

Synthesis and Crystal Structure of $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ ($0.130 \leq x \leq 0.166$)

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Solid solutions of $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ were prepared at 950°C for 12 h in air with a narrow composition range of x from 0.130 to 0.166. Thermal analysis revealed that the sample of $x = 0.143$ decomposed into MgO and Cu_2O above 1030°C. The stoichiometric oxygen content based on Cu II valence was confirmed with the weight loss after decomposition in $\text{H}_2:\text{Ar}$ (20%:80%) atmosphere. The X-ray powder diffraction pattern of the sample ($x = 0.143$) was analyzed by the Rietveld method. The structure is isostructural with CaCu_2O_3 , and related to a rock-salt-type superstructure with an orthorhombic cell, $a = 3.9906(1)$, $b = 9.3482(3)$, and $c = 3.1911(1)$ Å, space group $Pmmn$ (No. 59, setting 2). There are two metal atom sites in the structure. One metal atom site (4e) occupied by Cu atoms is in an elongated octahedron of oxygen atoms. The other site (2b) is statistically occupied by Cu and Mg atoms with fractions of 0.143 and 0.857, respectively. © 2001 Academic Press

Key Words: magnesium copper oxide; thermogravimetry; crystal structure; X-ray powder diffraction; Rietveld analysis.

INTRODUCTION

Recently, syntheses, crystal structures, and physical properties of oxides containing copper have been widely investigated due to interest in high- T_c superconductors and related compounds. The compounds prepared under flowing O_2 in the Mg–Cu–O system were investigated by Schmahl *et al.* (1). They reported a solid solution phase of $\text{Mg}_{1-x}\text{Cu}_x\text{O}$ ($0 \leq x \leq 0.22$) with a cubic rock-salt-type structure and MgCu_3O_4 . The peaks in the X-ray powder diffraction pattern of MgCu_3O_4 were indexed with an orthorhombic unit cell ($a = 3.989$, $b = 6.387$, and $c = 9.345$ Å), but the crystal structure was not analyzed. Details of the crystal structure of the $5\text{CuO}-2\text{MgO}$ compound were not reported in the phase diagram of $\text{MgO}-\text{Al}_2\text{O}_3-\text{CuO}$ (2). MgCu_2O_3 was reported by Driessens *et al.* (3) and Drenkhahn and Müller-Buschbaum (4). The crystal structure of MgCu_2O_3 was determined by X-ray diffraction with a single crystal synthesized using the KF flux (4). MgCu_2O_3 (orthorhombic, space group $Pmmn$, $a = 4.00$, $b = 9.35$, and $c = 3.19$ Å) is

isostructural with CaCu_2O_3 , guggenite α -type (5). Two phases, α - and β - MgCu_2O_3 , were reported in the files of the International Center for Diffraction Data (ICDD41-1364 and 41-1365) (6, 7). According to the description in the files, the α phase was prepared from a mixture of MgO and CuO powders with a Mg:Cu = 1:2 molar ratio. The mixture was heated at 950°C for 5 days in air in a Pt crucible. The crystal structure of the α phase was the same as that reported for the single crystal of MgCu_2O_3 (4). The α phase changed to the β phase at 1005°C in air. The β phase crystallized in an orthorhombic supercell ($a = 3.988$, $b = 40.55$, and $c = 3.186$ Å) of the α phase structure (6). A monoclinic phase of MgCu_2O_3 was also reported as a metastable phase in ICDD 41-1381(8). The crystal structures of the monoclinic MgCu_2O_3 and β - MgCu_2O_3 have not been clarified.

We reexamined the preparation of α - MgCu_2O_3 at several temperatures (900–1050°C) in air and could not obtain single phase of α - MgCu_2O_3 with the guggenite-type structure from the starting mixture of the composition of MgO:CuO = 1:2. The single phase was obtained from starting mixtures with the compositions around 2:5 molar ratio. Details of the results are described under Results and Discussion. The present paper reports on the synthesis and thermal and crystal structure analyses of this ternary cuprate phase.

EXPERIMENTAL

The starting materials used were MgO (99.99% purity) and CuO (99.99% purity) powders. The MgO and CuO powders were heated at 900°C for 1 h before weighing. The oxide powders were weighed in various MgO:CuO molar ratios, thoroughly mixed for 1 h with an agate mortar and a pestle, and then pressed into pellets. The pellets were placed in an alumina boat and heated at several temperatures (900–1050°C) for 12 h in air. After heating, the samples were furnace-cooled.

The pellet samples were powdered for the X-ray diffraction (XRD). The $\text{CuK}\alpha$ radiation was used on a

diffractometer with a pyrolytic graphite monochromator (Rigaku, RINT 2000). Lattice parameters of the compounds were refined by the least-squares method with the d -spacings calculated from the XRD angle of the peaks. The Rietveld analysis was carried out with the program RIETAN (9). The X-ray diffraction data were collected at a 2θ interval of 0.04° in the 2θ region from 10° to 120° .

The density of the samples was measured by pycnometry with water solvent at room temperature. Thermal properties of the sample were examined by thermogravimetry. In the measurement, weight loss and calorimetric signals were monitored from room temperature to 1400°C with a heating rate of $50^\circ\text{C}/\text{min}$ in air. The oxygen content of the sample was determined from the weight loss of the sample heated in a $\text{H}_2:\text{Ar}$ (20%:80%) atmosphere. Details of the measurement are described elsewhere (10).

RESULTS AND DISCUSSION

We tried to prepare a single α phase with the guggenite-type structure at several temperatures ($900\text{--}1050^\circ\text{C}$) at 12 h

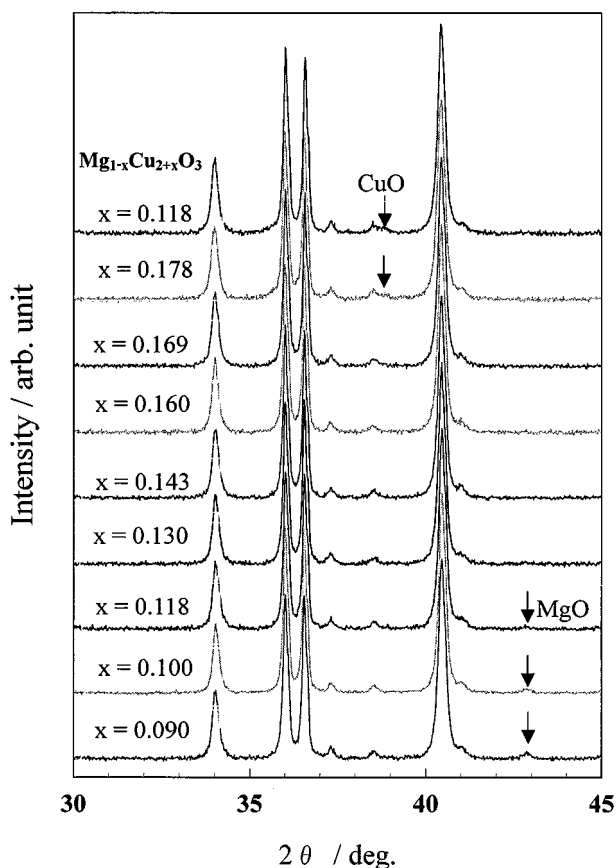


FIG. 1. X-ray powder diffraction patterns of samples prepared at 950°C from the starting mixtures with various molar ratios of $\text{MgO}:\text{CuO}$ from 2:4.6 to 2:5.4.

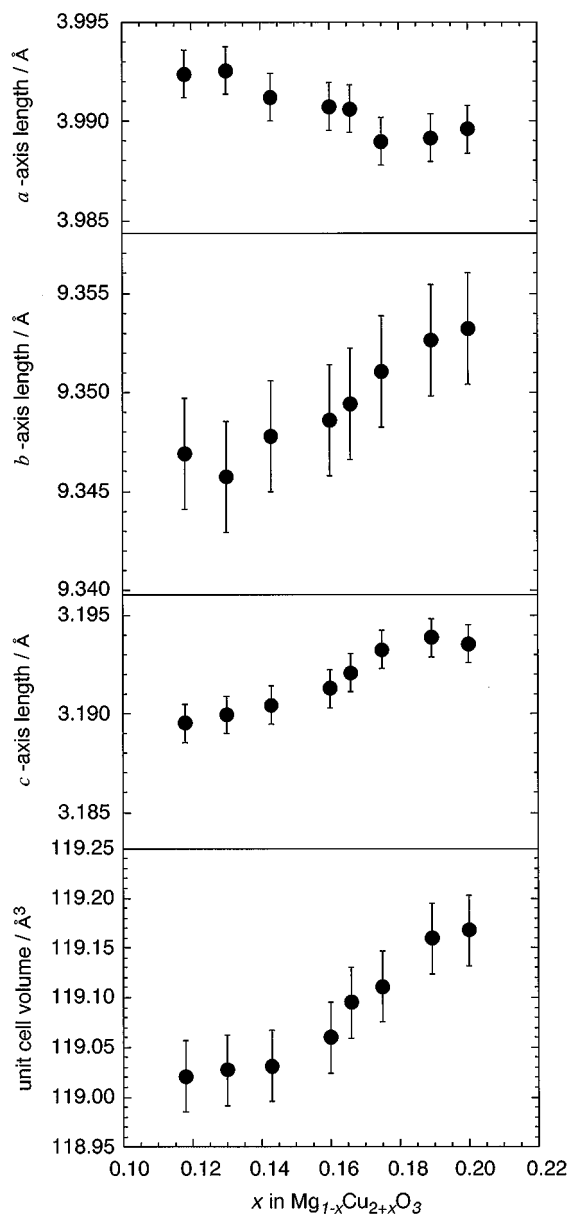


FIG. 2. Unit cell parameters and volume for $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$.

in air on an alumina boat using starting mixtures with compositions of $\text{MgO}:\text{CuO} = 1:2$ and $2:5$. In both the cases, MgO and CuO hardly reacted with each other at 900°C for 12 h in air. The single α phase was obtained at 950 and 975°C for 12 h in air using the starting mixture with the composition of $\text{MgO}:\text{CuO} = 2:5$, while the sample was a mixture of MgO and the α phase in the case of a 1:2 composition. The results mean that the single α phase could be obtained with excess CuO of 0.5 over the 1:2 ratio. A similar result for CaCu_2O_3 was reported by Ruck *et al.* (11). No reaction was observed between the sample pellet and the alumina boat in both cases. A negligible amount of

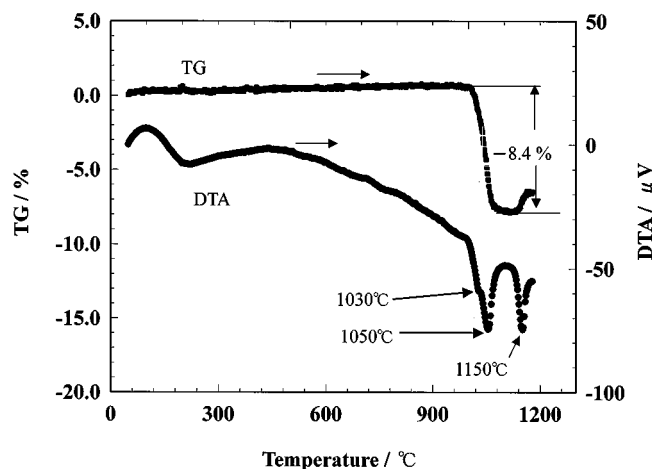


FIG. 3. TG and DTA profiles of $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ ($x = 0.143$).

weight loss (-0.08%) measured for the sample after the heating also supported that there was no reaction between them. We obtained similar results for the sample prepared in a Pt crucible, although the color of the pellet on the Pt crucible side changed. We also attempted to synthesize MgCu_3O_4 from a mixture with a composition of $\text{MgO}:\text{CuO} = 1:3$ in O_2 stream, exactly following the report by Schmahl *et al.* (1). However, we did not obtain the single phase but a mixture of the orthorhombic compound and CuO .

Figure 1 shows the X-ray powder diffraction patterns of the samples prepared at 950°C from the starting mixtures with various compositions. The single phase was obtained from the compositions $\text{MgO}:\text{CuO}$ from 1:2.45 to 1:2.60, which correspond to $0.130 \leq x \leq 0.166$ of $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$. X-ray diffraction peaks of CuO and MgO were detected at

$x > 0.166$ and $x < 0.130$, respectively. As shown in Fig. 2, the b - and c -axis lengths and cell volume increased and the a -axis length decreased with the increasing x . This indicates a presence of the solid solution in the narrow composition region.

The sample prepared at $\text{MgO}:\text{CuO} = 1:2.5$ ($x = 0.143$) at 950°C was used for the thermogravimetry and crystal structure analysis. The compound changed into a high-temperature phase above 1000°C . The X-ray diffraction peaks from the high-temperature phase quenched at room temperature could be explained with the data reported on $\beta\text{-MgCu}_2\text{O}_3$ (6). The compound decomposed into MgO and Cu_2O by heating at 1050°C for 12 h. These results, except the composition of the compound, were consistent with the reports on MgCu_2O_3 (4, 6).

The results of the sample characterized by the thermogravimetry in air is shown in Fig. 3. There was no weight loss up to 1000°C . Endothermic peaks were observed at 1030 and 1056°C with the total weight loss of 8.4% , which agreed with a loss of 8.36% calculated from the following reaction, $\text{Mg}_2\text{Cu}_5\text{O}_7 \rightarrow 2\text{MgO} + \frac{5}{2}\text{Cu}_2\text{O} + \frac{5}{2}\text{O}_2$. This result indicates that the decompose reaction begins around 1030°C . The peak at 1153°C seems to correspond to the melting of the $\text{MgO}-\text{Cu}_2\text{O}$ mixture. A small weight gain was observed after the melting. This gain would be caused by oxidation during the reaction between the crucible and the sample. From the result of the thermogravimetric measurement in the $\text{H}_2:\text{Ar}$ atmosphere, it was confirmed that the Cu valence was the II state.

Figure 4 shows the profile fit and difference patterns of the Rietveld analysis for the X-ray powder diffraction pattern of the sample $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ ($x = 0.143$) prepared at 950°C . The crystallographic data and the results of the refinement are listed in Table 1. Table 2 shows the

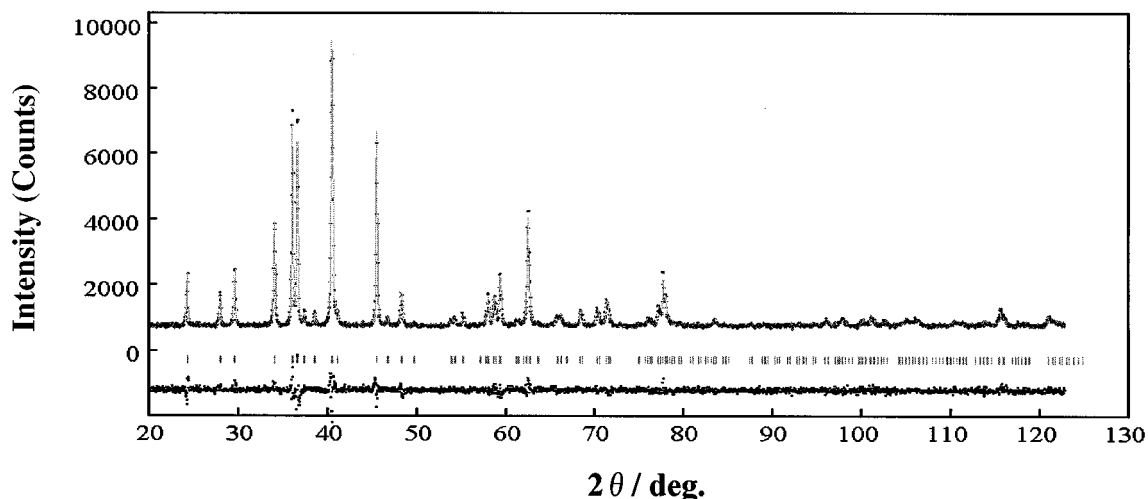


FIG. 4. The observed (dots) and calculated (solid) X-ray diffraction profiles for $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ ($x = 0.143$). Tick marks below the diffraction pattern represent the allowed Bragg reflections. The difference profile is located at the bottom of the figure.

TABLE 1
Crystallographic Data and Structure Refinement for
 $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ ($x = 0.143$)

Formula	$\text{Mg}_{0.857}\text{Cu}_{2.143}\text{O}_3$
Formula weight	205.01
Space group	$Pm\bar{m}n$ (No. 59, setting 2)
Unit cell dimensions	$a = 3.99063(10) \text{ \AA}$ $b = 9.3482(3) \text{ \AA}$ $c = 3.19105(10) \text{ \AA}$
Cell volume	$V = 119.04(6) \text{ \AA}^3$
Z	2
Density (calculated)	5.72 Mg/m^3
(measured)	5.85 Mg/m^3
Goodness-of-fit	$S = 1.405$
R indexes	$R_{\text{wp}} = 0.0398$ $R_p = 0.0295$ $R_f = 0.0210$ $R_{\bar{f}} = 0.0150$

TABLE 2
Atomic Coordinates and Isotropic Displacement Parameters for
 $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ ($x = 0.143$)

	Site	Occupancy	x	y	z	B (\AA^2)	
	Cu1/Mg1	4e	0.995(2)/0.005	$\frac{1}{4}$	0.0865(2)	0.1790(4)	0.39(5)
	Cu2/Mg2	2b	0.153/0.847	$\frac{1}{4}$	$\frac{3}{4}$	0.3666(12)	0.39 ^a
	O1	4e	1.000	$\frac{1}{4}$	0.5935(7)	0.875(2)	0.45(10)
	O2	2a	1.000	$\frac{1}{4}$	$\frac{1}{4}$	0.547(2)	0.45 ^b

^a Constrained with the value of Cu1/Mg1.

^b Constrained with the value of O1.

parameters of atomic position, occupation, and isotropic displacement. We adopted the crystal structure of MgCu_2O_3 as a starting model (4). There are two sites for

metal atoms. The refined occupation parameter shows that 4e site is almost fully occupied by Cu atoms. Cu and Mg atoms respectively occupy about 15 and 85% of the 2b site. The density calculated from the results of the refinement was 5.72 Mg/m^3 . This is close to the measured densities of 5.85 Mg/m^3 in our experiment, 5.85 Mg/m^3 for MgCu_3O_4 (1), and 5.57 Mg/m^3 for $\alpha\text{-MgCu}_2\text{O}_3$ (4).

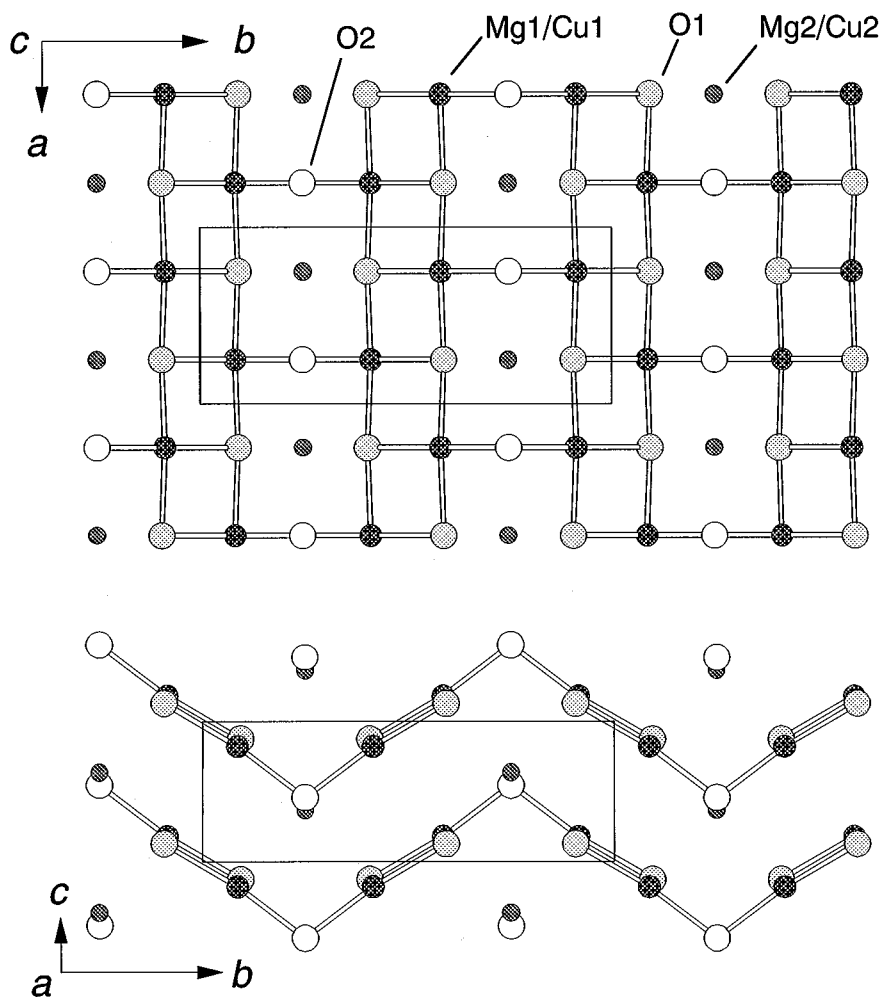


FIG. 5. Crystal structure of $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ ($x = 0.143$) projected on the a - b and b - c planes.

TABLE 3
Selected Interatomic Distances (\AA) for $Mg_{1-x}Cu_{2+x}O_3$
($x = 0.143$)

Cu1/Mg1-O1	1.942(6)	Mg2/Cu2-O1	$2.144(6) \times 2$
-O1	$2.0039(5) \times 2$	-O1	$2.185(6) \times 2$
-O1	2.787(6)	-O2	$2.0144(12) \times 2$
Cu1/Mg1-O2	1.927(4)		
-O2	2.531(6)		

The crystal structure of $Mg_{1-x}Cu_{2+x}O_3$ ($x = 0.143$) is illustrated in Fig. 5. Cu1-O square planes connect by sharing edges and apexes, and form a two-dimensional zigzag

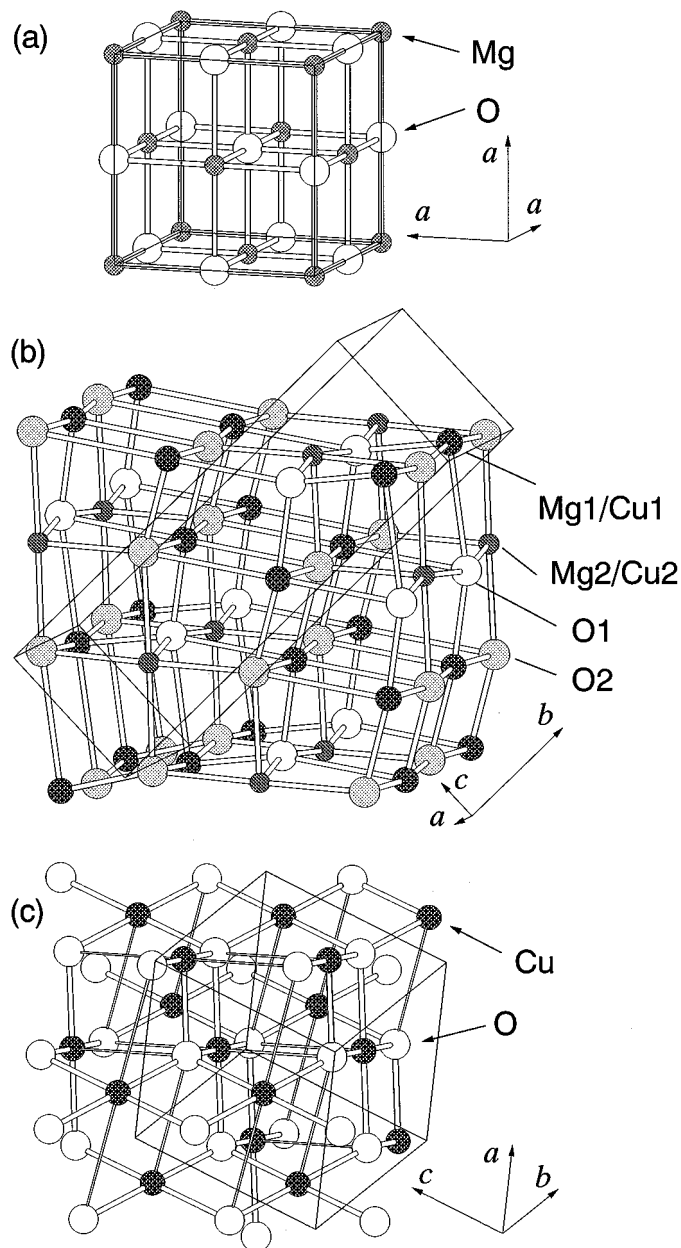


FIG. 6. Crystal structures of MgO, $Mg_{1-x}Cu_{2+x}O_3$ ($0.130 \leq x \leq 0.166$), and CuO.

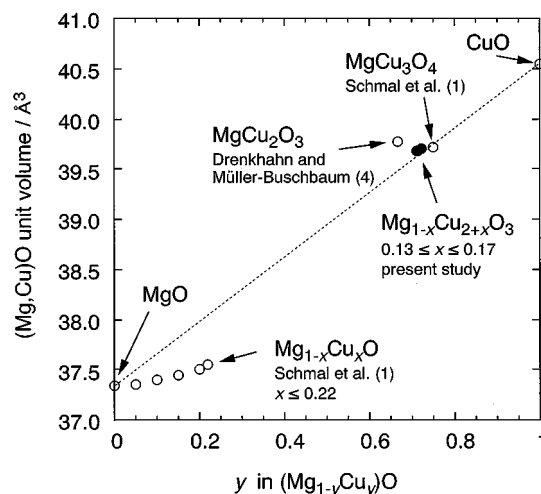


FIG. 7. $(Mg,Cu)O$ unit volume (\AA^3) versus y in $(Mg_{1-y}Cu)_yO$.

plane along the a - b plane. Cu-O distances in the planes were from 1.927(4) to 2.0039(5) \AA , an average 1.969 \AA (Table 3). These interatomic distances are a little longer than those observed in the square-planar CuO_2 plane in the superconducting cuprates (12). The average value of Cu1-O distances in the plane (1.969 \AA) was nearly equal to the Cu-O bond lengths of 1.9608 and 1.9509 \AA observed in CuO (13).

The structure of $Mg_{1-x}Cu_{2+x}O_3$ ($x = 0.143$) can also be related to a rock-salt-type superstructure as shown in Fig. 6. All metal atoms situated in distorted oxygen octahedra due to the Jahn-Teller effect of Cu (II). The octahedron containing Cu1 atoms elongates in one direction. The interatomic distances of Cu1-O1 and Cu1-O2 along the elongated direction were 2.787(6) and 2.531(6) \AA , respectively. The interatomic distance between the Cu atom and the apical oxygen atom of the elongated octahedron in CuO is 2.784 \AA (13). The interatomic distances of Mg2/Cu2-O were from 2.0144(12) to 2.185(6) \AA . The average of these distances (2.114 \AA) is a little longer than Mg-O distance of 2.106 \AA in a regular oxygen octahedron of MgO (14).

Figure 7 shows volumes of $(Mg,Cu)O$ units occupied in the structures of MgO-CuO compounds. The unit volume for $Mg_{1-x}Cu_{2+x}O_3$ ($0.130 \leq x \leq 0.166$) was plotted on the straight line between the volumes of MgO and CuO units. The unit volumes for $Mg_{1-x}Cu_xO$ solid solutions ($x \leq 0.22$) are smaller than the volumes expected from the MgO-CuO line. The solid solutions of $Mg_{1-x}Cu_xO$ maintain the regular octahedral coordination in the cubic rock-salt-type structure up to $x = 0.22$ (1). In the structure of $Mg_{1-x}Cu_{2+x}O_3$ ($0.130 \leq x \leq 0.166$), Mg atoms cannot fully occupy the 2b site. It seems that the replacement of about 15% Mg atoms by Cu atoms in the 2b site is necessary to stabilize the distorted coordination caused by the Jahn-Teller distortion of the neighbor Cu1-O octahedra.

SUMMARY

The orthorhombic compounds, $\text{Mg}_{1-x}\text{Cu}_{2+x}\text{O}_3$ ($0.130 \leq x \leq 0.166$), previously reported as MgCu_2O_3 and MgCu_3O_4 , were prepared by solid state reaction of MgO and CuO at 950°C in air. Cu II valency in this phase was confirmed by thermogravimetry. The solid solution phase, expressed with the structural formula $(\text{Mg}_{1-x}\text{Cu}_x)\text{Cu}_2\text{O}_3$, is isostructural with CaCu_2O_3 .

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REFERENCES

1. N. G. Schmahl, J. Barthel, and G. F. Eikerling, *Z. Anorg. Allg. Chem.* **332**, 230 (1964).
2. V. M. Ust'yantsev and L. S. Zholova, *Izv. Akad. Nauk SSSR Neorg. Mater.* **10**, 1272 (1974).
3. F. C. M. Driessens, G. D. Rieck, and H. N. Cönen, *J. Inorg. Nucl. Chem.* **30**, 747 (1968).
4. H. Drenkhahn and M. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **418**, 116 (1975).
5. C. L. Teske and M. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **371**, 325 (1969).
6. International Center for Diffraction Data, ICDD, 41-1365.
7. International Center for Diffraction Data, ICDD, 41-1364.
8. International Center for Diffraction Data, ICDD, 41-1381.
9. F. Izumi, in "The Rietveld Method" (R. A. Young, Ed.), Chap. 13. Oxford Univ. Press, Oxford (1993); Y.-I. Kim and F. Izumi, *J. Ceram. Soc. Jpn.* **102**, 401 (1994).
10. K. Oh-ishi, M. Kikuchi, Y. Syono, N. Kobayashi, and Y. Muto, *J. Solid State Chem.* **83**, 237 (1990).
11. K. Ruck *et al.*, *Solid State Chem.* **1**, 55 (2000).
12. T. Kajitani *et al.*, *Jpn. J. Appl. Phys. Ser. 7*, 59 (1991).
13. S. Åsbrink and L.-J. Norrby, *Acta Crystallogr. Sect. B* **26**, 8 (1970).
14. International Center for Diffraction Data, ICDD, 45-0846.