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A New Delafossite-Type Compound $CuYO_2$

I. Synthesis and Characterization

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Single crystals of a new delafossite-type compound $CuYO_2$ were grown from a Cu_2O–Y_2O_3 melt by slow cooling from 1210°C. The crystal is hexagonal, $P6_3/mmc$, $a = 3.5206(1)$ Å, $c = 11.418(1)$ Å, $Z = 2$ and $D_x = 5.01$ g/cm^3. Although the crystal belongs to the 2H-polytype of the delafossite family, selected peaks showed a large line broadening on the X-ray powder profile. Correspondingly, diffuse scattering along the c axis was observed for the reflections $h - k \neq 3n$ on the precession photographs. The approximate crystal structure was analyzed by means of single-crystal X-ray diffraction with a conventional R value of 0.106.

Introduction

Delafossite, $CuFeO_2$, is a mineral discovered by Pabst (*1*). About 30 isomorphic compounds have been reported. The delafossite type structural group has the formula $A^+B^{3+}O_2$ (A = Cu, Ag, Pd, and Pt; B = Al, Sc, Cr, Fe, Co, Ga, Rh, In, La, Pr, Nd, Sm, Eu, and Tl, etc.), and three polytypes (3R, 2H, and 6H) have been found. Shannon and co-workers synthesized a series of 3R-type delafossite-type compounds containing Pd^+ and Pt^+ in the A site, analyzed the crystal structures, and measured the anisotropies of their electrical conductivities (*2–4*). Haas and Kordes synthesized 3R-type $CuLnO_2$ (Ln = La, Pr, Nd, Sm, and Eu) and suggested that the delafossites with lanthanide ions have a shorter c length than other delafossite-type compounds (*5*). Okamoto *et al.* (*6*) and Hayashi *et al.* (*7*) synthesized 2H-type delafossites δ-$AgFeO_2$ and $Cu^+(Cu^{2+}, Ti^{4+})O_2$, respectively, and analyzed their crystal structures. Stählin *et al.* prepared 6H-type analogs, $AgMO_2$ (M = Fe, Co, and Cr) but did not determine their structures (*8*). Ishiguro *et al.* prepared $CuAlO_2$ single crystals from Cu_2O–Al_2O_3 molten salts, refined the crystal structure, and found the thermal vibration of the Cu^+ ion to be very anisotropic (*9*). They also investigated the structural change of $CuAlO_2$ at high temperatures (*10*).

No phase diagram has been reported for the Cu–Y–O system. Schemitz–DuMont investigated cupric yttrate $Cu_2Y_2O_5$ which has the same structure of $Cu_2In_2O_5$ (*11*). The ionic radius of the Y^{3+} ion at the octahedral site lies between those of lanthanoid ions and other smaller trivalent ions, and the structures of delafossite family are rather different between those containing larger B^{3+} ion and those containing smaller ones. Thus we were interested in the delafossite structure with the midsize ion Y^{3+}. This paper covers the synthesis, crystal growth, and crystal structure determination of the new delafossite-type compound $CuYO_2$.

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Experimental

Synthesis and crystal growth. Polycrystalline and single crystal $CuYO_2$ was prepared by solid state reaction and flux growth techniques, respectively. The chemicals used were 99.99% pure Y_2O_3 obtained from Soekawa Chemicals (Tokyo, Japan) and regent grade Cu_2O from Wako Pure Chemicals (Tokyo, Japan). From the preliminary experiments it was found that $CuYO_2$ could be synthesized under a restricted oxygen pressure ($P_{O_2} = 10^{-4}$–10^{-2} atm) at 1100°C, but the reaction rate was so slow that calcination in air had to precede the reaction under the proper atmosphere which gives pure polycrystalline $CuYO_2$. Cu_2O and Y_2O_3 were mixed in a Cu/Y ratio slightly greater than 1.0 with methanol. The intermediate reactant $Cu_2Y_2O_5$ was synthesized by heating the powder mixture in an Al_2O_3 Tammann tube at 1000°C in air for 1 day. The product was heated at 1100°C in a stream of N_2 and air (mixing ratio 25 : 1, and $P_{O_2} = 10^{-2}$ atm) or in an N_2 flow ($P_{O_2} = 10^{-4}$ atm) for 4 days. The excess copper oxide was removed from the reactants by leaching in aqueous ammonia for 2 days. The $CuYO_2$ powder specimen was identified by chemical analysis and powder X-ray diffraction analysis.

Single crystals were grown at $P_{O_2} = 10^{-4}$ atm. A mixture of Cu_2O (27.7g) and Y_2O_3 (2.3g) was packed into a high-purity recrystallized alumina Tammann tube (10 cm^3) which was located at the center of an electric furnace. Dried N_2 gas was passed through the reaction tube in the furnace at the rate of 200 cm^3/min. The furnace was heated at 200°C/hr to 1210°C, maintained at that temperature for 5 hr, then cooled at 2°C/hr to 1050°C. The sample was quenched to room temperature by pulling the Tammann tube to the upper part of the furnace. The $CuYO_2$ crystals were separated from the matrix (solidified copper oxide) by leaching in aqueous ammonia for 7 days. As-grown crystals were examined by optical microscopy and single-crystal X-ray diffraction techniques.

Crystal structure analysis. Powder X-ray diffraction patterns were obtained at 20°C using Cu$K\alpha$ radiation. The equipment was calibrated with Si. Unit cell dimensions were determined from 29 reflections in the range $15 \leqq 2\theta \leqq 140°$ (Cu$K\alpha$) with least-squares procedure. Single-crystal X-ray diffraction photographs were taken with a Buerger precession camera. A small triangular platelet crystal with dimensions $0.15 \times 0.15 \times 0.02$ mm^3 was used for the intensity measurements. Intensity data were collected on an automated four-circle diffractometer (Philips PW1100) with Mo$K\alpha$ radiation monochromated by a graphite single crystal. The ω-2θ scan technique was employed with a scanning speed 3°/min in ω and the scan width 2.0°. The scanning was repeated twice when the total counts were less than 10,000. The intensities were corrected for Lorentz polarization and absorption effect (μ = 403.8 cm^{-1}). In all, 286 independent reflection data, whose $|F|$'s were larger than $3\sigma(|F|)$, were obtained within the range $2\theta < 137°$ and used for the structure determination. The structure was refined with the full-matrix least-squares program LINUS (*13*) using anisotropic temperature factors. The predicted value from the cell dimensions and ionic radii as reported before (*12*) was used for the initial value of oxygen atom position. The atomic scattering factors for Cu^+ and Y^{3+} and the dispersion correction factors for Cu, Y, and O were taken from "International Tables for X-Ray Crystallography" (*14*), and the atomic scattering factors for O^{2-} were taken from those given by Tokonami (*15*).

Computations were carried out on a M-200H computer at the Computer Center of the Tokyo Institute of Technology.

Results and Discussion

Both $CuYO_2$ powder specimens synthesized in $P_{O_2} = 10^{-4}$ and 10^{-2} atm were light green. Single crystals grown in $P_{O_2} = 10^{-4}$ atm were transparent and light-green platelets with approximately 0.3 mm diameter and 0.05 mm thickness. From the X-ray powder profiles of both powder specimens, several peaks were found to be quite broad. All the lines, however, were indexed on a hexagonal cell as shown in Table I. The chemical compositions and the cell dimensions are listed in Table II. These values suggested that the new compound $CuYO_2$ was a nearly stoichiometric compound independent on the oxygen partial pressure in synthesis.

TABLE I

POWDER X-RAY DIFFRACTION DATA OF $CuYO_2$

P_{O_2} (atm)			10^{-4}		10^{-2}	
hkl			*d*	I/I_0	*d*	I/I_0
0	0	2	5.7167	25	5.7021	44
1	0	0	3.0491	18	3.0450	25
1	0	1[a]	2.9450	59	2.9478	69
0	0	4	2.8559	68	2.8524	77
1	0	2[a]	2.6929	38	2.6897	45
1	0	4[a]	2.0840	5	2.0840	5
1	0	5[a]	1.8268	6	1.8248	4
1	1	0	1.7603	100	1.7593	100
1	1	2	1.6823	12	1.6817	12
1	0	6[a]	1.6140	4	1.6143	6
2	0	0	1.5242	3	1.5242	5
2	0	1[a]	1.5105	6	1.5099	8
1	1	4	1.4986	45	1.4980	47
2	0	2	1.4733	7	1.4727	10
0	0	8	1.4276	8	1.4270	8
2	1	0	1.1526	4	1.1522	4
0	0	10	1.1465	4	1.1462	4
2	1	2[a]	1.1296	6	1.1296	8
1	1	8	1.1088	16	1.1086	15
3	0	0	1.0163	13	1.0164	12
3	0	2	1.0006	3	1.0007	3
1	1	10	0.9575	10	0.9576	11
0	0	12	0.9515	3	0.9516	3
3	0	6	0.8964	1	0.8963	1
2	2	0	0.8801	7	0.8802	6
2	2	2	0.8698	3	0.8699	3
3	1	0	0.8456	2	0.8456	3
2	2	4	0.8412	7	0.8411	9
1	1	12	0.8370	10	0.8370	10
3	0	8	0.8278	5	0.8279	6

[a] Diffused peak.

TABLE II

CHEMICAL COMPOSITIONS AND CELL DIMENSIONS OF POLYCRYSTALLINE $CuYO_2$

P_{O_2} (atm)		10^{-4}	10^{-2}
Chemical composition (wt%)	Cu	34.2(34.4)	34.3(34.4)
	Y	49.2(48.2)	48.0(48.2)
	Al	0.1(0.0)	0.1(0.0)
	O	16.6(17.4)	17.7(17.4)
Direct cell parameter	*a*(Å)	3.5206(1)	3.5205(2)
	c(Å)	11.418(1)	11.417(1)
	V(Å^3)	122.56(1)	122.54(2)
Reciprocal cell parameter	a^* (Å^{-1})	0.32799(1)	0.32799(2)
	c^* (Å^{-1})	0.087582(5)	0.087590(7)

Note. Figures in parentheses are calculated from the stoichiometric formula or estimated standard deviations.

Crystallographic data for $CuYO_2$ synthesized in $P_{O_2} = 10^{-4}$ atm are given in Table III. The systematic absence, *hhl* for *l* odd was observed on the Buerger precession photographs, which restricted the space group to $P\bar{6}2c$, $P6_3mc$, or $P6_3/mmc$. Selective diffuse scattering along the c^* direction was observed for the reflections $h - k \neq 3n$ on the photographs. The diffuse scattering explains the line broadening of the powder profile data and suggests that the 2H-type stacking mode frequently disordered in the $CuYO_2$ crystal. The approximate structure was analyzed based on a simple 2H-polytype model with the space group $P6_3/mmc$. The final conventional *R* value became 0.106 as the result of the refinement. At the final stage of the refinement, several peaks with the height of approximately 10 e/Å^3

TABLE III

CRYSTAL DATA FOR $CuYO_2$

Hexagonal
$P6_3/mmc$
$a = 3.5206(1)$ Å
$c = 11.418(1)$ Å
$V = 122.56(1)$ Å^3
$Z = 2$
$M = 184.45$
$D_x = 5.01$ g/cm^3

TABLE IV

FINAL POSITIONAL AND THERMAL PARAMETERS OF $CuYO_2$

Atom	x	y	z	U_{11}	U_{33}	B_{iso}
Cu	0	0	0	135(9)	57(9)	0.86
Y	0	0	0.5	47(4)	75(7)	0.42
O	0	0	0.0893(11)	69(23)	51(28)	0.49

Note. Values in parentheses are estimated deviations. The thermal parameters refer to the expression,

$$T = \exp(-10^{-4}\, 2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^*)),$$

where $U_{22} = U_{11}$, $U_{12} = 1/2U_{11}$, and $U_{23} = U_{13} = 0$. Isotropic temperature factors B_{iso} are calculated from the anisotropic thermal parameters, U_{11} and U_{33}.

still remained on the difference Fourier maps. These peaks can be basically explained by the stacking faults of the structure. Powder profile analysis with respect to the stacking disorder of the crystal will be mentioned in the next article (*17*). The final positional and thermal parameters are given in Table IV. Selected interatomic distances and bond angles are presented in Table V.

TABLE V

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) OF $CuYO_2$

Cu-O	(×2)	1.835(12)
Y-O	(×6)	2.276(5)
Cu-Cu^i	(×6)	3.524(1)
O-O^i	(×6)	3.524(1)
O-O^{ii}	(×6)	2.881(12)
O-Y-O^i	(×6)	101.5(2)
O-Y-O^{ii}	(×6)	78.5(2)
Cu-O-Y	(×3)	116.6(3)
Y-O^i-Y^i	(×3)	101.5(2)

Note. Symmetry codes:

None	x	y	z
(*i*)	x	$y-1$	z
(*ii*)	$y-1$	x	$-z$

The approximate structure of $CuYO_2$ is the same as other 2H-type delafossite compounds, δ-$AgFeO_2$ (*6*) and $Cu(Cu,Ti)O_2$ (*7*). The Cu^+ ions are lineally coordinated by two O^{2-} ions whereas Y^{3+} ions are octahedrally coordinated by six O^{2-} ions. The YO_6 octahedra share six edges each other to form the $\{YO_2^-\}_\infty$ sheets parallel to (001). The Cu^+ ions have the role of combining these layers. The stacking mode of the layer unit which consists of Cu^+ and $\{YO_2^-\}_\infty$ is resemble to the *hcp* structure. The Cu–O and the Y–O distances are 1.835 and 2.276 Å, respectively. They agreed well with the values calculated from the ionic radii, $^{II}Cu^+$ = 0.46, $^{VI}Y^{3+}$ = 0.900, and $^{IV}O^{2-}$ = 1.38Å, where II, IV, and VI are coordination numbers (*16*). The unshared O–O length $(O-O)^u$ and the shared one $(O-O)^s$ in a YO_6 octahedron are 3.524 and 2.276 Å, respectively. The ratio $(O-O)^u/(O-O)^s$ is 1.223 and is the highest value of all (Table VI). This indicates that the YO_6 octahedra in $CuYO_2$ have the most collapsed shape on (001) in the delafossite type structures which have been analyzed. The value of U_{11} component of the thermal parameter of the Cu^+ ion is larger than U_{33}, and the ratio $U_{11}/$

TABLE VI

ANISOTROPY OF THE THERMAL VIBRATION OF THE A^+ ION AND DISTORTION OF BO_6 OCTAHEDRON IN THE DELAFOSSITE ABO_2 COMPOUNDS

	U_{11}/U_{33} of A^+	$(O-O)^u/(O-O)^s$	Reference
$CuAlO_2$	1.74	1.126	(9)
$CuGaO_2$	3.00	1.127	—
$CuYO_2$	2.37	1.223	This work
$PtCoO_2$	—	1.137	(3)
$PdCoO_2$	—	1.106	(3)
$CuFeO_2$	—	1.122	(3)
α-$AgFeO_2$	—	1.123	(3)
δ-$AgFeO_2$	1.56	1.121	(6)
$Cu(Cu,Ti)O_2$	1.74	1.138	(7)

Note. $(O-O)^u$ and $(O-O)^s$ are the unshared and shared O–O length of the BO_6 octahedron, respectively.

U_{33} is 2.37 (Table VI). This large anisotropy in the thermal vibration of the A^+ ion is commonly found in the delafossite-type compounds.

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