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Abstract

Full Text

Chemistry

N. I. BASHILOVA and M. N. LYASHENKO

CRYSTALLOGRAPHIC STUDY OF SULFATES OF MONOVALENT THALLIUM

(Presented by Academician G. G. Urazov on 6 XII 1956)

As a result of the interaction of thallium sulfate with aqueous solutions of sulfuric acid, three acid thallium sulfates are formed ([1]):

$$Tl_3H(SO_4)_2,\ TlHSO_4 \text{ and } Tl_2H_4(SO_4)_3$$

The initial compound—Tl_2SO_4—has been studied by methods of crystallographic ([2]) and X-ray structural ([3,4]) analysis. The acid thallium sulfates, two of which were known previously ([5,6]), have been characterized only qualitatively by crystal-optical methods ([5]), and for one of them there are data from a goniometric study ([7]).

$Tl_3H(SO_4)_2$ crystallizes in the form of thin plates. They belong to the trigonal system ([7]). The refractive indices of this compound, determined by us by the immersion method, are presented in Table 1.

Table 1

Compound	Refractive indices N_p	Refractive indices N_m	Refractive indices N_g	Angle of the optical axes
$Tl_3H(SO_4)_2$	1.730	1.760	–	–
α-$TlHSO_4$	1.682	1.690	1.702	+78°
β-$TlHSO_4$	1.653	1.679	1.684	−45°
$Tl_2H_4(SO_4)_3$	–	1.619	–	–

$TlHSO_4$, in accordance with the indications of previous investigators ([5,6,8]), crystallizes in the form of square plates and needles.

Both kinds of crystals separately, when kept quietly for a long time in a solution saturated with respect to them, do not change their external form. However, upon prolonged stirring of the saturated solution with plate-like crystals of thallium bisulfate, crystals in the form of needles appear in the solid phase. At the same time the plates disappear, completely transforming into needles.

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It was necessary to determine whether thallium bisulfate is dimorphous, as previous investigators assumed ([5,8,9]), or whether the needle-like and plate-like crystals of $TlHSO_4$ belong to one and the same modification, and the difference in their external form is explained by the nonuniform development of the crystal faces.

For this purpose, crystals of thallium bisulfate were subjected to crystal-optical and goniometric study. The single crystals needed for this were grown in hermetically closed crystallizers: plates of thallium bisulfate—by slow crystallization from slightly supersaturated solutions; needles—by growth of separate, isolated, previously obtained crystals. Goniometric measurement of the crystals was made difficult by the fact that, because of hygroscopicity, their faces quickly lost their luster and the quality of the signals was average. The accuracy of measurement was $\pm 1^\circ$.

The results of the goniometric measurements are presented in Table 2.

According to the results of the goniometric measurements, the needle-shaped crystals of thallium bisulfate belong to the rhombic system, to the rhombodipyramidal type of symmetry. The elements of the crystal: $a : b : c = 0.23 : 1 : 0.31$.

Fig. 2. Microphotographs of $Tl_2H_4(SO_4)_3$ at different periods of crystallization. 120×

The following simple forms were observed on these thallium bisulfate crystals: {100}, {110}, {111}.

The direct zone of the crystals consists of a broad pinacoid {100} and a prism {110} with very narrow faces. The oblique zone is formed by the dipyramid {111}.

Crystallo-optical study of the needle-shaped crystals showed that these are biaxial positive crystals. The extinction is straight. The refractive indices, determined by the immersion method, and the angle of the optical axes, measured on a Fedorov stage, are presented in Table 1.

Table 2

Crystals	Face symbols	Face designations	Prism, °	ϕ° meas.	ϕ° calc.	Number of observations
Needles —α-$TlHSO_4$	100	a	90	90	–	8
Needles —α-$TlHSO_4$	110	m	90	30	30	8

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Fig. 1. General appearance of crystals of α-$TlHSO_4$ (a) and β-$TlHSO_4$ (b)

Figure 1: Fig. 1. General appearance of crystals of α-$TlHSO_4$ (a) and β-$TlHSO_4$ (b)

Crystals	Face symbols	Face designations	Prism, °	$\phi°$ meas.	$\phi°$ calc.	Number of observations
Needles —α-$TlHSO_4$	111	n	21	30	–	8
Plates —β-$TlHSO_4$	001	c	15	90	–	6
Plates —β-$TlHSO_4$	010	b	90	0	–	4
Plates —β-$TlHSO_4$	110	m	90	46	–	6

According to the results of goniometric measurements, the plate-shaped crystals of thallium bisulfate belong to the monoclinic system—the prismatic type of symmetry.

Crystal elements:—$a : b : c = 0.98 : 1 : ?$, $\beta = 105°$. Owing to the insufficient number of developed faces, the crystal elements cannot be fully calculated. Oblique faces were not observed on any of the crystals. These thallium bisulfate crystals have the following simple forms: {110}, {001}, {010}.

According to crystallo-optical analysis, the plate-shaped thallium bisulfate crystals are biaxial, negative. They have both symmetrical and oblique extinction. The extinction angle is 25°. The refractive indices and the angle of the optical axes of these crystals are shown in Table 1.

The results presented above show that, under ordinary conditions, thallium bisulfate crystallizes in two modifications—the needle-shaped α-modification and the plate-shaped β-modification (Fig. 1).

Fig. 1. General appearance of crystals of α-$TlHSO_4$ (a) and β-$TlHSO_4$ (b)

$Tl_2H_4(SO_4)_3$ crystallizes from very concentrated and viscous solutions ([1]), in which normal crystal growth is impeded. Therefore their form is very imperfect. The sequence of the crystallization process of $Tl_2H_4(SO_4)_3$, shown in Fig. 2, illustrates the formation of a granular microstructure (Fig. 2 v) from a dendritic one (Fig. 2 a, b).

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Crystals of $Tl_2H_4(SO_4)_3$ are isotropic. The magnitude of the refractive index of these crystals is given in Table 1.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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