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# PREPARATION AND THERMAL DECOMPOSITION OF BASIC COPPER(Ⅱ) SULFATES

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## ABSTRACT

The compositions and thermal behavior of basic copper(Ⅱ) sulfates, which were prepared by adding sodium hydroxide to copper(Ⅱ) sulfate in solutions, were examined extensively by means of chemical analysis, IR spectroscopy, X-ray diffractometry, and thermal analysis.

Synthetic brochantite and posnjakite were obtained by the methods used in the present study. The thermal decomposition processes of the compounds prepared to $Cu_2O$ were characterized by TG and DSC or DTA, as well as other physicochemical techniques.

## INTRODUCTION

It is well known that the bluish or bluish-green white precipitates obtained by adding hydroxide solution to copper(Ⅱ) sulfate solution are not simply copper(Ⅱ) hydroxide but basic copper(Ⅱ) sulfate[1]. The composition of the basic copper(Ⅱ) sulfate precipitated from solutions varies among different workers. Various precipitates with difference in composition results from solution depending on the preparation condition, that is, the concentration of solution mixed, rate of the mixing, pH of the solution, temperature and so on[2-7]. Reported thermal behaviors of these precipitates are also contradictory and not always reproducible[2-7].

It was felt that some additional work should be undertaken to clarify the composition, the crystal structure, and thermal behavior of the title compounds. Accordingly, chemical analysis, as well as IR spectroscopy and X-ray diffraction measurements were made on basic copper(Ⅱ) sulfates obtained under various conditions. TG and DSC(or DTA for high temperatures) were recorded simultaneously for the thermal decomposition of the basic copper(Ⅱ) sulfates. The results of the thermal analysis were proved by chemical and IR spectroscopic analyses of the intermediate compounds.

## EXPERIMENTAL

Precipitates of basic copper(Ⅱ) sulfates were obtained at various temperatures by adding an NaOH solution dropwise at a rate of ca. 1.0 ml $min^{-1}$ with stirring to 100 ml of $CuSO_4$ solution until the pH of the resulting solution was equal to 8.0. The effect of the concentration of the reactant solutions on the precipitates was examined.

The precipitates, dried in air and ground in a mortar, were characterized

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by means of IR spectroscopy and X-ray diffractometry using a Hitachi Spectrophotometer(EPI-G2) and a Rigaku diffractometer Miniflex, respectively.

About 20.0 mg of the samples were weighed into a platinum crucible of 5 mm in diameter and 2.5 mm in depth. TG-DSC (or TG-DTA) traces were recorded simultaneously at a heating rate of ca. 10 ℃ $min^{-1}$ in a flow of $N_2$ at a rate of 30 ml $min^{-1}$, using a Rigaku Thermoflex TG-DSC(8085E1) and TG-DTA(8076E1) apparatus. Ignited $Al_2O_3$ was used as reference material.

Determination of copper(II) and sulfate ions of the initial and intermediate compounds were made by iodometry using a standard solution of $Na_2S_2O_3$ and gravimetry as $BaSO_4$, respectively, after dissolving the sample in a dilute nitric acid.

## RESULTS AND DISCUSSION

The chemical analysis of the various synthetic basic copper(II) sulfates are given in Table 1, together with two kinds of X-ray diffraction patterns, A and B. The patterns A and B correspond to the minerals brochantite, $CuSO_4 \cdot 3Cu(OH)_2$ and posnjakite, $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$, respectively[2,5,6]. We see from Table 1 that the data of chemical analysis of copper(II) and sulfate ions correspond with the calculated values for the compositions of the two minerals. We also see that synthetic posnjakite precipitates from dilute solution at a lower temperature(5 ℃), whereas synthetic brochantite is obtained

TABLE 1
Determination of copper(II) and sulfate ions in the basic copper(II) sulfates precipitated under various conditions, and identification of the minerals brochantite and posnjakite by means of X-ray diffractometry

| Concentration of solutions, M | | Temp., | Weight % | | X-ray diffraction |
|---|---|---|---|---|---|
| $CuSO_4$ | NaOH | ℃ | Cu | $SO_4$ | pattern*1 |
| 1.00 | 1.00 | 5 | 55.61±0.53 | 23.27±0.07 | A |
| 1.00 | 1.00 | 25 | 55.03±0.35 | 21.75±0.56 | A |
| 1.00 | 1.00 | 50 | 56.24±0.28 | 21.65±0.31 | A |
| 0.10 | 0.20 | 5 | 56.00±0.16 | 22.73±0.05 | A |
| 0.10 | 0.20 | 25 | 57.28±0.23 | 21.28±0.07 | A |
| 0.10 | 0.20 | 50 | 56.39±0.36 | 21.37±0.09 | A |
| 0.01 | 0.02 | 5 | 53.80±0.48 | 20.49±0.32 | B |
| 0.01 | 0.02 | 50 | 55.57±0.18 | 21.85±0.24 | A |
| brochantite | | | 56.21*2 | 21.24*2 | A |
| posnjakite | | | 54.06*2 | 20.48*2 | B |

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*1 The patterns for brochantite and posnjakite are labeled as A and B, respectively.

*2 The calculated.

at higher temperatures. It was reported that the precipitate obtained by adding ca. 0.1 M NaOH solution to ca. 0.01 M $CuSO_4$ solution corresponds in composition to brochantite and posnjakite at higher and lower temperatures, respectively, than ca. 20 ℃[5]. In the present study, a distinct boundary temperature could not be specified. However, the precipitates obtained by adding 0.01 M NaOH solution to 0.01 M $CuSO_4$ solution in the temperature range 15-20 ℃ showed broad peaks in the X-ray diffraction pattern. This might be due to the mixing of two kinds of basic copper(II) sulfates such as brochantite and posnjakite.

Figures 1 and 2 show typical TG-DSC (or DTA at high temperatures) traces recorded simultaneously for the thermal decompositions of synthetic brochantite and posnjakite, respectively. Table 2 shows the chemical analysis of the stable intermediate products $A_3$, $A_5$, $B_4$, and $B_8$, labeled in Figs. 1 and 2. IR spectra of the initial and intermediate compouns are shown in Fig. 3. IR spectra of the initial compounds, $A_1$ and $B_1$, are also in good agreement with those of brochantite and posnjakite, respectively[5,7,8].

We can assume, for the thermal decompsition of synthetic brochantite, that the DSC peaks (a) and (b) are associated with the dehydroxylation, since the compound $A_3$ gives no OH bands in the IR spectrum and the weight percent of copper(II) and sulfate ions in the sample corresponds to that of $CuSO_4 \cdot 3CuO$. The mass-loss at this decompositon stage is listed in Table 3. This is also in agreement with the calculated values for the dehydroxylation of brochantite. According to the TG trace which was recorded simultaneously with the DSC, the two-step decomposition (see DSC peaks (a) and (b) in Fig. 1) may be described by the following reactions;

$$CuSO_4 \cdot 3Cu(OH)_2 \longrightarrow CuO \cdot CuSO_4 \cdot 2Cu(OH)_2 \longrightarrow CuO \cdot CuSO_4 + 2CuO,$$

which is in accordance with Margulis[2] and Ramamurthy and Secco[4]. It seems, however, that the intermediate compound $CuO \cdot CuSO_4 \cdot 2Cu(OH)_2$ was not isolated, at least in the present study, because it is not stable. It is intersting to

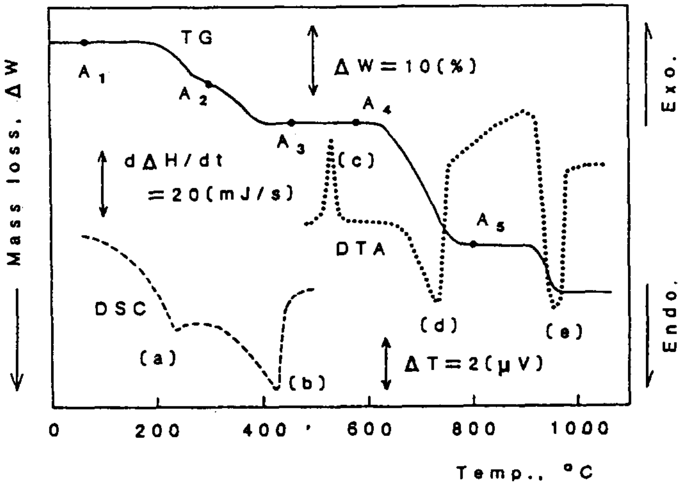

Fig. 1. Simultaneous TG-DSC(DTA) traces for the thermal decomposition of synthetic brochantite.

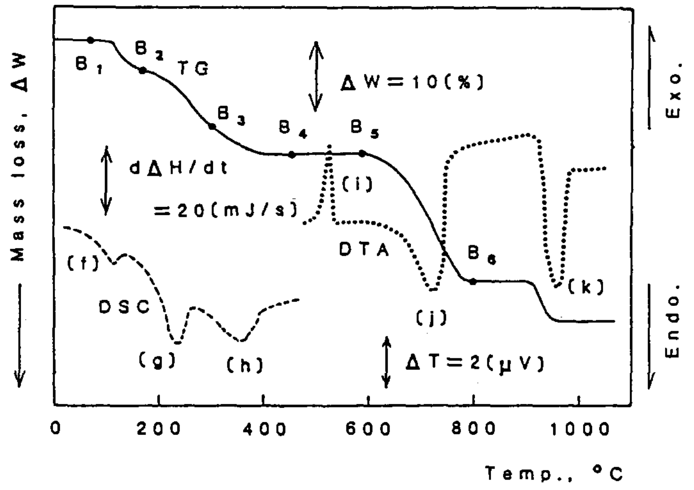

Fig. 2. Simultaneous TG-DSC(DTA) traces for the thermal decomposition of synthetic posnjakite.

TABLE 2
Determination of copper(II) and sulfate ions in intermediate compounds in the thermal decompositions of the synthetic brochantite and posnjakite

| Compound*[1] | Weight % | |
|---|---|---|
| | Cu | $SO_4$ |
| $A_3$ | 61.86±0.49 | 24.49±0.38 |
| $A_5$ | 79.72±0.59 | |
| $B_4$ | 64.19±0.34 | 24.12±0.09 |
| $B_8$ | 80.70±0.10 | |
| $CuSO_4 \cdot 3CuO$ | 63.84*[2] | 24.12*[2] |
| CuO | 79.90*[2] | |

*1 See Figs. 1 and 2.
*2 The calculated.

note that one of the absorption bands between 3550-3600 $cm^{-1}$ in the IR spectra of the compound $A_1$ disappears in those of the compound $A_2$. It is likely that the compound $A_3$ (also $A_4$) is a mixture of $CuSO_4 \cdot CuO$ and CuO in a mole ratio of 1:2 and the exothermic peak (c) is attributable to the crystallization of these compounds as reported earlier[3,4].

The endothermic peak (d) is ascribed to the removal of $SO_3$, as confirmed by chemical analysis and mass loss data (see Tables 2 and 3, respectively). The IR spectrum of compound $A_5$ does not exhibit any absorption band due to $SO_4$. The compound $A_5$ is obviously copper(II) oxide. It is clear that the endothermic peak (e) is due to the reduction of CuO into $Cu_2O$( see Table 3 ).

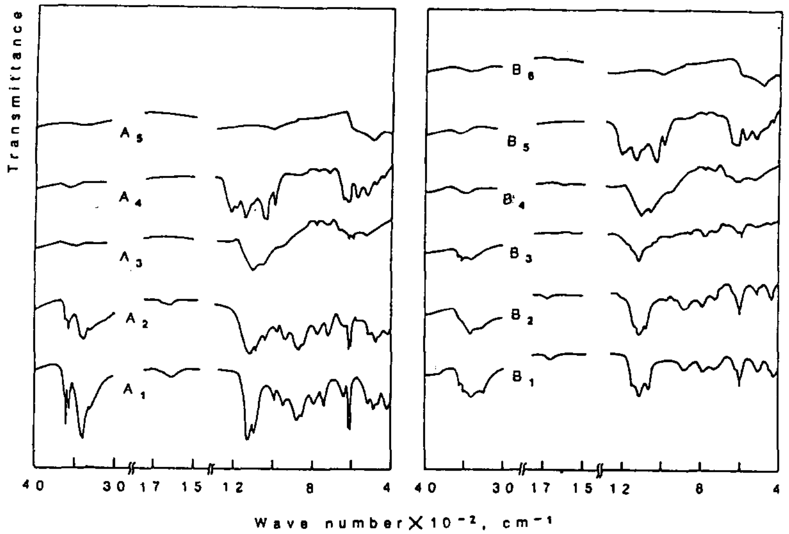

Fig. 3. IR spectra of synthetic brochantite and posnjakite and their intermediate compounds obtained from their thermal decompositions.

TABLE 3
The mass loss due to the successive decomposition of synthetic brochantite by means of TG

| Peak*1 | Mass-loss, % | |
|---|---|---|
| | Observed | Calculated*2 |
| (a) and (b) | 11.87±0.34 | 11.95($-3H_2O$) |
| (d) | 17.48±0.19 | 17.70($-SO_3$) |
| (e) | 6.98±0.11 | 7.07($-O_2$) |

*1 See Fig. 1.
*2 Assuming the composition, $CuSO_4 \cdot 3Cu(OH)_2$.

Concerning the decomposition of synthetic posnjakite, the endothermic peak (f) is associated with the dehydration of the monohydrate to its anhydrate (see Fig.2). From the TG traces, it seems that the brochantite form. This is not shown, however, from the IR spectrum of the compound $B_2$. This might be due to the rapid dehydration of posnjakite at a heating rate of ca. 10 K $min^{-1}$, which cannot allow the dehydration product to crystallize, prior to the subsequent dehydroxylation. It would be possible to obtain brochantite stably from posnjakite through the dehydration if we could dehydrate the monohydrate isothermally or quasi-isothermally. We see that the dehydroxylation stage exhibits two endothermic peaks, (g) and (h). In view of the DSC with peaks (g) and (h) in Fig. 2, it might be assumed that the dehydrated posnjakite, which in composition corresponds to brochantite, is dehydroxylated via an intermediate,

TABLE 4
The mass loss due to the successive decomposition of synthetic posnjakite by means of TG

| Peak*1 | Mass-loss, % | |
|---|---|---|
| | Observed | Calculated*2 |
| (f), (g) and (h) | 15.55±0.21 | 15.39($-4H_2O$) |
| (j) | 16.99±0.09 | 17.02($-SO_3$) |
| (k) | 6.79±0.14 | 6.80($-O_2$) |

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*1 See Fig. 2.
*2 Assuming the composition, $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$.

$CuO \cdot CuSO_4 \cdot 2Cu(OH)_2$, to $CuO \cdot CuSO_4 + 2CuO$. It is evident from Tables 2 and 4 that the compound $B_4$ corresponds in composition to $CuSO_4 \cdot 3CuO$. We also see that the peak temperature (i) in Fig. 2 is in accordance with that of (c) and that IR spectra of the compound $B_5$ are similar to those of $A_4$. This suggests that the compounds $B_4$ and $B_5$ have a mixed composition of $CuSO_4 \cdot CuO$ and CuO in a mole ratio of 1:2, as in the case of the compounds $A_3$ and $A_4$[4]. The subsequent endothermic peak (j), as well as peak (d), which is accompanied by mass loss, is associated with the removal of $SO_3$. The composition of $B_4$, CuO, was proved by mass loss data, the weight percent of copper(II) and sulfate ions, and IR spectra. The mass loss which corresponds to peak (k) is in good agreement with the calculated value for the reduction of CuO to $Cu_2O$, as listed in Table 4.

## CONCLUSION

The present precipitates correspond in composition to the minerals of brochantite and posnjakite. The following scheme was established for the thermal decomposition of synthetic posnjakite under the present experimental condition;

$$CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O \longrightarrow CuSO_4 \cdot 3Cu(OH)_2 \longrightarrow CuSO_4 \cdot CuO + 2CuO$$
$$\longrightarrow 4CuO \longrightarrow 2Cu_2O$$

The thermal decomposition of synthetic brochantite proceeded in a similar way to that of the synthetic posnjakite dehydrated.

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