z = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mg²⁺, Fe²⁺; T = Si⁴⁺, Al³⁺, B³⁺; B = B³⁺; V = (OH)⁻, O²⁻; W = (OH)⁻, F⁻, O²⁻. Note that the non-italicized letters X, Y, Z, T and B represent groups of cations at the ^[9]X, ^[6]Y, ^[6]Z, ^[4]T and ^[3]B

crystallographic sites (*italicized letters*) and the letters V and W represent groups of anions accommodated at the [3]-coordinated O3 and O1 crystallographic sites, respectively. Tourmaline-supergroup minerals are currently classified into three groups, vacant, alkali and calcic, based on the X-site occupancy (Henry et al. 2011). A further level of classification into subgroups is based on the charge arrangements at the Y and Z sites. Tourmalines are also distinguished by the dominant anion at the W position of the general formula into hydroxy-, fluor- and oxy-species.

Tourmaline gained more and more interest along the years surely because of its remarkable power to carry a lot of information about its genetic conditions (e.g., Federico et al. 1998; Dutrow and Henry 2011). However, tourmaline relevance stands even more in its role of boron and water carrier from the crust deep down the mantle and the implications it may have (Henry and Dutrow 1996; Ota et al. 2008a, b; Shimizu and Ogasawara 2013; Lussier et al. 2016). In fact, the boron and water released because of tourmaline breakdown reduce both the solidus temperature of the hosting rock and the viscosity of any associated melt (Pichavant 1981; Dingwell et al. 1992). Remarkably, how

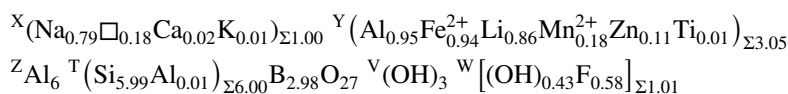
✉ Beatrice Celata
beatrice.celata@uniroma1.it

✉ Paolo Ballirano
paolo.ballirano@uniroma1.it

¹ Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale A. Moro 5, 00185 Rome, Italy

the breakdown conditions are reached in terms of structural variations has never been investigated so far, as well as it remains unclear when the deprotonation process exactly starts, i.e., if "water" is actually released throughout the breakdown process or way before the structural collapse as suggested, for example, by the studies of Filip et al. (2012) and Bosi et al. (2018b).

The present work aims at investigating the thermal behaviour of the fluor-elbaite, ideally $\text{Na}(\text{Li}_{1.5}\text{Al}_{1.5})\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{F}$ (Bosi et al. 2013) at room pressure. A Fe-bearing deep green fluor-elbaite sample from the Cruzeiro pegmatite (Minas Gerais, Brazil), previously fully characterized by Bosi et al. (2019b) with the formula:



was studied by in situ high-temperature X-ray powder diffraction (HT-XRPD) up to the structural breakdown.

Experimental

The fluor-elbaite crystal fragment was gently grinded in ethanol, in an agate mortar; the powder was then loaded in a 0.7 mm diameter SiO_2 -glass capillary kept open at one side. The capillary was fixed to a hollow corundum tube using a HT cement and mounted and aligned on a goniometer head. The capillary was inserted into the heating chamber for capillaries, developed by MRI and Bruker AXS, that is placed along the beam path of the diffractometer. Characteristics and thermal calibration procedure of the chamber are reported in Ballirano and Melis (2007).

In situ HT-XRPD data were measured on a Bruker AXS D8 Advance that operates in θ/θ geometry in transmission mode. The instrument is fitted with focussing multilayer graded (Göbel) mirrors placed along the incident beam and Soller slits on both the incident (2.3° opening angle) and diffracted (radial) beams. The data were collected using a position sensitive detector (PSD) VÅntec-1 operating at an opening angle of $6^\circ 2\theta$. Details of the data collection are reported in Table 1.

At the end of the heating run, the powder was cooled back at room temperature (RT) within the chamber, removed from the capillary, re-homogenised and charged in a new borosilicate-glass capillary. This procedure was followed to reduce the possible effect of textured recrystallization at the walls of the capillary. As a side effect, re-homogenisation involved also powder lying at the coldest extremity of the capillary where T , owing to thermal gradients, was significantly smaller than that reached in the analysed part of the sample. A measurement of this sample was performed outside the chamber.

Table 1 Miscellaneous data of the data collection and Rietveld refinements of the fluor-elbaite studied

2θ range ($^\circ$)	7–145
2θ step-size ($^\circ$)	0.021798
Counting time (s)	3
T_{max} ($^\circ\text{C}$)	850
T steps ($^\circ\text{C}$)	50
Rp (%)	1.772–2.275
Rwp (%)	2.392–3.312
R_{Bragg} (%)	0.907–1.303
DWd	0.801–1.363
χ^2	1.767–2.509

Definition of the statistical indicators, from Young (1993)

Data evaluation was performed by the Rietveld method using Topas 6 (Bruker 2016). The Fundamental Parameters Approach (FPA: Cheary and Coelho 1992) was used to describe the peak shape. The equation of Sabine et al. (1998) for a cylindrical sample was applied for absorption correction using the approach of Ballirano and Maras (2006) for handling the correlation existing between displacement parameters and absorption. In particular, isotropic displacement parameters were constrained as follow: $B_Y = B_Z = B_B = B_T$; $B_{O2} = B_{O3} = B_{O4} = B_{O5} = B_{O6} = B_{O7} = B_{O8}$. Preferred orientation effects were corrected using spherical harmonics (8th-order, nine refinable parameters) by selecting the number of appropriate terms following the procedure described by Ballirano (2003). As expected for data collected in transmission-mode on capillaries, the coefficients refined to small values. Starting structural data were those of Bosi et al. (2019b) and each refined structure at a given non-ambient T was used as input for the subsequent T . EoSFit7-GUI (Gonzalez-Platas et al. 2016) was used to analyse the dependence of the unit-cell parameters from T employing the equation of Berman (1988) for fitting the data. This equation has the advantage to permit accommodation of non-linear thermal expansion. It is expressed as $X_T = X_0 \left[1 + a_0(T - T_{\text{ref}}) + \frac{1}{2}a_1(T - T_{\text{ref}})^2 \right]$ with $X = V, a, c$. Miscellaneous information regarding the refinements is listed in Table 1 and a representative example of Rietveld plots is shown in Fig. 1. CIF files of the fluor-elbaite structure refined at the various T are given in Online Resource.

Results and discussion

Breakdown products of F-elbaite

The first evidence of fluor-elbaite structural breakdown was observed at 850 $^\circ\text{C}$ owing to the occurrence of very weak

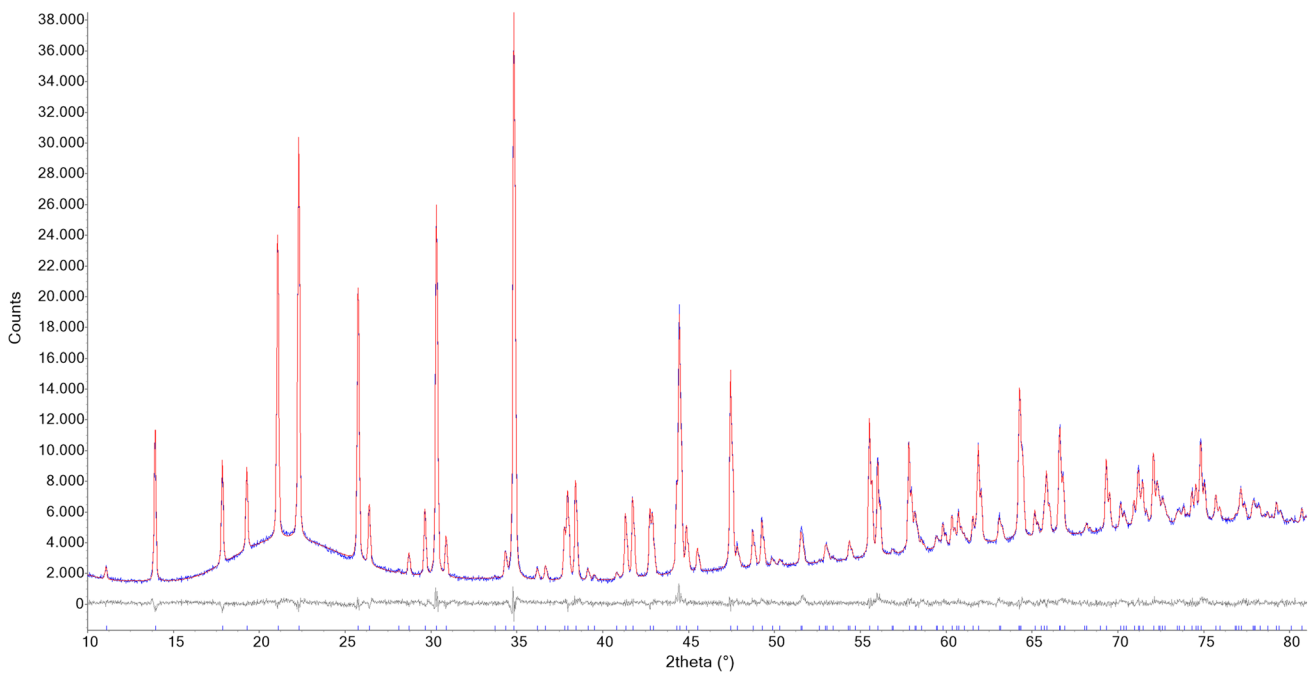


Fig. 1 Representative example of the Rietveld plots of the diffraction pattern collected at 423 K. Blue: experimental; red: calculated; grey: difference; vertical bars: position of calculated Bragg reflections of the fluor-elbaite studied

diffraction reflections assigned to a mullite-like phase. The breakdown was completed at the T of 900 °C. The quantitative phase analysis (QPA) of the sample cooled down at RT (Fig. 2) indicates the occurrence of prevailing mullite-like

phase plus minor hematite and traces of spinel as breakdown products. Furthermore, the increased intensity of the broad band centred at ca. 22° 2θ , in addition to the contribution of the capillary glass, also reveals the occurrence of some

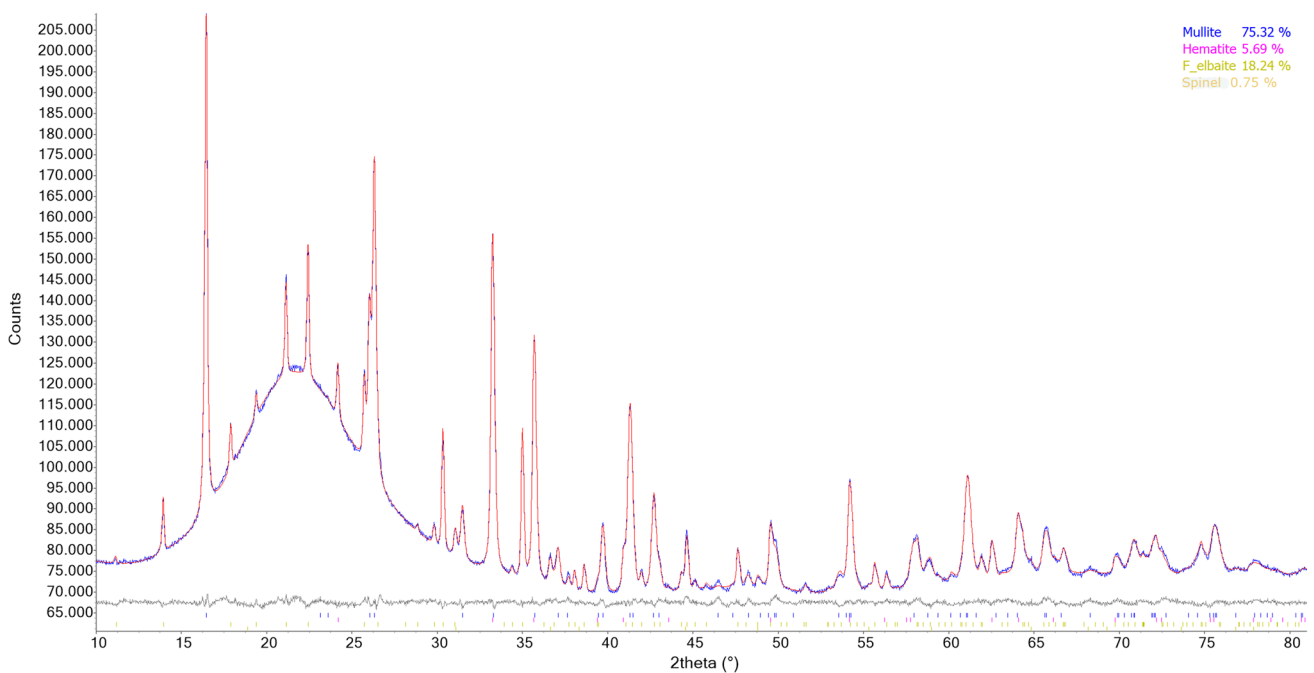


Fig. 2 Magnified 10–80° 2θ view of the Rietveld plots of the products of breakdown of the fluor-elbaite studied. Blue: experimental; red: calculated; grey: difference; vertical bars: position of calculated

Bragg reflections of (from above to below) mullite, hematite, fluor-elbaite (unreacted) and spinel

amorphous material, likely being the cooling product of a Si-rich hydrous fluid derived from the tourmaline breakdown. Relicts of unreacted fluor-elbaite were caused by the re-homogenisation of the powder (see “Experimental”).

Refined unit-cell parameters of the mullite-like phase, in the space group *Pbam*, were $a = 7.5382(2)$ Å, $b = 7.6749(2)$ Å, $c = 2.8385(1)$ Å, $V = 164.22(1)$ Å³ and are consistent with those of B-mullites (Lührs et al. 2014). An estimation of the B content was carried out using the regression equations proposed by Lührs et al. (2014), based on the *b*- and *c*-parameters ($b = -0.0030(2) \times B_2O_3$ mol.% + 7.6921(8): $R^2 = 0.99$; $c = -0.0041(2) \times B_2O_3$ mol.% + 2.8876(19): $R^2 = 0.96$). The results point out to a content of ca. 6–12 mol.% B_2O_3 , corresponding to the $Al_8B_2Si_2O_{19}$ – $Al_9BSi_2O_{19}$ compositional range. It is worth noting that the mineral boromullite, space group being *Cmc2₁*, $a = 5.7168(19)$ Å, $b = 15.023(5)$ Å, $c = 7.675(3)$ Å, $V = 659.2(7)$ Å³ with composition $Al_9BSi_2O_{19}$, has been described by Buick et al. (2008). However, attempts to use this superstructure as starting structure for the present B-mullite (using a $4 \times$ larger supercell $a' = 2c = 5.6770(1)$ Å, $b' = 2a = 15.0763(4)$ Å and $c' = b = 7.6749(2)$ Å, obtained by the transformation matrix 002/200/010) produced relatively strong unobserved reflections, clearly indicating the inability of the model to fit the data. Moreover, Werdning and Schreyer (1992) reported the orthorhombic unit-cell parameters $a = 5.681(2)$ Å, $b = 15.014(5)$ Å, $c = 7.671(4)$ Å, $V = 654.3(3)$ Å³ for a sample of $Al_8B_2Si_2O_{19}$ composition. It is interesting to notice that V' of the present sample, calculated from the $4 \times$ larger supercell, is equal to 656.88(3) Å³, which is a value located exactly halfway between those of $Al_8B_2Si_2O_{19}$ and $Al_9BSi_2O_{19}$.

Finally, the recently discovered (Li,Be)-bearing borosilicate mineral vránaite, ideally $Al_{16}B_4Si_4O_{38}$ (Novák et al. 2015; Cempírek et al. 2016), was also considered since it was found as a breakdown product of spodumene in the elbaite-subtype Manjaka granitic pegmatite (Novák et al. 2015), and its space group *I2/m* can be derived from the orthorhombic supergroup *Pbam* (Fischer and Schneider 2008) to which our structural refined data refer to. Vránaite cell parameters are $a = 10.383(1)$ Å, $b = 5.668(1)$ Å, $c = 10.823(1)$ Å, $\beta = 90.11(1)^\circ$, $V = 637.0(1)$ Å³. However, similarly to boromullite, attempts to fit the XRPD data using the structural parameters of vránaite produced significantly worse agreement indices than those obtained for B-mullite. In particular, the markedly different cell parameters resulted in a unit cell volume of ca. 657 Å³, significantly larger than that reported for vránaite.

Thus, a mullite-type phase of approximate $Al_{8.5}B_{1.5}Si_2O_{19}$ composition may represent the breakdown crystalline phase incorporating B.

Because the B/Si ratio observed in pristine fluor-elbaite was 1:2 and that of the present recrystallized B-mullite is

approximately 1.5:2, it is most likely that the Si-rich amorphous component retrieved at the end of the breakdown process is very poor in B.

Moreover, considering that pristine fluor-elbaite is a hydrated phase containing a definite amount of Na and Li and that no hydrated Na- and Li-bearing breakdown products are observed, it is very likely that the silicatic amorphous component may also contain Na and Li and H₂O, as commonly used in experimental investigation of tourmaline formation (e.g., Orlando et al. 2017).

The observed hematite accommodates the oxidised Fe and spinel probably accommodates the remaining Fe (Mn) and Al of the pristine fluor-elbaite.

Thermal expansion and HT structure modifications

Variation of unit-cell parameter values for the fluor-elbaite at each *T* is reported in Table 2, and the relative expansion of the same parameters as a function of *T* is shown in Fig. 3.

A non-linear thermal expansion is observed, with the occurrence of several discontinuities. The *a*-parameter deviates from the regularly increasing trend around 500 °C and shows a flattening, suddenly followed by a marked decrease that ends at 700 °C; above this *T*, the *a*-parameter increases again with approximately the same rate observed below 500 °C. The *c*-parameter experiences a different behaviour as the discontinuity occurs at a higher *T* (650 °C) and consists in an increased expansion rate. These opposite behaviours suggest the onset of two different structural

Table 2 Refined cell parameters at the various temperatures of the fluor-elbaite studied

<i>T</i> (°C)	<i>a</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
30	15.9187(1)	7.1283(1)	1564.35(2)
50	15.9199(1)	7.1297(1)	1564.87(3)
100	15.9228(1)	7.1328(1)	1566.15(2)
150	15.9262(1)	7.1362(1)	1567.56(3)
200	15.9298(1)	7.1398(1)	1569.04(3)
250	15.9345(1)	7.1441(1)	1570.92(3)
300	15.9387(1)	7.1481(1)	1572.64(3)
350	15.9435(1)	7.1527(1)	1574.59(3)
400	15.9475(1)	7.1572(1)	1576.37(3)
450	15.9504(1)	7.1618(1)	1577.97(3)
500	15.9489(2)	7.1662(1)	1578.63(5)
550	15.9361(3)	7.1701(1)	1576.94(7)
600	15.9193(3)	7.1748(1)	1574.48(6)
650	15.9087(2)	7.1842(1)	1574.63(4)
700	15.9077(1)	7.1965(1)	1577.14(3)
750	15.9097(1)	7.2040(1)	1579.16(3)
800	15.9134(1)	7.2099(1)	1581.20(3)
850	15.9138(2)	7.2181(1)	1583.07(5)

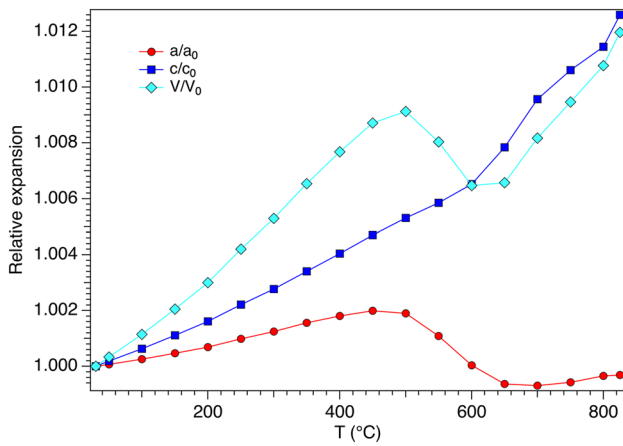


Fig. 3 Change of normalized unit-cell parameters with T for the fluor-elbaite studied

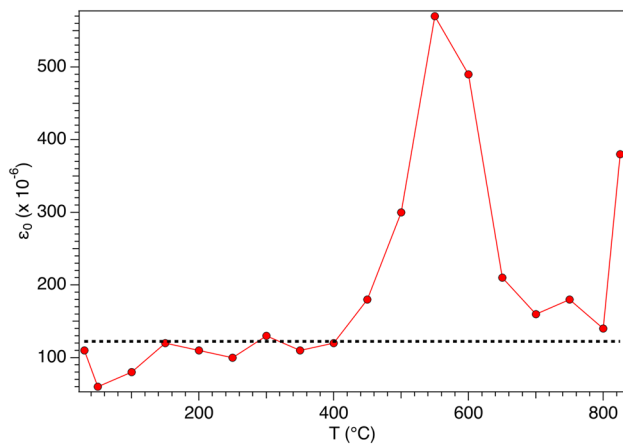


Fig. 4 Variation of ϵ_0 microstrain with T for the fluor-elbaite studied. The dotted horizontal line, corresponding to the ϵ_0 value at RT, is drawn as a guide for the eye

processes and are reflected by the net volume contraction occurring in the 500–600 °C thermal range, followed by the restart of volume increase after 650 °C.

It is worth noting that ϵ_0 microstrain (lattice strain), defined as $\beta_i = 4\epsilon_0 \tan \theta$, where β_i is the integral breadth of the j th reflection, refined as a part of the profile shape optimization (Ballirano and Sadun 2009), shows a significant increase in the same thermal range (450–700 °C) where the unit-cell parameters deviate from the regular trends (450–700 °C, Fig. 4).

Table 3 Relevant parameters of the fitting procedure by the Berman equation of the unit-cell parameters vs. T data of the fluor-elbaite studied

	V_0	a_0, c_0 (Å ³ , Å, Å)	a_0 ($\times 10^{-5}$ K ⁻¹)	a_1 ($\times 10^{-9}$ K ⁻²)	X_w^2
V (Å ³)	1564.38(6)		1.59(5)	2.6(3)	8.64
a (Å)	15.9188(2)		0.371(17)	0.66(10)	6.26
c (Å)	7.1284(1)		0.849(16)	1.32(9)	3.19

Temperature of reference = 30 °C (303 K)

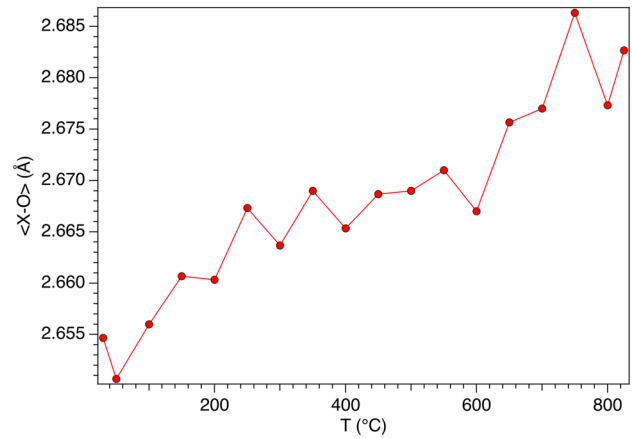
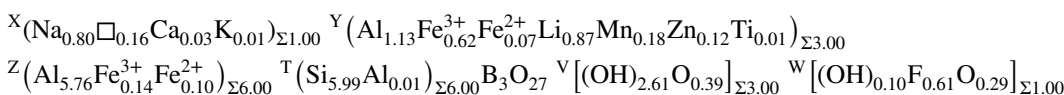


Fig. 5 Variation of $\langle X-O \rangle$ bond distances with T for the fluor-elbaite studied

The variation of the unit-cell parameters with T was modelled up to 400 °C, i.e., before the onset of structural modifications, using the Berman equation (Berman 1988). Table 3 reports the relevant parameters of the fitting procedure. The data indicate that the c -parameter is softer than the a -parameter against T .

As far as the structural modifications are referred to, the $\langle X-O \rangle$ mean bond distance shows an irregular increase with T (Fig. 5). In spite of a marked enlargement tentatively exhibited at higher temperature, the possibility of Na release and a consequent increase of the X -site vacant component, which might enlarge $\langle X-O \rangle$ (Bosi et al. 2005), is not fully supported by experimental data. Moreover, the modifications observed by Bosi et al. (2019b) on a single-crystal fragment of the same fluor-elbaite studied in this work, heated in air at the T of 800 °C and studied at RT by single crystal X-ray diffraction, confirmed that Na was not released after heating, as reported in their empirical formula,



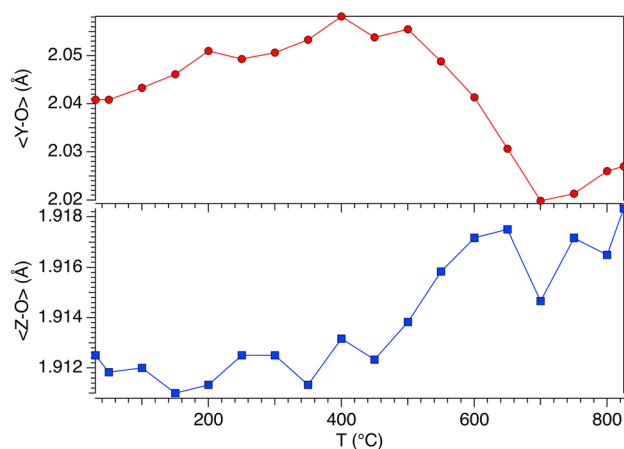


Fig. 6 Dependence of $\langle Y-O \rangle$ (upper panel) and $\langle Z-O \rangle$ (lower panel) bond distances from T for the fluor-elbaite studied

which has the same Na content of the pristine fluor-elbaite.

The dependence of $\langle Y-O \rangle$ and $\langle Z-O \rangle$ bond distances from T displays a different behaviour (Fig. 6). In particular, the $\langle Y-O \rangle$ bond distance regularly increases from 2.048 Å to 2.064 Å due to thermal expansion when T increases from RT to 500 °C, then contracts significantly to 2.027 Å in the range 500–700 °C and slightly increases again up to the breakdown T of 850 °C. Conversely, the $\langle Z-O \rangle$ bond distance regularly increases up to the breakdown, although an increment of the expansion is observed at 500 °C.

The $\langle Y-O \rangle$ and $\langle Z-O \rangle$ modifications observed in situ correlate nicely with the structural modifications observed by Bosi et al. (2019b) on the same fluor-elbaite as a result of their thermal treatment followed by ex situ study. In fact, these authors observed a marked $\langle Y-O \rangle$ shrinking together with limited $\langle Z-O \rangle$ enlargement which was interpreted as the occurrence of Fe^{2+} oxidation to Fe^{3+} , counterbalanced by the deprotonation of $(OH)^-$ groups and described by the reaction $(Fe^{2+}) + (OH)^- \rightarrow (Fe^{3+}) + (O^{2-}) + 1/2H_2(g)$. It is worth noting that the whole Fe content of the starting sample of fluor-elbaite was Fe^{2+} ; therefore, given that the empirical mean ionic radius of $[^{6}Fe^{3+}]$ is smaller than that of $[^{6}Fe^{2+}]$ [0.675(15) Å vs. 0.776(1) Å, respectively, Bosi (2018)], we may conclude that in fluor-elbaite the Fe oxidation starts at 500 °C and the heating is definitely the driving force that also rules the associated deprotonation (required to restore the overall charge balance even under reducing conditions, see Bosi et al. 2019b for details).

To explain the observed variation of Fe occupancy at the Y and Z sites with T (Fig. 7), the onset of an intracrystalline exchange process after 650 °C has to be hypothesized. After Fe^{2+} oxidation to Fe^{3+} , some amounts of Fe migrate from the larger YO_6 polyhedron to the adjacent smaller $ZAlO_6$ polyhedron, which in turn moves Al to the Y site. This process can be described by the intracrystalline order–disorder reaction

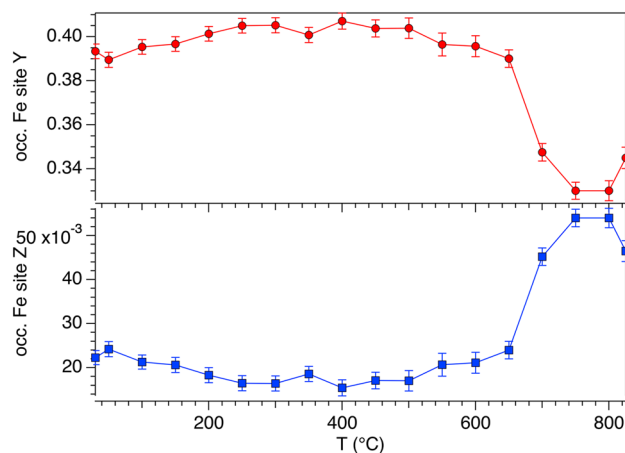


Fig. 7 Evolution with T of the Fe (+Mn) occupancy at the Y and Z sites for the fluor-elbaite studied

${}^YFe + {}^ZAl \rightarrow {}^ZFe + {}^YAl$, which was observed on thermally-treated tourmaline single-crystals by Bosi et al. (2019b) for fluor-elbaite, Bosi et al. (2018b) for lucchesiite and Filip et al. (2012) for schorl. In the studied fluor-elbaite, this process probably ends at 750 °C, when the Fe is reasonably supposed to be fully oxidized (Fig. 7).

Both the oxidation reaction of Fe^{2+} to Fe^{3+} at the Y site and the above reported intracrystalline order–disorder reaction contribute to explain the observed dependence of $\langle Y-O \rangle$ and $\langle Z-O \rangle$ from T (Fig. 6). In fact, the abrupt contraction of $\langle Y-O \rangle$ is consistent with the combination of the two reactions, which leads to the reduction of the aggregate size of the constituent cation $\langle {}^Yr \rangle$. As above mentioned, the empirical mean ionic radius of $[^{6}Fe^{3+}]$ is smaller than that of $[^{6}Fe^{2+}]$ [0.675(15) Å vs. 0.776(1) Å, respectively], and the empirical mean ionic radius of $[^{6}Al]$ is much smaller than that $[^{6}Fe^{3+}]$ [0.547(3) Å vs. 0.675(15) Å, Bosi (2018)]. The minor expansion of $\langle Z-O \rangle$ in the same thermal range is consistent with the smaller increase of the aggregate size of the constituent cation $\langle {}^Zr \rangle$ than $\langle {}^Yr \rangle$ caused by double multiplicity of the Z site with respect to Y . A similar behaviour was observed for both Fe-dominant/rich tourmalines (e.g., Filip et al. 2012; Bosi et al. 2018b, 2019b) and Fe-bearing amphiboles (Oberti et al. 2018; Pacella et al. 2020; Ballirano and Pacella 2020).

Conclusions

The thermal behaviour of fluor-elbaite was investigated up to structural breakdown through in situ HT-XRPD.

Well before the breakdown, heating the fluor-elbaite at 500 °C (773 K) in air was enough to set the Fe oxidation out, counterbalanced by the deprotonation reaction:

(Fe^{2+}) + (OH^-) \rightarrow (Fe^{3+}) + (O^{2-}) + $1/2\text{H}_2(\text{g})$. Since the capillary acted as a closed system, the early formation of an aqueous fluid may be envisaged at this stage. At a higher temperature, quantified around 650 °C (923 K), Fe starts to migrate from the Y to the Z sites, according to the intracrystalline order–disorder reaction ${}^Y\text{Fe} + {}^Z\text{Al} \rightarrow {}^Z\text{Fe} + {}^Y\text{Al}$.

Fluor-elbaite structural breakdown starts at 850 °C (1123 K), owing to the first occurrence of a mullite-like phase in the decomposition products, and the process is complete at 900 °C (1173 K). Tourmaline breakdown products have been identified as B-mullite (for the most part), hematite, spinel and a silicatic B-poor (Na, Li, H_2O)-bearing glass.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00269-021-01147-5>.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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