

Changes in Bornite (Cu_5FeS_4) after Heating in Air: Mössbauer Effect Study

M. KĄDZIOLKA-GAWEL^{a,*} AND Z. ADAMCZYK^b

^aInstitute of Physics, University of Silesia in Katowice, 75 Pułku Piechoty 1a, 41-500 Chorzów, Poland

^bInstitute of Applied Geology, Silesian University of Technology, Akademicka 2, 44-100 Gliwice, Poland

The phase transitions and structural behaviour in natural bornite sample were investigated after heat treatment in air in a temperature range of (180 ÷ 500) °C using high-resolution Faraday, X-ray diffraction and ⁵⁷Fe Mössbauer spectroscopy studies. X-ray diffraction and the Mössbauer spectroscopy results show that polymorph phases can exist only at high temperatures, and at a temperature of 220 °C a process of decomposition of bornite structure starts. Hematite is a main Fe-bearing phase and Cu is located mainly in copper oxides present in the sample after annealing at 500 °C.

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1. Introduction

Bornite (Cu_5FeS_4), also known as peacock ore, is a widespread natural mineral that is composed of non-toxic and earth-abundant elements. Natural bornite (L-bornite) crystallizes in the orthorhombic structure with space group *Pbca*. Two other cubic polymorphs (space group *Fm3m*) of this mineral are known: a high temperature form (H-bornite), above 262 °C, and an intermediate temperature form (I-bornite) observed in the 200 °C to 262 °C range [1–4]. Bornite is an interesting compound because it is one of the most important ore minerals for copper [5, 6]. It has special semiconducting and magnetic properties used in several high-tech materials, e.g. diluted magnetic semiconductors [3, 4, 7]. It shows great potential as a new economical and eco-friendly thermoelectric material.

A natural polycrystalline bornite from the Polkowice Mine, Poland, has been studied using powder X-ray diffraction (XRD), high-resolution Faraday (XRF) and ⁵⁷Fe Mössbauer spectroscopy. This paper investigates the structural changes in bornite after annealing at high temperatures. The Mössbauer spectroscopy was used to study the Fe-bearing phase transformation during the annealing process. X-ray powder diffraction was used to determine the changes in lattice parameters of low bornite phase and to identify phases which are created during the decomposition of bornite after annealing at high temperatures. The characterisation of phase transitions and the thermodynamic behaviour of bornite is of potential application in the modelling of ore deposit formation, because most important bornite-bearing mesothermal deposits are formed at temperatures above that of the low-intermediate transition.

2. Experimental procedure

The natural sample of bornite was chosen for detailed analyses. The bornite sample was taken from the Permian copper-silver deposit from the Fore-Sudetic Monocline and was collected in a Lubin mine located about 75 km NW of Wrocław in SW Poland. In the field of the Fore-Sudetic Monocline there occur mainly mineralized sulfides of sandstone, black shale and dolomite. The mineralization is zoned both laterally and vertically. Two types of mineralization dominate: Cu-Fe-S (bornite, chalcopyrite, pyrite) and Cu-S (chalcocite, djurleite, digenite, covellite). The bornite sample was collected from a monomineral vein with a thickness of 2 cm of sulfide mineralization, which was found in the ore of black shale.

Sample of bornite was pulverized in agate mortar and heated for 3 h in an electric furnace on air atmosphere under static conditions to several different temperatures: 180, 200, 220, 300, 350, 400, and 500 °C. After each heating treatment, the Mössbauer and XRD measurements at room temperature were taken.

The chemical composition of the bornite samples was determined using X-ray fluorescence ZSX Primus II Rigaku spectrometer. The spectrometer, equipped with the 4 kW, 60 kV Rh anode and wavelength dispersion detection system, allowed for the analysis of the elements from Be to U. No external standards were necessary. Only the internal standards coupled with the fundamental parameters method (theoretical relationship between the measured X-ray intensities and the concentrations of elements in the sample) were implemented.

To confirm bornite structure in the investigated sample and identify other minerals in the samples after the heating procedure, we used XRD studies. The XRD studies were conducted at room temperature using a Siemens D5000 X-ray diffractometer and Cu K_α . Rietveld refinement was performed in a licensed Xpert High Score Plus with PDF-4 crystallography database.

*corresponding author; e-mail:

mariola.kadziolka-gawel@us.edu.pl

^{57}Fe Mössbauer transmission spectra were recorded at room temperature by the use of a POLON type spectrometer and a linear arrangement of source $^{57}\text{Co}:\text{Rh}$ (~ 10 mCi), a multichannel analyser, an absorber and a detector. A gas proportional counter LND-45431 was used as a gamma-ray detector. The 2 keV escape peak and 14.4 keV gamma ray pulses were selected with a multichannel analyser. The spectrometer was calibrated at room temperature with $\alpha\text{-Fe}$ foil. The numerical analysis of the Mössbauer spectra was performed with the use of the WMOSS program (Ion Prisecaru, WMOSS4 Mössbauer Spectral Analysis Software, 2009–2016). The mineralogical analysis of the spectra was based on the Mössbauer Handbook Mineral Data [8].

3. Results and discussion

The chemical compositions obtained of the investigated bornite sample by XRF method are shown in Table I. Except main elements, like Cu, Fe, S, additional elements are also observed. On the basis of the values of element concentration listed in Table I, we can expect that there are a lot of inclusion defects in the investigated bornite structure or additional phases can be present in the investigated sample.

Selected diffractograms of the initial and annealed sample of bornite are present in Fig. 1. XRD pattern for the initial bornite sample shows diffraction lines that are associated with the bornite structure. On these diffractograms additional lines which come from quartz (SiO_2) and chalcopyrite (CuFeS_2) structure were also observed. These minerals often occur in copper ore [9] and the presence of quartz structure explains the existence of a big amount of Si in the investigated sample (Table I).

TABLE I

The chemical composition of the investigated bornite sample

Element	C	O	Mg	Al	Si	S
[wt.%]	5.03	12.18	1.18	2.29	4.64	14.51
Element	K	Ca	Fe	Cu	Ti	Ag
[wt.%]	0.68	3.02	9.18	46.98	0.06	0.11

TABLE II

The lattice parameters obtained by the Rietveld refinements of the initial and annealed bornite

Annealing temperature [°C]	Lattice constant		
	a [Å]	b [Å]	c [Å]
initial	10.946(8)	21.847(1)	10.963(2)
180	10.957(6)	21.876(1)	10.956(6)
200	10.950(1)	21.903(4)	10.951(2)
220	10.957(2)	21.871(1)	10.953(2)
300	10.958(3)	21.855(3)	10.970(3)
350	10.960(1)	21.895(8)	10.961(1)

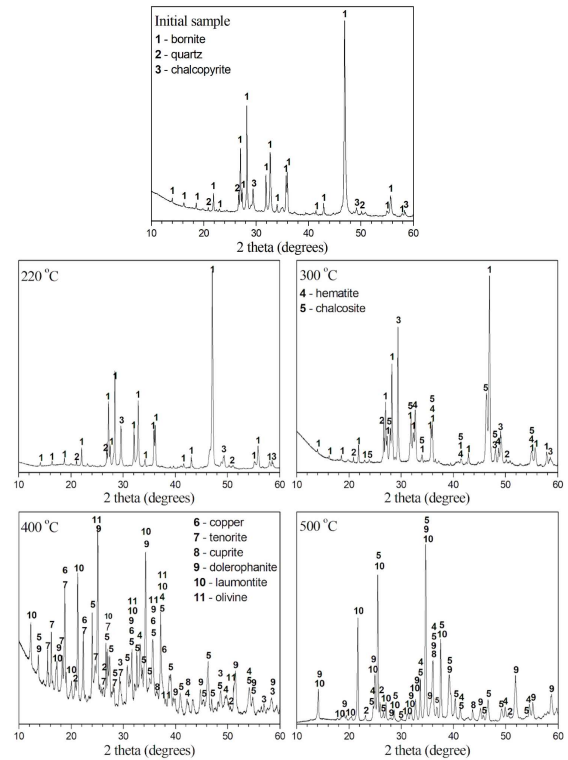


Fig. 1. XRD patterns of the initial and annealed sample of the investigated bornite.

Orthorhombic lattice parameters (space group $Pbca$) determined for bornite in the initial sample and the sample annealed up to a temperature of 350 °C are listed in Table II. The obtained lattice parameters are close to those presented in the literature [4, 10], small difference of the obtained parameters can be connected with some inclusions in bornite structure. After annealing of the sample up to a temperature of 220 °C on XRD diffractograms no additional lines connected with superstructure of bornite were observed. This means that polymorph phases exist only at high temperatures, not even a remainder, of such forms after heating at the particular temperatures was observed. Simultaneously, increase of intensity lines for chalcopyrite was observed. These results indicated that at 220 °C decomposition process of bornite started. Incorporation of Fe and Cu atoms from bornite structure causes visible changes of lattice parameters. On the diffractograms of the sample heated at 300 °C additional diffraction lines connected with hematite (Fe_2O_3) and chalcocite (Cu_2S) appear and intensity lines of chalcopyrite increase significantly. The decomposition process of bornite increases very fast with annealing temperature, after heating at 400 °C the lines connected with structure of Cu_5FeS_4 are not visible. In this diffractogram a lot of diffraction lines are present, these lines are generally related with Cu, S, and Fe oxides (tenorite CuO , cuprite Cu_2O , dolerophanite $\text{Cu}_2\text{O}(\text{SO}_4)$), pure copper, laumontite $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ and olivine $(\text{Mg,Fe})_2\text{SiO}_4$. Heating at a temperature of 500 °C causes mainly ordering the previously created phases.

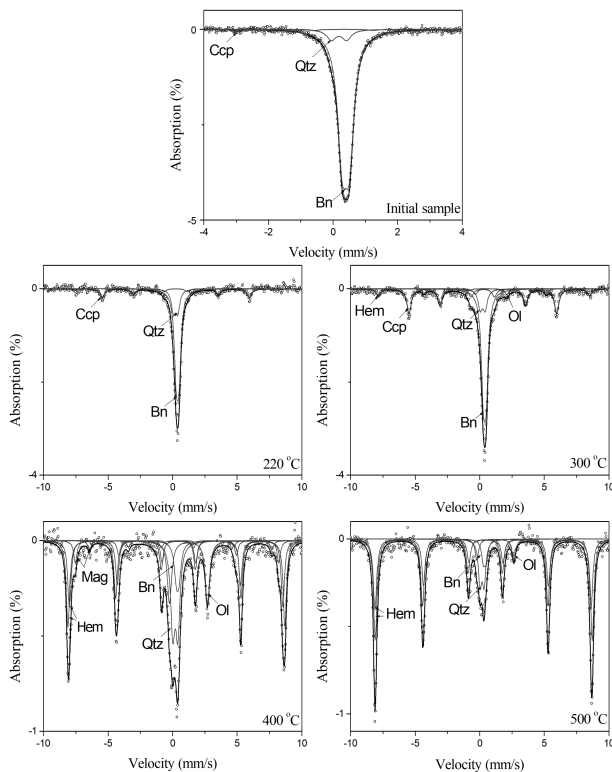


Fig. 2. Room temperature Mössbauer spectra and Mössbauer phases analysis of investigated bornite; Bn — bornite, CCp — chalcopyrite, Qtz — Fe^{3+} in quartz, Ol — olivine, Hem — hematite, Mag — magnetite.

The room temperature Mössbauer spectra of the initial and selected annealed bornite sample are presented in Fig. 2, while a relative area of fitted subspectra obtained after heating at high temperatures are presented in Fig. 3. The Mössbauer spectrum of non-heated bornite contains three components. The main component, which is a quadrupole split doublet with an isomer shift $I_s = 0.395$ mm/s and small quadrupole splitting $Q_s = 0.217$ mm/s, suggests that most probably Fe occupies only one crystallographic equivalent position with minor distortion in bornite structure. The values of I_s and Q_s are almost the same as observed in former Mössbauer studies of bornite [4, 11]. In that research one room temperature Mössbauer study of natural bornites from different localities show Q_s values in the range of 0.20–0.23 mm/s and I_s values in the range of 0.37–0.39 mm/s with respect to α -iron at room temperature. The current work shows almost the same Mössbauer parameters and this means that our sample is well-suited for high-temperature studies. After annealing process no significant changes of the hyperfine parameters of this doublet were observed, each time they remained in the ranges presented above, only contributions of this doublet changed much with the increase in temperature. Except the main doublet on the Mössbauer spectrum there is another one with $I_s = 0.183$ mm/s and $Q_s = 0.475$ mm/s visible, which is connected with Fe^{3+} in quartz structure [13]. A sextet with hyperfine magnetic field $B = 35.8$ T,

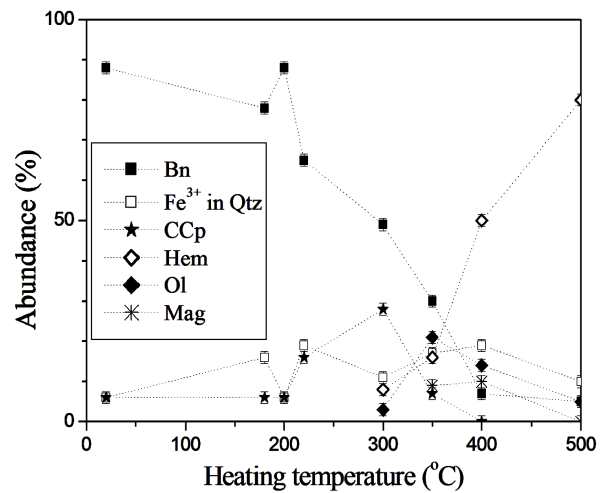


Fig. 3. Relative area of fitted Mössbauer subspectra obtained after heating at high temperatures for the investigated bornite sample.

$I_s = 0.355$ mm/s is related to the presence of chalcopyrite in the investigated sample. The observed components on the Mössbauer spectrum of the initial sample confirm the results of XRD measurements.

Heating the bornite sample at temperatures of 180 °C and 200 °C did not lead to any significant changes of both Mössbauer spectra and hyperfine parameters of the components present there. After heating at 220 °C the abundance of bornite doublets decreased and at the same time the abundance of chalcopyrite sextets increased. This effect is more noticeable after heating at 350 °C, when additional two components also appear, one of which is connected with non-magnetic Fe^{2+} and the other is a sextet connected with hematite ($B = 50.9$ T). With the increase in heating temperature the abundance of bornite doublets decreased, above 350 °C only a few percent contribution of this component is observed (Fig. 3). Also chalcopyrite is present on the Mössbauer spectrum only up to 350 °C. Heating temperature of 350 °C we can treat as the temperature at which the complete decomposition of bornite and chalcopyrite takes place. Heating at this temperature leads to incorporation of Fe^{2+} ions into olivine structure ($I_s = 1.21$ mm/s, $Q_s = 2.95$ mm/s) and the spinel structure of MgFe_2O_4 ($B = 44.3$ T, 48.5 T). Also, heating in air atmosphere causes oxidation of Fe^{2+} to Fe^{3+} ions and an increase in contribution of iron oxide like hematite. Hematite ($B = 51.9$ T, 52.3 T) contains more than 80% of all iron-bearing phases in the investigated samples of bornite after being heated at 500 °C.

4. Conclusions

The techniques applied have proven to be useful in the investigation to the phase transitions and structural behaviour in the natural bornite sample. XRD and ^{57}Fe Mössbauer spectroscopy results show that polymorphic forms related to superstructuring, with structural transitions at 180 and 265 °C, can exist at high temperatures.

There is no evidence at room temperature, not even a remainder, of such forms after heating at the particular temperatures. The Mössbauer spectroscopy results show that at a temperature of 220 °C the process of decomposition of bornite structure starts, which is clearly visible on XRD diffractograms obtained after heating at 300 °C. Up to heating in a temperature of 400 °C in the investigated sample there was domination of processes of incorporation of Cu and Fe ions from bornite and chalcopyrite phases and creation of, mainly, Cu and Fe oxides. XRD measurements indicate that sulphur dissolves in bornite and chalcopyrite is released as a soluble species SO_4^{2-} and builds mainly $\text{Cu}_2\text{O}(\text{SO}_4)$.

References

- [1] A. Putnis, J. Grace, *Contrib. Mineral. Petrol.* **55**, 311 (1976).
- [2] B. Grguric, A. Putnis, R. Harrison, *Am. Mineral.* **83**, 123 (1998).
- [3] M. Borgheresi, F. Di Benedetto, A. Caneschi, M. Romanelli, *Period Mineral.* **80**, 113 (2011).
- [4] J. Przewoźnik, J. Żukrowski, Ł. Gondek, K. Gąska, A. Lemański, C. Kapusta, A. Piestrzyński, *Nukleonika* **58**, 1 (2013).
- [5] D. Bourgarit, P. Rostan, E. Burger, L. Carozza, B. Mille, G. Artioli, *His. Met.* **42**, 11 (2008).
- [6] N. Pradhan, K. Nathasarma, K.S. Rao, L. Sukla, B. Mishra, *Miner. Eng.* **21**, 355 (2008).
- [7] P. Qiu, T. Zhang, Y. Qiu, X. Shi, L. Chen, *Energy Environm. Sci.* **7**, 4000 (2014).
- [8] *Mössbauer Mineral Handbook*, Eds. J.G. Stevens, A.M. Khasanov, J.W.B. Miller, H. Pollak, Zhe Li, Mössbauer Effect Data Center, Asheville (USA) 2005.
- [9] Y. Li, G. Qian, J. Li, A. Gerson, *Metals* **5**, 1566 (2015).
- [10] Y. Kanazawa, K. Koto, N. Morimoto, *Can. Mineral.* **16**, 397 (1978).
- [11] M.F. Collins, G. Longworth, M.G. Townsend, *Can. J. Phys.* **59**, 535 (1981).
- [12] R. Gainov, F. Vagizov, V. Golovanevskiy, V. Ksenofontov, G. Klingelhofer, V. Klekovkina, T.G. Shumilova, I. Penkov, *Hyperfine Interact.* **226**, 51 (2014).
- [13] M. Kądziołka-Gaweł, D. Smolka-Danielowska, *Nukleonika* **62**, 101 (2017).