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Crystallographic data for pure crystalline silver ferrite. By WILLIAM J. CROFT, N. C. TOMBS and R. E. ENGLAND, *Sperry Rand Research Center, Sudbury, Mass., U.S.A.*

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The formation of a silver ferrite of empirical formula AgFeO_2 by reactions involving iron hydroxides and silver compounds in aqueous suspensions was reported by Krause, Ernst, Gawryck & Kocay (1936). The initial interest of these authors was in use of the red-colored silver compound in identification of specific iron hydroxide compounds. The products obtained were apparently poorly crystallized and/or inhomogeneous, and the reported X-ray diffraction powder data consisted of only nine reflections. The unit cell deduced from these results was rhombohedral, $a_R = 4.61 \text{ \AA}$, $\alpha = 85^\circ 25'$.

The present work describes the preparation of silver ferrite, AgFeO_2 , in the form of single crystals from which optical and improved crystal data have been obtained.

The preparation involved the reaction of a mixture of silver oxide (Ag_2O) and α -ferric oxide (Fe_2O_3) under hydrothermal conditions in basic solutions, for example aqueous sodium hydroxide, concentrations from 3*M* to 12*M* being used successfully. The reaction system was sealed in a thin-walled platinum tube which was heated in a Stellite pressure vessel of conventional design. The reaction was essentially complete in 72 hr at 400 °C and 40,000 lb.in⁻², but no attempt was made to study the kinetics. Use of a slight excess of silver oxide ensured that no free ferric oxide remained. The unreacted silver oxide could be removed readily by treatment with dilute nitric acid. The reaction product consisted of shiny platelets up to about 2 mm on a side and about 0.2 mm thick, together with finer crystallized material. Both the platelets and the smaller crystallites gave the same X-ray powder pattern.

Emission spectrographic analysis showed only silver

and iron as major constituents. Of special interest is the fact that sodium was present to the extent of less than 1 p.p.m., although the crystallization took place in sodium hydroxide solution.

Up to 0.3% sodium has been reported in preparations from coprecipitated hydroxides (Krause & Pilawski, 1931).

Quantitative chemical analysis for silver and iron was performed by flame photometry. The sample and standards were dissolved in concentrated sulfuric acid which was then diluted. The analytical results confirmed a silver to iron atomic ratio of one to one.

Many of the thinner platelets were transparent and a rich ruby red color in transmission. They gave a uniaxial negative interference figure. The crystals were too deeply colored for refractive index determination, but the mean value is greater than 2. Some of the platelets were six-sided. The included angle between the edges has been measured microscopically to be 120°.

A group of platelets was mounted on a flat glass plate and examined in a diffractometer using nickel-filtered copper radiation (45 kV and 40 mA). A scintillation counter detector with pulse height discrimination was used. Assuming hexagonal symmetry, all of the 00*l* reflections were measured. With this as a basis the entire powder pattern (Table 1) was indexed on a hexagonal cell. The dimensions are $a = 3.041$, $c = 18.55 \text{ \AA}$. The true symmetry is rhombohedral. The dimensions of the primitive cell are $a_R = 6.427 \text{ \AA}$, $\alpha = 27^\circ 22'$. The pattern is indexed in the obverse position notation (*International Tables for X-ray Crystallography*, 1952). The powder pattern was made in a Straumanis-loaded camera, 114.59 mm diameter, using manganese-filtered iron radiation. Intensity measurements were made by visual estimation.

The density was measured in toluene, with a modified Bernan balance. A value of 6.39 g.cm⁻³ was obtained. The calculated value of 6.56 was obtained by using a value of 3 units of AgFeO_2 per hexagonal unit cell.

When heated in air, AgFeO_2 crystals are stable up to about 700 °C, at which temperature they decompose with loss of oxygen to yield metallic silver and $\alpha \text{ Fe}_2\text{O}_3$. In view of its transparency in the form of thin crystals, further study of the optical properties could be of interest. Likewise, the magnetic properties may merit investigation.

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References

- KRAUSE, A., ERNST, Z., GAWRYCK, ST. & KOCAY, W. (1936). *Z. anorg. Chem.* **228**, 352.
KRAUSE, A. & PILAWSKI, K. (1931). *Z. anorg. Chem.* **197**, 301.

Table 1. X-ray powder data for AgFeO_2

Hexagonal indices	Rhombohedral indices	d_c	d_o	I/I_0
003	111	6.183	6.188	w
006	222	3.091	3.091	s
101	100	2.607	2.607	w
012	110	2.533	2.532	s
104	211	2.290	2.290	m
009	333	2.061	2.062	w
107	322	1.868	1.869	w
018	332	1.740	1.742	m
0,0,12	444	1.546	1.548	w
110	10 $\bar{1}$	1.520	1.515	m+
1,0,10	433	1.516		
116	321	1.364	1.363	m-
202	200	1.303	1.303	w
024	220	1.266	1.266	w-
0,1,14	554	1.183	1.186	w+
208	422	1.145	1.145	w
1,1,12	543	1.084	1.085	w+
0,2,10	442	1.073	1.073	w
1,0,16	655	1.061	1.062	w
0,0,18	666	1.031	1.033	m-
122	21 $\bar{1}$	0.9897	0.9892	w-