

Bornite, Cu_5FeS_4 or $\text{Cu}_8\text{Fe}_4\text{S}_8$ - Experimental Versus Model Proposal.

Antonio L. Soares Jr.^{a,b} (PG), Thomas Heine^b (PQ), Hélio A. Duarte^a (PQ) and Heitor A. De Abreu^a (PQ).

^aUniversidade Federal de Minas Gerais, Departamento de Química – GPQIT, Belo Horizonte - Brazil. ^bJacobs University Bremen, Campus Ring, Bremen - Germany.
e-mail: antoniolsj@ufmg.br or alsoaresjr@gmail.com

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INTRODUCTION

Bornite (Cu_5FeS_4 ^[1] or $\text{Cu}_8\text{Fe}_4\text{S}_8$ ^[2]) is one of the minerals detected on the chalcopyrite surface during its leaching process^[3] for copper extraction. It is observed a dramatic decrease in the rate of leaching of copper and its mechanism at a molecular level is not well understood. Understanding the electronic structure of the bulk and surfaces of bornite is important for the proposal of a leaching mechanism. The orthorhombic Cu_5FeS_4 ^[1] (160 atom/cell) system is the best molecular formula proposed by experimental results and the cubic $\text{Cu}_8\text{Fe}_4\text{S}_8$ ^[2] (80 atom/cell) is a theoretical proposal which fixes some deviations found in the experimental results and crystallization. The aim of this work is the theoretical comparison between both structures with elucidation of the nature of the chemical bonding, structural and electronic properties through Density Functional Theory formalism.

METHODS

Quantum Espresso package in its parallel implementation with plane wave basis, PBE and PBESOL exchange–correlation (xc) functional with core electrons described by US and PAW pseudopotentials were used. In both arrangements, kinetic energy was set to 80 Ry and charge density cutoff was 400 Ry. The k-points density $2 \times 2 \times 2$ integrals by Monkhorst and Pack for $\text{Cu}_8\text{Fe}_4\text{S}_8$ and Gamma point for Cu_5FeS_4 were used.

RESULTS AND DISCUSSION

X-ray diffraction results for Cu_5FeS_4 exhibit fractional occupation in metallic centers, however our theoretical results show that occupation **4** and **5** in asymmetric unit of the cell is $30 \text{ kcal} \cdot \text{mol}^{-1}$ more stable than any other possible positions of iron atoms. Adopting these preferential positions to the iron atoms all other results were obtained. The PBE functional and US pseudopotential provided better results with structural properties variation less than 2% in both molecular proposals. Both structures show antiferromagnetic

behavior as detected in experimental results. Band gap of 0.86 eV was measured for Cu_5FeS_4 nanoparticles, but our results indicate metallic behavior in both cases, justified by the underestimated value of energy gap in DFT calculation. Although they had similar electronic behavior, as indicated by the DOS and band structure, PDOS results reveal that Cu_5FeS_4 presents large contributions from *d* orbitals localized on the iron atoms above the Fermi Level (FL) and $\text{Cu}_8\text{Fe}_4\text{S}_8$ exhibits some more contribution below the FL (Figure 1), suggesting the oxidation states +3 and +2, respectively, for the iron atoms. Charge distributions based on Bader's theory (AIM) confirm PDOS information, and suggest Cu^+ and S^{2-} . The AIM topological analysis and ELF shows the ionic character for M–S bond. The bulk compressibility of Cu_5FeS_4 is close to S and Cu local compressibility basins: $\kappa(\text{S}) \approx \kappa(\text{Cu}_5\text{FeS}_4) \approx \kappa(\text{Cu}) = 10.65 \text{ TPa}^{-1}$.

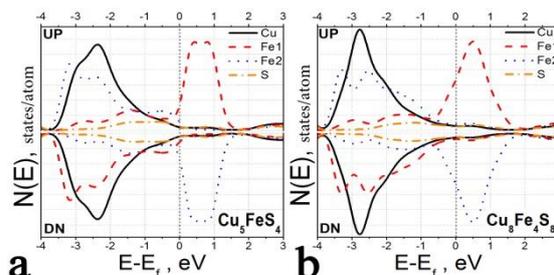


Figure 1. Projected Density Of States (PDOS)/atom for (a) Cu_5FeS_4 and (b) $\text{Cu}_8\text{Fe}_4\text{S}_8$.

CONCLUSIONS

Theoretical results of both structures could be described with accuracy. It was identified the metal occupation in Cu_5FeS_4 and it was shown that the $\text{Cu}_8\text{Fe}_4\text{S}_8$ does not represent a good model for the description of electronic distribution in native bornite (Cu_5FeS_4).

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