

THE LANGBEINITE $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ OBTAINED VIA SOLUTION FROM $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$ 1:2 M MIXTURES. II. ANALYSIS OF THE LANGBEINITE DECOMPOSITION *

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ABSTRACT

We have studied in detail the thermal decomposition of the langbeinite $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ prepared by evaporation of 1:2 M saturated solutions of $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$.

The decomposition has been followed by TG, DTA, DRX and IR spectroscopy. Data provided by these experimental techniques together with the results from chemical analysis and SEM, allow us to affirm that in the decomposition of $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ there are no stable intermediate compounds.

INTRODUCTION

In the DTA curve of the langbeinite studied, the endothermic peak corresponding to its decomposition has a submaximum which suggests the overlapping of several phenomena. We have studied this decomposition interval using the experimental techniques described in part I *.

EXPERIMENTAL

Samples

The langbeinite prepared as we described in part I was calcined at temperatures within the decomposition interval established from the TG curve. These temperatures, seven in all, were reached with a heating rate of 2.5 K min^{-1} .

Other samples were obtained by calcination of the langbeinite at temperatures close to the submaximum of the DTA curves recorded for $\beta = 2.5$ and 0.8 K min^{-1} .

* For part I of this study, see *Thermochim. Acta*, 144 (1989) 65.

Apparatus

The thermogravimetric apparatus was a Chevenard thermobalance 93 (Adamel) with a vertical furnace ($T = 1100^\circ\text{C}$), a photographic register, and a Staatlich Berlin porcelain crucible (A4/0). The temperature of the air surrounding the crucible was monitored. The sample weight was 200–300 mg. The heating rate β was 10, 5, 2.5 and 0.8 K min^{-1} . A Mettler TA3000 system was also used ($T = 1000^\circ\text{C}$) with an alumina microcrucible with sample weights of 30–40 mg.

The DTA apparatus was constructed in this laboratory using a vertical furnace with a temperature regulation system (Adamel). The sintered alumina holder ($19 \times 12.5 \times 14\text{ mm}$) was divided into two equal cavities with a wall thickness of 1.5 mm. A differential chromel–alumel thermocouple was used with a Metrohm Labograph E478 recorder. The temperature of the air surrounding the specimen holder was monitored. The heating rate β was 2.5 and 0.8 K min^{-1} .

X-Ray powder diffraction was performed on a Siemens D-500 diffractometer, with K-805 generator, Cu $K\alpha$ radiation, Ni filter and graphite monochromator. Experimental conditions were 40 Kv, 32 mA with a goniometer rate of 5 deg. min^{-1} , a paper speed of 300 mm h^{-1} , and a time constant of 1 s.

Infrared spectroscopy was performed on a Perkin–Elmer 599B spectrophotometer using KBr pellets and a sample concentration of $0.8\text{ mg sample}/300\text{ mg KBr}$.

The optical microscope used was an Ultraphot III Zeiss microscope. Samples were prepared as emulsions with a liquid having a refractive index of 1.543.

The electron microscope used was a Jeol JSM 35C with a resolution of 60 Å. Samples were prepared as solid suspensions in “carbon”; after liquid evaporation, samples were coated with an Au–Pd film.

A Beckman DU spectrophotometer was used to determine NH_3 at 420 nm, using a Nessler reagent, a standard solution of $(\text{NH}_4)_2\text{SO}_4$ ($0.001\text{ mg NH}_3\text{ ml}^{-1}$).

RESULTS AND DISCUSSION

TG

Table 1 lists the weight losses associated with several temperatures ($\beta = 2.5\text{ K min}^{-1}$, s.w. = 210 mg).

When the mass loss is small ($T < 275^\circ\text{C}$), the X-ray powder diffraction indicates that $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ is the sole component of the residue, although the relative intensity of its diffraction lines is disturbed.

TABLE 1

Weight loss (%) at different temperatures; TG curve ($\beta = 2.5 \text{ K min}^{-1}$)

T ($^{\circ}\text{C}$)	175	225	275	350	375	400	500
Δm (%)	0.26	0.93	1.34	5.16	11.65	15.37	23.50

The X-ray diffraction of the residue at $T = 350^{\circ}\text{C}$, weight loss approximately 5%, corresponds to two compounds: the main component is the langbeinite $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$, but it is rather altered because the relative intensity of its diffraction lines is considerably reduced. The other component is anhydrous cadmium sulphate which appears as traces in the residue and comes from the decomposition of the langbeinite which is just beginning. We observed the same phenomenon in the residue at $T = 375^{\circ}\text{C}$ and $T = 400^{\circ}\text{C}$, but here it is more pronounced, with mass losses double or triple the preceding one.

The breakdown of the langbeinite lattice is complete at $T = 500^{\circ}\text{C}$. At this temperature, the residue is monophasic CdSO_4 .

As well as a decrease in the intensity of the diffraction lines and the disappearance of some of them, the destruction of the langbeinite lattice is accompanied by the appearance of new diffraction lines. Curiously, these lines are the same as those found in some of the evaporation residue of 1:2 M $(\text{NH}_4)_2\text{SO}_4/\text{CdSO}_4$ saturated solutions.

Table 2 uses the spacing and relative intensities of these lines. The relative intensities reach maximum values for those samples heated at $375\text{--}400^{\circ}\text{C}$.

In the residue obtained in the interval $350\text{--}400^{\circ}\text{C}$, anhydrous CdSO_4 is found with its monohydrate. This hydrate is not stable at these temperatures; according to Walter-Lévy et al. [1] its dehydration occurs in the interval $165\text{--}225^{\circ}\text{C}$. Therefore, it must have been formed in a secondary reaction at room temperature between the anhydrous sulphate and environ-

TABLE 2

X-ray diffraction lines which have not been assigned, from the diffractograms of samples taken from the TG curve ($\beta = 2.5 \text{ K min}^{-1}$)

$T = 350^{\circ}\text{C}$		$T = 375^{\circ}\text{C}$		$T = 400^{\circ}\text{C}$	
d (\AA)	I/I_1	d (\AA)	I/I_1	d (\AA)	I/I_1
		8.3367	11	8.2765	15
6.1970	6	6.2100	42	6.1755	49
		5.0666	5		
4.3433	1	4.3539	13	4.3391	12
4.1524	2	4.1640	10	4.1524	7
3.0273	3	3.0334	30	3.0253	26
2.8959	6	2.9005	60	2.8923	58

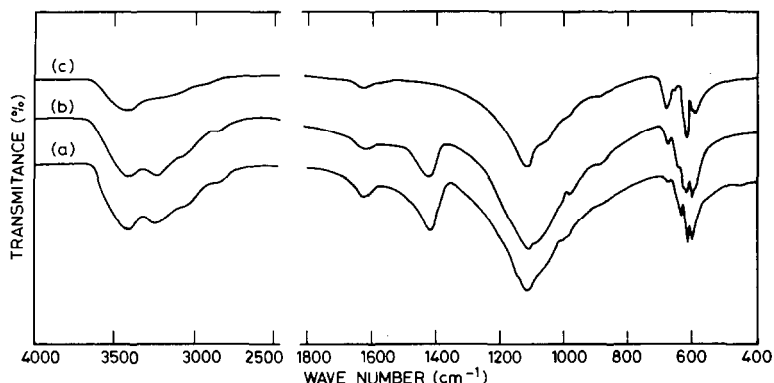


Fig. 1. Infrared spectrum of samples at different temperatures in the TG curve of $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ ($\beta = 2.5 \text{ K} \cdot \text{min}^{-1}$): (a) $T = 350^\circ \text{C}$; (b) $T = 375^\circ \text{C}$; (c) $T = 500^\circ \text{C}$.

mental water. Atmospheric moisture could have been absorbed by the decomposition products of ammonium sulphate (an unstable component of the langbeinite in the studied interval of temperatures), in particular by NH_4HSO_4 [2,3], $(\text{NH}_4)_2\text{S}_2\text{O}_7$ [4,5] and $\text{NH}_4\text{HSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ [6], which are all deliquescent.

Anhydrous cadmium sulphate retains gaseous products in the solid phase as well as in solution: it is a deliquescent solid [7] and gives rise to hydrates [8,9]. It behaves in the same way with ammonia gas [7,8], giving rise to several ammoniacal compounds whose X-ray diffraction patterns are unknown.

The residue of calcination at 350, 375 and 500 °C have also been analysed by infrared spectroscopy. In the spectrum of the residuum at 350 °C, the decomposition observed by TG and X-ray diffraction can be seen (Fig. 1(a)).

The characteristic absorptions of the SO_4^{2-} group of the double salt can be observed but their intensities are reduced, especially in the multiplet δ_{as} . At 675 cm^{-1} , there is a very small band which corresponds to δ_{as} of CdSO_4 .

In the spectrum of the residue at 375 °C (Fig. 1(b)), the multiplet assigned to δ_{as} of the anion of the double salt is less well resolved than in the residue at 350 °C: the absorption at 640 cm^{-1} is only a shoulder.

The 675 cm^{-1} absorption of CdSO_4 is more intense than in the preceding spectrum and also it is possible to observe a widening of the band that has its maximum at 600 cm^{-1} .

Likewise, the band centred at 1100 cm^{-1} loosely assigned to ν_{as} , is wider now and does not have any defined maximum; this may be due to the overlapping of the asymmetric stretchings of the SO_4^{2-} tetrahedrons of the langbeinite, CdSO_4 and $\text{CdSO}_4 \cdot \text{H}_2\text{O}$.

The spectrum of the residue at 500 °C (Fig. 1(c)) corresponds to anhydrous CdSO_4 .

DTA

$$\beta = 2.5 \text{ K min}^{-1}$$

The submaximum appears close to 400°C. We have used two samples heated to 385 and 400°C.

At $T = 385^\circ\text{C}$, the langbeinite lattice is quite broken down, and CdSO_4 appears with the langbeinite in its anhydrous and monohydrate forms.

The X-ray diffractogram includes several lines which cannot be assigned to any previously known compound. It can be seen that these lines coincide with those found in the residue taken from the TG curve (Tables 2 and 3).

In the samples heated to 400°C, it is very difficult to differentiate the langbeinite, whereas the two forms of CdSO_4 have considerably increased. The unassigned lines have also increased in number and in intensity; some of them even become the most intense in the diffractogram (Table 3).

$$\beta = 0.8 \text{ K min}^{-1}$$

We have taken samples at several temperatures: $T = 360^\circ\text{C}$ (before the submaximum), $T = 380^\circ\text{C}$ (temperature corresponding to the submaximum), 410 and 420°C (after the submaximum).

Although the heating rate is three times slower, the results do not differ from those obtained previously: the progressive disappearance of the langbeinite, which becomes the minor component in the residue at 410–420°C, and the parallel increase of cadmium sulphate. The unassigned lines are also present (Table 4).

TABLE 3

X-ray diffraction lines which have not been assigned, from the diffractograms of samples taken from the DTA curve ($\beta = 2.5 \text{ K min}^{-1}$)

$T = 385^\circ\text{C}$		$T = 400^\circ\text{C}$	
d (Å)	I/I_1	d (Å)	I/I_1
8.3782	5	8.3545	28
6.2449	18	6.2013	100
		5.5691	2
		5.0548	3
		4.6187	7
4.3666	4	4.3687	16
4.1775	2	4.1775	8
		3.6746	3
3.0374	6	3.0374	31
2.9033	17	2.9033	67
		2.5722	5

TABLE 4

X-ray diffraction lines which have not been assigned from the diffractograms of samples taken from the DTA curve ($\beta = 0.8 \text{ K min}^{-1}$)

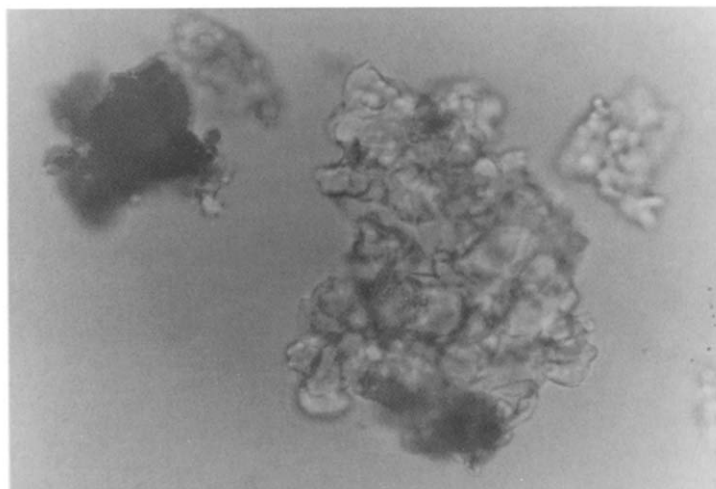
$T = 360^\circ \text{C}$		$T = 380^\circ \text{C}$		$T = 420^\circ \text{C}$	
$d \text{ (\AA)}$	I/I_1	$d \text{ (\AA)}$	I/I_1	$d \text{ (\AA)}$	I/I_1
8.3075	7	8.2765	16	8.3387	10
6.2013	19	6.1841	56	6.2187	20
4.3496	6	4.3433	13	4.3496	3
4.1620	3	4.1543	6		
3.0374	12	3.0324	17	3.0263	5
2.9033	26	2.8995	51	2.8996	16

Optical microscopy and SEM

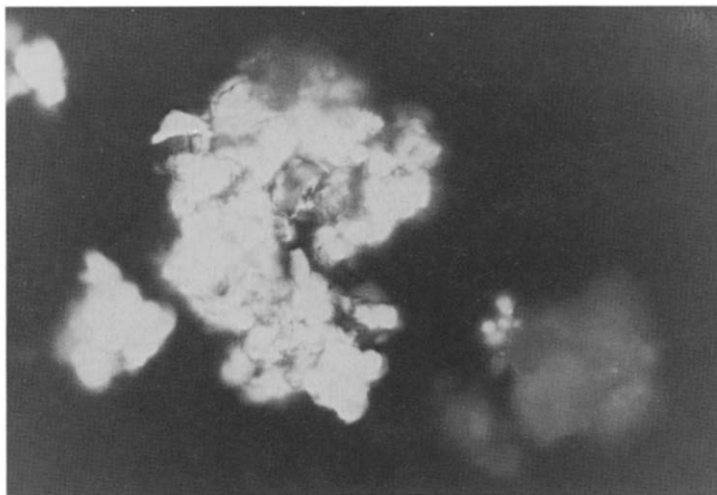
When the samples are first removed, they are pasty, which indicates the presence of molten materials. When they were cool, they were examined with an optical microscope and an SEM.

Photographs 1 and 2 correspond to a sample calcined at 400°C , at 470 magnifying power, the first with parallel nicols and the second with crossed nicols. In photograph 1, the alterations suffered by the langbeinite can be seen, and in photograph 2, the field is totally illuminated indicating its anisotropy; the langbeinite has disappeared, and therefore the cubic symmetry.

The SEM micrographs 3 and 4 are of the same sample. Both show alterations in the morphology of the langbeinite.



Photograph 1. Residue from calcination at $T = 400^\circ \text{C}$ of $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$. Optical microscope, $\times 470$, parallel nicols.



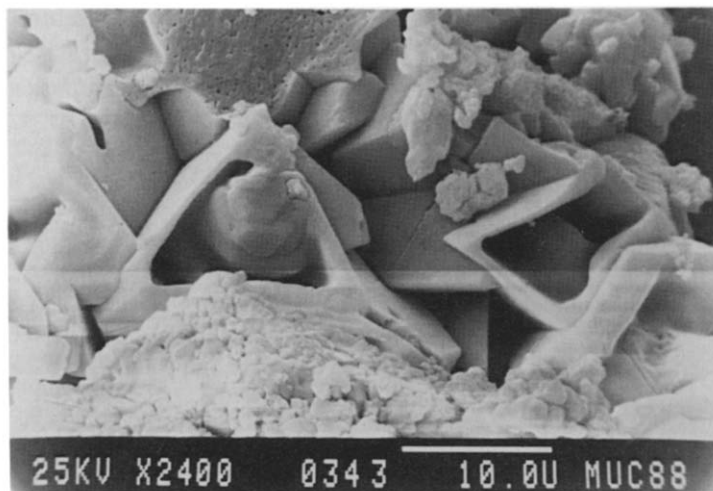
Photograph 2. Residue from calcination at $T = 400^{\circ}\text{C}$ of $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$. Optical microscope, $\times 470$, crossed nicols.



Photograph 3. Scanning electron micrograph of residue from calcination at $T = 400^{\circ}\text{C}$ of $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$, showing alterations in the morphology of the langbeinite.

Chemical analysis

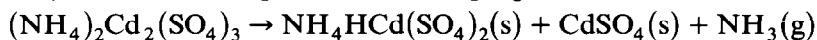
Prymova et al. [10] in their study on the thermal decomposition of Tutton's salt $(\text{NH}_4)_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and by comparison with $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, propose the existence of a stable compound, $\text{NH}_4\text{HCd}(\text{SO}_4)_2$, formed by decomposition of the langbeinite.



Photograph 4. Scanning electron micrograph of residue from calcination at $T = 400^\circ\text{C}$ of $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$, showing alterations in the morphology of the langbeinite.

The quantitative analysis of SO_4^{2-} and NH_4^+ can provide new complementary data in order to determine if the langbeinite decomposes with formation of the intermediate compound $\text{NH}_4\text{HCd}(\text{SO}_4)_2$.

For the langbeinite $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ the molar ratio $\text{SO}_4^{2-}/\text{NH}_4^+$ is $3/2 = 1.5$. For the proposed intermediate stage of decomposition, this ratio is $3/1 = 3$, according to the following equation



The difference between these two values means that the calculation of the molar ratio for samples of langbeinite calcined at temperatures under 450°C would be a suitable way to establish whether or not the langbeinite decomposition proceeds via an intermediate compound.

Calculating this ratio for two samples heated to 400°C , we have obtained the values $\text{SO}_4^{2-}/\text{NH}_4^+ = 1.93$ and 2.0 , which do not fit the theoretical values for $\text{NH}_4\text{HCd}(\text{SO}_4)_2$ or for $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$.

The samples analysed have an ammonia content lower than that of the langbeinite; this fact confirms its decomposition.

It has been indirectly confirmed that the unassigned lines of the X-ray diffractogram do not belong to a defined compound but to a distorted structure of the langbeinite.

We believe that this study confirms that the unassigned lines of the X-ray diffractogram do not correspond to any defined compound.

The appearance of these lines coincides with the dissociation of the langbeinite and with the progressive loss of the volatile components which produces alterations in the melting and volatilisation temperatures. These alterations can be detected in the DTA curves as changing endothermic peaks.

Also, the two components of the double salt $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$, and, therefore, the undissociated salt, can absorb water vapour and ammonia gas, a phenomenon which may originate from a displacement or reorientation of the crystalline planes, registered in the X-ray diffractogram by the new lines.

REFERENCES

- 1 L. Walter-Lévy, D. Groult and J.W. Visser, *Bull. Soc. Chim. Fr.*, 3-4, Pt-1 (1974) 383-6.
- 2 F. Burriel-Martí and M.E. García-Clavel, *Anales de Física y Química*, LIII-B (1957) 1285-1292.
- 3 L.A. Prymova and N.M. Selivanova, *Izv. Vyssh. Unchebn. Zaved. Khim-Khim. Tekhnol.*, 15(6) (1972) 817-820.
- 4 D.G. Ivanov and S.P. Kossev, *God. Vissh. Khimikotechnol. Inst.*, 12 (1965) 67; *Chem. Abstr.*, 69 (1968) 5580g.
- 5 E.V. Margullis, N.I. Kopylov and L.I. Beisekeeva, *Zh. Neorg. Khim.*, 11(7) (1966) 1673-8; *Chem. Abstr.*, 65 (1966) 13198f.
- 6 I. Konkoly Thege, *Thermochim. Acta*, 60 (1983) 149-159.
- 7 P. Pascal, *Nouveau Traité de Chimie Minérale*, vol. 5, Masson et C^{ie}, Paris, 1962, pp. 377, 378, 381.
- 8 G.G. Urazov and A.K. Kirakosyan, *Izv. Sektora. Fiz-Khim. Anal. Akad. Nauk. SSSR.*, 23 (1953) 249-57; *Chem. Abstr.*, 48 (1954) 9855gh.
- 9 A.S. Karnaukhov, T.P. Fedorenko and V.G. Shevchuck, *Yarosl. Gos. Pedagog. Inst.*, 95 (1971) 123-128; *Chem. Abstr.*, 78 (1973) 8482q.
- 10 L.A. Prymova, T.I. Khozhainova and N.M. Selivanova, *Chem. Abstr.*, 94 (1981) 113679n.