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The crystal structure of pierrotite, $Tl_2(Sb, As)_{10}S_{16}$

P. Engel, M. Gostojić

Laboratorium für Kristallographie, Universität Bern,
Freiestrasse 3, CH-3012 Bern, Schweiz

and W. Nowacki

Mineralogisches Institut, Universität Bern,
Baltzerstrasse 1, CH-3012 Bern, Schweiz

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Abstract. The crystal structure of pierrotite, $Tl_2(Sb,As)_{10}S_{16}$ has been determined. Four formula units are contained in the orthorhombic unit cell, which has dimensions $a = 38.746(8)$, $b = 8.816(2)$ and $c = 7.989(2)$ Å. The space group is $Pna2_1$. The structure was determined with direct methods and refined with block-diagonal least-squares using anisotropic temperature factors and anomalous dispersion correction to a final R-value of 0.072 for 2975 observed reflections.

The AsS_3 and SbS_3 pyramides together with the SbS_4 and SbS_5 coordination polyhedra build up a three-dimensional framework. The $Tl(1)S_9$ coordination polyhedra form $^1_\infty[TlS_6]$ columns along the c axis and the $Tl(2)S_9$ coordination polyhedra form $^2_\infty[TlS_7]$ layers parallel to the (100) crystal face. Pierrotite is the first sulfosalt which shows a three-dimensional $^3_\infty[(Sb,As)_{10}S_{16}]$ framework.

Introduction

In 1970 Guillemin et al. described a new mineral, named pierrotite, from Jas-Roux (Hautes-Alpes), France. E. Asselborn provided us with some crystals of dark brown to black colour from Jas-Roux. Preliminary single crystal investigations showed that among these crystals there were two different minerals. One of them was identified from the crystal data as pierrotite and the other as chabourneite (Johan et al., 1981, Nagl, 1979). The crystal data obtained for pierrotite are presented in Table 1 and show very good

Table 1. Crystal data of pierrotite

	Pierrotite	present work
lattice parameters	$a=8.77$ Å	$a'=38.746(8)$ Å
	$b=38.8$	$b'=8.816(2)$
	$c=8.03$	$c'=7.989(2)$
space group	$Pbn2_1$ or $Pbnm$	$Pna2_1$
formula	$Tl_2(Sb,As)_{10}S_{17}$	$Tl_2(Sb,As)_{10}S_{16}$
$C_{obs.}$	4.97 g cm^{-3}	
$C_{calc.}$	4.97	4.75 g cm^{-3}

Table 2. Comparison of the composition of pierrotite determined by X-ray structure analysis and microprobe analysis

	Tl	Sb	As	S	Σ
I $Tl_2Sb_6As_4S_{16}$ (cryst. str. anal.)	20.94	37.42	15.35	26.28	100.00
	20.97	37.70	15.73	26.47	100.87
	20.86	37.86	15.54	26.63	100.89
II electron	20.94	37.77	15.53	26.51	100.75
microprobe	20.82	37.62	15.50	26.90	100.84
analysis	20.40	37.86	15.63	26.85	100.74
	21.24	37.42	15.49	26.25	100.40
	21.45	37.29	15.38	26.40	100.52
mean	20.95	37.65	15.54	26.57	100.70
III pierrotite	19.95	44.9	8.8	26.4	100.0
Guillemin et al. (1970)	19.9	43.3	8.9	26.9	99.0

agreement with the published data (we used the standard space group $Pna2_1$ with $a'=b$, $b'=a$, $c'=c$).

The findings of the present crystal structure determination, which were in good agreement with the microprobe analysis, gave the formula $Tl_2Sb_6As_4S_{16}$ for pierrotite, in contrast to the formula $Tl_2(Sb,As)_{10}S_{17}$ proposed by Guillemin. However, the crystal we used showed a higher As content than the one used by Guillemin, as can be seen from Table 2.

Experimental

From a selected crystal we prepared a small sphere, $R=0.058$ mm, for the single crystal study. Preliminary Weissenberg photographs with Cu$K\alpha$ radiation indicated that the crystal belongs to the orthorhombic system.

Systematic extinctions are: $0kl$, $k+l=2n+1$; $h0l$, $h=2n+1$; $h00$, $h=2n+1$; $0k0$, $k=2n+1$; $00l$, $l=2n+1$, which permit $Pna2_1$ and $Pnam$ as possible space groups. The determination of the lattice parameters and the intensity measurements were made with the NONIUS CAD 4 diffractometer using Mo$K\alpha$-radiation and a graphite monochromator ($\lambda=0.71069$ Å). 15 reflections determined with the NONIUS peak hunting procedure in the range $13° < 2\theta < 27°$ were carefully centered. Accurate cell parameters were calculated by the least-square procedure. The lattice parameters are given in Table 1.

The chemical composition was determined by an electron microprobe analysis (Type ARL, ETH Zürich) by A. Edenharter. The results of the microprobe analysis are presented in Table 2.

The calculated density is $d_x=4.75$ g cm^{-3} for four formula units per unit cell. A total of 4242 independent reflections in the range $1.5° \leqslant 2\theta \leqslant 60°$ were measured with the $\omega-2\theta$ scanning technique. 2975 reflections with $I > 2.57\sigma(I)$ were obtained. The measured intensities were corrected for Lorentz-polarisation and absorption effects ($\mu=182.94$ cm^{-1}).

Structure determination and refinement

The structure factors were converted to normalized E-values. The statistical distribution of the E-values gave no clear indication for the centrosymmetric space group. The theoretical values are given in brackets.

		centric	non-centric
$\langle\|E\|\rangle$	0.847	(0.798)	(0.886)
$\langle\|E^2\|\rangle$	1.027	(1.0)	(1.0)
$\langle\|E^2-1\|\rangle$	0.855	(0.968)	(0.736)

Therefore we decided to determine the structure in the non-centric space group $Pna2_1$. The structure was determined using direct methods. The eight strongest maxima in the E-map were assumed to be the positions of the two Tl atoms and the six Sb atoms. The positions of the four As atoms and the sixteen S atoms were obtained by successive Fourier syntheses. Least-squares refinements including all atoms and isotropic temperature factors reduced the R-value to 0.098 for all observed reflections. The refinement was continued using anisotropic temperature factors and anomalous dispersion corrections: Tl: $\Delta f'=3.556$, $\Delta f''=9.659$; Sb: $\Delta f'=0.816$, $\Delta f''=1.546$; As: $\Delta f'=0.03$, $\Delta f''=2.007$; S: $\Delta f'=0.110$, $\Delta f''=0.124$ (taken from International Tables for X-ray Crystallography, Vol. IV). The final R-values are: $R=0.072$ for all observed reflections, $R_w=0.102$ and $R=0.138$ for all reflections.

All computations and drawings were made on the IBM 3033 computer of BEDAG (Bern) using the program system KRIPROG (Engel, 1978).

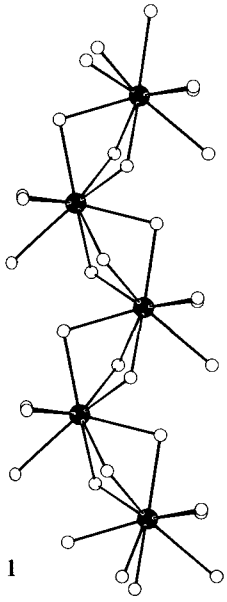
Table 3. The final atomic coordinates and anisotropic temperature factors for pierrotite, $Tl_2Sb_6As_4S_{16}$. $T=\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+kl\beta_{13}+kl\beta_{23})]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl(1)	0.03205(5)	0.4965(2)	0.0544(0)	0.00047(1)	0.0080(2)	0.0171(3)	0.0002(1)	0.0008(1)	0.0040(5)
Tl(2)	0.21783(4)	0.2442(2)	0.1351(3)	0.00041(1)	0.0072(2)	0.0157(3)	−0.0005(1)	0.0005(1)	0.0005(4)
Sb(1)	0.43813(7)	0.2642(3)	0.1299(5)	0.00030(1)	0.0046(3)	0.0117(5)	0.0000(1)	0.0002(2)	0.0011(6)
Sb(2)	0.48782(6)	0.4470(3)	0.5363(4)	0.00020(1)	0.0040(2)	0.0094(4)	0.0001(1)	0.0000(2)	−0.0004(6)
Sb(3)	0.17719(7)	0.5153(3)	0.5664(5)	0.00027(1)	0.0063(3)	0.0124(5)	0.0001(1)	0.0003(2)	−0.0006(7)
Sb(4)	0.27190(8)	0.1972(3)	0.6636(5)	0.00042(2)	0.0048(3)	0.0134(6)	−0.0008(1)	0.0000(2)	0.0000(7)
Sb(5)	0.35962(7)	0.3000(3)	0.3605(5)	0.00033(2)	0.0076(3)	0.0117(5)	0.0006(1)	−0.0007(2)	−0.0061(7)
Sb(6)	0.06980(7)	0.2956(3)	0.5530(5)	0.00029(1)	0.0071(3)	0.0098(4)	−0.0006(1)	0.0000(2)	−0.0012(7)
As(1)	0.1903(1)	0.0280(4)	0.5442(6)	0.00027(2)	0.0013(3)	0.0066(6)	0.0001(1)	0.0005(2)	0.0024(9)
As(2)	0.1280(1)	0.2360(4)	0.9002(6)	0.00015(2)	0.0027(4)	0.0077(6)	−0.0002(1)	−0.0005(2)	0.0007(9)
As(3)	0.1101(1)	0.9866(4)	0.2248(6)	0.00013(2)	0.0026(4)	0.0071(6)	0.0004(1)	0.0001(2)	0.0017(9)
As(4)	0.1232(1)	0.5360(4)	0.2263(6)	0.00032(3)	0.0023(4)	0.0073(6)	−0.0007(2)	0.0006(2)	−0.0003(7)
S(1)	0.3573(3)	0.2118(10)	0.9145(16)	0.00034(6)	0.0017(9)	0.0122(19)	−0.0002(4)	0.0013(6)	−0.0018(23)
S(2)	0.1484(3)	0.3350(10)	0.3771(14)	0.00025(6)	0.0021(9)	0.0083(17)	−0.0001(3)	−0.0004(5)	0.0013(20)
S(3)	0.3322(2)	0.0638(11)	0.5300(14)	0.00014(5)	0.0052(10)	0.0072(16)	0.0007(4)	0.0003(5)	0.0011(22)
S(4)	0.4155(2)	0.3010(10)	0.5787(13)	0.00014(4)	0.0030(8)	0.0073(16)	0.0005(3)	−0.0004(4)	−0.0041(19)
S(5)	0.0185(2)	0.2362(11)	0.7257(15)	0.00018(5)	0.0045(10)	0.0092(16)	0.0001(4)	0.0008(5)	−0.0015(23)
S(6)	0.2493(3)	0.0258(11)	0.4440(14)	0.00017(5)	0.0055(11)	0.0064(15)	−0.0002(4)	0.0000(5)	0.0000(22)
S(7)	0.4935(2)	0.2717(10)	0.2850(13)	0.00011(5)	0.0048(10)	0.0057(13)	0.0000(4)	0.0001(4)	−0.0001(20)
S(8)	0.2312(3)	0.5266(11)	0.4057(15)	0.00020(5)	0.0056(11)	0.0077(16)	0.0000(4)	0.0009(5)	0.0017(23)
S(9)	0.3391(2)	0.4749(10)	0.5764(15)	0.00014(5)	0.0038(9)	0.0089(16)	−0.0003(3)	0.0009(5)	−0.0040(21)
S(10)	0.4537(3)	0.0539(10)	0.9508(14)	0.00025(6)	0.0022(9)	0.0072(15)	−0.0002(4)	0.0004(5)	0.0003(19)
S(11)	0.0849(2)	0.1939(10)	0.0949(15)	0.00021(5)	0.0027(9)	0.0127(21)	0.0002(4)	0.0006(5)	−0.0008(22)
S(12)	0.0982(2)	0.4374(10)	0.7767(14)	0.00018(5)	0.0025(8)	0.0090(16)	−0.0006(4)	−0.0005(5)	0.0000(20)
S(13)	0.2985(2)	0.3261(10)	0.2293(15)	0.00014(5)	0.0033(9)	0.0105(17)	−0.0007(4)	−0.0005(5)	0.0006(23)
S(14)	0.4553(3)	0.4538(10)	0.9267(14)	0.00017(5)	0.0026(9)	0.0088(17)	−0.0002(4)	−0.0003(5)	0.0003(20)
S(15)	0.1154(3)	0.0656(9)	0.7035(13)	0.00035(6)	0.0013(8)	0.0072(16)	0.0006(4)	−0.0012(5)	0.0009(19)
S(16)	0.2040(2)	0.2332(10)	0.7191(15)	0.00016(5)	0.0038(10)	0.0090(16)	−0.0004(4)	−0.0006(5)	0.0011(23)

Description of the structure

The final atomic coordinates and thermal parameters are given in Table 3. A list of interatomic distances and bond angles is available upon request from the authors. In the pierrotite structure there are two independent Tl atoms, each of which is surrounded by nine S atoms with distances ranging from 3.18 −3.53 Å. The coordination polyhedron is a deformed trigonal prism, defined by six S atoms with three additional S atoms beyond the three prism faces. This type of coordination polyhedron for the Tl atom has also been observed in parapierrotite (Engel, 1980) and chabourneite (Nagl, 1979). The $Tl(1)S_9$ coordination polyhedra are connected by sharing a common face with neighbours to form infinite $^1_\infty[TlS_6]$ columns in the direction of the *c* axis, as can be seen in Figure 1. The $Tl(2)S_9$ coordination polyhedra are connected by sharing a common vertex with neighbours to form infinite $^2_\infty[TlS_7]$ layers parallel the (100) crystal face, as shown in Figure 2.

Sb(1), Sb(2), Sb(3) and Sb(6) are coordinated by three nearest S atoms in the range from 2.42 −2.59 Å. Sb(4) is coordinated by four S atoms. Two S atoms are closer, 2.453 and 2.475 Å, and the other two S atoms are further away, 2.687 and 2.825 Å. Sb(5) is coordinated by five S atoms. One S atom is at a distance of 2.446 Å and the other four S atoms are further away, 2.60



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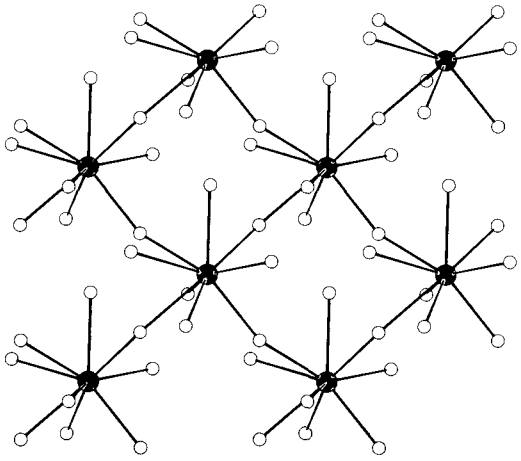

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Fig. 1. Cut out of the $^1_\infty[TlS_6]$ column. Parallel projection along the *b*-axis

Fig. 2. Cut out of the $^2_\infty[TlS_7]$ layer. Parallel projection along the *a*-axis

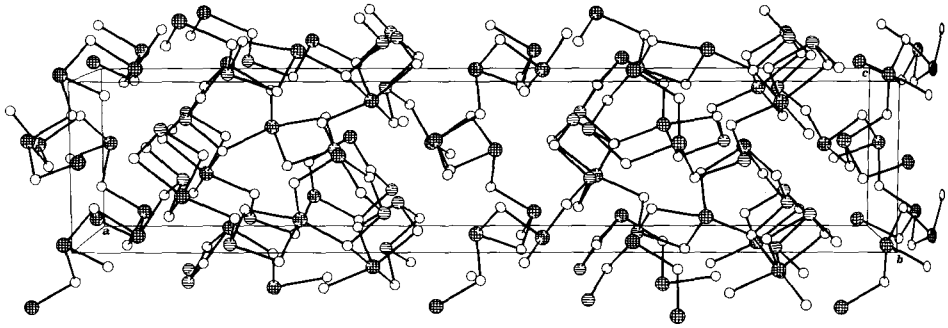

Fig. 3. The central projection of the $^3_\infty[(Sb,As)S_{1.6}]$ framework viewed along the *b*-axis

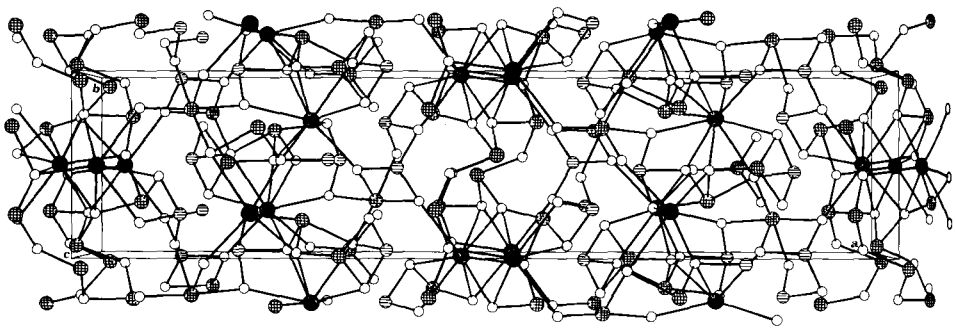

Fig. 4. The central projection of the structure of pierrotite viewed along the *c*-axis

−2.83 Å. The As atoms are coordinated by three S atoms in the range 2.23 −2.43 Å. The coordination polyhedron is a trigonal pyramid with the As atom at the apex. The Sb and As coordination polyhedra form a three-dimensional framework, shown in Figure 3. Even if for Sb(4) and Sb(5) only the three shortest bonds are taken the three-dimensional connectivity remains. The $^1_\infty[TlS_6]$ columns and the $^2_\infty[TlS_7]$ layers interpenetrate the $^3_\infty[(As,Sb)S_{1.6}]$ framework as shown in Figure 4. S(1), S(14) and S(15) are coordinated to only two (As,Sb) atoms. S(3) is coordinated to three (As,Sb) atoms and one Tl atom. The other S atoms are coordinated to two (As,Sb) atoms and one or two Tl atoms.

In pierrotite a three-dimensional framework of the (As, Sb) polyhedra was found for the first time. According to the classification of sulfosalts proposed by Nowacki (1969), pierrotite with S : (As, Sb) = 1.6 belongs to a new group V a_4 with a three-dimensional framework.

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