https://doi.org/10.46861/bmp.32.045 PŮVODNÍ PRÁCE/ORIGINAL PAPER

An intermediate member of the scorodite - strengite series, scorodite$_{56}$ - strengite$_{41}$, from Kutná hora ore district, Czech Republic: chemistry and X-ray powder diffraction study

Richard Pažout* and Jaroslav Maixner

*University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6, Czech Republic; *email: richard.pazout@vscht.cz*

Pažout R, Meixner J (2024) An intermediate member of the scorodite - strengite series, scorodite$_{56}$ - strengite$_{41}$, from Kutná hora ore district, Czech Republic: chemistry and X-ray powder diffraction study. Bull Mineral Petrolog 32(1): 45-49 ISSN 2570-7337

Abstact

A rare intermediate member of the scorodite - strengite series with an extraordinarily high degree of the anionic P for As substitution, technically a scorodite extremely rich in phosporus, scorodite$_{56}$ - strengite$_{41}$ (Scd$_{56}$ - Stg$_{41}$), was found and identified from mine dump material of the Rejzské pásmo Lode of the Kutná Hora ore district, Czech Republic. The mineral forms fine-grained, light brownish yellow crystalline masses and coatings, several milimeters in thickness on areas of tens of cm^2 on the surface of drusy quartz gangue with partially corroded galena and arsenopyrite. Chemical analyses revealed substantial amount of anionic phosphorus substituting for arsenic, ranging from 39.0 to 44.1 at. % of P (mean 41.0 %). Its chemical composition (mean of nine point analyses) corresponds to the empirical formula $(Fe^{3+}_{0.93}Al_{0.03}Pb_{0.01})_{\Sigma 0.97}[(As_{0.56}P_{0.41}S_{0.03})_{\Sigma 1.00}O_{4.00}]\cdot 2H_2O$. Such a scope of the P for As substitution in members of the scorodite - strengite series is rare and exceptional. X-ray powder diffraction data, unit-cell parameters and space group for the intermediate member are reported [*a* = 8.844(2) Å, *b* = 9.969(2) Å, *c* = 10.247(2) Å, unit-cell volume *V* = 903.39 Å^3, Z = 8 and space group *Pbca*]. No discontinuation of the solid solution between scorodite and strengite has been observed, X-ray powder difraction analysis unambiguously confirmed the existence of a single phase representing an intermediate member.

***Key words**: intermediate member, scorodite - strengite series, chemical composition, As - P substitution, indexed X-ray powder diffraction data, Kutná Hora ore district, Czech Republic*

Received 28. 4. 2024; accepted 25. 6. 2024

Introduction

Scorodite is a common hydrated iron arsenate mineral with the chemical formula $FeAsO_4\cdot 2H_2O$. It is found in hydrothermal deposits and as a secondary mineral in gossans worldwide. It can also be found as a primary mineral at hydrothermal deposits. It forms a solid-solution series with strengite ($FePO_4\cdot 2H_2O$) which occurs far more rarely than scorodite. The minerals scorodite and strengite are isostructural and form an isomorphous series. As evidenced in the literature, scorodite with P is much more frequent than strengite with As.

Murciego et al. (2009) observed zoned crystals of scorodite with an enrichment in P from the borders to the core with the P_2O_5 contents from 1 to 9 wt. %, while in the concentric textures the content of P_2O_5 varied from 0.7 to 6 wt. %. Murciego et al. (2011) studied secondary phases formed under natural weathering conditions from arsenopyrite in mine wastes from abandoned tungsten and tin exploitations of the Barruecopardo and Terrubias mining areas, Spain. They determined relatively high P contents (from 0.26 to 9.01 wt. % P_2O_5) and moderately low contents of S (up to 1.49 % SO_3) and concluded that this mineral is an intermediate member between scorodite and strengite, corresponding to P-rich scorodite or *phosphoscorodite* ($Fe(As,P)O_4\cdot 2H_2O$). According to Endo et al. (2008) the two minerals form only a partial solid-solution series and no continuous solid solution is produced due to the size difference between AsO_4^{3-} and PO_4^{3-}.

Higher contents of P_2O_5 in scorodite were reported by Llorens, Moro (2012), who studied phosphate assemblages of pegmatite dykes of from Jálama batholith in the Navasfrías Sn-W district, Salamanca, Spain. They described a phosphate-rich scorodite (up to 26 wt. % P_2O_5), which occurs on partly corroded arsenopyrite and rockbridgeite. This reference is nonetheless dubious because a) no data on chemical composition of scorodite are presented; and b) 26 wt. % P_2O_5 would represent an As-rich strengite with P > As and not scorodite.

The highest contents of P_2O_5 in scorodite and at the same time the highest contents of As_2O_5 in strengite were published from Jedová jáma mine near Vejprty, Czech Republic, by Pauliš et al. (2020). They described an intermediate member with continuously variable compositions from 15.0 wt. % P_2O_5 (P-rich scorodite Scd$_{59}$-Stg$_{41}$) up to 22.0 wt. % P_2O_5 (As-rich strengite Scd$_{43}$-Stg$_{56}$).

Sample

The samples with the intermediate mixed member of the scorodite - strengite series were found and identified from mine dump material of the Rejzské pásmo Lode of the Kutná Hora ore district, Czech Republic, deposited at the entrance of the 14 pomocníků (Fourteen Helpers) Gallery. The mineral forms fine-grained, light brownish

Fig. 1 *Photograph of the bulk sample with crystalline masses and coatings of the intermediate member of the scorodite - strengite series from Kutná Hora ore district, Czech Republic; field of view 1 cm.*

Fig. 2 *Photograph of the crystalline coatings of the intermediate member of the scorodite - strengite series from Kutná Hora ore district, Czech Republic; field of view 1.7 mm.*

yellow crystalline masses and coatings (Figs. 1 and 2), several milimeters in thickness on areas of tens of cm^2 on the surface of drusy quartz gangue with partially corroded galena and arsenopyrite lenses and crystals.

Methods of identification

The chemical composition was determined by the Cameca SX-100 electron microprobe (Masaryk University, Brno) operating in the wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 4 and 10 nA, and a beam diameter of 10 μm. The following lines and standards were used: *K*α: andradite (Fe), baryte (S), fluorapatite (P), sanidine (Al), ZnO (Zn); *L*α: InAs (As); and *M*α: vanadinite (Pb). Peak counting times (CT) were 20 s; CT for each background was one-half of the peak time. The raw intensities were converted to the concentrations automatically using the *PAP* (Pouchou and Pichoir 1985) matrix-correction algorithm.

The X-ray diffraction pattern was collected at room temperature using an X'Pert PRO θ-θ powder diffractometer with parafocusing Bragg-Brentano geometry and Cu $K\alpha_1$ radiation (λ = 1.5406 Å, generator setting: 40 kV, 30 mA). An ultrafast X'Celerator detector was employed to collect XRD data over the angular range from 4 to 68 °2θ with a step size of 0.02 °2θ and a counting time of 10 s. $step^{-1}$. The software package HighScore Plus V 4.0 of PANalytical, Almelo, Netherlands, was used to smooth the data, to fit the background and to eliminate the $K\alpha_2$ component.

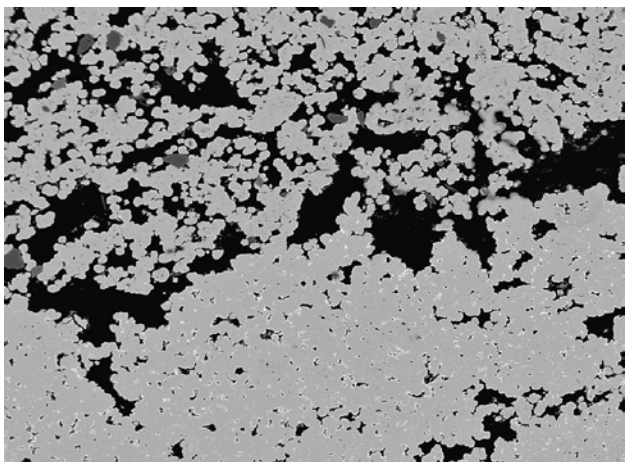

Fig. 3 *BSE image of the intermediate member of the scorodite - strengite series from Kutná Hora ore district, Czech Republic (polished section UN 287 of sample RES 1); field of view 750 μm.*

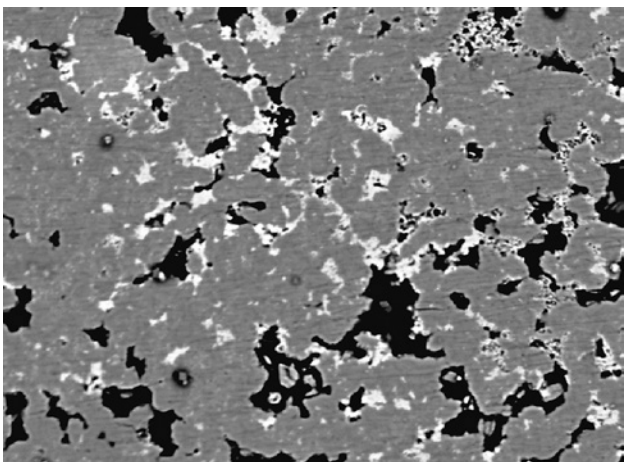

Fig. 4 *BSE image of the intermediate member of the scorodite - strengite series from Kutná Hora ore district, Czech Republic (polished section NAB 62 of sample RES 1). The white phase is an iron sulphate; field of view 130 μm.*

The top of smoothed peak method was used to determine the peak positions and intensities of the diffraction peaks. Automatic indexing of the experimental XRD pattern was done using DICVOL06 (Boultif, Louër 2004).

Chemistry

The chemical composition was studied on two polished sections (Figs. 3 and 4) obtained from the sample RES 1. The most distinct feature is the presence of considerable amounts of phosphorus next to arsenic (Table 1) in the anionic part of the structure with P_2O_5 contents ranging from 13.01 to 15.71 wt. %, corresponding to 0.39 to 0.44 *apfu* of P. Rather high totals of analytical points 4 and 5 are caused by different analytical conditions (current 10 nA).

The chemical composition (mean of nine point analyses) corresponds to the empirical formula $(Fe^{3+}_{0.93}Al_{0.03}Pb_{0.01})_{\Sigma 0.97}[(As_{0.56}P_{0.41}S_{0.03})_{\Sigma 1.00}O_{4.00}]\cdot 2H_2O$. Such a scope of the P for As substitution in members of the scorodite - strengite series is rare and exceptional and represents an intermediate member of the scorodite - strengite isomorphous series close to 1:1 ratio of As and P.

Table 1 *Chemical composition of the intermediate member of the scorodite-strengite series from Kutná Hora ore district, Czech Republic (wt. %, apfu).*

wt. %	1	2	3	4	5	6	7	8	9
PbO	0.42	0.52	2.77	1.26	0.61	0.73	0.25	0.16	0.00
ZnO	0.05	0.13	0.25	0.13	0.15	0.12	0.03	0.13	0.18
Fe_2O_3	34.62	34.98	34.14	38.35	38.48	35.51	34.44	33.99	34.67
Al_2O_3	0.69	0.65	0.58	0.63	0.68	0.58	0.77	0.96	0.65
As_2O_5	29.44	30.45	27.77	30.99	31.13	32.22	31.90	31.79	32.07
P_2O_5	14.38	14.13	13.17	14.58	15.71	13.08	13.44	13.16	13.01
SO_3	1.27	0.85	2.09	1.25	0.74	0.70	0.68	0.79	0.64
H_2O*	17.10	17.10	16.33	17.68	18.07	17.05	17.12	17.01	16.95
Total	97.98	98.81	97.09	104.86	105.57	99.98	98.62	97.99	98.17
Pb	0.004	0.005	0.027	0.011	0.005	0.007	0.002	0.002	0.000
Zn	0.001	0.003	0.007	0.003	0.004	0.003	0.001	0.003	0.005
Fe	0.913	0.923	0.943	0.979	0.961	0.939	0.908	0.902	0.923
Al	0.028	0.027	0.025	0.025	0.027	0.024	0.032	0.040	0.027
Σ cation	0.947	0.958	1.002	1.018	0.997	0.973	0.943	0.947	0.955
As	0.540	0.558	0.533	0.550	0.540	0.592	0.584	0.586	0.593
P	0.427	0.419	0.409	0.419	0.441	0.389	0.398	0.393	0.390
S	0.033	0.022	0.057	0.032	0.019	0.018	0.018	0.021	0.017
Σ anion	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
H_2O	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

The coefficients of the empirical fomulas are calculated on the basis of As+P+S = 1 *apfu*
H_2O* - the content calculated on the basis of the ideal content of 2 H_2O.

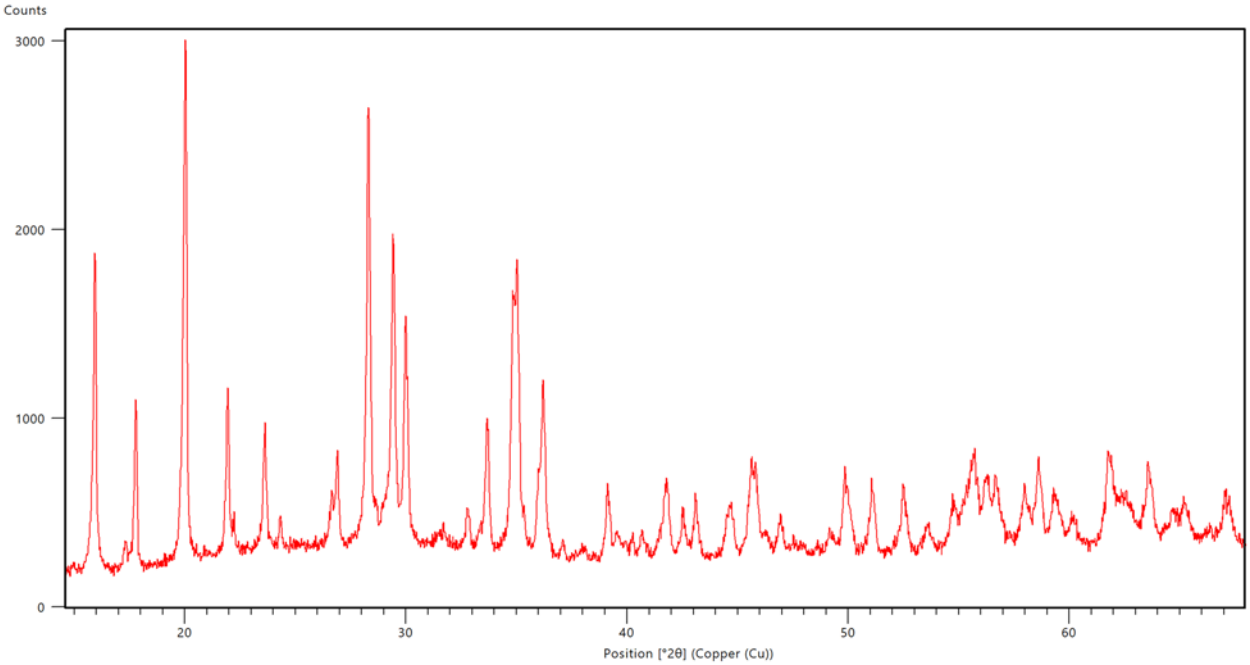

Fig. 5 *X-ray powder diffraction pattern of the intermediate member of the scorodite - strengite series from Kutná Hora ore district, Czech Republic. Cu Kα radiation (ƛ = 1.5418 Å).*

Table 2 *Indexed X-ray powder diffraction data for the intermediate member of the scorodite - strengite series. Only the peaks with I_{rel} of 1 or greater are presented [a = 8.844(2) Å, b = 9.969(2) Å, c = 10.247(2) Å, unit-cell volume V = 903.39 Å^3, Z = 8 and space group Pbca]. All measured lines were indexed and are consistent with the Pbca space group. The d-values were calculated using Cu Kα_1 radiation (λ = 1.5406 Å).*

$2\theta_{obs}$ (°)	d_{obs} (Å)	I_{rel}	*h*	*k*	*l*	$2\theta_{cal}$ (°)	d_{calc} (Å)	$\Delta 2\theta$
15.934	5.558	77	1	1	1	15.933	5.558	-0.0004
17.328	5.113	7	0	0	2	17.295	5.123	-0.0339
17.781	4.984	37	0	2	0	17.780	4.985	-0.0008
19.814	4.477	19	0	2	1	19.791	4.482	-0.0228
20.026	4.430	100	1	0	2	20.013	4.433	-0.0128
21.939	4.048	29	1	1	2	21.925	4.051	-0.0142
22.208	4.000	8	1	2	1	22.217	3.998	0.0089
23.624	3.763	23	2	1	1	23.643	3.760	0.0190
26.644	3.343	9	2	0	2	26.608	3.347	-0.0362
26.906	3.311	15	1	2	2	26.893	3.313	-0.0129
28.311	3.150	61	2	2	1	28.329	3.148	0.0178
29.429	3.033	41	1	1	3	29.406	3.035	-0.0227
29.996	2.977	31	1	3	1	29.996	2.977	0.0003
31.717	2.819	4	0	2	3	31.733	2.818	0.0152
32.813	2.727	6	3	1	1	32.839	2.725	0.0262
33.686	2.659	16	1	3	2	33.680	2.659	-0.0058
34.880	2.570	29	2	3	1	34.861	2.572	-0.0187
35.030	2.560	33	0	0	4	35.000	2.562	-0.0301
35.990	2.493	10	0	4	0	36.007	2.492	0.0167
36.224	2.478	18	3	1	2	36.265	2.475	0.0416
37.113	2.421	2	0	4	1	37.094	2.422	-0.0188
39.129	2.300	8	1	3	3	39.137	2.300	0.0086
39.535	2.278	3	0	2	4	39.521	2.278	-0.0139
40.232	2.240	3	0	4	2	40.205	2.241	-0.0268
40.679	2.216	3	2	0	4	40.671	2.217	-0.0077
41.739	2.162	7	2	1	4	41.710	2.164	-0.0294
42.511	2.125	5	2	4	1	42.528	2.124	0.0169
43.098	2.097	7	2	3	3	43.104	2.097	0.0061
44.565	2.032	4	4	0	2	44.601	2.030	0.0355
44.679	2.027	5	3	3	2	44.703	2.026	0.0245
45.609	1.987	9	4	1	2	45.567	1.989	-0.0417
45.818	1.979	9	1	3	4	45.852	1.977	0.0342
46.941	1.934	4	3	0	4	46.953	1.934	0.0126
49.179	1.851	3	3	3	3	49.137	1.853	-0.0412
49.852	1.828	8	2	1	5	49.850	1.828	-0.0027
51.091	1.786	6	0	4	4	51.090	1.786	-0.0014
52.507	1.741	6	2	2	5	52.485	1.742	-0.0223
53.602	1.708	3	0	0	6	53.623	1.708	0.0209
54.790	1.674	4	4	0	4	54.804	1.674	0.0136
55.351	1.658	5	3	1	5	55.324	1.659	-0.0264
55.708	1.649	7	5	1	2	55.701	1.649	-0.0070
56.274	1.633	6	4	4	1	56.298	1.633	0.0244
56.667	1.623	6	2	3	5	56.683	1.623	0.0159
57.991	1.589	5	1	2	6	57.983	1.589	-0.0078
58.612	1.574	7	4	4	2	58.603	1.574	-0.0092
59.338	1.556	4	1	6	2	59.353	1.556	0.0154
60.158	1.537	3	2	6	1	60.123	1.538	-0.0350
61.770	1.501	7	3	3	5	61.744	1.501	-0.0260
62.585	1.483	4	2	5	4	62.616	1.482	0.0317
63.585	1.462	6	3	1	6	63.602	1.462	0.0174
64.670	1.440	3	5	1	4	64.667	1.440	-0.0032
65.219	1.429	3	1	1	7	65.225	1.429	0.0066
67.061	1.395	4	3	4	5	67.057	1.395	-0.0040
67.234	1.391	4	1	4	6	67.240	1.391	0.0052

Table 3 The comparison of unit cell parameters of end and intermediate members of the scorodite - strengite series.

	a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	
scorodite	8.953(3)	10.038(2)	10.325(6)	927.91	Kitahama et al. (1975)
intermediate member	8.844(2)	9.969(2)	10.247(2)	903.39	this paper
strengite	8.722(3)	9.878(2)	10.1187(14)	871.79	Taxer, Bartl (2004)

In this context it was interesting to investigate whether the studied sample represents a partial solid-solution series represented by two phases (scorodite and strengite) or by a single phase representing an intermediate member of the series.

X-ray powder diffraction study

The experimental powder diffraction pattern is depicted in Figure 5. Automatic indexing results obtained by DICVOL06 (Table 2) show that the title compound is orthorhombic with the space group *Pbca* and unit-cell parameters: *a* = 8.844(2) Å, *b* = 9.969(2) Å, *c* = 10.247(2) Å, unit-cell volume *V* = 903.39 Å^3, Z = 8]. The figure of merits is F_{20} = 16.9673 (Smith, Snyder 1979). All lines were indexed and are consistent with the *Pbca* space group.

The results of the diffraction analysis clearly showed that: a) the sample is formed by a single phase of the scorodite - strengite series; b) the peak positions correspond to an intermediate member between scorodite and strengite (Table 3). Thus, no discontinuation of the solid solution between scorodite and strengite due to size difference between AsO_4^{3-} and PO_4^{3-}, reported by Endo et al. (2008) has been observed.

Conclusions

The studied scorodite with extraordinarily high P content is an intermediate member of the scorodite-strengite series, expressed as scorodite$_{56}$ - strengite$_{41}$. Chemistry and indexed powder diffraction data are presented. The study did not confirm previous statements by Endo et al. (2008) that scorodite and strengite form only a partial solid-solution series and no continuous solid solution is produced. X-ray powder diffraction study unambiguously confirmed the existence of a single phase that can be characterized as an intermediate member of the scorodite - strengite series (Scd$_{56}$ - Stg$_{41}$).

Acknowledgements

Our thanks go to Petr Pauliš and Jiří Sejkora for microprobe measurements. This work was financed by the Czech Science Foundation (GAČR project 15-18917S) to RP.

References

Boultif A, Louër D (2004) Powder pattern indexing with the dichotomy method. J Appl Crystallogr 37: 724-731

Endo S, Terada Y, Kato Y, Nakai I (2008) Chemical speciation of arsenic-accumulating mineral in a sedimentary iron deposit by synchrotron radiation multiple X-ray analytical techniques. Environ Sci Technol 42: 7152-7158

Kitahama K, Kiriyama R, Baba Y (1975) Refinement of the crystal structure of scorodite. Acta Crystallogr Sect B 31: 322-324

Llorens T, Moro MC (2012). Fe-Mn phosphate associations as indicators of the magmatic-hydrothermal and supergene evolution of the Jálama batholith in the Navasfrías Sn-W District, Salamanca, Spain. Mineral Mag 76: 1-24

Murciego A, Pellitero Pascual E, Angeles Rodríguez M, Álvarez Ayuso E, García Sánchez A, Rubio F, Rubio J (2009) Arsenopyrite weathering products in Barruecopardo mine tailings (Salamanca, Spain). Revista Sociedad Esp Miner 11: 133-134

Murciego A, Álvarez-Ayuso E, Pellitero E, Rodríguez M, García-Sánchez A, Tamayo A, Rubio J, Rubio F, Rubio J (2011). Study of arsenopyrite weathering products in mine wastes from abandoned tungsten and tin exploitations. J Hazard Mater 186: 590-601

Pauliš P, Dolníček Z, Gramblička R, Pour O (2020) Unusual vein Cu-Zn-Ag-Pb-As-Sb-Se-Sn-Bi mineralization from Jedová jáma mine near Vejprty in the Krušné hory Mts. (Czech Republic). Bull Mineral Petrol 28: 385-405 (in Czech with English abstract)

Pouchou J, Pichoir F (1985) „PAP" (φρz) procedure for improved quantitative microanalysis. In: Armstrong JT (ed): Microbeam Analysis: 104-106. San Francisco Press. San Francisco

Smith GS, Snyder RL (1979) F_N: A criterion for rating powder diffraction patterns and evaluating the reliability of powder indexing. J Appl Crystallogr 12: 60-65

Taxer K, Bartl H (2004) On the dimorphy between the variscite and clinovariscite group: refined fine-structural relationship of strengite and clinostrengite, $Fe(PO_4)\cdot 2H_2O$. Cryst Res Technol 39: 1080-1088