THE CHEMICAL FORMULA OF EMPRESSITE

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Abstract

Ag_5Te_3 is synthetic empressite. $Ag_{5-x}Te_3$ is the formula deduced, for the mineral, from cell dimensions and density of analyzed crystals.

Empressite was described by Bradley (1914, 1915) as a silver telluride AgTe and by Schaller (1914) as the silver end-member of the phase (Ag,Au)Te, which occurs as the mineral muthmannite. The formula rested on three determinations of type-locality material, two by Bradley (1914) and one by E. J. Dittus (*in* Bradley, 1915), which gave values $Ag_{0.97\pm0.01}Te_{1.00}$ in excellent agreement with one another. Nevertheless, in the light of later analyses and syntheses, it appears likely that native tellurium was admixed in the analyzed samples in such finely divided form that it was not recognized under the microscope. More recently a careful analysis by R. N. Williams, also on material from the type locality, gave the composition $Ag_{1.43}Te_{1.00}$ as reported by Thompson *et al.* (1951). These authors found the specific gravity to be 7.61 ± 0.01. They took x-ray patterns of powders as well as synthetic single crystals and showed that the empressite powder pattern is identical with that of a homogeneous fusion product of composition Ag_5Te_3. They concluded, however, that the general formula should be written $Ag_{2-x}Te_{1+x}$ with $0.1 \leqq x \leqq 0.5$, thus implying that silver and tellurium substitute for each other over an appreciable range of solid solution. Because of the difference in electronegativity of silver and tellurium and because these two elements are known to play very different roles in related compounds, this formula is unsatisfactory.

A recent study of the silver-tellurium phase diagram by Kracek and Ksanda (1955) establishes the existence of two and only two compounds in the Ag-Te system, namely: Ag_2Te, identical with hessite, and Ag_5Te_3, to which the compositions AgTe, Ag_7Te_5, Ag_3Te_2, $Ag_{12}Te_7$ and Ag_7Te_4 had previously been ascribed.

Professor Berry kindly sent us the single crystals of empressite which Thompson *et al.* (1951) had obtained by hydrosynthesis. We confirmed their cell dimensions on the precession camera, using CuKα radiation ($\lambda=1.5418$ Å); $a=13.49$ Å, $c=8.47_4$ Å, all ±0.3 per cent. The diffraction aspect is P***, with a pronounced pseudo-aspect $P6_3$** (all reflections $000l$ are missing when l is odd, except 0003). Unfortunately, because of scarcity of material, it was not possible to determine the specific gravity of these single crystals, and since their exact composition was not certain either, we proceeded with the x-ray and density studies of synthetic samples prepared by Kracek and Ksanda. A least-square analysis of the powder pattern of Ag_5Te_3 (62.50 at. per cent Ag) gives cell dimensions

$a = 13.46$ Å, $c = 8.47$ Å, all ± 0.3 per cent, $V = 1328$ Å^3. The observed specific gravity is 7.96 ± 1 per cent. Assuming 7 Ag_5Te_3 per cell the calculated specific gravity is 8.07. The intensities and cell dimensions of Ag_5Te_3 check those of the powder pattern of type-locality material given by Thompson *et al.* (1951, p. 468), namely: $a = 13.49$ Å (13.46 kX), $c = 8.48$ Å (8.46 kX), $V = 1336$ Å^3. Although the silver/tellurium ratio in this material, as noted above, is 1.43, not 1.67, and the specific gravity is 7.61 instead of 7.96, there is no doubt that the two patterns come from isostructural compounds, so that the ideal formula for empressite can only be Ag_5Te_3.

Because both composition and specific gravity are known for the sample from the Empress Mine, it is straightforward, once the ideal formula is established, to decide between the three possible types of solid solution.

1. Substitution solid solution. The formula is to be written $Ag_{5-x}Te_{3+x}$; $x = 0.29$. With seven formula units of $Ag_{4.71}Te_{3.29}$ per cell and a measured cell volume of 1336 Å^3, the calculated specific gravity is 8.1.

2. Addition solid solution. The formula is to be written Ag_5Te_{3+x}; $x = 0.50$. With seven formula units of $Ag_5Te_{3.50}$ and a measured cell volume of 1336 Å^3, the calculated specific gravity is 8.6.

3. Omission solid solution. The formula is to be written $Ag_{5-x}Te_3$; $x = 0.71$. With seven formula units of $Ag_{4.29}Te_{3.00}$ and a measured cell volume of 1336 Å^3, the calculated specific gravity is 7.4. Reasonable agreement between this value and the observed one (7.61) establishes the formula of empressite as $Ag_{5-x}Te_3$. Powder patterns of synthetic samples whose composition ranges from Ag_5Te_3 to $Ag_{4.50}Te_3$ show only the $Ag_{5-x}Te_3$ phase. Hessite lines are observed when as little as 0.66 at. per cent excess silver is present.

Cell dimensions calculated for $Ag_{4.74}Te_3$ and $Ag_{4.50}Te_3$ show no significant changes. The cell volume remains constant within experimental limits of error. If tellurium forms a hexagonal close-packed framework, random vacancies in the silver positions would not be expected to lead to measurable changes in cell dimensions.

References

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