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CRYSTALLOGRAPHICALY-CHEMICAL CHARACTERISTICS OF SPHALERITES FROM THE POLYMETALLIC Pb-Zn ORE DEPOSIT KIZEVAK (Raska, Serbia)

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ABSTRACT. With the X-ray, chemical and spectrochemical methods there were investigated monomineral concentrations of sphalerites from the polymetallic Pb-Zn ore deposit Kizevak (Raska, Serbia).
These sphalerites are from the different horizons of 670, 690 and 710m. Their colour vary from yellow, brownish-yellow, brown to brownish-red.
Obtained crystallographic parameters are within following ranges:
a_0 = 5.4184(6) – 5.4195(6)Å and V_0 = 159.08(5) – 159.18(6)Å^3.
Obtained chemical contents are within following ranges:
FeS = 1.29 – 12.28 mol.%; MnS = 0.08 – 0.21 mol.%; CdS = 0.23 – 0.32 mol.%; CuS = 0.01 – 0.30 mol.%; In = 0.0006 – 0.0600 % and Ga = 0.0004 – 0.0090 %.
It was confirmed that crystallographic parameters increase with the FeS content and decrease with the CuS content.

КРИСТАЛОГРАФСКИ-ХИМИЧНИ ХАРАКТЕРИСТИКИ НА СФАЛЕРИТИ ОТ ПОЛИМЕТАЛНО Pb-Zn РУДНО НАХОДИЩЕ КИШЕВАЦ (Раска, Сърбия)

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РЕЗЮМЕ. Мономинерални концентрации от сфалерит от полиметалното Pb-Zn находище край Кишевац (Раска, Сърбия) са изследвани с помощта на рентгенови, химични и спектрохимични методи.
Тези сфалерити са взети от различни хоризонти от 670, 690 и 710m. Цветът им варира от жълт, кафяво-жълт, кафяв до кафеникаво-червен.
Получените кристалографски параметри варират в следните граници:
a_0 = 5.4184(6) – 5.4195(6)Å и V_0 = 159.08(5) – 159.18(6)Å^3.
Полученото химично съдържание е в следните граници:
FeS = 1.29 – 12.28 mol.%; MnS = 0.08 – 0.21 mol.%; CdS = 0.23 – 0.32 mol.%; CuS = 0.01 – 0.30 mol.%; In = 0.0006 – 0.0600 % и Ga = 0.0004 – 0.0090 %.
Потвърждава се факта, че кристалографските параметри нарастват със съдържанието на FeS и намаляват със съдържанието на CuS.

Introduction

Interest for sphalerites begin to rise when Kullerud (1953) at basis of the experimental data established that solution of FeS in ZnS increase with the temperature, and that with the FeS content there is increase of the unit cell dimensions a_0.

However, later investigations of the synthetic and natural sphalerites arised to the considerable large disagreements, and even to the some contradictory results.

These disagreements manifested as in the view of the mutually relations of the crystallographic datas and chemical compositions, and also in the view of the sphalerite formation, then if sphalerite can or can not be useful as geothermometer, as geobarometer, etc.

Since up to date there are further polemics about the most of these questions, we shall in this investigations retain only at the relations between the crystallographical parameters and chemical compositions and compare the literature datas with the datas which are obtained for sphalerites from Kizevak.

According to that, we shall mention some of the most important papers which considerate this problematic.

Skinner *et al.* (1959) modified the datas and diagrams of Kullerud (1953) and obtained the bigger unit cell dimensions a_0 for the same FeS contents.

At contrast of Skinner *et al.* (1959) which established the linear variation of the unit cell dimensions a_0 by the FeS contents, Barton and Toulmin (1966) established nonlinear curve variation and even bigger values for the a_0.

Skinner (1961) investigated natural and synthetic sphalerites and established the increase of the unit cell dimensions a_0 not only with the FeS, but also with the MnS and CdS contents. These variations are linear.

On the other hand, some other authors (Scott, 1973) cited datas that the sphalerite phase relations are not changed even at the presence of several wt.% CdS.

Toulmin *et al.* (1991) conclude that the presence of geologically normal concentrations of such components as CdS, MnS, ZnSe, CoS and like does do not affect to the partial molar volume of FeS in sphalerite.

From other elements that can enter into the sphalerite structure and to influence to the variation of the crystallographic parameters, it seems that the most significant is the Cu content.

Investigations which were performed by Toulmin (1960) indicate that substitution of Cu in Fe-bearing sphalerites reduces the unit cell dimensions.

Later Wiggins and Craig (1980) confirmed this observation and represented an empirical equation describing the variation

of a_0 axis with composition of sphalerite in the system ZnS-FeS-CuS.

That CuS has much significant effect to the molar volume of the FeS in sphalerite was also confirmed by Toulmin *et al.* (1991).

In this paper there were represented the results of the investigations which were obtained with the X-ray, chemical and spectrochemical methods at sphalerites from different horizons and with different colors from the Kizevak ore deposit.

There were investigated the crystallographical parameters, chemical compositions and their mutually relations, especially the influence of the FeS and CuS contents to the unit cell dimensions, regardless that some other elements (Mn, Cd, In and Ga) are also determined.

Material preparation and applied methods

Sphalerites were first hand picked under the microscope.

In order to get monomineral concentrations, these hand picked sphalerites were purified with the electromagnetic separation and with the heavy liquids.

Control of all of the fractions was carried out under the microscope, nevertheless there were eliminated all the impurities.

The X-ray investigations of the samples were performed by the X-ray diffractometer for powder PHILIPS, PW 1009 and PW 1051.

There was used cobalt radiation (U=38 kV and I=8 mA) with the wave-lengths $\lambda CoK\alpha_1$=1.78897Å and $\lambda CoK\alpha_2$=1.79284Å, which was filtered by iron β-filter.

Goniometer speed was V_g=1/8° 2θ/min, and running paper speed was 400 mm/h.

It was used GM counter with mean plateau at 1550V. Sensitivity was 640 imp/s full scale, and RC constant was 4 s.

Samples were powdered, and preparations were made in the standard aluminium frame with dimensions 20 x 10 x 1.5 mm, and then they were recorded in the 2θ angle range from 30° to 120°.

There were accomplished measurements of the Bragg angles (2θ), and at basis of that values there were calculated interplanar spacings (d).

Precision of the diffractometer was controlled before and after the experiments with the metallic Si standard.

Calculation of the unit cell dimensions was accomplished with the programme LSUCRI (Garvey, 1987) for the personal computer.

Contents of the Fe, Mn and Cd were determined with the atomic absorption method with PERKIN-ELMER, model 306.

Contents of the Cu, In and Ga were determined with the spectrograph of high dispersion LITROU-HILGER, E-478, with the quartz and glass prism.

The measured spectral range was from 2700 to 5000Å.

Fusion of a mixture of spectrally pure carbon powder and sample, in a ratio of 1:1, was carried out in a DC arc with a current of 8 A.

The registration of the spectrum is carried out with a ten step rotating sector.

Germanium and palladium were used as the internal standards.

Control of the working graphs obtained at the basis of the synthetic standards, representing a basic intermediate acid rock was carried out with the international geochemical standards (USGS, ZGI).

Results and discussion

Horizon 670m

Powder diffraction patterns for the 15.611 brownish-yellow and 15.611 brownish-red sphalerite samples are represented at Table 1.

Table 1.

Powder diffraction patterns for the 15.611 brownish-yellow and 15.611 brownish-red sphalerite samples

JCPDS 05-0566	15.611 brownish-yellow		15.611 brownish-red	
h k l	d_{obs}	d_{calc}	d_{obs}	d_{calc}
1 1 1α_1	3.1335	3.1284	3.1369	3.1290
2 0 0α_1	2.7140	2.7093	2.7165	2.7098
2 0 0α_2	2.7155	2.7093	2.7155	2.7098
2 2 0α_1	1.9168	1.9158	1.9184	1.9161
2 2 0α_2	1.9174	1.9158	1.9186	1.9161
3 1 1α_1	1.6344	1.6338	1.6352	1.6340
3 1 1α_2	1.6355	1.6338	1.6348	1.6340
2 2 2α_1	1.5648	1.5642	1.5655	1.5645
2 2 2α_2	1.5652	1.5642	1.5656	1.5645
4 0 0α_1	1.3550	1.3547	1.3552	1.3549
4 0 0α_2	1.3552	1.3547	1.3553	1.3549
3 3 1α_1	1.2434	1.2431	1.2435	1.2433
3 3 1α_2	1.2433	1.2431	1.2435	1.2433
4 2 0α_1	1.2114	1.2116	1.2117	1.2118
4 2 0α_2	1.2115	1.2116	1.2116	1.2118
4 2 2α_1	1.1058	1.1061	1.1059	1.1063
4 2 2α_2	1.1060	1.1061	1.1060	1.1063
5 1 1α_1	1.0423	1.0428	1.0426	1.0430
5 1 1α_2	1.0425	1.0428	1.0426	1.0430

Chemical compositions (in %) for the 15.611 brownish-yellow and 15.611 brownish-red sphalerite samples are represented at Table 2.

Table 2.

Chemical compositions for the 15.611 brownish-yellow and 15.611 brownish-red sphalerite samples

Chemical composition	15.611 brownish-yellow	15.611 brownish-red
Fe	1.41	7.80
Mn	0.06	0.13
Cd	0.24	0.21
Cu	0.0300	0.0316
In	0.0018	0.0450
Ga	0.0008	0.0050
FeS	2.22	12.28
MnS	0.10	0.21
CdS	0.31	0.27
CuS	0.0451	0.0475

Horizon 690m

Powder diffraction patterns for the 15.623 yellow and 15.604 brown sphalerite samples are represented at Table 3.

Table 3.
Powder diffraction patterns for the 15.623 yellow and 15.604 brown sphalerite samples

JCPDS 05-0566	15.623 yellow		15.604 brown	
h k l	d_{obs}	d_{calc}	d_{obs}	d_{calc}
1 1 1α_1	3.1332	3.1284	3.1322	3.1286
2 0 0α_1	2.7124	2.7093	2.7128	2.7095
2 0 0α_2	2.7133	2.7093	2.7104	2.7095
2 2 0α_1	1.9168	1.9158	1.9156	1.9159
2 2 0α_2	1.9177	1.9158	1.9168	1.9159
3 1 1α_1	1.6342	1.6338	1.6341	1.6339
3 1 1α_2	1.6349	1.6338	1.6354	1.6339
2 2 2α_1	1.5646	1.5642	1.5644	1.5643
2 2 2α_2	1.5644	1.5642	1.5644	1.5643
4 0 0α_1	1.3548	1.3546	1.3550	1.3547
4 0 0α_2	1.3547	1.3546	1.3550	1.3547
3 3 1α_1	1.2429	1.2431	1.2428	1.2432
3 3 1α_2	1.2430	1.2431	1.2433	1.2432
4 2 0α_1	1.2113	1.2116	1.2113	1.2117
4 2 0α_2	1.2122	1.2116	1.2119	1.2117
4 2 2α_1	1.1058	1.1061	1.1058	1.1061
4 2 2α_2	1.1059	1.1061	1.1059	1.1061
5 1 1α_1	1.0426	1.0428	1.0427	1.0429
5 1 1α_2	1.0427	1.0428	1.0430	1.0429

Chemical compositions (in %) for the 15.623 yellow and 15.604 brown sphalerite samples are represented at Table 4.

Table 4.
Chemical compositions for the 15.623 yellow and 15.604 brown sphalerite samples

Chemical composition	15.623 yellow	15.604 brown
Fe	1.35	5.19
Mn	0.05	0.07
Cd	0.25	0.18
Cu	0.0170	0.2000
In	0.0006	0.0130
Ga	0.0032	0.0025
FeS	2.12	8.17
MnS	0.08	0.11
CdS	0.32	0.23
CuS	0.0256	0.3009

Horizon 710m

Powder diffraction patterns for the 15.635 yellow and 15.633 yellow sphalerite samples are represented at Table 5.

Table 5.
Powder diffraction patterns for the 15.635 yellow and 15.633 yellow sphalerite samples

JCPDS 05-0566	15.635 yellow		15.633 yellow	
h k l	d_{obs}	d_{calc}	d_{obs}	d_{calc}
1 1 1α_1	3.1352	3.1283	3.1356	3.1284
1 1 1α_2	3.1356	3.1283	/	/
2 0 0α_1	2.7140	2.7092	2.7140	2.7092
2 0 0α_2	2.7145	2.7092	2.7127	2.7092
2 2 0α_1	1.9166	1.9157	1.9167	1.9157
2 2 0α_2	1.9169	1.9157	1.9177	1.9157
3 1 1α_1	1.6345	1.6337	1.6347	1.6337
3 1 1α_2	1.6352	1.6337	1.6353	1.6337
2 2 2α_1	1.5650	1.5642	1.5646	1.5642
2 2 2α_2	1.5649	1.5642	1.5651	1.5642
4 0 0α_1	1.3545	1.3546	1.3547	1.3546
4 0 0α_2	1.3551	1.3546	1.3547	1.3546
3 3 1α_1	1.2431	1.2431	1.2430	1.2431
3 3 1α_2	1.2434	1.2431	1.2428	1.2431
4 2 0α_1	1.2112	1.2116	1.2115	1.2116
4 2 0α_2	1.2116	1.2116	1.2120	1.2116
4 2 2α_1	1.1059	1.1060	1.1057	1.1060
4 2 2α_2	1.1060	1.1060	1.1059	1.1060
5 1 1α_1	1.0423	1.0428	1.0425	1.0428
5 1 1α_2	1.0424	1.0428	1.0426	1.0428

Chemical compositions (in %) for the 15.635 yellow and 15.633 yellow sphalerite samples are represented at Table 6.

Table 6.
Chemical compositions for the 15.635 yellow and 15.633 yellow sphalerite samples

Chemical composition	15.635 yellow	15.633 yellow
Fe	0.82	1.06
Mn	0.05	0.05
Cd	0.22	0.21
Cu	0.0070	0.0316
In	0.0300	0.0100
Ga	0.0004	0.0005
FeS	1.29	1.67
MnS	0.08	0.08
CdS	0.28	0.27
CuS	0.0105	0.0475

Powder diffraction patterns for the 15.634 brown and 15.629 brown sphalerite samples are represented at Table 7.

Table 7.
Powder diffraction patterns for the 15.634 brown and 15.629 brown sphalerite samples

JCPDS 05-0566	15.634 brown		15.629 brown	
h k l	d_{obs}	d_{calc}	d_{obs}	d_{calc}
1 1 1α_1	3.1351	3.1285	3.1356	3.1287
1 1 1α_2	3.1354	3.1285	/	/
2 0 0α_1	2.7145	2.7093	2.7153	2.7095
2 0 0α_2	2.7121	2.7093	2.7136	2.7095
2 2 0α_1	1.9173	1.9158	1.9174	1.9159
2 2 0α_2	1.9168	1.9158	1.9174	1.9159
3 1 1α_1	1.6344	1.6338	1.6346	1.6339
3 1 1α_2	1.6351	1.6338	1.6348	1.6339
2 2 2α_1	1.5649	1.5642	1.5648	1.5643
2 2 2α_2	1.5654	1.5642	1.5656	1.5643
4 0 0α_1	1.3548	1.3547	1.3548	1.3548
4 0 0α_2	1.3545	1.3547	1.3542	1.3548
3 3 1α_1	1.2429	1.2431	1.2431	1.2432
3 3 1α_2	1.2429	1.2431	1.2434	1.2432

4 2 0α_1	1.2119	1.2117	1.2115	1.2117
4 2 0α_2	1.2118	1.2117	1.2114	1.2117
4 2 2α_1	1.1056	1.1061	1.1058	1.1062
4 2 2α_2	1.1056	1.1061	1.1064	1.1062
5 1 1α_1	1.0425	1.0428	1.0426	1.0429
5 1 1α_2	1.0430	1.0428	1.0429	1.0429

Chemical compositions (in %) for the 15.634 brown and 15.629 brown sphalerite samples are represented at Table 8.

Table 8.
Chemical compositions for the 15.634 brown and 15.629 brown sphalerite samples

Chemical composition	15.634 brown	15.629 brown
Fe	2.88	4.06
Mn	0.11	0.05
Cd	0.21	0.21
Cu	0.1200	0.0320
In	0.0060	0.0600
Ga	0.0008	0.0090
FeS	4.53	6.39
MnS	0.17	0.08
CdS	0.27	0.27
CuS	0.1805	0.0481

Relation between the calculated unit cell dimensions and the FeS and CuS contents

Unit cell dimensions were calculated in the space group F $\bar{4}$3m (Swanson and Fuyat, 1953) with the 19 and 20 reflections which are represented at Tables 1, 3, 5 and 7.

Axis a_0 are represented in Å, while the volumes V_0 are represented in Å^3.

For the comparison, together with the crystallographical parameters there are also represented values of the FeS and CuS contents (in %) from Tables 2, 4, 6 and 8.

These results are represented at Table 9.

Table 9.
Calculated unit cell dimensions and the FeS and CuS contents

	a_0	V_0	FeS	CuS
JCPDS 05-0566	5.406	157.99		
15.635 yellow	5.4184(6)	159.08(5)	1.29	0.01
15.633 yellow	5.4185(5)	159.09(4)	1.67	0.05
15.623 yellow	5.4186(4)	159.10(4)	2.12	0.03
15.611 brownish -yellow	5.4186(6)	159.10(5)	2.22	0.04
15.634 brown	5.4187(5)	159.10(5)	4.53	0.18
15.629 brown	5.4190(5)	159.14(5)	6.39	0.05
15.604 brown	5.4189(4)	159.13(3)	8.17	0.30
15.611 brownish -red	5.4195(6)	159.18(6)	12.28	0.05

From Tables 1-9 it can be seen that the d-values and calculated unit cell dimensions (a_0 and V_0) of sphalerites increase with the FeS contents.

Only at the 15.634 brown and 15.604 brown sphalerite samples it can be seen the irregularities of increasing of the crystallographic parameters regard to the composition, but it can be consider within the range of the standard error.

Although it is in the range of the standard error, this lower unit cell dimensions are most probably caused by the considerable bigger CuS contents (0.18 and 0.30 %) regard to the other investigated sphalerites.

Variation of the unit cell dimension a_0 by the FeS contents for the yellow and brown sphalerites from Kizevak is represented at Figure 1, together with the variation lines by Skinner *et al.* (1959) and Barton and Toulmin (1966).

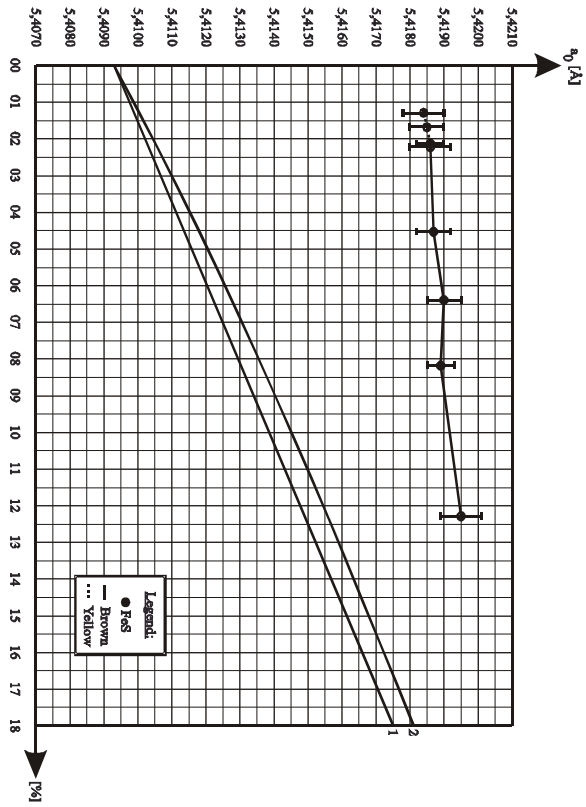

Fig. 1. Variation of the unit cell dimension a_0 by the FeS contents for the yellow and brown sphalerites from Kizevak.
Lines: 1 by Skinner *et al.* (1959) and 2 by Barton and Toulmin (1966)

From Figure 1 it can be clearly seen that there is reducing of the unit cell dimensions for the 15.634 brown and 15.604 brown sphalerite samples.

At such manner there were confirmed the conclusions of Toulmin (1960), Wiggins and Craig (1980) and Toulmin *et al.* (1991) that substitution of the Cu in Fe-sphalerites decrease the unit cell dimensions.

From Figure 1 it can be also seen the differences between the variation of the unit cell dimension a_0 by the FeS contents for the sphalerites from Kizevak regard to the variation lines by Skinner *et al.* (1959) and Barton and Toulmin (1966).

That differences are considerable and they decrease with the increasing of the FeS content.

Also, it was established that sphalerite compositions and their unit cell dimensions are more or less different at different

depths and also they are different for the yellow and brown varietys (by their predominated color).

Regard to the literature datas (Swanson and Fuyat (1953), JCPDS 05-0566), all investigated sphalerites has considerable bigger unit cell dimensions than pure ZnS.

It can not be find the appropriate explanation for these differences, except that sphalerites from Kizevak was formed under the different P-T-X conditions than sphalerites from the literature datas.

Conclusion

With the X-ray, chemical and spectrochemical methods there were investigated monomineral concentrations of the yellow and brown (by their predominated color) sphalerite varietys from the polymetallic Pb-Zn ore deposit Kizevak from the different horizons at 670, 690 and 710m.

Results of the X-ray investigations are represented at Tables 1, 3, 5 and 7, and the results of the chemical and spectrochemical compositions at Tables 2, 4, 6 and 8.

There were calculated sphalerite unit cell dimensions for which it was confirmed that increase with the increasing of the FeS contents and which decrease with the increasing of the CuS content (Table 9 and Figure 1).

Sphalerite compositions and their unit cell dimensions are more or less different at different depths, and also they are different for the yellow and brown varietys.

Calculated unit cell dimensions from the X-ray investigations are considerable bigger related to that from the literature datas, while the difference between them decrease with the increasing of the FeS contents.

It was presumed that these differences are caused by the different P-T-X conditions of the formation of the sphalerites from Kizevak regard to the sphalerites from the literature datas.

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