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Tillmannsite, $(Ag_3Hg)(V,As)O_4$, a new mineral: its description and crystal structure

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Abstract: Tillmannsite, $(Ag_3Hg)(V,As)O_4$, was found in the old copper mines of Roua (Alpes-Maritimes, France), associated with pecoraite, vésigniéite, olivenite, kolfanite, janggunite, chlorargyrite, cuprite, native copper, native silver, native silver containing 2 % of mercury, domeykite, djurleite and algodonite. It forms aggregates (0.2 mm diameter) consisting of pseudooctahedral crystals (50 µm maximum dimension). The crystals are red, brownish red. The mineral is tetragonal, $I\bar{4}$, a = 7.727(7) Å, c = 4.648(5) Å, V = 277.5(5) Å^3, Z = 2 and D_{calc} = 7.733(3) g/cm^3 . The strongest lines in the X-ray powder diffraction pattern (d_{obs} in Å, (hkl), I_{vis}) are: 5.45, (110), 25; 2.772, (211), 100; 2.324, (002), 30; 2.254, (301), 20. Luster is adamantine translucent, streak is brownish red; crystals are uniaxial (+) with $\omega - 2.3$, $\varepsilon - 2.5$ at 589 nm. Pleochroism is intense with ε = red orange intense, ω = orange brown. The crystal structure was solved from data collected using synchrotron radiation by traditional direct methods and refined using 350 observed unique reflections to R(F) = 0.037, Rw(F^2) = 0.075. The structure of tillmannsite containes isolated tetrahedra $(V,As)O_4$ and tetrahedral clusters (Ag_3Hg) formed by metallic atoms. Each (Ag,Hg) metallic atom is coordinated by 3 metallic neighbors and by 3 oxygens.

Key-words: tillmannsite, crystal structure, vanadate, silver, mercury, Roua (France).

Introduction

Tillmannsite, $(Ag_3Hg)(V,As)O_4$, is a new mineral discovered in samples collected by Danielle Mari, Gilbert Mari and Pierre Rolland in the old copper mines of Roua, which are situated in the northwestern part of the Alpes-Maritimes department (France). The mineral name honors Professor Ekkehart Tillmanns (born 1941) from Institute of Mineralogy and Crystallography of Wien, Austria. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type material is preserved in the Department of Mineralogy of the Natural History Museum of Geneva, Switzerland, under reference no. 478.006.

Occurrence

The new mineral herewith described occurs in the Roua copper occurrences in the upper part of the Var valley (the Daluis gorge) at the western margin of the Barrot Dome. The metallogeny and geology of this Dome have been studied by Vinchon (1984) and Mari (1992). In the Roua ore deposit, the cupriferous mineralisation is hosted in a gangue formed by dolomite, calcite and aragonite, and consists of native copper, cuprite, domeykite, algodonite, koutekite and native silver. Detailed mineralogical study of this ore deposit produced several secondary, rare and unknown mineral species (Sarp *et al.*, 1994, 1995, 1996). The new mineral described here occurs in small geodes in association with pecoraite, vésigniéite, olivenite, kolfanite, janggunite, chlorargyrite, cuprite, native copper, native silver, native silver containing 2 % of mercury, domeykite, djurleite and algodonite. It is a secondary alteration mineral.

Physical and optical properties

Tillmannsite occurs as aggregates of maximum size 0.2 mm in diameter, which are formed by pseudooctahedral crystals of maximum size 50 µm. The crystals are occasionally twinned by contact on (100) and they do not

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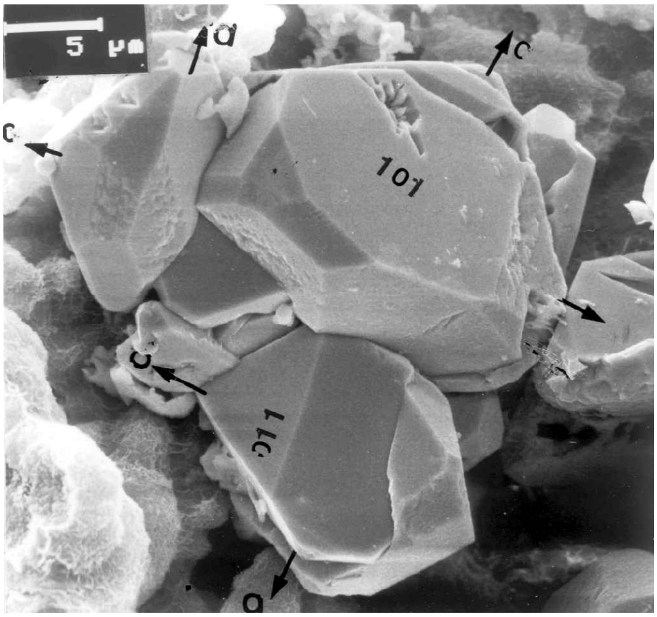

Fig. 1. SEM image of tillmannsite crystals of pseudooctahedral habitus.

possess a cleavage. The most developed forms are (111), (110), (100), (101) and minor (001) (Fig. 1). The crystals are red, brownish red, translucent, with adamantine luster and brownish red streak. The mineral is very brittle with conchoidal fracture. The Mohs' hardness and the density could not be measured because of the small grain size. Calculated density is 7.769 (based on the empirical formula) and 7.733(3) g/cm^3 (based on the ideal formula). The mineral is not soluble in HC1. It is nonfluorescent and has intense pleochroism: ε = red orange intense, ω = orange brown. Tillmannsite is uniaxial positive. The refractive indices, which are high, could not be measured by index oils. They were determined by reflectance measurements on oriented crystals in a polished section and yielded ω –2.3, ε – 2.5 (at 589 nm).

Table 1. Chemical analysis (wt.%) of tillmannsite.

	Average of 14 analysis	Range of 14 analysis	Standard deviation	Ideal formula*
Ag	49.82	48.22-51.95	1.1	50.07
Hg	30.40	29.73-31.17	0.5	31.04
V	5.32	4.53-6.27	0.4	5.51
As	4.23	3.72-4.99	0.4	3.48
O	9.90	9.38-10.42	0.4	9.90
Total	99.67			100.00

*For $(Ag_3Hg)(V_{0-7}, As_{03})O_4$

Table 2. X-ray powder diffraction data for tillmannsite (in Å).

hkl	d_{calc}	d_{obs}	I_{obs}	I_{calc}
110	5.464	5.45	25	23
101	3.983	3.98	5	6
200	3.864	3.863	<5	6
211	2.773	2.772	100	100
220	2.732	2.735	10	2
310	2.444	2.446	10	22
002	2.324	2.324	30	12
301	2.253	2.254	20	15
112	2.139	2.138	10	7
202	1.992	1.992	10	5
321	1.946	1.950	10	12
400	1.932	1.932	10	2
411	1.738	1.740	15	2
420	1.728	1.727	5	9
312	1.684	1.683	15	17

Chemical composition

Tillmannsite was analyzed with a Cameca SX 50 electron microprobe, using operating voltage of 20 kV, beam current of 30 nA, and a beam diameter of 5 μm. Qualitative examination showed only Ag, Hg, V, As and O. For quantitative analysis, AgAsS (Ag, As), HgTe (Hg), V metal (V) and vanadinite (O) were used as standards. The results are given in Table 1. The empirical formula based on (Ag + Hg) = 4 is: $Ag_{3.01}Hg_{0.99}V_{0.68}As_{0.36}O_{4.03}$ and the idealized formula, $(Ag_3Hg)(V,As)O_4$, was confirmed by the structure determination. The Gladstone-Dale calculation (Mandarino, 1981) give the excellent compatibility: $1- K_P/K_C = -0.034$.

X-ray crystallography

Powder diffraction data for tillmannsite (Table 2) were obtained using a Gandolfi camera (114.6 mm diameter, Ni-filtered Cu$K\alpha$). The relative intensities of the reflections were estimated visually. A single crystal with dimensions 40 x 20 x 10 μm^3 was first tested by the precession method (Ni-filtered Cu$K\alpha$) and the same crystal was used for the structure determination at room temperature. Details of the single crystal X-ray data collection and structure refinement of tillmannsite are given in Table 3. The data were collected at λ = 0.6941 Å using a Bruker AXS SMART CCD area detector diffractometer on station 9.8 of the Synchrotron Radiation Source located at the CCLRC Daresbury Laboratory (Cernik *et al.*, 1997). A nominal full sphere of diffraction data was collected with ω-rotations and processed (Clegg *et al.*, 1998). This yielded refined tetragonal cell constants of a = 7.727(7) Å, c = 4.648(5) Å, V = 277.5(5) Å^3 are in accordance with the unit cell parameters calculated from powder data: a = 7.731(2) Å, c = 4.647(2) Å, V = 277.8(2) Å^3.

SHELXTL (Sheldrick, 2000) was used for structure solution and refinement (space group $I\bar{4}$) by using 919 reflections merged to 363 independent reflections, of which 350 reflections have $I > 2\sigma(I)$ with R(int) = 0.05. A difference Fourier map with residual peaks around (Ag,Hg) and (V,As) atoms showed that their positions should be refined using the anharmonic thermal displacement factors (Gram-Charlier expansion of tensors F(ijklmn)). The program JANA98 (Petricek & Dusek, 1998) was used in the structure refinement using full-matrix least-squares refinement on F^2. The Ag/Hg and V/As ratio in cationic sites indicated by the refinement are in good agreement

Table 3. Crystal data, structure solution and refinement for tillmannsite.,

Chemical formula	$(Ag_3Hg)(V,As)O_4$
Molecular weight	651.13
Temperature	293(2) K
Radiation and wavelength	synchrotron, 0.6941 Å
Crystal system, space group	tetragonal, $I\bar{4}$
Unit cell dimensions	a = 7.727(7) Å c = 4.648(5) Å
Volume	277.5(5) $Å^3$
Z	2
Density (calculated)	7.790 g/cm^3
Absorption coefficient μ	41.67 mm^{-1}
F(000)	562
Crystal colour	red
Crystal size	0.04 x 0.02 x 0.01 mm^3
Data collection method	Bruker AXS SMART CCD diffractometer, ω rotation with narrow frames
θ range for data collection	3.73 to 29.56°
Index ranges	$-6 \le h \le 10, -10 \le k \le 9, -6 \le l \le 6$
Intensity decay	10%
Reflections collected	919
Independent reflections	363 (R_{int} = 0.050)
Reflections with $I>2\sigma(I)$	350
Absorption correction	multiscans
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	54
$R(F)_{obs}$ [$I>2\sigma(I)$]	0.037
$Rw(F^2)$ [$I>2\sigma(I)$]	0.075
R indices (all data)	R(F) = 0.039, $Rw(F^2)$ = 0.075
Largest diff. peak and hole	1.80 and -1.78 e/$Å^3$

with the results of chemical analysis (Table 1). The final difference Fourier map was featureless: δρ maximum and minimum were 1.80 e/$Å^3$ and -1.78 e/$Å^3$. The atomic coordinates, displacement parameters, selected interatomic distances and bond angles are presented in Tables 4 and 5.

The value of density calculated on the basis of the structural formula is 7.733(3) g/cm^3. The intensity calculations (Yvon *et al.*, 1977) for tillmannsite (Table 2) demonstrated the agreement between the X-ray powder diffraction and the single-crystal data. The figures were obtained with the use of the program ATOMS (Dowty, 1995).

Table 4. Final positional and displacement parameters ($Å^2$) for tillmannsite.

Atom	Wyckoff notation	*x*	*y*	*z*	*B**
(Ag,Hg)	8g	0.5707(2)	0.6624(2)	0.2896(3)	2.01(6)
(V, As)	2c	0.5	0	0.75	1.5(1)
O	8g	0.659(1)	0.9159(9)	0.548(2)	1.8(2)

*The equivalent isotropic displacement was converted from the anisotropic parameters.

Table 5. Selected interatomic distances (Å) and angles (°) for tillmannsite.

(Ag,Hg)-O	2.395(1)	(V, As) - O x 4	1.678(8)
-O	2.407(8)		
-O	2.449(8)	O- (V, As) -O x 4	108.3(4)
Av.	2.417	O- (V, As) - O x 2	111.8(4)
		Av.	109.5
(Ag,Hg)-(Ag,Hg) x2	2.752(2)		
- (Ag,Hg)	2.738(2)		
Av.	2.747		

Description of the structure

The structure of tillmannsite contains isolated $(V,As)O_4$ tetrahedra and tetrahedral clusters (Ag_3Hg) formed by metallic atoms (Fig. 2). A disordered distribution of Ag and Hg atoms within the latter structural units, revealed on the basis of XRD data, can be considered as a specific feature of tillmannsite in respect to chemically related synthetic $AgHg_2PO_4$ and $AgHg_2AsO_4$ (Masse *et al.,* 1978) where Ag and Hg atoms are completely ordered and form the dimers O_2Ag-AgO_2 and O_3Hg-HgO_3. In tillmannsite, each (Ag,Hg) metallic atom is coordinated by 3 metallic neighbours and by 3 oxygens (Fig. 2).

The analysis of the metal-metal bond lengths in mercury and silver compounds (Table 6) confirms the conclusion about disordered distribution of Ag and Hg atoms in tillmannsite. Tetrahedral clusters $(Ag_3Hg)^{3+}$ revealed in tillmannsite are unique in spite of the fact that mercury is characterized by the low-valence state in many minerals (Pervukhin *et al*., 1999). From the almost 100 Hg-minerals known so far, about 20 contain the dimers $[Hg_2]^{2+}$: for example, halogenides – calomel, Hg_2Cl_2, moschelite, Hg_2I_2; oxides – poyarkovite, Hg_3ClO, hanawaltite, $Hg_6Hg[Cl,(OH)]_2O_3$ or shakhovite, $Hg_4Sb(OH)_3O_3$ *etc.* Triangles of $[Hg_3]^{4+}$ have been observed only in a few

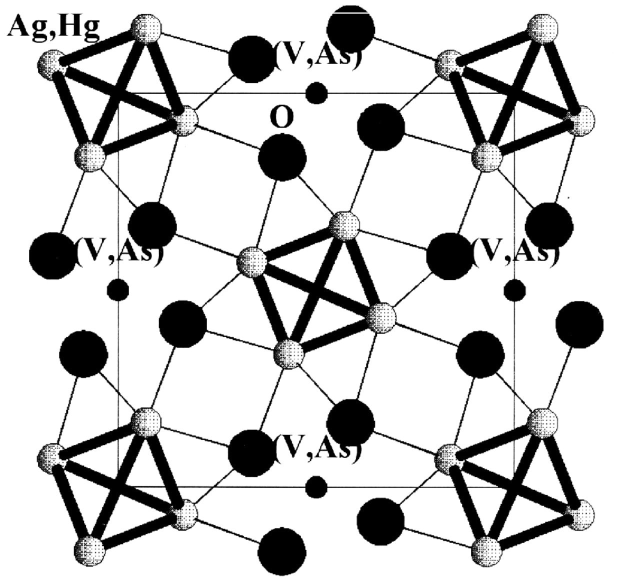

Fig. 2. Projection of tillmannsite along [001] with marked bonds between Ag,Hg atoms and surrounding O atoms.

minerals, namely in kuznetsovite, $Hg_2HgCl(AsO_4)$, and terlinguaite, Hg_2ClO, and there are no known minerals with tetrahedral clusters formed by Hg atoms. However the discrete Ag_3Sn heteroclusters were recently reported in synthetic Ag_3SnP_7 (Shatruk *et al.*, 2000).

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Table 6. The metal-metal bonds in Ag and Hg compounds.

Compound	Bond lengths, Å	References
	Hg-Hg	
$(Hg_2)_3(AsO_4)_2$	2.535	Kamenar & Kaitner, 1973
$Hg_2(H_2PO_4)_2$	2.499	Nilsson, 1975
$AgHg_2PO_4$	2.608	Masse *et al.*, 1978
$HgVO_3$	2.543	Wessels & Jeitschko, 1996
Hg_2VO_4	2.536	Wessels & Jeitschko, 1996
$Hg_4Sb(OH)_3O_3$	2.543	Tillmanns *et al.*, 1982
Tillmannsite $(Ag_3Hg)(V,As)O_4$	(Ag,Hg)-(Ag,Hg 2.730-2.737	This work
	Ag-Ag	
$AgHg_2PO_4$	2.824	Masse *et al.*, 1978
Ag_3SnP_7	2.904-3.230	Shatruk *et al.*, 2000

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