

Original paper

Distribution of Bi in the crystal structure of Bi-rich jamesonite, $\text{FePb}_4(\text{Sb}_{5.48}\text{Bi}_{0.52})_{\Sigma 6}\text{S}_{14}$

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Crystal structure of Bi-rich jamesonite, $\text{FePb}_4\text{Sb}_6\text{S}_{14}$, from Kutná Hora ore district, Czech Republic was solved from single-crystal X-ray diffraction data to establish whether bismuth shows a preference for any of the three antimony sites in the structure and whether increasing content of the element is placed in one specific site in the structure or is distributed over more sites. Jamesonite is monoclinic, $P2_1/c$, with $a = 4.0237(3)$, $b = 19.1136(17)$, $c = 15.7813(15)$ Å, $\beta = 91.799(7)^\circ$, $V = 1213.10(18)$ Å³, $Z = 2$, $D_{\text{calc.}} = 5.7746$ g·cm⁻³. The structural formula derived from the refinement is $\text{FePb}_4(\text{Sb}_{5.48}\text{Bi}_{0.52})_{\Sigma 6}\text{S}_{14}$. The structure refinement ($R = 5.22$ %) of a needle-like crystal documents that out of three antimony sites in the structure, bismuth shows a preference for Sb1 and Sb3 sites in the lone-electron pair micelle of the $[\text{Pb}_4\text{Sb}_6\text{S}_{13}]$ substructure motif while the site Sb2 closest to the Fe octahedron is least inclined to accept bismuth. The refinement also reveals that bismuth content is simultaneously distributed over all three antimony sites and that the placement of bismuth first and preferentially into one antimony site does not take place.

Keywords: Bi-rich jamesonite, crystal structure, distribution of Bi, prediction, Kutná Hora, Czech Republic

Received: 4 November 2020; **accepted:** 3 December 2020; **handling editor:** J. Plášil

Electronic supplementary material. Supplementary crystallographic data are available online at the Journal web site (<http://dx.doi.org/10.3190/jgeosci.316>).

1. Introduction

Sulfosalts containing both Bi and Sb are relatively rare in nature (Cook 1997; Pažout et al. 2017). Minerals containing both Sb and Bi as essential constituents include tintinaite, kobellite, izoklakeite, giessenite, jaskolskiite, terywallaceite, staročeskéite, oscarkempffite, clinoscarkempffite, garavellite and aramayoite. The second group is represented by Bi sulfosalts with significantly increased Sb content represented by Sb-bearing members of the lillianite branch of the lillianite homologous series. An almost complete transition of Bi-sulfosalts of lillianite series with $N = 4$ to Sb-rich members, recently observed in Kutná Hora ore district, is unique on the world scale (Pažout 2017). The third group comprises Sb sulfosalts with significantly increased Bi content, including Bi-rich varieties of jamesonite, boulangerite and owyheite.

The issue of the distribution of bismuth substituting for antimony in Sb sulfosalts is an essential issue in the crystal chemistry of sulfosalts concerning the definition of new minerals. According to the IMA rules, as soon as the rising content of a minor element substituting for a major one (Bi for Sb in the case of jamesonite) causes the prevalence of minor element in any particular site in the crystal structure, the phase is entitled to be proposed as a new mineral species even if the cell and symmetry are the same as for the phase without minor element.

The lowest Bi content in Bi-rich jamesonite that if placed in a single site would cause a predominance of Bi over Sb in that site (and thus would become eligible to be proposed as a new mineral species) is one-sixth of the total atomic metal content of Bi+Sb which corresponds to Bi/(Bi+Sb) ratio equal to 0.17 (corresponding to ~10.2 wt. % of Bi in jamesonite). On the other hand, if distributed strictly evenly over all three antimony sites in the structure, the content of Bi would have to be at least 50 % of the total atomic metal content of Bi+Sb (corresponding to Bi/(Bi+Sb) ratio equal to 0.50 and to ~29 wt. % of Bi in jamesonite). Therefore, the study is aimed at documenting the behavior of bismuth substituting for antimony and find out whether bismuth shows a preference for any of the three antimony sites in the structure and whether the Bi content is placed in a single site or is distributed over more sites.

2. Sample

The crystal of Bi-rich jamesonite investigated by single-crystal X-ray diffraction was recovered from the specimen, which was found by the author on medieval mine dumps of Staročeské pásmo Lode of the Kutná Hora ore district, Czech Republic. The sample was extracted from a specimen of quartz gangue (ST 187) with fairly rich accumulations of grains with silver grey metallic luster and crystal aggregates of several millimeters in size of

Tab. 1 Crystallographic data and refinement details for Bi-rich jamesonite from Kutná Hora, Czech Republic.

Crystal data	
Structure formula	FePb ₄ (Sb _{5.48} Bi _{0.52}) _{Σ6} S ₁₄
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit-cell parameters: <i>a</i> , <i>b</i> , <i>c</i> [Å]	4.0237(3), 19.1136(17), 15.7813(15)
β [°]	91.799(7)
Unit-cell volume [Å ³]	1213.09(19)
<i>Z</i>	2
Calculated density [g/cm ³]	5.7746
Crystal size [mm]	0.23 × 0.03 × 0.02
<i>F</i> ₀₀₀	1801
Data collection	
Diffractometer	Rigaku SuperNova, Atlas S2 detector
Temperature [K]	298.1
Radiation, wavelength [Å]	MoK α , 0.71073 (50 kV, 30 mA)
θ range for data collection [°]	2.49–29.59
Limiting Miller indices	<i>h</i> = –5→5, <i>k</i> = –26→25, <i>l</i> = –20 → 20
Axis, frame width (°), time per frame (s)	ω , 1, 65
Total reflections collected	8133
Unique reflections	7586
Unique observed reflections, criterion	4292, [<i>I</i> > 3 σ (<i>I</i>)]
Absorption coefficient [mm ^{–1}], type	36.52; multi-scan
<i>T</i> _{min} / <i>T</i> _{max}	0.935/1
<i>R</i> _{int}	0.0865
Structure refinement by Jana2006	
Refined parameters, restraints, constraints	118, 0, 27
<i>R</i> , <i>wR</i> (obs)	6.36, 5.22
<i>R</i> , <i>wR</i> (all)	10.94, 5.66
GOF obs/all	1.77, 1.44
Weighting scheme, weights	σ , $w = 1/(\sigma^2(I) + 0.0001I^2)$
Largest diffraction peak and hole (e [–] /Å ³)	5.52, –4.02

Ag–Pb–Bi–Sb sulfosalts of lillianite homologous series, accompanied by jamesonite. Jamesonite forms grey metallic needles up to several millimeters in size.

3. Single-crystal X-ray crystallography

A tiny needle-like metallic crystal of jamesonite with dimensions 0.23 × 0.03 × 0.02 mm, was selected under the optical stereomicroscope. The intensity data were collected using Rigaku SuperNova single-crystal diffractometer equipped with Atlas S2 CCD detector and monochromated MoK α radiation from a conventional sealed X-ray tube (55 kV, 30 mA), collimated with fiber optics Mo-Enhance collimator. The monoclinic unit cell was refined by a least-squares algorithm using the CrysAlis Pro Package (Agilent Technologies 2014) from 3476 reflections and gave *a* = 4.0237(3) Å, *b* = 19.1136(17) Å, *c* = 15.7813(15) Å, β = 91.799(7)°, with *V* = 1213.09(19) Å³, and *Z* = 2. From the total of 8133 measured diffractions, 7586 were independent and

4292 from them were classified as observed [*I*_{obs} > 3 σ (*I*)]. Data were corrected for background, Lorentz and polarization effects, and a multi-scan correction for absorption was applied, resulting in *R*_{int} of the merged data equal to 0.0865.

The crystal structure was solved from X-ray diffraction data by the charge-flipping algorithm (Palatinus and Chapuis 2007) independently from the previous structure solutions (Matsushita and Ueda 2003; Léone et al. 2003). The obtained model was refined by the full-matrix least-squares of the Jana2006 program (Petříček et al. 2014) based on *F*. All atoms were found from the structure solution. In the next step, all atoms were refined with isotropic displacement parameters, followed by splitting of atomic positions of the three Sb sites and introducing bismuth in the refinement. Occupancies of the two metals were set to 50 % each and refined. The atom numbering scheme remains the same as in the paper by Léone et al. (2003). Finally,

the anisotropic displacement parameters of all atoms were successfully refined. Because *R*-factors were still higher than expected, a careful look into the refinement listing revealed a possible problem with non-matching reflections. Since it is difficult to reveal non-matching reflections after averaging, unaveraged reflection data were used. A criterion of skipping non-matching reflections with $|F_{\text{obs}} - F_{\text{calc}}| > 5 * \sigma(F_{\text{obs}})$ was used, resulting in the discarding of 547 reflections from the refinement, which led to a significant improvement of *R*-factors. The final refinement including all atoms refined with anisotropic displacement parameters converged to an *R*_{obs} = 0.0636, *wR*_{obs} = 0.0522 with a GOF = 1.77 for 4272 unique observed reflections. Details of the data collection and crystallographic and structure refinement parameters are listed in Tab. 1. Final atom coordinates, occupancies and isotropic displacement parameters are given in Tab. 2; anisotropic displacement parameters are given in Tab. 3. The CIF file, also containing a block with reflections, is deposited at the Journal's web page www.jgeosci.org.

4. Results and discussion

The structure of jamesonite was solved by the minimum-function method as early as 1957 (Niizeki and Buerger 1957) and described in detail by Matsushita and Ueda (2003) and by Léone et al. (2003), including a detailed discussion of substructure building blocks in terms of modular approach and impact on optical, electric and magnetic properties. The structure of jamesonite consists of two components of rod-shaped substructures. One is $[\text{Pb}_4\text{Sb}_6\text{S}_{13}]$

substructure (a Bi_2Te_3 -type, also called SnS archetype) consisting of all lead and antimony sites. The other is a rod-shaped substructure which is formed by the FeS_6 octahedron (Matsushita and Ueda 2003). According to Léone et al. (2003) – the same cell setting as in this study – the projection of the structure along a shows rods $(\text{Pb}_4\text{Sb}_6\text{S}_{14})^\infty$ parallel to a , constituted by two SnS-type ribbons (each two-atom thick); these two ribbons are connected by 2×3 Sb atoms weakly bonded to opposite S atoms due to their lone electron pairs, while the Pb atoms are located at the margins. These rods are connected along c by iron atoms in octahedral coordination, forming rod-layers parallel to (010). The connection between two adjacent rod-layers is assumed by Pb–S bonds. FeS_6 octahedra are connected by two opposite edges, forming single chains $(\text{FeS}_6)^\infty$ parallel to a .

Nevertheless, none of the previous studies dealt with partial substitution of antimony sites by bismuth, so no information was available on whether there is a preference of Bi for any of the Sb sites and whether the element is distributed firstly in one site or evenly over more sites.

Tab. 2 Atom coordinate, occupancies and isotropic displacement parameters for the crystal structure of Bi-rich jamesonite from Kutná Hora, Czech Republic.

Atom	Occupancy	x/a	y/b	z/c	U_{eq}
Pb1	1	0.55614(15)	0.76150(3)	0.42622(4)	0.0231(2)
Pb2	1	0.53480(15)	0.86007(4)	0.18315(5)	0.0264(2)
Sb1	Sb 0.883(7)	1.1100(2)	0.95297(5)	0.39658(7)	0.0217(4)
	Bi 0.117(7)	1.1100(2)	0.95297(5)	0.39658(7)	0.0217(4)
Sb2	Sb 0.965(6)	1.0861(2)	1.06421(5)	0.17973(7)	0.0194(4)
	Bi 0.035(6)	1.0861(2)	1.06421(5)	0.17973(7)	0.0194(4)
Sb3	Sb 0.892(7)	1.1120(2)	0.84136(5)	0.63134(7)	0.0261(4)
	Bi 0.108(7)	1.1120(2)	0.84136(5)	0.63134(7)	0.0261(4)
S1	1	0.5508(9)	0.8974(2)	0.5031(3)	0.0245(14)
S2	1	1.0500(9)	0.84056(19)	0.3175(2)	0.0162(12)
S3	1	1.0214(9)	0.95643(18)	0.0956(2)	0.0158(12)
S4	1	1.0697(9)	0.7311(2)	0.5508(2)	0.0189(12)
S5	1	1.5280(9)	0.9971(2)	0.2841(3)	0.0214(13)
S6	1	1.5817(11)	0.7945(2)	0.7244(3)	0.0277(14)
S7	1	1.5128(9)	1.10537(19)	0.0791(3)	0.0184(12)

The structural refinement results clearly showed that out of three antimony sites in the structure, bismuth shows a preference for Sb1 and Sb3 sites, while the site Sb2 is much less inclined to accept bismuth. The occupancies of the three Sb sites are as follows: Sb3 has 89.2 % Sb and 10.8 % of Bi, Sb2 contains 96.5 % of Sb and 3.5 % of Bi and Sb1 has 88.3 % of Sb and 11.7 % of Bi. The inspection of interatomic distances (Tab. 4) and comparison with the structure of jamesonite of Léone et al. (2003) showed that the Sb1/Bi1 and Sb3/Bi3 sites have more considerable differences in M –S bond lengths (up to 0.05 Å) than Sb2/Bi2 site. However, when each site's average bond length is considered, no significant differences in bond lengths appear. The mean M –S bond lengths of each metal site differ only in the order of 0.015 Å, which is negligible to conclude the reasons for the observed distribution of Bi among the Sb sites. The Sb1 and Sb3 sites are positioned in the Sb–S ribbons of the $[\text{Pb}_4\text{Sb}_6\text{S}_{13}]$ substructure motif running approximately parallel to [021] and have a pronounced lone-electron pair micelle. The site Sb2 is positioned closest to the Fe octahedron

Tab. 3 Anisotropic displacement parameters (in Å²) for the crystal structure of Bi-rich jamesonite from Kutná Hora, Czech Republic.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0203(3)	0.0158(3)	0.0331(4)	−0.0016(3)	0.0011(3)	0.0010(3)
Pb2	0.0192(3)	0.0283(4)	0.0318(4)	−0.0016(3)	−0.0001(3)	0.0037(3)
Sb1	0.0262(7)	0.0138(6)	0.0253(7)	−0.0005(4)	0.0024(4)	0.0028(4)
Sb2	0.0202(7)	0.0124(6)	0.0260(7)	−0.0012(4)	0.0076(4)	−0.0029(5)
Sb3	0.0312(7)	0.0188(7)	0.0278(7)	0.0062(4)	−0.0074(5)	−0.0048(5)
Fe1	0.0331(19)	0.0044(15)	0.031(2)	−0.0046(14)	0.0082(15)	−0.0063(14)
S1	0.021(2)	0.019(2)	0.032(3)	0.0036(18)	−0.0058(18)	−0.010(2)
S2	0.023(2)	0.0094(19)	0.017(2)	−0.0010(16)	0.0001(17)	0.0039(16)
S3	0.029(2)	0.0043(18)	0.015(2)	0.0007(15)	0.0027(17)	−0.0013(15)
S4	0.029(2)	0.0072(18)	0.021(2)	0.0001(17)	0.0045(18)	−0.0044(17)
S5	0.017(2)	0.019(2)	0.029(2)	−0.0076(16)	0.0046(17)	0.0057(18)
S6	0.040(3)	0.010(2)	0.033(3)	0.0075(18)	−0.004(2)	−0.0032(19)
S7	0.022(2)	0.0097(19)	0.024(2)	0.0011(15)	0.0047(17)	−0.0032(17)

Tab. 4 Interatomic distances in Bi-rich jamesonite as obtained by the current study (left column) and in the study of Léone et al. (2003) (right column). Distances up to 3.7 Å are shown.

Pb1	S4	2.867(2)	Pb1	S4	2.874
	S1	2.867(2)		S1	2.899
	S4	2.877(2)		S4	2.902
	S7	2.998(3)		S7	2.950
	S2	3.026(2)		S2	3.033
	S2	3.065(2)		S2	3.066
	S6	3.365(3)		S6	3.345
	mean	3.010		mean	3.010
Pb2	S2	2.941(3)	Pb2	S2	2.940
	S2	2.949(2)		S2	2.955
	S6	3.03(3)		S6	3.048
	S3	3.051(2)		S3	3.047
	S3	3.064(2)		S3	3.056
	S5	3.066(2)		S5	3.077
	S4	3.265(2)		S4	3.230
	S4	3.510(2)		S4	3.474
	mean	3.109		mean	3.103
Sb1 Bi1	S2	2.493(2)	Sb1	S2	2.450
	S5	2.623(2)		S5	2.584
	S5	3.014(2)		S5	3.007
	S1	2.630(2)		S1	2.577
	S1	3.043(2)		S1	3.074
	S1	3.523(2)		S1	3.537
	mean	2.887		mean	2.872
Sb2 Bi2	S3	2.460(2)	Sb2	S3	2.443
	S7	2.502(2)		S7	2.487
	S5	2.709(2)		S5	2.714
	S7	2.869(2)		S7	2.872
	S5	3.104(2)		S5	3.113
	S6	3.354(2)		S6	3.332
	mean	2.833		mean	2.827
	Fe1	3.552(3)		Fe	3.541
	Sb3 Bi3	3.597(3)		Sb3	3.622
Sb3 Bi3	S4	2.463(2)	Sb3	S4	2.436
	S6	2.521(2)		S6	2.479
	S6	2.776(2)		S6	2.808
	S1	2.930(2)		S1	2.890
	S1	3.171(2)		S1	3.193
	S5	3.645(2)		S5	3.642
	mean	2.918		mean	2.908
	Sb2 Bi2	3.596(3)		Sb2	3.622
Fe1	S7	2.369(2)	Fe	S7	2.396
	S7	2.369(2)		S7	2.397
	S3	2.619(2)		S3	2.615
	S3	2.619(2)		S3	2.615
	S3	2.678(2)		S3	2.682
	S3	2.678(2)		S3	2.682
	mean	2.555		mean	2.565
	Sb2 Bi2	3.553(3)		Sb2	3.541
	Sb2 Bi2	3.553(3)		Sb2	3.542

with the shortest Sb2–Fe distance of 3.553(1) Å. The refinement also revealed that bismuth content is simultaneously distributed over all three antimony sites and that the placement of bismuth first and preferentially into only one antimony site does not occur.

If we attempt to hypothetically predict how much Bi has to be in Bi-rich jamesonite to have a prevalence of Bi in any particular Sb site and to become eligible to be proposed as a new mineral, we come out with the following assumptions based on the structural study in this paper. Assuming the trend of substituting the antimony sites with additional bismuth does not change with higher bismuth contents and progresses linearly, we can approximately assume that the Sb1 and Sb 3 sites will have to be filled with Bi to acquire occupancies of 50 % of Bi (with Sb1 slightly ahead by 0.9 %, so by the time Sb3 acquires 50 % of Bi, the Sb1 site will already have a prevalence of Bi and the phase is a new mineral) at which stage the Sb2 site will have an occupancy of Bi of ~41.5 %. Expressed in atomic proportions and weight percent, this situation – which results in a new mineral species – will occur when the Bi for Sb substitution reaches 47 %, corresponding to ~28 wt. % of Bi.

Acknowledgements. Michal Dušek and Václav Petříček (Institute of Physics, ASCR, v.v.i.) are thanked for their help with data collection/reduction and processing of non-matching reflections respectively. Comments by an anonymous reviewer improved substantially the early version of the manuscript. This research was financially supported by the Czech Science Foundation (GAČR project 15-18917S).

Electronic supplementary material. Supplementary crystallographic data are available online at the Journal web site (<http://dx.doi.org/10.3190/jgeosci.316>).

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