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# THERMAL DECOMPOSITION OF BASIC COPPER SULPHATE MONOHYDRATE

*I. Uzunov, D. Klissurski and L. Teocharov*

Institute of General and Inorganic Chemistry, Bulg. Acad. of Sciences, Sofia 1040, Bulgaria

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## Abstract

The thermal decomposition of copper sulphate hydroxide hydrate, $(CuO\cdot CuSO_4)\cdot 2Cu(OH)_2\cdot H_2O$, to copper oxysulphate and CuO was investigated by X-ray phase analysis, IR spectroscopy, complex thermal analysis and electron microscopy.

The effect of water vapour and time of treatment on the formation of decomposition products with a large surface area is studied.

The strong decrease in specific surface area of the precipitate (from 80 $m^2/g$ to 20 $m^2/g$) thermally treated at a temperature above 250°C is associated with the elimination of water having a coordination bond with the $Cu^{2+}$ ion. During this process, the interplanar distances of the crystal lattice of copper sulphate hydroxide hydrate decrease. The time of decomposition of this compound essentially affects the decrease of the specific surface area.

When the decomposition proceeds in an atmosphere containing water vapour sintering processes are predominating and the phase obtained has a considerably smaller specific surface area than in cases of decomposition under dry air.

**Keywords**: copper hydroxide hydrate, copper oxysulphate, mechanism of decomposition, thermal decomposition

## Introduction

Copper(II) hydroxide is a suitable initial compound for the preparation of high-dispersity copper(II) oxide. Precipitation of $Cu(OH)_2$ with NaOH solution from copper salt solutions is used very often for obtaining $Cu(OH)_2$.

When the excess of the precipitant is not sufficient, basic salts with a constant composition of the type $CuA\cdot Cu(OH)_2$ (where $A = SO_4^{2-}$, $NO_3^-$ and $Cl^-$) may be formed during the preparation.

For this reason it is of interest to study the thermal behaviour of this class of compounds.

In the present paper basic copper sulphate-monohydrate is dealt with.

The data available in the literature concern mainly the ways of preparation of a basic salt with a definite composition [1–7]. Investigations associated with the

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elucidation of the structure and bonds in the so-called basic sulphates of the types nMeO·mMeSO$_4$ and pMeSO$_4$·qMe(OH)$_2$ have been published [8–11].

The present paper deals with the thermal decomposition of basic copper sulphate from a different viewpoint. New information not only on the thermal behaviour of the compound but also on the texture and dispersity of the initial compound and decomposition products is obtained.

The formation of intermediate phases and the changes in texture of the samples after thermal decomposition have been investigated by X-ray phase analysis, IR spectroscopy, thermal analysis and electron microscopy.

The results obtained confirm the decomposition mechanism of basic copper sulphate hydroxide hydrate proposed by most of the authors and add new data on the phase formation within different temperature ranges that correlate with the dispersity of the decomposition products.

In this connection, an investigation has been carried out in order to establish the effect of temperature, time and atmosphere on the specific surface area of the decomposition products.

## Experimental

Basic copper sulphate hydroxide hydrate was prepared by the precipitation method described in the literature using a NaOH:CuSO$_4$ ratio of 1.5:1 and $pH = 4$, which ensures the formation of a compound with the desired composition [8, 12–14]. The precipitate was dried at 80°C in air.

The phase composition of the samples was determined by X-ray phase analysis with K$_\alpha$Cu radiation. The IR spectra were obtained in a KBr pellet within the range 400–4000 cm$^{-1}$. Thermal analysis was performed at a heating rate of 10 deg·min$^{-1}$ in air, using a platinum crucible. The electron micrographs were taken with transmission and scanning using different magnifications.

Basic copper sulphate monohydrate was heated for 3 h at 250, 450, 500 and 800°C, respectively.

The specific surface area of the samples obtained at different temperatures was determined by the B.E.T. Method.

The decomposition of the samples in dry and humid air was performed using an outlet as flow of 7.2 l/h and a partial pressure of 2.33 kPa.

## Results and discussion

After washing and drying, the blue-green precipitate was subjected to complex thermal analysis (TG, DTA and DTG). The TA curves are given in Fig. 1.

The DTA curve shows a broad and well expressed endothermic effect with a maximum at 410°C, a strong endothermic effect at 655°C and a narrow exothermic effect beginning at 485°C.

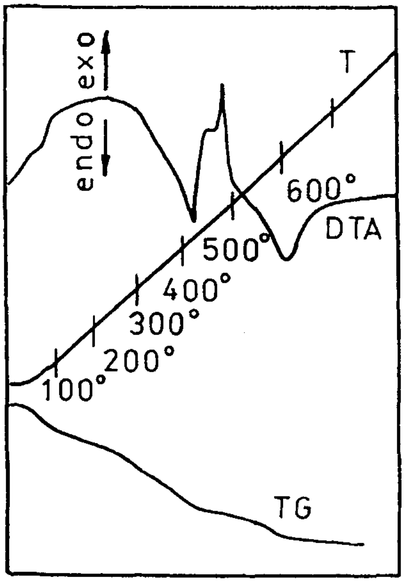


**Fig. 1** Complex thermal analysis (TG, DTG and DTA) of basic copper sulphate monohydrate

X-ray phase analysis has shown that the phase composition of the precipitate corresponds to basic copper sulphate monohydrate, $CuO{\cdot}CuSO_4{\cdot}2Cu(OH)_2{\cdot}H_2O$ (Fig. 2) [8, 15]. This means that the first endothermic effect concerns the decomposition of $Cu(OH)_2$ from the double compound. This temperature is much higher than the dehydration temperature of copper(II) hydroxide and of $Cu(OH)_2{\cdot}H_2O$.

If we accept the decomposition mechanism of basic copper sulphate monohydrate proposed by Margulis [8], i.e.:

$$CuO{\cdot}CuSO_4{\cdot}2Cu(OH)_2{\cdot}H_2O = (CuO{\cdot}CuSO_4){\cdot}2Cu(OH)_2 + H_2O \tag{a}$$

$$(CuO{\cdot}CuSO_4){\cdot}2Cu(OH)_2 = CuO{\cdot}CuSO_4 + 2CuO + H_2O \tag{b}$$

$$CuO{\cdot}CuSO_4 = 2CuO + SO_3 \tag{c}$$

then, the second endothermic effect is associated with the decomposition of copper oxysulphate.

The exothermic effect at 485°C is ascribed to the crystallization of the new phases of $CuO{\cdot}CuSO_4$ and CuO.

These facts are also confirmed by X-ray data obtained for samples decomposed at temperatures within the region of the exothermic effect.

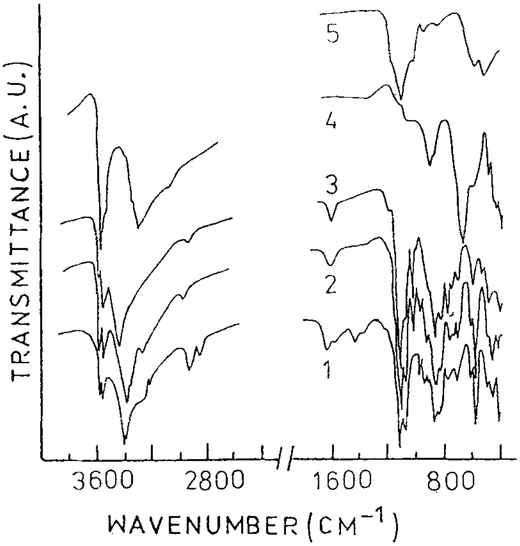


**Fig. 2** IR spectra: (1) initial sample, and samples heated at (2) 250°C, (3) 450°C, (4) 500°C and (5) 800°C

The TG data confirm the composition of the initial compound. The complete decomposition to copper(II) oxide is accompanied by a weight loss of about 20 wt% (theoretical value 21 wt%). In addition, the shape of the TG curve indicates that the water of crystallization is evolved within a wide temperature interval, reaching a temperature above 500°C. This means that the water formed is tightly bound to the crystal lattice of the compound by a coordination and/or hydrogen bond. In the literature this type of water is determined as zeolite water [16, 17].

These peculiarities of the dehydration process may be connected with high temperature hydrolysis with further water loss [18–20].

The changes occurring during the thermal decomposition of basic copper sulphate monohydrate have been studied on samples heated isothermally at preset temperatures.

Figure 2 shows the IR spectra of different samples.

The absorption spectrum of the initial sample confirms the composition of the basic copper sulphate monohydrate [7, 21, 22]. According to the X-ray analysis, the structure of the initial compound is similar to the structure of brochanite, i.e. it is monoclinic.

The characteristic frequencies of copper hydroxy sulphate in the IR absorption region will depend on the OH and $SO_4$ groups.

The stretching modes of the OH groups are shifted to 3200–3600 cm$^{-1}$. This depends on the bond of the group with the rest of the molecule. The presence of three types of hydroxy bridges in the initial compound is confirmed by the stretching modes at 3560 and 3587 cm$^{-1}$ and the bending modes at 727 and 780 cm$^{-1}$ which correspond to $O_5H$ and $O_6H$ groups, not involved in the formation of hydrogen bonds. The existence of a relatively strong hydrogen bond is confirmed by the absorption at 3267 and 940 cm$^{-1}$. The absorption at 3393 cm$^{-1}$, which corresponds to the stretching modes, and the absorption at 873 cm$^{-1}$, associated with bending modes, confirm the presence of a third type of hydrogen bond which is not especially strong [10].

The availability of a zeolite type of water in the initial compound determines the absorption at 1653 and 1453 cm$^{-1}$ which is related to the bending modes of the H–O–H bond [16, 17].

**Table 1** Characteristic infrared adsorption band frequencies

| Assignment | Frequency/cm$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | Initial compound | 250°C | 450°C | 500°C | 800°C |
| $\nu_{OH}$ | 3587 | 3600 | 3580 | 3580 | |
| | 3560 | 3575 | 3500 | 3500 | |
| | 3393 | 3400 | | 3430 | |
| | 3267 | 3310 | | | |
| $\delta_{OH}$ | 940 | 950 | 890 | 890 | |
| | 873 | 885 | 860 | 860 | |
| | 780 | 860 | 800 | 805 | |
| | 727 | 790 | 765 | 765 | |
| | | 740 | | | |
| $\delta_{OH}^*$ | 1653 | 1650 | 1640 | 1640 | |
| $SO_4$ | 1113 | 1135 | 1210 | 1220 | 1200 |
| $\nu_3$ | 1087 | 1095 | 1160 | 1160 | 1145 |
| | | 1045 | 1125 | 1120 | 1110 |
| | | | 1080 | 1085 | |
| | | | 1050 | | |
| $\nu_1$ | 983 | 995 | 1010 | 1000 | 950 |
| $\nu_4$ | 640 | 685 | 645 | 645 | 595 |
| | 600 | 610 | 588 | 585 | |
| $\nu_2{\cdot}\nu_{Cu-O}$ | 567 | 510 | 525 | 535 | 540 |
| | 500 | 490 | 445 | 495 | 460 |
| | 467 | 420 | | 470 | |
| | | | | 430 | |

$\delta^*$ – zeolitic water, [16, 17]

The absorption at 400–500 $cm^{-1}$ is associated with the stretching modes of the Cu–O bond.

Forming bonds with the $Cu(OH)_4O_2$ and $Cu(OH)_5O$ groups, the sulphate ion participates in the formation of the crystal unit cell of basic copper sulphate [10].

Hence, the vibration spectrum of $SO_4$ would also depend on the crystal surroundings. The coordination of the multiatomic ligand to Cu and its interaction with OH will cause a decrease of symmetry. This determines the multiplet structure of the bands reflecting absorption by $SO_4$ [23, 24].

The characteristic IR frequencies the $SO_4$ ion and the behaviour of these frequencies are presented in Table 1.

The multiplet absorption bands and the stretching mode $\nu_1$ indicate that in basic copper sulphate monohydrate the $[SO_4]^{2-}$ ligand has a monodentate bonding with the $Cu^{2+}$ ion (symmetry $C_{3v}$) [23].

After heating the basic copper sulphate monohydrate at 250°C, part of the crystallization water is evolved (Fig. 1). The IR spectrum reveals the change in coordination of $[SO_4]^{2-}$ from monodentate to bidentate. The absorption at 600, 640, 995, 1045, 1095 and 1135 $cm^{-1}$ is attributed to stretching modes of $C_{2v}$ position symmetry for $[SO_4]^{2-}$. The main bands that correspond to the Cu–O–H bond are preserved.

With rising temperature of decomposition, the coordination of $[SO_4]^{2-}$ becomes lower than $C_{2v}$. The coordination is determined by the $Cu_3O_2SO_4$ structure which contains a copper oxysulphate anion, $[(CuO)_2SO_4]^{2-}$ and by the molecularly dispersed free CuO [11].

Characteristic bands of this coordination are observed with samples heated at 450 and 500°C, respectively (Fig. 2). The sample obtained at 450°C still exhibits bands that correspond to a bidentate coordination of the sulphate ion.

In samples heated up to 500°C, the bands for $[OH]^{1-}$ not participating in the formation of hydroxy bridges, are preserved. This confirms the coordination binding of part of the water in the complex compound basic copper sulphate monohydrate.

Complete removal of the water of crystallization and decomposition of the hydroxide are observed only at 800°C. The IR spectrum of the same sample still contains the bands characteristic of the stretching modes of the oxysulphate anion. The remaining bands in the spectrum correspond to the Cu–O bond.

The mechanism of thermal decomposition of basic copper sulphate monohydrate can also be studied on the basis of X-ray data (Fig. 3).

The decomposition process was also investigated by the determination of the specific surface area of the solid decomposition products at different temperatures (Fig. 4).

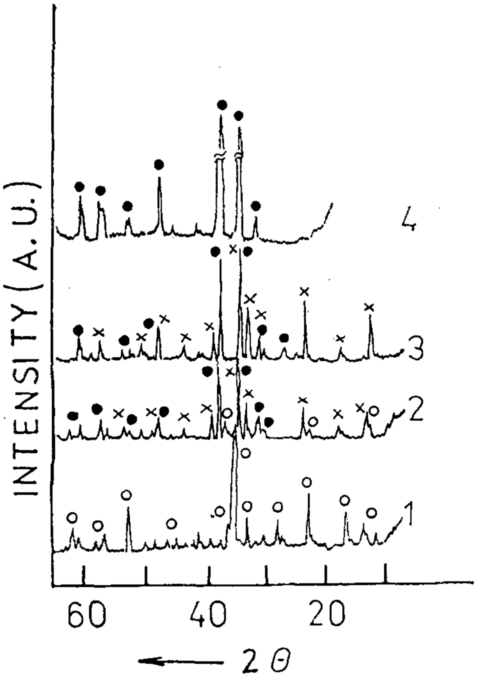


**Fig. 3** X-ray phase analysis: (1) initial sample, and samples heated at (2) 450°C, (3) 500°C and (4) 800°C

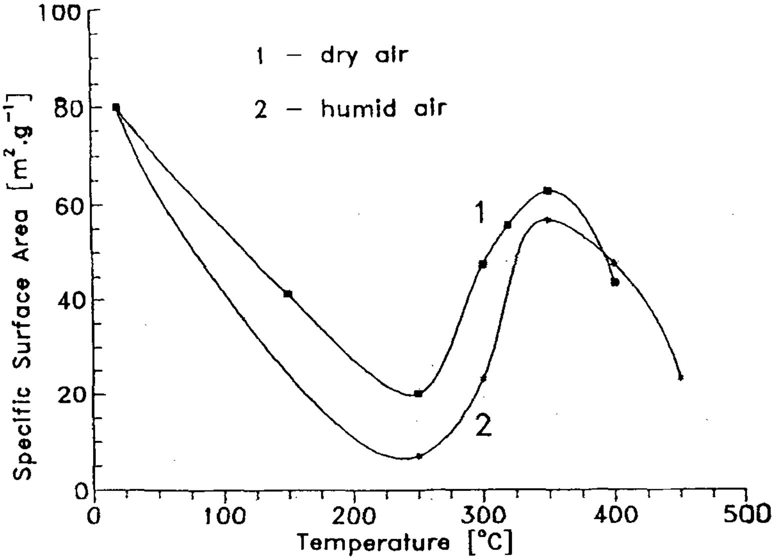


**Fig. 4** Dependence of the specific surface area on the decomposition on temperature

The decomposition was carried out in dry air and in air saturated with water vapour. Both curves show similar changes in the specific surface area for the same time. The strong decrease of the surface area at temperatures up to 250°C is attributed to low-temperature sintering. The gradual separation of the coordinatively bound water favours the sintering, this effect becoming stronger in the presence of water vapour. The decomposition of the hydroxide part of the complex at 350°C is associated with a fragmentation of the solid phase, i.e. with an increase of the specific surface area. Up to this temperature the amorphous character of the solid phase prevails. Recrystallization processes leading to additional decrease of the specific surface area occur above 400°C.

Figure 5 shows the effect of the time of decomposition on the specific surface area of the products. The same character of the curves depending on the atmosphere of decomposition is preserved.

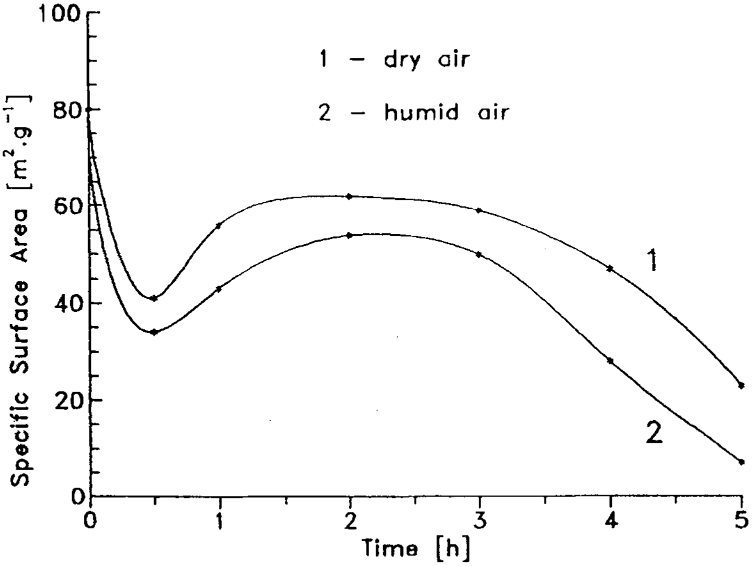
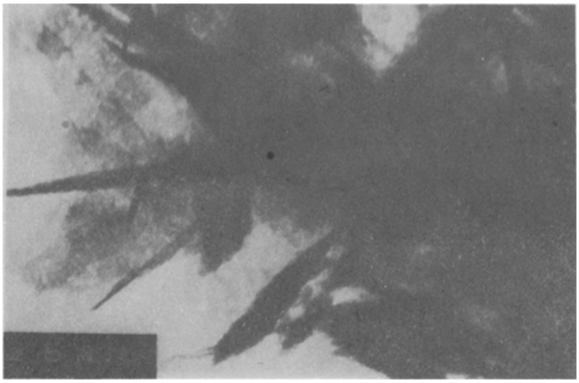


**Fig. 5** Dependence of the specific surface area on the duration of decomposition at 350°C

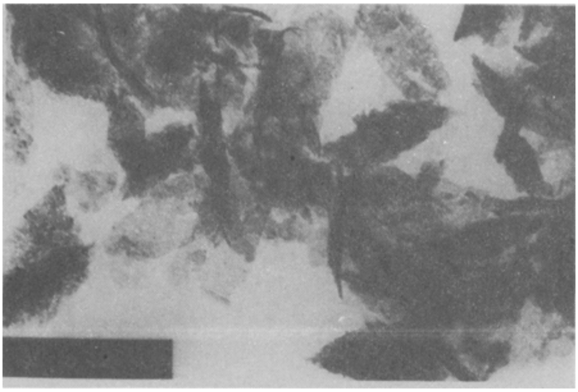
The change in texture of the basic copper sulphate hydroxyhydrate after heating was studied by electron microscopy.

The photographs of the initial sample show the needles of the complex compound. After heating at 250°C, crystals in the shape of irregular plates appear. The growth of separate crystals up to 320°C is due to low-temperature sintering. The sample heated up to 450°C clearly shows the fragmentation of the solid-phase products of decomposition. The decomposition of the sulphate part of the complex and the high-temperature sintering of copper(II) oxide can also be seen in the last photograph.

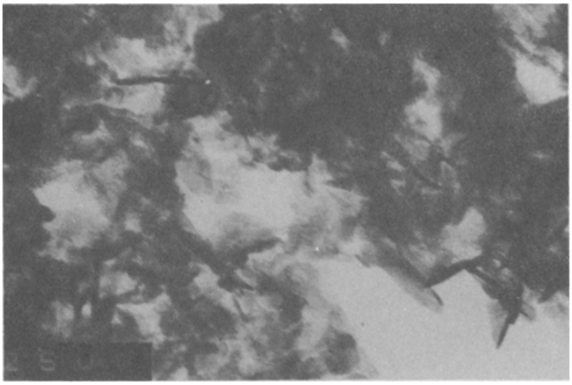
**Photograph 1** Initial sample; transmission; electron microscope magnification × 40 000



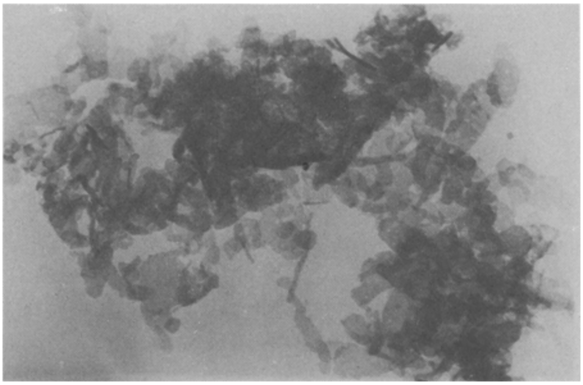
**Photograph 2** Initial sample; transmission; electron microscope magnification × 50 000



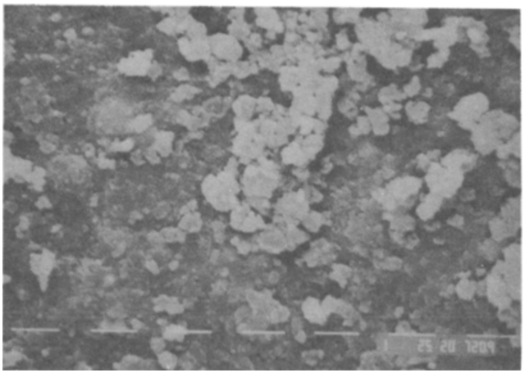
**Photograph 3** Heating at 250°C; transmission; electron microscope magnification × 40 000



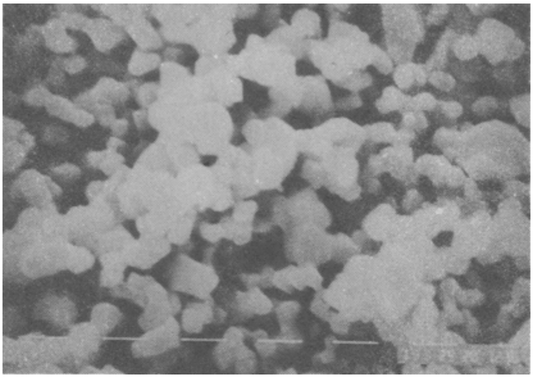
**Photograph 4** heating at 320°C; transmission; electron microscope magnification × 50 000



**Photograph 5** Heating at 450°C; transmission; electron microscope magnification × 50 000



**Photograph 6** Heating at 450°C; scanning; electron microscope magnification × 10 000



**Photograph 7** Heating at 800°C; scanning; electron microscope magnification × 10 000

## Conclusions

The methods of X-ray phase analysis, IR spectroscopy, thermal analysis and electron microscopy are used to investigate the thermal decomposition of basic copper sulphate monohydrate.

The stepwise mechanism of decomposition of the complex compound $CuO{\cdot}CuSO_4{\cdot}2Cu(OH)_2{\cdot}H_2O$ has been confirmed.

The IR data have shown that the water of crystallization is bonded coordinatively to the lattice of the compound and is eliminated above 500°C. This favours the process of low-temperature sintering of the solid decomposition products. The decomposition in an atmosphere of water vapour also leads to sintering of the products.

The evolution of the water of crystallization changes the coordination of the $[SO_4]^{2-}$ ion from bidentate to monodentate and to a simpler symmetry.

It has been established that the changes in phase composition of the solid decomposition products are associated with alteration of their texture and specific surface area.

## References

1 J. W. Mellor, Comprehensive Treatise Inorg. Theor. Chem., 3 (1956) 261.
2 A. S. Tikhonov, N. K. Vitchenko, O. D. Talalaeva and P. Y. Yakshova, (Russ.), Zh. Neorg. Khim., 2 (1957) 2197.
3 V. L. Heifets and A. L. Rotinyan, (Russ.), Zh. Obshchei Khim., 24 (1954) 930.
4 A. K. Kirakosyan and A. V. Stogova, (Russ.), Zh. Neorg. Khim., 5 (1960) 2088.
5 E. Posnjak and E. Tunell, Amer. J. Sci., 18 (1929) 1.
6 J. Gauthier, Bull. Soc. Chim. France, (1956) 661.
7 H. Tanaka, M. Kawano and N. Koga, Thermochim. Acta, 182 (1991) 281.

8 E. V. Margulis, (Russ.), Zh. Neorg. Khim., 7 (1962) 1811.
9 P. Ramamurthy and E. A. Secco, Can. J. Chem., 48 (1970) 3510.
10 E. A. Secco, Can. J. Chem., 66 (1988) 329.
11 E. A. Secco, Can. J. Chem., 66 (1988) 337.
12 E. V. Margulis, L. I. Beisekeeva, E. D. Maletina and N. I. Kopilov, (Russ.), Zh. Neorg. Khim., 10 (1965) 972.
13 L. Markov, Kh. Dobrev and R. Ioncheva, (Russ.), Zh. Neorg. Khim., 32 (1987) 688.
14 H. Tanaka and N. Koga, J. Chem. Educ., 67 (1990) 612.
15 JCPDS Powder Diffraction File (1979).
16 L. Bertsch and H. W. Habgood, J. Phys. Chem., 67 (1963) 1621.
17 J. L. Carter, P. J. Lucchesi and D. J. Yates, J. Phys. Chem., 68 (1964) 1385.
18 V. N. Makatun, Chemistry of Inorg. Hydrates, Nauka i technika, Minsk 1985 (Russ.).
19 V. A. Logvinenko, Thermal Anal. of Coord. Compounds and Clathrates, (Russ.), Ed. 'Nauka', Novosibirsk 1982.
20 V. A. Logvinenko, F. Paulik and J. Paulik, Quasi-equilibrium Thermogravimetry, Nauka, Novosibirsk 1989 (Russ.).
21 H. Jaggy and H. R. Oswald, Acta Cristallogr., 14 (1961) 1041.
22 V. V. Pechkovskii and M. S. Gaisinovich, (Russ.), Zh. Neorg. Khim., 9 (1964) 2299.
23 G. Nikolov, Structure and Properties of Coordination Compounds, Nauka i Izkustvo, Sofia 1977.
24 K. Nakamoto, IR Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, N. Y., 1962.

**Zusammenfassung** — Mittels Röntgenphasenanalyse, IR-Spektroskopie, komplexer Thermoanalyse und Elektronenmikroskopie wurde die thermische Zersetzung von Kupfersulfat-hydroxidhydrat $(CuOCuSO_4)\cdot 2Cu(OH)_2\cdot H_2O$ zu Kupferoxysulfat und CuO untersucht.

Der Einfluß von Wasserdampf und Behandlungszeit auf die Bildung der Zersetzungsprodukte mit großer Oberfläche wurde untersucht.

Die starke Abnahme der spezifischen Oberfläche von Präzipitaten (von 80 $m^2/g$ auf 20 $m^2/g$), die bei einer Temperatur oberhalb 250°C thermisch behandelt wurden, ist mit der Abspaltung von Wasser verbunden, die am $Cu^{2+}$-Ion koordinativ gebunden sind. Bei diesem Vorgang nimmt der interplanare Abstand des Kristallgitters von Kupfersulfat-hydroxidhydrat ab. Die Zeit für die Zersetzung dieser Verbindung nimmt wesentlichen Einfluß auf die Abnahme der spezifischen Oberfläche.

Erfolgt die Zersetzung in einer wasserdampfhaltigen Atmosphäre, dominieren Schrumpfungsprozesse und die erhaltene Phase hat eine eindeutig geringere spezifische Oberfläche als bei der Zersetzung in trockener Luft.