

# Synthesis of the Delafossite-Type $\text{CuInO}_2$

M. Shimode,<sup>\*,1</sup> M. Sasaki,<sup>†</sup> and K. Mukaida<sup>†</sup>

<sup>\*</sup>Division of Chemical and Material Engineering, Muroran Institute of Technology, 27-1 Mizumoto, Muroran, Hokkaido 050-8585, Japan; and

<sup>†</sup>Department of Material Science and Engineering, Faculty of Engineering, Muroran Institute of Technology, 27-1 Mizumoto, Muroran, Hokkaido 050-8585, Japan

Received April 6, 1999; in revised form November 23, 1999; accepted December 13, 1999

A new delafossite type oxide  $\text{CuInO}_2$  was synthesized by cation exchange reaction of  $\text{CuCl}$  with  $\text{LiInO}_2$ , which was produced from  $\text{Li}_2\text{O}$  and  $\text{In}(\text{OH})_3$ . An almost single phase was obtained at  $350^\circ\text{C}$  for 144 h. The structure of  $\text{CuInO}_2$  was refined by Rietveld analysis and the final  $S$  value became 1.1636.  $\text{CuInO}_2$  is rhombohedral,  $R\text{-}3m$ ,  $a = 3.2922 \text{ \AA}$ ,  $c = 17.388 \text{ \AA}$ . © 2000 Academic Press

**Key Words:** Delafossite-type oxide; solid state reaction; structure refinement.

## INTRODUCTION

Delafossite,  $\text{CuFeO}_2$  was discovered by Pabst who also reported its structure (1). The crystal structure of the delafossite-type oxide with formula  $\text{ABO}_2$  ( $A$ , monovalent metal;  $B$ , trivalent metal), can be described as the alternate stacking of edge-shared  $\text{BO}_2^-$  octahedral layers and  $A^+$ -ion layers perpendicular to the  $c$  axis. Each  $A^+$  ion layer is linearly coordinated by two  $\text{O}^{2-}$  ions (2). Shannon *et al.* (2) synthesized the series containing the noble metal ions  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Pd}^+$ , and  $\text{Pt}^+$  ions in the  $A$  site. The oxides with a noble metal are difficult to prepare by a conventional solid state reaction, because noble metal oxides used as reagents frequently decompose before reaction occurs. So they used various preparation techniques such as hydrothermal, metathetical, and oxidizing flux reactions. Regarding  $B$  site new members of delafossite-type  $\text{ABO}_2$ , Ishiguro *et al.* (3) synthesized  $\text{CuYO}_2$ , and Doumerc *et al.* (4) prepared  $\text{CuScO}_2$ .

Figure 1 shows the structure field map for various  $\text{ABO}_2$  oxides (2–6). On the delafossite-type oxide  $\text{ABO}_2$  with  $\text{Cu}^+$  ion in the  $A$  site, there are many material systems which contain small ions in the 0.54 to 0.67 Å range, and large lanthanoid ions, in the 0.95 to 1.06 Å range in the  $B$  site. However, only very few compounds have midsize ions in the

$B$  site. The ionic radius of  $\text{In}^{3+}$  (0.8 Å) ion is situated in this intermediate range.

Gessner (7) reported the preparation of  $\text{CuInO}_2$  using an exchange reaction of  $\text{CuCl}$  and  $\text{NaInO}_2$ . However, the crystal structure of the reaction product has not been refined. Thus, a new Cu-containing delafossite oxide with  $\text{In}^{3+}$  ion in the  $B$  site was tried to synthesize and analyze the structure.

## EXPERIMENTAL

### Synthesis

Preparation of  $\text{CuInO}_2$  was tried both by solid state reaction using the same procedure as that for synthesizing  $\text{CuFeO}_2$  (5) and  $\text{CuAlO}_2$  (6) and by cation exchange reaction, which is employed in the synthesis of  $\text{CuScO}_2$  (4). Each preparation method is given as follows.

**Solid state reaction.**  $\text{Cu}_2\text{O}$  (Kojundo Chemical Lab. Co., Ltd., 99%) and  $\text{In}_2\text{O}_3$  (Kojundo Chemical Lab. Co., Ltd., 99.9%) or  $\text{In}(\text{OH})_3$  powder (Kojundo Chemical Lab. Co., Ltd., 99.99%) were mixed in a dry process (mixing ratio:  $\text{Cu}:\text{In} = 50:50$  at %) and shaped by CIP method (pressure of 60 MPa, pressing time of 60 s). Shaped specimens were heated at  $1000^\circ$  or  $1100^\circ\text{C}$  for 24 h in Ar (heating rate,  $250^\circ\text{C h}^{-1}$ ; flowing rate,  $3.3 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ ).

**Cation exchange reaction.** Gessner (7) applied  $\text{NaInO}_2$  with  $\alpha\text{-NaFeO}_2$ -type structure in an exchange reaction with  $\text{CuCl}$ . In this work,  $\text{LiInO}_2$  with  $\alpha\text{-LiFeO}_2$ -type structure was used as a reactant for an exchange reaction with  $\text{CuCl}$  and the following exchange reaction was assumed:



$\text{LiInO}_2$  was prepared by solid state reaction as a first stage.  $\text{Li}_2\text{O}$  (Kojundo Chemical Lab. Co., Ltd., 99%) and  $\text{In}(\text{OH})_3$  were mixed in a dry process (mixing ratio:  $\text{Li}:\text{In} = 50:50$  at%), shaped, and heated at  $550^\circ\text{C}$  for 72 h in air (heating rate:  $250^\circ\text{C h}^{-1}$ ). The  $\text{LiInO}_2$  powder obtained was mixed with  $\text{CuCl}$  (Kishida Chemical Co., Ltd., 98%) in

<sup>1</sup>To whom correspondence should be addressed. E-mail: shimode@whale.cc.muroran-it.ac.jp.



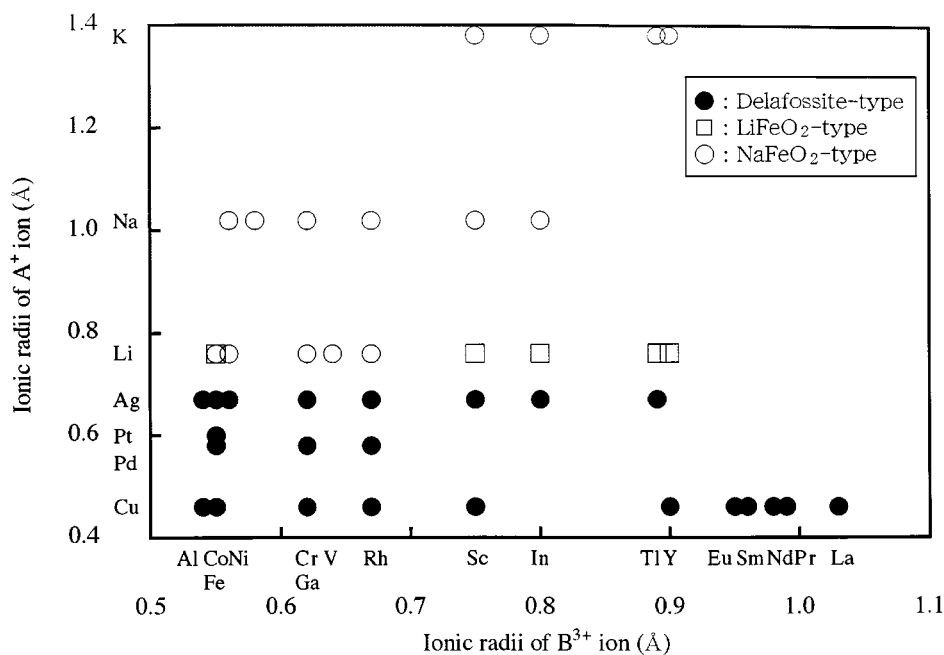


FIG. 1. Structure field map for various  $ABO_2$  compounds. Structural data were taken from (2–6).

a dry process (mixing ratio: Cu: Li = 50: 50 at%). Molded specimens were sealed in an evacuated silica glass tube and heated between 350 and 600°C. After the heat treatment, the reaction products were washed with distilled water to leach out the remaining LiCl and then dried.

#### Crystal Structure Analysis

The powder specimens obtained were evaluated by X-ray diffraction (Rigaku Denki, RV-200) with  $\text{CuK}\alpha_1$  radiation. Intensity data were collected from 5° to 80° in  $2\theta$  at room temperature; scan speed,  $4^\circ\text{min}^{-1}$ ; scan step,  $0.04^\circ$ . The structure and the lattice parameters were refined by Rietveld analysis using the computer program RIETAN-97  $\beta$  (8). For the Rietveld analysis, X-ray diffraction measurement was performed in  $2\theta$  range from 5° to 140°, at room temperature; scan speed,  $2^\circ\text{min}^{-1}$ ; scan step,  $0.02^\circ$ . For this analysis, the Voigt function was used for the diffraction profile and all atom occupations were fixed to 1.

## RESULTS AND DISCUSSION

The relationship between reaction conditions and products is summarized in Table 1. Generally, the delafossite-type compounds including  $\text{Cu}^+$  ion in the *A* site are produced by solid state reaction of the oxides. However, solid state reaction occurred neither in the  $\text{Cu}_2\text{O}$ – $\text{In}_2\text{O}_3$  nor in the  $\text{Cu}_2\text{O}$ – $\text{In}(\text{OH})_3$  system at any investigated heat treatment conditions. This result agrees with that of Hahn and Lorentz (9).

$\text{LiInO}_2$  used in cation exchange reaction was obtained under the heat treatment condition described in the Experimental section.  $\text{LiInO}_2$  obtained was refined as tetragonal symmetry; space group,  $I41/amd$ ; the lattice parameters of the tetragonal cell,  $a = 4.3166$ ,  $c = 9.3498 \text{ \AA}$  by Rietveld analysis. This lattice parameters nearly agree with the values reported in the JCPDS card (10) ( $a = 4.3143$ ,  $c = 9.3419 \text{ \AA}$ ).

The diffraction peaks of  $\text{CuCl}$  and  $\text{LiInO}_2$  disappeared for the products obtained by cation exchange reaction under various heat treatment conditions. For the specimens synthesized at 450–600°C for 72 h, the main phases formed were  $\text{Cu}_2\text{O}$  and  $\text{In}_2\text{O}_3$ . For any products obtained by

TABLE 1  
Relationship between Reaction Conditions and Products for the Cu–In–O System

Reaction system	Heat treatment conditions	Products
Solid state reaction by $\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$	1100°C, 24 h	$\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$
	1000°C, 24 h	$\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$
Solid state reaction by $\text{Cu}_2\text{O}$ and $\text{In}(\text{OH})_3$	1100°C, 24 h	$\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$
	1000°C, 24 h	$\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$
Cation exchange reaction from $\text{CuCl}$ and $\text{LiInO}_2$	600°C, 72 h	$\text{CuInO}_2$ , $\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$
	550°C, 72 h	$\text{CuInO}_2$ , $\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$
	450°C, 72 h	$\text{CuInO}_2$ , $\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$
	350°C, 72 h	$\text{CuInO}_2$ , $\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3$
	350°C, 144 h	$\text{CuInO}_2$ , $\text{Cu}_2\text{O}$ and unknown phase

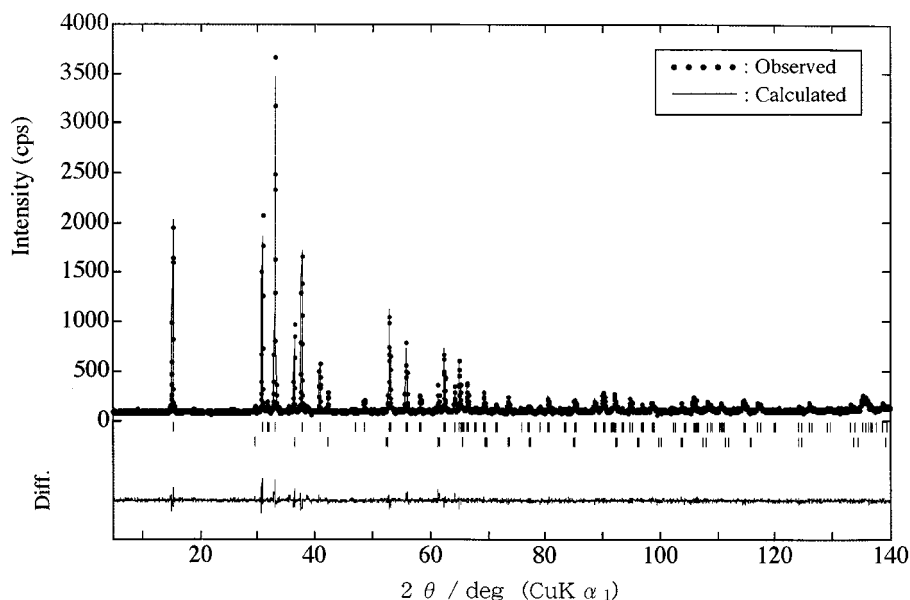


FIG. 2. Calculated, difference plots by Rietveld refinement and observed XRD pattern for the Cu–In–O system obtained by cation exchange reaction at 350°C for 144 h. Rietveld refinement was achieved with two phases of  $R\text{-}3m$   $\text{CuInO}_2$  and  $Pn\text{-}3m$   $\text{Cu}_2\text{O}$ .

cation exchange reaction, unknown diffraction peaks which could not be attributed in the JCPDS cards tended to increase with decreasing heat treatment temperature. The main product prepared at 350°C for 144 h was of unknown phase. No phase has been reported in the Cu–In–O system except  $\text{CuIn}_2\text{O}_5$  synthesized by Bergerhoff *et al.* (11) and  $\text{CuInO}_2$  prepared by Gessner (7). The diffraction pattern of the unknown phase did not correspond to  $\text{CuIn}_2\text{O}_5$ . Some X-ray diffraction peaks of the unknown phase fit those of the compound synthesized by Gessner (7). The pattern of the products synthesized by cation exchange reaction is similar to that of the delafossite-type  $\text{AgInO}_2$  (12).

Thus, the unknown phase obtained by cation exchange reaction was assumed to be the delafossite-type  $\text{CuInO}_2$  with space group  $R\text{-}3m$ , and its structure was refined by Rietveld analysis. Rietveld analysis performed on the sample obtained at 350°C for 144 h with the highest diffraction intensities. For the product obtained in the same reaction condition described above, the diffraction peaks were

around  $2\theta$  (deg), of 35° and 40°. These peaks were assigned to (411) and (332) of  $\text{In}_2\text{O}_3$ , and Rietveld analysis was carried out with the three phases of the delafossite-type

TABLE 3  
Diffraction Data for  $\text{CuInO}_2$  Obtained by Cation Exchange Reaction

$h$	$k$	$l$	$d_{\text{cat.}}$	$d_{\text{obs.}}$	$I/I_0$	$h$	$k$	$l$	$d_{\text{cat.}}$	$d_{\text{obs.}}$	$I/I_0$
0	0	3	5.7960	5.8241	45	1	1	12	1.8077	1.0882	6
0	0	6	2.8980	2.9043	57	1	2	2	1.0696	1.0697	6
1	0	1	2.8136	2.8220	3	2	1	4	1.0460	1.0464	4
0	1	2	2.7092	2.7153	100	1	2	5	1.0293	1.0297	2
1	0	4	2.3841	2.3878	45	1	0	16	1.0155	1.0163	3
0	1	5	2.2048	2.2077	13	2	1	7	0.9886	0.9887	1
0	0	9	1.9320	1.9317	1	0	0	18	0.9660	0.9660	6
1	0	7	1.8729	0.8747	4	0	1	17	0.9628	0.9630	1
0	1	8	1.7285	1.7312	30	3	0	0	0.9504	0.9507	3
1	1	0	1.6461	1.6483	24	1	1	15	0.9478	0.9480	1
1	1	3	1.5835	1.5848	6	2	0	14	0.9365	0.9369	2
1	0	10	1.4845	1.4861	19	2	1	10	0.9156	0.9162	3
0	0	12	1.4490	1.4503	8	0	3	6	0.9031	0.9032	3
1	1	6	1.4313	1.4320	16	3	0	6			
0	2	1	1.4208	1.4189	1	1	2	11	0.8904	0.8905	1
2	0	2	1.4068	1.4075	10	1	0	19	0.8714	0.8718	2
0	1	11	1.3825	1.3825	1	0	2	16	0.8643	0.8644	2
0	2	4	1.3546	1.3558	6	3	0	9	0.8528	0.8526	1
2	0	5	1.3191	1.3200	2	0	3	9			
1	1	9	1.2530	1.2551	1	2	1	13	0.8392	0.8392	1
0	2	7	1.2364	1.2368	2	1	1	18	0.8331	0.8333	5
1	0	13	1.2109	1.2120	2	0	1	20	0.8316	0.8318	4
2	0	8	1.1921	1.1929	5	0	0	21	0.8280	0.8281	1
0	1	14	1.1387	1.1393	4	2	2	0	0.8231	0.8230	2
0	2	10	1.1024	1.1033	3						

TABLE 2

Rietveld Refinement Results of  $\text{CuInO}_2$  (Space Group:  $R\text{-}3m$ )

$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$R_{\text{wp}}$	$R_{\text{e}}$	$S$	$R_{\text{B}}$	$R_{\text{F}}$
3.2922(1)	17.388(4)	163.21	10.44	8.97	1.1636	4.47	3.82

Note.  $R_{\text{wp}}$ ,  $R$ -weighted pattern;  $R_{\text{e}}$ ,  $R$ -expected;  $S$ , goodness-of-fit between calculated and observed data,  $S = R_{\text{wp}}/R_{\text{e}}$ ;  $R_{\text{B}}$ ,  $R$ -Bragg factor;  $R_{\text{F}}$ ,  $R$ -structure factor.

**TABLE 4**  
Atom Positions and Isotropic Atomic Displacement Parameters of  $\text{CuInO}_2$  (Space Group:  $R-3m$ )

Atom	$x$	$y$	$z$	$B_{\text{iso.}} (\text{\AA}^2)$
Cu	0	0	0	0.9196(5)
In	0	0	0.5	0.1799(9)
O	0	0	0.1061(45)	0.4077(3)

$\text{CuInO}_2$ ,  $\text{Cu}_2\text{O}$ , and  $\text{In}_2\text{O}_3$ . However, the refinement result did not fit with the observed X-ray diffraction pattern especially in the  $\text{In}_2\text{O}_3$  because of lower diffraction intensities for  $\text{In}_2\text{O}_3$ . As a result, these diffraction peaks are assigned to an unknown phase. Therefore, the structure refinement was performed for a two-phase mixture of the delafossite-type  $\text{CuInO}_2$  and  $\text{Cu}_2\text{O}$ . Figure 2 shows the fitting profile calculated by Rietveld refinement, the observed X-ray diffraction data, and their difference plots. The refinement results are listed in Table 2. In this work,  $S$  (goodness-of-fit between calculated and observed data) was used in order to verify the validity of the refinement result. For Rietveld analysis, the most important  $R$  factor is  $R_{\text{wp}}$  ( $R$ -weighted pattern). However,  $R_{\text{wp}}$  depends heavily on the specimen and the measurement conditions of X-ray diffraction. Best  $R_{\text{wp}}$  statistically anticipated, is  $R_e$  ( $R$ -expected). Thus,  $S$  defined as  $S = R_{\text{wp}}/R_e$ , indicates a quality of the fit between calculated and observed data. If the  $S$  value is lower than 1.3, refinement is suitable. Judging from the low  $S$  value in Table 2, the unknown phase obtained in this work can be assumed to be  $\text{CuInO}_2$  with delafossite-type structure. It is concluded that the unknown phase is a new compound,  $\text{CuInO}_2$ , converted from  $\text{LiInO}_2$  with ordered rock-salt structure into delafossite-type structure by the cation exchange reaction of Li to Cu.

The composition of  $\text{CuInO}_2$  has been confirmed “ $\text{CuInO}_2$ ” by Rietveld refinement. A chemical analysis does not work on the  $\text{Cu}_2\text{O}$ -containing  $\text{CuInO}_2$ .

**TABLE 5**  
Selected Interatomic Distances ( $\text{\AA}$ ) and Bond Angles (deg.) for  $\text{CuInO}_2$  (Space Group:  $R-3m$ )

Cu–O	( $\times 2$ )	1.845(7)
In <sup>(iii)</sup> –O	( $\times 6$ )	2.172(6)
O–O <sup>(i)</sup>	( $\times 6$ )	3.292(0)
O–O <sup>(iv)</sup>	( $\times 6$ )	2.835(9)
O–In <sup>(ii)</sup> –O <sup>(i)</sup>	( $\times 6$ )	98.52(7)
O–In <sup>(ii)</sup> –O <sup>(iv)</sup>	( $\times 6$ )	81.48(2)
Cu–O–In <sup>(iii)</sup>	( $\times 6$ )	118.97(6)
In <sup>(ii)</sup> –O–In <sup>(iii)</sup>	( $\times 6$ )	98.52(7)

Note. Symmetry codes: (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)  $x + 2/3, y + 1/3, 1/3 - z$ .

**TABLE 6**  
Lattice Parameters for  $\text{CuInO}_2$  and Various Delafossite-Type Compounds

Compounds	$a$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	Reference
$\text{CuAlO}_2$	2.8604	16.953	(6)
$\text{CuCrO}_2$	2.9761	17.102	(2)
$\text{CuFeO}_2$	3.0347	17.162	(14)
$\text{CuScO}_2$	3.2155	17.089	(4)
$\text{CuInO}_2$	3.2922	17.388	This work
$\text{CuEuO}_2$	3.6311	17.069	(15)
$\text{CuNdO}_2$	3.7137	17.092	(16)
$\text{AgAlO}_2$	2.8902	18.272	(2)
$\text{AgFeO}_2$	3.0391	18.590	(2)
$\text{AgScO}_2$	3.2112	18.538	(2)
$\text{AgInO}_2$	3.2772	18.881	(2)
$\text{AgTiO}_2$	3.5682	18.818	(2)

Table 3 shows diffraction data of  $\text{CuInO}_2$  obtained by cation exchange reaction. All of the diffraction peaks of  $\text{CuInO}_2$  can be marked on a rhombohedral cell.

The atom positions and isotropic atomic displacement parameters are given in Table 4. Selected interatomic distances and bond angles are shown in Table 5. In the structure of delafossite-type  $\text{ABO}_2$ ,  $A^+$  ions are surrounded by two linear  $\text{O}^{2-}$  ions and  $B^{3+}$  ions are surrounded by six  $\text{O}^{2-}$  ions. Cu–O and In–O distances are 1.845 and 2.172  $\text{\AA}$ , respectively. They agree well with the values calculated from the effective ionic radii (13),  $\text{Cu}^+ = 0.46$ ,  $\text{In}^{3+} = 0.80$ ,  $\text{O}^{2-} = 1.38$   $\text{\AA}$ . Table 6 compares the lattice parameters of  $\text{CuInO}_2$  with those of the other delafossite-type compounds previously reported. In the series containing  $\text{Cu}^+$  ion in the  $A$  site, and  $a$  axis increases with increasing ionic radii in the  $B$  site, whereas the  $c$  axis of  $\text{CuInO}_2$  is the longest axis. A similar tendency is found in the series with the  $\text{Ag}^+$  ion in the  $A$  site.

## CONCLUSIONS

The preparation of a new delafossite-type compound,  $\text{ABO}_2$ , containing  $\text{Cu}^+$  ion in the  $A$  site and  $\text{In}^{3+}$  ion in the  $B$  site, was attempted by cation exchange reaction of Li to Cu in the  $\text{CuCl-LiInO}_2$  system and by solid state reaction. No reaction occurred in the  $\text{Cu}_2\text{O-In}_2\text{O}_3$  and  $\text{Cu}_2\text{O-In(OH)}_3$  systems under various heat treatment conditions.  $\text{CuInO}_2$  was obtained only by cation exchange reaction. Rietveld refinement confirmed that the composition is  $\text{CuInO}_2$  and that the structure is of delafossite-type with lattice parameters of the rhombohedral cell,  $a = 3.2992$ ,  $c = 17.388$   $\text{\AA}$ .

## ACKNOWLEDGMENT

The authors thank Dr. Hisanori Yamane at Tohoku University for Rietveld analysis.

## REFERENCES

1. A. Pabst, *Am. Mineral.* **31**, 539 (1946).
2. R. D. Shannon and D. B. Rogers, *Inorg. Chem.* **10**, 713 (1971).
3. T. Ishiguro, N. Nishizawa, N. Mizutani, and M. Kato, *J. Solid State Chem.* **49**, 232 (1983).
4. J. Doumerc, A. Ammar, A. Wichainchai, M. Pouchard, and P. Hagemmuller, *J. Phys. Chem. Solids* **48**(1), 37 (1987).
5. H. Wiedersich, J. W. Savage, A. H. Muir, and D. G. Swarthout, *Mineral. Mag.* **36**, 643 (1968).
6. T. Ishiguro, A. Kitazawa, N. Mizutani, and M. Kato, *J. Solid State Chem.* **40**, 170 (1981).
7. W. Gessner, *Silikattechnik* **21**, 45 (1970).
8. F. Izumi, "The Rietveld Method" (R. A. Young, Ed.). Oxford Univ. Press, London, 1993.
9. H. Hahn and C. Lorent, *Z. Anorg. Allg. Chem.* **279**, 281 (1955).
10. JCPDS Card File, 43-1131.
11. G. Bergerhoff and H. Kasper, *Acta Crystallogr. Sect. B* **24**, 388 (1968).
12. JCPDS Card File, 21-1077.
13. R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
14. JCPDS Card File, 39-0246.
15. JCPDS Card File, 37-1356.
16. JCPDS Card File, 37-1358.