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SHORT COMMUNICATION

Chemical and crystallographical investigations on edenharderite ($\text{TlPbAs}_3\text{S}_6$)*

Peter Berlepsch¹

Abstract

Edenharderite ($\text{TlPbAs}_3\text{S}_6$) was analyzed in detail by means of an electron microprobe. The analyses clearly showed that Sb is always present in edenharderite (max. 2.7 wt%), a feature not known until now. A correlation between As and Sb could not be observed.

A structural analysis on the mineral edenharderite was performed. The structure of natural edenharderite is not significantly different from that of the synthetic compound $\text{TlPbAs}_3\text{S}_6$. Some structural data for both the mineral and the synthetic compound are compared.

Keywords: edenharderite, Tl-As-sulphosalts, microprobe analyses, crystal structure, Lengenbach (Binntal, Switzerland).

Introduction

The aim of the present work, which is part of the current research project on new minerals from the Lengenbach quarry, Binntal, Switzerland (see e.g. GRAESER et al., 1992), is to show the results of detailed chemical and crystallographical investigations on the mineral edenharderite ($\text{TlPbAs}_3\text{S}_6$).

Edenharderite (orthorhombic; $a = 15.465(3)$, $b = 47.507(8)$, $c = 5.843(2)$, space group $Fdd2$) was described as a new mineral by GRAESER and SCHWANDER (1992). It is one of at least eleven Tl-As-sulphosalts that were found in the Lengenbach quarry so far (S. Graeser in HOFMANN et al., 1993). The crystal structure of a new compound synthesized by A. Edenharder (in NOWACKI et al., 1982), with the chemical composition $\text{TlPbAs}_3\text{S}_6$ has been published by BALIC-ZUNIC and ENGEL (1983). From comparison of the single-crystal X-ray data of the two compounds GRAESER and SCHWANDER (1992) concluded that both edenharderite and the synthetic compound are identical phases.

The discovery of another new mineral

(jentschite, monoclinic., space group $P2_1/n$; GRAESER and EDENHARTER, in prep; GRAESER, EDENHARTER and BERLEPSCH, 1995) with similar chemical composition (idealized: $\text{TlPbAs}_2\text{SbS}_6$) but different symmetry requires a series of detailed chemical and crystallographical investigations. To get the basis for detailed comparison between the two minerals, the chemistry of edenharderite was studied and a structure refinement on the mineral was performed.

Chemical investigations

EXPERIMENTAL

Because limited amounts of material were available, only a few crystals were analyzed. For the chemical analyses with an electron microprobe six crystals were separated from six different rock samples. On these samples edenharderite (associated with various other Tl-sulphosalts) had already been identified by X-ray methods (Gandolfi camera) sometimes ago. All samples originate from the Lengenbach quarry, which is the

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Tab. 1 Summarized microprobe analyses (all wt%) of three crystals (above). The standard deviation (σ_{n-1}) and the analytical error (a. e.) are given for the edenharterite phases only. Normalized edenharterite formulae (Tl = 1) and charge balances (below).

		L 19746				L 20435		L 20486		
	N a. e.	Edenharterite 14	Baumhauerite 9	Unknown 8		Edenharterite 10		Edenharterite 25	Baumhauerite 5	
		wt% σ_{n-1}	wt%	wt%		wt% σ_{n-1}		wt% σ_{n-1}	wt%	
Tl	0.5	24.64 0.60	4.66	4.34		24.71 0.38		24.51 0.47	5.37	
Pb	0.5	23.69 0.83	44.88	42.22		23.44 0.45		23.36 0.46	45.33	
As	0.2	25.69 0.49	24.62	27.48		27.03 0.30		27.14 0.35	23.86	
Sb	0.03	1.60 0.45	0.98	0.84		1.32 0.22		1.00 0.14	1.67	
S	0.6	23.86 0.27	24.68	25.85		23.50 0.20		23.33 0.26	23.28	
Sn		<0.04 ---	<0.04	<0.04		<0.04 ---		<0.04 ---	<0.04	
Cu	0.04*	0.05 0.04	0.07	0.04		<0.04 ---		<0.04 ---	<0.04	
Zn		<0.05 0.02	<0.05	<0.05		---		<0.05 ---	<0.04	
Σ		99.55	99.91	100.79		100.02		99.35	99.51	

N = number of analyses; a. e. = analytical error (wt%, from count statistics on edenharterite); * = detection limit

Sample	Normalised edenharterite formulae (Tl = 1)	Σ As+Sb (at%)	c. b.
L 19746	$Tl_1 Pb_{0.95 \pm 0.05} (As_{2.85 \pm 0.08} Sb_{0.11 \pm 0.03}) S_{6.18 \pm 0.19}$	2.96 ± 0.09	-0.6 ± 0.2
L 20435	$Tl_1 Pb_{0.94 \pm 0.02} (As_{2.98 \pm 0.06} Sb_{0.09 \pm 0.02}) S_{6.06 \pm 0.11}$	3.07 ± 0.06	-0.0 ± 0.1
L 20486	$Tl_1 Pb_{0.94 \pm 0.03} (As_{3.02 \pm 0.08} Sb_{0.07 \pm 0.01}) S_{6.07 \pm 0.17}$	3.09 ± 0.08	-0.0 ± 0.2
c. b. = charge balance			

only locality where edenharterite has been found so far. Unfortunately semi-quantitative EDS analyses performed with a PHILIPS SEM 515 (equipped with EDS system) showed that only three of the six crystals had the composition of edenharterite.

CHEMICAL COMPOSITION

Quantitative chemical analyses were carried out on all six crystals by means of an electron microprobe (JEOL JXA-8600 superprobe, ZAF correction). The elements S, As, Sb, Tl, Pb and Cu, Zn, Ag, Sn were quantitatively analyzed using the following standards: TlAs₂ (S K_{α} PET, As L_{α} TAP and Tl M_{α} PET), Sb₂S₃ (Sb L_{α} PET) as well as PbS (Pb M_{α} PET), CuFeS₂ (Cu K_{α} LiF), ZnS (Zn K_{α} LiF), Ag₂S (Ag L_{β} PET) and SnS (Sn L_{β} PET). The conditions of measurement were: acceleration voltage 15 kV, beam current 20 nA, scanned area 15 μm^2 . The results of the analyses are summarized in table 1.

The crystal L 19746 is inhomogenous (Fig. 1) and composed of three different Sb-bearing phases; edenharterite ($TlPbAs_3S_6$), baumhauerite ($Pb_3As_5S_9$) and an unknown phase ($Pb_3(As,Sb)_5S_{11}$). The crystal L 20435 is homogeneous edenharterite. Crystal L 20486 is inhomogenous and consists mainly of edenharterite with minor amounts of baumhauerite. The formulae of edenharterite differ from those given by GRAESER and SCHWANDER (1992) particularly by higher contents of As+Sb and S, but they are similar with respect to Tl and Pb.

The remaining three crystals are wallsite ($TlPb(Cu,Ag)As_2S_5$, L 24582), an intergrowth of jordanite ($Pb_{14}(As,Sb)_6S_{23}$, L 18989) with an unidentified Pb-As-sulphosalt and another Pb-As-sulphosalt (L 24626) with extremely small lamellae of probably edenharterite. The latter three samples are not discussed in detail.

In the original description of the chemical composition of edenharterite (GRAESER and SCHWANDER, 1992) very small amounts of Sn but no Sb were reported. In contrast to that, all

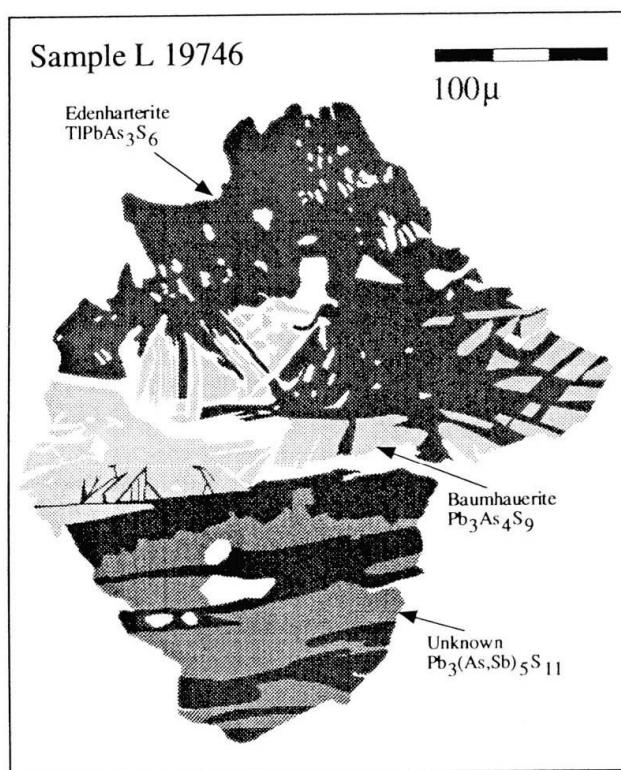


Fig. 1 The inhomogeneous crystal L 19746: schematic presentation of the three different phases (all Sb bearing) edenharterite ($\text{TiPbAs}_3\text{S}_6$), baumhauerite ($\text{Pb}_3\text{As}_4\text{S}_9$) and an unknown sulfosalt ($\text{Pb}_3(\text{As},\text{Sb})_5\text{S}_{11}$).

recently analyzed crystals of edenharterite contain significant amounts of Sb (max. 2.7 wt%) like the associated baumhauerite. Traces of Sn, Cu and Zn but no Ag were also found in some cases.

The variations in the chemical composition of edenharterite are small (Fig. 2). With the given analytical error (Tab. 1) the three crystals of edenharterite exhibit almost homogenous composition. A distinct correlation between As and Sb could not be observed (Fig. 3).

From these observations it can be seen that a limited substitution of As by Sb exists in edenharterite. Compared to the synthetic compound, which is a pure As-edenharterite, natural edenharterite contains up to 2.7 wt% of Sb (= 0.19 mol%).

Structure refinement

EXPERIMENTAL

A structure determination of the mineral edenharterite has not been performed so far. According to the X-ray data and chemical composition it was suggested that both the natural and the syn-

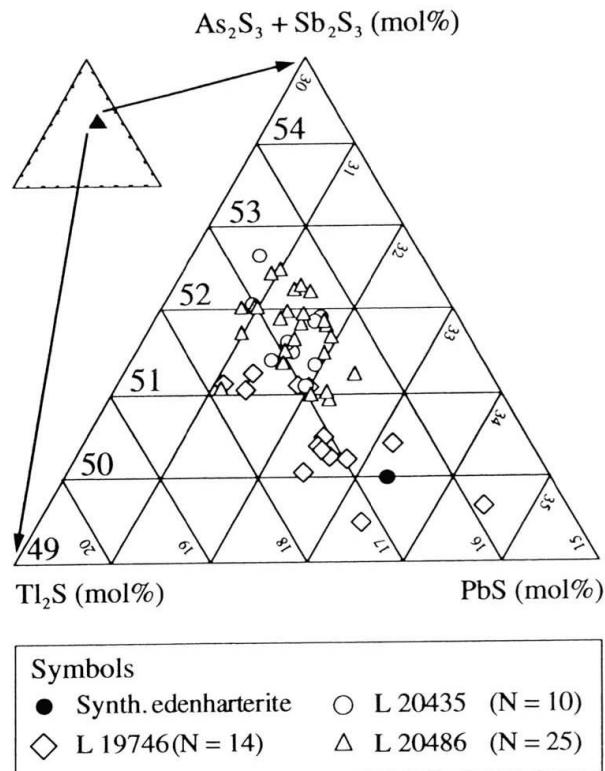


Fig. 2 Triangular plot with Tl_2S (mol%), PbS (mol%) and $\text{As}_2\text{S}_3 + \text{Sb}_2\text{S}_3$ (mol%) which shows almost no variations in the chemical composition of edenharterite within the analytical error.

thetic compound represent identical structures. To verify this and to check whether or not the substitution of As by Sb has an influence on the crystal structure of edenharterite, a structure refinement was executed.

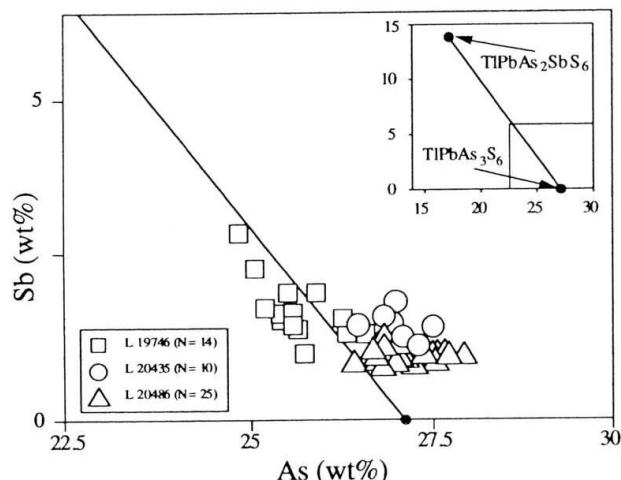


Fig. 3 Variation diagram with Sb (wt%) against As (wt%). Poor correlation between As and Sb can be observed. The line indicates the theoretical correlation curve for perfect substitution of As by Sb between $\text{TiPbAs}_3\text{S}_6$ and $\text{TiPbAs}_2\text{SbS}_6$.

The X-ray data collection was performed on a platy crystal, measuring about $0.045 \times 0.19 \times 0.26$ mm, by means of an ENRAF NONIUS FR 590 CAD4 automatic single-crystal diffractometer with Kappa geometry. The lattice parameters were determined and refined, using 25 reflections within the angular range $26.76^\circ < \vartheta < 52.16^\circ$. Diffraction intensities were measured within the range $5.4^\circ < 2\vartheta < 155^\circ$, using graphite monochromatized Cu K_α radiation ($\lambda = 1.54178 \text{ \AA}$) and operating in the ω - 2ϑ scan mode. Data reduction included background and Lorentz-polarization corrections. The data were empirically corrected for absorption by using ψ scans.

The obtained space group ($F2dd$) and cell parameters (orthorhombic; $a = 5.848(1)$, $b = 15.478(2)$, $c = 47.600(9)$) are in agreement with the data from GRAESER and SCHWANDER (1992) as well as with own results from Weissenberg and precession investigations. Based on 1155 independent reflections ($I_{\text{obs}} > 3\sigma[I_{\text{obs}}]$), the structure was solved using the model by BALIC-ZUNIC and ENGEL (1983) and refined anisotropically to a R -value = 13.8%. In agreement with the rules of DONNAY and ONDIK (1973) for orientation of unit cells, the space group was subsequently transformed into $Fdd2$.

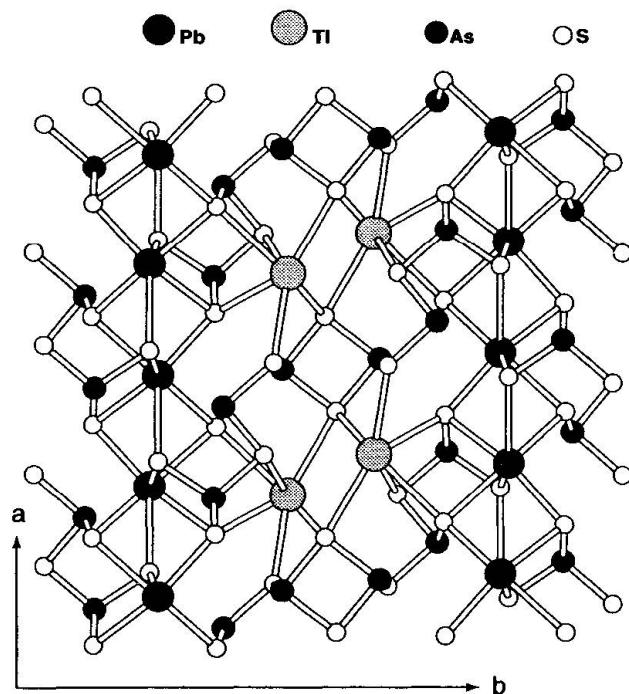


Fig. 4 Central projection of the edenharderite structure (only part of the unit cell) along the c -axis. The structure consists of As_6S_{12} clusters which themselves are connected to the PbS_3 planes, thus forming the full crystal structure of edenharderite (Fig. 4). The As-S distances range from 2.23 \AA to 2.32 \AA identical with the data from BALIC-ZUNIC and ENGEL (1983).

DISCUSSION

The structure by BALIC-ZUNIC and ENGEL (1983) for the synthetic compound ($\text{TlPbAs}_3\text{S}_6$) and the structure of edenharderite (this paper) can easily be converted into each other. The poor value of R does not permit detailed conclusions.

Thallium: Tl is surrounded by one As- and nine S-atoms in a distance ranging from 3.17 \AA to 3.87 \AA . For the graphical presentation (Fig. 4) some restrictions were made. Bonds between Tl and S are drawn only for atoms closer than the nearest As atom. In this case seven Tl-S bonds are drawn in a range from 3.17 \AA to 3.42 \AA . Tl forms As_6S_{12} double chains along [001]. For the synthetic compound BALIC-ZUNIC and ENGEL (1983) indicate a seven plus two coordination of S-atoms around Tl, seven S-atoms in a range from 3.17 \AA to 3.39 \AA , and two more distant S-atoms (3.67 \AA and 3.88 \AA).

Lead: For the Pb-atoms the situation is similar. In general, the distances between Pb and S are smaller than those between Tl and S, which actually permits to distinguish these two atoms within the same structure (EDENHARTER, 1976). In the range up to 3.73 \AA Pb, like Tl, is surrounded by ten atoms. In contrast to Tl, Pb is surrounded by seven S- and three As-atoms. The restriction used for drawing Tl-S bonds can be neglected for Pb, because all seven S-atoms are closer than the nearest As-atom. Seven Pb-S bonds were drawn in a range from 2.74 \AA to 3.51 \AA . Pb forms As_6S_{12} double chains along [001] and PbS_3 planes parallel to (010) (Fig. 4). For the synthetic compound, BALIC-ZUNIC and ENGEL (1983) indicate a five plus two coordination of S-atoms around Pb. Five close S-atoms in a range from 2.80 \AA to 3.06 \AA and two more distant S-atoms (3.33 \AA and 3.48 \AA).

Arsenic: As forms the apex of a trigonal pyramid with S-atoms at the base. Six As_6S_{12} pyramids are connected to form As_6S_{12} clusters which themselves are connected to the As_6S_{12} double chains and the PbS_3 planes, thus forming the full crystal structure of edenharderite (Fig. 4). The As-S distances range from 2.23 \AA to 2.32 \AA identical with the data from BALIC-ZUNIC and ENGEL (1983).

Conclusions

In contrast to the original description of GRAESER and SCHWANDER (1992), Sb could be identified in all measured edenharderite crystals. Sb-contents vary from approximately 1 to 2.7 wt% (0.06 to 0.19 mol%). The presence of Sb in edenharderite was not known until now; it is of

special interest for the comparison of edenharterite and jentschite.

The structure refinement of edenharterite revealed, as expected, very similar crystal structures for both the synthetic compound and the mineral. Due to the poor R-value, no detailed conclusions can be made. The incorporation of Sb up to 2.7 wt% into the lattice of edenharterite has no influence to the formation of the mineral.

The next step in the current work will be a detailed study of jentschite to describe its chemistry, its chemical variations and its structure. This study may give the informations for understanding the structural change from orthorhombic to monoclinic symmetry.

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