

Table 3. *Distribution of atoms in the garnet and  $\text{C}_{12}\text{A}_7$  structures (see also Fig. 1)*

Fractional coordinates of representative atoms are also given.

Garnet $[\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3]^*$ 1a3d		$\text{C}_{12}\text{A}_7$ ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{X}$ ) 143d
O 96h 0.2043, 0.2882, 0.0978	(a)	O(1) 48e 0.1997, 0.2818, 0.1022
	(c)	O(2) 16c x, x, x; x = 0.3151
Si 24d $\frac{1}{2}, 0, \frac{1}{2}$	(a)	Al(2) 12a $\frac{1}{2}, 0, \frac{1}{2}$
	(b)	X (= Cl) 12b $\frac{1}{2}, 0, \frac{1}{2}$
Al 16a $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	(c)	Al(1) 16c x, x, x; x = 0.2329
Ca 24c $\frac{1}{2}, 0, \frac{1}{2}$	(d)	Ca(1) 24d 0.1059, 0, $\frac{1}{2}$

(a) Half of the  $\text{SiO}_4$  tetrahedra of the garnet structure are retained in  $\text{C}_{12}\text{A}_7$ , as  $\text{Al}(2)\text{O}_4$  tetrahedra, avoiding any pairs of  $\text{SiO}_4$  related by a centre of symmetry.

(b) Those sites from which  $\text{SiO}_4$  have been omitted are available for occupancy by the X atoms of  $\text{C}_{12}\text{A}_7$ , e.g. Cl in this case.

(c) Al of garnet is retained in  $\text{C}_{12}\text{A}_7$ , but its coordination is reduced from octahedral to tetrahedral by replacing triplets of garnet O omitted as indicated in (a) above by a single O(2).

(d) Ca of garnet is retained in  $\text{C}_{12}\text{A}_7$ , but again as a result of the omission of  $\text{SiO}_4$  as in (a) above its coordination by oxygen is reduced from 8 (cubic) to the distorted sixfold coordination described by Williams (1973). Occupancy of the 'empty'  $\text{SiO}_4$  site by X (here Cl) as in (b) above will then restore some of the symmetry of the Ca coordination again exactly as described by Williams (1973).

\* Data from Wyckoff (1968).

Glasser, 1987). These properties combine with high thermal stability;  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  melts at  $\sim 1670$  K. However, the structure type has hitherto appeared to be confined to Ca, Al and O, with only limited OH, F and Cl inclusion. The present study shows that further chemical tailoring is possible, leading to the synthesis of materials with potentially useful properties.

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## Crystal Structure of $\text{KLiSO}_4$ at 200 K: a Neutron Diffraction Study

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**Abstract.**  $M_r = 142.10$ , trigonal,  $P31c$ ,  $a = 5.129$ ,  $c = 8.639$  Å,  $V = 196.82$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.397$  g cm<sup>-3</sup>,  $\lambda(\text{neutron}) = 1.176$  Å,  $\mu_c = 0.74$  cm<sup>-1</sup>,  $T = 200$  K. Refinement for the ordered structure with 593 reflections with  $(\sin\theta)/\lambda \leq 0.57$  Å<sup>-1</sup> gave  $R(F^2) = 0.055$ . The study has revealed merohedral twinning of

the crystal about (110), with twin components in nearly equal proportion, and large thermal vibration for the oxygens. Displacing the oxygens into three disordered positions gave a somewhat better  $R$  factor.

**Introduction.** The crystal structure of  $\text{KLiSO}_4$  at room temperature was determined by Bradley (1925). It crystallizes in space group  $P6_3$  ( $F1$  phase). In recent years much work has been done to study the behaviour

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of the oxygens which form the tetrahedra. In the ideal structure model these oxygens are ordered, but exhibit unusually high temperature factors. Karppinen, Lundgren & Liminga (1983) explained the anomalous temperature factors as the results of highly anharmonic thermal motion of the oxygens. By contrast, Bhakay-Tamhane, Sequeira & Chidambaram (1984) treated O(1) atoms, which form the vertices of the tetrahedra, as occupying threefold split positions with occupancy of 1/3. Schulz, Zucker & Frech (1985) found that both oxygens show large and strongly anharmonic thermal motion as well as static disorder. They explained the thermal vibration as the coupled rotational vibration of the oxygens around the S atoms.

KLiSO<sub>4</sub> undergoes several phase transitions. A phase (*F2*) has been reported in a temperature range of about 250–180 K. Bansal, Deb, Roy & Sahni (1980), in their Raman scattering experiment, proposed space group *P31c*, caused by cooperative reorientation of SO<sub>4</sub> tetrahedra. Tomaszewski & Lukaszewicz (1982) assume space group *P6<sub>3</sub>mc* to explain their X-ray diffraction data. Holuj & Drozdowski (1981) found in an EDR study that this phase may have an incommensurate structure. Bhakay-Tamhane, Sequeira & Chidambaram (1985) found, in a single-crystal neutron diffraction study in this temperature range, that there are two types of domain in *P31c* in nearly equal amounts. In their experiment, the *F2* phase was always mixed with the *F1* phase, and no structural parameters were presented.

The phase transition between *F1* and *F2* has been found to exhibit a rather large hysteresis. In the cooling cycle the transition occurred at about 205 K while in the heating cycle it appeared at about 250 K (Bansal *et al.*, 1980; Tomaszewski & Lukaszewicz, 1982, 1983; Bhakay-Tamhane *et al.*, 1985). Tomaszewski & Lukaszewicz (1983) found that in the cooling cycle the *F2* phase is always mixed with *F1* phase until it transforms to another phase (*F3*), and pure *F2* phase can be obtained only in the heating cycle from *F3* to *F2*. Bhakay-Tamhane *et al.* (1985), in their single-crystal neutron diffraction study, could not get a pure phase even in the heating cycle.

This study was carried out to determine the precise structure of KLiSO<sub>4</sub> in the *F2* phase.

**Experimental.** The specimen crystal (0.18 × 0.21 × 0.31 cm) was cut from a large crystal. Low-temperature data were collected using a refrigerator on the P32 four-circle diffractometer at SILOE reactor in Centre d'Etudes Nucleaires de Grenoble, France. A Cu monochromator was used,  $\lambda = 1.176 \text{ \AA}$ . The sample was cooled to 150 K for an hour, and then heated slowly to 200 K. Lattice constants determined from 19 centred single-crystal reflections by least-squares refinement of the orientation matrix.  $\omega$  scan mode up to  $(\sin\theta)/\lambda = 0.57 \text{ \AA}^{-1}$ . 660 reflections ( $\pm h, -k, \pm l$ ) were

collected, of which 134 are independent. The mutual agreement factor for the intensities of a standard reflection, which was repeated after every 40 reflections, was better than 0.02. The Friedel pairs were averaged; those of 21 reflections which were observed negative were retained as negative. 593 reflections were used for the structure refinements.

Data reduction was carried out using *COLLSN* (Lehmann, 1977, unpublished). An absorption correction was made ( $\mu_c = 0.74 \text{ cm}^{-1}$ ) using *DISTAE* (modified by Tasset from *DISTAO*, 1981, unpublished). PRIME computer, installed at CENG DRF, France, was used for this work. All the programs mentioned above were modified by one of the authors (Boucherle) for PRIME.

No satellite reflections are observed in the diffraction data, so the incommensurate structure should be ruled out. The intensity of the 111 reflection, which is rather strong at room temperature, is zero at 200 K. It indicates that no *F1* phase is mixed with *F2* phase. The systematic absences are consistent with space groups *P31c* and *P6<sub>3</sub>mc*.

The refinement of the ordered structure in space group *P6<sub>3</sub>mc*, which was assumed by Tomaszewski & Lukaszewicz (1982), could not converge satisfactorily. In general, there are two positions related by a (110) mirror plane in one cell, each of which corresponds to space group *P6<sub>3</sub>*. O(2), which is at the general position, is disordered at these two positions with equal occupancy. For this disordered model, the structure was refined with isotropic extinction and anisotropic temperature factors. It gave a rather high residual  $R(F^2) = 0.280$ .

At this stage, the space group *P31c* was adopted in the refinements. Using the model proposed by Bansal *et al.* (1980), the refinement with isotropic extinction and isotropic temperature factors gave  $R(F^2) = 0.237$ .

In our diffraction data, the differences between the intensities  $I(hkl)$  and  $I(h\bar{k}l)$  are much smaller than that calculated in space group *P31c*. It hinted that the merohedral twinning of the crystal at 200 K, found first by Bhakay-Tamhane *et al.* (1985), should be considered. Two models (*A* and *B*), reflected by the (110) mirror plane in the space group *P31c*, can be obtained by the cooperative reorientation of SO<sub>4</sub> tetrahedra in space group *P6<sub>3</sub>* (Fig. 1). During the phase transition from *F1* to *F2*, two domains, corresponding to models *A* and *B* respectively, are formed. The intensity of each reflection is the sum of the intensities of two domains:

$$F^2(hkl) = (1-f)F_A^2(hkl) + fF_B^2(hkl), \quad (1)$$

where  $f$  is the fraction of model *B* in the crystal.

The full-matrix least-squares program *ORXFLS4* [a modified version of *ORFLS* (Busing, Martin & Levy, 1962)] was used in the structural refinements. In order to refine the twinned crystal, this program was modified by one of the authors (Zhang). The fraction  $f$

was introduced into *ORXFLS4* as an extra parameter. The calculation of intensity was carried out according to (1). 0.5 was chosen as the initial value of *f*. The positional parameters in *P6<sub>3</sub>*, reported by Schulz *et al.* (1985) were adopted as the starting parameters. With isotropic extinction and isotropic temperature factors the refinement of the structure reduced the residual dramatically to 0.072. Because the diffraction data show anisotropic extinction, a type II anisotropic extinction correction was made. With anisotropic temperature factors the refinement converged at  $R(F^2) = 0.055$  with  $f = 0.464$  (3). Altogether 28 variables were refined in the last cycle. The elements of the extinction tensor are

$$\begin{aligned} Z(11) &= 3.9 (5) & Z(22) &= 3.9 (5) & Z(33) &= 20.6 (32) \\ Z(12) &= 1.1 (4) & Z(13) &= -1.4 (8) & Z(23) &= 0.5 (7). \end{aligned}$$

The crystallographic parameters, r.m.s. displacements along the principal axis of thermal vibration, and selected bond lengths and angles are shown in Tables 1, 2 and 3 (ordered structure), respectively.\*

The temperature factors of oxygens are unusually high and strongly anisotropic, rather similar to those at room temperature reported by Schultz *et al.* (1985). Both O(1) and O(2) show large motion normal to the S—O bonds.

On changing the position of O(1) from the threefold axis with other parameters fixed, a minimum *R* factor was obtained at about  $x = 0.32$ ,  $y = 0.67$ ,  $z = 0.04$ . Using the split O(1) model the structure was refined with anisotropic temperature factors (34 variables were refined). The *R* factor was reduced a little:  $R(F^2) = 0.052$ . By splitting O(2) into three positions with occupancy of 1/3 for each one, with other parameters fixed, the *R* factor was reduced further. In order to

\* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44551 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

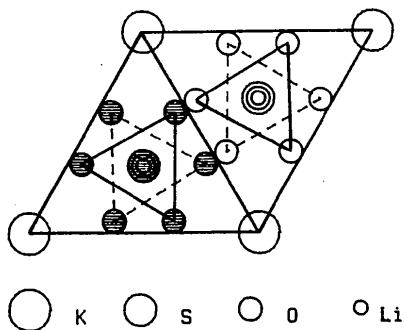


Fig. 1. View of KLiSO<sub>4</sub> in space group *P31c* in the direction [001]. The shaded circles are separated from open circles by  $c/2$ . The solid triangles and the dashed triangles represent the orientations of SO<sub>4</sub> tetrahedra in models *A* and *B*, respectively.

Table 1. Atomic coordinates and thermal parameters

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{iso}/B_{eq}(\text{\AA}^2)$
Ordered structure				
K	0	0	0	1.27 (5)
Li			0.8156 (6)	0.89 (10)
S			0.2049 (3)	0.74 (7)
O(1)			0.0350 (3)	2.44 (5)
O(2)	0.0591 (2)	0.6589 (2)	0.2595 (3)	1.65 (3)
Disordered structure				
K	0	0	0	1.27 (3)
Li			0.8162 (5)	1.05 (5)
S			0.2052 (3)	0.70 (4)
O(1)	0.2824 (7)	0.6571 (14)	0.0369 (5)	0.82 (4)
O(21)	0.0603 (10)	0.6811 (10)	0.2595 (11)	0.65 (12)
O(22)	0.0715 (7)	0.6502 (11)	0.2844 (7)	1.11 (10)
O(23)	0.0461 (8)	0.6433 (10)	0.2414 (6)	0.44 (11)

Table 2. Selected r.m.s. displacements along the principal directions of vibration and the corresponding direction cosines in a Cartesian system

Ordered structure	$U(\text{\AA}^2)$			
	$\cos\alpha$	$\cos\beta$	$\cos\gamma$	
O(1)	$U_{11} = 0.205$	1.0000	0.0000	0.0000
	$U_{22} = 0.205$	0.0000	1.0000	0.0000
	$U_{33} = 0.093$	0.0000	0.0000	1.0000
O(2)	$U_{11} = 0.098$	0.8755	-0.3662	-0.3153
	$U_{22} = 0.125$	0.4080	0.9098	0.0760
	$U_{33} = 0.193$	0.2590	-0.1952	0.9460

The *x* axis of the Cartesian system is perpendicular to the *bc* plane in the cell, *y* and *z* are in the directions of *b* and *c* respectively.

Table 3. Selected bond lengths (Å) and angles (°)

Ordered structure		Disordered structure	
S—O(1)	1.47	S—O(1)	1.47
S—O(2)	1.46	S—O(21)	1.51
		S—O(22)	1.47
		S—O(23)	1.45
O(1)—S—O(2)	109	O(1)—S—O(21 <sup>i</sup> )	111
		O(1)—S—O(22)	108
		O(1)—S—O(23 <sup>ii</sup> )	108
O(2)—S—O(2 <sup>i</sup> )	110	O(21 <sup>i</sup> )—S—O(22)	102
		O(21 <sup>i</sup> )—S—O(23 <sup>ii</sup> )	119
		O(22)—S—O(23 <sup>ii</sup> )	109
Li—O(1 <sup>iii</sup> )	1.90	Li—O(1 <sup>iii</sup> )	1.92
Li—O(2 <sup>iv</sup> )	1.93	Li—O(21 <sup>v</sup> )	1.97
		Li—O(22 <sup>vi</sup> )	1.91
		Li—O(23 <sup>vi</sup> )	1.91

Labeling of positions: (i)  $1-y, 1+x-y, z$ ; (ii)  $-x+y, 1-x, z$ ; (iii)  $x, y, 1+z$ ; (iv)  $-x, -x+y, z+0.5$ ; (v)  $1+x-y, 1-y, z+0.5$ ; (vi)  $y, 1+x, z+0.5$ .

avoid too many parameters being refined, isotropic temperature factors were adopted in the refinements of the O(2) disordered structure. The refinement with 29 variables gave  $R(F^2) = 0.051$ ,  $f = 0.464$  (3). The positional and thermal parameters are shown in Table 1, selected bond lengths and angles in Table 3 (disordered structure).

Scattering lengths for K, Li, S and O were taken from Sears (1984). An IBM-158 computer, installed at

the Institute of Physics, Chinese Academy of Sciences, Beijing, was used for the structure refinements.

**Discussion.** As mentioned before, the phase transition from  $P6_3$  to  $P31c$  is associated with the cooperative reorientation of the  $\text{SO}_4$  tetrahedra (Bansal *et al.*, 1980). The rotation of one of the two tetrahedra in one cell in  $P6_3$  causes two types of domain in  $P31c$ , in equal proportions. No matter whether the crystal is merohedrally twinned or not at room temperature, the twin fraction in  $P31c$  should be the same. In this experiment the twin fraction  $f$  is 0.464 (4); the small difference of  $f$  from  $\frac{1}{2}$  may be caused by the inhomogeneous distribution of the defects in the crystal.

The splitting of both O(1) and O(2) into three sites means that the rigid  $\text{SO}_4$  tetrahedra are disordered in three positions with equal probability, which is rather similar to the results at room temperature reported by Schulz *et al.* (1985).

With the method reported by Tomaszewski & Lukaszewicz (1983), pure  $P31c$  phase was obtained in our experiment. Using a similar method, Bhakay-Tamhane *et al.* (1985) did not obtain a pure phase in a single crystal grown by themselves. During the transformation from  $F1$  to  $F2$ , one of the two tetrahedra turns about  $57^\circ$ . This rotation may be sensitive to the concentration of defects in the crystal, which depends on the growth conditions.

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## Structure of Yttrium Nitrate Trihydrate

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**Abstract.**  $\text{Y}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ ,  $M_r = 328.97$ , triclinic,  $P\bar{1}$ ,  $a = 6.946$  (2),  $b = 7.323$  (1),  $c = 10.948$  (1) Å,  $\alpha = 71.47$  (1),  $\beta = 78.38$  (1),  $\gamma = 67.64$  (1)°,  $V = 486.2$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.246$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54184$  Å,  $\mu = 93.7$  cm<sup>-1</sup>,  $F(000) = 324$ ,  $T = 296$  (1) K,  $R = 0.028$  for 1878 unique observed reflections. The compound was prepared by thermal decomposition of crystals of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Merck, Art. 12516) at 382 K. Three bidentate nitrate groups and three water molecules produce a nine-coordinated Y atom. The coordination polyhedra are linked by hydrogen bonds into a three-dimensional network.

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**Introduction.** Differential thermal analysis of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  shows two strong endothermic peaks at 361 and 378 K. At the first peak a complex of  $[\text{Y}(\text{H}_2\text{O})_5(\text{NO}_3)_2][\text{Y}(\text{H}_2\text{O})_2(\text{NO}_3)_4]$  (Radivojević, Milinski, Ribár & Lazar, 1984) arises and at the second one the title compound is formed which has been grown from the melt of hexahydrate at 382 K. The crystals were sealed into Lindemann capillary tubes.

**Experimental.** A crystal  $ca$   $0.20 \times 0.25 \times 0.40$  mm was mounted on a CAD-4 diffractometer equipped with graphite monochromator. Scan range  $3.0 < 2\theta < 150^\circ$ ,

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