

## Single-Crystal Growth and Crystal Structure Refinement of $\text{CuAlO}_2$

T. ISHIGURO, A. KITAZAWA, N. MIZUTANI, AND M. KATO\*

*Department of Inorganic Materials, Faculty of Engineering,  
Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan*

Received April 6, 1981; in revised form July 9, 1981

Single crystals of the delafossite-type compound  $\text{CuAlO}_2$  were grown from  $\text{Al}_2\text{O}_3\text{-Cu}_2\text{O}$  melt by a slow-cooling method from  $1200^\circ\text{C}$ . Three types were found in as-grown crystals (single crystals, short-columnar twin crystals with concave angles, and laminar twin crystals). The twinning form is similar to the spinel-type twin.  $\text{CuAlO}_2$  is rhombohedral,  $R\bar{3}m$ ,  $a = 2.8604(7)$ ,  $c = 16.953(5)$  Å,  $Z = 3$ ,  $D_x = 5.12$  g/cm<sup>3</sup> and  $D_m = 5.06$  g/cm<sup>3</sup>. The crystal structure of  $\text{CuAlO}_2$  was analyzed by means of single-crystal X-ray diffraction with a conventional  $R$  value = 0.038. The value of the  $U_{11}$  component of the thermal parameter of  $\text{Cu}^+$  was twice as large as  $U_{33}$ .

### Introduction

The delafossite-type compounds have the formula  $ABO_2$  ( $A = \text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Pd}^+$ , and  $\text{Pt}^+$ , and  $B = \text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ , and  $\text{Rh}^{3+}$ , etc.). The compounds whose structures have been determined by the single-crystal X-ray method are  $\text{PtCoO}_2(3R)$  (2),  $\text{PdCoO}_2(3R)$  (2),  $\text{CuFeO}_2(3R)$  (2),  $\alpha\text{-AgFeO}_2(3R)$  (2),  $\delta\text{-AgFeO}_2(2H)$  (4) and  $\text{Cu}(\text{Cu}_{0.5}\text{Ti}_{0.5})\text{O}_2(2H)$  (5), where the 3R and 2H are the notation of polytypes proposed by Ramsdell (6). Rogers *et al.* have studied the delafossite-type compounds systematically, and classified them into two types due to their electrical behavior (3). One type, including  $\text{Pt}^+$  or  $\text{Pd}^+$  ( $d^9$  ion) as the  $A^+$  ion, shows metallic conductivity and the other, including  $\text{Ag}^+$  or  $\text{Cu}^+$  ( $d^{10}$  ion), shows semiconductivity.

Generally, the delafossite-type compounds containing  $\text{Cu}^+$  melt incongruently at high temperature, so that it is difficult to get single crystals large enough to measure

the electrical conductivity. Although the crystal growth of these compounds was studied under hydrothermal conditions by Shannon *et al.* (1), the sizes of as-grown crystals were relatively small. Gadalla and White have reported that the  $\text{CuAlO}_2\text{-Cu}_2\text{O}$  system has a eutectic point about  $1130^\circ\text{C}$  (7). The authors succeeded in the growth of the single crystals of  $\text{CuAlO}_2$  by using a  $\text{Cu}_2\text{O}$  flux.

Hahn and Lorent have studied the crystal structure of  $\text{CuAlO}_2$  with the powder X-ray method and reported the positional parameter  $z$  of  $\text{O}^{2-}$  to be 0.12 (8). This paper covers the crystal growth and crystal structure refinement of  $\text{CuAlO}_2$ .

### Experimental

#### Single-Crystal Preparation

Single crystals of  $\text{CuAlO}_2$  were grown by slow-cooling the melt of a mixture of  $\text{CuAlO}_2$  powder and  $\text{Cu}_2\text{O}$ . The reagent grade copper oxide (mixture of 40 mole%  $\text{Cu}_2\text{O}$  and 60 mole%  $\text{CuO}$ ) and  $\text{Al}_2\text{O}_3$  were mixed in a  $\text{Cu/Al}$  ratio slightly greater than

\* To whom correspondence should be addressed.

1.0 by wet-ball milling with methanol.  $\text{CuAlO}_2$  powder was prepared by calcining this mixture in an  $\text{Al}_2\text{O}_3$  crucible at  $1050^\circ\text{C}$  for 4 days in air. The excess copper oxide was removed from the heated material by leaching in  $1N$   $\text{HNO}_3$  at  $100^\circ\text{C}$  for 2 days. The  $\text{CuAlO}_2$  powder was identified by chemical analysis and powder X-ray diffraction to determine the phase.

A mixture of  $\text{CuAlO}_2$  powder (5 g) and copper oxide powder (45 g) was packed into a high-purity alumina  $30\text{-cm}^3$  crucible. The crucible covered with mullite bricks was located at the center of the electrical furnace, and the temperature of the furnace was measured on the surface of the bricks by a Pt-13%Rh thermocouple. The furnace was heated at  $200^\circ\text{C/hr}$  to  $1200^\circ\text{C}$ , maintained at that temperature for 5 hr, cooled to  $1050^\circ\text{C}$  with various cooling rates (10, 2, and  $0.5^\circ\text{C/hr}$ ), and cooled to the room temperature by turning off the power of the furnace. The  $\text{CuAlO}_2$  crystals were separated from a matrix of solidified copper oxide flux by leaching in  $1N$   $\text{HNO}_3$  at  $100^\circ\text{C}$  for 4 days.

#### *Crystal Structure Analysis*

The powder X-ray diffraction patterns were obtained at  $20^\circ\text{C}$  using  $\text{CuK}\alpha$  radiation. The equipment was calibrated with Si standard. Unit cell dimensions were determined by a least-squares procedure. An optical microscope and Buerger precession camera were used for determining the relation between twinning and crystal shape. A small octahedral shape crystal with dimensions  $0.2 \times 0.2 \times 0.2$  mm was used for intensity measurements. Intensity data were collected on an automated four-circle diffractometer Philips PW1100 with  $\text{MoK}\alpha$  radiation monochromated by a graphite single crystal. The  $\omega$ - $2\theta$  scan technique was employed with a scanning speed of  $6^\circ/\text{min}$  in  $\omega$  and the scan width  $(1.3 + 0.2 \tan \theta)^\circ$ . The scanning was repeated twice when the total counts were less than 10,000. The in-

tensities were corrected for Lorentz-polarization and absorption effects ( $\mu = 138.1 \text{ cm}^{-1}$ ). In all, 333 independent reflection data, whose  $|F|$ 's were larger than  $3\sigma(|F|)$ , were obtained within the range  $2\theta < 160^\circ$  and used for the structure determination. The starting positions of all atoms were assumed to be the same as  $\text{CuFeO}_2$  (2). The structure was refined with the full-matrix least-squares program Linus (9) using anisotropic temperature factors. Secondary extinction effects were taken into consideration. The weighting scheme described by Hughes (10) was adopted:  $w = 1.0$  if  $|F_o| < 250.0$ , and  $w = (250.0/|F_o|)^2$  if  $|F_o| \geq 250.0$ . The atomic scattering factors for  $\text{Cu}^+$  and  $\text{Al}^{3+}$  and the dispersion correction factors for Cu, Al, and O were taken from "International Tables for X-Ray Crystallography" (11), and the atomic scattering factors for  $\text{O}^{2-}$  were taken from those given by Tokonami (12).

## **Results and Discussion**

### *Crystal Growth*

The  $\text{CuAlO}_2$  powder was dark blue, and its powder X-ray pattern agreed well with that of the JCPDS card (13). This shows that the  $\text{CuAlO}_2$  does not decompose easily to  $\text{CuAl}_2\text{O}_4$  and  $\text{CuO}$  (or  $\text{Cu}_2\text{O}$ ), although it seems unstable below  $1030^\circ\text{C}$  from phase diagram (7). The  $\text{CuAlO}_2$  single crystals were grown by slow-cooling to  $1050^\circ\text{C}$  from  $1200^\circ\text{C}$  above the liquidus line at the  $\text{Al}_2\text{O}_3$  rich side of the eutectic point. The chemical compositions of powder and single crystals are given in Table I and are in good agreement with the theoretical value based on the stoichiometric compound.

As-grown crystals are classified into three groups (single crystals, short-columnar twin crystals with concave angles and laminar twin crystals without apparent concave angles). The change of the cooling rate affects not only the crystal size but also the kind of crystal grown (Table II). The single

TABLE I  
CHEMICAL ANALYSIS OF CuAlO<sub>2</sub> SPECIMEN (wt%)

Atom	Theoretical	Polycrystalline	Single crystal
Cu	51.9	50.6	51.8
Al	22.0	22.1	22.1
Fe	—	0.10	—
Ni	—	<0.02	—
Co	—	<0.02	—
Na	—	0.01	—
O	26.1	27.2	26.1

crystals were grown only at an extremely slow cooling rate. Figure 1 shows the microscopic photographs and schematic crystal shapes. The single crystals have octahedral or rhombohedral shapes, whereas the twin crystals have triangular or hexagonal short-columnar shapes with concave angles or laminar shapes without apparent concave angles. Twinning occurs by a 60° rotation around the *c* axis. The twinning form is similar to the spinel-type contact twin observed in diamond. The hexagonal short-columnar shape twin crystal is found to be constituted from three individuals (see Fig. 1b). The (*hk*1) precession photograph of the single crystal has three-fold symmetry but that of the twin crystal with concave angles has pseudo six-fold symmetry. The reason why the laminar crystals without apparent concave angles are found to be twinned is that the pattern of their precession photograph is identical to that of twin crystals with concave angles.

TABLE II

THE RELATIONSHIPS BETWEEN THE COOLING RATE AND THE MAXIMUM DIAMETER (mm) OF AS-GROWN CRYSTALS

Cooling rate (°C/hr)	Laminar twin crystals	Columnar twin crystals	Single crystals
10	0.1	X	X
2	2	1	X
0.5	5	2	1

Note. X: not obtained.

TABLE III  
CRYSTAL DATA FOR CuAlO<sub>2</sub>

Rhombohedral
$R\bar{3}m$
$a = 2.8604(7) \text{ \AA}$
$c = 16.953(5) \text{ \AA}$
$Z = 3$
$M = 122.52$
$D_x = 5.12 \text{ g/cm}^3$
$D_m = 5.06 \text{ g/cm}^3$

TABLE IV  
FINAL POSITIONAL AND THERMAL PARAMETERS

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{33}$	$B_{180}$
Cu	0	0	0	113(1)	65(1)	0.76
Al	0	0	0.5	57(1)	76(3)	0.50
O	0	0	0.10979(8)	75(2)	75(3)	0.59

Note. Values in parentheses are estimated deviations. The thermal parameters refer to the expression,  $T = \exp(-10^{-4} \cdot 2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^*))$ , where  $U_{22} = U_{11}$ ,  $U_{12} = 1/2U_{11}$  and  $U_{23} = U_{31} = 0$ . Isotropic temperature factors  $B_{180}$  are calculated from the anisotropic thermal parameters,  $U_{11}$  and  $U_{33}$ .

TABLE V  
SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)

Cu—O	(×2)	1.861(1)
Al <sup>III</sup> —O	(×6)	1.912(1)
Cu—Cu <sup>I</sup>	(×6)	2.860(1)
O—O <sup>I</sup>	(×6)	2.860(1)
O—O <sup>IV</sup>	(×6)	2.539(2)
O—Al <sup>III</sup> —O <sup>I</sup>	(×6)	96.81(4)
O—Al <sup>III</sup> —O <sup>IV</sup>	(×6)	83.19(4)
Cu—O—Al <sup>III</sup>	(×3)	120.28(4)
Al <sup>III</sup> —O—Al <sup>III</sup>	(×3)	96.81(4)

Symmetry code

none	<i>x</i>	<i>y</i>	<i>z</i>
(i)	<i>x</i>	<i>y</i> - 1	<i>z</i>
(ii)	<i>x</i> + $\frac{1}{2}$	<i>y</i> + $\frac{2}{3}$	<i>z</i> - $\frac{1}{3}$
(iii)	<i>x</i> + $\frac{1}{2}$	<i>y</i> - $\frac{1}{3}$	<i>z</i> - $\frac{1}{3}$
(iv)	<i>x</i> + $\frac{2}{3}$	<i>y</i> + $\frac{1}{3}$	$\frac{1}{3}$ - <i>z</i>

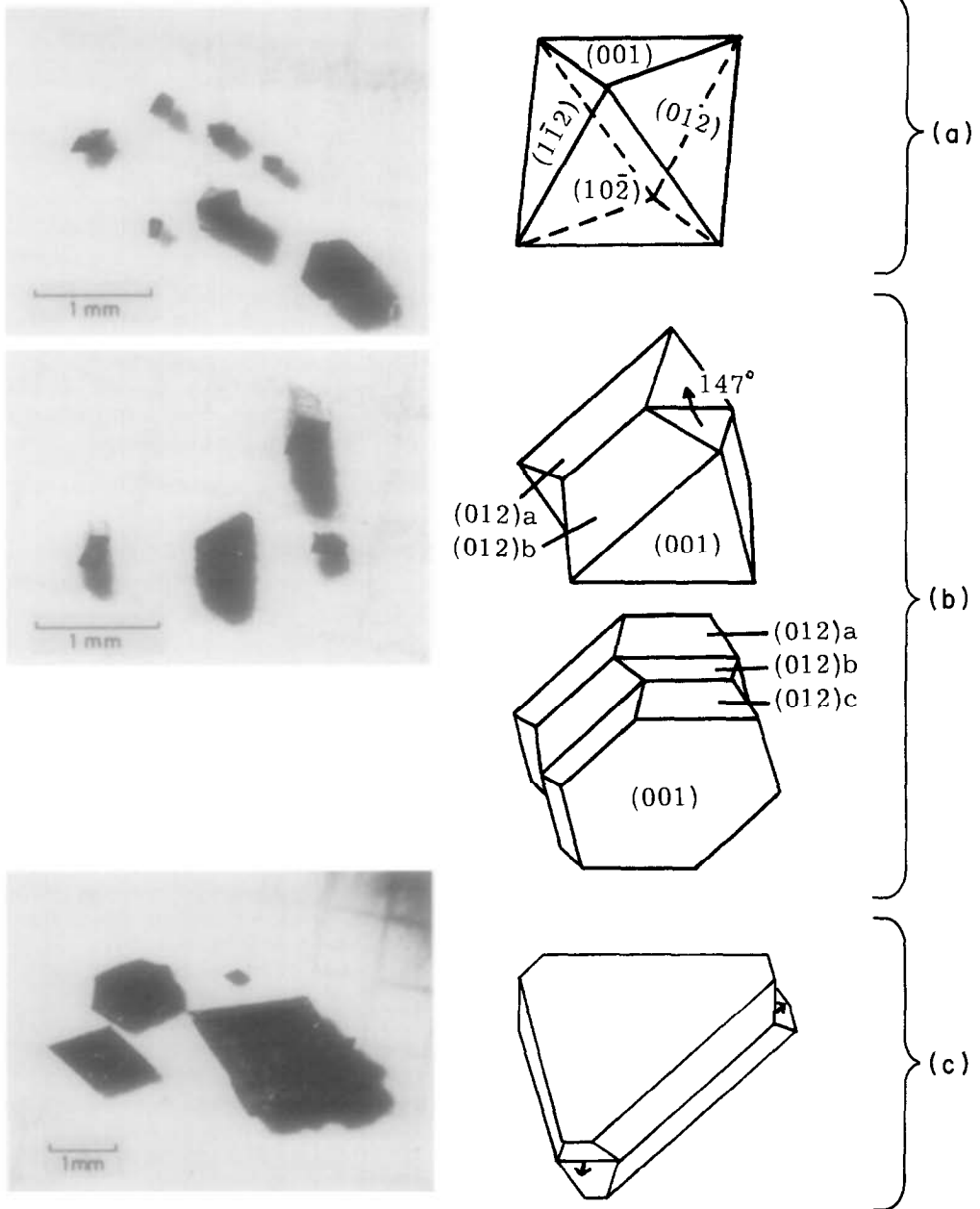


FIG. 1. The microscopic photographs and their schematic shapes of (a) single crystals, (b) short-columnar twin crystals with concave angles, and (c) laminar twin crystals without apparent concave angles.

### Crystal Structure

Crystallographic data for  $\text{CuAlO}_2$  is given in Table III. The systematic absences observed on Buerger precession photographs were  $hkl$  for  $-h + k + l = 3n$ , which lead to the space groups  $R3m$ ,  $R32$  or  $R\bar{3}m$ . The structural model based on the space group  $R\bar{3}m$  gave a satisfactory result for the structure refinement. The final conventional  $R$  value was 0.038 after correction for the secondary extinction effect. There were no noticeable peaks on the difference Fourier maps. The final observed and calculated structure factors are deposited.<sup>1</sup> And the final positional parameters are given in Table IV. Selected interatomic distances and bond angles are presented in Table V.

In the structure,  $\text{Cu}^+$  ions are linearly coordinated by two  $\text{O}^{2-}$  ions whereas  $\text{Al}^{3+}$  ions are octahedrally coordinated by six  $\text{O}^{2-}$  ions. The  $\text{AlO}_6$  octahedra share six edges each other to form sheets parallel to (001). The  $\text{Cu}^+$  ions have the role of combining these octahedral layers. The  $\text{O}^{2-}$  ion is surrounded tetrahedrally by one  $\text{Cu}^+$  and three  $\text{Al}^{3+}$  ions. The Cu–O and the Al–O distances are 1.861 and 1.912 Å, respectively. They agreed well with the value calculated with the ionic radii,  $r(\text{Cu}^+) = 0.46$ ,  $r(\text{Al}^{3+}) = 0.535$  and  $r(\text{O}^{2-}) = 1.38$  Å (14). The unshared and shared O–O length in a  $\text{AlO}_6$  octahedron are 2.860 and 2.539 Å, respectively. The  $\text{AlO}_6$  octahedron is collapsed in the direction of the three-fold axis ( $c$  axis), chiefly due to the electrostatic repulsion between Al atoms linked across the shared

octahedral edges. The Cu–Cu distance in the cation network layer is 2.860 Å, the smallest value in the Cu delafossite-type compounds.

The value of the  $U_{11}$  component of the thermal parameter of  $\text{Cu}^+$  ion is twice as large as  $U_{33}$  (see Table IV). The short Cu–Cu distance and the anisotropic electron distribution suggest that the nonbonding orbital of cuprous ions creates the semiconduction band in the cation network layers perpendicular to the  $c$  axis. Furthermore because the  $\text{AlO}_2$  octahedral layers are nonconductive, we propose that  $\text{CuAlO}_2$  is a strongly anisotropic semiconductor.

### Acknowledgment

The authors wish to thank to Dr. N. Ishizawa for helpful discussions. Computations were carried out on M-180 and M-200H computers at the Computer Center of the Tokyo Institute of Technology.

### References

1. R. D. SHANNON, D. B. ROGERS, AND C. T. PREWITT, *Inorg. Chem.* **10**, 713 (1971).
2. C. T. PREWITT, R. D. SHANNON, AND D. B. ROGERS, *Inorg. Chem.* **10**, 719 (1971).
3. D. B. ROGERS, R. D. SHANNON, C. T. PREWITT, AND J. L. GILLSON, *Inorg. Chem.* **10**, 723 (1971).
4. S. OKAMOTO, S. I. OKAMOTO, AND T. ITO, *Acta Crystallogr. Sect. B* **28**, 1774 (1972).
5. K. HAYASHI, N. MIZUTANI, AND M. KATO, *Nippon Kagakukaishi*, **6** (1974).
6. L. S. RAMSDELL, *Amer. Mineral.* **32**, 64 (1947).
7. A. M. M. GADALLA AND J. WHITE, *Trans. Brit. Ceram. Soc.* **63**(1), 57 (1964).
8. H. HAHN AND C. LORENT, *Z. Anorg. Allg. Chem.* **279**, 281 (1955).
9. P. COPPENS AND W. D. HAMILTON, *Acta Crystallogr. Sect. A* **26**, 71 (1970).
10. E. W. HUGHES, *J. Amer. Chem. Soc.* **63**, 1737 (1941).
11. "International Tables for X-Ray Crystallography," Vol. IV, p. 73. Kynoch Press, Birmingham (1974).
12. M. TOKONAMI, *Acta Crystallogr.* **19**, 486 (1965).
13. JCPDS Card File, 9-185, ASTM, Philadelphia (1959).
14. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).

<sup>1</sup> See NAPS document No. 03891 for 3 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513 Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 for up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for an additional 10 pages of material. Remit \$1.50 for postage of any microfiche orders.