



Article

Zvěstovite-(Zn), $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$, a new tetrahedrite-group mineral from Zvěstov, Czech Republic

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Abstract

The new mineral, zvěstovite-(Zn), ideally $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$, was found in quartz–baryte gangue at the mine dump of the abandoned small deposit of Zvěstov, central Bohemia, Czech Republic. Zvěstovite-(Zn) is associated with tennantite-(Zn), tetrahedrite-(Zn), argentotennantite-(Zn), acanthite and supergene azurite and malachite. The new mineral occurs as rare relic anhedral grains rimmed by acanthite, up to 100 μm in size. Zvěstovite-(Zn) is grey, Mohs hardness is *ca.* 3½–4, in agreement with other members of the tetrahedrite group; the calculated density is 5.16 $\text{g}\cdot\text{cm}^{-3}$. In reflected light, zvěstovite-(Zn) is grey with a greenish tint, without birefractance, pleochroism or anisotropy. Deep red internal reflections are ubiquitous. Reflectance values of zvěstovite-(Zn) in air (*R*%) are: 28.5 at 470 nm, 26.9 at 546 nm, 25.5 at 589 nm and 23.8 at 650 nm. The empirical formula for zvěstovite-(Zn), based on electron-microprobe analyses ($n = 4$), is $\text{Ag}_{6.27}[(\text{Ag}_{3.90}\text{Cu}_{0.38})_{\Sigma 4.28}(\text{Zn}_{1.60}\text{Fe}_{0.09}\text{Cd}_{0.03})_{\Sigma 1.72}]_{\Sigma 6.00}(\text{As}_{2.26}\text{Sb}_{1.48})_{\Sigma 3.74}\text{S}_{12.50}$. The ideal formula is $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$, which requires (in wt.%) Ag 56.01, Zn 6.79, As 15.56 and S 21.64, total 100.00. Zvěstovite-(Zn) is cubic, $I\bar{4}3m$, with unit-cell parameters: $a = 10.850(2)$ Å, $V = 1277.3(8)$ Å³ and $Z = 2$. The strongest reflections of the calculated powder X-ray diffraction pattern [d , Å (I) (hkl)] are: 3.1321(100) (222), 2.7125(21) (400), 1.9809(11) (521), 1.9180(31) (440) and 1.6357(15) (622). According to the single-crystal X-ray diffraction data ($R_{\text{obs}} = 0.051$), the crystal structure of zvěstovite-(Zn) agrees with the general features of the members of the tetrahedrite group. Zvěstovite-(Zn) is named after its type locality, Zvěstov; the suffix indicates the dominant divalent C-constituent, according to the approved nomenclature of the tetrahedrite group. It is the As-isotype of rozhdestvenskayaite-(Zn). The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2020-061).

Keywords: zvěstovite-(Zn), new mineral, tetrahedrite group, silver, arsenic, crystal structure, Zvěstov, Czech Republic

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Introduction

Tetrahedrite-group minerals are the most common sulfosalts in different kinds of hydrothermal ore deposits. They form a complex isotypic series characterised by multiple homo- and heterovalent substitutions, representing an interesting link between mineralogy and ore geochemistry (Moëlo *et al.*, 2008; Biagioni *et al.*, 2020a). The classification and nomenclature of the tetrahedrite-group minerals, in keeping with the current International Mineralogical Association (IMA) rules (Mills *et al.*, 2009; Bosi *et al.*, 2019) was published recently by Biagioni *et al.* (2020a). The general structural formula of minerals belonging to this group can be written as $M^{(2)}\text{A}_6M^{(1)}(\text{B}_4\text{C}_2)_{\Sigma 6}X^{(3)}\text{D}_4\text{S}^{(1)}\text{Y}_{12}\text{S}^{(2)}\text{Z}$, where $\text{A} = \text{Cu}^+$, Ag^+ , \square (vacancy) and $(\text{Ag}_6)^{4+}$ cluster; $\text{B} = \text{Cu}^+$ and Ag^+ ; $\text{C} = \text{Zn}^{2+}$, Fe^{2+} , Hg^{2+} , Cd^{2+} , Ni^{2+} , Mn^{2+} , Cu^{2+} , Cu^+ and Fe^{3+} ; $\text{D} = \text{Sb}^{3+}$, As^{3+} , Bi^{3+} and Te^{4+} ; $\text{Y} = \text{S}^{2-}$ and Se^{2-} ; and $\text{Z} = \text{S}^{2-}$, Se^{2-} and \square (Biagioni *et al.*, 2020a).

Silver-rich members with 3–6 Ag atoms per formula unit (apfu) (the A constituent, now the freibergite/arsenofreibergite

series) have been known for a long time. Indeed, ‘freibergite’ was first described from the Hab Acht Mine near Freiberg, Saxony, Germany by Weissenbach (1831) and named by Kenngott (1853). Currently IMA-accepted minerals belonging to the freibergite series are argentotetrahedrite-(Fe) (Welch *et al.*, 2018), argentotetrahedrite-(Hg) (Wu *et al.*, 2021), argentotetrahedrite-(Zn) (Sejkora *et al.*, 2021), kenoargentotetrahedrite-(Fe) (the former ‘freibergite’ – Welch *et al.*, 2018; Biagioni *et al.*, 2020a) and kenoargentotetrahedrite-(Zn) (Qu *et al.*, 2021). The arsenofreibergite series comprises fewer species, being currently represented only by argentotennantite-(Zn) (Spiridonov *et al.*, 1986; Biagioni *et al.*, 2020a) and kenoargentotennantite-(Fe) (Biagioni *et al.*, 2020b).

The Ag-rich members of the tetrahedrite group, however, are known from many occurrences worldwide and at some deposits represent the main Ag ore, extremely Ag-rich members, with $\text{Ag} > 8$ apfu (~45 wt.% Ag; as both the A and B constituents), are distinctly rarer. The first documented find is probably from the Kutná Hora deposit (Czech Republic) where Kvaček *et al.* (1975) described ‘tetrahedrite’ with ~8 Ag apfu (and with Fe and Sb dominant as C and D constituents, respectively). Later, Paar *et al.* (1978) found ‘freibergite’ (Zn–Sb) with 8.6–10.5 Ag apfu in material from the “Knappenstube” mine, Hochtor, Salzburg (Austria). The Fe- and As-dominant member with 8.8 Ag apfu was reported from the Manson Lode deposit, Kelantan,

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Malaysia by Gan (1980). Ixer and Stanley (1983) analysed a Zn- and As-dominant member occurring as inclusion in galena from the Sark's Hope mine, Sark, Channel Islands, with ~8 Ag apfu. In the 1990s, further findings of extremely Ag-rich members of the tetrahedrite group were reported from China and Russia. Li and Wang (1990) described 'freibergite' (Fe–Sb dominant) from the Dachang ore field, Guangxi (China), with 9.0–9.6 Ag apfu and with $a = 10.950 \text{ \AA}$. Zhdanov *et al.* (1992) described Ag-rich 'tetrahedrite' (Fe–Sb dominant) from the deposit of Khachakchan, Verkhoian-Kolyma region, Russia, with Ag content ranging between 10.2 and 10.7 apfu and a unit-cell parameter $a = 10.92 \text{ \AA}$. Later, Samusikov and Gamyranin (1994) presented an almost Ag-pure sample (52 wt.% Ag, with only 0.7 wt.% Cu; $a = 10.90 \text{ \AA}$) from Yakutia, Russia and named it 'tarynite' from the locality. However, no official proposal was submitted to the then 'Commission on New Minerals and Mineral Names' of the IMA by these authors. Foit and Ulbricht (2001) documented 'tetrahedrite' samples (Hg and Sb dominant) from the O'Keefe pit, Steens-Pueblo, Oregon, USA with 9.3 Ag apfu. The Zn and As dominant 'argentotennantite' with 9.1 Ag apfu was described by Koch and Heider (2018) from the Frische Lutter mine, Bad Lauterberg, Harz, Germany. The first IMA-approved member of tetrahedrite group with Ag > 8 apfu was rozhdestvenskayaite-(Zn), $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$, described by Welch *et al.* (2018) from the Moctezuma mine, Sonora, Mexico.

During a systematic investigation of tetrahedrite-group minerals from the Czech Republic, a sample characterised by an extremely Ag-rich composition and with As > Sb was identified. This new mineral and its name were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA (IMA2020-061, Sejkora *et al.*, 2020). Zvěstovite-(Zn) is named after the type locality, Zvěstov, Czech Republic; the suffix indicates the dominance of Zn as the C constituent, according to the approved nomenclature of the tetrahedrite group (Biagioni *et al.*, 2020a). The holotype material (polished section) is deposited in the mineralogical collection of the Department of Mineralogy and Petrology of the National Museum, Prague, Czech Republic (catalogue number P1P 50/2020). The crystal used for the single-crystal X-ray diffraction study is stored in the mineralogical collection of the Museo di Storia Naturale of the Università di Pisa, Via Roma 79, Calci (PI), under catalogue number 19921.

Occurrence and mineral description

Occurrence

One hand-sized specimen of zvěstovite-(Zn) was collected at the mine dump in the southern part of the abandoned small deposit of Zvěstov (Stříbrnice), which is located 1200 m NNE from the village of Zvěstov. This locality is 10 km SW of Vlašim, central Bohemia region, Czech Republic. The GPS coordinates of the occurrence of zvěstovite-(Zn) are 49°38'39.069"N, 14°47'51.993"E. The Zvěstov deposit is represented by an irregular hydrothermal vein system ~1300 m long, with thickness ~20–50 cm and a vertical extent (verified by prospect borehole) of ~60 m (Nouza, 1988). There are no written records about historical mining at this deposit (Velebil, 2004). A fragment of a ceramic mug found in the studied mine dump was dated at the turn of the 15th and 16th Centuries (Velebil *et al.*, 2016). The exploration was last carried out here in the years 1956–1957 (Nouza, 1988). The quartz + baryte veins of the Zvěstov deposit host grains of

galena, sphalerite, chalcopryrite, pyrite, arsenopyrite and minerals of the tetrahedrite group (Nouza, 1988; Velebil *et al.*, 2016). This deposit is one of the small ore occurrences connected with the Blanice Graben (Fig. 1), which represents an ~200 km long NNE–SSW trending crustal-scale brittle tectonic zone in the Moldanubian Unit with minimal sinistral movement of ~17 km (Zachariáš and Hübst, 2012). It hosts low-fineness Au mineralisation (Roudný, Dobrá Voda) and younger Ag–Pb–Zn mineralisations (e.g. Ratibořské Hory – Stará Vožice, Rudolfovo or Stříbrná Skalice).

The holotype specimen of zvěstovite-(Zn) is a fragment of a quartz + baryte vein with sulfide disseminations [tennantite-(Zn), tetrahedrite-(Zn), argentotennantite-(Zn) and acanthite], as well as clasts of the host rocks (gneiss); it is partly supergenically altered, originating azurite and malachite.

Physical and optical properties

Zvěstovite-(Zn) forms relic anhedral grains rimmed by acanthite (Fig. 2), up to 100 μm in size. The mineral is grey in colour and is opaque in transmitted light; it has a metallic lustre. No cleavage was observed; it is brittle with a conchoidal fracture. The calculated density ($Z = 2$) for the empirical formula is 5.16 g.cm^{-3} . Mohs hardness is assumed at 3½–4 by analogy with other members of the tetrahedrite group. In reflected light, zvěstovite-(Zn) is grey with a greenish tint, without birefractance, pleochroism and anisotropy. Internal reflections are ubiquitous and deep red in colour. Reflectance spectra were measured in air with a TIDAS MSP400 spectrophotometer attached to a Leica microscope (50 \times objective) using a WTiC (Zeiss no. 370) standard, with a square sample measurement field of ca. $7 \mu\text{m} \times 7 \mu\text{m}$. The results from the 400–700 nm range are given in Table 1 and plotted in Fig. 3 in comparison with published data (Welch *et al.*, 2018) for rozhdestvenskayaite-(Zn), argentotetrahedrite-(Fe) and kenoargentotetrahedrite-(Fe) (originally 'freibergite').

Chemical composition

Chemical analyses were performed using a Cameca SX100 electron microprobe (National Museum, Prague) operating in wavelength-dispersive mode (25 kV, 20 nA and 1 μm wide beam). The following standards and X-ray lines were used to minimise line overlaps: Ag (AgL α), Au (AuM α), Bi (BiM β), CdTe (CdL α), Co (CoK α), chalcopryrite (CuK α , SK α), pyrite (FeK α), HgTe (HgM α), Ni (NiK α), NiAs (AsL α), PbS (PbM α), PbSe (SeL α), PbTe (TeL α), Sb₂S₃ (SbL α), TlBrI (TlL α) and ZnS (ZnK α). Peak counting times were 20 s for all elements, and 10 s for each background. Gold, Bi, Co, Hg, Ni, Pb, Se, Te and Tl were found to be below the detection limits (0.02–0.05 wt.%). Raw intensities were converted to the concentrations of elements using the automatic 'PAP' (Pouchou and Pichoir, 1985) matrix-correction procedure.

Analytical data for the zvěstovite-(Zn) grain used for single-crystal study are given in Table 2. On the basis of $\Sigma Me = 16$ apfu, the empirical chemical formula is $\text{Ag}_{6.27}[(\text{Ag}_{3.90}\text{Cu}_{0.38})_{\Sigma 4.28}(\text{Zn}_{1.60}\text{Fe}_{0.09}\text{Cd}_{0.03})_{\Sigma 1.72}](\text{As}_{2.26}\text{Sb}_{1.48})_{\Sigma 3.74}\text{S}_{12.50}$. The ideal formula is $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{As}_4\text{S}_{13}$, which requires Ag 56.01, Zn 6.79, As 15.56 and S 21.64, a total of 100.00 wt.%. Representative analyses for all zvěstovite-(Zn) grains in the holotype sample are given in Table 3. The grains studied show distinct AgCu₋₁ substitution (Fig. 4) with Ag and Cu contents 8.23–10.51 apfu and 0.10–2.00 apfu, respectively. The dominant Me^{2+} is Zn (1.55–1.85 apfu)

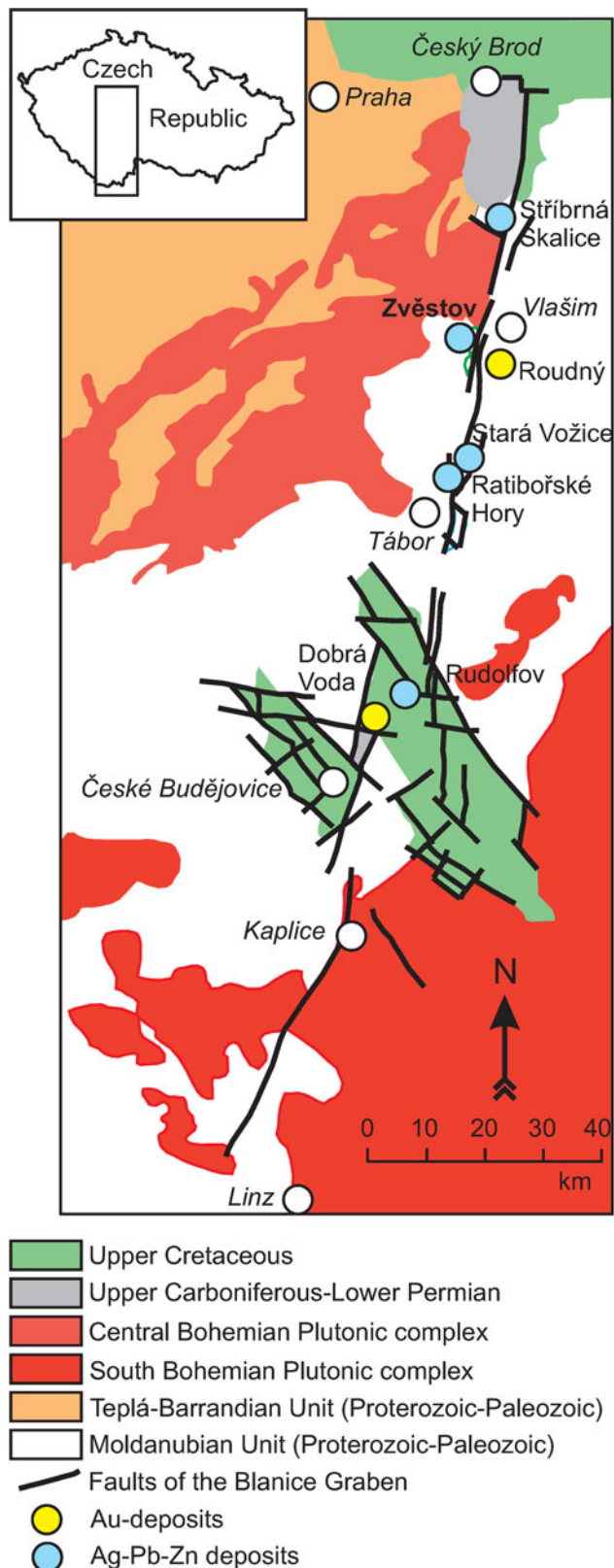


Fig. 1. Simplified geological map of the Blanice Graben and surrounding units with location of Au and Ag-Pb-Zn hydrothermal vein-type deposits (modified from Zachariáš and Hübst, 2012).

accompanied by minor Fe (0.07–0.15 apfu) and Cd (0.02–0.05 apfu). Arsenic (2.05–2.37 apfu) always prevails over Sb (1.35–1.79 apfu). The determined contents of S are in the range

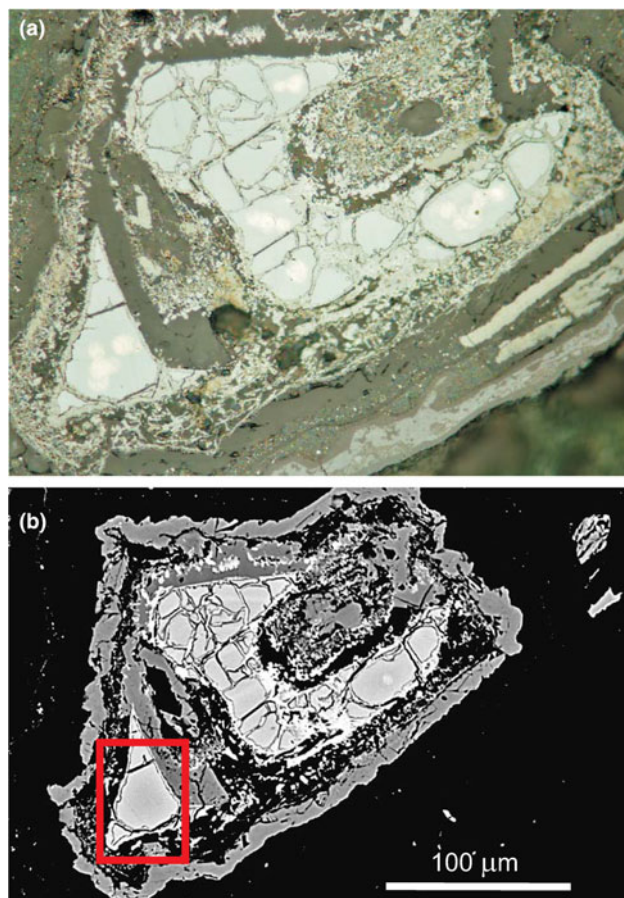


Fig. 2. Zvěstovite-(Zn), as relict grains rimmed by acanthite; (a) reflected light photo, partly crossed polarisers; (b) back-scattered electron photo, where the area of extracted fragment for single-crystal X-ray diffraction study is outlined in red. Holotype material (catalogue number P1P 50/2020).

12.32–12.99 apfu, values of S > 12.50 apfu were found for 9 of the 14 point analyses (Table 3).

X-ray diffraction data

Powder X-ray diffraction data could not be collected, due to the paucity of available material. Consequently, powder X-ray diffraction data, given in Table 4, were calculated using the software *PowderCell 2.3* (Kraus and Nolze, 1996) on the basis of the structural model discussed below.

A short prismatic fragment of zvěstovite-(Zn), 50 μm × 40 μm × 30 μm, extracted from the polished section analysed using electron microprobe (Fig. 2), was mounted on a glass fibre and examined with a Bruker Smart Breeze diffractometer equipped with an air-cooled CCD detector (Dipartimento di Scienze della Terra, Università di Pisa), and graphite-monochromatised MoK α radiation. The detector-to-crystal distance was 50 mm. Data were collected using ω scan mode, in 0.5° slices, with an exposure time of 45 s per frame. Owing to the small crystal size and the weakness of the observed reflections, intensity data collection was possible up to $2\theta = \sim 47^\circ$. From the total of 2367 reflections, 199 were independent and 193 classified as unique observed with $I > 4\sigma(I)$. The data were corrected for Lorentz and polarisation factors and absorption using the software package *Apex3* (Bruker AXS Inc., 2016).

Table 1. Reflectance values (%) for zvěstovite-(Zn).

λ (nm)	<i>R</i>	λ (nm)	<i>R</i>	λ (nm)	<i>R</i>
400	29.1	520	27.6	620	24.5
420	29.2	540	27.1	640	24.0
440	29.0	546	26.9	650	23.8
460	28.7	560	26.5	660	23.6
470	28.5	580	25.9	680	23.2
480	28.3	589	25.5	700	22.9
500	27.9	600	25.1		

The reference wavelengths required by the Commission on Ore Mineralogy (COM) are given in bold.

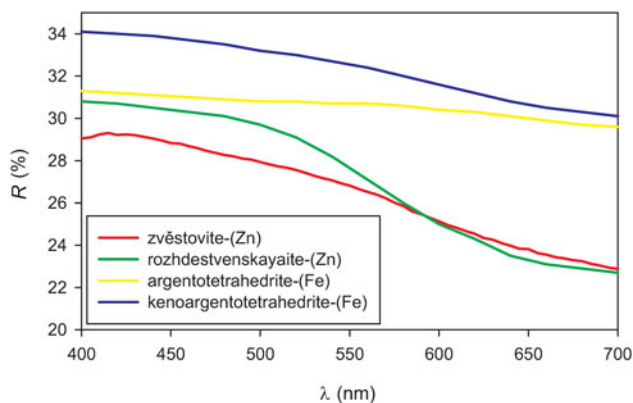


Fig. 3. Reflectance curve for zvěstovite-(Zn) compared with published data (Welch *et al.*, 2018) for rozhdstvenskayaite-(Zn), argentotetraedrite-(Fe) and kenoargentotetraedrite-(Fe).

Table 2. Chemical data (wt.%) for zvěstovite-(Zn) crystal used for the single-crystal X-ray study ($n = 4$) and chemical formula (apfu) based on $\Sigma Me = 16$ apfu.

Constituent	Mean	Range	S.D. (σ)	Apfu	S.D. (σ)
Cu	1.23	0.34–1.84	0.65	0.38	0.20
Ag	55.60	53.73–57.47	1.52	10.17	0.25
Fe	0.24	0.22–0.26	0.02	0.09	0.01
Zn	5.29	5.17–5.43	0.11	1.60	0.04
Cd	0.18	0.15–0.24	0.04	0.03	0.01
As	8.57	8.39–8.73	0.17	2.26	0.06
Sb	9.11	8.53–9.41	0.39	1.48	0.06
S	20.30	20.16–20.51	0.15	12.50	0.09
Total	100.52	99.58–101.07	0.64		

S.D. – standard deviation

The crystal structure of zvěstovite-(Zn) was refined using *Shelxl*-2018 (Sheldrick, 2015) starting from the atomic coordinates of rozhdstvenskayaite-(Zn) (Welch *et al.*, 2018). The occurrence of a racemic twin was modelled [twin ratio 0.4(2)]. The following neutral scattering curves, taken from the *International Tables for Crystallography* (Wilson, 1992) were used: Ag vs. vacancy at $M(2)$; Ag vs. Zn at $M(1)$; As vs. Sb at $X(3)$; and S at $S(1)$ and $S(2)$ sites. An isotropic model converged to $R_1 = 0.09$, thus confirming the correctness of the structural model. Site occupancies at the split $M(2a)$ and $M(2b)$ positions were found close to a full Ag occupancy at $M(2)$; consequently, in the latest stages of the refinement, the sum of the site occupancies at the two split sites was constrained to full occupancy. The anisotropic structural model converged to $R_1 = 0.0508$ for 193 reflections with $F_o > 4\sigma(F_o)$

and 27 refined parameters. Details of data collection and refinement are given in Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters are reported in Table 6. Table 7 reports selected bond distances. Finally, Table 8 gives the bond-valence sums (BVS) obtained using the bond-valence parameters of Brese and O’Keeffe (1991). Anisotropic displacement parameters are reported in the crystallographic information file, which has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

Crystal structure of zvěstovite-(Zn)

The crystal structure of zvěstovite-(Zn) agrees with the general features of the members of the tetrahedrite group. The $M(2)$ site was found to be split into two sub-positions, labelled $M(2a)$ and $M(2b)$ (Fig. 5), similar to those reported by Makovicky *et al.* (2005) in Cu-excess unsubstituted tennantite, and by Welch *et al.* (2018) in rozhdstvenskayaite-(Zn). Both positions are triangularly coordinated. The observed distances agree with the Ag-pure nature of this position, in agreement with figure 5 of Welch *et al.* (2018). The BVS calculated at these two sub-positions, assuming the full occupancy by Ag, results in a good agreement for $M(2b)$ [BVS = 0.97 valence units, vu], whereas the BVS at $M(2a)$ shows an important overbonding [BVS = 1.62 vu]. Indeed, whereas the mean $\langle M(2b)-S \rangle$ distance is 2.57 Å, the $\langle M(2a)-S \rangle$ is 2.39 Å, too short with respect to ideal $\langle Ag-S \rangle$ in three-fold coordination, 2.56 Å. This short average distance is mainly related to the short $M(2a)-S(2)$ distance. This behaviour was observed by Johnson *et al.* (1988) who highlight that three-fold Ag is distinctly aspherical, with the increase of the $M(2)-S(1)$ distance, related to the increasing Ag content in tetrahedrite-group minerals, being significantly larger than that observed for the $M(2)-S(2)$ bond. Indeed, Welch *et al.* (2018) reported a similar short $M(2a)-S(2)$ distance (2.284 Å) in rozhdstvenskayaite-(Zn). $M(2a)$ and $M(2b)$ show an elongate displacement ellipsoid having their elongation axes oriented approximately along a line connecting two $M(2b)$ positions with the $M(2a)$ site located between them. The distances $M(2a)-M(2b)$ and $M(2b)-M(2b)$ are 1.00(5) and 1.97(11) Å, to be compared with the corresponding $Cu2A-Cu2B$ and $Cu2B-Cu2B$ distances of 1.08(2) and 2.00(3) Å reported by Makovicky *et al.* (2005) for Cu-excess tennantite. Welch *et al.* (2018) proposed a split-site model for rozhdstvenskayaite-(Zn) using isotropic displacement parameters for the two split positions labelled $A1$ and $A2$, and they found distances $A1-A2$ and $A2-A2$ of 0.789(5) and 1.545(9) Å, respectively.

The tetrahedrally coordinated $M(1)$ site (Fig. 6) has a bond distance of 2.497(6) Å, in agreement with the $M(1)-S(1)$ distance reported for rozhdstvenskayaite-(Zn), i.e. 2.496(2) Å (Welch *et al.*, 2018). On the basis of the electron microprobe analysis, the site population ($Ag_{0.65}Zn_{0.27}Cu_{0.06}Fe_{0.02}$) can be proposed. The bond-valence sum at this site is 1.44 vu, in agreement with the theoretical value (1.31 vu, assuming all Cu as monovalent and Fe as Fe^{3+}).

The $X(3)$ site (Fig. 6) has bond distance of 2.322(8) Å and it shows a mixed ($As_{0.60}Sb_{0.40}$) site occupancy, in agreement with chemical data. The bond-valence sum is 3.21 vu. Taking into account the bond-valence approach, a better site occupation factor at $X(3)$ would be ($As_{0.70}Sb_{0.30}$), corresponding to ($As_{2.80}Sb_{1.20}$) apfu, with an $As/(As+Sb)$ slightly higher than that determined through electron microprobe (0.70 against 0.60).

Table 3. Representative analyses (wt.%) for zvěstovite-(Zn) from Zvěstov.*

	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]
Wt.%														
Ag	53.73	55.54	55.64	57.47	46.55	47.16	47.40	47.97	47.75	50.33	51.57	52.06	53.49	54.73
Cu	1.54	1.84	1.19	0.34	6.65	5.73	5.79	5.22	5.31	3.62	2.82	2.55	1.40	0.32
Fe	0.25	0.25	0.26	0.22	0.44	0.32	0.34	0.34	0.28	0.43	0.24	0.23	0.24	0.18
Cd	0.17	0.16	0.15	0.24	0.20	0.21	0.20	0.16	0.31	0.23	0.22	0.28	0.18	0.18
Zn	5.43	5.17	5.29	5.27	6.16	6.23	6.28	6.20	5.76	6.15	5.22	5.51	5.26	5.25
Sb	9.25	9.24	9.41	8.53	9.47	10.88	10.66	10.89	10.46	10.55	9.06	8.89	8.87	10.29
As	8.70	8.39	8.46	8.73	9.08	8.25	8.31	8.26	8.23	8.24	8.64	8.82	8.80	7.50
S	20.51	20.16	20.27	20.28	21.65	21.60	21.58	21.56	20.84	21.21	20.36	20.34	20.03	19.57
Total	99.58	100.74	100.65	101.07	100.20	100.38	100.56	100.60	98.94	100.76	98.13	98.68	98.27	98.02
Atoms per formula unit														
Ag	9.919	10.089	10.171	10.507	8.229	8.430	8.441	8.584	8.660	9.060	9.582	9.600	9.985	10.379
Cu	0.484	0.568	0.369	0.104	1.996	1.739	1.750	1.586	1.635	1.106	0.889	0.798	0.444	0.103
Ag + Cu	10.403	10.657	10.540	10.611	10.225	10.169	10.191	10.170	10.295	10.166	10.471	10.398	10.429	10.482
Fe	0.088	0.087	0.091	0.077	0.150	0.110	0.117	0.118	0.098	0.150	0.086	0.082	0.087	0.066
Cd	0.030	0.028	0.026	0.042	0.034	0.036	0.034	0.027	0.054	0.040	0.039	0.050	0.032	0.033
Zn	1.653	1.549	1.595	1.589	1.797	1.838	1.845	1.831	1.724	1.827	1.600	1.677	1.620	1.643
ΣMe^{2+}	1.771	1.664	1.712	1.708	1.981	1.984	1.996	1.976	1.876	2.016	1.726	1.808	1.739	1.742
Sb	1.513	1.487	1.523	1.382	1.483	1.723	1.682	1.727	1.681	1.683	1.491	1.452	1.467	1.729
As	2.313	2.193	2.225	2.299	2.311	2.123	2.131	2.128	2.149	2.136	2.311	2.342	2.365	2.048
Sb + As	3.826	3.680	3.749	3.681	3.794	3.847	3.812	3.855	3.830	3.818	3.803	3.794	3.832	3.777
S	12.741	12.318	12.463	12.472	12.876	12.990	12.928	12.979	12.715	12.844	12.727	12.618	12.579	12.485

*[1–4] crystal used for the single-crystal study; [5–14] other grains in holotype sample; coefficients of the empirical formula were calculated on the basis 16 *Me* apfu.

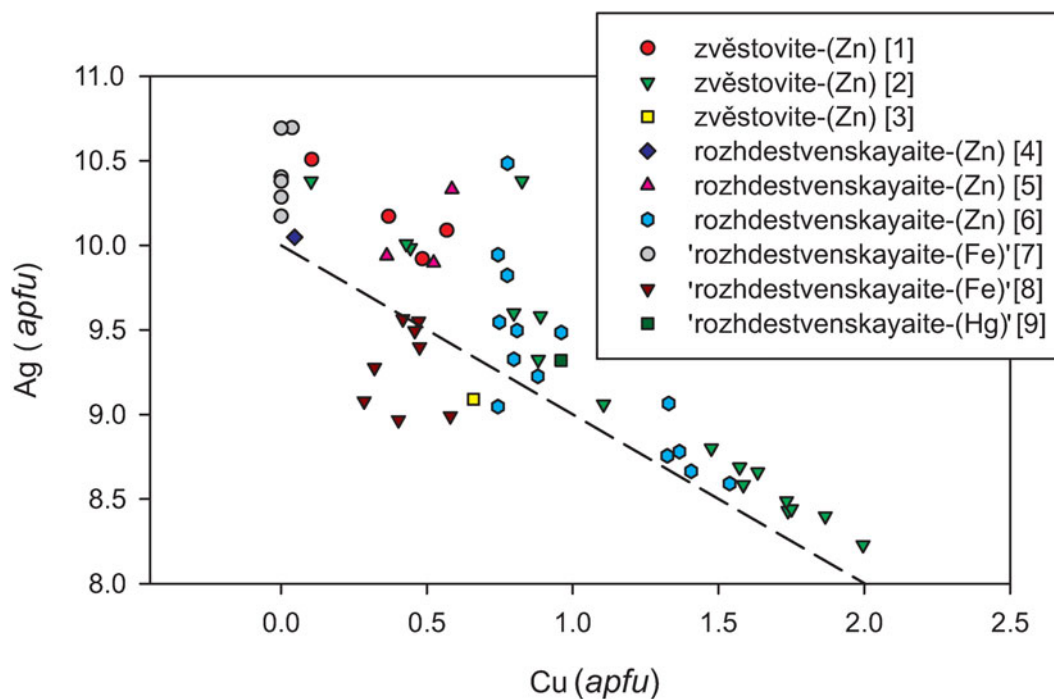


Fig. 4. Relation between Ag vs. Cu contents (apfu) in the zvěstovite and rozhdestvenskayaite series. Dashed line indicates the ideal $Cu + Ag = 10$ apfu. Zvěstovite-(Zn): [1] holotype sample – grain used for crystal structure study; [2] holotype sample – other grains; [3] Bad Lauterberg (Koch and Heider, 2018). Rozhdestvenskayaite-(Zn): [4] Moctezuma mine (Welch *et al.*, 2018); [5] Moctezuma mine (Sejkora, unpublished data), [6] Knappenstube (Paar *et al.*, 1978). Not approved 'rozhdestvenskayaite-(Fe)': [7] Khachakchan (Zhdanov *et al.*, 1992); [8] Dachang (Li and Wang, 1990). Not approved 'rozhdestvenskayaite-(Hg)': [9] O'Keefe pit, Steens-Pueblo (Foit and Ulbricht, 2001).

All the geometrical features of the studied samples agree with its isotopic relationships with rozhdestvenskayaite-(Zn) (Welch *et al.*, 2018). In addition, the volume of the $S(2)(Ag_6)$ octahedron, calculated using the $M(2a)$ position, is $\sim 15.3 \text{ \AA}^3$, agreeing with the volume observed in rozhdestvenskayaite-(Zn), i.e. 15.9 \AA^3 (Welch *et al.*, 2018). The refinement of the $S(2)$ site as fully occupied

results in a high U_{eq} value, $0.086(13) \text{ \AA}^2$, similar to that reported by Welch *et al.* (2018), i.e. $0.095(5) \text{ \AA}^2$. The occurrence of a minor vacancy at $S(2)$ may be possible, but the occurrence of Ag–Ag bonds as reported in kenoargentotetrahdrite-(Fe) was not observed. In addition, the high U_{eq} value, coupled with the short $M(2a)$ – $S(2)$, could be the result of the dynamic disorder

Table 4. Calculated powder X-ray diffraction data for zvěstovite-(Zn).*

l_{calc}	d_{calc} (Å)	hkl	l_{calc}	d_{calc} (Å)	hkl
6	7.6720	1 1 0	11	1.9809	5 2 1
4	4.4294	2 1 1	31	1.9180	4 4 0
100	3.1321	2 2 2	4	1.8607	4 3 3
1	2.8998	3 2 1	1	1.8083	4 4 2
21	2.7125	4 0 0	3	1.7601	6 1 1
5	2.5574	3 3 0	1	1.7601	5 3 2
1	2.5574	4 1 1	1	1.7155	6 2 0
1	2.3132	3 3 2	15	1.6357	6 2 2
1	2.2148	4 2 2	2	1.5660	4 4 4
1	2.1278	5 1 0	2	1.5344	7 1 0
5	2.1278	4 3 1			

*Intensity and d_{hkl} were calculated using the software PowderCell/2.3 (Kraus and Nolze, 1996) on the basis of the structural data given in Tables 5 and 6. Only reflections with $I_{\text{rel.}} \geq 0.5$ are listed. The five strongest reflections are given in bold.

Table 5. Summary of data collection conditions and refinement parameters for zvěstovite-(Zn).

Crystal data	
X-ray formula	Ag _{9.97} Zn _{2.03} (As _{2.40} Sb _{1.60})S ₁₃
Crystal size (mm)	0.050 × 0.040 × 0.030
Cell setting, space group	Cubic, $I\bar{4}3m$
a (Å)	10.850(2)
V (Å ³)	1277.3(8)
Z	2
Data collection	
Radiation, wavelength (Å)	MoK α , $\lambda = 0.71073$
Temperature (K)	293(2)
$2\theta_{\text{max}}$ (°)	46.63
Measured reflections	2367
Unique reflections	199
Reflections with $F_o > 4\sigma(F_o)$	193
R_{int}	0.0717
$R\sigma$	0.0393
Range of h, k, l	$-12 \leq h \leq 11, -12 \leq k \leq 11, -11 \leq l \leq 12$
Refinement	
R [$F_o > 4\sigma(F_o)$]	0.0508
R (all data)	0.0534
wR (on F_o^2)*	0.1585
Goof	1.256
Absolute structure parameter**	0.4(2)
No. of least-squares parameters	27
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e ⁻ Å ⁻³)	0.74 [at 0.99 Å from X(3)] -1.18 [at 1.61 Å from S(2)]

* $w = 1/[\sigma^2(F_o^2) + (0.0827P)^2 + 30.0580P]$, where $P = (F_o^2 + 2F_c^2)/3$

**Flack (1983)

Table 6. Atoms, atom coordinates and or equivalent isotropic displacement parameters (Å²) for zvěstovite-(Zn).

Site	Wyck.	s.o.f.	x/a	y/b	z/c	U_{eq}
M(2a)	12e	Ag _{0.53(6)}	0.2078(12)	0	0	0.048(9)
M(2b)	24g	Ag _{0.23(3)}	0.2229(12)	0.064(4)	-0.064(4)	0.052(10)
M(1)	12d	Ag _{0.66(7)} Zn _{0.34(7)}	1/4	1/2	0	0.0440(18)
X(3)	8c	As _{0.60(7)} Sb _{0.40(7)}	0.2594(4)	0.2594(4)	0.2594(4)	0.035(2)
S(1)	24g	S _{1.00}	0.1231(6)	0.1231(6)	0.3529(8)	0.035(3)
S(2)	2a	S _{1.00}	0	0	0	0.086(13)

Wyck – Wyckoff position; s.o.f. – site occupation factor

probably affecting both the positions of the M(2) and S(2) atoms. Indeed, an ordered distribution of S, with more reasonable Me–S distances, may be achieved through the splitting of S(2) in positions displaced from the (0,0,0) position.

Table 7. Selected bond distances (in Å) for zvěstovite-(Zn).

M(1)–S(1) ×4	2.497(6)	X(3)–S(1) ×3	2.322(8)
M(2a)–S(2)	2.255(13)		
M(2a)–S(1) ×2	2.458(12)		
M(2b)–S(1) ×2	2.55(2)		
M(2b)–S(2)	2.61(3)		

Table 8. Weighted bond-valence sums (in valence units) in zvěstovite-(Zn).

Site	M(1)	M(2a)	M(2b)	X(3)	Σ anions	theor.
S(1)	^{2x} →0.36 ^{x4}	0.23 ^{x2}	0.16 ^{x2}	1.07 ^{x3}	2.18	2.00
S(2)		^{6x} →0.40	^{6x} →0.14		3.24	2.00
Σ cations	1.44	0.86	0.46	3.21		
theor.	1.27	0.53	0.47	3.00		

Discussion

Recalculation of chemical formulae of Ag-rich tetrahedrites

There are several different approaches to recalculate the chemical formula of the minerals belonging to the tetrahedrite group.

- (1) Normalisation on the basis $\Sigma S(+Se) = 13$ apfu, which prevails in the older literature especially. However, there is clear crystallographic evidence of the possible occurrence of vacancies at the S(2) site (e.g. Rozhdestvenskaya *et al.*, 1993; Welch *et al.*, 2018; Škácha *et al.*, 2020). Moreover, it is recognised that the S content of tetrahedrite-group minerals determined by electron microprobe can be substantially affected by analytical uncertainty, as seen in many published analyses (e.g. Repstock *et al.*, 2016; Wang *et al.*, 2018). Thus, this recalculation basis is clearly unsatisfactory as it assumes a fixed (S + Se) content, which in reality can be highly variable (Welch *et al.*, 2018).
- (2) Normalisation on the basis of $\Sigma Me = 16$ apfu. This recalculation assumes that no vacancies occur at M(2), M(1) and X(3). However, vacancies are known there, especially in the case of goldfieldite (Makovicky and Karup-Møller, 2017; Biagioni *et al.*, 2020a) or pošepnýite (Škácha *et al.*, 2020). Consequently, this normalisation can be used in several cases, but it should be avoided for Te-rich members of the tetrahedrite group.
- (3) Normalisation on the basis of (As + Sb + Bi + Te) = 4 apfu. Previous studies (e.g. Johnson *et al.*, 1986) revealed negligible variations with respect to the ideal number of D atoms that occur.
- (4) Normalisation on the basis of all 29 apfu for the general formula. This recalculation could mask some S deficit (e.g. only 12 apfu S instead 13 in the case of kenoargentotetrahedrite-(Fe); Biagioni *et al.*, 2020a) or vacancies at M(2) and M(1) sites (Biagioni *et al.*, 2020a; Škácha *et al.*, 2020).

Silver-rich members of the tetrahedrite group can show variable S contents, related to the possible occurrence of a S vacancy at S(2) and presence of (Ag₆)⁴⁺ clusters. Consequently, chemical formulae of these compounds should be normalised on the basis of normalisation procedures (2) or (3). For zvěstovite-(Zn) the normalisation on the basis of $\Sigma Me = 16$ apfu gives the formula (Ag_{10.17}Cu_{0.38}Zn_{1.60}Fe_{0.09}Cd_{0.03}) Σ _{12.27}(As_{2.26}Sb_{1.48}) Σ _{3.74}S_{12.50}. On the basis of the crystal structure refinement the following crystal-chemical formula can be written: Ag_{6.27}(Ag_{3.90}Cu_{0.38}Zn_{1.60}Fe_{0.09}

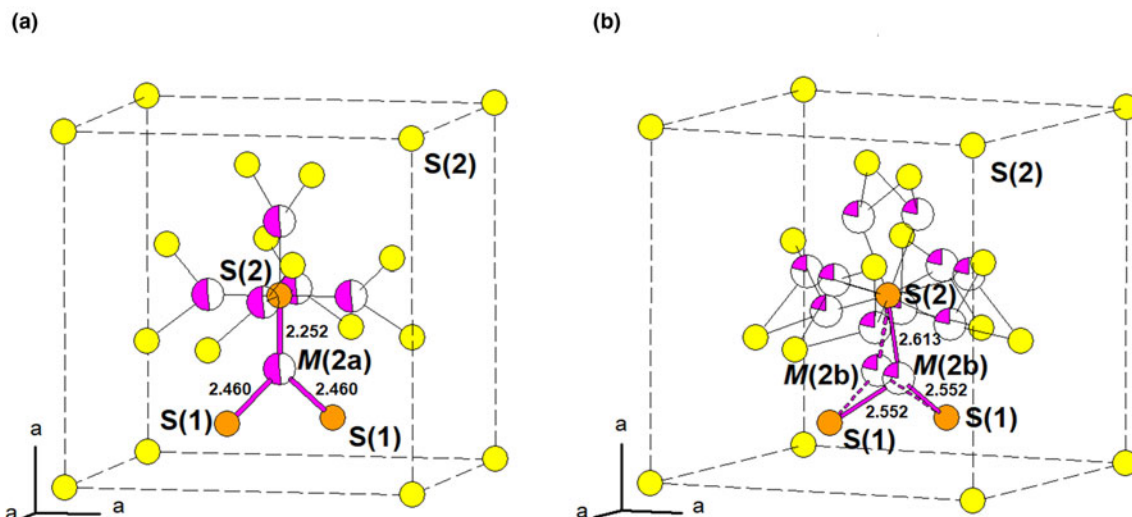


Fig. 5. Coordination of the two split sites $M(2a)$ and $M(2b)$ (a and b, respectively).

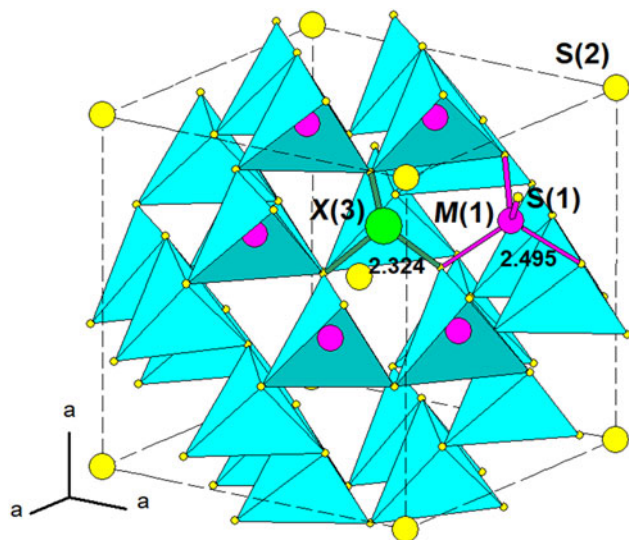


Fig. 6. Coordination of the $M(1)$ and $X(3)$ sites.

$Cd_{0.03}\Sigma_{6.00}(As_{2.26}Sb_{1.48})\Sigma_{3.74}S_{12.50}$. The alternative empirical formula, based on $As + Sb = 4$ apfu, is $(Ag_{10.90}Cu_{0.41}Zn_{1.71}Fe_{0.09}Cd_{0.03})\Sigma_{13.14}(As_{2.42}Sb_{1.58})\Sigma_{4.00}S_{13.39}$. On the basis of the crystal structure, the following crystal-chemical formula can be written as $Ag_{7.14}(Ag_{3.76}Cu_{0.41}Zn_{1.71}Fe_{0.09}Cd_{0.03})\Sigma_{6.00}(As_{2.42}Sb_{1.58})\Sigma_{4.00}S_{13.39}$. In both cases, the $Ev(\%)$ value, where $Ev(\%) = [\Sigma(val+) - \Sigma(val-)] \times 100 / \Sigma(val-)$, assuming all Cu as Cu^+ and Fe as Fe^{3+} , is +0.7(8), ranges between +0.1 and +1.9.

Ag excess in *zvěstovite*-(Zn)

The observed Ag(+Cu) excess in *zvěstovite*-(Zn) has to be discussed. The occurrence of a Cu excess is known in tennantite (e.g. Makovicky *et al.*, 2005); moreover, Maske and Skinner (1971) reported a compositional field between $Cu_{12.3}As_4S_{13}$ and $Cu_{13.7}As_4S_{13}$ for synthetic tennantite. Possibly, a similar mechanism could also act in Ag-bearing members of the tetrahedrite group, although no previous data are available. The excess of

Ag (0.27 apfu in the formula normalised on $\Sigma Me = 16$ apfu, and 1.14 apfu in the formula normalised on the sum of Sb and As), would correspond to a value of electrons per site (assuming a six-fold multiplicity of the site in a formula unit) ranging between ~ 2 and ~ 9 electrons. No additional maxima in the difference-Fourier maps, suggesting the occurrence of possible additional Ag sites having a low occupancy, were detected.

Another possibility is that the Ag excess could be related to a deficiency in the sum of D cations. One could propose that the observed excess of Ag (0.27 apfu) and the (As + Sb) and S deficit (0.26 and 0.50 apfu, respectively) occurring in *zvěstovite*-(Zn) may be explained through the substitution $(As/Sb)^{3+} + S^{2-} = Ag^+ + \square$. The site scattering refined at the $X(3)$ site is 40.25 electrons; assuming that the Ag excess occurs at the $X(3)$ site, the calculated site scattering, with the population $(As_{0.56}Sb_{0.37}Ag_{0.07})$, would be 40.64 electrons, in agreement with the observed value. However, assuming a full occupancy at the $X(3)$ site by As and Sb only, the calculated site scattering would be 40.11 electrons. Moreover, the average $\langle X(3)-S \rangle$ distance suggests a higher As/(As + Sb) atomic ratio, compatible with the occurrence of higher amounts of smaller cations; on the contrary, the presence of Ag should probably increase the bond length. However, taking into account the relatively low quality of the structural refinement, the very minor Ag substitution, and the absence of any hints suggesting detectable S vacancies, there is no proof supporting this substitution in *zvěstovite*-(Zn).

As *zvěstovite*-(Zn) could be an ionic conductor, the analytical shift observed with respect to the ideal stoichiometry could be due to the migration of some Ag at the surface of the polished section under the electron beam. Considering that some Ag-excess was observed in other Ag-rich members of the tetrahedrite group, more data are required to solve this issue. Previous authors (e.g. Lind and Makovicky, 1982; Makovicky and Karup-Møller, 1994) discussed the analytical problems arising during electron microprobe analysis of tetrahedrite-group minerals. In particular, they stressed the analytical shifts related to the choice of different standards as well as the apparent Cu migration under the electron beam, leading to a shift of all Cu-enriched tetrahedrites towards the minimum Cu content.

Table 9. Comparison of members of the zvěstovite and rozhdestvenskayaite series.

Mineral	zvěstovite-(Zn)	rozhdestvenskayaite-(Zn)	'rozhdestvenskayaite-(Fe)'	'rozhdestvenskayaite-(Fe)'
Source	Zvěstov	Moctezuma	Dachang	Khachakchan
Reference	this paper	Welch <i>et al.</i> (2018)	Li and Wang (1990)	Zhdanov <i>et al.</i> (1992)
A	Ag _{6.27}	Ag _{6.05}	Ag _{5.98}	Ag _{6.28}
B	Ag _{3.90} Cu _{0.10}	Ag _{4.00}	Ag _{3.58} Cu _{0.42}	Ag _{4.00}
C	Zn _{1.60} Cu _{0.28} Fe _{0.09} Cd _{0.03}	Zn _{1.62} Cd _{0.17} Fe _{0.09} Cu _{0.05}	Fe _{1.96} Zn _{0.14}	Fe _{0.97} Zn _{0.77} Hg _{0.15}
D	As _{2.26} Sb _{1.48}	Sb _{3.70} As _{0.34}	Sb _{3.92}	Sb _{3.75} As _{0.08}
<i>a</i> (Å)	10.850(2)	10.9845(5)	10.950	10.92

Note: 'rozhdestvenskayaite-(Fe)' is not currently an approved member of this series.

Zvěstovite-(Zn) in the framework of the tetrahedrite group

Zvěstovite-(Zn) has isotopic relations with its Sb-analogue, rozhdestvenskayaite-(Zn) (Welch *et al.*, 2018). Both minerals are currently unassigned members of the tetrahedrite group. However, as detailed above, several occurrences of potential new minerals suggest that, in addition to the potential rozhdestvenskayaite series already proposed in Biagioni *et al.* (2020a), the zvěstovite series, characterised by the chemical constituents A = Ag, B = Ag, and D = As, is likely to be created.

A comparison between selected data of zvěstovite-(Zn) and valid or potential members of the not-yet formally existing rozhdestvenskayaite series is shown in Table 9. Although zvěstovite-(Zn) does not correspond to any valid or invalid unnamed mineral (Smith and Nickel, 2007), tetrahedrite-group minerals having chemical compositions corresponding to that of zvěstovite-(Zn) were reported previously from the Sark's Hope mine, Sark, Channel Islands, by Ixer and Stanley (1983), and from the Frische Lutter mine, near Bad Lauterberg, Harz, Germany, by Koch and Heider (2018). A potential Fe-analogue, 'zvěstovite-(Fe)', was described by Gan (1980) from the Manson Lode deposit, North Kentalan, Malaysia.

Stability of Ag-rich members of the tetrahedrite group

The two Ag-pure members of the tetrahedrite group can be considered as mixtures of ZnS with two simple Ag sulfosalts, i.e. ideal zvěstovite-(Zn) as $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{As}_4\text{S}_{13} = 2\text{ZnS} + 3\text{Ag}_3\text{AsS}_3 + \text{AgAsS}_2$ and ideal rozhdestvenskayaite-(Zn) as $\text{Ag}_6(\text{Ag}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13} = 2\text{ZnS} + 3\text{Ag}_3\text{SbS}_3 + \text{AgSbS}_2$.

In Ag-rich sulfide ores, such simple Ag sulfosalts are very common and associated frequently with sphalerite, which would favour the formation of these two Ag-pure members of the tetrahedrite group, contrary to the observations. Their rarity may be due to crystal-chemical constraints related to Ag coordination with S. These two tetrahedrite-group minerals have major IVAg^+ together with III Ag^+ , while simple Ag sulfosalts have major III Ag^+ and II Ag^+ . Thus, contrary to Cu^+ , it appears more difficult to stabilise Ag^+ in tetrahedral coordination relative to triangular or linear coordination, and it is possible that such a stabilisation is subordinated to low-*T* conditions.

Conclusion

Zvěstovite-(Zn) is a new Ag-rich member of the tetrahedrite group, isotopic with rozhdestvenskayaite-(Zn), and the first mineral of a potential new series (i.e. the zvěstovite series). Its crystal chemical study improves the knowledge of this important group of sulfosalts and provides further data for a better understanding

of Ag-rich tetrahedrites. Indeed, only accurate structural investigations on samples characterised by different chemical compositions will allow us to achieve a full understanding of the relations between Ag and S contents in these complex chalcogenides, which can pose such severe difficulties in their correct classification.

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Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2021.57>

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