Structure and Phase Transition of $[(CH_2OH)_3CNH_3]_2SiF_6$

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Single crystals of $(TRIS)_2SiF_6$ were grown and characterised by X-ray analysis, differential scanning calorimetry (DSC) and optical investigations. They were bond to be trigonal, space group $P\bar{3}$, with the unit cell dimensions $a = 7.699(1)$, $c = 7.818(2)$ Å. The SiF_6^{2-} anions, located in large cavities formed by hydrogen bonded cations, are strongly disordered at room temperature. The DSC measurements revealed a first-order phase transition at $T_C \approx 177$ K with a hysteresis of 4 K. The nature of the transition was confirmed by a sharp increase of the linear birefringence below T_C. Optical observations under a polarizing microscope showed a domain structure of the low temperature phase, characteristic of ferroelastic materials.

Key words: Phase Transition; X-ray Crystal Structure; Birefringence Domain Structure.

1. Introduction

Tris-hydroxymethylaminomethane (TRIS) [1] and some compounds containing TRIS belong to the non-centrosymmetrical (polar) structures. They are expected to be useful as electrooptic and second harmonic generation (SHG) materials [2 – 3]. The TRIS crystal undergoes a phase transition from the polar to a plastic phase showing reorientational freedom of its pseudoglobular molecules. In the present work, single crystals of a new TRIS cation related compound, *i.e.* $[(CH_2OH)_3CNH_3]_2SiF_6$, were grown, and their structure and potential phase transition was studied.

2. Experimental Section

The crystals of $[(CH_2OH)_3CNH_3]_2SiF_6$, were grown from water solutions containing TRIS and an excess of H_2SiF_6. The single crystals were obtained by slow evaporation at 303 K. Good quality samples of 0.3 – 1 cm^3 volume were obtained within 3 – 4 weeks. The crystals were colourless, and their shape suggested the trigonal symmetry.

The X-ray diffraction measurements were performed with a four-circle crystal diffractometer KM-4 / CCD (Kuma Diffraction) with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were determined by 740 reflections. The intensity data were collected with an ω-scan technique, $\Delta\omega = 1.0°$ per step, frame exposure 30 s. The 960 images, taken in 6 sets at different ω-values, covered about 90% of the Ewald sphere. To control the

Table 1. The crystal data and experimental parameters used for the intensity data collection and structure refinement.

Formula	$[(CH_2OH)_3CNH_3]_2$ SiF_6
Formula weight	386.38
Crystal system, space group	Trigonal, $P\bar{3}$
Unit cell dimensions (Å)	$a = 7.699(1)$ $b = 7.699(1)$ $c = 7.818(2)$ $\gamma = 120°$
Volume (Å^3)	401.32(13)
Z, Calculated density (Mg/m^3)	1, 1.599
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Absorption coefficient (mm^{-1})	0.239
F(000)	202
Crystal size (mm)	$0.33 \times 0.30 \times 0.30$
θ range for data collection	5.48 to 47.31°
Limiting indices	$-8 \leq h \leq 15$, $-15 \leq k \leq 15$, $-16 \leq l \leq 10$
Reflections collected / unique	7263 / 2223 [R(int) = 0.021]
Completeness to $\theta = 47.31$	89.3%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2223 / 0 / 39
Goodness-of-fit on F^2	1.312
Final R indices [$I > 2.5\sigma(I)$]	$R_1 = 0.0970, wR_2 = 0.3609$
R indices (all data)	$R_1 = 0.1544, wR_2 = 0.3977$
Largest diff. peak and hole (eÅ^{-3})	2.148 and -0.971

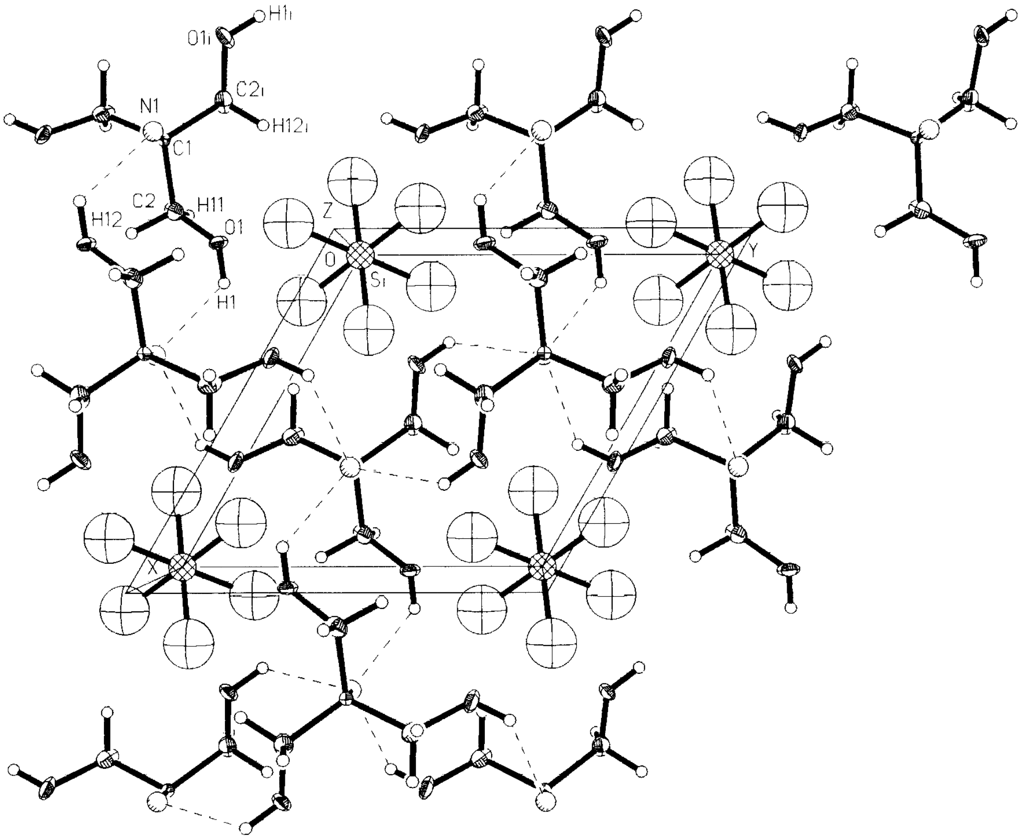

Fig. 1. Crystal structure of $[(CH_2OH)_3CNH_3]_2SiF_6^{2-}$ with atom numbering and hydrogen bonds.

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)
N(1)	6667	3333	5064(3)	27(1)
C(1)	6667	3333	3146(3)	28(1)
C(2)	8831(3)	4573(3)	2547(2)	37(1)
O(1)	9868(2)	6418(2)	3442(2)	40(1)
Si	0	0	0	26(1)
F(1)	0	0	2169(2)	69(1)
F(2)	2459(8)	1124(11)	−260(5)	85(1)

The site occupation factor for F(2) is 0.5.

Table 3. Selected bond lengths (Å) and angles (°) of (TRIS)$_2$SiF$_6$.

N(1)-C(1)	1.499(3)	C(1)-C(2)	1.522(2)
C(1)-C(2)$^{\#1}$	1.522(2)	C(1)-C(2)$^{\#2}$	1.522(3)
C(2)-O(1)	1.418(2)	N(1)-H(1)	0.978(3)
C(2)-H(11)	0.970(3)	C(2)-H(12)	0.956(3)
Si-F(1)	1.696(2)	Si-F(2)	1.654(5)
N(1)-C(1)-C(2)	107.9(1)	N(1)-C(1)-C(2)$^{\#1}$	107.9(1)
N(1)-C(1)-C(2)$^{\#2}$	107.9(1)	C(2)-C(1)-C(2)$^{\#2}$	110.9(1)
C(2)#1-C(1)-C(2)	110.9(1)	C(2)#1-C(1)-C(2)$^{\#2}$	110.9(1)
O(1)-C(2)-C(1)	111.6(1)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+y+1, 1-x, z$; $^{\#2}$ $1-y, x-y, z$.

stability of the crystal and the electronics, one image was selected as a standard and monitored after every 40 images. The intensities were integrated and corrected for Lorentz polarization and absorption effects. The data collection and reduction were carried out using the Kuma Diffraction software [4]. Details of the crystal and the experiments are summarized in Table 1.

The structure of the $P\bar{3}$ space group was found by direct methods, which revealed the positions of the cation subunits. The location of the SiF_6^{2-} group encountered some difficulties. Fourier syntheses showed the Si atom at the position *1a* (0 0 0) together with numerous peaks around, which could correspond to the fluorine atoms, but were smeared out in the equatorial plane of the distorted polyhedron. One of the peaks, fulfilling the bond distance conditions, was taken as the F(2) atom. The positions of all non-hydrogen atoms, but fluorine, were refined with anisotropic thermal vibration amplitudes, using a full-matrix least-squares method and the SHELX97 program [5]. Hydrogen atoms introduced at calculated positions were riding on their carrier atoms with refined U parameters ($\text{Å}^2 \times 10^3$). The positions of the atoms and the isotropic equivalent isotropic thermal parameters are given in Table 2.

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7 apparatus with scanning rates 5 – 20 K/min in the temperature range 100 – 390 K. The temperature dependence of the linear birefringence in the crystal was measured by means of a rotating analyser set-up [6]. The optical observations under a polarizing microscope and the pictures were registered with a CCD camera.

3. Results and Discussion

The formula unit consists of two $(CH_2OH)_3CNH_3^+$ cations and the disordered SiF_6^{2-} anion (Figure 1). In the unit cell the NH_3 and C(1) atoms take the special position $2d(2/3,1/3,z)$, therefore the configuration of the cation has tree-fold point symmetry with three equivalent C—CH_2OH groups about the NH_3—C(1) bond (Table 3). At the same time, the F(2)-atom of the SiF_6 polyhedron shows strong disorder, which may result from a superposition of possible orientations about the $\bar{3}$ axis which the thermally activated anion may adopt. The structure is stabilised by hydrogen bonds of the type N—H··· O, with the distance $N(1)\cdots O(1)_{2-x,1-y,1-z} = 2.83(2)$ Å and the

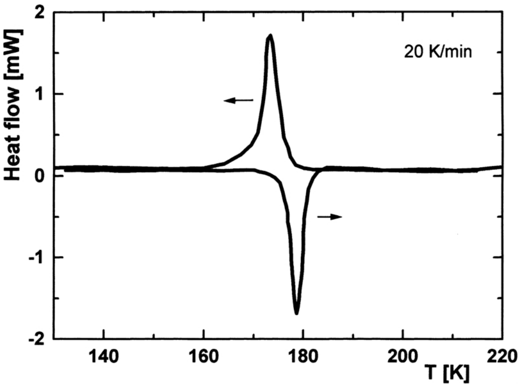

Fig. 2. Heat flow (DSC) in the temperature range 160 – 180 K for $(TRIS)_2SiF_6$ crystals.

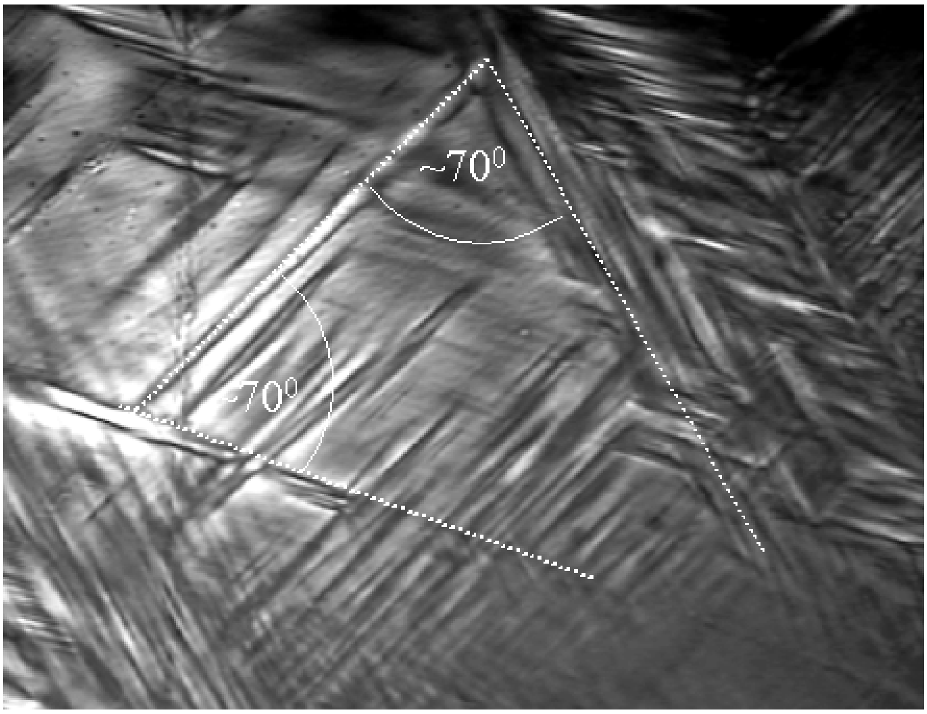

Fig. 3. Domain structure of $(TRIS)_2SiF_6$ below 178 K.

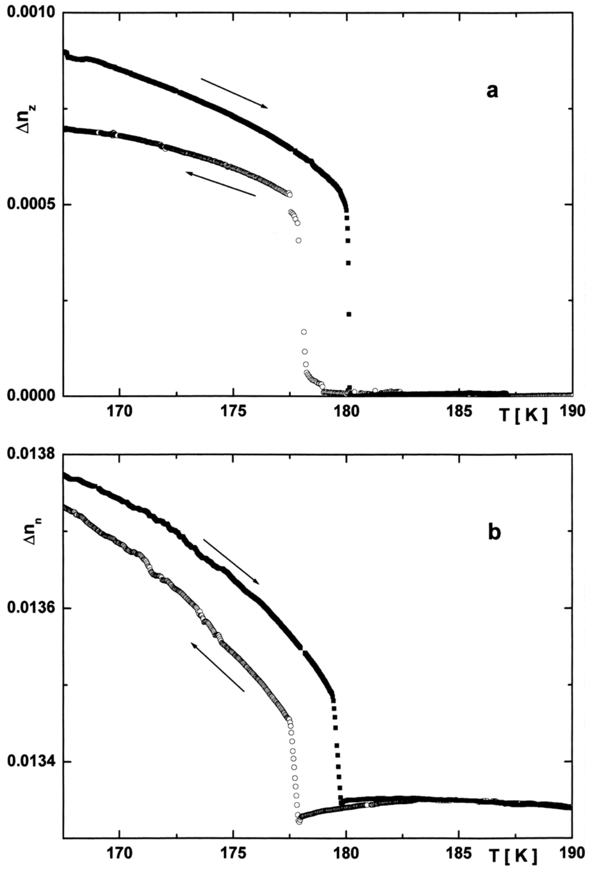

Fig. 4. Temperature dependence of the linear birefringence in $(TRIS)_2SiF_6$ in a vicinity of the phase transition: a: measured along the triad axis, b: measured along the direction normal to the triad axis.

angle N(1)—H···O(1) = 142°. These linkages reduce the flexibility of the cationic groups forming a type of large cavities, filled with the rotating SiF_6^{2-} anions. Important interatomic distances and angles are listed in Table 3. The bond lengths observed in the anion deviate slightly from the normal values, as is typical for such disordered groups. The disorder influences the value of the conventional discrepancy factors *R*, which are somewhat high, despite of the good internal consistency of the symmetry equivalent reflections (Table 1).

Additional material comprising anisotropic thermal displacements and a full list of bond distances and angles is available from the authors.

The temperature dependence of the heat flow (DSC) revealed an anomaly at about 180 K on cooling and 176 K on heating (Figure 2). The scan rate was set to 20 K/min. The shape of the anomaly is typical of the first-order phase transition (PT). The entropy of the transition equals to 4,4 J/molK.

The position of the optical indicatrix, observed under a polarizing microscope at room temperature, was consistent with the trigonal symmetry of the crystal. The phase front, passing close to T_C, confirms the first-order nature of the transition. The domain structure, appearing below T_C, evidenced that the crystal symmetry has changed, since the pattern of the domains shown in Fig. 3 suggested that the threefold axis has vanished in the low temperature phase. We could also observe a coexistence of the two phases, characteristic of the first order phase transitions. The angles between the domain walls are far from 30° or 60°, what can be caused by a significant spontaneous deformation. The pattern of the domains in the sample, cleaved parallel to the (101) plane, shows that the preferred orientation of the domain walls is nearly parallel to the cleavage plane. According to Sapriel [7], no permissible ferroelastic domain walls can be expected when the crystal transforms from trigonal $P\bar{3}$ to the lower symmetry phase. The only possibility is a triclinic, ferroelastic phase with three orientational states but no strain-free (*i.e.* no permissible) ones.

The large number of very narrow domains in the low temperature phase did not allow precise measurements of the birefringence with a rotating analyzer. Nevertheless, this experiment yielded some information on the character of the PT. The temperature dependent evolution of the linear birefringence in the sample, cut normal to the triad axis (Fig. 4a), shows that down to T_C the birefringence measured along the **c**-axis is zero, as expected in optically monoaxial crystals. The jump-like appearance of birefringence, observed close to T_C, gives clear evidence of the first-order nature of the PT and of the change of the crystal symmetry. Temperature dependent changes of birefringence were also observed along the direction perpendicular to the threefold axis, both at the room- and low temperature phases (Fig. 4b).

Summarising the results of our investigations, we state:

- The Domain structure, observed in the low temperature phase and the character of the temperature dependent changes of birefringence indicate that the new crystal has at least potential ferroelastic properties.
- The molecular mechanism of the first-order phase transition at $T_C = 177$ K in $[(CH_2OH)_3CNH_3]_2SiF_6$

seems to be related to a freezing of the reorientational motion of the SiF_6^{2-} anions. The room temperature phase can be described by the space group $P\bar{3}$, with strongly disordered SiF_6^{2-} anions.

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