The Rietveld Structure Refinement of the Marcasite Crystals from Herja Ore Deposit Using X-ray Powder Diffraction Data

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Abstract

The crystal structure of marcasite sampled from Herja ore deposit (Maramures region, Romania) has been refined using X-Ray powder diffraction data and the Rietveld method. Marcasite is the metastable dimorph of FeS2 crystallized in the orthorhombic system, and rapidly inverts to pyrite when is heated above 500°C. Genetically, marcasite appears under low-temperature conditions, both in sedimentary rocks and in hydrothermal veins. The Rietveld refinements were carried out using the computer program Topas 4.1 (Bruker-AXS). Pseudo-Voigt (pV) profile function was used for the fit of the peaks. Rietveld refinement using X-Ray powder diffraction data of marcasite crystals in space group Pnnm (No.58), a=4.4339Å, b=5.3887Å, c=3.3620Å (2-sigma=0.0037), Z=2, confirm the basic marcasite structure.

Key words: *marcasite crystal structure, X-ray powder diffraction, Rietveld refinement, Herja ore deposit, Neogene volcanites, Gutai Mountains*

Introduction

The crystal structure of the marcasite sample from Herja ore deposit (Maramures district, northern Romania) was refined using X-Ray powder diffraction data and the Rietveld method. The studied sample (figure 1) was collected by George Barzoi during field trip to the Herja mining exploitation in the summer practice held in Baia Mare region in July 2012.

From geological point of view, the Herja ore deposit belongs to the Neogene volcanites zone of Eastern Carpathians, locally being situated in the Gutai Mountains. Herja ore deposits it's a largest hydrothermal vein systems of Pannonian age hosted into Sarmatian-Pannonian volcanic rocks and Neogene and Paleogene rocks in the metallogenic district surrounding the Baia Mare city. [1],[2]. The mining exploitation is close to the small village of Chiuzbaia, 7 km east-north-east of Baia Mare city. The polymetallic mineralized veins contains a wide variety of metallic minerals: sphalerite, galena, pyrite, pyrrhotite, stibnite, chalcopyrite, arsenopyrite, jamesonite, tetrahedrite, semseyite, and non-metallic minerals: quartz, siderite, ankerite, calcite, gypsum, baryte and vivianite. The hydrothermal veins show different types of structures: massive, rubanate, brecciated and concentric [3].

Marcasite is the metastable dimorph of FeS_2, and rapidly inverts to pyrite when is heated above 500°C. Minerals with the marcasite structure type have the formula AX_2, where A = Fe, Co, Ni, Ru, Os, and X = S, Se, Te, As and Sb. Marcasite is typically formed under low-temperature highly acidic conditions, both in sedimentary environments (shales, limestones, and coals) and in hydrothermal veins formed by ascending solutions. The marcasite crystals themselves are of

diamond shaped, tabular habit, and flattened parallel to (001). The diamond shapes are outlined by (110). The crystals are typically tabular on (010), also pyramidal, prismatic, and, rarely, capillary; curved faces common. Also, stalactitic, reniform, fine-granular massive; cockscomb and spearhead shapes due to twinning on (101). [4],[5],[6],[7],[8].

Fig.1. Polymetallic sample with iron sulphides (pyrite and marcasite) from Herja ore deposit

The marcasite has a 6-3 coordination structure. Marcasite is composed of Fe and S in the atomic state, both types of the atoms having almost identical radii. Marcasite, like pyrite, has Fe atoms in octahedral coordination with S, and S atoms tetrahedrally coordinated to three Fe atoms and one S atom. The difference between the marcasite and pyrite structures is found in the linking of the Fe-centered octahedra. In the marcasite structure, Fe-centered octahedra share two edges in planes normal to (001); in pyrite the octahedra are linked at corners. The pyrite structure can be obtained from that of marcasite by rotation of half of the S groups through 90º. [4],[7],[8]

The marcasite crystal structure aroused a great interest since the beginning of the last century. X-ray diffraction studies of the marcasite structure were made by several authors: [4],[9],[10]. The first attempts to investigate the crystal structure of marcasite have been made by Huggins [9] and de Jong [10]. Huggins [9] presented a marcasite structure based on a rearrangement of major units of the pyrite structure. De Jong [10] has attempted experimentally to analyze a crystal of marcasite from Bohemia, using the X-ray powder method with Fe-Kα radiation. The solving of the crystal structure of marcasite belongs to Buerger [4], in his paper being founded the details of a complete X-ray determination (Mo-Kα radiation) of the marcasite crystal structure in the space group *Pnnm*.

Experimental Data

The sample was ground in an agate mortar with pestle through fine grinding. X-ray powder diffraction data were measured at 24ºC using an automated Bruker D8 Advance θ-θ diffractometer, with Cu-Kα radiation (λ = 1,54Å; 40kV; 40mA), a LynxEye solid-state Si detector and Bragg-Brentano geometry. Kβ radiation was eliminated by a Ni filter. Primary and secondary Soller slits were 2.5º. A fixed aperture and divergence slit of 0.6mm, a 0.6mm antidivergence slit and 0.1mm width detector slit were used. X-ray diffraction data were obtained using 0.1º 2θ steps from 20º to 60º 2θ counting for 5 s per step. The powder was placed into a cavity mount in an attempt to minimize preferred orientation.

Results and Discussions

The Rietveld refinement was carried out using Diffracplus TOPAS 4.1 (Bruker-AXS) computer program. Pseudo-Voigt (pV) profile function was used for the fit of the peaks; the result of measurement shows that the peaks shape is Lorentzian. Rietveld refinement using X-ray powder diffraction data of marcasite sample in the space group *Pnnm* (No.58) [11]: *a*=4.4339Å, *b*=5.3887Å, *c*=3.3620Å (2-sigma=0.0037), Z=2, Rwp=5.28, Rexp=5.00, Rp=4.06, confirm the basic marcasite structure. The goodness-of-fit GOF (Rwp/Rexp) was 1.06, and Durbin-Watson *d*-statistic (DW) was 2.20, both indicating a good refinement [12],[13],[14].

Qualitative analysis was carried out using Diffracplus EVA computer program (Bruker-AXS) and is presented in figure 2. Figure 3 shows a graphical representation of final Rietveld refinement (calculated data), the observed data and the difference between them.
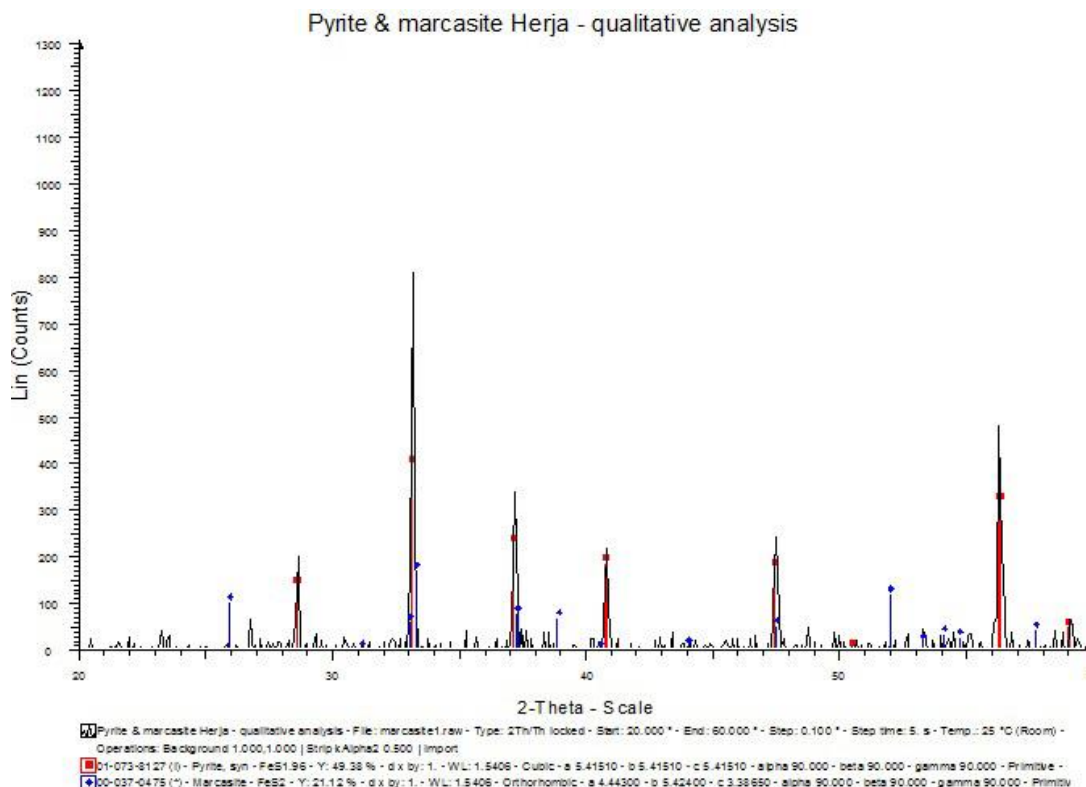

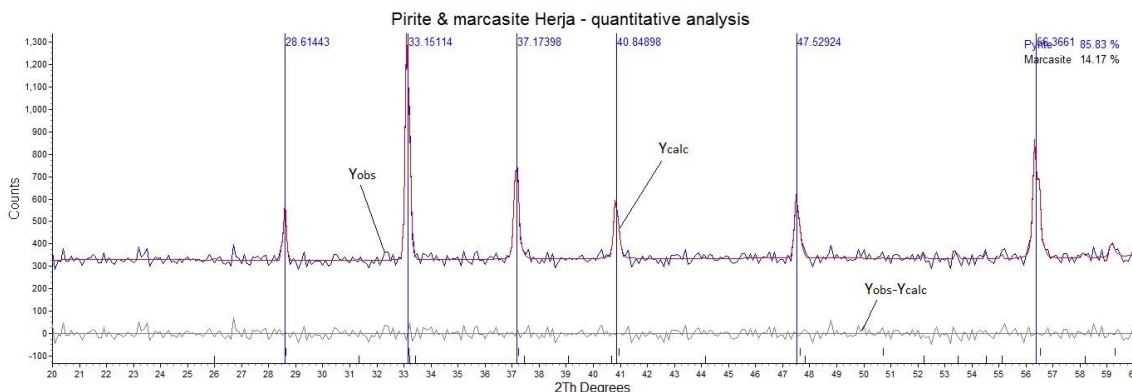**Fig.2**. Qualitative analysis of the marcasite sample from Herja ore deposit

Fig.3. Final Rietveld refinement showing the observed (Yobs) and calculated (Ycalc) X-ray diffraction patterns and difference pattern between both (Yobs-Ycalc).

The parameters which represent the quality of the Rietveld refinement are found in the Table 1. The crystal structure in the figure 4 shows the position of the atoms and the bonds between atoms in refined structure of marcasite. The Fe–S bond lengths vary between 2.15 and 2.26Å; and S–S bond lengths between 2.34 and 3.07Å. The atomic positional parameters for the marcasite structure resulted from the Rietveld refinements are presented in the Table 2.

Table 1. Rietveld refinement quality parameters

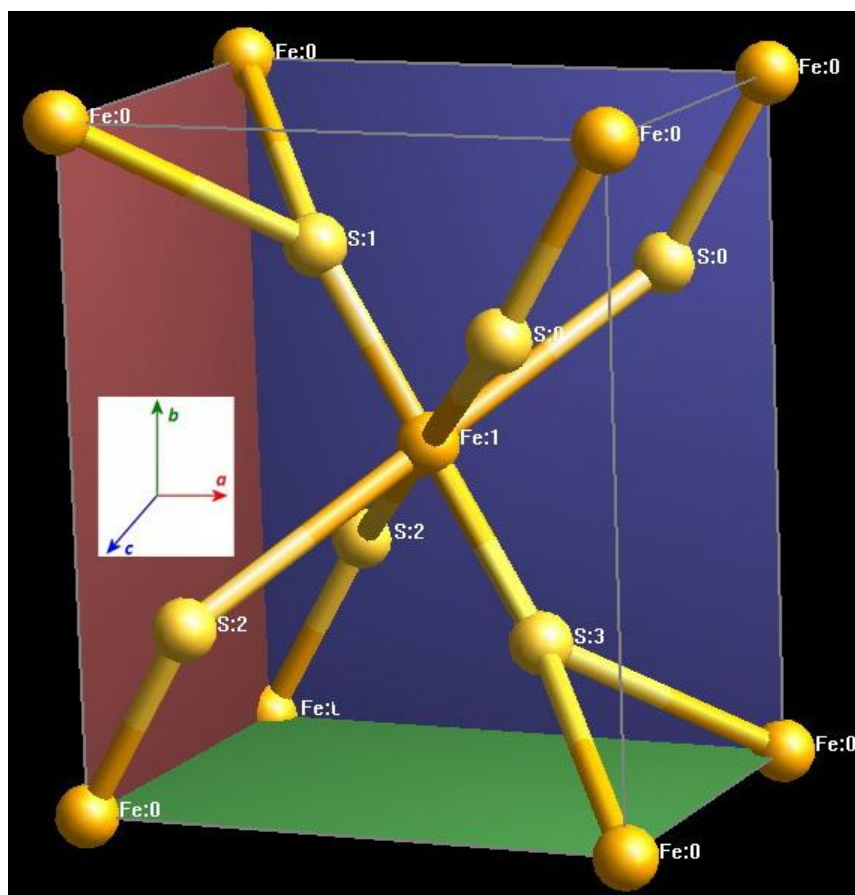| Parameter	Value	2-sigma
a (Å)	4.4339	0.0037
b (Å)	5.3887	0.0038
c (Å)	3.3620	0.0037
Cry size L (nm)	999.95	0.0135
Cry density (g/cm^3)	4.960	0.0080
Cell Volume (Å^3)	80.3297	0.1257
R Bragg	3.6890	-
Rexp (%)	5.00	-
Rwp (%)	5.28	-
Rp (%)	4.06	-
GOF	1.06	-
DW	2.20	-

Fig.4. The position and the bonds between the atoms in the refined structure of marcasite.

Table 2. Atomic positional parameters for the marcasite structure resulted from Rietveld refinement

Atom	Np	x	y	z	Occ	Beq	2-sigma
Fe	2	0.00000	0.00000	0.00000	1	1.794	0.0179
S	4	0.20000	0.28225	0.00000	1	0.9912	0.0836

Figure 5 shows a 3D view of marcasite structure with Fe atoms in octahedral coordination with S, and S atoms tetrahedrally coordinated to three Fe atoms and one S atom, resulted from Rietveld refinement.
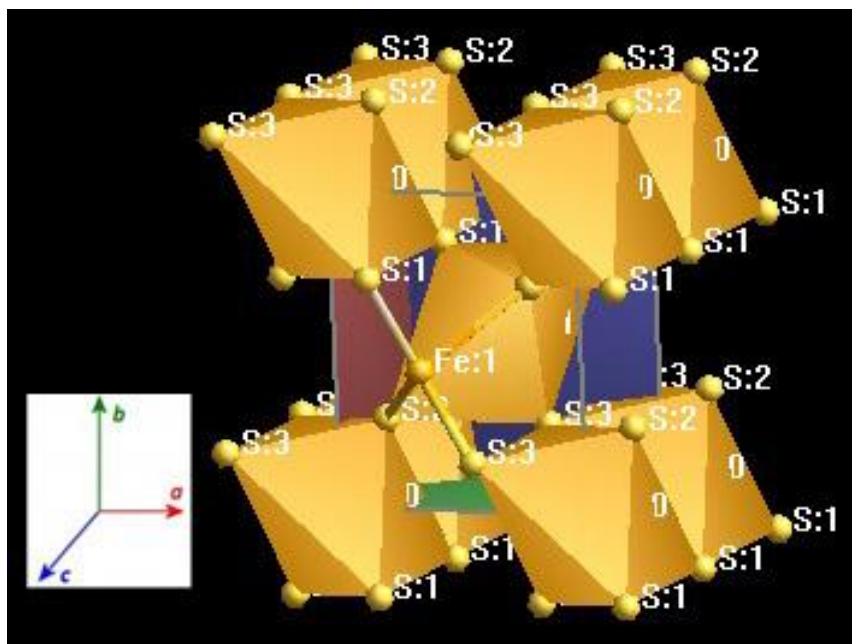
Fig.5. 3D view of marcasite structure resulted from Rietveld refinement

Conclusions

The crystal structure of marcasite from Herja ore deposit (Gutai Mountains, Romania) was refined by means of the Rietveld method using X-ray powder diffraction data. The results led to the conclusion that the sample belongs to space group *Pnnm* (No.58) and confirmed the basic marcasite structure. The figures of merit [13],[14] were: goodness-of-fit GOF=1.06, χ^2=1.123 and Durbin-Watson *d*-statistic=2.20, and indicate a good refinement.

The paper provides a new set of the unit cell parameters and fractional coordinates that define the marcasite structure. Note that it is the first time when a Rietveld refinement is made on marcasite crystals from Herja ore deposit.

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Rafinarea Rietveld a structurii cristaline a marcasitei din zacamantul Herja utilizând date de difracţia razelor X pe pulberi

Rezumat

Structura cristalină a cristalelor de marcasita prelevate din zacamantul Herja (regiunea Maramures, Romania) a fost rafinată folosind difracţia de raze X pe pulberi şi metoda Rietveld. Marcasita este o modificatie polimorfa metastabila a FeS2, cristalizata in sistemul rombic, si care trece rapid in pirita la temperaturi mai mari de 500ºC. Genetic, marcasita apare in conditii de temperatura joasa, atat in roci sedimentare cat si in filoane hidrotermale. Rafinarea Rietveld a fost realizată cu ajutorul programului de calculator TOPAS 4.1 (Bruker-AXS). Pentru potrivirea peakurilor a fost folosită funcţia pseudo-Voigt (pV). Rafinarea Rietveld utilizând date de difracţie de raze X pe pulberi a eşantionului de marcasita în grupul spaţial Pnnm (No.58), a=4.4339Å, b=5.3887Å, c=3.3620Å (2-sigma=0.0037), Z=2, a confirmat structura de bază a marcasitei.