JOURNAL OF SOLID STATE CHEMISTRY **41**, 132–137 (1982)

High Temperature Structural Investigation of the Delafossite Type Compound $CuAlO_2$

T. ISHIGURO, N. ISHIZAWA, N. MIZUTANI, AND M. KATO*

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

Received August 24, 1981

Crystal structure parameters were determined for the delafossite type compound $CuAlO_2$ at 295, 450, 600, 750, 900, and 1200 K with single crystal high temperature X-ray diffraction technique. Anisotropic refinements result in conventional R values of 0.021, 0.027, 0.029, 0.030, 0.032, and 0.036 at respective temperatures. Crystals of $CuAlO_2$ have the rhombohedral space group $R\bar{3}m$ with a = 2.8584(7), c = 16.958(3) Å and Z = 3 at 295 K. The mean thermal expansion coefficient for the dimension a is 11.0×10^{-6} K^{-1} about three times larger than 4.1×10^{-6} K^{-1} for c. In the structure, the AlO_6 octahedra are linked by their O–O edges and form AlO_2 layers perpendicular to the c axis with the thickness corresponding to the height of an octahedron. With increasing temperature, the AlO_6 octahedra expand along the directions of the basal plane, while expansion scarcely occurs along the c axis. The Cu atom lying between the AlO_2 layers shows a large anisotropic behavior in the thermal vibration. The temperature factor for Cu atom in the basal plane becomes very large (0.044 Å^2) at 1200 K, but the ratio of the temperature factor perpendicular to c to that parallel to c does not change appreciably with increasing temperature.

Introduction

The delafossite $CuFeO_2$ type structural group have 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.). Soller and Thompson solved the structure of the delafossite type compound $CuFeO_2$ by X-ray powder diffractometry (*1*). Since then, many investigators have studied delafossite type compounds. Shannon, Prewitt, Rogers, and Gillson measured the electrical conductivity of several delafossite type compounds and found that the conductivity along the basal plane is much larger than the conductivity perpendicular to the plane (*2–4*). They discussed the anisotropic conduction from the d–s hybridized orbital of the A site ions, and classified these compounds into two types, metallic conductor (containing Pd or Pt) and semiconductor (containing Cu or Ag). Copper aluminum delafossite $CuAlO_2$ is expected to have a larger anisotropy than other Cu-delafossites owing to the existence of the semiconductive Cu layers and the nonconductive AlO_2 layers in the structure (*5*). High temperature X-ray diffraction study was thus undertaken in order to elucidate the anisotropic behavior of $CuAlO_2$ at high temperatures from the structural aspects and to afford information on crystal chemistry of the delafossite type compounds.

Experimental

Single crystals of $CuAlO_2$ were grown by slow-cooling the melt of the mixture of

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[*] To whom correspondence should be addressed.

0022-4596/82/020132-06$02.00/0

$CuAlO_2$ powder and Cu_2O added as flux. The condition of crystal growth was described in the previous paper (5). A single crystal with octahedral shape found in an as-grown batch was ground to a sphere for the high-temperature X-ray study. The crystal was mounted on a quartz glass capillary with $ZrSiO_4$ cement. A Philips PW1100 four-circle diffractometer equipped with a small specimen-heating apparatus (6) was used for the determination of the cell dimensions and the collection of intensity data at 295, 450, 600, 750, 900, and 1200 K. The specimen was heated in a hot N_2 gas stream to avoid oxidation. The temperature of the specimen was measured with a 0.08 mm Pt–Pt 13% Rh thermocouple placed at a point about 0.1 mm away from the specimen and was kept constant within ±5 K during the measurements. Cell dimensions at each temperature were calculated from the 17 reflections in the range $3.5 < \theta < 23°$ (Mo$K\alpha$) with least-squares procedure and listed in Table I.

TABLE I

CELL DIMENSIONS AND UNIT CELL VOLUMES OF $CuAlO_2$ AT VARIOUS TEMPERATURES

T(K)	a(Å)	c(Å)	V(Å³)
295	2.8584(7)	16.958(3)	119.99(6)
450	2.8643(8)	16.974(3)	120.60(7)
600	2.8668(11)	16.981(4)	120.86(9)
750	2.8729(10)	16.988(4)	121.42(9)
900	2.8778(10)	17.001(4)	121.94(9)
1200	2.8915(9)	17.034(3)	123.35(8)

Intensities were collected with Mo$K\alpha$ radiation monochromated with a graphite plate. The ω-2θ scan technique was employed with scanning speeds of 6°/min in ω for the measurement at 295 K and of 4°/min in ω for the measurements at high temperatures. At 295 K, 1608 intensity data were obtained in the whole reciprocal space within the range $\sin\theta/\lambda < 1.08$ Å^{-1}. At 450, 600, 750, 900, and 1200 K, 184, 185, 181, 174, and 163 intensity data were respectively obtained within the range $\sin\theta/\lambda < 1.08$ Å^{-1} in the asymmetric space determined by Laue symmetry. After the correction for the Lorentz and polarization factors, the correction coefficients K_{hkl} for the 295 K data set were calculated using the expression, $K_{hkl} = F_{hkl}/F_m$, where F_m is the mean value of all the observed reflections equivalent to the hkl reflection. The correction coefficients were then applied to the corresponding reflections obtained at higher

TABLE II

REFINED POSITIONAL AND THERMAL PARAMETERS[a]

		Thermal parameters (×10⁻⁴ Å²)					
		Cu		Al		O	
T(K)	Positional parameter z of O	U_{11}	U_{33}	U_{11}	U_{33}	U_{11}	U_{33}
295	0.10978(6)	124(1)	69(1)	68(2)	78(2)	91(2)	80(3)
450	0.10980(8)	171(2)	85(2)	79(2)	101(3)	102(3)	99(4)
600	0.10981(8)	218(2)	93(2)	85(2)	116(3)	113(3)	114(4)
750	0.1097(1)	266(3)	118(2)	104(2)	144(3)	134(3)	131(4)
900	0.1098(1)	329(3)	133(2)	116(3)	161(4)	158(4)	141(5)
1200	0.1098(1)	437(5)	172(3)	149(4)	211(5)	199(5)	173(6)

[a] Positional parameters (x y z) of Cu and Al are (0 0 0) and (0 0 0.5), respectively, and both x and y of O (oxygen) equal to 0. The anisotropic thermal parameters are given by $T = \exp(-2\pi^2 \Sigma_{ij} U_{ij} a_i^* a_j^*)$, and herein, $U_{22} = U_{11}$, $U_{12} = 0.5\ U_{11}$, and $U_{23} = U_{13} = 0$ for all atoms.

TABLE III

SELECTED INTERATOMIC DISTANCES (Å), BOND ANGLES (°), AND SHAPE PARAMETERS OF AlO_6 OCTAHEDRON (Å)[a]

		295 K	450 K	600 K	750 K	900 K	1200 K
Cu–O	×2	1.8617(11)	1.8638(14)	1.8647(14)	1.8675(18)	1.8707(18)	1.8743(17)
$\mathrm{Al^{ii}}$–O	×6	1.9116(6)	1.9148(8)	1.9162(9)	1.9204(10)	1.9223(10)	1.9301(10)
Cu–$\mathrm{Cu^{i}}$	×6	2.8584(7)	2.8643(8)	2.8668(11)	2.8729(10)	2.8778(10)	2.8915(9)
O–$\mathrm{O^{i}}$	×6	2.8584(7)	2.8643(8)	2.8668(11)	2.8729(10)	2.8778(10)	2.8915(9)
O–$\mathrm{O^{iv}}$	×6	2.5388(12)	2.5419(15)	2.5432(16)	2.5460(19)	2.5464(19)	2.5544(19)
O–$\mathrm{Al^{ii}}$–$\mathrm{O^{i}}$	×6	96.78(3)	96.83(4)	96.85(5)	96.97(5)	97.06(5)	97.15(5)
O–$\mathrm{Al^{ii}}$–$\mathrm{O^{iv}}$	×6	83.22(3)	83.18(4)	83.15(4)	83.10(5)	83.01(5)	82.92(5)
Cu–O–$\mathrm{Al^{ii}}$	×3	120.31(3)	120.27(4)	120.25(4)	120.16(5)	120.09(5)	120.02(5)
$\mathrm{Al^{ii}}$–O–$\mathrm{Al^{iii}}$	×3	96.78(4)	96.83(5)	96.85(5)	96.97(5)	97.06(5)	97.15(5)
Shape	x	2.8584(7)	2.8643(8)	2.8668(11)	2.8729(10)	2.8778(10)	2.8915(9)
Parameter	z	1.9293(8)	1.9304(9)	1.9309(10)	1.9277(10)	1.9256(10)	1.9294(10)

[a] Symmetry code:

none	x	y	z
(i)	x	$y - 1$	z
(ii)	$x + 1/3$	$y + 2/3$	$z - 1/3$
(iii)	$x + 1/3$	$y - 1/3$	$z - 1/3$
(iv)	$x + 2/3$	$y + 1/3$	$1/3 - z$

temperatures. Absorption corrections were carried out assuming the specimen to be a sphere with 0.25 mm in diameter ($\mu = 138.1\ \mathrm{cm^{-1}}$). In all, 189 at 295 K, 182 at 450 K, 183 at 600 K, 179 at 750 K, 172 at 900 K, and 161 at 1200 K independent reflections having nonzero values were used for further calculation.

Refinement

Refinement of the structure of $CuAlO_2$ at each temperature was carried out with the full matrix least-squares program LINUS (*7*). The positional parameters obtained from previous study (*5*) were adopted for the starting values of the structure at each temperature. Anisotropic temperature factors were used for all atoms. Isotropic secondary extinction effects were taken into consideration (*8*). The weighting scheme, $w = 1/\sigma(|F_o|)$, was adopted where $\sigma(|F_o|)$ being the estimated deviation of the observed structure factor calculated from the counting statistics. The atomic scattering factors for Cu^+ and Al^{3+} and the real and imaginary dispersion terms for Cu, Al, and O were taken from International Tables for X-ray Crystallography (*9*). The atomic scattering factors for O^{2-} were given by Tokonami (*10*). The final conventional R values were 0.021, 0.027, 0.029, 0.030, 0.032, and 0.036 for structures at 295, 450, 600, 750, 900, and 1200 K, respectively. Final positional and thermal parameters are given in Table II.[1] Selected interatomic distances and bond angles are listed in Table III.

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[1] See NAPS document No. 03891 for 3 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Accession Number. Institutions and organizations may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

Discussion

Description of the Structure

The structure of $CuAlO_2$ at 1200 K is shown in Fig. 1. The structure can be considered as the alternative stacking of the AlO_2 and Cu layers perpendicular to the *c* axis. The AlO_6 octahedra are linked by their edges, forming AlO_2 layers with thickness corresponding to the height of the octahedron. The Cu atom is linearly coordinated by two oxygen atoms which belong to the AlO_2 layers.

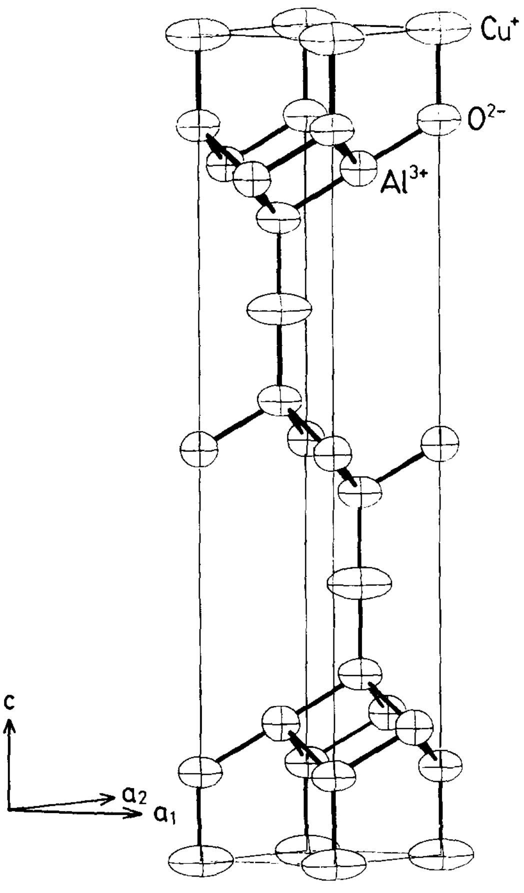

FIG. 1. The crystal structure of $CuAlO_2$ at 1200 K, showing thermal-vibration ellipsoids at 90% probability.

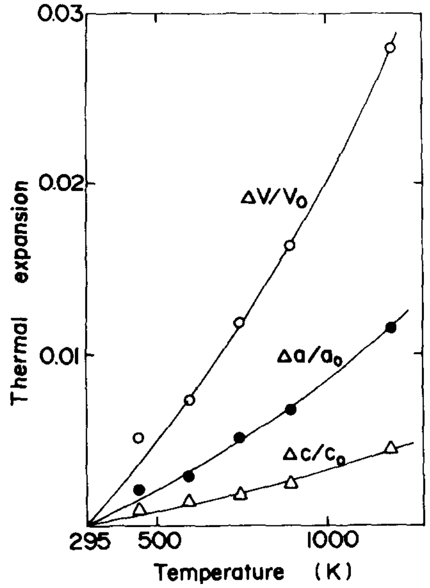

FIG. 2. Changes of cell dimensions and unit cell volume of $CuAlO_2$ as a function of temperature.

Thermal Expansion of the Unit Cell Parameters

The thermal expansion of cell dimensions and unit cell volume is shown in Fig. 2, where Δx is the difference of *x* between 295 K and the corresponding temperature. The mean thermal expansion coefficients (hereafter MTEC) for the temperature region 295–1200 K are 11.0×10^{-6} and 4.1×10^{-6} K^{-1} for the dimensions *a* and *c*, respectively. The MTEC of $CuAlO_2$ along *a* is close to the values of α-Al_2O_3, 10.0×10^{-6} K^{-1} along *a* and 11.2×10^{-6} K^{-1} along *c* (*11*), and the MTEC of $CuAlO_2$ along *c* lies between 1.9×10^{-6} K^{-1} of Cu_2O (*12*) and those of α-Al_2O_3.

Thermal Expansion of Interatomic Distances

The changes with temperature of the interatomic distances are shown in Fig. 3. The changes of shape parameters *x* and *z* of an AlO_6 octahedron are also shown in Fig. 3, where *x* is the basal edge length and *z* the

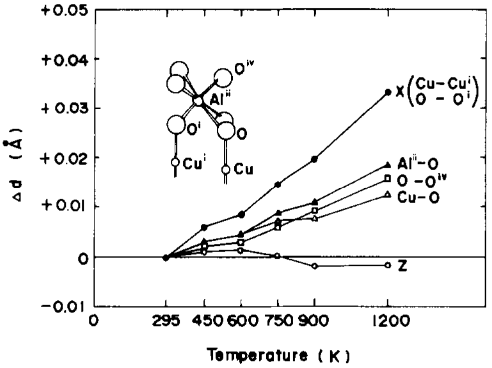

FIG. 3. Changes of typical interatomic distances and shape parameters x and z of AlO_6 octahedron as a function of temperature. The subscript for each atom indicates the symmetry code defined in Table III.

height along the c axis. The x is equal to the interatomic distances O–O^{i} and Cu–Cu^{i}. All interatomic distances and x increase with temperature, whereas little change occurs in z. Namely, the AlO_6 octahedron expands along the direction in the basal plane, but the height along the c axis was kept nearly constant at high temperature. This result is in clear contrast with the structural change of α-Al_2O_3 in which the oxygen octahedron surrounding the Al atom becomes more regular with increasing temperature, chiefly due to the O–O repulsion (*11*). From the viewpoint of Pauling's fifth rule (*13*), the unshared edge (e.g., O–O^{i}) of the AlO_6 octahedron in the basal plane should expand more than the shared edge (e.g., O–O^{iv}). This partly explains the two-dimensional expansion of AlO_2 layers in the basal plane. The MTEC for Al^{ii}–O, Cu–O, O–O^{iv}, and O–O^{i} (equal to Cu–Cu^{i} and x) were 9.6×10^{-6}, 7.8×10^{-6}, 5.2×10^{-6}, and 11.3×10^{-6} K^{-1}, respectively. The MTEC of Al^{ii}–O agrees with 11.2×10^{-6} K^{-1}, the MTEC of Al–O in α-Al_2O_3 calculated from the data of the interatomic distances of Ishizawa *et al.* (*11*) and Haga *et al.* (*14*). On the other hand, the MTEC for Cu–O is larger than 1.9×10^{-6} K^{-1}, the value of Cu–O in Cu_2O (*14*). The Cu_2O and $CuAlO_2$ structures have a similarity in that two oxygen atoms are coordinated to Cu atoms with the linear linkages of O–Cu–O. These structures, however, differ in the point that the O–Cu–O linkages form three-dimensional networks in the Cu_2O structure but exist independently between AlO_2 layers in the $CuAlO_2$ structure. The existence of OCu_4 tetrahedron in the Cu_2O structure presumably obstructs the free extention of the Cu–O bond as is found in the $CuAlO_2$ structure. Thus, the MTEC of Cu–O in Cu_2O structure is kept at a low value.

Positional and Thermal Parameters

The z parameter of the O atom scarcely changes with temperature and the value is approximately 0.1098. The mean-square displacements $\langle u^2\rangle$(Å^2) of each atom in the directions perpendicular and parallel to c are plotted as a function of temperature in Fig. 4. In each direction $\langle u^2\rangle$ data are represented by the single straight lines through the origin with very small deviations, indicating that the classical harmonic oscillator model proposed by Debye (*15*) explains well the thermal vibration of the constituent atoms in the $CuAlO_2$ structure within the temperature range studied. The basal plane component of $\langle u^2\rangle$ of the Cu atom becomes very large (0.044 Å^2) at 1200 K, but the

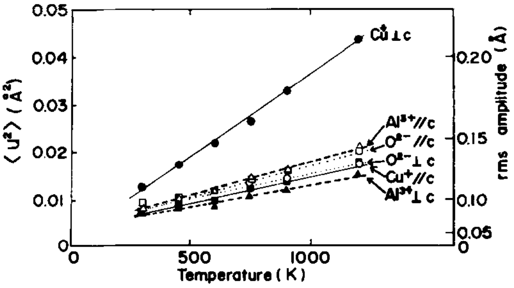

FIG. 4. Changes of the mean-square displacements $\langle u^2\rangle$ of each atom in the directions perpendicular and parallel to the c axis as a function of temperature. Right vertical axis is graduated in the rms ampritude $\langle u^2\rangle^{1/2}$ of the thermal ellipsoid.

ratio of $\langle u^2 \rangle$ perpendicular to c to that parallel to c does not change appreciably with increasing temperature.

Acknowledgment

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

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