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Study of the temperature dependence of the structure of KY_3F_{10}

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Abstract

KY_3F_{10} ($Fm\bar{3}m$, $Z = 8$) is an anion-excess fluorite-related superstructure, which is employed as a room-temperature laser, when doped with rare-earths. Earlier conductivity measurements have revealed two thermally activated processes below and above 600 K. In this work we studied the high-temperature behaviour of KY_3F_{10} in the temperature range from 293 K up to 800 K at ambient pressure using x-ray powder and single crystal diffraction. No structural phase transition is observed in this temperature range and the structure determinations reveal that the change of structural parameters, interatomic distances, and angles with temperature is very small. A prominent maximum observed in the difference Fourier maps, which corresponds to the centre of an empty F_8 cube, might be one of the interstitial sites involved in the conduction mechanism.

1. Introduction

At ambient conditions potassium tryttrium decafluoride KY_3F_{10} ($Fm\bar{3}m$, $Z = 8$) is a $2 \times 2 \times 2$ superstructure of fluorite and is isostructural to γ - KYb_3F_{10} and KTb_3F_{10} . The trivalent cations are incorporated into distorted square antiprisms. The K is coordinated tetrahedrally by four inner fluorine atoms at distances of approximately 2.7 Å; twelve further anions are positioned at longer distances (≈ 3.2 Å).

The compound is an anion-excess fluorite-related superstructure and is a representative of the series M_nX_{2n+2} with $n = 4$. As pointed out by [1], the basic building unit in these structures consists of six square antiprisms which share common corners in such a way that an

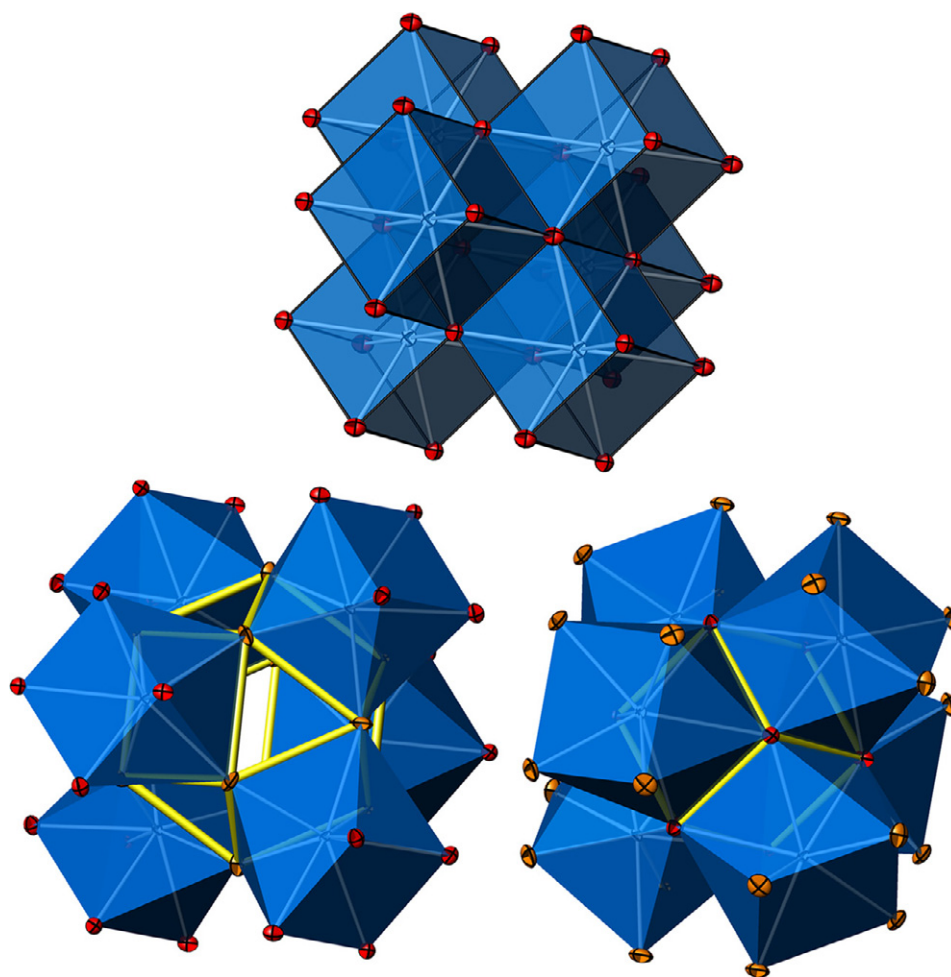


Figure 1. Top: the M_6X_{32} -unit in fluorite (top); bottom: the M_6X_{36} (left) and M_6X_{32} (right) units in KY_3F_{10} . F1 (dark grey) and F2 (light grey) atoms are shown with their thermal ellipsoids at a 50% probability level. The empty cube and cuboctahedron for the units in KY_3F_{10} , respectively, are indicated.

(This figure is in colour only in the electronic version)

empty cuboctahedron is formed at the centre of the unit. These units can be directly derived from the fluorite structure: in fluorite each cation is coordinated by a cube of eight anions. Six edge-sharing MX_8 form a $[M_6X_{32}]$ -unit, which is built around an empty X_8 cube in its centre (see figure 1, top). In KY_3F_{10} the cation coordination polyhedra (around Y) have transformed to square antiprisms which, by incorporation of four additional anions, now share corners and enclose an empty cuboctahedron forming $[M_6X_{36}]$ -units (figure 1, bottom left).

These $[M_6X_{36}]$ -units are further connected to generate $[M_6X_{32}]$ -units (see figure 1, bottom right), which like in the corresponding unit in the fluorite structure possess an empty X_8 cube at their centre. It should be noted that in other anion-excess structures the centric cuboctahedral site of the $[M_6X_{36}]$ -unit can be occupied by a further fluorine anion, leading to $[M_6X_{37}]$ -units [1].

An alternative description of KY_3F_{10} is based on the two ionic groups $[KY_3F_8]^{2+}$ and $[KY_3F_{12}]^{2-}$, which alternate in the directions of the cubic axes [2].

Table 1. Crystallographic data and details of the structure determination of KY₃F₁₀.

Empirical formula	KY ₃ F ₁₀			
Space group	$Fm\bar{3}m$			
Formula units	8			
X-ray density (g cm ³)	4.22			
F(000)	1808			
Wavelength	Mo K α			
hkl_{\min} ; hkl_{\max}	$\bar{1}\bar{8}, \bar{1}\bar{8}, \bar{1}\bar{8}; 18, 18, 18$			
Structure refinement	Jana2000 [11]			
Weighting scheme	$w = 1/[\sigma(F_{\text{obs}})^2 + (0.01 F_{\text{obs}})^2]$			
Diffractometer	Stoe IPDS II			
Distance	60 mm			
	308 K	428 K	583 K	723 K
	Crystal 2	Crystal 1	Crystal 1	Crystal 2
Run 1: ϕ , ω , $\delta\omega$ (deg)	0, 1–180, 1	0, 1–180, 1	0, 1–180, 1	0, 1–180, 1
Run 2: ϕ , ω , $\delta\omega$ (deg)	90, 1–59, 1	90, 1–180, 1	90, 1–165, 1	90, 1–93, 1
Time per frame (s)	180	150	150	180
Coefficient A [12]	11.8	14.0	14.0	11.8
Coefficient B [12]	0.7	5.7	5.7	0.7
Effective mosaic spread [12]	0.02	0.038	0.038	0.02
Lattice parameter [\AA]	11.5541(8)	11.5723(7)	11.5984(7)	11.6234(9)
Volume (\AA^3)	1542.4(2)	1549.7(2)	1560.3(2)	1570.4(2)
2θ -region (deg)	6.1–70.1	6.1–70.4	6.1–70.2	6.1–70.1
Number of reflections total	5122	6071	6013	5464
Number of reflections $\geq 3\sigma$	3886	4787	4659	3845
Absorption correction	Gaussian [13]			
T_{\min}	0.0569	0.0509	0.0508	0.0426
T_{\max}	0.1429	0.1192	0.1186	0.1208
Number of faces	17	20	20	17
Absorption coefficient (mm^{-1})	22.8	22.8	22.7	22.7
Extinction coefficient	0.218(6)	0.191(5)	0.146(9)	0.065(4)
$R_{\text{int}} > 3\sigma$	0.0599	0.0562	0.0579	0.0817
R_{int} all	0.0603	0.0563	0.0568	0.0826
Number of unique reflections $> 3\sigma$ /all	207/209	209/213	209/215	212/213

When doped with rare-earths, KY₃F₁₀ is a material employed as a room-temperature laser operating at 1.5, 1.85, 2.3, and 2.9 μm [3–5]. It is considered to be intrinsically disordered, with fluorine linked in Frenkel pairs [6]. The ionic conductivity is believed to be mainly due to the fluorine migration in the crystal lattice. Dielectric constant and ac and dc electrical conductivity measurements have revealed the presence of two thermally activated processes below and above 600 K, associated with different conductivity mechanisms [6, 7]. It is possible that at high temperatures potassium–fluorine pseudo-Schottky defects are present. It is not clear whether the conductivity change at around 600 K is accompanied by a structural transformation of the fluorite-derived crystal structure. Raman scattering measurements as a function of temperature have shown that the band linewidths are associated with the thermally activated fluorine diffusion and atomic displacements around the interstitial sites [8, 9].

Investigations at non-ambient conditions [10] have indicated that upon compression to above 7.5 GPa at room temperature, a new polymorph of KY₃F₁₀ ($Pm\bar{3}m$, $Z = 1$) is formed in which the potassium and yttrium atoms occupy the ideal fcc fluorite positions. Fluorine atoms are disordered and split on partially occupied sites. The same polymorph is obtained at lower pressures and higher temperatures.

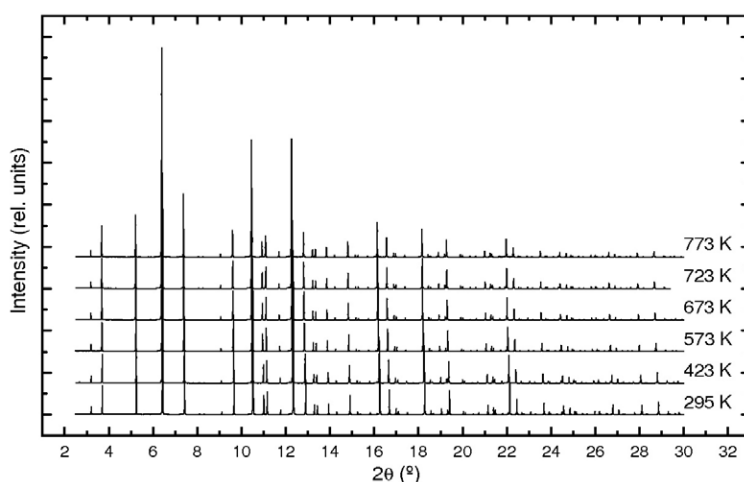


Figure 2. Powder diffraction diagrams of KY_3F_{10} as a function of temperature.

In this work we want to elucidate the high-temperature behaviour of the $2 \times 2 \times 2$ fluorite superstructure in KY_3F_{10} in the temperature range between 295 and 800 K at ambient pressure, using both powder and single crystal x-ray diffraction. Our aim is to check whether the ionic conductivity anomalies at around 600 K are due to a structural transformation and whether any conclusion about the conductivity mechanism can be drawn from the structural data.

2. Experimental details

The x-ray powder diagrams of KY_3F_{10} were measured in Debye–Scherrer geometry (using glass capillaries with an inner diameter of 0.3 mm) using a two-circle high-resolution multi-analyser diffractometer on the BM1B station at the ESRF (Grenoble, France). The 2θ region was 1.5° – 30° , the angular step was 0.0025° , and the temperature range 295–773 K at atmospheric pressure. The measurements were carried out at a wavelength of $0.374\,79(1)\text{ \AA}$.

For the single crystal investigations a suitable specimen of KY_3F_{10} was enclosed in a capillary and its diffraction intensities were measured with a Stoe IPDS II diffractometer at different temperatures (308, 428, 583, and 723 K) using the heating device HEATSTREAM (Stoe). After cooling down to room temperature another measurement was carried out. To secure reproducibility we repeated the room-temperature measurements and the measurement at the highest temperature with a second crystal. For further experimental details see table 1.

3. Results and discussion

An inspection of the powder x-ray diagrams reveals that no phase transition is observed in KY_3F_{10} in the entire temperature range studied here (see figure 2).

The refined lattice parameter and unit cell volume from powder data at 295 K are $a = 11.543\,98(6)\text{ \AA}$ and $V = 1538.39\text{ \AA}^3$. The thermal expansion coefficients are shown in figure 3. The linear thermal expansion coefficient α_{11} along the a -axis is defined as $\alpha_{11} = (da/dT)/a$. It is fitted with the linear function $\alpha_{11} = 1.370\,78 \times 10^{-5} + 2.537\,71 \times 10^{-9}T$ ($\alpha_{11} = 1.45 \times 10^{-5}\text{ K}^{-1}$ at $T = 295\text{ K}$). The bulk thermal-expansion coefficient α is defined as $(dV/dT)/V$ and is fitted with the function $\alpha = 4.102\,39 \times 10^{-5} + 7.801\,17 \times 10^{-9}T$ ($\alpha = 4.33 \times 10^{-5}\text{ K}^{-1}$ at $T = 295\text{ K}$).

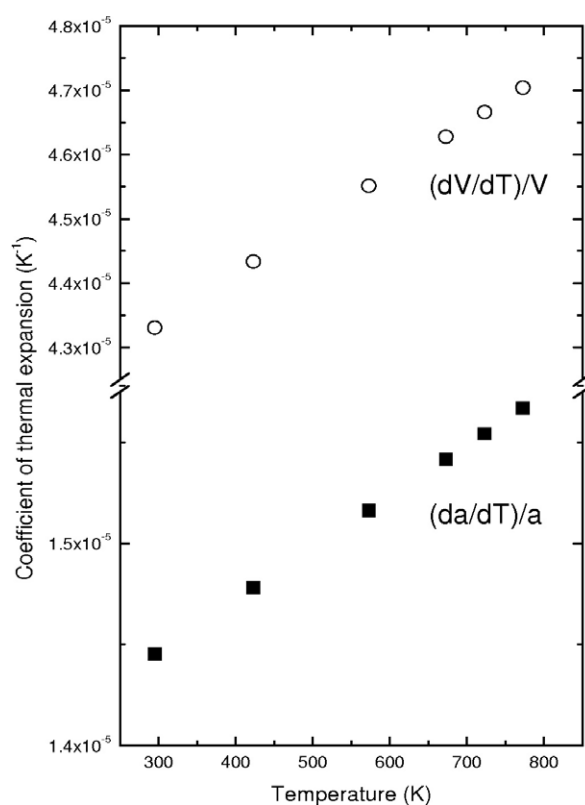


Figure 3. Temperature dependence of the coefficients of thermal expansion: $a_{295\text{ K}} = 11.543\,98(6)\text{ \AA}$ and $V_{295\text{ K}} = 1538.39\text{ \AA}^3$.

The single crystal investigations confirm the stability of the crystal structure in the temperature range studied. The structure refinements at the different temperatures were carried out with the program Jana2000 [11] using the coordinates from [2] as the starting model.

Two different models were refined. In the first one the structures were refined assuming the ideal Wyckoff positions of the $Fm\bar{3}m$ structure (Y in 24e, K in 8c, F1 in 32f, and F2 in 48i). As the displacement parameters of potassium were unusually large, we also tried a second model in which the potassium atom was displaced from its ideal position in Wyckoff position 8c ($\equiv 1/4, 1/4, 1/4$) to the more general position 32f (x, x, x). The deviation from the ideal x -coordinate of $1/4$ is relatively small and increases with rising temperature. As expected, the displacement parameters of K in the second model are considerably smaller when compared to the first model.

For model 2 the overall agreement factors are slightly lower than for model 1 (see table 2). Though the effect is not very large, it might be considered significant, especially if one takes into account that the number of refinable parameters is only increased by two (model 1: 13; model 2: 15).

Atomic coordinates and isotropic temperature parameters for model 1 are given in table 3; selected interatomic distances are given in table 4.⁶

⁶ Further details of the crystallographic investigations corresponding to model 1 and 2 can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein–Leopoldshafen, Germany, on quoting the depository numbers CSD 416080–416087.

Table 2. Final agreement factors for the refinements of the structure of KY₃F₁₀ at the different temperatures; S = goodness of fit, NP = number of parameters.

Model 1: K in the ideal position 8c (0.25, 0.25, 0.25)								
<i>T</i>	<i>R</i> (obs)	<i>Rw</i> (obs)	<i>R</i> (all)	<i>Rw</i> (all)	<i>S</i> (obs)	<i>S</i> (all)	<i>NP</i>	
308	0.0383	0.0448	0.0393	0.0451	3.34	3.34	13	Crystal 2
428	0.0330	0.0473	0.0337	0.0475	3.56	3.56	13	Crystal 1
583	0.0331	0.0461	0.0341	0.0462	3.37	3.35	13	Crystal 1
723	0.0364	0.0449	0.0378	0.0453	3.04	3.03	13	Crystal 2
Model 2: K in Wyckoff position 32f (<i>x</i> , <i>x</i> , <i>x</i>)								
<i>T</i> (K)	<i>R</i> (obs)	<i>Rw</i> (obs)	<i>R</i> (all)	<i>Rw</i> (all)	<i>S</i> (obs)	<i>S</i> (all)	<i>NP</i>	
308	0.0373	0.0433	0.0382	0.0436	3.33	3.27	15	Crystal 2
428	0.0313	0.0422	0.0320	0.0423	3.19	3.19	15	Crystal 1
583	0.0305	0.0404	0.0315	0.0406	2.98	2.96	15	Crystal 1
723	0.0351	0.0402	0.0362	0.0407	2.76	2.74	15	Crystal 2

Table 3. Atomic coordinates and isotropic displacement parameters of KY₃F₁₀ corresponding to model 1; standard deviations are given in parentheses.

<i>T</i> (K)	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i> _{iso}
308	Y	0.240 24(6)	0	0	0.0127(2)
428	Y	0.240 42(7)	0	0	0.0108(2)
583	Y	0.240 57(6)	0	0	0.0134(2)
723	Y	0.240 75(6)	0	0	0.0203(2)
308	Y	0.240 23(6)	0	0	0.0128(2)
308	K	0.25	0.25	0.25	0.0336(8)
428	K	0.25	0.25	0.25	0.0396(6)
583	K	0.25	0.25	0.25	0.0497(7)
723	K	0.25	0.25	0.25	0.0617(8)
308	F1	0.1115(2)	0.1115(2)	0.1115(2)	0.0172(4)
428	F1	0.1116(3)	0.1116(3)	0.1116(3)	0.0172(5)
583	F1	0.1116(3)	0.1116(3)	0.1116(3)	0.0221(5)
723	F1	0.1114(3)	0.1114(3)	0.1114(3)	0.0302(6)
308	F2	0.5	0.1659(2)	0.1659(2)	0.0219(7)
428	F2	0.5	0.1659(3)	0.1659(3)	0.0227(8)
583	F2	0.5	0.1656(3)	0.1656(3)	0.0287(9)
723	F2	0.5	0.1657(3)	0.1657(3)	0.0394(11)

Table 4. Selected interatomic distances of KY₃F₁₀ in (Å) corresponding to model 1; standard deviations are given in parentheses.

<i>T</i>	Y–F1	Y–F2	K–F1	K–F2	F1–F1	F1–F2	F2–F2'	F2–F2''
308	2.352(2)	2.202(3)	2.771(3)	3.1985(11)	2.578(4)	2.944(4)	2.747(4)	2.711(3)
428	2.357(3)	2.205(3)	2.774(3)	3.2037(13)	2.583(4)	2.948(4)	2.753(4)	2.715(3)
583	2.364(3)	2.208(3)	2.781(3)	3.2131(13)	2.588(5)	2.957(4)	2.768(4)	2.716(3)
723	2.369(3)	2.212(3)	2.791(3)	3.2194(14)	2.589(5)	2.965(4)	2.772(5)	2.724(3)

The refinements show that the changes for most of the structural parameters are very small with varying temperature. Thus, for example, the atomic coordinates of the fluorine atoms stay basically constant over the whole temperature range. The *x*-coordinate of the Y atom on the

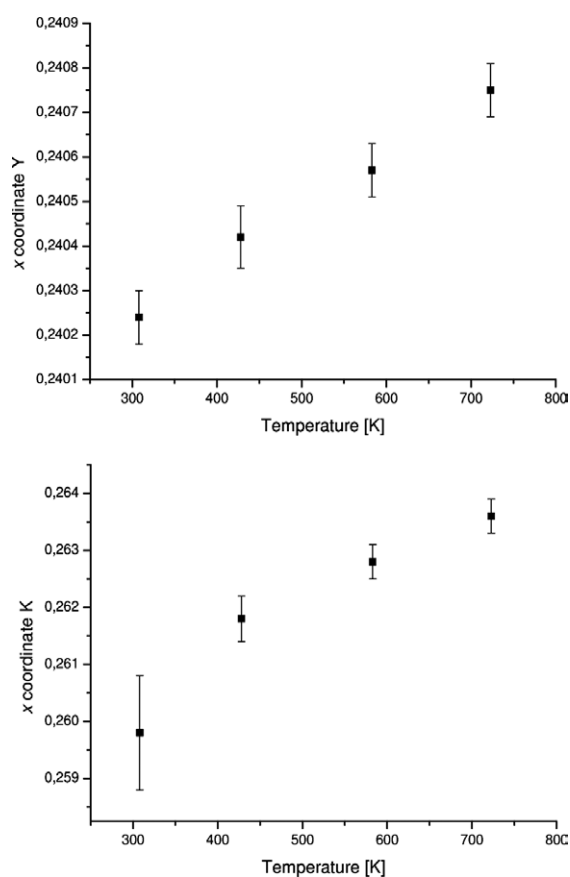


Figure 4. Value of the x -coordinate of yttrium and K (in Wyckoff Position 32f; model 2, see text) as a function of temperature.

other hand shows a slight tendency to approach the more ideal value of 0.25 with increasing temperature and the refinements corresponding to model 2 show that the x -coordinate of the K atom shows larger deviations from the ideal coordinate of 0.25 with increasing temperature (see figure 4).

As can be seen from table 4, all relevant interatomic distances increase only slightly with temperature, leading to the observed increase in lattice parameters and overall volume. The changes in interatomic angles are also extremely small. The displacement parameters show the expected increase with rising temperature and the only striking feature is the comparatively large displacement parameter of K (see figure 5).

As already mentioned before, two thermally activated processes have been observed for KY_3F_{10} and were associated with different conductivity mechanisms [6, 7]. Several interstitial sites for the fluorine in the ionic conducting phase were postulated. Thus, for example, the position $1/4, 1/4, 0$ is mentioned by [9].

It is tempting to assume that the partial occupancy of interstitial sites involved in the conductivity mechanism could give rise to maxima in the difference Fourier synthesis. Furthermore, one would expect these maxima to become more pronounced with rising temperature. On the basis of these considerations we decided to look very carefully at the

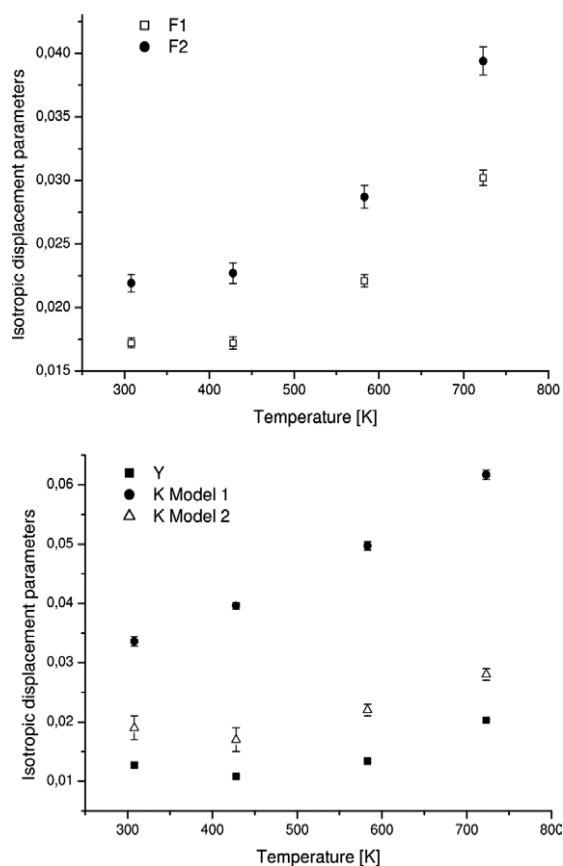


Figure 5. Isotropic displacement parameters as a function of temperature.

difference Fourier synthesis corresponding to the different temperatures. We report here on the Fourier synthesis corresponding to refinement model 1, yet model 2 gives basically identical results.

The position at the centre of the cuboctahedra (coordinates $1/2, 0, 0$), which is known to be occupied by additional fluorine atoms in other anion-excess fluorite-related superstructures, seems to be a reasonable candidate for possible interstitial sites. Surprisingly this position corresponds to a minimum in the difference Fourier synthesis. In addition, the $1/4, 1/4, 0$ position suggested in [9] does not appear with any appreciable weight at all.

On the other hand, the position which corresponds to the centre of the empty F_8 cube (coordinates $0, 0, 0$) appears as one of the most prominent maxima in the difference Fourier map. Indeed, of all the maxima of considerable weight it is the only one that is characterized by reasonable interatomic distances ($\approx 2.24 \text{ \AA}$ to the fluorine atoms forming the cube). The evolution of the difference Fourier map around the $0, 0, 0$ position with temperature is shown in figure 6. As can be seen this maximum considerably gains in importance with rising temperature (0.41 e/\AA^3 at 308 K as compared to 2.32 e/\AA^3 at 723 K) and sharpens significantly. A comparison of the two maps corresponding to room temperature (before and after heating) even suggests a small memory effect.

As a trial, we introduced the position at $0, 0, 0$ into the different refinement models, yet when we refined the occupancy of this position we never obtained a value significantly different

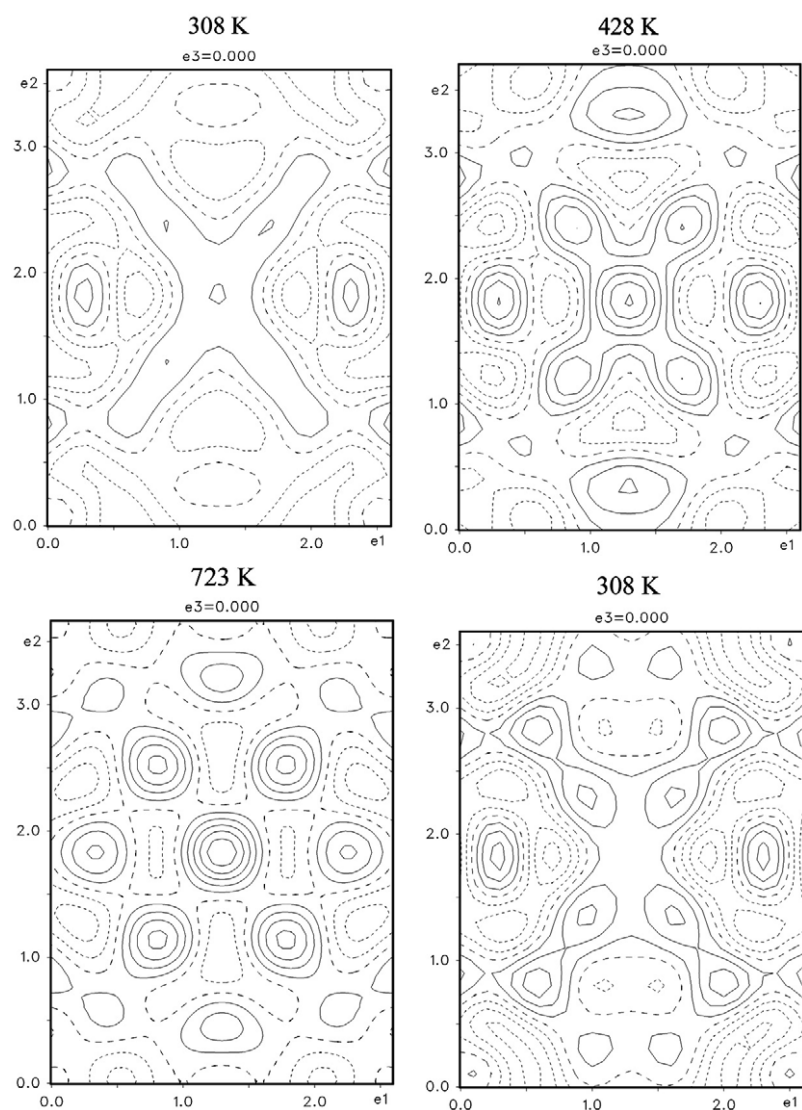


Figure 6. Difference Fourier synthesis around the maximum at 0, 0, 0. The point e1 corresponds to $F1^{x,x,x}$, point e2 corresponds to $F1^{x,x,-x}$, and the upper right corner corresponds to $F^{-x,-x,-x}$. Contour lines correspond to 0.2 (positive = full lines and negative = broken lines). The first difference Fourier at 308 K is before heating; the second one is after heating.

from zero. The anisotropic displacement parameters of the F1 atoms, which should slightly increase, if the occupancy of the F1 position is reduced, also do not show any significant effect (see figure 5).

In the structure of KY_3F_{10} the empty cuboctahedra are built by F2 atoms, while the empty cubes are built up by F1 atoms which also form the tetrahedral coordinations around the K atoms. Thus, any interstitial F atom occupying the centre of the empty cube must have left its normal site in the K coordination sphere. In this context, it is interesting that, according to the refinement model, the K atoms are displaced in the direction away from the corners of the

coordinating tetrahedron. This might well be a consequence of vacant corners, in which case K would be more attracted towards the remaining three coordinating F atoms. In this respect the behaviour of K with rising temperature could be in direct connection with the fluorine migration mechanism.

Finally, we would like to point out that, on the basis of our structural data, we were not able to identify any feature which might be related to the anomaly in the conductivity around 600 K observed by [6, 7].

4. Conclusions

In the description of fluorite-related superstructures, it is common to consider mainly the anions as they are significantly displaced from the ideal fluorite sites. However, in the fluorite superstructure in KY_3F_{10} the yttrium atoms are also shifted from the ideal positions derived from the fluorite structure. At high temperatures and atmospheric pressure, the x -coordinate of the Y atom in fact exhibits a tendency to approach its ideal value, an observation which correlates well with the results of previous high-temperature high-pressure investigations [10]. Furthermore, the results of this study show that the high-temperature mobility of fluorine atoms in the structure of KY_3F_{10} might involve the central position of the F_8 cube (formed by F1 atoms) rather than the central site of the empty cuboctahedra (formed by F2 atoms) as expected from comparison with other fluorite-related superstructures [1]. Our x-ray diffraction experiments also do not reveal any other crystallographically allowed sites or interstitials for the fluorine thermal conductivity. As the F1 atoms are those fluorines in the structure which are strongly bonded to potassium, their migration might have a direct influence on the coordination of the K site. These observations further suggest that a homologous series of $KY_{3-x}Me_xF_{10+x}$ compounds derived from the anion-excess fluoride of the KY_3F_{10} type ($Fm\bar{3}m$, $Z = 8$) might exist, in which the trivalent cations are substituted by tetravalent cations and at the same time additional fluorine atoms are accommodated in the empty cubes for charge balance.

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