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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)	$8{\cdot}177 \pm 0{\cdot}010$	$8{\cdot}137 \pm 0{\cdot}010$
α	$31°\ 24' \pm 15'$	$32°\ 18' \pm 15'$
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 $6{\cdot}60 \pm 0{\cdot}04$ 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.