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The crystal structure of Na_2SO_4III*

B. N. Mehrotra

School of Physics, University Sains Malaysia, Penang, Malaysia

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Abstract. This modification of sodium sulfate exists between 200°C to 228°C. Single crystals of Na_2SO_4III are grown by metastable nucleation from aqueous solutions at 50°C.

Sodium sulphate III is orthorhombic with space group *Cmcm* and cell constants $a = 5.607$ Å, $b = 8.955$ Å, $c = 6.967$ Å, $Z = 4$. The structure has been refined to $R = 4.5\%$. The structure consists of tetrahedral and octahedral framework. The thermal vibrations of most of the atoms are large along the *c*-axis.

Introduction

The complicated polymorphyism of sodium sulfate has been investigated by Mehrotra et al. (1975).

$$Na_2SO_4\ V \xleftrightarrow{\sim 180\ C} IV \xleftrightarrow{200\ C} III \xleftrightarrow{228\ C} II \xleftrightarrow{235\ C} I \xleftrightarrow{883\ C} \text{melt}.$$

Na_2SO_4III is a stable modification in the temperature range 200 to 228°C. It can be quenched from the melt at room temperature and remains metastable for a long time if kept dry.

The earlier investigations of the structure were based on powder data, leading to several conflicting space groups:

Pnbn (Frevel, 1940); $I\bar{4}2d$ (Dasgupta, 1953) and *Cmcm* (Fischmeister, 1954). The first structure proposal originates from Frevel.

The present investigation with single crystal work confirms the space group *Cmcm*.

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* Parts of this work are contained in the Ph.D. thesis of the author (1973) and in a paper presented in the Tenth International Conference of Crystallography, Amsterdam (1975).

There are only two compounds known with Na_2SO_4III structure type:

Compound		a (Å)	b (Å)	c (Å)	b/a	Literature
Na_2SO_4III	20°C	5.592	8.926	6.953	1.596	Wyckoff (1960)
	20°C	5.607	8.955	6.967	1.597	This work
	225°C	5.610	9.160	7.000	1.632	This work
Na_2CrO_4	20°C	5.861	9.259	7.138	1.579	Wyckoff (1960)
	20°C	5.950	9.241	7.137	1.579	This work

In this paper the complete structure of Na_2SO_4III is worked out.

Crystal data

Na_2SO_4III: $M = 142.06$, space group *Cmcm*. $a = 5.607 \pm 0.001$ Å, $b = 8.955 \pm 0.002$ Å, $c = 6.967 \pm 0.001$ Å, $V = 349.82$ Å^3, $Z = 4$, $D_c = 2.698$ g/cm^3.

Experimental

Preparation of single crystals of Na_2SO_4III:

Sodium sulfate (from Merck, Germany) was dissolved in distilled water. The aqueous solution, when evaporated above 32°C yielded crystals of Na_2SO_4V (space group *Fddd*), which were bipyramidal in shape. When the aqueous solution was evaporated quickly (at temperatures of 50°C, 60°C etc.) a few long cylindrical crystals of Na_2SO_4III were obtained along with bipyramidal crystals. The growth of these cylindrical crystals can be explained only due to spontaneous nucleation under metastable conditions.

The crystal used for intensity measurements had the dimensions 0.68 mm (maximum) and 0.20 mm (minimum). Intensities of 1059 reflections were collected with the Siemens automatic diffractometer (AED) with Zr filtered

Table 1. Atomic parameters and isotropic temperature factors of Na_2SO_4III. Standard deviations (in parentheses) refer to the last significant figures

Atom	Point symmetry	x	y	z	B
Na(1)	*mm*	0.0	0.1881(2)	0.25	1.88(3)
Na(2)	2/*m*	0.0	0.5	0.0	1.05(2)
S	*mm*	0.0	0.8486(1)	0.25	0.33(2)
O(1)	*m*	0.2848(4)	0.4453(3)	0.25	0.95(2)
O(2)	*m*	0.0	0.2446(3)	0.5776(3)	1.84(4)

Table 2. Root mean square amplitude $\sqrt{U_{ij}^2}$ and the angles θ (°) between the ellipsoids axes and the crystal axes of Na_2SO_4III

Atom	RMS amplitude (Å)	ϕ_1 (°)	ϕ_2 (°)	ϕ_3 (°)
Na(1)	0.122	90.0	0.0	90.0
	0.145	90.0	90.0	0.0
	0.186	0.0	90.0	90.0
Na(2)	0.118	90.0	75.5	165.5
	0.138	90.0	165.5	75.7
	0.138	0.0	90.0	90.0
S	0.083	90.0	0.0	90.0
	0.087	0.0	90.0	90.0
	0.099	90.0	90.0	0.0
O(1)	0.089	144.6	54.6	90.0
	0.137	90.0	90.0	0.0
	0.162	54.6	35.4	90.0
O(2)	0.082	90.0	141.9	51.9
	0.166	0.0	90.0	90.0
	0.176	90.0	128.1	141.9

Mo radiation using $\theta - 2\theta$ scan. All reflections were corrected for absorption by the program ORABS. Out of 1059 reflections, 27 reflections were not significantly different from zero.

The structure proposal of Frevel (1940) was worked out. The refinement with anisotropic temperature factors led to a value of $R = 4.5\%$. All calculations were carried out by of X-ray crystallographic program of Stewart et al. (1970).

Description of the structure

The atomic parameters and root mean square amplitudes of the atoms of the asymmetric unit are given in Tables 1 and 2.

Figure 1 shows the projection of the structure along the (001) plane. The structure consists of deformed tetrahedra and octahedra (Table 3). The tetrahedra lie on the intersection of the mirror planes (001) and (100). The symmetry of the tetrahedra is *m*2*m*.

There are two types of octahdra:

1. One with symmetry *m*2*m* – it is connected with four corners and one edge of the neighbouring tetrahedron.

2. The other octahedron with symmetry 2/*m*11 – it is connected with six different tetrahedra.

Both tetrahedra have a common face (Fig. 2).

Table 3. Bond length (Å) and angles (°) in SO_4^{2-} tetrahedron and NaO_6 octahedron of Na_2SO_4III. Standard deviations in parentheses refer to the last significant figures

S–O in $(SO_4)^{2-}$	O–O in $(SO_4)^{2-}$	O–S–O in $(SO_4)^{2-}$	Na–O in NaO_6
1.485(1)×2	2.412(1)×2	108.69(1)	2.803(1)×2
1.463(1)×2	2.406(1)×4	110.35(1)	2.425(1)×2
Average 1.474		109.44(1)	2.338(1)×2
			2.413(1)×4
			2.350(1)×4

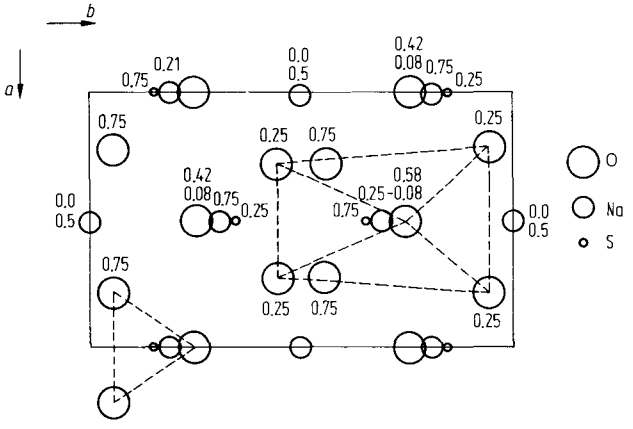

Fig. 1. Projection of the structure of Na_2SO_4III on (001)

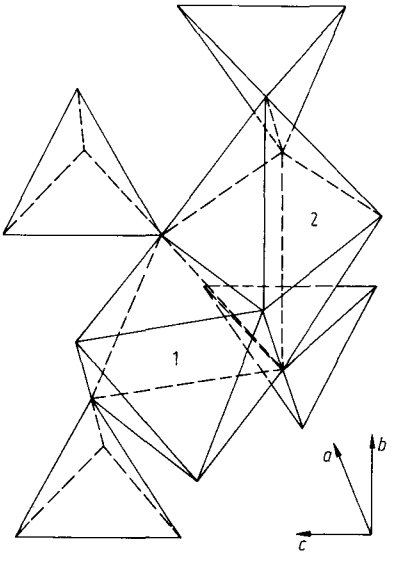

Fig. 2. Correlation of tetrahedra and octahedra in Na_2SO_4III; 1. octahedron with Na at 2/*m*; 2. octahedron with Na at *mm*

For most of the atoms, the thermal vibrations are large along the *c*-axis. This is in agreement with the coefficient of thermal expansion (Fischmeister, 1962), the values of which are noticeably large also along the *c*-axis.

The list of structure factors can be obtained from the author on request.

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