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Synthesis of $\text{Cu}(\text{OH})_2$ and CuO by soft chemistry

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Abstract - The ternary diagram $\text{CuO-Na}_2\text{O-H}_2\text{O}$ has been investigated, in order to understand the conditions of stability of $\text{Cu}(\text{OH})_2$ and CuO . Solubility curves and domains of pure solid phases, $\text{Na}_2\text{Cu}(\text{OH})_4$ and CuO , have been determined. This study shows that CuO is less soluble than $\text{Cu}(\text{OH})_2$, the latter of which does not exist in equilibrium in the ternary system. Synthesis of pure $\text{Cu}(\text{OH})_2$, is achieved from $\text{Na}_2\text{Cu}(\text{OH})_4$. This salt is diluted in a large amount of water and this procedure avoids the formation of CuO through the complex ion $\text{Cu}(\text{OH})_4^{2-}$. The synthesis of pure CuO , at room temperature, required a new route. Copper metal is oxidized by dioxygen in concentrated ammonia solutions. The solid obtained is relatively well-crystallized, despite the way of synthesis used.

INTRODUCTION

The synthesis of pure copper (II) hydroxide is not easy because of the lack of stability of this phase in basic solutions (many publications mentioned this fact [1]-[5]). Previously, we presented a new method of synthesis, in order to obtain pure hydroxide $\text{Cu}(\text{OH})_2$ from $\text{Na}_2\text{Cu}(\text{OH})_4$ [6]. In a parallel work, we recently published [7] the synthesis of cobalt, nickel and cadmium hydroxides, in oxidizing the related metal by dioxygen in presence of ammonia. In the same way, in the case of copper metal, it is not copper hydroxide but copper oxide which is obtained.

The syntheses are always performed at room temperature and normal pressure. Soluble copper salts are never used as a source of Cu^{2+} . They introduce parasitic anions which induce a pollution of the solids or the formation of copper hydroxysalts. The aim of this present publication is the study of the ternary diagram $\text{CuO-Na}_2\text{O-H}_2\text{O}$, at room temperature and normal pressure, in order to define the conditions of stability of $\text{Cu}(\text{OH})_2$ and CuO , and consequently, to explain and discuss the mentioned methods of synthesis.

THE TERNARY DIAGRAM : CuO-Na₂O-H₂O

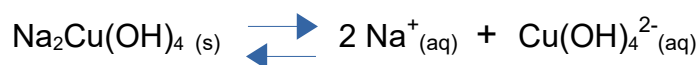
The study of the ternary diagram requires the synthesis of Na₂Cu(OH)₄ [6]. Na₂Cu(OH)₄ is obtained from a starting system which contains 10 moles of NaOH for one mole of a reactive CuO (Sédéma ref.: 3011406). A homogeneous starting system is slowly hydrated by water vapour thanks to the hygroscopic character of sodium hydroxide, sheltered from carbon dioxide. The reacting system at the beginning of hydration has the composition in weight : 64.5% Na₂O, 16.5% CuO, 19% H₂O. During the hydration process, its representative point on the diagram, follows the straight line from this composition, towards the figurative point of pure water (fig.1). The evolution was controlled by weighing in order to determine the amount of water and, then, the new composition of the system. When the composition is 35% Na₂O, 9% CuO, 56% H₂O, the system is left during one month to reach equilibrium between blue crystals of Na₂Cu(OH)₄ which appear and their mother-liquor. Then, the slow hydration process is continued further. Chemical analyses, performed for sodium and copper with an inductively coupled plasma spectrometer JY34, were carried out, on the saturated solution. Samples corresponding to eight systems situated on the line of ratio NaOH/CuO = 10 , could be analyzed. Sample weight was approximately 100 mg while the weight of the whole system, was more of 25 g. Moreover, a visual observation of the reacting system in evolution, allows for the confirmation of the limits of crystallization domains of the solid phases. The results of chemical analyses are reported in the table and shown in figure 2, and the ternary diagram is drawn in weight percent, in figure 1. Three solid phases containing copper exist in this diagram (fig.1): Na₂Cu(OH)₄, Cu(OH)₂ and CuO. Their solubility curves are located very near the base line H₂O-Na₂O, due to their weak solubility (fig.2).

Weight %	saturated solutions							
	1	2	3	4	5	6	7	8
% Na ₂ O	42.5	35	29.6	29.0	27.9	26.0	8.1	2.4*10 ⁻⁵
% CuO	0.062	0.222	0.360	0.220	0.120	0.076	0.013	1.5*10 ⁻⁶

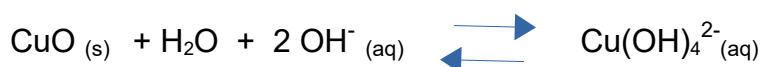
TABLE : - Chemical composition of saturated solutions
in the diagram : CuO-Na₂O-H₂O

The solution saturated in both Na₂Cu(OH)₄ and CuO is situated at 29.6% of Na₂O and 0.36% of CuO (point N° 3). This point corresponds to the intersection of the two solubility curves and permits to define accurately the limits of the domains of pure solids, Na₂Cu(OH)₄ and CuO. These domains are dotted on figure 1. The part of the domain of Na₂Cu(OH)₄ beyond 45% of Na₂O , has not been investigated because systems are too concentrated for solution sampling. Moreover, hydrates of sodium hydroxide can exist in this region. The domain of Cu(OH)₂ does not appear on the diagram because this phase is metastable in these conditions and cannot be obtained by a slow hydrolysis. The straight line on which are located the representative points of the system during the hydration process is drawn.

In figure 2, the solubility curve located beyond 30% Na₂O, corresponds to the following equilibrium :

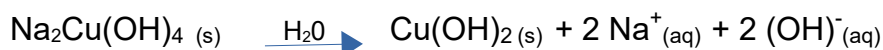


When concentration of Na⁺ decreases, an increase of solubilized copper is well observed. However, the determination of the solubility product of Na₂Cu(OH)₄ is not possible: the very strong concentration of sodium hydroxide, which is larger than 13 mol./l , implies that activity coefficients are unknown. The second solubility curve, below 30% Na₂O , corresponds to the solubility equilibrium of CuO :



In this case, when hydroxide ion concentration decreases, solubilized copper decreases also. When the hydration process is finished, copper oxide is filtered, washed with water and then is left several days under partial vacuum in a dry box with KOH pellets. It is a relatively well crystallized phase, if we consider the conditions of preparation (fig.3b).

The synthesis of Cu(OH)₂ is exposed in a previous publication [6]. The system, whose composition is 35% Na₂O, 9% CuO, 56% H₂O, containing crystals of Na₂Cu(OH)₄ and their mother-liquor, is quickly introduced in a large amount of water (approximately 2 liters for 10 g of mixture). This imperative synthesis procedure is justified by the fact that copper hydroxide is not stable in sodium hydroxide solutions and gives rise quickly to CuO. On the diagram this procedure corresponds to a jump over the domain of CuO and is represented by the bow, drawn in figure 1. The hydrolysis reaction is summarized in the following scheme :



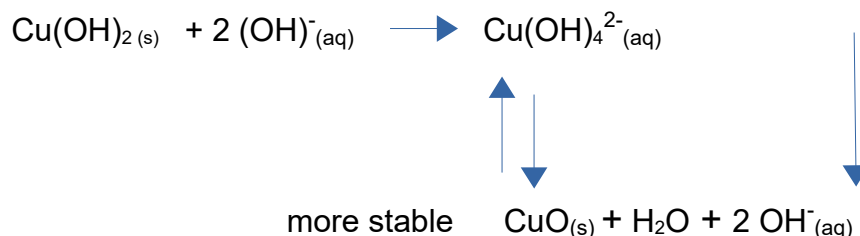
A few minutes later, copper hydroxide is filtered, washed with water and then left several days under partial vacuum, in a dry box using KOH pellets. The yield is 70%. The solid obtained is relatively well crystallized (fig.3a). Chemical and thermal analyses show that copper hydroxide obtained by this way contains approximately 3% of adsorbed water [6].

COMPARISON OF THE STABILITIES OF Cu(OH)₂ AND CuO

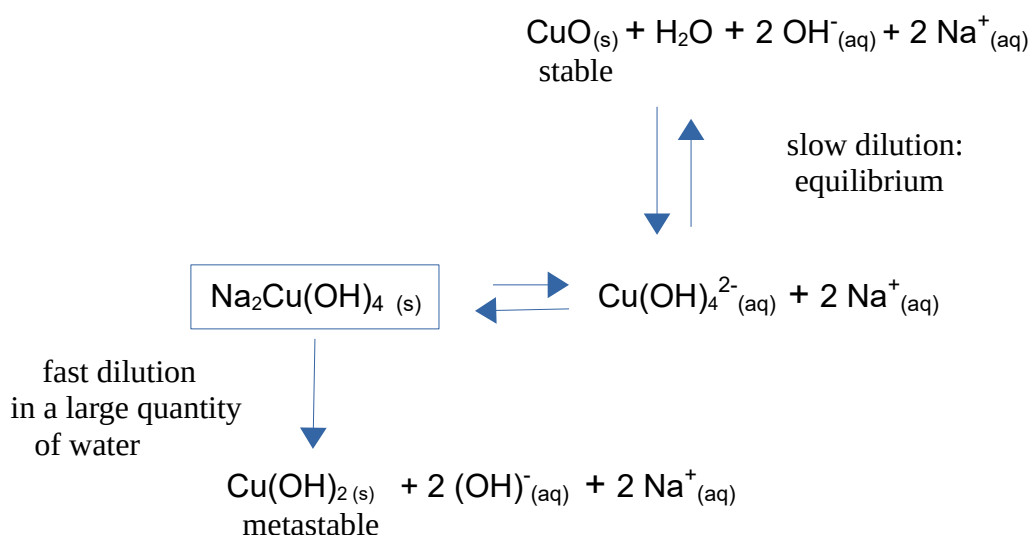
In order to confirm the role of hydroxide ions in the instability of copper hydroxide, the solubilities of pure Cu(OH)₂, and pure CuO in pure water, have been determined at room temperature. In pure water, copper hydroxide is practically stable during several weeks. After one month, the solid phase is lightly darkened, but traces of CuO can be seen on X-ray patterns and IR spectra, only after 2 months. Therefore, transformation in copper oxide is extremely slow in pure water, at room temperature. Copper in saturated solutions, was analyzed by ICP . Results show that Cu(OH)₂ is more soluble than CuO :

$$S(\text{Cu(OH)}_2) \sim 1.3 \times 10^{-5} \text{ mol. / l}; S(\text{CuO}) \sim 2 \times 10^{-7} \text{ mol. / l}$$

The reaction of hydroxide ions with Cu(OH)_2 can be explained by the formation of the complex ion Cu(OH)_4^{2-} in the solution, which then gives rise to the stable compound CuO :



The weak concentration of hydroxide ion in pure water explains why Cu(OH)_2 is practically stable, at room temperature. If we consider now, the reactions of formation of Cu(OH)_2 and of CuO , from $\text{Na}_2\text{Cu(OH)}_4$ (s) , they can be summarized in the following scheme :



The fast hydrolysis of $\text{Na}_2\text{Cu(OH)}_4$ crystals was observed with a binocular lens. Crystals are transformed quickly into Cu(OH)_2 . This transformation could be explained by a topotactic reaction. Nevertheless, structural correlations between the crystal structures of $\text{Na}_2\text{Cu(OH)}_4$ [8] and Cu(OH)_2 [3] have not been established, so far. That could explain why Cu(OH)_2 obtained by this way, is relatively well crystallized. We tried then, to apply the same procedure for the synthesis of Cu(OH)_2 from copper salts. Trials of synthesis by precipitation with sodium hydroxide solutions failed, even when precipitates are quickly and abundantly washed in order to eliminate OH^- . The reason is that grain size is very weak in this case. An X-ray pattern, performed on the blue gel obtained from copper sulfate by addition of sodium hydroxide, shows evidently, a very bad crystalline state. The presence of salt anions may be responsible for this fact. In these conditions, solid phases give rise to CuO in a few hours. Finally, it is possible to conclude that the stability of Cu(OH)_2 depends on three important factors :

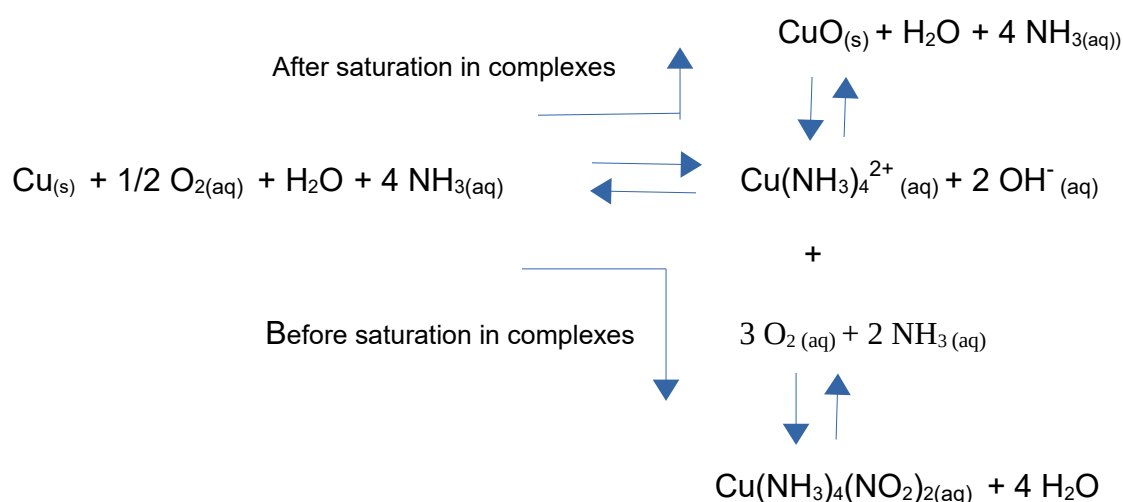
- 1) - Temperature [5],
- 2) - Grain size,
- 3) - Hydroxide ion concentration.

These factors also influence the synthesis of CuO from copper metal in presence of ammonia.

SYNTHESIS OF CuO BY OXIDATION OF COPPER METAL IN AMMONIA

In a previous publication [7], we described a new way of synthesis of hydroxides, in oxidizing the metals by dioxygen in concentrated ammonia. In the case of copper, hydroxide is never obtained but it is always copper(II) oxide because of the basicity of the solution. It should be noted that this result is perfectly consistent with that obtained in the ternary system CuO-Na₂O-H₂O. Consequently, this study leads to an original way of synthesis of CuO.

In addition, another important phenomenon happens. It is the oxidation of ammonia which leads to nitrite ion. This phenomenon was mentioned in very early works [9][10] and its kinetic study was recently published [11][12]. The formation of copper tetraammine nitrite complexes is responsible for the oxidation of ammonia, because of the great stability of these complexes, due to the Jahn-Teller effect, very important in the case of divalent copper. The solubility of copper depends on the ammonia concentration and on the amount of nitrite which is formed during the kinetic process. When the solution is saturated in complexes, oxidation of copper metal continues and the precipitate of CuO appears. A whole sight of these reactions can be summarized in the following scheme:



When all copper metal powder has reacted, CuO is filtered and washed abundantly with water and then dried under partial vacuum in presence of concentrated sulfuric acid at room temperature. Copper oxide appears under the form of a black fine-grained powder. An X-ray pattern obtained on a RIGAKU D-MAX II diffractometer shows that the solid is relatively well crystallized (fig.3c), in spite of the preparation method used. The refined parameters of the monoclinic cell are compared with those of standard CuO:

Present work

$$a(\text{\AA}) = 4.687(5), \quad b(\text{\AA}) = 3.434(4), \quad c(\text{\AA}) = 5.119(5\text{\AA}), \quad \beta^\circ = 99.2(1)$$

Powder Diffraction File

$$a(\text{\AA}) = 4.685 \quad , \quad b(\text{\AA}) = 3.423 \quad , \quad c(\text{\AA}) = 5.132 \quad , \quad \beta^\circ = 99.52 \quad [14]$$

CONCLUSION

The study of the ternary diagram CuO-Na₂O-H₂O , allows to conclude that copper hydroxide cannot exist in equilibrium with saturated solutions; the reason being that copper oxide alone, is stable. In fact, Cu(OH)₂, is more soluble than CuO in pure water, and the ratio between solubilities is near 100. The solubility product of copper hydroxide, given in literature is approximately 10⁻²⁰ . We think that this value is wrong. Chemical analyses, performed on a pure copper hydroxide, are convenient with a value near 10⁻¹⁵ . On other hand the value 10⁻²⁰ would rather correspond to the solubility product of CuO. Before our works, it was not possible to prepare pure Cu(OH)₂. The solubility product of Cu(OH)₂, has probably been determined with the saturated solutions obtained from copper salt solutions in presence of hydroxide ions. In these conditions, another equilibrium gives rise to the complex ion Cu(OH)₄²⁻ . The consequence is lower values for free copper(II) ion and hydroxide ion, concentrations.

Synthesis of pure Cu(OH)₂ becomes possible with a fast hydrolysis of Na₂Cu(OH)₄. A quick elimination of OH⁻ ions permits to stabilize the hydroxide, which otherwise, slowly turns into CuO.

Synthesis of CuO from copper metal by oxidation in concentrated ammonia is an interesting way for the preparation of a pure copper oxide at room temperature. It is worth remembering that the usual method for the preparation of pure CuO requires high temperature in order to obtain the thermal decomposition of hydroxysalts.

REFERENCES

- [1] G.NATTA, Gazz. Chim. Ital., 1928, **58**, p.344.
- [2] R.FRICKE and J.KUBACH, Z. Electrochem., 1949, **53**, p.76.
- [3] H.JAGGI and H.R.OSWALD, Acta Cryst., 1961, **4**, p.1041.
- [4] J.D.GRICE and E.GASPARINI, Can.Minéral., 1981, **19**, p.337.
- [5] P.PASCAL, Nouveau traité de chimie minérale, MASSON éditeurs , 1957, **t.III**, p.229.
- [6] Y.CUDENNEC, A.LECERF, A.RIOU and A.GERAULT, Eur.J.Solid State Inorg. Chem., 1988, **25**, p.351.
- [7] A.LECERF and Y.CUDENNEC, Mater.Res.Bull., 1994, **29**, p.1255.
- [8] A.RIOU, Y.CUDENNEC and Y.GERAULT, Acta Cryst., 1989, **C45**, p.374.
- [9] PELIGOT, C.R.Acad.Sci.Paris, 1861, **53**, p.209.
- [10] H.BASSETT and R.G.DURRANT, J.Chem.Soc., 1922, p.2630.
- [11] Y.CUDENNEC, A.RIOU, K.ROCHDI, Y.GERAULT and A.LECERF, Eur.J.Solid State Inorg.Chem.,1993, **30**, p.77.
- [12] Y.CUDENNEC, N.LELOUS and A.LECERF, C.R.Acad.Sci.Paris, 1995, **320IIb**, p.309.
- [13] H.R.OSWALD, A.RELLER, H.W.SCHMALLE and E.DUBLER, Acta Cryst., 1990, **C46**, p.2279.
- [14] Standard CuO , P.D.F N° 41-254.

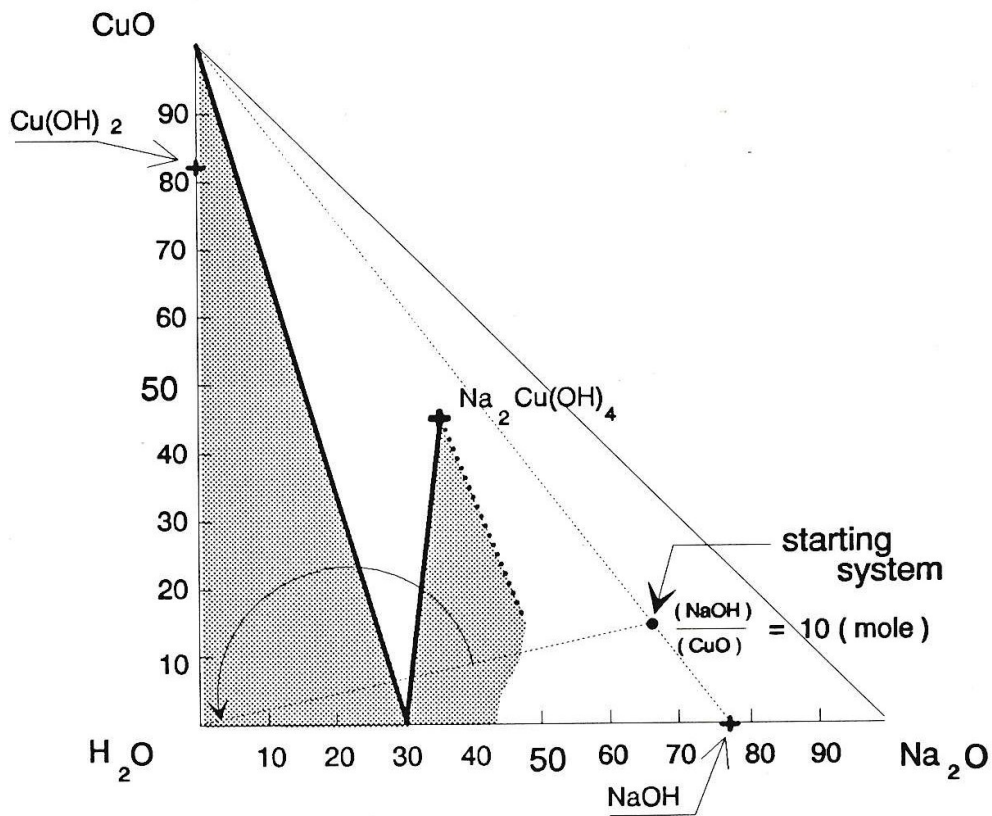


Fig. 1 - Ternary diagram : CuO , Na_2O , H_2O (weight %)

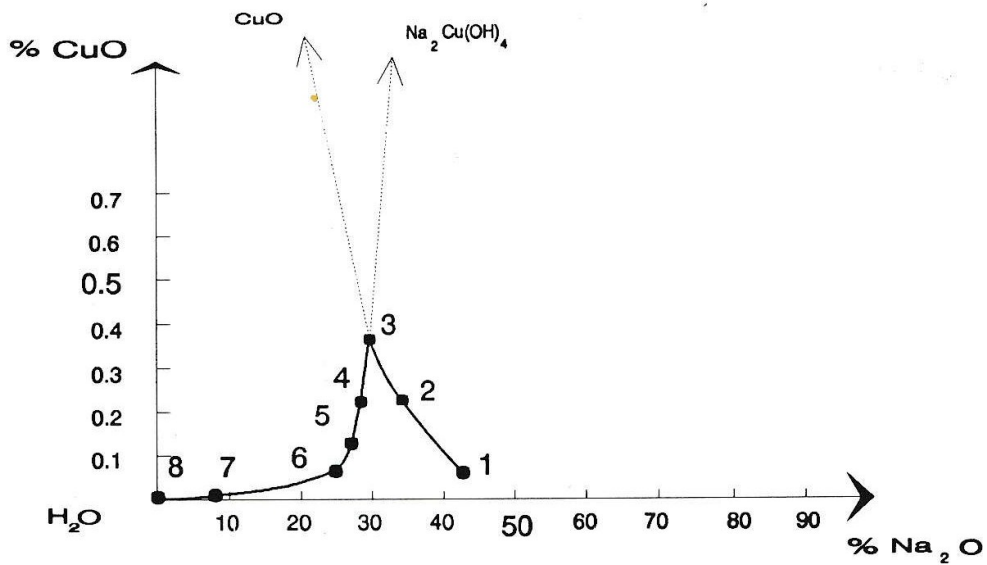


Fig. 2 - Ternary diagram : Solubility curves (weight %)

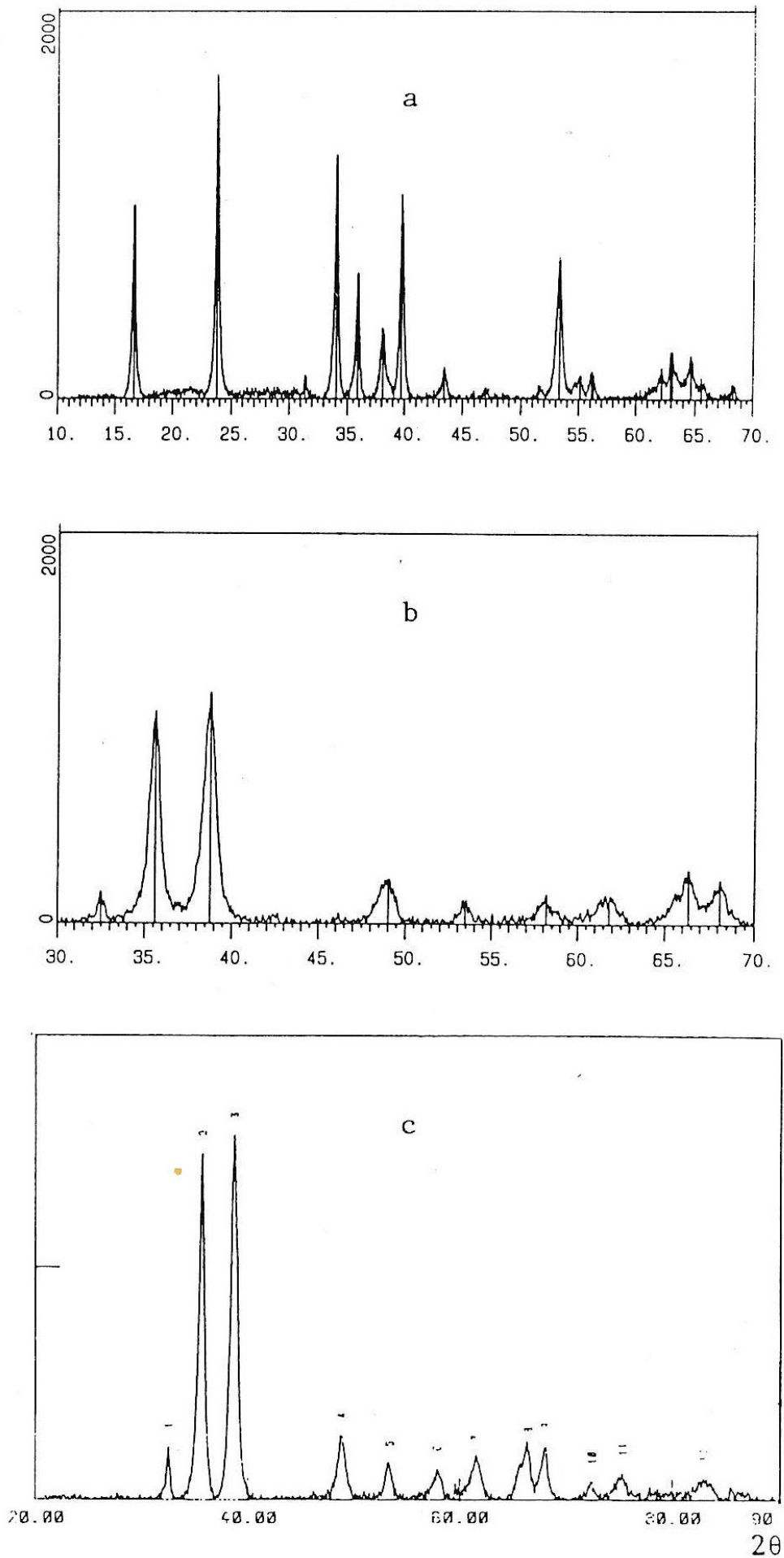


Fig. 3- X-ray powder patterns

- a) $\text{Cu}(\text{OH})_2(\text{s})$ from $\text{Na}_2\text{Cu}(\text{OH})_4$
- b) $\text{CuO}(\text{s})$ from $\text{Na}_2\text{Cu}(\text{OH})_4$
- c) $\text{CuO}(\text{s})$ from copper metal

