THE CHEMICAL FORMULA OF EMMRESSITE

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

ABSTRACT

Ag₆Te₃ is synthetic empressite. Ag₆₋₄Te₃ 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±₀.₀₁Te₁.₀₀ 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 Ag₀.₈₇Te₁.₀₀ 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 Ag₆Te₃. They concluded, however, that the general formula should be written Agₓ₋₄Teₓ₄ 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: Ag₅Te, identical with hessite, and Ag₆Te₃, to which the compositions AgTe, Ag₄Te₄, Ag₃Te₅, Ag₂Te₆, Ag₁Te₇ 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 003). 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 Ag₆Te₃ (62.50 at. per cent Ag) gives cell dimensions...
CHEMICAL FORMULA OF EMPRESSITE 723

The observed specific gravity is 7.96 ± 1 per cent. Assuming 7 Ag₅Te₈ per cell, the calculated specific gravity is 8.07. The intensities and cell dimensions of Ag₅Te₈ 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 Ag₅Te₈.

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 Ag₅₋ₓTe₈₊ₓ; \( x = 0.29 \). With seven formula units of Ag₄.₇Te₂.₉₉ 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 Ag₅Te₈₊ₓ; \( x = 0.50 \). With seven formula units of Ag₅Te₈.₃₀ 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₋ₓTe₈; \( x = 0.71 \). With seven formula units of Ag₄.₂₉Te₂.₀₆ 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₋ₓTe₈. Powder patterns of synthetic samples whose composition ranges from Ag₅Te₈ to Ag₄.₆₀Te₈ show only the Ag₅₋ₓTe₈ phase. Hessite lines are observed when as little as 0.66 at. per cent excess silver is present.

Cell dimensions calculated for Ag₄.₇₄Te₈ and Ag₄.₆₀Te₈ 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


Kracek, F. C., and Kranda, C. J. (1955), Phase relations in the system silver-tellurium, in manuscript.


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