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SYNTHESIS AND CRYSTAL DATA OF A Cu-FREE "MENEGHINITE"

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ABSTRACT

A Cu-free "meneghinite" was synthesized in the Pb-Sb-S system at 635°C. This phase is orthorhombic, *Pbnm, a* 11.36, *b* 23.98, *c* 4.10Å. The symmetry and unit-cell dimensions correspond to the subcell of the Cu-bearing mineral. The metal-rich formula $Pb_{3+x}Sb_2S_6$ is proposed for the Cu-free phase.

SOMMAIRE

De la "ménéghinite" exempte de cuivre a été synthétisée dans le système Pb-Sb-S à 635°C. Cette phase est orthorhombique, *Pbnm, a* 11.36, *b* 23.98, *c* 4.10Å. Par ses paramètres et sa symétrie, cette maille correspond à la maille sous-multiple du minéral $CuPb_{13}Sb_7S_{24}$. La formule $Pb_{3+x}Sb_2S_6$ est proposée pour la phase exempte de cuivre.

(Traduit par la Rédaction)

The existence of a much disputed Cu-free "meneghinite" in the Pb-Sb-S system has been experimentally confirmed in two cases (Wang 1973; Jambor 1975). This note gives the experimental details for the work done several years ago, which has been partly repeated by the author, on this Cu-free phase.

Samples containing stoichiometric PbS and Sb_2S_3 in the mole ratio between 3.2:1 and 3.0:1 (corresponding to compositions of phase II of Salanci & Moh 1970) were heated in evacuated silica-glass tubes at 630°C and ground three times within the first week. Powder patterns taken at this stage were identical to that of phase II of Salanci & Moh (1970) and phase I of Craig *et al.* (1973). The samples were then brought to melt at 640°C, ground once more, and held in the temperature range 628-635°C for three additional weeks. The quenched products consisted mainly of well-formed, prismatic crystals associated with small amounts of fine-grained PbS. Reheating of the original phase II samples of Salanci & Moh at 635°C, without melting, yielded similar results. Most of the crystal grains thus obtained are bounded by well-developed {120}. The grains are up to 0.2 mm in cross section.

Precession photographs of a prismatic crystal indicated orthorhombic symmetry, *a* 11.36, *b* 23.98, *c* 4.10Å, V=1117Å^3, space group *Pbnm*. These single-crystal data correspond to the subcell of Cu-bearing natural meneghinite where Cu tends to order in the structure and is essential for the natural phase (Berry & Moddle 1941; Euler & Hellner 1960). The *hk*0 pattern closely resembles the orthorhombic $2PbS.Sb_2S_3$ phase (Wang 1973). The powder data are identical to those published by Jambor (1975) for the Cu-free "meneghinite". Microprobe analysis of a single crystal, confirmed by X-ray study, gave an atomic ratio Pb:Sb= 12.6:8. These crystals are considered to be more Sb-rich than the starting material since a small amount of PbS is present in the quenched products. The microprobe analysis for S was not of sufficiently high reliability to show whether the composition of the analyzed crystal falls on the $PbS\text{-}Sb_2S_3$ join. However, addition of 0.2 wt. % sulfur to phase II yielded at 630°C a mixture of PbS and boulangerite, which eliminates the possibility of a sulfur-rich composition for both phase II and "meneghinite". On the other hand, formation of "meneghinite" was favored in samples which contained a slight excess of antimony.

The experimental results described above clearly show the existence of a Cu-free "meneghinite" in the ternary system Pb-Sb-S at temperatures up to 635°C. The atomic ratio Pb:Sb=12.6:8 obtained in the present study for "meneghinite" agrees fairly well with the results of Jambor (1975) where the ratio is 12.4:8. The slightly Sb-rich sample analyzed by Jambor probably represents the other composition limit of the Cu-free phase at 550°C because his crystals were prepared from an Sb-rich starting material.

On the basis of these experimental data and of a structural consideration (Euler & Hellner 1960), the author proposes a metal-rich formula $4(Pb_{3+x}Sb_2S_6)$ for the Cu-free "meneghinite", where $0.15 \geqq x > 0$. For x=0, this formula degenerates to that of the Sb-rich composition limit of phase II of Salanci & Moh (1970), i.e., phase I of Craig *et al.* (1973).

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