Crystal structure of silver thallium phosphate, $Ag_3Tl_2(PO_4)_3$

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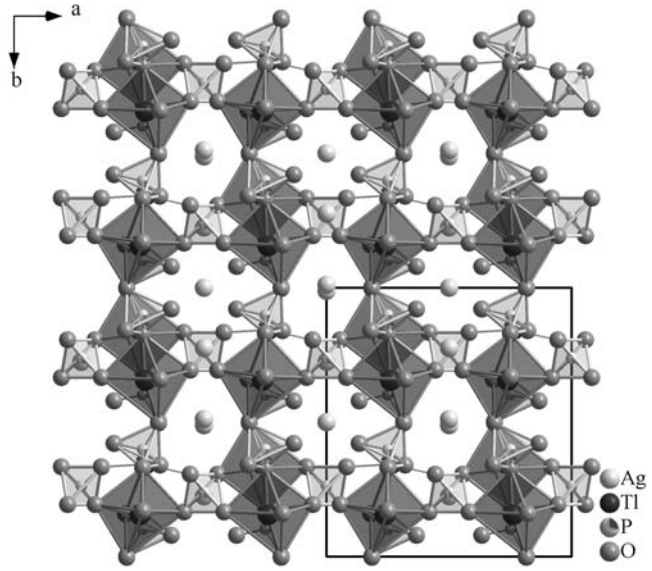

Abstract

$Ag_3O_{12}P_3Tl_2$, monoclinic, $C12/c1$ (no. 15), a = 13.138(3) Å, b = 13.111(3) Å, c = 6.725(1) Å, β = 114.62(3)°, V = 1053.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.145, T = 293 K.

Source of material

$Ag_3Tl_2(PO_4)_3$ was prepared by reacting Ag_2O (freshly precipitated from $AgNO_3$ and KOH solutions), Tl_2O_3 (freshly precipitated from $Tl(NO_3)_3 \cdot 3H_2O$ and KOH solutions) and $(NH_4)_2HPO_4$ (Acros Organics, > 99 %) in stainless-steel autoclave at elevated oxygen pressure and temperature [1]. Stoichiometric amounts of the starting materials were intimately mixed and placed into gold tubes which were sealed on one side and mechanically closed on the other. In a typical experiment, 300 mg of the starting mixture was heated up to 500 °C for 100 h at $p(O_2)$ = 25 MPa. In order to grow single crystals, suitable for an X-ray diffraction analysis, 1.0 mL H_2O was added to the starting mixture as a mineralizer. The crystalline product was filtered off, washed with deionized water and dried in air. The yellow crystals of $Ag_3Tl_2(PO_4)_3$ are stable towards air and moisture.

Discussion

Ligth yellow crystals of $Ag_3Tl_2(PO_4)_3$ have been encountered during the systematic investigation of silver thallium phosphates. The title compound is isostructural to β-$Ag_3In_2(PO_4)_3$ [2]. Two distorted octahedra TlO_6 are connected by a shared edge to form Tl_2O_{10} bioctahedra. The Tl—O bond distances vary from 2.140 to 2.234 Å, the O–Tl–O angles are between 81.263° and 111.716°. The bond lengths are thus in the expected range, and similar to those found in Na_5TlO_4 [3]. The phosphorus atoms are surrounded by 4 oxygen atoms, forming slightly distorted tetrahedra.The P—O bond distances are in the range of 1.533 to 1.564 Å, the O–P–O angles lie between 105.526° and 112.254°. The TlO_6 octahedra and the PO_4 tetrahedra are connected via corners, building a three-dimensional framework. The silver atoms are coordinated by six and eight oxygen atoms. The $Ag2O_6$ octahedron is moderately distorted with Ag—O bond distances in the range from 2.387 to 2.663 Å. Ag1 and Ag3 are coordinated by 8 oxygen atoms with Ag—O bond distances in the range between 2.480 and 2.877 Å (Ag1), 2.758 and 2.939 Å (Ag3), respectively. The structure can be regarded as alluaudite-like with a general formula $[X2][X1][M1][M2]_2(PO_4)_3$. The X1 (½ 0 0) position is occupied by Ag2 atoms while the X2 (0 0 0) position is vacant. The M1 position is occupied by Ag1 and Ag3, whereas the M2 position is occupied by the Tl atoms.

Table 1. Data collection and handling.

Crystal:	yellow irregular, size 0.03 × 0.03 × 0.05 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	365.00 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4426, 930
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 924
$N(param)_{refined}$:	95
Programs:	SHELXS-97, SHELXL-97 [4], DIAMOND [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	4*e*	½	0.2242(2)	¼	0.032(1)	0.036(1)	0.040(2)	0	0.016(1)	0
Ag(2)	4*b*	½	0	0	0.032(1)	0.028(1)	0.032(1)	0.005(1)	0.002(1)	–0.0032(9)
Ag(3)	4*e*	½	0.5112(3)	¾	0.043(2)	0.066(2)	0.053(2)	0	0.017(1)	0
Tl(1)	8*f*	0.23879(5)	0.15586(5)	0.6699(1)	0.0153(6)	0.0166(6)	0.0195(6)	–0.0006(2)	0.0071(4)	0.0011(2)
P(1)	4*e*	½	0.2379(5)	¾	0.012(3)	0.017(3)	0.019(3)	0	0.005(2)	0

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Table 2. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	8*f*	0.418(1)	0.166(1)	0.796(2)	0.023(7)	0.016(7)	0.031(8)	0.000(5)	0.008(6)	0.003(5)
O(2)	8*f*	0.633(1)	0.079(1)	1.326(2)	0.020(7)	0.031(8)	0.028(7)	–0.005(6)	0.009(6)	–0.001(6)
O(3)	8*f*	0.444(1)	0.306(1)	0.548(2)	0.019(6)	0.019(7)	0.020(7)	–0.001(5)	0.005(5)	0.004(5)
P(2)	8*f*	0.7506(4)	0.1021(4)	1.3524(7)	0.017(2)	0.015(2)	0.018(2)	–0.001(2)	0.009(2)	0.000(2)
O(4)	8*f*	0.180(1)	0.1594(9)	0.932(2)	0.022(7)	0.016(7)	0.024(7)	0.003(5)	0.015(6)	0.002(5)
O(5)	8*f*	0.186(1)	–0.003(1)	0.650(2)	0.018(6)	0.020(7)	0.021(7)	0.000(5)	0.006(5)	–0.001(5)
O(6)	8*f*	0.750(1)	0.170(1)	1.162(2)	0.028(8)	0.015(7)	0.020(7)	0.000(5)	0.010(6)	–0.002(5)

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