

SYNTHESIS AND THERMAL INVESTIGATION OF $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$

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(Received May 29, 1993; in revised form February 5, 1994)

Abstract

The synthesis and thermal decomposition of $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ in both air and nitrogen are described. The synthesis was performed by two different procedures, but in both cases the same product was obtained, corresponding to the general formula given above.

The crystals obtained were investigated by methods of X-ray powder diffraction, and chemical and thermal analysis. The differences in thermal decomposition in air and nitrogen are discussed.

Keywords: $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, synthesis, thermal decomposition

Introduction

There are many data on the double sulfates of cadmium with sodium. In Gmelins Handbuch [1], the syntheses of $\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$, $\text{CdSO}_4 \cdot 2\text{Na}_2\text{SO}_4$, $\text{CdSO}_4 \cdot 3\text{Na}_2\text{SO}_4$ and $3\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$ are described. All these compounds were obtained by treating a mixture of solid cadmium sulfate and sodium sulfate in appropriate molar ratios at different temperatures. In the same reference, the synthesis of sodium cadmium sulfate dihydrate is mentioned. There are also some data on the thermal decomposition of sulfates and double sulfates of cadmium.

Arhipov *et al.* [2] studied the dehydration of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ by means of TG, DTA and X-ray powder diffraction. The basic sulfate was studied by Walter-Levy [3]. The synthesis and structural investigation of a basic sulfate of cadmium with potassium and cesium [4] have also been performed.

There are likewise structural data on $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and its thermal decomposition in air and in vacuum [5]. The results of these investigations show that in a flow of air, at a heating rate of $20 \text{ deg} \cdot \text{h}^{-1}$, dehydration takes place at about 100°C . The anhydrous double salt is stable in the interval $110\text{--}550^\circ\text{C}$, and it then starts to decompose, with melting at about 680°C . The decomposition of the salt subsequently accelerates, but it is still not finished at 1000°C .

In vacuum (10^{-5} mm Hg and a heating rate of $10 \text{ deg}\cdot\text{h}^{-1}$), dehydration takes place at about 65°C . Up to 550°C the anhydrous double salt is stable, and it then decomposes up to 800°C .

However, there are no literature data on the thermal decomposition in an inert atmosphere. The purpose of our investigation, therefore, was to study the thermal behavior in both air and nitrogen. The results obtained were compared with the literature data [5].

Experimental

Procedure

– The double sulfate with general formula $\text{Na}_2\text{Cd}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$ was obtained by two different procedures:

1. By slow evaporation of an aqueous mixture of $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ and $\text{CdSO}_4\cdot 8/3\text{H}_2\text{O}$ in a molar ratio of 1:1.

2. By decreasing the solubility of the salt, by adding a few drops of absolute ethanol to an aqueous mixture of the simple salts.

In the first case, the crystallization took place very slowly, while in the second case the white crystals were obtained almost immediately. The crystals obtained were filtered off, washed with a solution of ethanol and dried in air. The product was identified by chemical analysis, X-ray powder diffraction and TG and DTA analysis.

Apparatus and methods

– Gravimetric methods were used for the determination of the water and the sulfate group. Sodium was determined by flame atomic absorption spectrometry, and cadmium by complexometry.

The X-ray powder diffraction patterns were obtained on a JEOL diffractometer, model JDX-7E, with Ni-filtered $\text{CuK}\alpha$ radiation, and with a goniometer, model DX-GO-F.

TG and DTA analyses were performed on a NETZSCH thermoanalyser in air in the range $20\text{--}1500^\circ\text{C}$, and in nitrogen in the range $20\text{--}1000^\circ\text{C}$, at a heating rate of $10 \text{ deg}\cdot\text{min}^{-1}$. The isothermal measurements at 260 and 600°C in air were recorded on the same instrument in Pt crucibles, with $\alpha\text{-Al}_2\text{O}_3$ as reference substance.

Results and discussion

The results of the chemical analyses of the compounds obtained by the two different methods are given in Table 1. It can be seen that in both cases the

Table 1 Results of chemical and TG analyses of $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$

%	Theoretical	Experimental	
		by slow evaporation	by decreasing the solubility
H_2O	9.32	9.00	9.45
Cd	29.08	30.08	30.00
SO_4	49.70	50.90	49.20
Na	11.80	12.60	11.20

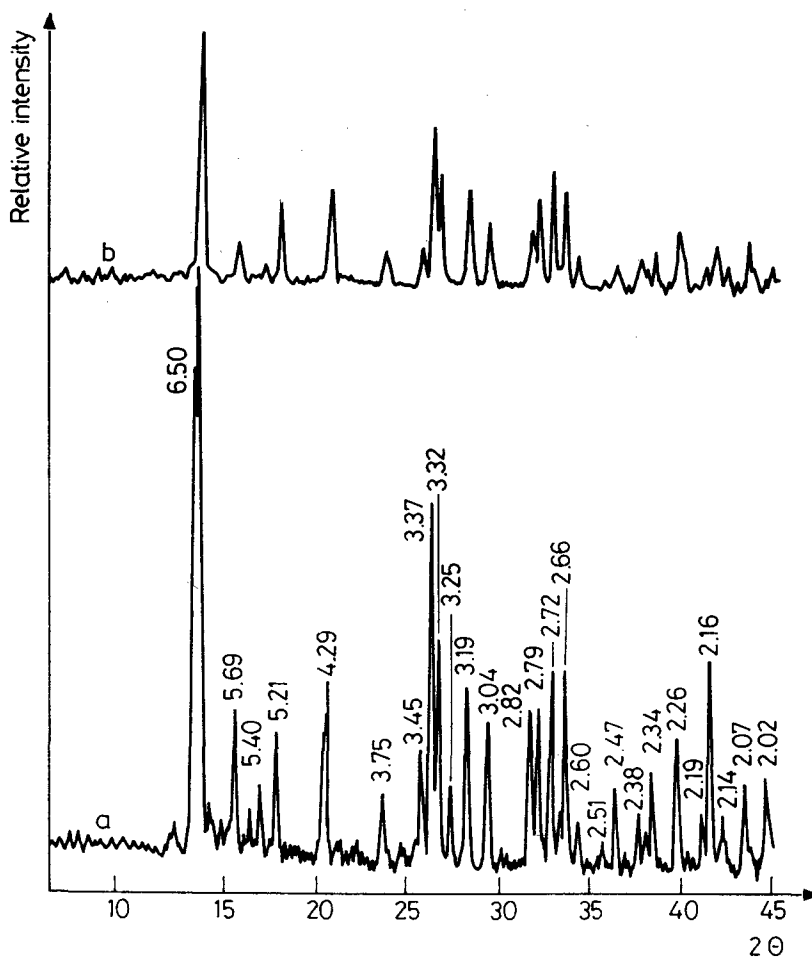


Fig. 1 X-ray powder diffraction patterns of $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, a) by slow evaporation; b) by decreasing the solubility. The d -values given by Cot in Å are: 6.50; 5.67; 5.20; 4.32; 3.75; 3.45; 3.37; 3.32; 3.26; 3.15; 3.04; 2.82; 2.79; 2.73; 2.67; 2.61; 2.51; 2.47; 2.39; 2.34; 2.26; 2.19; 2.17; 2.14; 2.07; 2.03; 2.00; 1.87; 1.86; 1.83; 1.82; 1.79; 1.76 Å

same compound was obtained, corresponding to the general formula $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$.

X-ray powder diffraction patterns of the crystals are shown in Fig. 1. It can be seen that the crystals obtained by the two different methods have the same structure. The crystals obtained by slow evaporation were usually larger. In this paper, therefore only the results of investigation the double sulfate obtained by this method are presented.

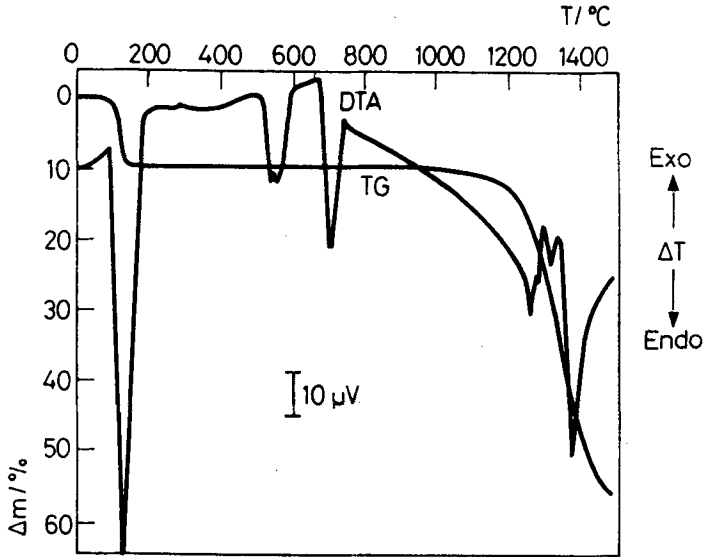


Fig. 2 TG and DTA curves of $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, at temperature of 20–1500°C, recorded in air, heating rate 10 deg·min⁻¹

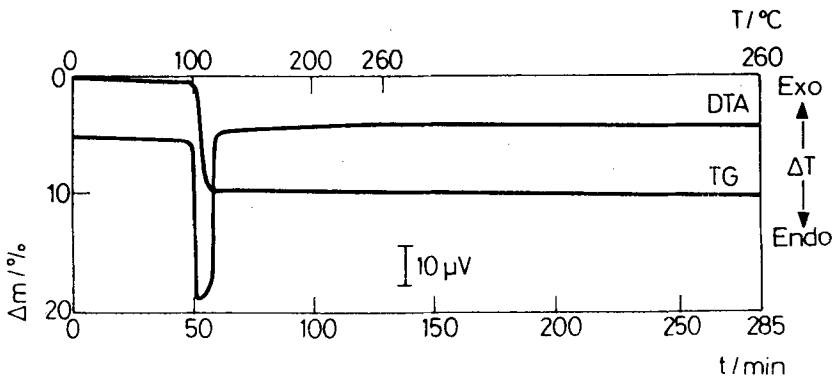


Fig. 3 TG and DTA curves of $\text{Na}_2\text{Cd}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, at temperature range of 20–260°C, recorded in air, heating rate to 260°C, 2 deg·min⁻¹

The TG and DTA curves recorded in air at a heating rate of $10 \text{ deg}\cdot\text{min}^{-1}$ are given in Fig. 2.

Dehydration takes place in the interval $90\text{--}190^\circ\text{C}$, with an endotherm at 120°C . At 540 , 560 and 700°C , there are some endotherms not connected with mass loss, which suggested that phase transitions were probably taking place. The anhydrous double salts decomposes at about 1000°C , which is not in agreement with the literature data [5].

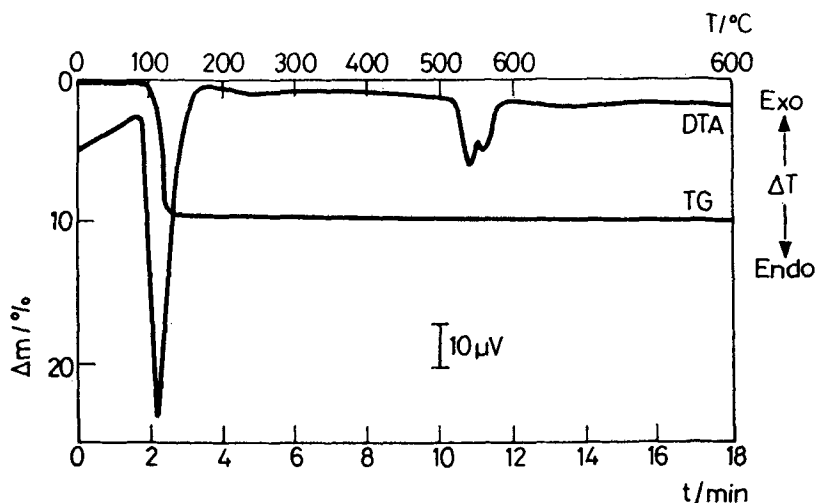


Fig. 4 TG and DTA curves of $\text{Na}_2\text{Cd}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$, at temperature range of $20\text{--}600^\circ\text{C}$, recorded in air, heating rate to 600°C , $2 \text{ deg}\cdot\text{min}^{-1}$

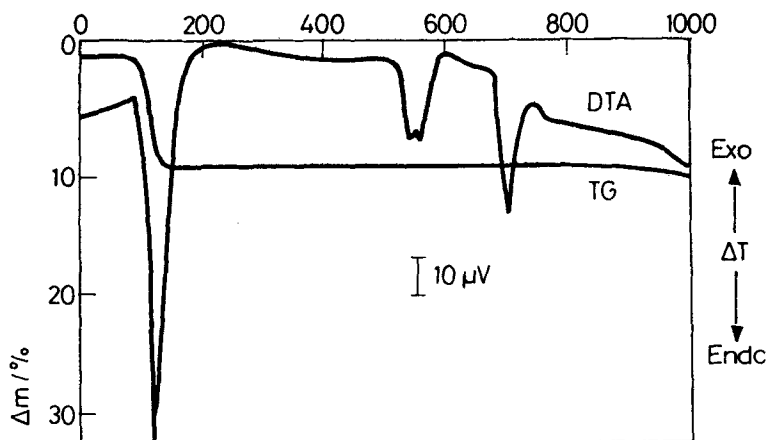


Fig. 5 TG and DTA curves of $\text{Na}_2\text{Cd}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$, at temperature range of $20\text{--}1000^\circ\text{C}$, recorded in nitrogen, heating rate $10 \text{ deg}\cdot\text{min}^{-1}$

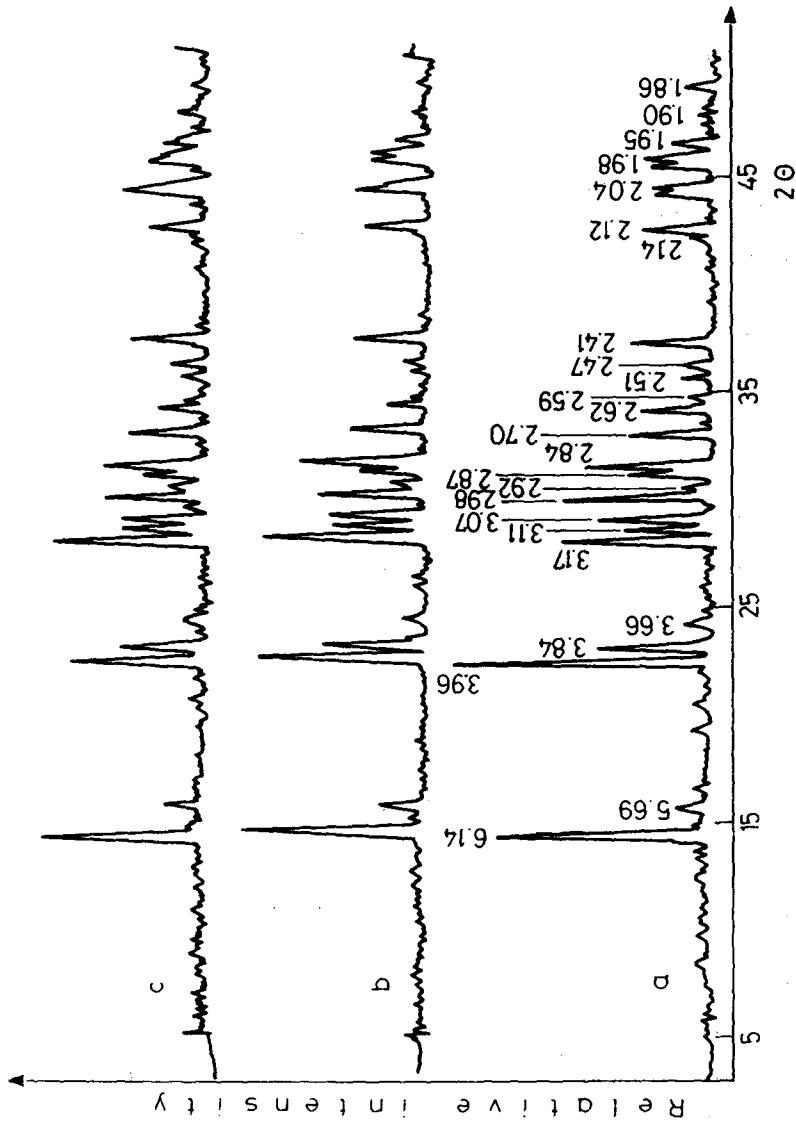


Fig. 6 X-ray diffraction patterns of residues: a) at 260°C; b) at 600°C; c) at 1000°C. The d -values of $\text{Na}_2\text{Cd}(\text{SO}_4)_2$ given by Cot in Å, are: 6.02; 5.59; 3.92; 3.82; 3.63; 3.14; 3.09; 3.04; 2.95; 2.91; 2.82; 2.69; 2.61; 2.58; 2.51; 2.47; 2.39; 2.12; 2.06; 2.04; 1.98; 1.95; 1.92 and 1.89 Å

In order to establish what kind of transitions took place, isothermal measurements at 260 and 600°C were carried out, and the residues of the thermal decomposition were identified by X-ray powder diffraction.

The TG curve obtained at 260°C at a heating rate of 2 deg·min⁻¹ is presented in Fig. 3. The substance was then heated at 260°C for about 150 min. The experimental mass loss at this temperature (9.25%) is in good agreement with the value calculated for two water molecules (9.35%). The residue is white. The X-ray powder diffraction patterns (Fig. 6a) show that it is a crystal substance with a structure different from that of the initial substance. Cot *et al.* have reported that the crystal structure of Na₂Cd(SO₄)₂·2H₂O is monoclinic, with space group *P2₁/c* [5]. In the same paper, there are data on the *d* values of the anhydrous salt, obtained from the X-ray powder diffraction patterns. No other literature data have been reported on the crystal structure of the anhydrous salt. The X-ray powder diffraction patterns and the *d* values of the residue at 260°C are given in Fig. 6a. The obtained *d* values are in agreement with the literature data given by Cot *et al.*

The isothermal measurement at 600°C (Fig. 4) was performed under the same experimental conditions as the previous ones, but at a heating rate of 5 deg·min⁻¹, followed by heating at 600°C for about 60 min. The residue was a white melt with a crystal structure almost identical to that of the crystals previously obtained at 260°C. This was confirmed by the X-ray powder diffraction patterns (Fig. 6b).

Thermal decomposition in an inert atmosphere (nitrogen) was performed at a heating rate of 10 deg·min⁻¹. The TG and DTA curves are given in Fig. 5. It is evident that the decomposition in an inert atmosphere is almost identical to that in air. The decomposition of the sulfate in nitrogen takes place above 1000°C, as in air (Fig. 2).

The X-ray powder diffraction of the residue obtained in nitrogen is almost the same as that obtained in air. At about 700°C, an endotherm appears in the DTA curve, which is not accompanied by any mass loss. It is probably due to phase transitions, but this crystal form (at 700°C) is not stable, so only the initial crystal form exists at lower temperatures. This can be concluded from the X-ray powder diffraction patterns of the residues obtained at 260, 600 and 1000°C (Fig. 6).

Conclusion

From the discussion given above, it can be concluded that:

1. The substance Na₂Cd(SO₄)₂·2H₂O can be synthesized by slow evaporation of an aqueous mixture of CdSO₄·8/3H₂O and Na₂SO₄·10H₂O in a molar ratio of 1:1, or by decreasing the solubility of the same solution with ethanol.

2. In both cases the same product was obtained, but with different degrees of crystallinity.

3. The product obtained by slow evaporation had a higher degree of crystallinity.

4. In both air and nitrogen, dehydration takes place in the temperature range 90–190°C. Decomposition of the sulfate in air takes place above 1000°C, as in nitrogen. This is not in agreement with the literature data given by Cot *et al.* [5], probably because of the difference in heating rate (20 deg·h⁻¹ in air and 10 deg·h⁻¹ in vacuum [5], and 10 deg·min⁻¹ in our measurements, both in air and in nitrogen).

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Zusammenfassung — Es wird die Herstellung und die thermische Zersetzung von Na₂Cd(SO₄)₂·2H₂O sowohl in Luft als auch in Stickstoff beschrieben. Die Synthese erfolgte mittels zwei verschiedener Verfahren, jedoch wurde in beiden Fällen das gleiche Produkt mit obiger allgemeinen Formel erhalten.

Die erhaltenen Kristalle wurden mittels Röntgenpulverdiffraktion, chemischer als auch thermischer Analyse untersucht. Die Unterschiede zwischen der thermischen Zersetzung in Luft beziehungsweise Stickstoff werden diskutiert.