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The crystal structures of $TlSbTe_2$ and $TlBiTe_2$.

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In a recent publication Semiletov & Man (1959) have reported on the crystal structures of $TlSbS_2$ and $TlBiSe_2$. These were found to be of the disordered NaCl type and it was surmised in their paper that certain other thallium compounds might also have this structure. However, there exist ordered structures which are closely related to the disordered NaCl type. Geller & Wernick (1959) have found that for $AgBiSe_2$ and $AgBiS_2$ there is a high temperature phase of the disordered NaCl type, while at room temperature a hexagonal phase exists. At intermediate temperatures there is a rhombohedral structure formed by ordering of the cations in layers perpendicular to one of the cubic [111] directions. We have synthesized and examined two of the compounds mentioned by Semiletov & Man, $TlSbTe_2$ and $TlBiTe_2$. These compounds have been found to be isostructural with the intermediate phases of $AgBiSe_2$ and $AgBiS_2$.

Specimens of $TlSbTe_2$ and $TlBiTe_2$ were prepared directly from the elements in evacuated fused silica ampules. The materials were heated to 600 °C., mixed and then cooled at a rate of about 10° min.$^{-1}$. By differential thermal analysis $TlSbTe_2$ was found to have a melting temperature of 480 °C. and $TlBiTe_2$ of 535 °C. In neither case were thermal effects observed below the melting temperatures.

Table 1. *Crystallographic data for* $TlSbTe_2$ *and* $TlBiTe_2$

	$TlSbTe_2$	$TlBiTe_2$
Crystal system	Rhombohedral	Rhombohedral
Systematically absent spectra	None	None
Space group	$R\bar{3}m$–D^5_{3d}	$R\bar{3}m$–D^5_{3d}
a_0 (Å)	8·177 ± 0·010	8·137 ± 0·010
α	31° 24′ ± 15′	32° 18′ ± 15′
Z	1	1
Calculated density (g.cm.$^{-3}$)	7·34	8·15
Measured density (g.cm.$^{-3}$)	7·26	8·06

X-ray powder patterns of both materials were indexed on the basis of a primitive rhombohedral cell and the crystallographic data referred to this unit cell are given in Table 1. Long exposure oscillation photographs of a small crystal separated from a Bridgman grown ingot of $TlSbTe_2$, revealed no additional reflection which would have required a larger unit cell. In the case of $TlBiTe_2$ suitable single crystals were not found, and the space-group assignment is consequently less definitive.

The atoms occupy the following special positions of the space group $R\bar{3}m$:

$$\text{Tl in } (a)\ 0, 0, 0;\ \text{Sb or Bi in } (b)\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2};$$
$$2\ \text{Te in } (c)\ \pm x, x, x\ .$$

The Te free parameter x was adjusted to give the best agreement between calculated and observed intensities, as measured on a Norelco diffractometer using powdered samples, and this was found with $x = 0{\cdot}243$ for $TlSbTe_2$ and $x = 0{\cdot}250$ for $TlBiTe_2$. In the latter case almost equally good agreement was obtained through the range 0·245–0·255. R, defined as $\Sigma|I_o - I_c|/\Sigma I_o$, was 0·074 for $TlSbTe_2$ (17 measured intensities) and 0·053 for $TlBiTe_2$ (14 measured intensities) using these parameters. In $TlSbTe_2$ the interatomic distances for Tl–Te are 3·30 Å and for Sb–Te are 3·11 Å both ±0·05 Å. If the Tl–Te distances are equal in both compounds then the x parameter in $TlBiTe_2$ becomes 0·246, which is consistent with the experimental data, and the Bi–Te distances would then be 3·19 Å.

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A new phase in the zinc-zirconium system.

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An intermetallic compound Zn_2Zr_3 has been isolated by precipitation from a solution of zinc and zirconium in molten magnesium. It is not mentioned in a recent comprehensive study of the Zn–Zr system (Chiotti & Kilp, 1959) nor in the earlier literature (Hansen, 1958; Pearson, 1958).

A representative sample of the new phase, consisting of those crystals retained on 100-mesh screening, contained 68·0% Zr by weight (calculated, 67·7%) and showed a density of 6·60 ± 0·04 g.cm.$^{-3}$. Data gathered from Weissenberg and rotation photographs of single crystals, together with data from powdered specimens, indicate a simple tetragonal unit cell with edges

$$a = 7{\cdot}633 \pm 0{\cdot}004,\ c = 6{\cdot}965 \pm 0{\cdot}004\ \text{Å},\ c/a = 0{\cdot}9125\ .$$

The density, calculated on the basis of 4 Zn_2Zr_3 in each cell, is 6·62 g.cm.$^{-3}$. The sole criterion observed for the non-extinction of reflections is $k+l$ even for $0kl$, which allows the three space groups $P4_2nm$, $P\bar{4}n2$, and $P4_2/mnm$.

Powder data recorded with a GE camera of diameter 143·2 mm., using Cu $K\alpha$ radiation, are listed in Table 1.

Table 1. *Powder data for* Zn_2Zr_3

hkl	I/I_1	*d* (obs.)	*d* (calc.)
112	20	2·92 Å	2·926 Å
220	44	2·69	2·699
022	75	2·57	2·572
221	38	2·52	2·516
122	100	2·44	2·438
130	63	2·41	2·414
131	63	2·28	2·281
013	31	2·23	2·221
222, 113	15	2·13	2·133, 2·133
230	18	2·12	2·117
132	20	1·98	1·984
140	22	1·85	1·851
232	18	1·81	1·809
331, 004	22	1·74	1·742, 1·741
033, 240	5	1·71 *B*	1·715, 1·707
042, 133	3	1·67	1·673, 1·673
114	3	1·65	1·657
142	31	1·63	1·635
332	31	1·595	1·598
124	22	1·550	1·551
242, 340	22	1·529	1·533, 1·527
—	3	1·511	—
—	20	1·490 *B*	—
—	38	1·460	—
—	31	1·447	—
—	15	1·421	—
—	38	1·410	—
—	5	1·387	—
—	38	1·372	—
—	31	1·346	—
—	31	1·310	—
—	44	1·271	—
—	8	1·252	—
—	18	1·236	—
—	5	1·218	—
—	20	1·205	—
—	15	1·187	—
—	5	1·170	—
—	3	1·160	—
—	10	1·135 *B*	—
—	8	1·109	—
—	5	1·097	—
—	10	1·078 *B*	—
—	10	1·065	—
—	13	1·042	—
—	5	1·033	—
—	5	1·027	—
—	8	1·018	—
—	8	1·010	—
—	5	1·000	—
—	8	0·990	—
—	5	0·983	—
—	8	0·974	—
—	8	0·960	—

Note that *B* indicates a *broad* line.

Relative intensities were established by visual comparison against calibrated standards.

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X-ray investigation of the anhydrous cadmium and mercuric sulphates.

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Continuing the systematic X-ray investigation of the unstable anhydrous sulphates of bivalent metals undertaken by our Department, we are studying the structure determination of $CdSO_4$ and $HgSO_4$. The two substances were found to be isostructural and different from the sulphates studied so far. In this preliminary communication are given the unit-cell dimensions and the space group of the compounds.

According to the literature both substances crystallize in the orthorhombic system. Crystallographic measurements are given only for $CdSO_4$, which, however, owing to the chance approximation of the angle $(011):(01\bar{1})$ to that of $ZnSO_4$, was erroneously assumed to be isomorphous to it (Groth, 1908). The values of the angles $(110):(1\bar{1}0) = 89°\ 58'$ and $(011):(01\bar{1}) = 70°\ 52'$ given by Groth, differ considerably from the values 89° 48′ and 71° 26′ respectively, measured on crystals prepared by us. The latter represent the mean of a series of measurements on different crystals, which yielded somewhat differing values because of imperfect face growth. Their approximation to the values 89° 49′ and 71° 20′ respectively, calculated from the lattice constants, is closer than that of the values given in Groth.

No crystallographic measurements on $HgSO_4$ crystals have been reported in the literature. On the crystals prepared by us the values of the interfacial angles, corresponding to those of $CdSO_4$ given above, are 89° 27′ and 72° 28′, in satisfactory agreement with the values 89° 34′ and 72° 27′ calculated from the lattice constants.

The systematic extinctions on Weissenberg and precession photographs made necessary a reorientation of the crystal axes, so as to make the space-group symbol agree with that given in the *International Tables* (1952). The changes are as follows:

$$\text{Groth } a \rightarrow c_0,\ \text{Groth } b \rightarrow a_0,\ \text{Groth } c \rightarrow b_0\ .$$

The cell dimensions given below were obtained from powder diagrams, taken with a calibrated 9 cm. Unicam camera for $CdSO_4$ and with a Norelco diffractometer for $HgSO_4$. The indexing of the powder diagrams was carried out by using the lattice constants obtained from