Synthesis and Crystal Structure of AgInO$_2$

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Single crystals of AgInO$_2$ were obtained by hydrothermal reaction of Ag$_2$O and In$_2$O$_3$ in NaOH at elevated temperature and O$_2$ pressure. The delafossite type crystal structure was refined using single crystal X-ray diffractometer data ($R3m$; a_{hex} = 327.68(7), c_{hex} = 1887.8(7) pm; Z = 3; R_w = 0.022; 171 independent structure factors). In–O and Ag–O bond distances are 217.4(4) and 207.6(8) pm, respectively. Structure and bond characteristics are discussed. © 1987 Academic Press, Inc.

Introduction

The Ag-delafossites are promising candidates for further studies on previously postulated Ag$^+$–Ag$^+$ bonding interactions (*1*). As the compounds all crystallize in the same (delafossite) structure, the possibility of varying the Ag–Ag distances over a wide range (~290–360 pm), without essentially changing other Ag-related parameters, arises. This would allow an almost matrix-independent evaluation of physical properties effected by the Ag–Ag distance. In order to provide a quantitative basis for these investigations, accurate crystallographic data concerning bond lengths and angles are necessary.

Although a large number of Ag-delafossites have been prepared (*2*) only few have been studied structurally in detail (AgAlO$_2$ (*3*) and AgFeO$_2$ (*4*)). Data on bond lengths etc. is therefore not available, with the aforementioned exceptions.

The present paper deals with the struc-tural properties of the compound AgInO$_2$, first described by Shannon *et al.* (*2*), and compares the Ag-delafossites structurally characterized to date.

Experimental

Synthesis

Crystals of AgInO$_2$ were obtained by heating 1 g of an equimolar mixture of Ag$_2$O and In$_2$O$_3$ in 5 g of a 40 wt% aqueous NaOH solution at 580°C for 4 days, cooling to 450°C at 10°C/hr and subsequently removing the heat source. The reaction was carried out in a gold tube within an autoclave under high (200 MPa) oxygen partial pressure, to prevent reaction with the container and decomposition of Ag$_2$O, respectively. Orange-yellow single crystals of AgInO$_2$ in the form of pseudo-hexagonal platelets of up to 0.05 mm thick and 0.2 mm in diameter resulted. The crystals were washed on the filter with large amounts of water to remove

the adsorbed NaOH solution. Failure to find Na by photometric analysis set an upper limit of 0.05% for the concentration of this element in the product.

Crystal Data and Structure Refinement

Rotation, Weissenberg, and precession photographs were taken in order to determine the crystal system and possible space groups, while unit cell parameters were refined from Guinier powder data ($CuK\alpha_1$, low quartz as internal standard): Rhombohedral, $R\bar{3}m$, a_{hex} = 327.68(7), c_{hex} =

TABLE I
POWDER DATA OF $AgInO_2$

h k l	d_o (pm)	I_o	h k l	d_o (pm)	I_o
0 0 3	629.59	1	1 1 6	145.36	9
0 0 6	314.81	8	2 0 2	140.29	5
0 1 2	271.81	8	0 2 4	135.88	5
1 0 4	243.33	7	0 1 14	121.77	1
0 1 8	181.52	5	2 0 8		
1 1 0	163.74	10	1 1 12	113.43	4
1 1 3	158.42	4	0 2 10		
0 0 12	157.26	8			
1 0 10					

TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS OF R-$AgInO_2$

h	k	l	10FO	10FC	h	k	l	10FO	10FC	h	k	l	10FO	10FC	h	k	l	10FO	10FC	h	k	l	10FO	10FC
-1	2	0	1701	1730	0	3	0	1096	1073	-2	4	0	917	909	-1	5	0	618	618	-1	1	1	215	-194
-2	3	1	53	52	-4	4	1	117	117	-1	4	1	104	104	0	5	1	149	136	0	1	2	1709	2057
-2	2	2	1436	1436	-1	3	2	1150	1131	-3	4	2	798	808	0	4	2	692	705	-5	5	2	503	494
-2	5	2	613	621	0	0	3	280	268	-1	2	3	224	223	-3	3	3	205	208	0	3	3	203	208
-2	4	3	206	206	-4	5	3	206	204	-1	5	3	208	204	-1	1	4	1468	1687	0	2	4	1258	1247
-2	3	4	1010	998	-4	4	4	613	629	-1	4	4	710	720	-3	5	4	545	552	0	5	4	442	438
0	1	5	368	364	-2	2	5	283	291	-1	3	5	257	262	-3	4	5	235	240	0	4	5	231	235
-5	5	5	227	221	-2	5	5	231	231	0	0	6	1549	1852	-1	2	6	1312	1328	-3	3	6	911	899
0	3	6	913	899	-2	4	6	764	760	-4	5	6	519	524	-1	5	6	522	524	0	2	7	110	96
-2	3	7	124	122	-4	4	7	153	155	-1	4	7	145	147	-3	5	7	162	159	0	5	7	169	162
0	1	8	1611	1738	-2	2	8	1346	1330	-1	3	8	1097	1075	-3	4	8	790	794	0	4	8	696	700
-2	5	8	616	617	0	0	9	288	-257	-1	2	9	73	-77	-3	3	9	43	40	0	3	9	63	40
-2	4	9	78	66	-4	5	9	116	106	-1	5	9	117	106	-1	1	10	1546	1593	0	2	10	1284	1257
-2	3	10	1055	1033	-4	4	10	678	684	-1	4	10	772	773	-3	5	10	603	605	-2	2	11	65	61
-1	3	11	92	91	-3	4	11	129	124	0	4	11	142	133	-2	5	11	141	140	0	0	12	1514	1417
-1	2	12	1166	1131	-3	3	12	813	806	0	3	12	818	806	-2	4	12	699	699	-4	5	12	492	487
-1	5	12	496	487	-1	1	13	197	204	0	2	13	191	197	-2	3	13	189	196	-4	4	13	203	201
-1	4	13	201	200	-3	5	13	203	200	0	1	14	1182	1137	-2	2	14	961	945	-1	3	14	809	803
-3	4	14	598	610	0	4	14	532	540	-2	5	14	476	478	0	0	15	107	119	-1	2	15	136	134
-3	3	15	158	156	0	3	15	156	156	-2	4	15	165	164	-4	5	15	185	173	-1	5	15	182	173
-1	1	16	1200	1148	0	2	16	988	962	-2	3	16	836	830	-4	4	16	564	569	-1	4	16	632	639
-3	5	16	508	506	0	1	17	66	-67	-1	3	17	39	25	-3	4	17	81	69	0	4	17	78	84
-2	5	17	116	94	0	0	18	1346	1212	-1	2	18	1051	1017	-3	3	18	778	769	0	3	18	780	770
-2	4	18	686	684	-1	1	19	75	-87	-4	4	19	74	66	-1	4	19	75	51	0	1	20	1017	999
-2	2	20	869	857	-1	3	20	745	751	-3	4	20	585	589	0	4	20	530	524	-1	2	21	76	60
-3	3	21	117	102	0	3	21	104	102	-2	4	21	127	115	-1	1	22	838	839	0	2	22	723	725
-2	3	22	625	635	-1	4	22	494	497	0	1	23	77	88	-2	2	23	110	108	-1	3	23	129	124
-3	4	23	148	145	0	0	24	872	834	-1	2	24	718	722	-3	3	24	558	560	0	3	24	550	560
-2	4	24	505	496	-2	3	25	57	44	0	1	26	798	816	-2	2	26	695	717	-1	3	26	624	635
0	0	27	103	-117	-1	1	28	748	772	0	2	28	660	682	-2	3	28	598	607	0	0	30	689	677
-1	2	30	587	597	0	2	31	75	52	0	1	32	538	559										

Atom	x	y	z	U11	U33	U(equ)
Ag	0	0	0	0.0171(3)	0.0050(6)	0.0102
In	0	0	$\frac{1}{2}$	0.0062(3)	0.0081(5)	0.0058
O	0	0	0.1100(4)	0.0085(9)	0.005(3)	0.0058

Note. Thermal parameters are of the form: $T = \exp[-2\pi^2(U11a^{*2}h^2 + \cdots + U23b^*c^*kl + \cdots)]\text{Å}^2$.

1887.8(7) pm, D_{calc} = 7.23 mg/m³, Z = 3. Powder data are given in Table I. The intensities of 2832 reflections were measured (2θ = 3–80°) using an automated diffractometer (Siemens-Stoe AED 2) and graphite monochromated MoKα radiation (scan width = 2.4+ $((\lambda_{\alpha2} - \lambda_{\alpha1})/\lambda_{\bar{\alpha}}) \cdot \tan \theta$). After averaging, applying absorption and LP-correction (μ(MoKα) = 165.73 cm, min. and max. transmission coefficients of 0.3411 and 0.6133, respectively), 171 independent structure factors, which are given in Table II, remained for refinement. Final R values of R = 0.033 and R_w = 0.022, with weights derived from counting statistics, were obtained. The atom parameters are given in Table III.

Results and Discussion

$AgInO_2$ is isostructural with $AgFeO_2$, $CuFeO_2$ (4), $CuAlO_2$ (5), $CuGaO_2$, and $CuYO_2$ (6), and has the delafossite structure. Oxygen atoms are stacked in the layer sequence (AABBCC) with Ag in linear coordination (AA, BB, and CC), and In in the octahedral sites (AB, BC, and CA). Bond distances and angles for $AgInO_2$ are given in Table IV. The accurate crystallographic data of Ag-delafossites studied to date is compiled in Table V. The change in the ratio $(O-M^{3+}-O^{III})/(O-M^{3+}-O^{II})$, which is a sensitive measure of the deformation (flat-

tening along the c axis) of the MO_6 octahedra, is insignificant (within the e.s.d's.) in going from Al (1.182) to In (1.190), whereas a significant increase is observed in the corresponding Cu-containing delafossites (Al (1.162), Y(1.287)) (6). In spite of the near constancy of the deformation of the MO_6 octahedra, the increase in In–O bond length as compared to that of the Al–O bond results in a 13% increase in the a unit cell dimension and a mere 3% in the c unit cell dimension. This is partially due to the fact that roughly 2/3 of the c unit cell parameter is determined by Ag–O bonds, whereas these do not contribute to the a unit cell dimension. Furthermore, the increase in the dimensions of the MO_6 octahedra in the direction of the c axis is partially compensated by the decrease in Ag–O bond length in going from Al to In. Considering the Ag–O bond lengths, a significant increase with decreasing Ag–Ag distance is observed, leading to an apparent decrease in the valence sum of Ag by about 10% (7). This increase in Ag–O bond length could be a compensation for bonding interaction between adjacent Ag atoms in the same layer (1, 6, 8). The large value of the temperature factor U11 of all Ag atoms, and the highly anisotropic nature thereof, as demonstrated by the ratio U11/U33, could be further supporting evidence.

The nonconformity of $AgFeO_2$ could possibly be due to a partial transfer of charge between Fe and Ag.

Ag–O	207.6(8)	(2×)	O–In–O⁽ᴵ⁾	180
In–O	217.4(4)	(6×)	O–In–O⁽ᴵᴵ⁾	82.2(2)
O–Ag–O⁽ᴵ⁾	180		O–In–O⁽ᴵᴵᴵ⁾	97.8(2)

Note. Symmetry code (I) $-x$, $-y$, $-z$; (II) $-x$, x, $-z$; (III) $-y$, $-x$, z.

TABLE V

CRYSTALLOGRAPHIC AND BOND DATA OF Ag-DELAFOSSITES

	$2H\text{-}AgAlO_2$	$AgFeO_2$	$AgInO_2$
Reference	(3)	(4)	This work
c (pm)	1221.9(7)	1859.0(2)	1887.8(7)
Ag–Ag (pm)	289.6(1)	303.91(2)	327.68(7)
Ag–O (pm)	210.1(5)	206.7(8)	207.6(8)
M–O (pm)	192.5(3)	203.5(4)	217.4(4)
$O\text{-}M^{3+}\text{-}O^{(III)}$ (°)	97.5(3)	96.6	97.8(2)
$(O\text{-}M^{3+}\text{-}O^{(III)})/(O\text{-}M^{3+}\text{-}O^{(II)})$	1.182	1.158	1.190
U11 (Ag)	0.061(3)	—	0.171(3)
U11/U33 (Ag)	2.35	—	3.42
Valence of one M–O bond (5)	0.477	0.460	$(0.482)^a$
Valence of one Ag–O bond (5)	0.567	0.640	0.620
Total valence on O (1 × (Ag–O) + 3 × (M^{3+}–O))	1.999	2.020	$(2.067)^a$
Total valence on M (6 × (M^{3+}–O)	2.864	2.761	$(2.895)^a$
Total valence on Ag (2 × (Ag–O)	1.134	1.280	1.239

^{a} Parentheses indicate uncertainty in the constants (7) used in the valence calculations.

Acknowledgments

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