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THE LANGBEINITE $(NH_4)_2Cd_2(SO_4)_3$ OBTAINED VIA SOLUTION FROM MIXTURES OF $(NH_4)_2SO_4/CdSO_4$ IN MOLAR RATIO 1:2.

III. EVOLUTION OF THE SAMPLES

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ABSTRACT

Samples taken during thermal decomposition of the langbeinite $(NH_4)_2Cd_2(SO_4)_3$ evolve in the same way at room temperature and after cyclical heatings (thermogravimetric and differential scanning calorimetric analyses). This evolution, indicated by alterations in the X-ray diffractograms, is due to evolving of NH_3 absorbed by the langbeinite lattice during its thermal decomposition.

INTRODUCTION

The solids formed by evaporation of saturated solutions of $(NH_4)_2SO_4/CdSO_4$ in molar ratio 1 : 2 change over time or with heating. The products of their calcination also evolve, and this evolution takes place in the same way.

EXPERIMENTAL

Samples

(1) Evaporation residua at 95 °C of saturated solutions of $(NH_4)_2SO_4/CdSO_4$ in molar ratio 1 : 2. (2) The langbeinite $(NH_4)_2Cd_2(SO_4)_3$ and the products of its calcination at temperatures as given in Parts I [1] and II [2] of this work.

Apparatus

Differential scanning calorimetry (DSC)

Mettler DSC 20, $T = 600\,^\circ C$. Standard aluminum sealed crucibles were used. The reference crucible was empty. Sample weight 8–10 mg, $\beta = 10$ K min^{-1}, flow of purge gas (air) = 50 ml min^{-1}.

Thermogravimetric analysis (TG)

Mettler TA3000 system, $T = 1000\,^\circ C$. Alumina microcrucible. Sample weight = 30–40 mg, $\beta = 10\ K\ min^{-1}$.

X-ray powder diffraction

Siemens D-500 diffractometer, with K-805 generator, Cu $K\alpha$ radiation, Ni filter and graphite monochromater: 40 kV, 32 mA, goniometer rate 5° min^{-1}, paper speed 300 mm h^{-1}, time constant 1 s.

RESULTS AND DISCUSSION

In Part I we saw that the evaporation residua were only slightly crystalline and the X-ray powder diffractions difficult to identify. In some of these residua we found several non-assigned diffraction lines (see Tables 2, 3 and 4 in Part II) which resulted from the langbeinite calcination at $T > 300\,^\circ C$.

On calcining the evaporation residua at $T < 300\,^\circ C$ these lines disappear, but with further heating they reappear at $T = 400\,^\circ C$ (see Part II).

Evolution at room temperature

As well as the evaporation residua calcined at 400 °C, the langbeinite (heated to temperatures within the interval 175–400 °C, and kept into closed tubes at room temperature) also evolves.

This evolution is relatively slow; all the samples remain stable for periods of time of less than 15 days. Its occurrence is indicated by X-ray diffraction data. (1) All the non-assigned lines disappear. (2) The relative intensities of the diffraction lines of the langbeinite return to almost their theoretical values. (3) Anhydrous cadmium sulphate does not appear in the evolved samples; only the monohydrate is present. Since the anhydrous sulphate is the only solid product of the langbeinite decomposition, formation of the monohydrate must take place through gradual hydration of the anhydrous sulphate over time.

Table 1 gives the pairs of lines whose relative intensities change with time. These pairs are formed by lines assigned to the langbeinite and non-assigned lines.

Figures 1 and 2 reproduce the section of the diffractogram showing these pairs of lines.

It can be seen that the non-assigned lines originate from certain lines on the diffractogram assigned to the langbeinite, lines whose intensities decrease in parallel with the increase in intensity of the non-assigned lines. The pairs of lines also indicate evolution over time, with an increase in the intensity of the langbeinite lines and a decrease in the intensity of their accompanying lines.

TABLE 1

Evolution at room temperature: changes in the relative intensities of pairs of diffraction lines

Sample	Initial diffractogram					Diffractogram of evolved sample				
	$(NH_4)Cd_2(SO_4)_3$ lines			Non-assigned lines		$(NH_4)_2Cd_2(SO_4)_3$ lines			Non-assigned lines	
	2θ	$(I/I_1)_{exp}$	$(I/I_1)_{theor}$	2θ	I/I_1	2θ	$(I/I_1)_{exp}$	$(I/I_1)_{theor}$	2θ	I/I_1
$T = 325\,°C$	14.80	32	50	14.28	6	14.94	60	50	14.38	5
(TG: 2.5 K min^{-1})	31.20	9	10	30.85	6	31.38	11	10		
$T = 350\,°C$	14.83	58	50	14.20	5	15.00	69	50		
(TG: 2.5 K min^{-1})	31.15	7	10	30.78	3	31.30	10	10		
$T = 375\,°C$	14.80	17	50	14.25	42	15.00	45	50		
(TG: 2.5 K min^{-1})	30.80	60	10			31.38	11	10		
$T = 400\,°C$	14.75	7	50	14.33	49	14.95	35	50		
(TG: 2.5 K min^{-1})	30.78	5	10			31.40	8	10		
$T = 400\,°C$	14.75	9	50	14.27	100	15.00	54	50		
(DTA: 2.5 K min^{-1})	19.00	12	65	19.20	7	19.38	55	65		
	30.77	67	10			31.35	8	10		

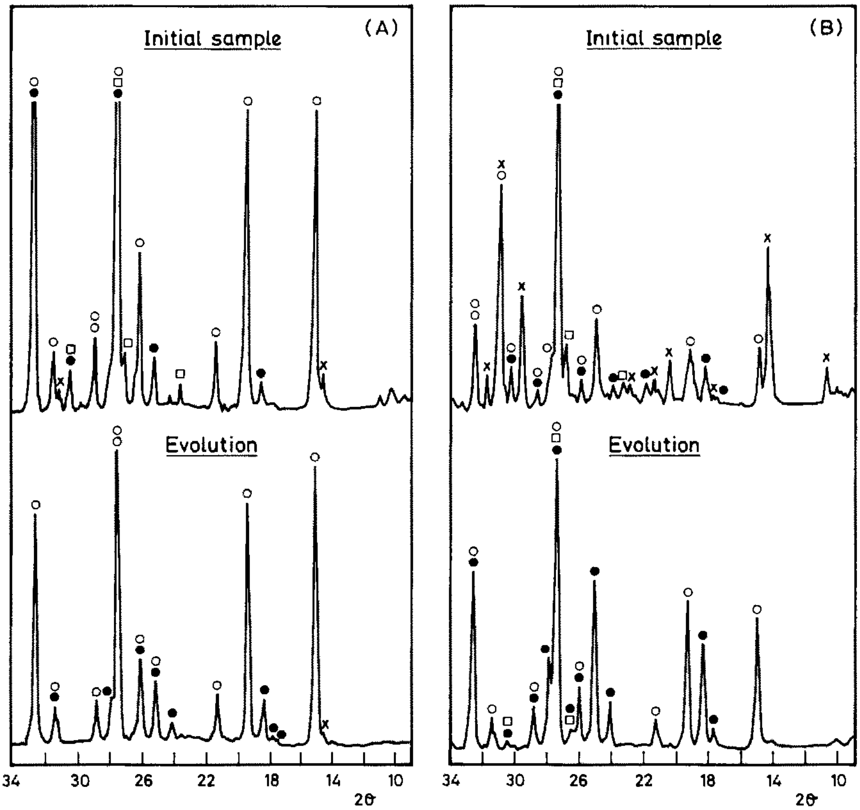

Fig. 1. Evolution at room temperature of residua of calcination, at different temperatures, of $(NH_4)_2Cd_2(SO_4)_3$: A $T = 350\,°C$ (TG curve, $\beta = 2.5$ K min^{-1}); B $T = 375\,°C$ (TG curve, $\beta = 2.5$ K min^{-1}).

Identical evolution has been found even in some *non-calcined* evaporation residua and over periods of less than two weeks.

Evolution on cyclical heatings

For this study, we used a residuum at $T = 400\,°C$. At this temperature the langbeinite is decomposing and the non-assigned lines in its diffractogram have their highest values of relative intensity.

The same residue was treated with three cyclical heatings, always to 120 °C, and the DTA curves were recorded ($\beta = 10$ K min^{-1}). Figure 3 reproduces these curves.

On the first heating (curve 1°) an endothermic peak with maximum at 98 °C was recorded. The intensity of this peak, and similarly the maximum temperature, decreases with further heating and then disappears totally (curve 3°).

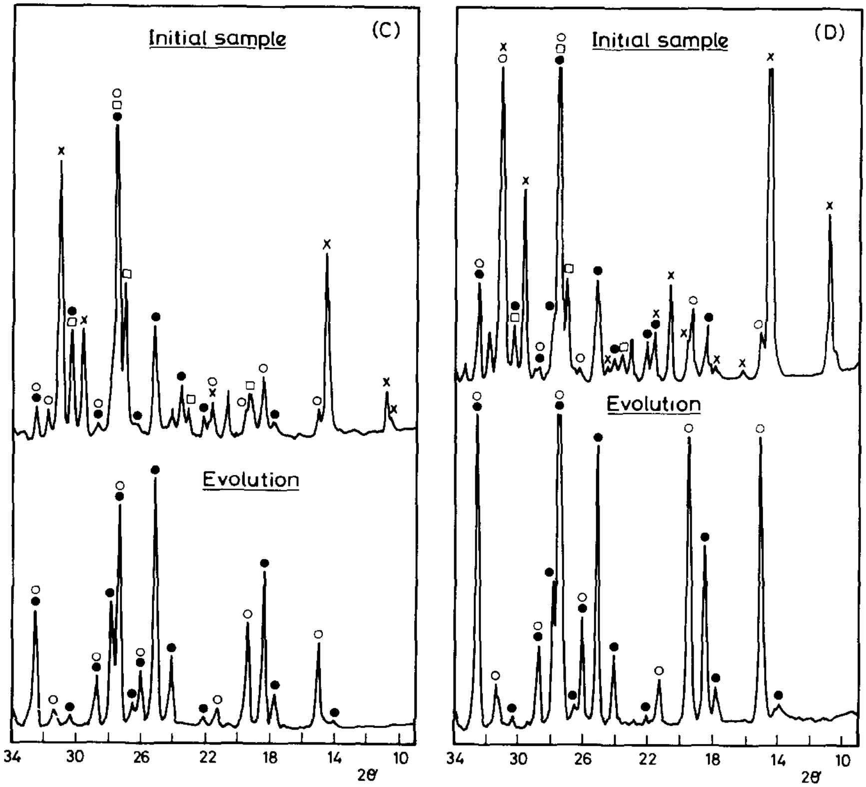

Fig. 2. Evolution at room temperature of residua of calcination, at different temperatures, of $(NH_4)_2Cd_2(SO_4)_3$: C $T = 400\,°C$ (TG curve, $\beta = 2.5$ K min^{-1}); D $T = 400\,°C$ (DTA curve, $\beta = 2.5$ K min^{-1}).

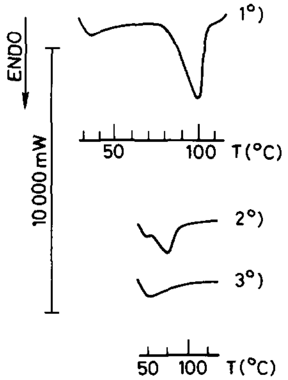

Fig. 3. Cyclical DSC ($\beta = 10$ K min^{-1}): initial sample, calcination residue of $(NH_4)_2Cd_2(SO_4)_3$ at $T = 400\,°C$.

TABLE 2

Cyclical DSC: changes in the relative intensities of pairs of diffraction lines

Initial sample					Residuum of the third heating				
$(NH_4)_2Cd_2(SO_4)_3$ lines			Non-assigned lines		$(NH_4)_2Cd_2(SO_4)_3$ lines			Non-assigned lines	
2θ	$(I/I_1)_{exp}$	$(I/I_1)_{theor}$	2θ	I/I_1	2θ	$(I/I_1)_{exp}$	$(I/I_1)_{theor}$	2θ	I/I_1
			10.65	22					
14.85	17	50	14.28	67	15.00	12	50	14.45	41
19.18	14	65			19.45	19	65		
30.80	68	10			31.00	38	10		

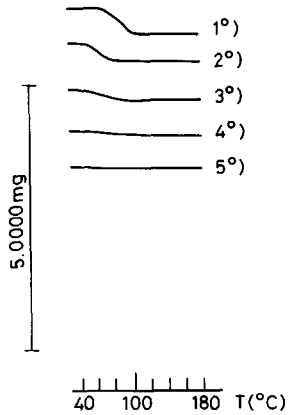

Fig. 4. Cyclical TG ($\beta = 10$ K min^{-1}): initial sample, calcination residue of $(NH_4)_2Cd_2(SO_4)_3$ at $T = 400$ ° C.

X-ray diffraction analysis of these samples evolved through heating gives the same results (Table 2) as those given in Table 1 for evolution at room temperature.

Two other residua at $T = 400$ ° C were used for TG analyses. A TG curve to 700 ° C ($\beta = 10$ K min^{-1}) was recorded for the first sample. The first loss, ending at approximately 100 ° C, represents a mass loss of 1.2%. The second occurring between 200 and 450 ° C, corresponds to the langbeinite decomposition.

Using the same operative method as for the DSC experiments, the second sample was treated with five cyclical heatings to $T_f = 140$ ° C ($\beta = 10$ K min^{-1}). Before the residue of each heating was used as the sample for the next heating, it was cooled to room temperature in the furnace using a purge gas circulation of (150 ml min^{-1}).

Figure 4 gives the five TG curves. The weight loss decreases in proportion to the heating, until the fourth curve where the weight loss is nil.

The X-ray diffractogram for the residue of the fourth curve is clearly different to the diffractogram for the initial sample (Table 3). These TG results indicate that the transformation undergone by the ammonium–cadmium langbeinite when calcined to temperatures of between 200 and 400 ° C is accompanied by small weight gains, which probably represent absorption by the sample of part of the ammonia evolved in the decomposition: probably ammonia because this gaseous compound is the first to be evolved during the decomposition of the ammonium sulphate.

The ammonia retained is probably intercalated between the planes of the langbeinite lattice, which would originate the new diffraction lines we have found so far. The relative intensity of these lines would increase in proportion to the amount of ammonia intercalated; in parallel, the original lines of the langbeinite would disappear.

TABLE 3

Cyclical TG: changes in the relative intensities of pairs of diffraction lines

Initial sample					Residuum of the fifth heating				
$(NH_4)_2Cd_2(SO_4)_3$ lines			Non-assigned lines		$(NH_4)_2Cd_2(SO_4)_3$ lines			Non-assigned lines	
2θ	$(I/I_1)_{exp}$	$(I/I_1)_{theor}$	2θ	I/I_1	2θ	$(I/I_1)_{exp}$	$(I/I_1)_{theor}$	2θ	I/I_1
			10.65	22					
14.85	17	50	14.28	67	15.00	29	50	14.45	12
19.18	14	65			19.30	34	65		
30.80	68	10			30.90	12	10		

The elimination of the retained ammonia which takes place at room temperature or, more quickly, through heating at temperatures below 100 ° C would bring about the return to the original langbeinite lattice.

At temperatures over 400 ° C the langbeinite decomposition is so advanced that the lattice has crumbled, and the absorption phenomenon that occurs at temperatures below 400 ° C cannot take place.

In summary, from the concordant results obtained by the various experiments outlined in these reports, we conclude that no intermediate compound is produced in the transformation of langbeinite to cadmium sulphate

$(NH_4)_2Cd_2(SO_4)_3 \rightarrow 2\ CdSO_4$

REFERENCES

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2 M.E. García-Clavel and M.P. Severt-Buxados, Thermochim. Acta. 144 (1989) 225.