

The crystallochemical mechanism of formation of vacancies in goldfieldite structure

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The mineral goldfieldite is characterized by general formula $Cu_{6-x}(Cu,Fe,Zn)_6(As,Sb)_4S_{13-y}$. The Sb-goldfieldite and As-goldfieldite structures have been solved (R-value 0,05) to get information on structural defects. Experimental data for the two structures were collected on an automated single-crystal diffractometer "NONIUS" CAD-4 SDP.

The As-goldfieldite crystal turned out to be more suitable for revealing the structure vacancies due to the large content of Te (% Cu=43.38; Sb=0.23; As=5.30; Te=25.74; S=25.56). The site occupancies refinement showed that Sb-goldfieldite and As-goldfieldite structures are characterized by cation-deficient model. It is mainly connected with appearing Cu-vacancies during the entering of Te^{4+} instead of Sb^{3+} and As^{3+} in the fahlore structure type. All Cu-vacancies are located in one-position (12e) only, where Cu has the triangular coordination and is characterized by markedly anisotropic thermal motion. The octahedral site (2a) can be occupied with S_2 also incompletely. But the deviation from full occupation is not so significant (no more than twice of the standard error). Probably complex interconnected redistribution of the amount of vacancies both in Cu (12e) and S (2a) position occurs in the goldfieldite structure, depending on the relation of Te and (As,Sb). Through the structure refinement the greatest number of vacancies (1.8) has been discovered in As-goldfieldite structure. The exact chemical formula of As-goldfieldite structure is $Cu_{24-1.8(2)}(Te_{5.9(2)}As_{2.1(2)}S_{24+1.7(2)})$.

Dmitrieva M.T., Ephremov V.A., Kovalenker V.A. Doklady AN SSSR, 297, 687 (1987).