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Crystal growth and reinvestigation of the crystal structure of crednerite, $CuMnO_2$

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Abstract. Single crystals of nearly stoichiometric $CuMnO_2$ were grown using a $LiBO_2$ flux. They crystallize in the monoclinic space group *C*2/*m* with cell parameters $a = 557.8(6)$ pm, $b = 288.1(2)$ pm, $c = 588.6(7)$ pm, $\beta = 104.00(5)°$ and $Z = 2$. The structure can be described as a close packing of linear $[O-Cu-O]^{3-}$ groups parallel to the *c*-axis where Mn^{III}-ions occupy edge sharing MnO_6 octahedra forming layers perpendicular to the *c*-axis. It is closely related to that of delafossite, $CuFeO_2$, but the Jahn-Teller effect of Mn^{III}-ions breaks the three-fold symmetry.

1. Introduction

The mineral crednerite was discovered by Credner (1848) in Friedrichroda (Thuringia) and Rammelsberg (1848) attributed the formula $3\,CuO : 2\,Mn_2O_3$ to it. McAndrew (1956) investigated samples from another ore (Mendip Hills, Somerset) as well as synthetic products. The composition was described as $Cu_2Mn_2O_5$; a monoclinic unit cell and three possible space groups – *C*2/*m*, *C*2 or *Cm* – were proposed. Kondrashev (1958) found the composition $CuMnO_2$ and determined the crystal structure on synthetic polycrystalline samples in space group *C*2/*m*. Later, the analysis of a natural product from the Anti-Atlas (Morocco) revealed a composition of about $CuMnO_2$ and the powder diffraction data were indexed on the basis of a monoclinic cell (Gaudefroy, Dietrich, Permingeat, Picot, 1966).

Up to now, all the investigations suffer from the lack of single crystal data. The present paper reports on the structure refinement of crednerite using single crystal X-ray diffraction.

2. Experimental

2.1 Sample preparation

Following the phase diagram of the system Cu – Mn – O in air (Driessens, Rieck, 1967) experiments to prepare polycrystalline samples of $CuMnO_2$ were carried out by annealing mixtures of CuO and $MnCO_3$ at 1333–1373 K. Neither samples cooled down in the furnace nor quenched ones produced a single phase. In addition to the X-ray diffraction peaks of crednerite those of a spinel phase were also observed. Rienäcker and Werner (1964) prepared $CuMnO_2$ by the reaction of CuO and Mn_2O_3 in an inert atmosphere or vacuo. Adapting that method we obtained pure $CuMnO_2$ by heating an intimate mixture of Cu, CuO and Mn_2O_3 in an evacuated and sealed silica tube at 1233 K for 72 h; then the tube was quenched. The product is a black powder. X-ray diffraction data are given in Table 1. A ratio Cu/Mn of 1 ± 0.02 was found by electron microprobe analysis. Assuming that the two-fold coordinate accounts for a copper d^{10} configu-

Table 1. Powder X-ray data of $CuMnO_2$, $a = 559.6(3)$ pm, $b = 288.0(1)$ pm, $c = 589.9(2)$ pm, $\beta = 104.02(3)°$. Space group *C*2/*m*.

h k l	d_{obs}	d_{calc}	I_{obs}	I_{calc}
0 0 1	5.716	5.7232	10	5
0 0 2	2.8609	2.8617	76	76
2 0 0	2.7163	2.7147	100	95
1 1 0	2.5477	2.5443	17	14
1 1 −1	2.4318	2.4296	80	100
2 0 −2	2.2596	2.2621	28	25
1 1 1	2.2347	2.2328	42	48
0 0 3	1.9055	1.9078	10	5
2 0 2	1.7663	1.7673	23	27
1 1 −3	1.6158	1.6170	34	42
3 1 −1	1.5625	1.5625	36	35
1 1 3	1.4490	1.4494	23	24
0 2 0	1.4410	1.4401	20	14
0 0 4	1.4288	1.4309	17	6
3 1 1	1.4120	1.4098	16	12
3 1 −3	1.3340	1.3360	15	17
0 2 2	1.2868	1.2864	14	11
2 2 0	1.2730	1.2722	16	14
2 2 −2	1.2123	1.2148	11	7

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ration, iodometric titration gave an oxidation state of 3.00 ± 0.02 for the Mn-ions. Further details about phase relations and physical properties of $CuMnO_2$ and solid solutions $Cu_{1+x}Mn_{1-x}O_2$ $(0 \leq x \leq 0.2)$ are or will be reported in separate papers (Doumerc, Trari, Töpfer, Fournès, Grenier, Pouchard, Hagenmuller, in press.).

Single crystals were grown in a flux of lithium borate (1 g $CuMnO_2$/3 g $LiBO_2$) in an alumina crucible under an argon atmosphere. The mixture was heated up to 1273 K at 100°/h. After 6 h the melt was slowly cooled down to 1113 K at 2°/h. The reaction product was leached out with warm water. The obtained material consists of a black phase $Cu_{1+x}Mn_{1-x}O_2$, CuO and $LiMn_2O_4$.

2.2 Structure determination

Powder X-ray diffraction patterns were obtained at 293 K using CuK_α radiation and Bragg-Brentano geometry. The equipment was calibrated with Si. Unit cell dimensions were determined from 15 reflections in the range $10° \leq 2\theta \leq 100°$ using a least square method.

For single crystal data collection a needle shaped crystal with dimensions $0.014 \times 0.182 \times 0.014$ mm^3 was chosen. Preliminary investigations with Weissenberg and Buerger photographs showed the crystal to belong to the C lattice mode of the monoclinic system. Intensities were collected on an automatic diffractometer (Enraf-Nonius CAD4). Details of the structure analysis are given in Table 2.

3. Results

All reflections of the polycrystalline $CuMnO_2$ specimen prepared in a silica tube could be indexed with a monoclinic cell (Table 1)[1]; the lattice parameters are $a = 559.6(3)$ pm, $b = 288.0(1)$ pm, $c = 589.9(2)$ pm and $\beta = 104.02(3)°$. These values are in good agreement with the data of McAndrew (1956) while they slightly differ from those of Kondrashev (1958), especially for the a and β parameters. These discrepancies and the fact that Kondrashev prepared the samples at about 1273 K in air suggest that his material was enriched in copper and belongs to the $Cu_{1+x}Mn_{1-x}O_2$ $(0 \leq x \leq 0.2)$ series (Trari, 1994).

The results of the structure determination of the single crystal in space group $C2/m$ are given in Table 2. Refinements in the non centrosymmetric $C2$ and Cm groups did not improve significantly the model. They confirm those reported by Kondrashev (1958) for a powder investigation.

Table 2. Details of structure refinement for crednerite single crystal.

Crystal system	Monoclinic
Space group; z	$C2/m$; 2
Lattice constants (pm, °)	$a = 557.8(6)$, $b = 288.1(2)$, $c = 588.6(7)$, $\beta = 104.00(5)$
Molar volume (cm^3/mol)	27.64
Density calc. (g/cm^3)	5.445
Radiation	MoK_α
Monochromator	Graphite
Min./max. transmission factors (absorption correction with crystal shape and size)	0.53/0.68
Scan range	$-11 \leq h \leq 11$ $-5 \leq k \leq 5$ $-11 \leq k \leq 11$
Number of measured reflections	3008
Number of independent reflections	229 $(F_0^2 \geq 3\sigma(F_0^2))$
$R_{INT} = \left(\sum_j \sum_i \lvert F_{0_{i,j}} - F_{0_j} \rvert\right) / \sum F_0$	0.027
Structure refinement program	SHELX-76
R	2.47%
R_w	2.56% $(w = 0.446/\sigma^2(F_0))$

The comparison of the lattice constants of the single crystal (Table 2) with those of crushed crystals grown in the $LiBO_2$ melt ($a = 557.71(9)$ pm, $b = 288.51(6)$ pm, $c = 588.44(9)$ pm and $\beta = 104.00(1)°$) shows that the chosen crystal is representative of the batch.

The three following features suggest that the composition of the investigated crystal is not exactly $CuMnO_2$ and that the crystal contains a slight excess of copper.

(i) For the series $Cu_{1+x}Mn_{1-x}O_2$ $(0 \leq x \leq 0.2)$ a variation of the parameters a and β with composition was observed while b and c remain nearly constant (Trari, 1994). The value of the parameter a of the investigated crystal corresponds to a composition of about $x = 0.04$.

(ii) Wavelength dispersive microprobe analysis of the investigated crystal (average of 25 different aligned points) gives for composition: $Cu_{1.04}Mn_{0.96}O_2$ $(x = 0.04)$.

(iii) Refinement of the atomic positions and thermal parameters leads to a slightly improved R value for $x = 0.04$ with respect to $x = 0$.

The atomic positions and the thermal parameters are given in Table 3 and selected interatomic distances in Table 4.

4. Discussion

In the structure of $CuMnO_2$ each Mn^{III} ion is bonded to six oxygen ions forming a distorted octahedron. Each MnO_6 octahedron shares six edges with six neighbors located in the same layer. These layers are linked by two-fold coordinated Cu^I ions. The unit cell is drawn in Fig. 1 showing that the structure can also be described as a close packing of linear $(O-Cu-O)^{3-}$ groups parallel to the c-axis where the octahedral sites are occupied by Mn^{III} ions.

The Cu – O distance of 183.4 pm is in the range of those generally found for two-fold coordinated Cu^I ions. The Cu-atoms form rows in the [010] direction with a

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[1] Additional material to this paper can be ordered referring to the no. CSD 58518, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of F_o/F_c-data is available from the author up to one year after the publication has appeared.

Table 3. Atomic positions and thermal parameters (10^4 pm^2) for $Cu_{1.04}Mn_{0.96}O_2$.

Atom	Multiplicity and Wyckoff letter	Site symmetry	x	y	z	Occupancy
Cu	$2d$	$2/m$	0	1/2	1/2	1
Mn/Cu	$2a$	$2/m$	0	0	0	0.96/0.04
O	$4i$	m	0.4070(5)	0	0.1789(5)	1

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Cu	0.0168(7)	0.0102(9)	0.0049(5)	0	0.0006(5)	0	0.0109(5)
Mn/Cu	0.0063(6)	0.0038(7)	0.0059(6)	0	0.0029(5)	0	0.0051(4)
O	0.0089(10)	0.043(10)	0.0062(9)	0	0.0022(8)	0	0.0064(6)

Thermal parameters refer to equation $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \ldots + 2U_{13}hla^*c^*))$.

Table 4. Selected interatomic distances (pm) and angles (°).

Mn	O^i	O^{ii}	O^{iii}	O^{iv}	O	O^v
O^i	**192.9**	385.9	288.5	256.2	279.2	314.0
O^{ii}	180.0	**192.9**	256.2	288.5	314.0	279.2
O^{iii}	96.8	83.2	**192.9**	385.9	279.2	314.0
O^{iv}	83.2	96.8	180.0	**192.9**	314.0	279.2
O	83.2	96.8	83.2	96.8	**226.0**	451.9
O^v	96.8	83.2	96.8	83.2	180.0	**226.0**

Cu	O^{iv}	O^{vi}
O^{iv}	**183.4**	366.9
O^{vi}	180.9	**183.4**

O	Cu^{vii}	Mn^i	Mn^{iii}	Mn
Cu^{vii}	**183.4**	327.7	327.7	353.0
Mn^i	121.0	**192.9**	288.5	314.0
Mn^{iii}	121.0	96.8	**192.9**	314.0
Mn	118.8	96.8	96.8	**226.0**

Symmetry code: (i) $-x + 1/2, y + 1/2, -z$; (ii) $x - 1/2, y - 1/2, z$; (iii) $-x + 1/2, y - 1/2, -z$; (iv) $x - 1/2, y + 1/2, z$; (v) $-x, y, -z$; (vi) $-x + 1/2, y + 1/2, 1 - z$; (vii) $x + 1/2, y - 1/2, z$.

Cu—Cu distance of 288.1 pm; the Cu—Cu distance between these rows is 313.9 pm. The strong anisotropy of the structure is also visible in comparing the thermal parameters: the U_{11} component of the Cu^I ions is more than three times larger than the U_{33} component and also significantly larger than U_{22}. As the Mn sublattice corresponds to the Cu one by a $(b + c)/2$ translation, the Mn—Mn distances differ in the same way as the Cu—Cu ones giving rise to a pseudo-1D arrangement accounting for the temperature dependence of the magnetic properties (Doumerc et al., in press).

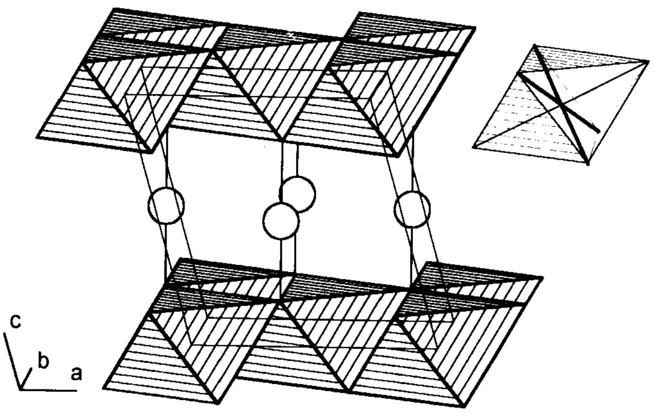

Fig. 1. Unit cell of crednerite with MnO_6 octahedra (hatched) and Cu ions (empty circles). In the separated octahedron bold lines correspond to short Mn—O distances.

The MnO_6 octahedra are elongated with four short and two long Mn—O distances (Table 4). Such a distortion is a typical feature of Mn^{III} ions in an octahedral site due to the Jahn-Teller effect.

Unlike $CuMnO_2$, many oxides of the general formula $CuM^{III}O_2$ crystallize with the delafossite-type structure which can be considered as a parent structure of crednerite. Depending on the stacking of the $[CuO_2]^{3-}$ groups in the c-direction different polytypes can be distinguished. The most common ones are the $3R$ ($R\bar{3}m$) and the $2H$ ($P6_3/mmc$) types (Shannon, Rogers, Prewitt, 1971; Doumerc, Ammar, Wichainchai, Pouchard, Hagenmuller, 1987). The delafossite structure is of higher symmetry than the crednerite one. It exhibits a three-fold axis and therefore single interatomic Cu—Cu, M—M and M—O distances. In delafossite the octahedra are flattened resulting in two different values for the O—O distances. The ratio of the length of the unshared MnO_6-octahedron edge $(O-O)^u$ over that of the edge common to two neighboring octahedra $(O-O)^s$, $(O-O)^u/(O-O)^s$, has been used to classify delafossite type oxides (Doumerc et al., 1987). This ratio has been shown to increase with the ionic radii of the M^{III} ions. In $CuMnO_2$ the additional influence of the Jahn-Teller distortion induces a further differentiation in both "in plane" and "common edge" O – O distances (Table 4).

As the composition of the studied crystal seems to be about $Cu_{1.04}Mn_{0.96}O_2$, a small number of copper ions occupy the octahedral positions. The distribution of the cations may be expressed by the formula $Cu^{I}_{1.00}(Cu^{II}_{0.04}Mn^{III}_{0.92}Mn^{IV}_{0.04})O_2$ where cations occupying the octahedral $2a$ positions are written in parentheses. Regarding empirical site preference energies Cu^{II} ions are enabled to occupy octahedral positions. In order to satisfy charge balance an equivalent amount of Mn^{IV} has to be formed. Further discussion about cation valence distribution and physical properties of $Cu_{1+x}Mn_{1-x}O_2$ $(0 \leq x \leq 0.2)$ materials will be reported in a next paper.

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