

BRIEF COMMUNICATION

On the Synthesis and Crystal Structure of $\text{Ba}_6\text{Cu}_{12}\text{Fe}_{13}\text{S}_{27}$: A Rebuttal Statement

Jaime Llanos¹ and Carlos Mujica

Departamento de Química, Facultad de Ciencias, Universidad Católica del Norte, Casilla 1280, Antofagasta, Chile

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The authors of the preceding critical discussion of our paper "Synthesis and Crystal Structure of $\text{Ba}_6\text{Cu}_{12}\text{Fe}_{13}\text{S}_{27}$ " claim that the compound is not new. Indeed, owensite, $(\text{Ba,Pb})_6(\text{Cu,Fe,Ni})_{25}\text{S}_{27}$ was the first barium base metal sulfide mineral found and structurally characterized (1,2). Nevertheless, we synthesized and solved the crystal structure of a compound with the chemical composition $\text{Ba}_6\text{Cu}_{12}\text{Fe}_{13}\text{S}_{27}$, which is isotypic but not identical with owensite (3).

We agree with the authors that the reference attributed to the synthesis of chalcopyrite was incorrect. The synthesis details were actually taken from ref 4. Following the procedure described in that paper, we obtained a homogeneous material, which was characterized as chalcopyrite by X-ray diffraction and chemical analysis. The purity of this material was sufficiently good to prepare $\text{Ba}_6\text{Cu}_{12}\text{Fe}_{13}\text{S}_{27}$ as a single phase. Moreover, material prepared in the same manner was also used in the successful synthesis of the alkali metal base sulfides NaCuFeS_2 , KCuFeS_2 , and CsCuFeS_2 (5–7).

On the other hand, it is well known that Cu and Fe cannot be differentiated by X-ray diffraction methods. Nevertheless, we were able to show by XPS studies that only Cu(I) is present in the structure of the phase $\text{Ba}_6\text{Cu}_{12}\text{Fe}_{13}\text{S}_{27}$. According to the stereochemical behavior of Cu(I), which can adopt a tetrahedral, linear, planar, distorted square planar, or square pyramidal, but never octahedral coordination (8), we assumed that only Fe ions can occupy the position $1b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), which is octahedrally surrounded by sulfur. In owensite, the authors use an "average" transition metal atom, assuming a random distribution of Cu, Fe, and Ni in both tetrahedral and octahedral sites. Copper ions with oxidation state $1+$ must be located only

in the tetrahedral positions. If the copper ions had the oxidation state $2+$, the octahedra around these atoms would be Jahn-Teller distorted, which is not the case. We can then conclude that the use of an "average" atom in this position is incorrect.

Finally, there is no discrepancy in the assignment of the space group. All djerfisherite-like structures crystallize in the cubic system with space group $Pm\bar{3}m$ (No. 221) (9). The notation $Pm3m$, which the authors claim as correct, corresponds to the short symbol used in the 1935 edition of the International Tables. The 1983 edition of the International Tables uses $Pm\bar{3}m$ as the short symbol for this space group (10).

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¹To whom correspondence should be addressed.