# Synthesis, Crystal Structure Determination, and Physical Properties of Ag<sub>5</sub>IO<sub>6</sub>

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Dedicated to Professor Herbert Jacobs on the Occasion of his 70<sup>th</sup> Birthday.

**Abstract.** The silver iodate(VII), Ag<sub>3</sub>IO<sub>6</sub>, was obtained by reacting a stoichiometric mixture of Ag<sub>2</sub>O and KIO<sub>3</sub>, at elevated oxygen pressure, adding a small portion of distilled water. The synthesis was done at 673 K and 270 MPa of oxygen pressure. The crystal structure was solved by direct methods based on single crystal diffraction data ( $R\bar{3}c$ , Z = 6, a = 5.9366(1), c = 32.1471(6) Å, 323 independent reflections, R<sub>1</sub> = 2.31 %). According to conductivity measurements, Ag<sub>5</sub>IO<sub>6</sub> is semiconducting with a specific resistance

# of 0.08 Ωcm at 300 K. The activation energy was determined as 7.4(1) meV in the temperature range of 220 – 300 K, and 4.3(1) meV in the temperature range of 90 – 180 K. The optical band gap for $Ag_5IO_6$ is 1.4 eV. $Ag_5IO_6$ is diamagnetic with a magnetic susceptibility of $-4.4 \times 10^{-4}$ emu/mol.

Keywords: Silver iodate(VII); Oxygen pressure; Crystal structure

# Introduction

In spite of the fact that the structure of orthoperiodic acid ( $H_5IO_6$ ) was solved rather long ago [1], only few examples of fully deprotonated salts of this acid are known to date [2–5]. Continuing the studies on ternary silver oxide systems at elevated oxygen pressure [6–8], now including the Ag-I-O system, we obtained the silver orthoperiodate Ag<sub>5</sub>IO<sub>6</sub> – the next silver iodate in addition to already known AgIO<sub>3</sub> [9] and AgIO<sub>4</sub> [10]. The silver orthoperiodate was first mentioned in 1941 [11], however its constitution has remained unconfirmed, and, in particular, no crystal structure analysis was performed. The synthesis, crystal structure and properties of Ag<sub>5</sub>IO<sub>6</sub> are discussed herein.

## **Experimental Part**

Reacting a mixture of  $Ag_2O$  and  $KIO_3$  (Aldrich 99.5 %) in a molar ratio of 5:2, to which 1 mL of distilled water was added to enhance reactivity and crystal formation, at elevated oxygen pressure, has yielded  $Ag_5IO_6$  as a coarse crystalline, shiny black product.  $Ag_2O$  was obtained by adding aqueous KOH to a  $AgNO_3$  (Sigma-Aldrich 99+%) aqueous solution. The 5:2 mixture was annealed for 36 hours in gold crucibles, placed in a stainless-steel autoclave [12], at 673 K and 270 MPa of oxygen pressure. The  $Ag_5IO_6$  product was washed out using distilled water and dried in air at 340 K

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**Table 1** Observed powder reflections for  $Ag_5IO_6$  (d > 1.5 Å). Results of a profile fit using the positional parameters from the single crystal investigation (Tab. 2-4).

Nr.	h	k	1	d / Å	I / %
1	0	0	6	5.3580	0.3
2	1	0	2	4.8971	1.1
3	1	0	4	4.3311	0.6
4	1	0	8	3.1662	9.8
5	1	1	0	2.9684	7.1
6	1	1	3	2.8607	33.1
7	1	0	10	2.7258	4.1
8	0	0	12	2.6790	21.8
9	1	1	6	2.5966	100.0
10	2	0	2	2.5385	1.5
11	0	2	4	2.4485	3.3
12	1	1	9	2.2830	33.8
13	2	0	8	2.1655	1.4
14	1	0	14	2.0967	3.0
15	1	1	12	1.9888	3.8
16	2	1	1	1.9398	1.3
17	2	1	2	1.9292	0.5
18	2	1	4	1.8889	0.6
19	1	0	16	1.8714	0.4
20	2	1	5	1.8602	2.9
21	2	1	7	1.7897	0.2
22	0	0	18	1.7860	0.8
23	2	1	8	1.7495	1.3
24	1	0	15	1.7376	8.9
25	3	0	0	1.7138	25.0
26	2	0	14	1.7126	5.5
27	3	0	6	1.6324	0.1
28	2	1	11	1.6182	0.4
29	2	0	16	1.5831	0.4
30	1	0	20	1.5342	3.9
31	1	1	18	1.5304	10.0
32	2	1	13	1.5280	0.9

for 5 hours. The as obtained coarse crystalline  $Ag_5IO_6$  is insensitive to air and light, and decomposes at 690 K leaving metallic silver and AgI as solid residues.

The *single crystal diffraction data* were collected on a Stoe IPDS II diffractometer (Mo-K $\alpha$  radiation, graphite monochromator) at 293 K. The crystal structure was solved by direct methods and refined using full-matrix least-squares techniques [13]. The final re-



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**Table 2** X-ray and crystallographic data<sup>a)</sup> for  $Ag_5IO_6$ .

Crystal data Empirical formula Formula weight / g mol <sup>-1</sup> Crystal system Space group, Z Lattice constants (from powder) $a \mid \mathring{A}$ $c \mid \mathring{A}$ $V \mid \mathring{A}^3$ Calculated density / g cm <sup>-3</sup> Crystal shape, color Crystal size / mm	Ag <sub>5</sub> IO <sub>6</sub> 762.4 rhombohedral $R$ $\overline{3}$ c (No. 167), 6 5.9366(1) 32.1471(6) 981.18(3) 7.740 hexagonal plate, black 0.1 $\times$ 0.1 $\times$ 0.03
Data collectionDiffractometerMonochromatorWavelength / ÅTemperature / K2 $\theta$ range for data collectionhkl-rangeTotal no. reflectionUnique reflectionsUnique reflections with $I > 2\sigma(I)$ Absorption coefficient / mm <sup>-1</sup> F(000)	STOE IPDS II Graphite 0.71073 293 20 < 60 $-8 \le h \le 4, 0 \le k \le 8, -45 \le l \le 45$ 1118 323 286 19.40 2016
Structure refinement Structure solution, refinement Parameters refined R <sub>1</sub> $I > 2\sigma(I)$ , all data wR <sub>2</sub> $I > 2\sigma(I)$ , all data $\Delta F_{max}$ , $\Delta F_{min} / e Å^{-3}$ Extinction coefficient	ShelXL'97 21 0.0288, 0.0231 0.0499, 0.0516 1.20, -1.52 0.0017(1)

<sup>a)</sup> Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-415893, the name of authors, and citation of the paper.

**Table 3** Atomic coordinates and isotropic thermal displacement parameters  $(U_{eq})$  for Ag<sub>5</sub>IO<sub>6</sub>.

Atom	Site	x	у	Z	$U_{eq} \; (in \; \mathring{A}^2)$
I1	6 <i>b</i>	0	0	0	0.0086(2)
Ag1	18 <i>e</i>	0.30460(9)	0	1/4	0.0204(2)
Ag2	12c	0	0	0.15546(3)	0.0211(2)
0Ĩ	36 <i>f</i>	0.2779(6)	0.3030(6)	0.0341(1)	0.0155(6)

Table 4 Anisotropic displacement parameters  $^{a)}$  (in  ${\rm \AA}^2)$  for  ${\rm Ag}_5 {\rm IO}_6.$ 

Atom	U11	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
I1 Ag1 Ag2 O1	0.0082(2) 0.0235(3) 0.0140(2) 0.0147(15)	U <sub>11</sub> 0.0194(3) U <sub>11</sub> 0.0186(17)	0.0093(3) 0.0171(3) 0.0354(4) 0.0158(13)	0.00412(12) 0.00970(14) 0.00698(12) 0.0102(13)	$0 \\ -0.00343(9) \\ 0 \\ -0.0070(12)$	$0 \\ -0.00687(19) \\ 0 \\ -0.0028(13)$

<sup>a)</sup> The anisotropic displacement factors exponent takes the form:

 $-2\pi^{2}(a^{*2}h^{2}U_{11} + b^{*2}k^{2}U_{22} + c^{*2}l^{2}U_{33} + 2b^{*}c^{*}klU_{23} + 2a^{*}c^{*}hlU_{13} + 2a^{*}b^{*}hkU_{12})$ 

finement included anisotropic displacement parameters for all atoms. X-ray investigations on powder samples were performed using the Stoe StadiP diffractometer, supplied with a position sensitive detector and a curved germanium monochromator, with Cu-K<sub> $\alpha$ 1</sub> radiation ( $\lambda = 1.54056$  Å) at room temperature. The data were collected in the range of 10 to 90 degrees in 20. The profile refinement was performed with the JANA2000 program package

[14], using the atomic coordinates from the single crystal investigation as starting parameters. See Table 1 for experimental d values and relative intensities, and Table 2 for the crystallographic data.

*Magnetic measurements* were performed on a SQUID-Magnetometer (MPMS 5.5, Quantum Design) between 5 and 320 K in magnetic fields of  $1 \times 10^{-3}$ , 0.1, 1 and 5 T. The electric conductivity was measured using the four-point method, for which a 6 mm of diameter, and 1 mm of height, pellet was pressed and annealed at 473 K for 10 hours in an oxygen flow to improve intergranular contacts. Metallic silver contacts were used.

Thermal analyses were carried out using a DTA/TG device (STA 409, Netzsch) coupled with a quadrupole mass spectrometer (QMG 421, Balzers). The sample was heated at a rate of 10 °C/min in a corundum crucible under dry argon. Low-temperature DSC measurements were performed on a Perkin Elmer Pyris 1 calorimeter in the temperature range of 100 - 300 K in aluminium crucibles. A diffuse reflectance spectrum was recorded on a Perkin Elmer Lambda 9 UV/VIS/NIR Spectrophotometer.

#### **Results and Discussion**

Ag<sub>5</sub>IO<sub>6</sub> has been obtained by solid state reaction of Ag<sub>2</sub>O and KIO<sub>3</sub> at elevated oxygen pressure [12], as a coarse crystalline black product. Experimental X-ray powder diffraction patterns (Tab. 1), which could be indexed assuming a rhomohedral crystal system with the refined lattice parameters a = 5.9366(1), c = 32.1471(6) Å, have shown, that the sample was single phase and the measured pattern agrees perfectly with the calculated one.

The crystal structure of the silver periodate(VII) was determined from single crystal data collected at 293 K. For the details of the structure refinement and for crystallographic data see Tables 2 - 4. Interatomic distances, coordination numbers (CN), effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR) [15] are given in Table 5.

Iodine atoms are located in the origin of the rhombohedral unit cell and are surrounded by six oxygen atoms. In spite of the fact that the site symmetry of the iodine atoms is  $C_{3i}$ , the coordination environment of iodine is a regular octahedron (within the limits of experimental error), and the  $O_h$  point group symmetry is fulfilled (see Fig. 1 and Tab. 6).

**Table 5** Interatomic distances (in Å), coordination numbers (CN),effective coordination numbers (ECoN) and mean fictive ionic radii(MEFIR, in Å) [14] for  $Ag_5IO_6$ .

Atom	O1	CN	ECoN	MEFIR
Il	1.908 ×6	6	6.0	0.51
Agl	2.246 ×2 2.655 ×2 2.809 ×2	6	3.3	0.88
Ag2	2.469 ×3 2.552 ×3	6	5.9	1.08
CN	6			
ECoN	4.6			
MEFIR	1.43			

0-I1-0	90.2(2)° ×6
	89.8(2)° ×6
	180.0(2)° ×3
O-Ag1-O	66.4(1)° ×2
0	$80.5(1)^{\circ} \times 2$
	$91.1(1)^{\circ} \times 2$
	$96.2(1)^{\circ} \times 2$
	$122.9(1)^{\circ} \times 2$
	$132.4(1)^{\circ} \times 2$
	76.7(1)°
	130.4(1)°
	159.9(1)°
O-Ag2-O	64.8(1)° ×3
0	$90.7(1)^{\circ} \times 3$
	91.5(1)° ×3
	$111.5(1)^{\circ} \times 3$
	$155.4(1)^{\circ} \times 3$

Table 6Selected angles for Ag<sub>5</sub>IO<sub>6</sub>.

Ag1 and Ag2 are either surrounded by six oxygen atoms, forming distorted trigonal prisms and distorted octahedra, respectively. In both cases the silver atoms are shifted from the centers of the polyhedra to achieve low coordination numbers, as preferred by Ag<sup>+</sup>. The coordination of Ag1 can be described as basically two-fold with Ag-O distances of 2.246 Å and an O-Ag-O angle of 159.9°, two oxygen atoms in the second coordination sphere with Ag-O distances of 2.655 Å, and two oxygen atoms in the third coordination sphere with Ag–O distances of 2.809 Å, altogether forming the distorted trigonal prism configuration. The first coordination sphere of Ag2 can be described as regular trigonal with the silver atom positioned slightly below the plane of oxygen atoms with Ag–O distances of 2.469 Å. The second coordination sphere is formed by three further oxygen atoms, completing the distorted octahedron (see Fig. 1 and Tab. 5-6).

The Ag–Ag distances in  $Ag_5IO_6$  are 3.108 Å and thus are shorter than to the sum of the *van der Waals* contacts of 3.40 Å [16]. However, these distances are significantly larger than those commonly found in silver-rich oxides [17]. The cation partial structure of  $Ag_5IO_6$  may be described as a heavily distorted face-centered cubic (*fcc*) structure of metallic silver, in which 1/6 of the silver atoms are substituted by iodine. Moreover, it can be related to the MoAl<sub>5</sub> type [18] with silver atoms instead of aluminum and iodine



Fig. 2 Crystal structure of  $Ag_5IO_6$ . (a) Packing scheme.  $IO_6$  octahedra are black,  $Ag2O_6$  distorted octahedra are light gray, Ag1 atoms are connected to six oxygen atoms forming a distorted trigonal prism geometry. (b) Packing of oxygen atoms composed of blocks of two layers of close packed oxygen atoms.

atoms replacing molybdenum, thus providing another example for the cationic partial structure in ternary oxides corresponding to the structure of binary intermetallic compounds [19].

The crystal structure of  $Ag_5IO_6$  can be described as blocks of close packed oxygen atoms with 50 % of octahedral voids filled by silver and iodine in a ratio of 2:1, forming  $[Ag_2IO_6]^{3-}$  slabs, and  $[Ag_3]^{3+}$  layers of silver atoms in a distorted trigonal prismatic coordination, connecting the blocks one to the other (Fig. 2). The structure of the  $[Ag_2IO_6]^{3-}$  blocks resembles the respective partial structure of lithium hexaoxometalates [20].

According to the conductivity measurements in the temperature range 5 – 300 K,  $Ag_5IO_6$  is a semiconductor with a specific resistance of 0.08  $\Omega$ cm at 300 K. A least squares fit of the  $\rho(T)$  data was performed using the equation (1), which corresponds to the intragranular conductivity.

$$\rho = \rho_0 e^{\frac{E}{kT}} \tag{1}$$



**Fig. 1** Coordination polyhedra of cations in  $Ag_5IO_6$ . (a) Regular octahedron, 11, (b) distorted trigonal prism, Ag1, (c) distorted octahedron, Ag2; iodine atom is black, light gray spheres represent silver atoms, and dark gray spheres represent oxygen atoms.



Fig. 3 Electric conductivity data for Ag<sub>5</sub>IO<sub>6</sub>. The specific resistance and linearized specific resistance (in inset) behaviors for Ag<sub>5</sub>IO<sub>6</sub>.



Fig. 4 Diffuse reflectance spectrum for  $Ag_5IO_6$  (R-reflectance).

The behavior of the specific resistance for  $Ag_5IO_6$  shows two regions, which correspond to different activation energies (Fig. 3). The best fits yield  $E_a = 7.4(1) \text{ meV}$  in the temperature range of 220 - 300 K, and  $E_a = 4.3(1) \text{ meV}$  in the temperature range of 90 - 180 K (full lines in the inset of Fig. 3). The change of activation energy in the temperature range of 180 - 220 K may indicate a phase transition. However, no temperature dependent effects were detected by low-temperature DSC measurements in the temperature range of 100 - 300 K. The optical band gap was determined from diffuse reflectance data and was found as 1.4 eV (Fig. 4). The large discrepancy between the optical band gap energy value and the activation energy as determined from conductivity measurements may be rationalized by assuming a significant contribution of ionic conductivity to the cumulative one, which was measured.

According to magnetic measurements,  $Ag_5IO_6$  is diamagnetic with a magnetic susceptibility of  $-4.4 \times 10^{-4}$  emu/mol (Fig. 5).



Fig. 5 Magnetic susceptibility data for Ag<sub>5</sub>IO<sub>6</sub>.

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