Polymorphism, structures and phase transformation of $K_3[SO_4]F$

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The phase $K_3[SO_4]F$ was found to be dimorphic, undergoing a reversible tetragonal (β) to cubic (α) phase transition at 585 °C. The room-temperature polymorph, β-$K_3[SO_4]F$, is isostructural with Ba_3SiO_5, as confirmed by Rietveld refinement of X-ray powder diffraction data: $a = 7.2961(5)$, $c = 10.854(1)$ Å, $R = 0.0689$ and $R_{wp} = 0.0907$. The α form is cubic, $a \approx 5.43$ Å, with probable space group $Pm\bar{3}m$. Partial Rietveld refinement suggested that it has an anti-perovskite structure. Lattice parameter measurements as a function of temperature showed no discontinuity at the α–β transition, which is therefore suggested to be a displacive second-order transition.

The compound $K_3[SO_4]F$ was synthesised as part of an investigation into compounds of the type $M_3[TO_4]X$, where T is a tetrahedral cation, M a medium to large cation and X an anion not bonded to the tetrahedra. These structures were described by Eysel and Breuer[1] in terms of close packed layers. The 'basic layer' has the hexagonal plane group $p3m1$ and the approximate lattice parameter $a \approx 7$ Å with a thickness of $c \approx 3$ Å. The repeat unit of the basic layer contains one formula unit $M_3[TO_4]X$. The M and TO_4 ions are depicted as small and large spheres, respectively, in Fig. 1(*a*). The additional anion, X, which has the choice of four possible positions, two above and two below the $M_3[TO_4]$ plane, is represented by shaded spheres. The packing of the layers is controlled by the orientation of the tetrahedra and the occupation of the X site; in Fig. 1 the tetrahedra are represented by circles to show all possible orientations. A side view of the basic layer is given in Fig. 1(*b*), showing more clearly the possible positions of the X sites relative to the $M_3[TO_4]$ layer. These layers may be stacked in the same manner as conventional close-packed structures; thus an infinite number of polytypes is possible.

Many related layered structures of general formula $M_3[TO_4]X$ have been reported. The compound $(Cd,Pb)_3[SiO_4]O$ has two polymorphs, both of which have two-layer structures.[2] The room-temperature polymorph has a pseudo-hexagonal, triclinic unit cell [space group $P1$ (no. 1)] which transforms to a hexagonal cell [space group $p3m1$ (no. 156) or $P3$ (no. 143)] at ≈700 °C. A number of three-layer structures exist of the type $M_3[TO_4]O$ with M = Pb, Cd, Sr or Ba and T = Si or Ge; all have pseudo-cubic cells. The subgroup relations for the three-layer compounds were detailed by Eysel and Breuer and are summarised in Scheme 1. The cement clinker phase Ca_3SiO_5 has a number of different polymorphs, which are all related to $M_3[TO_4]X$ and have nine-layer structures.[3] Another cement phase, of nominal formula $Ca_{12}Si_4O_{19}F_2$, may have a related, two-layer structure; Eysel and Breuer[1] propose a stoichiometry of $Ca_{11}\square Si_4O_{18}F_2$ with fluorine ions occupying sites not bonded to tetrahedra.

A summary of some of the previously studied oxides, their unit cells and pseudo-cubic and -hexagonal subcells is given in Table 1. In addition to these, a large number of compounds of general formula M_3TO_5 with $M_3 = Ba_3$, Ba_2Sr, Ba_2La or Sr_2La and T = Ti, V, Cr, Mn, Fe, Co, Al, Ga or Ge have been detailed by Mansmann.[7] These are isostructural with Ba_3SiO_5 and Cs_3CoCl_5[6,8] and other M_3CoX_5 compounds (M = Rb or Cs, X = Br or Cl). A range of beryllium fluorides, M_3BeF_5 also form with related structures;[9] for M = Cs, Rb or K the phase is isostructural with Sr_3SiO_5, but for M = Na, two polymorphs are observed, both having nine-layer structures similar to the T and R polymorphs of Ca_3SiO_5.[3]

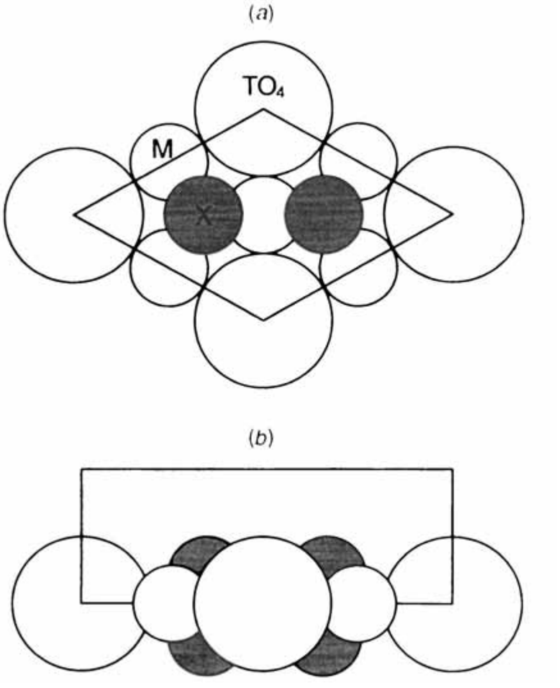


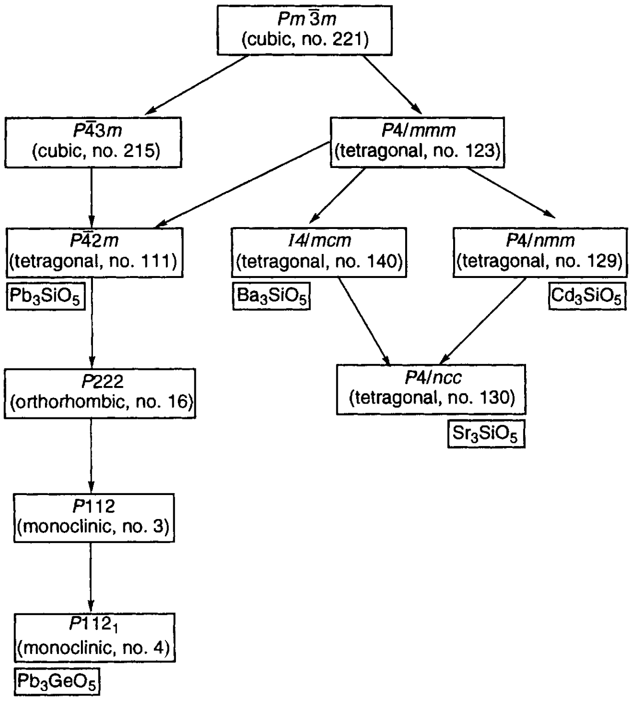
Fig. 1 Basic structural unit of $M_3[TO_4]X$ compounds: (*a*) plan view, (*b*) side view. Small spheres are M, large spheres TO_4; shaded spheres show X occupying possible positions above and below the plane

The phase $K_3[SO_4]F$ was first identified in a phase-diagram study of the binary system KF–K_2SO_4.[10] A fuller study of the systems AF–A_2SO_4 (A = Li, K, Rb or Cs)[11] noted the occurrence of a phase transition in $K_3[SO_4]F$ at ≈578 °C. The room-temperature polymorph is reported as tetragonal, $a = 7.301$, $c = 10.863$ Å, transforming to cubic, $a \approx 5.46$ Å at 585 °C.[12] The similarity between the X-ray powder diffraction patterns of $K_3[SO_4]F$ and $K_3[PO_3F]F$ was also noted.[12] One may expect the sodium analogue to have a similar powder pattern; $Na_3[SO_4]F$ is the mineral kogarkoite and is monoclinic, space group $P2_1/m$, $a = 18.074$, $b = 6.958$, $c = 11.443$ Å and $\beta = 107.71°$.[13] In the layer scheme of Eysel and Breuer,[1] $Na_3[SO_4]F$ can be considered to be a nine-layer structure. Since there is no obvious similarity between the X-ray diffraction (XRD) patterns of $Na_3[SO_4]F$ and $K_3[SO_4]F$ and therefore the structures of the $K_3[SO_4]F$ polymorphs are not known, a structural investigation of the two polymorphs of $K_3[SO_4]F$ was carried out.

Table 1 Summary of data for some oxides $M_3[TO_4]O$ (lengths in Å, angles in °)

Compound	Space group	Original cell *a*	*b*	*c*	α	β	γ	Pseudo-cubic *a*	*b*	*c*	Pseudo-hexagonal *a*	*b*	*c*	Ref.
Basic layer	*p*3*m*1[a]	7	7	3	90	90	120	4.95	4.95	4.24	7	7	3	
$(Cd,Pb)_3SiO_5$	*P*1	12.253	7.074	5.933	90.42	90.00	90.00	5.002	5.002	5.933	7.074	7.074	5.933	2
$(Cd,Pb)_3GeO_5$	*P*1	12.512	7.226	5.982	90.37	90	90	5.110	5.110	5.982	7.226	7.226	5.982	2
$(Cd,Pb)_3SiO_5$	*p*3*m*1[a]	7.231	7.231	6.003	90	90	120	5.113	5.113	6.003	7.231	7.231	6.003	2
$(Cd,Pb)_3GeO_5$	*p*3*m*1[a]	7.133	7.133	5.990	90	90	120	5.044	5.044	5.990	7.133	7.133	5.990	2
Cd_3SiO_5	*P*4/*nmm*	6.842	6.842	4.952	90	90	90	4.838	4.838	4.952	6.923	6.923	8.446	4
Sr_3SiO_5	*P*4/*ncc*	6.948	6.948	10.753	90	90	90	4.913	4.913	5.376	7.283	7.283	8.785	5
Ba_3SiO_5	*I*4/*mcm*	7.307	7.307	11.228	90	90	90	5.167	5.167	5.614	7.630	7.630	9.215	6
Pb_3SiO_5 (stable)	$P2_1/c$	11.980	10.114	10.342	90	90	109.1	5.990	5.057	5.171	7.913	7.233	9.391	2
(meta-stable)	*P*42*m*	5.392	5.392	5.172	90	90	90	5.392	5.392	5.172	7.471	7.471	9.214	2
Pb_3GeO_5	$P2_1$	5.484	5.265	10.450	90	90	92.57	5.484	5.265	5.225	7.575	7.418	9.225	2
Ca_3SiO_5 (T_I)	*C*1	24.398	14.212	25.103	89.91	89.69	89.69	4.980	5.025	5.021	7.043	7.106	25.103	3
(T_{III})	*C*1	24.633	14.290	25.412	90.06	89.86	89.91	5.028	5.052	5.082	7.111	7.145	25.412	3
(M_I)	*Cm*	12.332	7.142	25.420	90	89.85	90	5.034	5.050	5.084	7.120	7.142	25.420	3
(M_I)	*Cm*	12.342	7.143	25.434	90	90.0	90	5.039	5.051	5.087	7.126	7.143	25.434	3
(R)[b]	*R*3*m*	12.384	7.150	25.560	90	90	90	5.055	5.055	5.112	7.150	7.150	25.560	3

[a] Point group describing the basic layer. [b] Pseudo-orthohexagonal lattice constants from ref. 3.



Scheme 1 Subgroup relations for three-layer compounds in the system $M_3[TO_4]X$ (after ref. 1)

Experimental

Potassium fluoride sulfate, $K_3[SO_4]F$, was prepared by solid-state reaction of a stoichiometric mixture of AnalaR K_2SO_4 and KF fired at 700 °C for 24 h. Initial indexing of the room-temperature powder pattern was carried out using the Stoe auto-indexing program INDEX[14] and least-squares refinement gave a tetragonal unit cell of $a = 7.2961(5)$ and $c = 10.854(1)$ Å. Examination of systematic absences gave three possible space groups *I*4*cm*, *I*4̄*c*2 and *I*4/*mcm*. A survey of other compounds of the type $M_3[TO_4]X$ indicated that $K_3[SO_4]F$ might be isostructural with $Ba_3[SiO_4]O$, which crystallises in the space group *I*4/*mcm*.[6] Therefore, a theoretical powder pattern was generated for $K_3[SO_4]F$ using the atomic coordinates for $Ba_3[SiO_4]O$ and was found to be similar to the observed powder pattern. A second phase, identified as β-K_2SO_4 (arcanite),[15] was present in the sample, but in sufficiently small quantity as to allow successful Rietveld refinement of the $K_3[SO_4]F$ structure.

X-Ray diffraction data for Rietveld refinement were collected with a Stoe Stadi/P diffractometer in transmission mode using a small linear position sensitive detector and a germanium monochromator providing Cu-Kα_1 radiation ($\lambda = 1.540\ 56$ Å). A scan range of $5 \leqslant 2\theta \leqslant 110°$ in steps of 2° was used in the refinement; the detector resolution was 0.02°. Refinement was carried out using a squared Lorentzian function to model peak shape. This has been found to give the best fit for the peak-shape profile on the Stoe diffractometer. Initially, 16 profile parameters were refined, including two cell parameters, instrumental zeropoint, and scale factor. The variation of the full width at half maximum was described by three Tchebychev polynomials. The background was also modelled using a series of shifted Tchebychev polynomials up to the ninth degree; this was found necessary in the room-temperature refinement because of a rather modulated background profile. Starting parameters for the structural refinement were taken from the $Ba_3[SiO_4]O$ structure,[6] with F on the O(1) site, and these converged well with final shifts for all parameters of less than 10^{-4}. In the final refinement, three positional and five thermal parameters were refined giving final *R* factors of $R = 0.0753$, $R_{wp} = 0.1090$ and $R_I = 0.0544$; these dropped to $R = 0.0689$ and $R_{wp} = 0.0907$ when contributions from the K_2SO_4 phase were excluded.

Refinements were tested for a false minimum in *R* by shifts of each positional parameter by up to ±0.15%, but convergence to the same values always occurred. Greater shifts caused convergence to symmetry-related positions.

Since it has been reported that $K_3[SO_4]F$ undergoes a phase transition at ≈580 °C[11,12] a high-temperature study was carried out. Using the Stoe high-temperature attachment the sample was heated to 700 °C, with measurements taken in the range $26 \leqslant 2\theta \leqslant 75°$ at periodic temperature intervals. For each temperature the pattern was indexed using an automatic indexing program, and the unit cell obtained from this procedure was refined using the Stoe program LATREF.[16]

Differential thermal analysis was carried out on a Stanton Redcroft DTA675 (1640) instrument, using Al_2O_3 as a reference; no peaks due to the phase transition were observed.

Results

Crystal data and refined values for the structural parameters of the room-temperaturature polymorph of $K_3[SO_4]F$ are given in Table 2(*a*). Plots of the experimental X-ray diffraction patterns and difference data after Rietveld refinement are shown in Fig. 2.

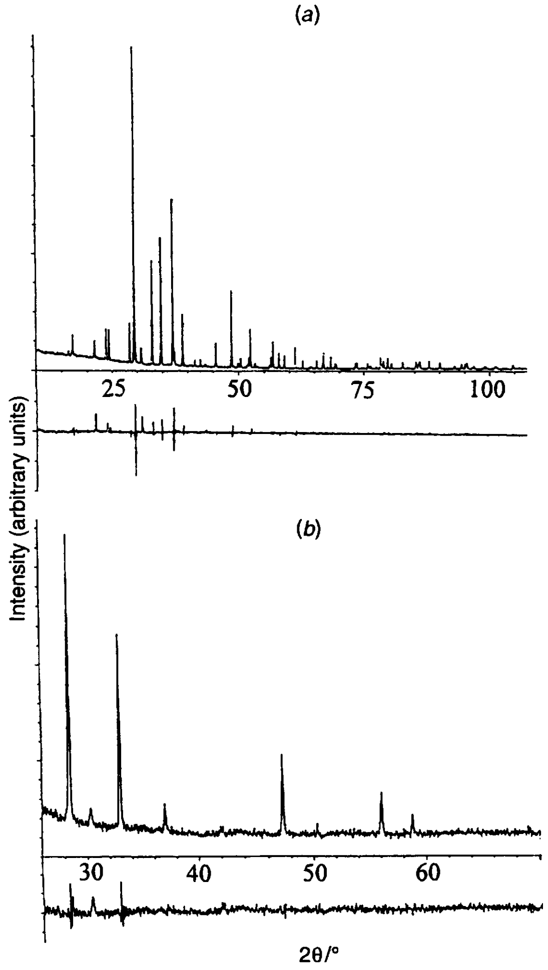


Fig. 2 Rietveld refinement profile fit for (*a*) β-$K_3[SO_4]F$ at 30 °C and (*b*) α-$K_3[SO_4]F$ at 600 °C

Table 2 Atomic coordinates with estimated standard deviations in parentheses

Space group *I*4/*mcm* (no. 140): a = 7.2961(3), c = 10.8537(5) Å

Atom	Position	X/a	Y/b	Z/c	U_{iso}/Å^2
K(1)	4a	0.00(—)	0.00(—)	0.25(—)	0.023(3)
K(2)	8h	0.1940(4)	0.6940(4)	0.00(—)	0.017(2)
S	4b	0.00(—)	0.50(—)	0.25(—)	0.013(3)
F	4c	0.00(—)	0.00(—)	0.00(—)	0.013(6)
O	16l	0.1150(7)	0.6150(7)	0.6740(8)	0.023(5)

(*b*) α-$K_3[SO_4]F$: a = 5.433(1) Å

Atom	Position *Pm*$\bar{3}$*m* (no. 221)	*P*$\bar{4}$3*m* (no. 215):	X/a	Y/b	Z/c	U_{iso}/Å^2
K	3d	3d	0.00(—)	0.00(—)	0.50(—)	0.07(4)
S	1b	1b	0.50(—)	0.50(—)	0.50(—)	0.60(8)
F	1a	1a	0.00(—)	0.00(—)	0.00(—)	0.18(8)
O	8g	4e	0.32(6)	0.32(—)	0.32(6)	0.7(3)

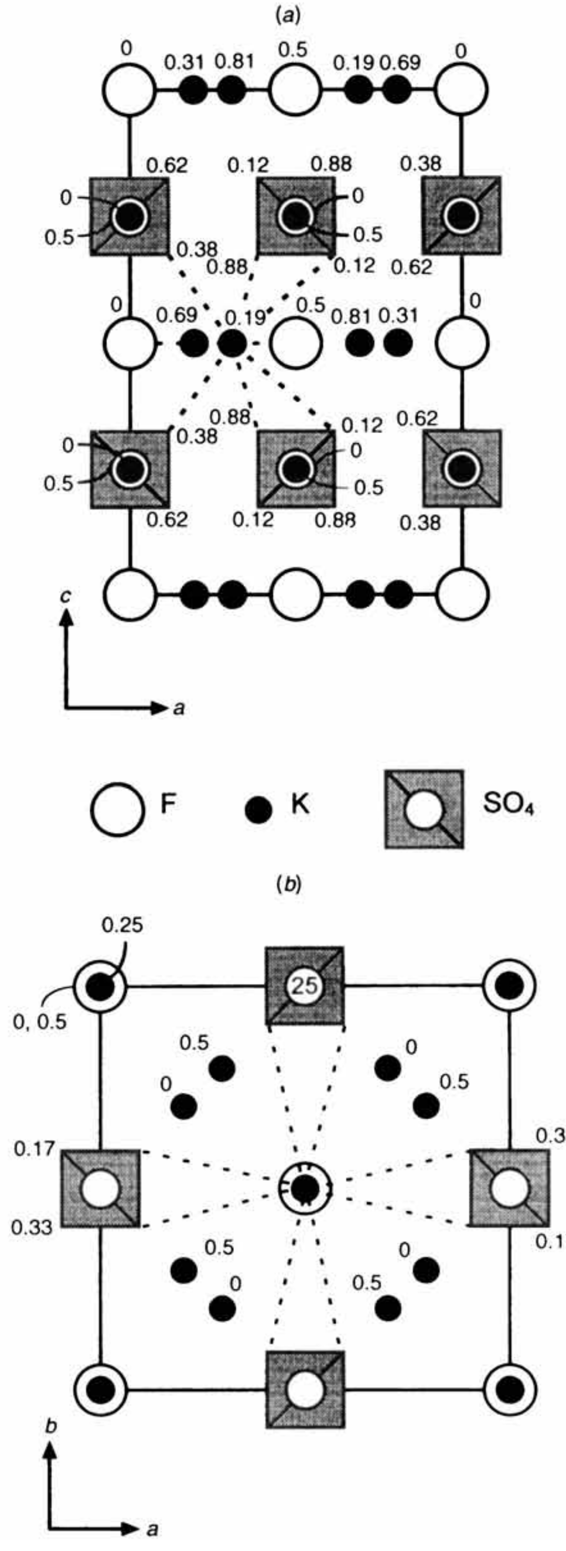


Fig. 3 Projections of the β-$K_3[SO_4]F$ structure along (*a*) [010] and (*b*) [001] (only atoms with *c* heights between 0 and 0.5 are shown)

The room-temperature polymorph of $K_3[SO_4]F$, designated β, is isostructural with compounds such as $Ba_3[SiO_4]O$ and Cs_3CoCl_5.[6,8] Projections of the structure along the [010] and [001] directions are shown in Fig. 3(*a*) and 3(*b*), respectively. Layers of K^+ and F^- ions lying in the *xy* plane are separated by layers of SO_4 tetrahedra and K^+ ions; thus, the structure may also be thought of as a layered double salt $KF{\cdot}K_2SO_4$. The SO_4 tetrahedra are slightly distorted with O–S–O angles of 109.0 and 110.4°, and S–O bond lengths of 1.445 Å. Atom K(1), which lies in the 'K_2SO_4' layers, is co-ordinated by eight oxygen atoms from four surrounding SO_4 tetrahedra and two fluorine atoms above and below in the *c* direction, with bond lengths of 3.045 and 2.713 Å for K(1)–O and K(1)–F, respectively [Fig. 3(*a*)]. Atom K(2) within the 'KF' layers, is co-ordinated by six oxygens, three above and three below in the *c* direction, and two fluorine atoms within the 'KF' layer, with bond lengths of 2.997 and 2.643 Å for K(2)–O and K(2)–F respectively [Fig. 3(*b*)]. The fluorine atoms are octahedrally co-ordinated to six potassium ions, four within the KF layers (2.643 Å) and one above and below in the *c* direction (2.713 Å).

As with all other $M_3[TO_4]X$ structures, the unit cell is

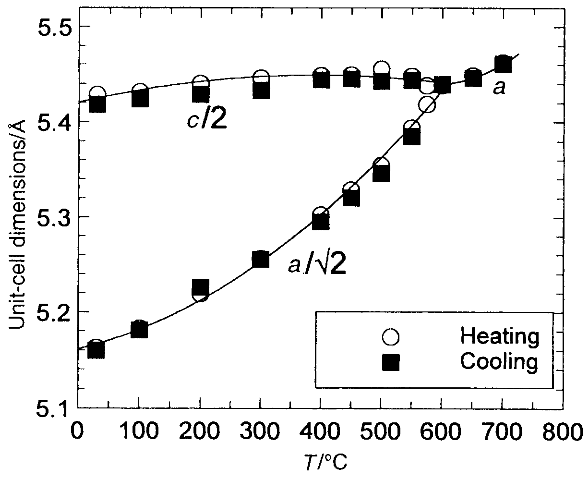


Fig. 4 Unit-cell parameters *versus* temperature for $K_3[SO_4]F$, showing the tetragonal–cubic transition

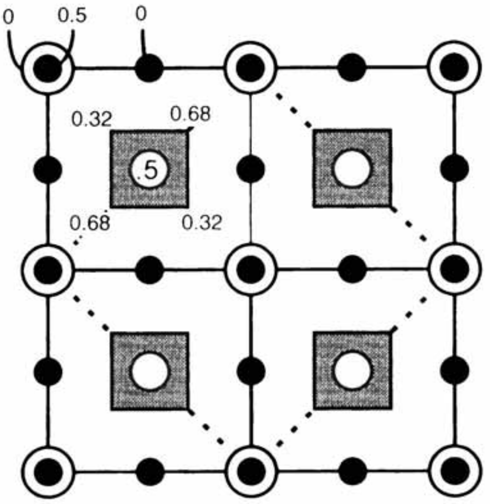


Fig. 5 Projection of the α-$K_3[SO_4]F$ structure. The equivalent tetragonal unit cell is indicated by dashed lines. The SO_4 anions are represented by shaded squares; these indicate the disorder of tetrahedra as for the space group $P\bar{4}3m$. Potassium ions are represented by filled circles and fluorine by open circles

pseudo-cubic, with $a_{cub} = a_{tet}/\sqrt{2} = 5.159$ Å and $c_{cub} = c_{tet}/2 = 5.427$ Å. Fig. 4 shows the variation of these pseudo-cubic cell parameters with temperature, showing a transition from tetragonal to cubic symmetry at 585 ± 10 °C. At 600 °C the unit cell was indexed as cubic, with $a = 5.438$ Å. High-temperature Rietveld refinement using data recorded at 600 °C was attempted in order to identify the space group and structure of the high-temperature polymorph, designated α-$K_3[SO_4]F$.[17] At this temperature the second phase was identified as α-K_2SO_4. Initially, structure refinement was attempted in the space group $Pm\bar{3}m$, with K, S and F in appropriate positions for the anti-perovskite structure.[18] The oxygen was placed in position 8g at a distance 1.52 Å from S, with occupancy 0.5, thus modelling an SO_4 tetrahedron of random orientation and average S–O bond length.[19] Refinement was also carried out in the space group $P\bar{4}3m$, with oxygen on the 4e position and full occupancy. This gave tetrahedra of specific orientation. The results of both refinements are given in Table 2(*b*). Although cubic symmetry was confirmed, as were the sites of both the potassium and sulfur atoms, no distinction could be made between the space groups $Pm\bar{3}m$ and $P\bar{4}3m$ because the refinements converged to the same *R* factors. Therefore, on the basis of our results we cannot distinguish between these two cubic space groups. The choice between them depends on whether or not the tetrahedra are disordered or ordered, respectively. A projection of the cubic structure is shown in Fig. 5; four cells are drawn and the corresponding tetragonal cell for the low-temperature polymorph is indicated by dotted lines. The orientation shown for the tetrahedra assumes space group $P\bar{4}3m$.

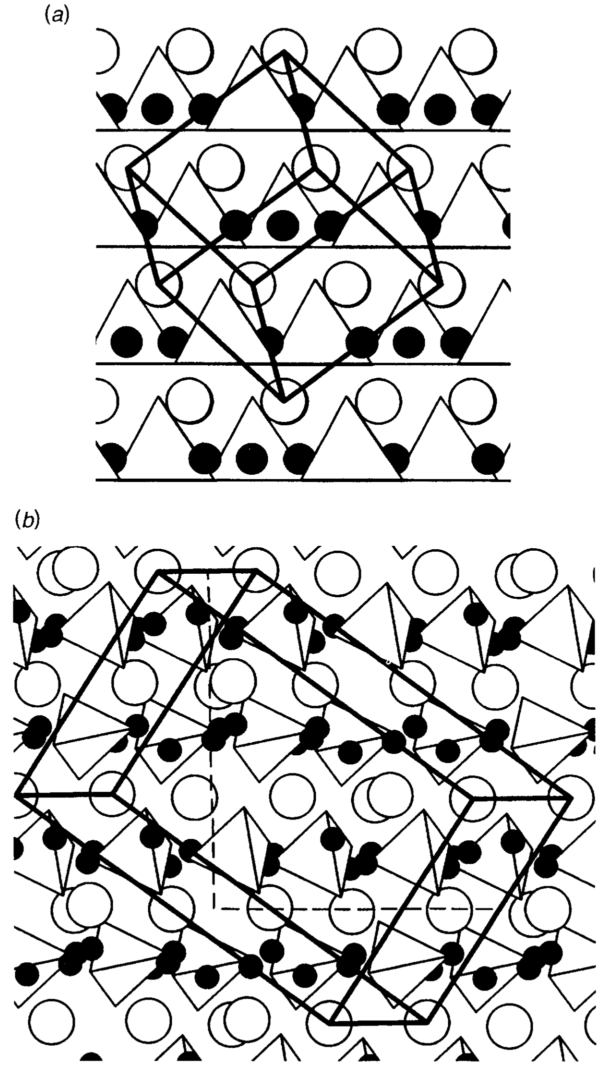


Fig. 6 (*a*) The structure of α-$K_3[SO_4]F$, showing the layers parallel to the face diagonal and perpendicular to the body diagonal. (*b*) The tetragonal β-$K_3[SO_4]F$ structure, showing the layers approximately parallel to the *ac*/*bc* face diagonal. The pseudo-hexagonal axes are indicated by the dashed axes

Discussion

Considering the previously described trigonal layer, Fig. 1, as the basic structural unit, both α- and β-$K_3[SO_4]F$ may be classified as three-layer structures, according to the classification of Eysel and Breuer;[1] the trigonal sub-cell is similar to that of Ba_3SiO_5 in Table 1. Fig. 6(*a*) shows the cubic α structure oriented in such a way as to show the 'basic' layers which lie parallel to the face diagonals of the cubic cell. For the purposes of this diagram the SO_4 tetrahedra are oriented as for the $P\bar{4}3m$ space group. Each layer consists of SO_4 tetrahedra separated by potassium ions, with the fluorine ions occupying positions above and below the 'K_3SO_4' layer. By comparison with the basic trigonal layer shown in Fig. 1, adjacent layers in the $K_3[SO_4]F$ structure are shifted by $\frac{1}{3}$ along the long diagonal of the unit cell relative to the first layer [Fig. 1(*a*)]. This means that the apical ion X(= F), which can occupy any of four sites as shown in Fig. 1(*b*), fits into a void in the next layer.

Fig. 6(*b*) shows the similar layered nature of the tetragonal β structure; in this case the layers run parallel to the long

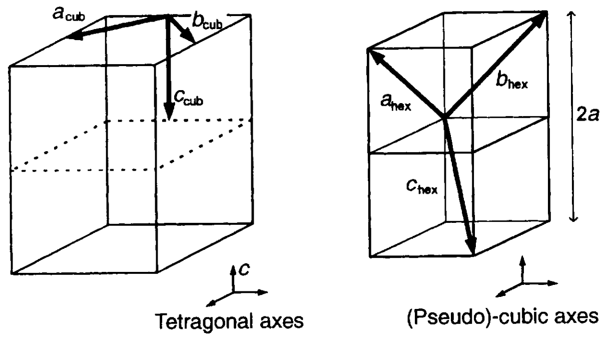


Fig. 7 Relation between the hexagonal (R-centred), cubic (Fig. 4) and tetragonal (Fig. 3) cells of the $K_3[SO_4]F$ structures

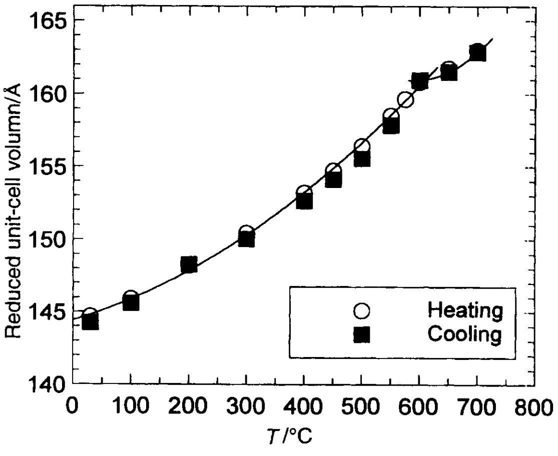


Fig. 8 Plot of volume per formula unit *versus* temperature for $K_3[SO_4]F$

face diagonal of the tetragonal cell. The (pseudo)-hexagonal axes are also indicated; the relationships between the symmetries of the two polymorphs and the trigonal basic layer are summarised in Fig. 7. The simple mathematical transformation between the tetragonal, cubic and hexagonal cells may be described as follows: $a_{tet} = \sqrt{2}a_{cub} = a_{hex}$, $c_{tet} = 2c_{cub}$ and $c_{hex} = \sqrt{c_{cub}^2 + 2a_{cub}^2}$. There are no previously reported $M_3[TO_4]X$ structures with cubic symmetry, but all known three-layer structures are pseudo-cubic, Table 1, as is the tetragonal β polymorph of $K_3[SO_4]F$. The sub group relationships for the three-layer structures given in Scheme 1 indicate that the cubic polymorph should have the space group $Pm\bar{3}m$, since the tetragonal polymorph then belongs to a subgroup.

Another way of describing the cubic structure is to consider the SO_4 tetrahedra as being represented by spheres; the structure can then be thought of as an anti-perovskite with the formula $\{SO_4\}FK_3$, with SO_4 at the body centre of the unit cell. Again, these structures are close packed, since the packing layers have the constitution $\{SO_4\}K_3$ with F^- ions occupying $\frac{1}{4}$ of the available octahedral sites, *i.e.* those sites co-ordinated to K^+ and not to SO_4^{2-}.

The principal structural difference between the α and β polymorphs lies in the orientation of the SO_4^{2-} tetrahedra, their rotation and inclination causing the lowering of symmetry in the β form. Hence, the transition $Pm\bar{3}m/P\bar{4}3m$ <=> $I4/mcm$ can be described as displacive, with tilting of the SO_4 tetrahedra and small shifts of the K(2) atoms. Alternatively, the transition may be described in terms of how the free energy of the system varies as the transition temperature is transgressed. A first-order transition is defined as one in which a discontinuity occurs in the first-order derivatives of the free energy, with respect to temperature and pressure; these derivatives correspond to entropy and volume respectively. Second-order transitions are characterised by discontinuities in the second-order derivatives of the free energy, *i.e.* in the heat capacity, C_p, thermal expansion, α, and compressibility, β. The graph of volume *versus* temperature, Fig. 8, shows little or no discontinuity in the unit-cell volume, but a change in gradient, and thus thermal expansion, α, is evident. The α <=> β transition of the $K_3[SO_4]F$ polymorphs can therefore be described as a displacive second-order phase transition, consistent with the absence of any DTA effect, and therefore of any measurable enthalpy, at the transition temperature.

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