

BRIEF COMMUNICATION

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

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We are pleased to read that the pure end-member of the mineral owensite (1, 2) has been synthesized (3). However, we take exception to the statement "The new $\text{Ba}_6\text{Cu}_{12}\text{Fe}_{13}\text{S}_{27}$, a new djerfisherite-like compound, ..." because it is not new. Owensite is, however, the *first* barium base metal sulfide mineral to be found. It was found during a study of the Cu–Ni–Pt–Pd mineralization at the Wellgreen deposit, Yukon, Canada (4).

We also take exception to the sentence "Synthetic chalcopyrite ..." because the reference attributed to details of synthesis (5) is incorrect. That particular paper describes a crystal structure refinement of a natural chalcopyrite crystal obtained from Western Mines (now known as the Myra Falls deposit), Vancouver Island, Canada, and that paper does *not* discuss or refer to synthesis of chalcopyrite. Synthetic tetragonal CuFeS_2 , equivalent to the mineral chalcopyrite, is known to be difficult to synthesize as a single homogeneous phase due to low-temperature reactions between metastable phases after cooling from above its incongruent melting temperature (6). Therefore, details of the synthesis would be interesting, especially since the authors (3) only used X-ray powder diffraction (not described) to verify the homogeneity of their synthetic product. It is unlikely that they produced pure synthetic chalcopyrite, most probably having a mixture of Cu–Fe–S phases which are difficult to distinguish by most X-ray powder diffraction methods due to the superposition of major lines of *fcc* and *pc* compounds with lines of the tetragonal chalcopyrite structure (6, 7).

It is unfortunate that the authors (3) and the referees of this journal were apparently unaware of earlier papers on the mineralogy (1) and the crystal structure of owensite (2). Had they read these papers, they would have noted that the Cu and Fe atoms in owensite could not be differentiated in different sites and therefore an "average" atom had to be

used for the Cu/Fe/Ni metal type. This resulted in a different space group assignment (*Pm3m*) that best fits the results on owensite (2) and which is the same space group in which previous djerfisherite-like structures, such as djerfisherite and thalfensite, have been described (8–10). Nature can be chemically more complex than the inorganic compounds synthesized in the laboratory. For example, owensite was determined to also contain Pb and Ni, with an average empirical formula $(\text{Ba}_{5.42}\text{Pb}_{0.56})(\text{Cu}_{12.87}\text{Fe}_{11.7}\text{Ni}_{0.14})\text{S}_{27.31}$, obtained by quantitative wavelength-dispersive spectrometry using an electron microprobe to analyze grains ranging from 15×22 to $43 \times 110 \mu\text{m}$ in size. The presence of disordered Pb in the Ba site also severely complicated the structure determination (2).

We hope that this note will help inform readers of the wealth of crystal structural information that is available in the mineralogical literature. There are many inorganic compounds that were first found and characterized as minerals, djerfisherite in particular (11).

REFERENCES

1. J. H. G. Laflamme, A. C. Roberts, A. J. Criddle, and L. J. Cabri, *Can. Mineral.* **33**, 665 (1995).
2. J. T. Szymański, *Can. Mineral.* **33**, 671 (1995).
3. J. Llanos, C. Mujica, O. Wittke, P. Gómez-Romero, and R. Ramírez, *J. Solid State Chem.* **128**, 62 (1997).
4. S. R. Hall and J. M. Stewart, *Acta Crystallogr. B* **29**, 579 (1973).
5. L. J. Cabri, L. J. Hulbert, J. H. G. Laflamme, R. Lastra, S. H. Sie, C. G. Ryan, and J. L. Campbell, *Explor. Min. Geol.* **2**, 105 (1993).
6. L. J. Cabri, *Econ. Geol.* **68**, 443 (1973).
7. L. J. Cabri and S. R. Hall, *Am. Mineral.* **57**, 689 (1972).
8. M. T. Dmitrieva, V. V. Ilyukhin, and G. B. Bokii, *Acta Crystallogr. A* **34** (Suppl.), S186 (1978).
9. M. T. Dmitrieva, V. V. Ilyukhin, and G. B. Bokii, *Sov. Phys. Crystallogr.* **24**, 683 (1979).
10. N. S. Rudashevskiy, A. M. Karpenkov, G. S. Shipova, N. N. Shishkin, and V. A. Ryabkin, *Vses. Mineral. Oro., Zapadno-Sib. Otd., Tr.* **108**, 696 (1979).
11. A. D. Genkin, N. V. Troneva, and N. N. Zhuravlev, *Geochem. Int.* **7**, 693 (1970).

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