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THE LANGBEINITE $(NH_4)_2Cd_2(SO_4)_3$ OBTAINED VIA SOLUTION FROM $(NH_4)_2SO_4/CdSO_4$ 1:2 M MIXTURES. I. SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

The name "langbeinite" was given to the anhydrous double sulphate of potassium and magnesium that occurs naturally in deposits of potassium salts, with other various double salts.

This important mineral gives its name to a large group of double salts with similar crystalline structures and which have the general formula $(A^+)_2(B^{2+})_2(XO_4^{2-})_3$ where X = S or Cr.

INTRODUCTION

The double sulphate salts with langbeinite-type structure have great technical interest because of their physical and structural properties, for example, the ferroelectric and ferroelastic ones.

A ferroelectric phase transition in this family was first found in $(NH_4)_2Cd_2(SO_4)_3$, in 1956 [1]. At almost the same time, an analogous transition was discovered in ammonium sulphate [2]. This langbeinite also displays triboluminiscence, an optical property discovered in this compound in 1980 [3].

To study these properties and others, several authors [4–8] prepared these compounds by evaporation of saturated aqueous solutions of the respective sulphates in 1:2 molar ratio.

The technical interest in langbeinites has led to numerous publications. However, scientific interest has been limited, almost exclusively, to the study of the crystalline structure.

Therefore, with the exception of Nagaishi et al. [9] who prepared an ammonium–manganese langbeinite by reaction of ammonium sulphate with MnO_2 in a 1:4 stoichiometric ratio and also very superficially studied its thermal behaviour, it is not easy to find publications referring to the study of the thermal characteristics of these compounds.

EXPERIMENTAL

Materials

The $(NH_4)_2SO_4$ was acquired commercially (a.r. Riedel). $CdSO_4$ was prepared in the laboratory from $3CdSO_4 \cdot 8H_2O$ (a.r. Carlo Erba) by dehydration at 600 °C for four hours in a muffle furnace. The composition was identified by X-ray powder diffraction.

Samples

The samples were prepared by evaporating to dryness the saturated aqueous solutions of 1 : 2 M mixtures of $(NH_4)_2SO_4/CdSO_4$, on a hot plate at 90–95 °C.

Apparatus

The thermogravimetric apparatus was a Chevenard thermobalance 93 (Adamel), with a vertical furnace, ($T = 1100$ °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 ($T = 1000$ °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 ($19 \times 12.5 \times 14$ 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 a K-805 generator, Cu $K\alpha$ radiation, Ni filter and graphite monochromater. 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 mg sample/300 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.

RESULTS AND DISCUSSION

Identification of the residue

The residue from the evaporation of the saturated aqueous solution of the 1 : 2 M mixture of $(NH_4)_2SO_4/CdSO_4$ was first identified by X-ray powder diffraction.

This technique reveals that the solid phase is really a mixture of two or three components: $(NH_4)_2Cd_2(SO_4)_3$, $CdSO_4$ and $(NH_4)_2Cd(SO_4)_2 \cdot 6H_2O$; the latter two are present in minor amounts.

Sometimes (Table 1), the X-ray diffractogram includes several lines which are not possible to identify in a direct manner.

However, heating of the residue to temperatures under 300 ° C, provides a langbeinite of ammonium and cadmium (CAS) which is practically pure: its X-ray diffractogram coincides with the standard one (file ASTM 21-791).

The crystals belong to the cubic system and its lattice was determined in 1900 by Mallet [10] and was also specified by Zemann and Zemann [11]. Other authors have established that at room temperature the CAS crystal presents a distorted cubic structure [8]. However, its morphology is unknown.

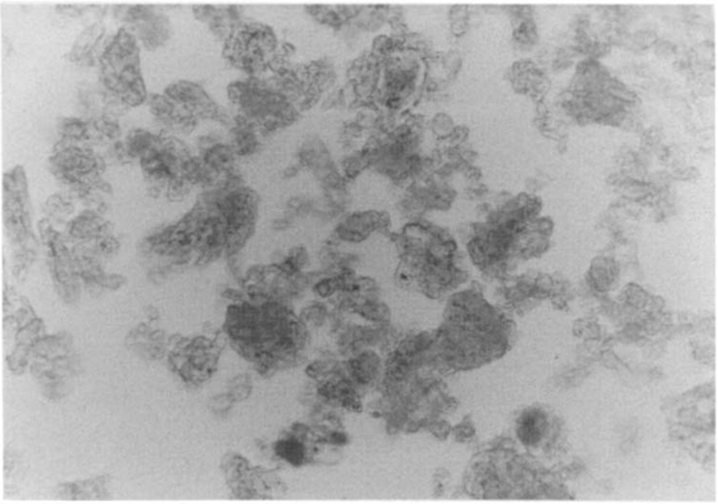
Photograph 1 shows a residue which has been heated to 200 ° C; this was taken through an optical microscope with × 144 magnification and parallel nicols. There is an unchanging field of very small crystals similar to common salt. These crystals, because they are cubic, are isotropic and absorb all the incident luminous radiation if the nicols are crossed, when the field becomes dark. For that reason, in photograph 2, there is an isotropic mass with some small illuminated zones due to the impurities that accompany langbeinite. These impurities are $CdSO_4 \cdot H_2O$ which crystallizes in the monoclinic system and therefore is anisotropic.

The SEM micrographs (3, 4 and 5) of the langbeinite crystals show a triangular morphology which corresponds to (111) growth planes of its cubic symmetry.

TABLE 1

Unassigned lines in the X-ray diffractogram of the evaporation residue of 1:2 M saturated solutions of $(NH_4)_2SO_4/CdSO_4$

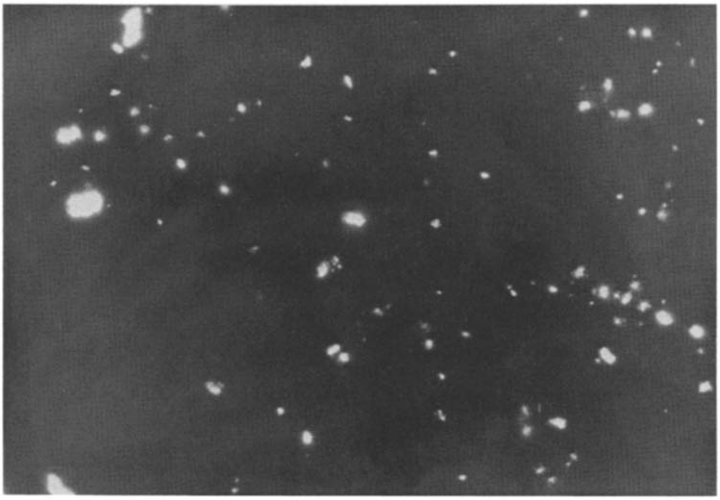
2θ	d (Å)	I/I_1
10.59	8.3466	7
12.73	6.9479	3
14.21	6.2274	23
29.39	3.0364	11
30.75	2.9051	19
33.95	2.6383	2
38.97	2.3092	2



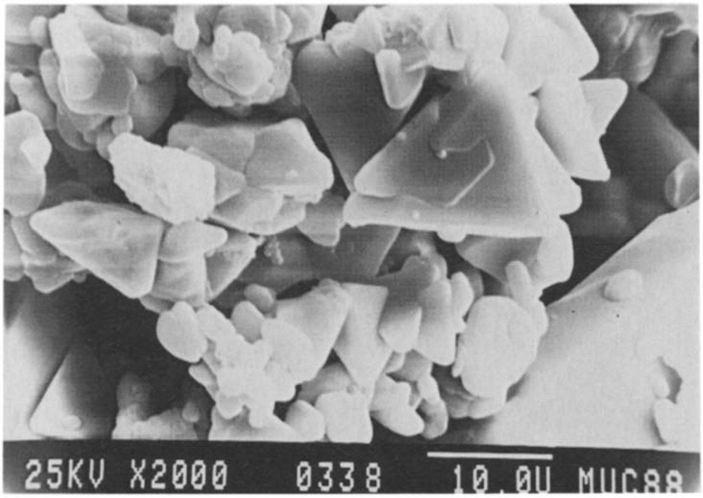
Photograph 1. $(NH_4)_2Cd_2(SO_4)_3$. Optical microscope: ×144, parallel nicols.

The same evaporation residue heated to 200 °C has been studied by infrared spectroscopy. Figure 1 shows the spectrum recorded. It contains the absorptions described as internal vibrations of SO_4^{2-} tetrahedra, according to the published data (Table 2). Table 3 details the infrared frequencies assigned to vibration of the NH_4^+ monovalent ion.

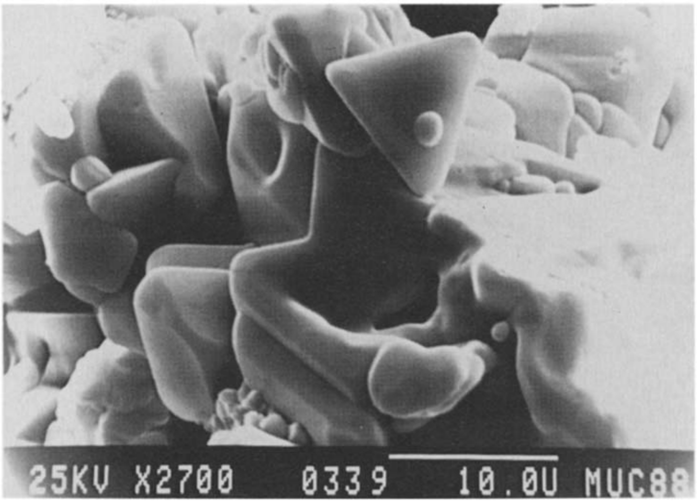
In conclusion, it is not possible to prepare a fairly pure langbeinite of cadmium and ammonium by evaporation of the 1 : 2 molar ratio saturated solution of the respective sulphates.



Photograph 2. $(NH_4)_2Cd_2(SO_4)_3$. Optical microscope: ×144, crossed nicols.



Photograph 3. Scanning electron micrograph of $(NH_4)_2Cd_2(SO_4)_3$.



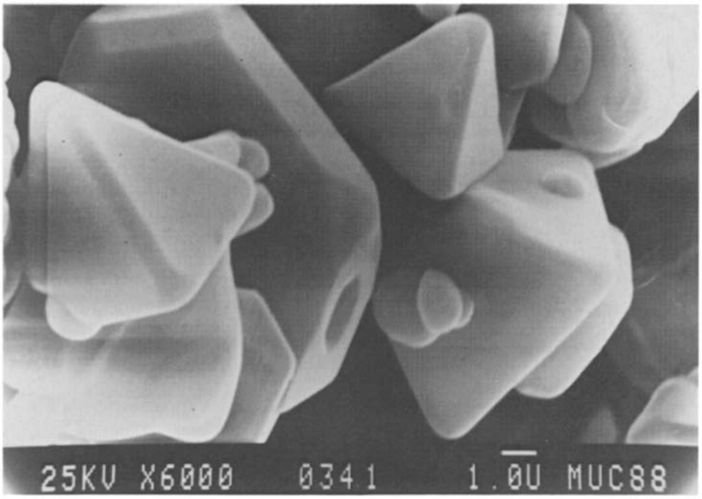
Photograph 4. Scanning electron micrograph of $(NH_4)_2Cd_2$ $(SO_4)_3$.

TABLE 2

Infrared spectrum of $(NH_4)_2Cd_2(SO_4)_3$: internal vibrations of SO_4^{2-} tetrahedron

Frequency (cm^{-1})	Assignation	References
1110 s	ν_{as}	12, 13, 14, 15
1007 sh	ν_s	12, 13, 14, 15
637 m		12,13,14
617 s	δ_{as}	12, 13, 14, 15
600 s		13, 14
460 vw	δ_s	12, 13, 15

s = strong; m = medium; vw = very weak; sh = shoulder.



Photograph 5. Scanning electron micrograph of $(NH_4)_2Cd_2(SO_4)_3$.

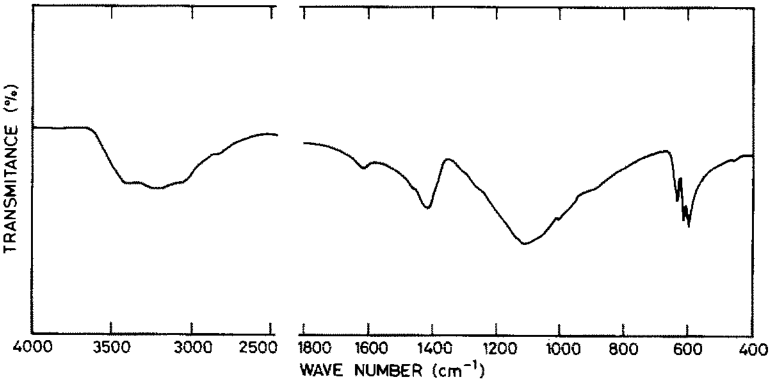


Fig. 1. Infrared spectrum of $(NH_4)_2Cd_2(SO_4)_3$: evaporation residue of 1:2 M saturated solutions of $(NH_4)_2SO_4/CdSO_4$ heated to 200 °C.

TABLE 3

Infrared spectrum of $(NH_4)_2Cd_2(SO_4)_3$: vibrations of the NH_4^+ ion

Frequency (cm^{-1})	Assignation	References
3230 s	ν_{as}	12, 14, 15
3050 vw		15
2840 vw		15
1420 s	δ_{as}	12, 14, 15
1480 m	δ_s	12, 15

s = strong; m = medium; vw = very weak; sh = shoulder.

This double sulphate does not always grow well crystallized and is accompanied by impurities in varying proportions. To eliminate these impurities, the evaporation residue must be heated to temperatures under 300 °C. As well as purifying the langbeinite, this heating improves its crystallization.

Thermal behaviour of the residue

In this part of the study we have used TG and DTA techniques.

TG study

This was performed with $\beta = 10$, 5 and 2.5 K min^{-1}. Figure 2 shows the TG and DTG curves for $\beta = 10$ K min^{-1}. There are two weight losses: the first, from room temperature to 200 °C, represents 0.5% of the initial weight and the second, from approximately 200 to 500 °C, corresponds to 22.5%. This second loss is continuous, which shows that the decomposition process does not involve stable intermediate compounds.

To provide heated samples to be analyzed by X-ray powder diffraction, other TG curves at slower heating rates, $\beta = 5$ and 2.5 K min^{-1} were recorded.

In Fig. 3, there are two new curves with the same weight losses as in Fig. 2. But, the first loss, which ends at about 150–140 °C, has a different size for each sample. It is a small loss, never surpassing 3% of the initial weight; it corresponds to loss of the volatile impurities, H_2O in particular. From this weight loss information, it is possible to know the amount of langbeinite grown by evaporation of the saturated solution of the ammonium and cadmium sulphates.

The horizontal position, from 150 to 240 °C, indicates a thermally stable phase. The X-ray diffractogram of a sample heated to 200 °C practically coincides with that for $(NH_4)_2Cd_2(SO_4)_3$.

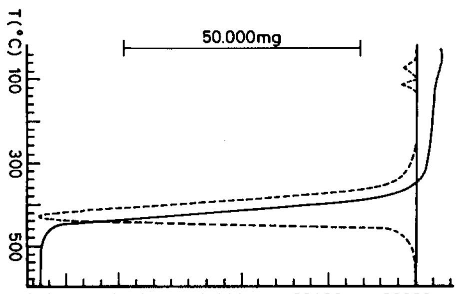


Fig. 2. TG and DTG curves of the evaporation residue of 1:2 M saturated solutions of $(NH_4)_2SO_4/CdSO_4$. Heating rate = 10 K min^{-1}.

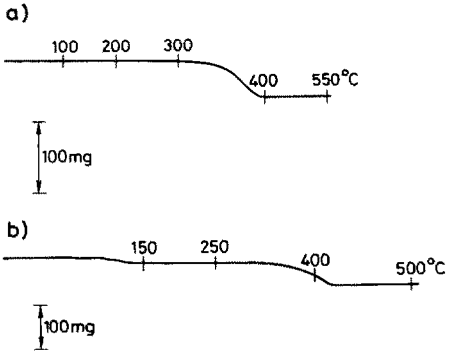


Fig. 3. TG curve of the evaporation residue of 1 : 2 M saturated solutions of $(NH_4)_2SO_4/CdSO_4$. Heating rate: (a) $\beta = 5$ K min^{-1}, (b) $\beta = 2.5$ K min^{-1}.

The second loss, between 240 and 450 ° C, does not show an inflexion point which could correspond to some solid phase intermediate between the langbeinite and the cadmium sulphate; the latter is the sole compound present in the residue at 500 ° C.

Therefore, the weight loss produced between 240 and 450 ° C, which varies for each sample from 23.8 to 24.1%, corresponds to the decomposition of the langbeinite by a unique process

$$(NH_4)_2Cd_2(SO_4)_3 \rightarrow 2CdSO_4(s) + SO_3(g) + 2NH_3(g) + H_2O(g).$$

The theoretical weight loss associated with this equation is 24.07%.

DTA study

This was carried out at two heating rates $\beta = 2.5$ and 0.8 K min^{-1}, in order to obtain a good separation of the thermal phenomena.

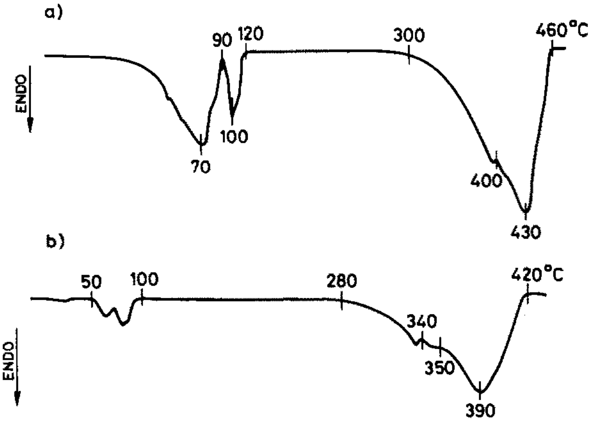


Fig. 4. DTA curves of the evaporation residue of 1:2 M saturated solutions of $(NH_4)_2SO_4/CdSO_4$. Heating rate: (a) $\beta = 2.5$ K min^{-1}, (b) $\beta = 0.8$ K min^{-1}.

Both curves are shown in Fig. 4. Several endothermic peaks appear at temperatures under 150 ° C, curve 4(a), and under 100 ° C, curve 4(b); these correspond to the weight losses observed in TG. The number and size of these peaks are variable and are caused by the loss of the volatile impurities.

Subsequently, there is a unique wide intense endothermic peak between 290 and 470 ° C.

The identification by X-ray powder diffraction of the samples taken at 200 and 500 ° C, confirms the presence, at both temperatures, of a single phase, $(NH_4)_2Cd_2(SO_4)_3$ and α-$CdSO_4$, respectively.

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