



High pressure sintering of a pure, compact and malleable chalcopyrite block



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ABSTRACT

In this work, a high pressure sintering method to prepare a pure, compact, and malleable chalcopyrite block at 0.6 GPa/270 °C in a cubic multi anvil press was introduced. The phase composition and elemental distribution of the pure sintered chalcopyrite block were investigated in comparison to a natural chalcopyrite ore and an impure sintered chalcopyrite block by X-ray diffraction (XRD), reflected light photographs and electron probe microanalysis techniques (EPMA). The results showed that the sample was with pure and stable chalcopyrite phase. The density and ductility of the pure sintered chalcopyrite were measured by density analyzer and grinding machine, respectively, indicating it was highly compact and easily machined.

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1. Introduction

Chalcopyrite, CuFeS_2 , is a natural mineral with special optical, electrical, chemical, dynamic and magnetic properties. To study these properties of chalcopyrite, many researches such as electrochemical corrosion, electrical conductivity and elastic wave of chalcopyrite need pure and compact chalcopyrite blocks with fixed shape as the experimental materials. However, chalcopyrite is often paragenetic with other sulfide minerals like pyrite, pyrrhotite, galena and sphalerite in hydrothermal ore-forming process [1,2]. Pyrrhotite is a material with the NiAs structure. Its crystal system changed from monoclinic forms to hexagonal forms at temperatures above 254 °C [3]. Having other minerals in the chalcopyrite, each face and part of the chalcopyrite is different, which effects the experimental results. Moreover, the grade of raw chalcopyrite is becoming lower with mining of chalcopyrite. Therefore, it is necessary to sinter pure, compact and malleable chalcopyrite blocks.

As important semiconductor materials, CuFeS_2 crystals with different morphologies have been synthesized by solid state sintering process [4], hydrothermal method [5,6] and solventothermal process^a [7–9]. The products of the last three methods were

$\text{Cu}^{1+}\text{Fe}^{3+}(\text{S}^{2-})_2$ -type chalcopyrite, while the ionic state of CuFeS_2 produced by sintering process was $\text{Cu}^{2+}\text{Fe}^{2+}(\text{S}^{2-})_2$. The ionic state of the natural chalcopyrite was still controversial and the synthesis products are all CuFeS_2 powders [10]. Methods of sintering pure and compact chalcopyrite blocks have not been reported so far.

In this work, a high pressure sintering method was devised to prepare a pure, compact and malleable chalcopyrite block. Density analyzer, X-ray diffraction (XRD), reflected light photographs, electron probe microanalysis (EPMA) and the pictures of the chalcopyrite blocks before and after grinding were used to testify the density, purity and ductility of our obtained chalcopyrite samples.

2. Experiments

2.1. Sample preparation

Sample N Cpy was the natural chalcopyrite ore from Baiyinchang, in Gansu Province, China. Sample I Cpy was the impure chalcopyrite particles in the region from 80 mesh to 100 mesh after flotation of Sample N Cpy to remove calcite particles. Sample P Cpy was the pure chalcopyrite particles separating from Sample I Cpy in the same size region. After cleaning Sample P Cpy in acetone and dehydrated ethanol respectively, the particles were wet ground into powder with their size under 200 mesh. The experimental assembly was presented in Fig. 1. The chalcopyrite powder was made into cylinder and sealed into a silver capsule of 6 mm in diameter and 5 mm length. Using NaCl as the pressure transmitting medium

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^a A method of crystal formation that depends on the organic solvents in high temperature and pressure.

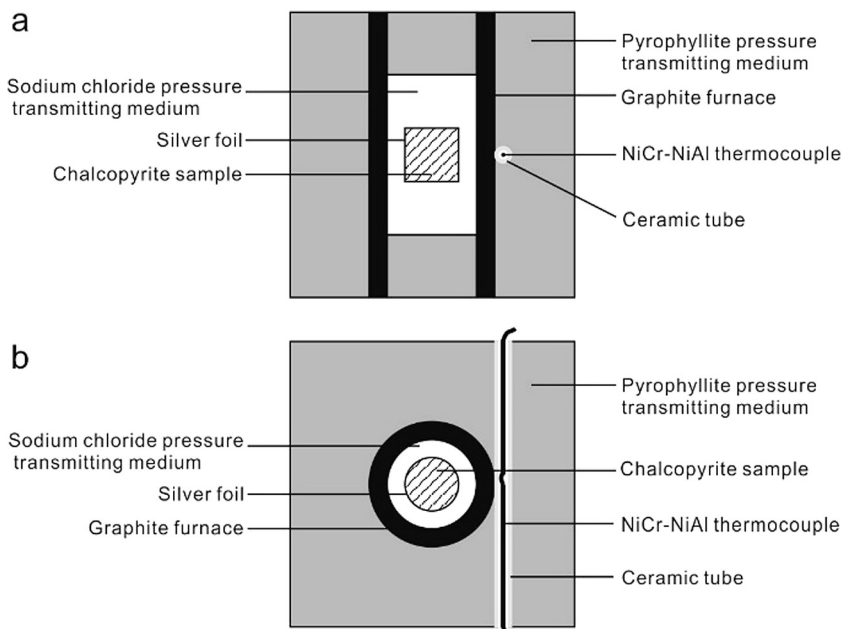


Fig. 1. Sectional view (a) and vertical view (b) of the experimental assembly.

and graphite as the furnace, the high pressure sintering experiment was performed in a cubic multi anvil press at 0.6 GPa and 270 °C with the reaction time of 1 h. Removing the silver foil on the surface, a high pressure sintered pure chalcopyrite block (Sample HP Cpy) was obtained. Choosing Sample I Cpy as the starting material and doing the same process as before, a high pressure sintered impure chalcopyrite block (Sample HI Cpy) was also obtained.

2.2. Characterization

The density of Sample HP Cpy was measured by an automatic density analyzer (ULTRAPYC 1200e). The phase compositions of Sample HP Cpy, HI Cpy, P Cpy and I Cpy were identified by powder X-ray diffraction (XRD). The surface morphologies of Sample HP Cpy, HI Cpy and N Cpy were determined by reflected light photographs. The elemental distribution and compositional variation of chalcopyrite phase for the three samples were examined by electron probe microanalysis (EPMA). Moreover, the ductility of Sample HP Cpy was tested by a grinding machine.

3. Result and discussion

Chalcopyrite has a tetragonal structure with space group $I\bar{4}2d$, lattice parameters $a = 5.289 \text{ \AA}$ and $c = 10.423 \text{ \AA}$. The unit cell density of chalcopyrite we calculated from lattice parameters is $4.178 \text{ g}\cdot\text{cm}^{-3}$. The density of our sintered pure chalcopyrite block (Sample HP Cpy) measured by the automatic density analyzer ULTRAPYC 1200e is $4.0096 \pm 0.0174 \text{ g}\cdot\text{cm}^{-3}$, which is close to the theoretical density of chalcopyrite, that is, the sample is compact.

Fig. 2 shows the XRD results of Sample I Cpy, P Cpy, HI Cpy and HP Cpy. Because pure chalcopyrite particles were picked out as the starting materials in Sample P Cpy and HP Cpy, all reflections can be indexed to the chalcopyrite. Diffraction peaks of pyrite and quartz were not detected in the two samples, while they were observed in Sample I Cpy and HI Cpy.

Fig. 3a–c exhibits the reflected light photographs of Sample HP Cpy, HI Cpy and N Cpy. It is obvious the sintered products Sample HP Cpy and Sample HI Cpy are more compact and even than Sample N Cpy. The surface of Sample N Cpy is uneven with many

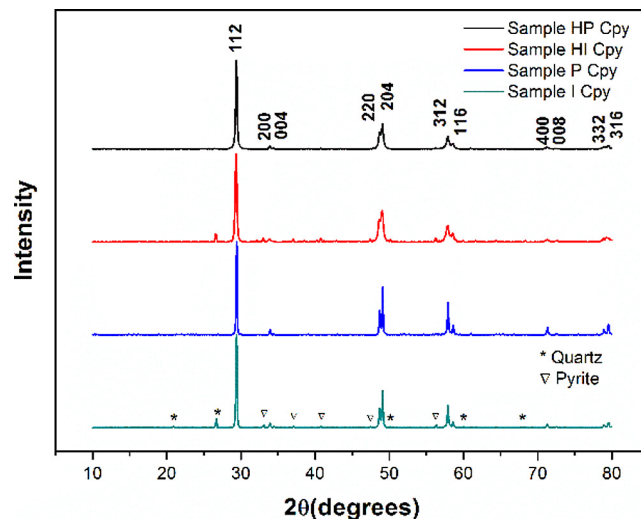


Fig. 2. X-ray diffraction patterns of Sample HP Cpy, Sample HI Cpy, Sample P Cpy and Sample I Cpy.

potholes and cracks. While Sample HP Cpy is with pure chalcopyrite phase, Sample HI Cpy is homogeneously dispersed with pyrite and quartz particles and Sample N Cpy is consisted with pyrite, quartz and calcite by large area, indicating the high purity of Sample HP Cpy.

The same phenomenon was found in the EPMA element maps of Cu, Fe and S for the three samples. Element Cu, Fe and S homogeneously covered in Sample HP Cpy (Fig. 3a₂–a₄), showing the sample is pure and compact. Concentration and deficiency of Element Cu, Fe and S were found with particle distribution in Sample HI Cpy (Fig. 3b₂–b₄). The particles with deficiency of element Cu, Fe and S are quartz after removing of calcite by flotation and the particles with deficiency of element Cu but concentration of element Fe and S are pyrite. That is, the sample contains pyrite and quartz. In Sample N Cpy (Fig. 3c₂–c₄), deficiency and concentration of element Cu, Fe and S exist with large area, indicating that chalcopyrite, pyrite, quartz and calcite regional coexist. Fig. 3a₅–c₅

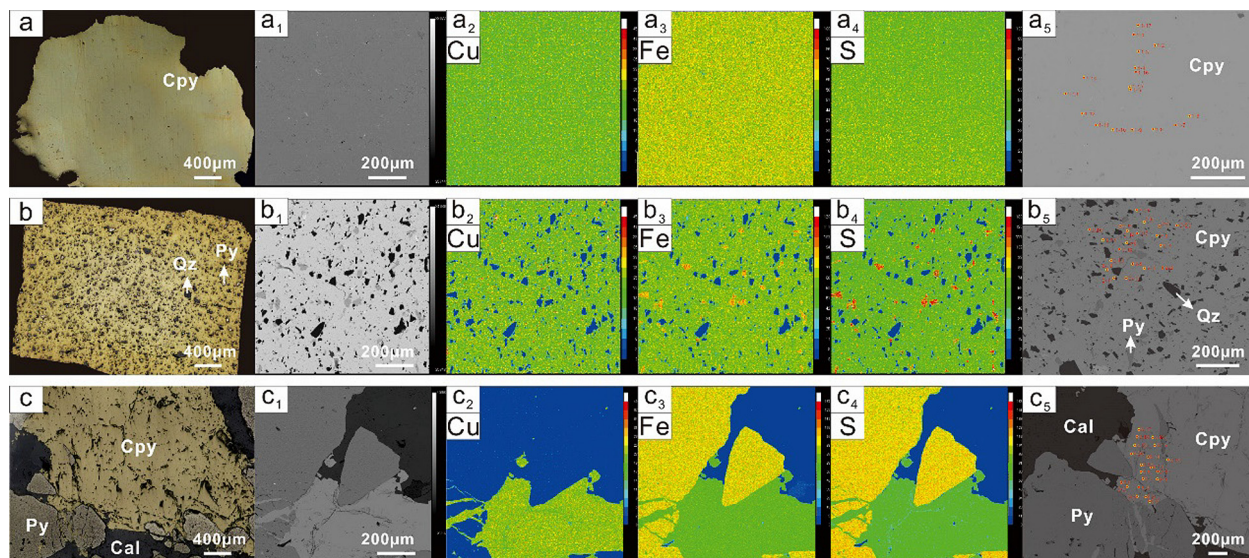


Fig. 3. Reflected light photographs of Sample HP Cpy (a), Sample HI Cpy (b) and Sample N Cpy (c), EPMA-BSE images of Sample HP Cpy (a₁ and a₅), Sample HI Cpy (b₁ and b₅) and Sample N Cpy (c₁ and c₅) (Circle and label denote EPMA spot position and number of the spot, respectively). Abbreviation: Cpy chalcopyrite; Qz quartz; Py pyrite; Cal calcite), and major EPMA element maps (Cu, Fe, S) of the three samples (Sample HP Cpy: a₂–a₄; Sample HI Cpy: b₂–b₄; Sample N Cpy: c₂–c₄).

Table 1

Average major elements (wt%) compositions of chalcopyrite in Sample HP Cpy, Sample HI Cpy and Sample N Cpy.

Sample name	Cu	Fe	S
Sample HP Cpy	34.230	29.396	34.348
Sample HI Cpy	35.316	29.824	34.750
Sample N Cpy	34.458	29.821	34.561

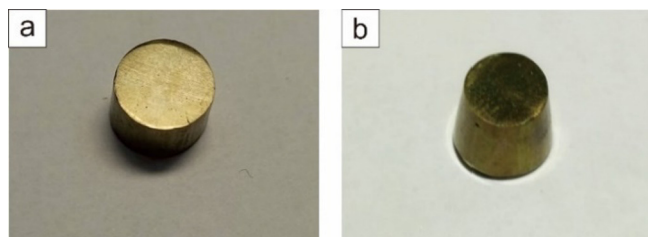


Fig. 4. Pictures of the pure, compact and malleable chalcopyrite blocks before grinding (a) and after grinding (b).

presents the EPMA-BSE images of the three samples with EPMA spot positions. Average major elements (wt%) compositions of chalcopyrite are given in Table 1. Calculated from the chalcopyrite quantitative data of Sample HP Cpy, Sample HI Cpy and Sample N Cpy, the formula of the three samples are $\text{Cu}_{1.00}\text{Fe}_{0.98}\text{S}_2$, $\text{Cu}_{1.02}\text{Fe}_{0.98}\text{S}_2$, $\text{Cu}_{1.00}\text{Fe}_{0.99}\text{S}_2$, respectively, which means that high pressure sintering won't change their element composition.

Fig. 4 shows the pictures of Sample HP Cpy before and after wheel grinding. Though the high pressure sintered product is cylindrical, it could be made into circular truncated cone by a grinding machine, which means our malleable sample could be made into fixed shape.

4. Conclusion

Choosing pure natural chalcopyrite particles as the starting material, the chalcopyrite block sintered around 0.6 GPa/270 °C in a cubic multi anvil press was pure, compact and malleable. Its

density was $4.0096 \pm 0.0174 \text{ g}\cdot\text{cm}^{-3}$, close to the unit cell density, showing the sample is compact. No impurity was detected by XRD, uniform distribution of chalcopyrite was observed by reflected light photographs and EPMA mapping analysis of Cu, Fe and S and the formula calculated from the quantitative EPMA was $\text{Cu}_{1.00}\text{Fe}_{0.98}\text{S}_2$, showing the sample is pure and stable. Finally, the columnar chalcopyrite block was made into circular truncated cone, showing the sample could be well machined. Therefore, the high pressure sintered product is a pure, compact and malleable chalcopyrite block.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.matlet.2017.04.053>.

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