THE CHEMICAL FORMULA OF EMPRESSITE

GABRIELLE DONNAY, F. C. KRACEK, AND W. R. ROWLAND, JR.,
Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D. C.

ABSTRACT

Ag₅Te₃ is synthetic empressite. Ag₅₋₁Te₃ 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 Ag₀.₉₇±₀.₀₂Te₃.₀₀ 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 Ag₁.₄₅Te₁.₀₀ 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 Ag₅Te₃. They concluded, however, that the general formula should be written Ag₅₋ₓTe₅₊₂ with 0.1 ≤ x ≤ 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: Ag₂Te, identical with hessite, and Ag₅Te₃, to which the compositions Ag₅Te, Ag₇Te₃, Ag₅Te₃, Ag₁₂Te₇, and Ag₇Te₄ 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 (λ = 1.5418 Å); a = 13.49 Å, c = 8.474 Å, all ± 0.3 per cent. The diffraction aspect is P***, with a pronounced pseudo-aspect P6₃** (all reflections 00l 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 Ag₅Te₃ (62.50 at. per cent Ag) gives cell dimensions.
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\[ a = 13.46 \, \text{Å}, \, c = 8.47 \, \text{Å}, \, \text{all} \pm 0.3 \, \text{per cent}, \, V = 1328 \, \text{Å}^3. \]

The observed specific gravity is 7.96 ± 1 per cent. Assuming 7 Ag₅Te₃ per cell the calculated specific gravity is 8.07. The intensities and cell dimensions of Ag₅Te₃ check those of the powder pattern of type-locality material given by Thompson et al. (1951, p. 468), namely: \( a = 13.49 \, \text{Å} \) (13.46 kX), \( c = 8.48 \, \text{Å} \) (8.46 kX), \( V = 1336 \, \text{Å}^3. \) 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 Ag₅Te₃.

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 Ag₁₋₅xTe₅₊₂x; \( x = 0.29 \). With seven formula units of Ag₄.₇Th₃.₂₉ per cell and a measured cell volume of 1336 Å³, the calculated specific gravity is 8.1.

2. Addition solid solution. The formula is to be written Ag₅Te₃₊₂x; \( x = 0.50 \). With seven formula units of Ag₅Te₃.₅₀ and a measured cell volume of 1336 Å³, the calculated specific gravity is 8.6.

3. Omission solid solution. The formula is to be written Ag₅₋₇xTe₃; \( x = 0.71 \). With seven formula units of Ag₄.₂₉Te₃.₆₀ and a measured cell volume of 1336 Å³, the calculated specific gravity is 7.4. Reasonable agreement between this value and the observed one (7.61) establishes the formula of empressite as Ag₅₋₇xTe₃. Powder patterns of synthetic samples whose composition ranges from Ag₅Te₃ to Ag₄.₅₀Te₃ show only the Ag₅₋₇xTe₃ phase. Hessite lines are observed when as little as 0.66 at. per cent excess silver is present.

Cell dimensions calculated for Ag₄.₇₄Te₃ and Ag₄.₆₀Te₃ 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


Krakek, F. C., AND Ksanda, C. J. (1955), Phase relations in the system silver-tellurium, in manuscript.


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