Acta Cryst. (1964). **17**, 757

Some ternary thallium chalcogenides.

By C. CREVECOEUR, *Laboratory of Inorganic Chemistry, University of Leyden, The Netherlands*

(*Received* 28 *October* 1963)

Isomorphous compounds of the composition Tl_3BX_4, in which B = V, Nb, Ta and X = S, Se, were prepared by heating weighed quantities of the elements in evacuated sealed Pyrex tubes at 500 °C. The X-ray powder diagrams can be indexed on a cubic body-centered lattice (Table 1),

Table 1. *Properties of isomorphous compounds* Tl_3BX_4

Compound	Colour	Cell edge (Å)	Density, experimental (g.cm^{-3})	Density, X-ray (g.cm^{-3})
Tl_3VS_4	black violet	7·51	6·16	6·22
Tl_3NbS_4	ochre	7·65		
Tl_3TaS_4	orange	7·67		
Tl_3VSe_4	black	7·74		
Tl_3NbSe_4	pink	7·85		
Tl_3TaSe_4	brown	7·88	7·28	7·56

containing two formula units Tl_3BX_4 per unit cell. Thus 6 Tl, 2 B and 8 X atoms have to be accommodated. This can be accomplished in a simple way in space group $I\bar{4}3m$ or in one of its subgroups, with

Tl in the positions (6*b*): $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$
B (2*a*): 000
X (8*c*): xxx; $x\bar{x}\bar{x}$; $\bar{x}x\bar{x}$; $\bar{x}\bar{x}x$
} $+000$; $+\frac{1}{2}\frac{1}{2}\frac{1}{2}$

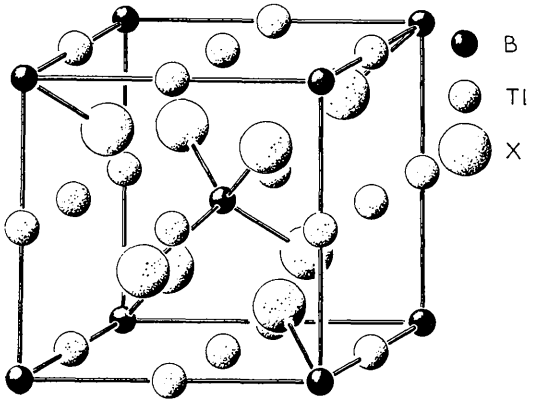

Fig. 1. The structure of Tl_3BX_4 (B = V, Nb, Ta; X = S, Se).

The diffraction patterns show a fading out towards the higher diffraction angles; the lines are rather broad. This is probably due to deformation of the crystals during grinding of the samples. This is confirmed by a Weissenberg photograph of Tl_3TaS_4 with sharp reflexions to the edge of the film.

Since the reflexion intensities suffer seriously from absorption effects and only twenty lines were measured it is clear that the positional x parameter of the X atoms could only be determined approximately from these data.

A reasonable agreement between calculated and observed structure factors is attained with $x = 0{\cdot}175$ for Tl_3VS_4 and $x = 0{\cdot}18$ for Tl_3TaSe_4 giving discrepancy indices of 0·155 and 0·17 respectively (Table 2).

The diffraction patterns of the selenides showed additional reflexions which in the case of Tl_3TaSe_4 could

Table 2. *Observed and calculated structure factors* (Cu $K\alpha$ radiation)

	Tl_3VS_4		Tl_3TaSe_4	
hkl	F_o*	F_c	F_o†	F_c
110	10·6	7·8	3·1	2·2
200	31·1	23·7	28·8	20·4
211	16·7	14·2	16·6	13·8
220	32·7	33·1	42·2	39·3
310	15·4	12·6	11·7	9·5
222	18·6	19·8	20·5	22·0
321	8·9	8·5	7·8	5·7
400	14·2	13·7	17·7	17·0
411 } 330	8·4	8·5	15·3	19·3
420	24·1	24·9	32·1	34·0
332	9·9	7·4	5·0	8·0
422	17·8	19·6	23·9	28·9
510 } 431	6·0	8·7	9·9	6·2
521	8·6	6·1	8·9	6·6
440	11·6	9·8	13·9	16·6
530 } 433	6·9	8·3	9·5	9·3
600 } 442	14·9	18·0	27·2	35·0
611 } 532	6·2	6·8	8·0	7·5
620	11·5	8·4	13·4	14·7
541	0	3·5	7·8	5·0
622	10·1	8·4	19·5	19·0

* Values taken from Debye-Scherrer photograph
† Values taken from Guinier-de Wolff photograph

be attributed to a secondary phase. Thus it is possible that slight deviations of the composition proposed can occur.

The arrangement in Tl_3BX_4 can be considered as a substituted CsCl structure with contraction of four X atoms around the B atom.

For instance in Tl_3VS_4 V is surrounded by 4 S at 2·3 Å and Tl by 4 S at 3·1 Å and 4 S at 3·7 Å.

The author is indebted to Drs. J. M. van der Berg for assistance in this structure determination.