Crystallographic Evidence for the Existence of the Phases In_4Se_3 and In_4Te_3 which contain the Homonuclear Triatomic Cation $(In_3)^{5+}$

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Summary The compounds previously reported as In_2Te and In_2Se are shown to be In_4Te_3 and In_4Se_3 respectively; both materials contain the cation $(In_3)^{5+}$, which is analogous to the recently proposed $(Hg_3)^{2+}$.

GROCHOWSKI, MASON, SCHMITT, and SMITH,[1] in a review of the phase diagram of the indium-tellurium system, found no evidence, as a result of d.t.a. and peritectic zone-refining experiments, for the existence of the phase reported as In_2Te.[2,3] They proposed the existence of In_9Te_7.

Mixtures of indium and tellurium in correct stoicheiometric proportions to produce In_2Te and In_9Te_7 were placed in sealed evacuated tubes, heated to 500 °C for 24 h, and then subjected to directional freezing. From both preparations black, shiny, needle-like single crystals were extracted; these had unit-cell parameters almost identical with those reported for "In_2Te",[3] and were very similar to those of "In_2Se".[4] An attempted preparation of "In_2Se" also produced shiny black needles having unit cell parameters almost exactly equal to those given by Man and Semiletov.[4] Further *X*-ray investigation suggested that the selenide and telluride were isomorphous There is, thus, a conflict between the structural results of Man and Semiletov[4] and the compositional conclusions of Grochowski *et al.*[1]

To resolve this anomaly, *X*-ray structure investigations were carried out on both phases, and showed that they were isomorphous. *Crystal data:* In_4Se_3, orthorhombic, space group *Pnnm* (No. 58), $Z = 4$, $D_c = 6{\cdot}02$, $a = 15{\cdot}297$, $b = 12{\cdot}308$, $c = 4{\cdot}081$ Å; In_4Te_3, orthombic, space group *Pnnm* (No. 58), $Z = 4$, $D_c = 6{\cdot}32$, $a = 15{\cdot}63$, $b = 12{\cdot}76$, $c = 4{\cdot}44$ Å.

Three-dimensional *X*-ray single-crystal data were collected, for the selenide on a Siemens automatic single-crystal diffractometer using Cu-K_α radiation, and for the telluride photographically using Mo-K_α radiation; the data for the selenide was corrected for absorption. The structures were solved by Patterson methods and refined by block-diagonal least squares to give final residuals of 6 and 8% for the selenide and telluride respectively.

It was found conclusively that both structures contain four formula units of In_4X_3 per cell (X = Se, Te). This is

in almost exact agreement with the formula one obtains from the 43 atom % Te, reported for the phase by Grochowski *et al.*,[1] but differs from the formula, In_9Te_7, which they proposed.

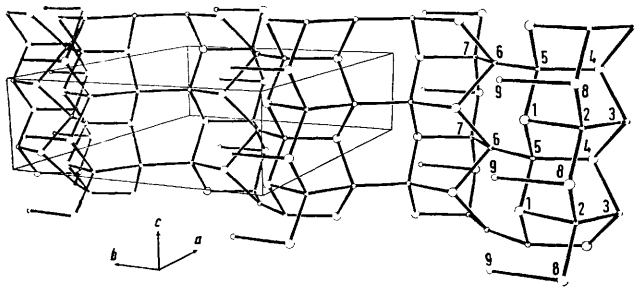

FIGURE. *Part of one of the pair of centro-symmetrically related continuous sheets of the structure of* In_4Te_3 *and* In_4Se_3. *The small circles are* In *atoms and the large circles* Te *or* Se *atoms. The part of the structure shown is from* −1 *to* +2 *cell translations in the* b *direction and from* −1 *to* +1·5 *in* c. *The asymmetric unit consists of atoms* 1—5, 8, *and* 9.

The Figure shows the structural arrangement for In_4Te_3 together with the suggested method of bonding. This, which is based on an analysis of interatomic distances, indicates that this material is composed of endless interlocking chains running parallel to *c*, consisting of five-membered indium–tellurium rings (atoms 1—5) the chains being cross linked by strong indium–indium–indium bonds (atoms 5—7) to form a continuous sheet lying perpendicular to *a*. These bonds, averaging 2·78 Å, indicate the presence of the homonuclear triatomic cation $(In_3)^{5+}$, analogous to the $(Hg_3)^{2+}$ ion.[5] Thus in ionic terms the formula of the phase would be $In^+(In_3)^{5+}3Te^{2-}$.

A similar system of bonding holds for In_4Se_3, suggesting the ionic formula $In^+(In_3)^{5+}3Se^{2-}$. The Table contains the relevant In–Te, In–Se, and In–In distances. The closest In–In non-bonded distances were 3·44 and 3·45 Å for In_4Se_3 and In_4Te_3 respectively. The crystal structures of In_6S_7[6] and In_6Se_7[7] also contain short In–In bonds of 2·74 and 2·76 Å respectively, indicating the presence of the diatomic cation $(In_2)_4^+$.

TABLE

Bond lengths

Bond Atom numbers[a]	Bond length/Å In_4Se_3	In_4Te_3
1–2	2·65	2·90
1–5	2·69	2·90
1–9	3·41	3·48
2–3	2·76	2·77
2–8	2·64	2·84
3–4	2·78	3·00
4–5	2·62	2·80
5–6	2·78	2·79
8–9	2·97	3·19

[a] The atom numbers refer to those in the Figure.

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