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Structural Studies on some 3d Mixed Oxides MO-CuO Systems*

J. S. Ahn
Dept. of Industrial Chemistry

S. Yoon
Dept. of Materials Science

<Abstract> (Received June 10, 1980)

Crystal structures of $M_{1-x}Cu_xO$ (M; Ni, Co, Fe) have been studied by *X*-ray powder diffractometry. Samples were prepared through wet process, i.e., decomposition of carbonate precipitations.

$Ni_{1-x}Cu_xO$ system showed a B1 type single phase in the range of $0 \leqslant x \leqslant 0.10$. As x exceeded 0.12, a second phase which could be indexed by CuO structure began to appear.

In $Co_{1-x}Cu_xO$ system, cubic+ferrite, cubic+ferrite+CuO and ferrite+CuO phases were found as x increases from 0.05.

$Fe_{1-x}Cu_xO$ system showed no B1 phase through the observed range $x \geqslant 0.05$ and the structure could be identified as magnetite+CuO mixed phase.

3d천이원소의 혼합산화물의 제조 및 결정 구조 연구*

안 성 수
공 업 화 학 과

윤 석 길
재 료 공 학 과

<요 약> (1980. 6.10 접수)

X-선 회절을 이용하여 3d천이원소 혼합산화물 $M_{1-x}Cu_xO$(M; Ni, Co, Fe)의 결정구조를 알아보았다. 시료는 탄산염을 침전시켜 열분해하는 습식방법에 의하여 얻었다. $Ni_{1-x}Cu_xO$인 경우는 $x \geqslant 0.10$일때 NiO와 같은 구조를 가지고 있음을 알 수 있었으며 x가 0.12를 넘으면서부터 CuO로 해석될 수 있는 제2상이 나타남을 볼 수 있었다. $Co_{1-x}Cu_xO$와 $Fe_{1-x}Cu_xO$의 경우는 조사된 범위($x \geqslant 0.05$)에서는 입방구조로 된 단상은 없었으며 Co의 경우 입방+ferrite 및 ferrite+CuO, Fe의 경우 magnetite+CuO의 혼합상만을 볼 수 있었다.

I. Introuction

Many research work have been made on 3d metal mixed oxides. NiO-MnO[1] and NiO-CoO[2] were reported to form a complete solid solution. FeO-MnO also makes a solid solution above 1150° C.[3] Mixed oxides of 3d metals with other metals, e.g., Mg, Ca, Zn were studied on their structures.[3][1]

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Electrical and magnetic properties of some mixed oxides have been reported by several workers. For instances, Roth investigated the antifferromagnetic structures of pure oxides.[5] Alvazov and Gurov worked on changes in χ and T_N in the systems NiO-MnO and NiO-CoO.[6] Sakada et al. reported the resistivity of NiO-CoO binary system.[7]

In this paper, crystal structures of 3d metal mixed oxide systems NiO-CuO, CoO-CuO and FeO-CuO were reported. The prime interest of this work was given on finding whether B1 (NaCl) type structure was realized inspite of inclusion of CuO which is monoclinic.

Ⅱ. Experiments and Results

1. Sample preparation

The samples were made through wet process using reagent grade or analytical grade chemicals. 0.5M solutions of Copper(Ⅱ)nitrate and each one of Nickel, Cobalt and Iron(Ⅱ)nitrates were mixed to make composite solutions with designed atomic ratio between metal ions.

100ml of the composite nitrate solution was added by drops into 150ml of 0.5M sodium carbonate solution with shaking. The precipitations were filtered and washed with distilled water. After drying at 120°C in an electric oven, the carbonates were decomposed at 800°C for 8 hours in a vacuum drying oven. Weight losses due to removal of carbon dioxide for each sample was checked.

X-ray diffractometer was employed to get crystallographic data.

2. $Ni_{1-x}Cu_xO$ system

It was found that CuO not more than 10mol% ($x \leqslant 0.10$) made a solid solution with NiO in B1 (NaCl) type structure. As x exceeded 0.12, however, a second phase began to appear. The second phase could be indexed by the CuO monoclinic system. x being increased, the cubic phase decresed its portion and CuO phase increased. The cubic phase sustained until $x=0.80$, but in the sample $x=0.90$, no cubic phase was recognized (Table 1). Lattice parameters of cubic phase monotonically increased with x in the region $x \leqslant 0.10$ from 4.180 Å and then remained roughly constant until $x=0.80$. (Fig. 1)

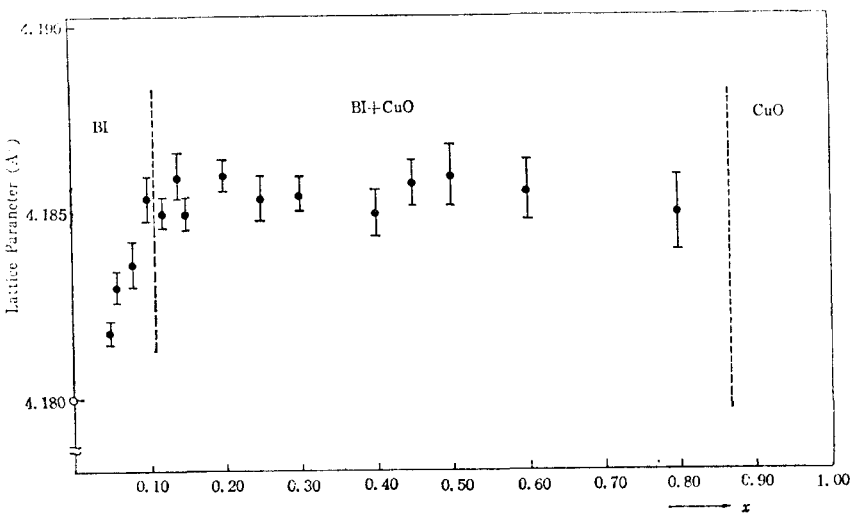

Fig. 1. Lattice Parameters of B1 Phase, $Ni_{1-x}Cu_xO$

Table 1. Crystal Structures of $Ni_{1-x}Cu_xO$ system.

Oxide	Structures	Lattice parameters, Å (Cubic phase)	Remarks
NiO*	B1 (NaCl)	4.180 ± 0.001	*Ref. (1) (2) (8)
$Ni_{0.95}Cu_{0.05}O$	B1 (NaCl)	4.1818±0.0003	
$Ni_{0.91}Cu_{0.06}O$	B1 (NaCl)	4.1830±0.0004	
$Ni_{0.92}Cu_{0.08}O$	B1 (NaCl)	4.1836±0.0006	
$Ni_{0.90}Cu_{0.10}O$	B1 (NaCl)	4.1854±0.0006	
$Ni_{0.88}Cu_{0.12}O$	B1 + CuO	4.1850±0.0004	
$Ni_{0.86}Cu_{0.14}O$	B1 + CuO	4.1860±0.0006	
$Ni_{0.85}Cu_{0.15}O$	B1 + CuO	4.1850±0.0004	
$Ni_{0.80}Cu_{0.20}O$	B1 + CuO	4.1860±0.0004	
$Ni_{0.75}Cu_{0.25}O$	B1 + CuO	4.1854±0.0006	
$Ni_{0.70}Cu_{0.30}O$	B1 + CuO	4.1855±0.0003	
$Ni_{0.60}Cu_{0.40}O$	B1 + CuO	4.1850±0.0006	
$Ni_{0.55}Cu_{0.45}O$	B1 + CuO	4.1858±0.0006	
$Ni_{0.50}Cu_{0.50}O$	B1 + CuO	4.1860±0.0006	
$Ni_{0.40}Cu_{0.60}O$	B1 + CuO	4.1856±0.0008	
$Ni_{0.20}Cu_{0.80}O$	B1 + CuO	4.1850±0.0010	
$Ni_{0.10}Cu_{0.90}O$	CuO phase only	—	

3. $Co_{1-x}Cu_xO$ system

Samples with x=0.05, 0.10, 0.15, 0.20, 0.30, 0.50, 0.80, 0.90, were examined. Although all the samples showed multiphase, B1 structure was found in the range up to x=0.80. The second phase appearing in the low Cu content range could be interpreted as Co ferrite ($CoO \cdot Co_2O_3$) with possible Cu substitutions. Another phase which appeared at $x \geqslant 0.20$ was identified as CuO structure. The amount of B1 and ferrite phase decreased as x increased. At x=0.90 only CuO phase was found. (Table 2) As seen from Fig2, lattice parameters of B1 structure remained virtually constant at 4.265 Å. In the region $x \geqslant 0.50$, however, B1 diffraction lines were too weak to be used for calculation of lattice parameters.

4. $Fe_{1-x}Cu_xO$ system

Throughout the investigated range $0.05 \leqslant x \leqslant 0.90$, no B1 phase was identified. Instead, the

Table 2. Crystal structures of Co_{1-x} Cu_x system

Oxide	Structure	Lattice parmeters, Å (of B1 structure)	Remarks
CoO*	B1	4.26	*Ref. (1)(2)
$Co_{0.95}Cu_{0.05}O$	B1+ferrite	4.266±0.002	
$Co_{0.90}Cu_{0.10}O$	B1+ferrite	4.264±0.001	
$Co_{0.85}Cu_{0.15}O$	B1+ferrite	4.263±0.001	
$Co_{0.80}Cu_{0.20}O$	B1+ferrite+CuO	4.265±0.003	
$Co_{0.70}Cu_{0.30}O$	B1+ferrite+CuO	4.226±0.002	
$Co_{0.50}Cu_{0.50}O$	B1+ferrite+CuO	4.275±0.005	calc. from
$Co_{0.20}Cu_{0.80}O$	B1+ferrite+CuO	4.27 ±0.01	v.w. lines
$Co_{0.10}Cu_{0.90}O$	CuO	—	

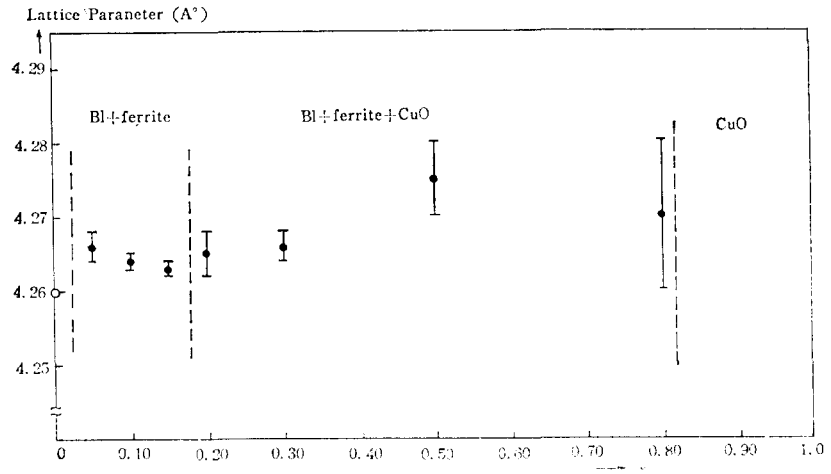

Fig. 2. Lattice parameters of B1 phase, Co_{1-x} Cu_xO

diffraction lines could be indexed by magnetite ($FeO \cdot Fe_2O_3$ with possible inclusions of Cu ferrite) and CuO structures. The amount of CuO phase seemed to increase with increasing x and at $x=0.90$ only CuO phase was observed.

Ⅲ. Discussions and Conclusion

It has been known that CuO has monoclinic structure whereas NiO, CoO and FeO show rock-salt (B1) type structure. There are quite a few reports on mixed oxides between 3d metals except for CuO. This may be understood by the fact that CuO does not easily form a solid solution with other 3d metal oxides. Rooksby (9), however, reported that addition of 5mol% of CuO to NiO reduced the structural distortion of NiO at 20°C.

In this work, it was found that only very small contents of CuO, formed a solid solution in B1 structure with other 3d metal oxides, say, not more than 10mol% in NiO, less than 5mol% in CoO and possibly far less than 5mol% in FeO (B1 phase was not found in 5mol% CuO-FeO). Solution heat treatment with subsequent quenching might be helpful to increase CuO solubility and to homogenize the sample[9]. In the case of $Co_{1-x}Cu_xO$, B1 lines were very weak and broadend. in the region $x \geqslant 0.50$ where three different phases (B1+ferrite+CuO) were recognized. This region possibly could be divided into two bi-phase regions like other 3d mixed oxides (e.g. (4)). It was noticed that, in all the investigated systems, only CuO phase was detected at $x \geqslant 0.90$.

Conductivity and magnetic susceptibility measurements and neutron diffraction studies will provide informations on the electronic states of metal ions and useful clues on magnetic interactions among 3d metals.

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