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Preparation of CdS by Thermal Decomposition of Double Salts and Saturated Solutions of the Systems $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH

M. Stoev*, **S. Ruseva**, and **B. Keremidchieva**

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria

Summary. The solubility isotherms of the systems $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH have been investigated at 25 °C. Reagents for the equilibrium existence of the salts $Cd(HCOO)_2$, $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$, $CS(NH_2)_2$, $Cd(CH_3COO)_2$, $Cd(CH_3COO)_2 \cdot CS(NH_2)_2$, and $Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$ are found. The preparation of CdS by thermal decomposition of double salts and from saturated solutions by the dip technique are discussed.

Keywords. Solubility; Double salt; Decomposition; Cadmium sulfide.

Herstellung von CdS durch thermische Zersetzung von Doppelsalzen und gesättigten Lösungen der Systeme $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH und $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH

Zusammenfassung. Untersucht werden die Löslichkeitsisothermen der Systeme $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH und $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH bei 25 °C. Die Kristallisationsfelder der Salze $Cd(HCOO)_2$, $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$, $CS(NH_2)_2$, $Cd(CH_3COO)_2$, $Cd(CH_3COO)_2 \cdot CS(NH_2)_2$ und $Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$ werden bestimmt. Die Herstellung von CdS durch thermische Zersetzung von Doppelsalzen und gesättigten Lösungen anhand des Tauchverfahrens wird diskutiert.

Introduction

CdS based thin solid films are widely used in solid state devices such as photoconductors, solar cells, thin film transistors and electroluminescence cells. The application of chemical methods (solution growth, spray pyrolysis and dip technique) to the preparation of CdS films requires knowledge of the solubility diagrams of the type cadmium salt–thiourea–solvent. The solubility diagram of the system $Cd(CH_3COO)_2$–$CS(NH_2)_2$–H_2O is known [1], whereas no data are available on systems of the type cadmium salt–thiourea–organic solvent, from which CdS films are obtained using the dip technique [2]. The present paper represents a continuation of our studies on the crystallization of salts in the cadium salt–thiourea–methanol systems [3], from which semiconducting materials may be obtained. The subject of our investigation were the solubility diagrams of the ternary systems $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH at 25 °C. It was aimed at obtaining CdS from these systems by thermal decomposition of double salts and from saturated solutions using the dip technique.

Table 1. Solubility isotherms for the $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH systems at 25 °C

No.	Liquid phase (mass %)			Wet residue (mass %)		Equil. sol. phase
$Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH						
	CH_3OH	$CS(NH_2)_2$	$Cd(HCOO)_2$	$CS(NH_2)_2$	$Cd(HCOO)_2$	
1	99.20	0.00	0.80	–	–	$Cd(HCOO)_2$
2	98.98	0.10	0.92	10.55	48.41	$Cd(HCOO)_2$ + $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$
3	97.39	1.48	1.13	31.00	40.57	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$
4	96.51	1.99	1.50	32.50	42.94	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$
5	92.84	5.18	1.98	31.15	40.39	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$
6	90.36	7.78	1.86	27.21	33.33	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$
7	84.82	13.21	1.97	35.00	42.01	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$
8	82.21	14.82	2.97	53.00	24.95	$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ + $CS(NH_2)_2$
9	83.61	14.72	1.67	59.23	1.00	$CS(NH_2)_2$
10	85.83	13.37	0.80	72.42	0.50	$CS(NH_2)_2$
11	88.05	11.95	0.00	–	–	$CS(NH_2)_2$
$Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH						
	CH_3OH	$CS(NH_2)_2$	$Cd(CH_3COO)_2$	$CS(NH_2)_2$	$Cd(CH_3COO)_2$	
1	82.39	0.00	17.61	–	–	$Cd(CH_3COO)_2$
2	81.22	0.29	18.49	0.27	57.66	$Cd(CH_3COO)_2$
3	78.91	1.05	20.04	1.02	62.66	$Cd(CH_3COO)_2$
4	76.72	1.57	21.71	13.69	68.62	$Cd(CH_3COO)_2$ + $Cd(CH_3COO)_2 \cdot CS(NH_2)_2$
5	85.85	0.42	13.73	17.50	56.67	$Cd(CH_3COO)_2 \cdot CS(NH_2)_2$
6	94.80	0.82	4.38	18.01	53.24	$Cd(CH_3COO)_2 \cdot CS(NH_2)_2$
7	95.06	1.14	3.80	15.27	45.52	$Cd(CH_3COO)_2 \cdot CS(NH_2)_2$
8	96.03	1.18	2.79	15.14	46.02	$Cd(CH_3COO)_2 \cdot CS(NH_2)_2$
9	91.41	3.37	5.22	19.35	44.29	$Cd(CH_3COO)_2 \cdot CS(NH_2)_2$ + $Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$
10	90.37	4.59	5.04	31.44	48.37	$Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$
11	84.77	8.01	7.22	31.48	47.94	$Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$
12	56.11	24.99	18.90	38.68	56.42	$Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$
13	52.33	26.98	20.69	38.15	54.27	$Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$
14	42.29	33.65	24.06	43.66	41.99	$Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$ + $CS(NH_2)_2$
15	46.86	31.66	21.48	94.00	4.66	$CS(NH_2)_2$
16	71.21	18.94	9.85	73.80	3.16	$CS(NH_2)_2$
17	76.61	17.22	6.17	83.57	1.52	$CS(NH_2)_2$
18	80.24	16.09	3.67	92.45	0.42	$CS(NH_2)_2$
19	85.29	13.67	1.04	90.52	0.36	$CS(NH_2)_2$
20	87.32	12.68	–	–	–	$CS(NH_2)_2$

Results and Discussion

Equilibria in the $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH systems at 25 °C

The results concerning the equilibria in the systems $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH are presented in Table 1. The solubility isotherm of the system $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH at 25 °C, given in Fig. 1, shows the equilibrium coexistence of the solid phases $Cd(HCOO)_2$, $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$, and $CS(NH_2)_2$. In the ternary systems the anhydrous salts $Cd(HCOO)_2$ and $CS(NH_2)_2$ are not solvated by methanol in the form of crystalline solvates, and the appearing double salt $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ is incongruently soluble. The solubility isotherm of the system $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH at 25 °C (Fig. 2) consists of four regions of equilibrium coexistence of the salts $Cd(CH_3COO)_2$, $Cd(CH_3COO)_2 \cdot CS(NH_2)_2$, $Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$, and $CS(NH_2)_2$. The double salt $Cd(CH_3COO)_2 \cdot CS(NH_2)_2$ can be obtained from the solution by isothermal evaporation of the methanol.

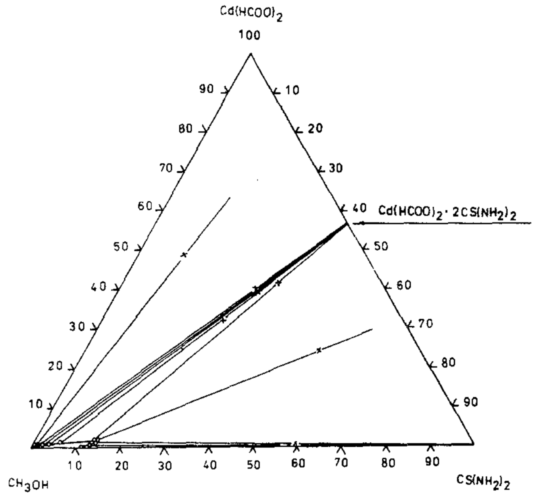

Fig. 1. Solubility isotherm of the $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH system at 25 °C

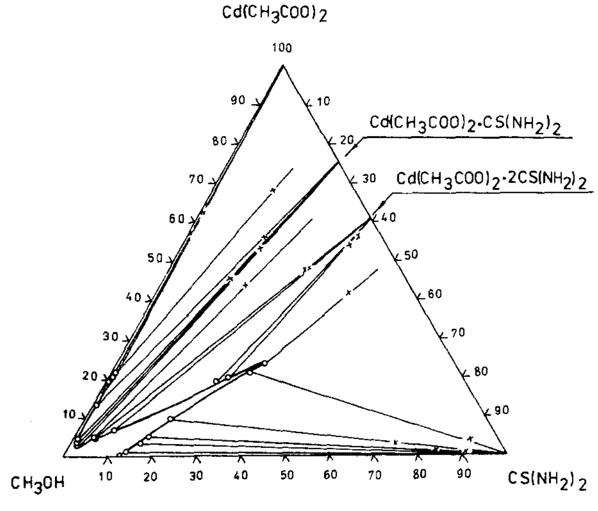

Fig. 2. Solubility isotherm of the $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH systems at 25 °C

Preparation of CdS by thermal decomposition of double salts and saturated solutions

The double salts $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$, $Cd(CH_3COO)_2 \cdot CS(NH_2)_2$, and $Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$ prepared from the systems under consideration were subjected to DTA and TG analyses. Figure 3 presents the DTA curves of the double salts and the thiourea, while the thermal data are given in Table 2.

With rising temperature, the thiourea melts at 170 °C, while the corresponding double salts melt as follows: $Cd(HCOO)_2 \cdot CS(NH_2)_2$ at 160 °C, $Cd(CH_3COO)_2 \cdot CS(NH_2)_2$ at 130 °C, and $Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$ at 150 °C. Further heating of the double salts leads to dissociation of $CS(NH_2)_2$ at 230 °C and 370 °C, complete decomposition of thiourea being achieved at 620 °C. Anhydrous $Cd(HCOO)_2$ decomposes at 255–400 °C [11], and $Cd(CH_3COO)_2$ at 250–340 °C [12], the final decomposition product being CdO. Above the melting temperature, the double salts are dissociated by decomposition of the thiourea and the formate and acetate anions, the weight losses being due to evolving gases. The decomposition of $CS(NH_2)_2$ is accompanied by evolution of H_2S, which reacts with the cadium salts, forming CdS [13]. For that reason, the weight losses during experiments on double salt decom-

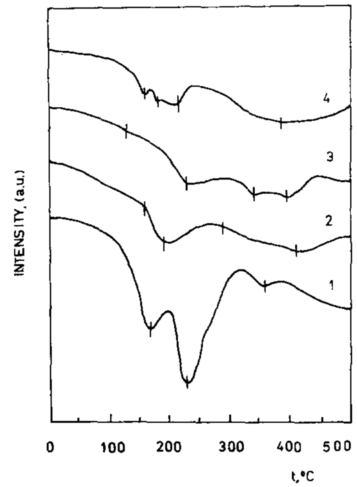

Fig. 3. DTA curves of $CS(NH_2)_2$, 670 mg (1); $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$, 340 mg (2); $Cd(CH_3COO)_2 \cdot CS(NH_2)_2$, 420 mg (3); $Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$, 450 m (4)

Table 2. Thermal data from T, DTA, DTG and TG curves concerning samples from the $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH systems

Sample	Melting point T (°C)	Dissociation peak maximum T (°C)	Theor. value of $CS(NH_2)_2$ (mass %)	Weight losses at 400 °C (mass %)
$CS(NH_2)_2$	170	230, 370	100.00	83.58
$Cd(HCOO)_2 \cdot 2CS(NH_2)_2$	160	190, 280, 400	42.92	54.41
$Cd(CH_3COO)_2 \cdot CS(NH_2)_2$	130	220, 330, 390	24.83	42.86
$Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$	150	180, 220, 380	39.79	74.44

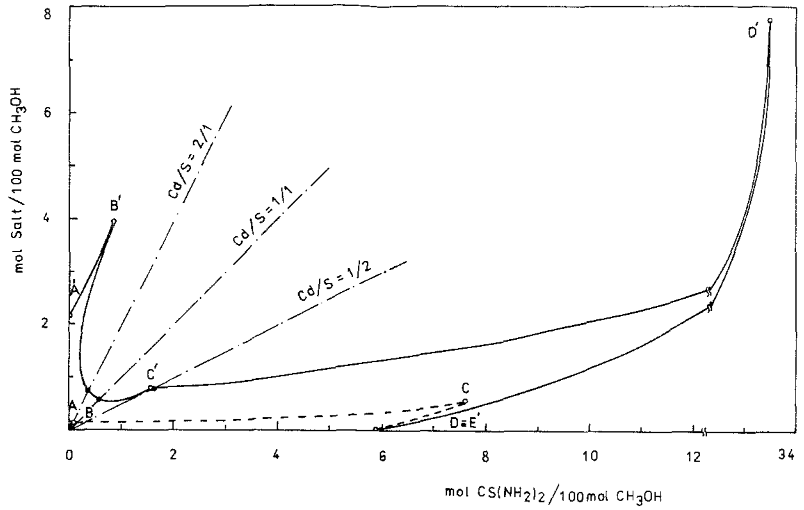

Fig. 4. Graphic determination of the concentrations of the saturated solutions $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH used for preparation of CdS films by the dip technique with Cd:S ratios of 2:1, 1:1, and 1:2; ——— : $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH, ----- : $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH, $AB = Cd(HCOO)_2$, $BC = Cd(HCOO)_2 \cdot 2CS(NH_2)_2$, $CD = D'E' = CS(NH_2)_2$, $A'B' = Cd(CH_3COO)_2$, $B'C' = Cd(CH_3COO)_2 \cdot CS(NH_2)_2$, $C'D' = Cd(CH_3COO)_2 \cdot 2CS(NH_2)_2$

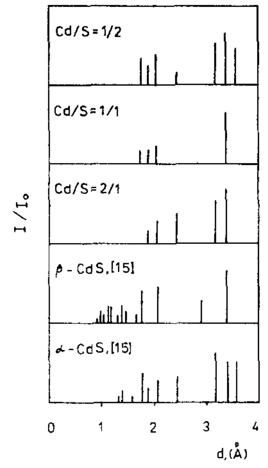

Fig. 5. X-ray analysis of CdS samples obtained by the dip technique from saturated $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH solutions after 5 min at 400 °C in air

position are larger than those theoretically calculated for the thiourea. The CdS obtained at 400 °C is unstable at higher temperatures, sublimates easily and is oxidized by the oxygen from the air to CdO. Decomposition of the double salts in order to obtain CdS must take place in a short time (5 min) at temperatures not exceeding 400 °C. Figure 4 shows the solubility isotherms of the systems $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH and $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH used for graphical determination of the concentrations of solutions for the preparation of cadmium sulfide films by the dip technique. Glass substrates were placed into the saturated solutions of the double salts, whose compositions were found from the point of intersection of the solubility isotherm of the ternary system with the line for the present composition of the film. Slow removal of the substrates from the solutions led to evaporation of the methanol from the substrate surfaces and formation of a film of congruently soluble double salts or simple salts. The films obtained by the dip technique were calcined at 400 °C under air in a furnace for 5 min. The CdS films obtained from the saturated solutions of the system $Cd(HCOO)_2$–$CS(NH_2)_2$–CH_3OH were amorphous. Figure 5 illustrates the effect of the saturated solution compositions of the system $Cd(CH_3COO)_2$–$CS(NH_2)_2$–CH_3OH on the structure of the CdS film established by X-ray diffraction. In the CdS films obtained by the dip technique there are cubic and hexagonal structures similar to CdS films obtained by spray pyrolysis [14].

Experimental

In the systems under investigation, equilibria were achieved by intense stirring and thermostatting the liquid and the solid phases at 25 °C ± 0.1 °C for 24 h. The solid and liquid equilibrium phases were separated by filtering on a G4 filter and their compositions were determined by chemical analyses. Determination of Cd^{2+} was performed by direct complexometric titration with Eryochrome Black T as indicator and 0.05 *M EDTA* in an ammonia buffer (*pH* 10) [4]. The amount of thiourea was established by its oxidation with hydrogen peroxide to sulfate ions and determination of the latter by classical gravimetric analysis [5]. The methanol content was calculated as the difference to 100%. The compositions of the solid phases were determined graphically by *Schreinemaker*'s method [6], X-ray and DTA analysis. The X-ray analysis was carried out with a DRON-2 X-ray diffractometer using a Cu anode, K_α radiation and a Ni filter for β radiation. The DTA analysis was performed in a corundum crucible at a heating rate of 10 °C/min under air using a Paulik-Paulik-Erdey derivatograph. The samples investigated were $CS(NH_2)_2$ (a.r., Merck) as well as $Cd(HCOO)_2$ and $Cd(CH_3COO)_2$ obtained by dehydration of $Cd(HCOO)_2 \cdot 2H_2O$ (a.r.) and $Cd(CH_3COO)_2 \cdot 2H_2O$ (a.r.) in a thermal way [7, 8]. Anhydrous CH_3OH was obtained by a standard dehydration procedure [9]. The amount of water in the dehydrated initial substances and in the systems was controlled by potentiometric titration with the reagent of K. Fischer [10].

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