Monatshefte für Chemie 125, 599–606 (1994)

Monatshefte für Chemie
Chemical Monthly
© Springer-Verlag 1994
Printed in Austria

Preparation of Cadmium Sulfide from $CdCl_2(CdBr_2, CdI_2)$-$CS(NH_2)_2$-CH_3OH Systems

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Summary. The solubility isotherms of the ternary systems CdX_2-$CS(NH_2)_2$-CH_3OH (X = Cl, Br, I) at 25 °C have been investigated. The fields of equilibrium existence of the salts $CdCl_2 \cdot 2CH_3OH$, $CdCl_2 \cdot 2CS(NH_2)_2$, $CS(NH_2)_2$, $CdBr_2 \cdot 3CH_3OH$, $CdBr_2 \cdot CS(NH_2)_2$, $CdBr_2 \cdot 2CS(NH_2)_2$, CdI_2 and $CdI_2 \cdot 2CS(NH_2)_2$ were determined. The formation of CdS by thermal dissociation of double salts and saturated solutions is discussed.

Keywords. Cadmium Sulfide; Equilibrium; Solubility isotherm; Thermal dissociation.

Kadmiumsulfid-Herstellung aus $CdCl_2(CdBr_2,CdI_2)$-$CS(NH_2)_2$-CH_3OH – Systemen

Zusammenfassung. Die Löslichkeitskurven der ternären Systeme CdX_2-$CS(NH_2)_2$-CH_3OH (X = Cl, Br, I) wurden untersucht. Die Gleichgewichtsbereiche der Salze $CdCl_2 \cdot 2CH_3OH$, $CdCl_2 \cdot 2CS(NH_2)_2$, $CS(NH_2)_2$, $CdBr_2 \cdot 3CH_3OH$, $CdBr_2 \cdot CS(NH_2)_2$, $CdBr_2 \cdot 2CS(NH_2)_2$, CdI_2 und $CdI_2 \cdot 2CS(NH_2)_2$ wurden bestimmt. Die Bildung von CdS als durch thermische Zersetzung von Doppelsalzen und gesättigten Lösungen wird diskutiert.

Introduction

The present investigations in nonaqueous medium with the participation of thiourea represent a continuation of our previous studies on the equilibria in the systems $CdCl_2$-H_2O-CH_3OH [1], $CdBr_2$-H_2O-CH_3OH [2] and $CS(NH_2)_2$-H_2O-$CH_3OH(C_2H_5OH)$ [3]. Semiconducting materials based on CdS are prepared from the systems $CdCl_2(CdBr_2)$-$CS(NH_2)_2$-H_2O [4] and CdI_2-$CS(NH_2)_2$-H_2O [5] in an aqueous medium using chemical precipitation [6] and spray pyrolysis [7]. Our investigations of the systems CdX_2-$CS(NH_2)_2$-CH_3OH (X = Cl, Br, I) in a nonaqueous medium mark the beginning of studies on the role of the solvent during the preparation of double salts and solutions for CdS-based semiconducting thin solid films using a dip technique [8] and thermal dissociation.

Experimental

The equilibria in the ternary systems were established by intensive stirring and thermostatting of the samples in an ultrathermostat at 25 °C (±0.1 °C) for 24 h. The equilibrium liquid and solid phases were separated by filtering through a G4 filter and their compositions were determined by chemical analyses. The Cd^{2+} content was determined by direct complexometric titration with Eriochrome Black T as indicator and by 0.05 *M EDTA* in an ammonium buffer (*pH* 10) [9]. The amount of thiourea was found by its oxidation with hydrogen peroxide to sulfate ions followed by their determination by the classical gravimetric analysis [10]. The remaining percentage (to 100 mass%) was ascribed to methanol. The compositions of the equilibrium solid phases were established by *Schreinemaker's* method [11], X-ray, DTA and DTG analyses. X-ray analysis was performed with a DRON-2 diffractometer using a Cu-anode, K_α radiation and a Ni-filter for β radiation. The DTA and DTG analyses of the samples were carried out in a corundum crucible with a heating rate of 10 °C/min under air using a *Paulik-Paulik-Erday* derivatograph [12]. The samples investigated were $CS(NH_2)_2$ (*p.a.*, Merck) and thermally dehydrated $CdCl_2$ and $CdBr_2$ (from $CdCl_2 \cdot 2.5H_2O$ (*p.a.*) and $CdBr_2 \cdot 4H_2O$, (*p.a.*), respectively) [13, 14]. Anhydrous CH_3OH was prepared by a standard dehydration procedure [15]. The amount of water in the dehydrated initial substances and in the system was controlled by potentiometric titration with the reagent of *K. Fisher* [16].

Results and Discussion

Equilibria in the $CdCl_2(CdBr_2,CdI_2)$-$CS(NH_2)_2$-CH_3OH systems at 25 °C

The results concerning the equilibria in the systems $CdCl_2$-$CS(NH_2)_2$-CH_3OH, $CdBr_2$-$CS(NH_2)_2$-CH_3OH, and CdI_2-$CS(NH_2)_2$-CH_3OH are given in Table 1. The solubility isotherm of the $CdCl_2$-$CS(NH_2)_2$-CH_3OH system presented in Fig. 1 indicates the equilibrium coexistence of the solid phases $CdCl_2 \cdot 2CH_3OH$, $CdCl_2 \cdot 2CS(NH_2)_2$ and $CS(NH_2)_2$. The crystalline solvate $CdCl_2 \cdot 2CH_3OH$ exists in the binary system $CdCl_2$-CH_3OH [17] and is strongly hygroscopic. The increase in concentration of the thiourea in the systems ensures a constant $CdCl_2$ concentration in the solution and formation of a region of equilibrium existence of the double salt $CdCl_2 \cdot 2CS(NH_2)_2$ [18]. The field of the thiourea exists within a narrow concentration range (from 84.46–88.05 mass% CH_3OH). The solubility isotherm of the $CdBr_2$-$CS(NH_2)_2$-CH_3OH system is presented in Fig. 2. It consists of four fields of equilibrium coexistence of the salts $CdBr_2 \cdot 3CH_3OH$, $CdBr_2 \cdot CS(NH_2)_2$, $CdBr_2 \cdot 2CS(NH_2)_2$ and $CS(NH_2)_2$. The increase in the thiourea concentration leads to an increase in the solubility of $CdBr_2$ in the field of equilibrium existence of the crystalline solvate $CdBr_2 \cdot 3CH_3OH$ present in the binary system $CdBr_2$-CH_3OH [17]. The fields of equilibrium coexistence of the double salts $CdBr_2 \cdot CS(NH_2)_2$ and $CdBr_2 \cdot 2CS(NH_2)_2$ [19] are characterized by a complicated complexation due to a salting-out process and a subsequent enhancement of the $CdBr_2$ solubility. The double salt $CdBr_2 \cdot 2CS(NH_2)_2$ is congruently soluble and can be obtained from the solution by isothermal evaporation of the methanol. The solubility isotherm of the system CdI_2-$CS(NH_2)_2$-CH_3OH shown in Fig. 3 evidences the equilibrium state of the salts CdI_2, $CdI_2 \cdot 2CS(NH_2)_2$ [19] and $CS(NH_2)_2$. The solubility of CdI_2 increases with the thiourea concentration in the field of CdI_2 and above 10.70 mass% $CS(NH_2)_2$ salting-out of $CdI_2 \cdot 2CS(NH_2)_2$ and $CS(NH_2)_2$ begins. The introduction of a negligible amount of water into the solutions of the anhydrous ternary systems under consideration leads to deposition of CdS. This circumstance might be used for distinguishing between the preparation of CdS in nonaqueous medium and its formation in a mixed water-methanol solvent.

Table 1. Solubility isotherms for the CdX_2-$CS(NH_2)_2$-CH_3OH (X = Cl, Br, I) Systems at 25 °C

No.	Liquid phase (mass %)			Wet residue (mass %)		Equil. sol. phase
$CdCl_2$-$CS(NH_2)_2$-CH_3OH						
	CH_3OH	$CS(NH_2)_2$	$CdCl_2$	$CS(NH_2)_2$	$CdCl_2$	
1	98.40	0.00	1.55	–	–	$CdCl_2 \cdot 2CH_3OH$
2	97.71	0.43	1.86	8.73	33.56	$CdCl_2 \cdot 2CH_3OH$ + $CdCl_2 \cdot 2CS(NH_2)_2$
3	97.24	1.37	1.39	33.55	40.36	$CdCl_2 \cdot 2CS(NH_2)_2$
4	92.08	5.22	2.70	38.75	46.68	$CdCl_2 \cdot 2CS(NH_2)_2$
5	91.00	6.95	2.05	28.00	31.50	$CdCl_2 \cdot 2CS(NH_2)_2$
6	90.50	7.42	2.08	29.01	33.35	$CdCl_2 \cdot 2CS(NH_2)_2$
7	89.38	8.73	1.89	31.05	33.95	$CdCl_2 \cdot 2CS(NH_2)_2$
8	85.32	12.91	1.77	30.00	31.21	$CdCl_2 \cdot 2CS(NH_2)_2$
9	85.46	12.57	1.97	46.97	29.82	$CdCl_2 \cdot 2CS(NH_2)_2$
10	84.47	13.13	2.40	51.48	1.00	$CdCl_2 \cdot 2CS(NH_2)_2$ + $CS(NH_2)_2$
11	98.31	13.83	1.69	75.50	0.89	$CS(NH_2)_2$
12	85.31	12.70	1.99	82.71	0.54	$CS(NH_2)_2$
13	88.05	11.95	0.00	–	–	$CS(NH_2)_2$
						$CS(NH_2)_2$
$CdBr_2$-$CS(NH_2)_2$-CH_3OH						
	CH_3OH	$CS(NH_2)_2$	$CdBr_2$	$CS(NH_2)_2$	$CdBr_2$	
1	84.50	0.00	15.50	–	–	$CdBr_2 \cdot 3CH_3OH$
2	72.84	3.15	24.01	0.28	65.57	$CdBr_2 \cdot 3CH_3OH$
3	64.60	6.04	29.36	2.22	60.10	$CdBr_2 \cdot 3CH_3OH$
4	62.34	6.07	31.59	2.60	59.38	$CdBr_2 \cdot 3CH_3OH$
5	61.67	6.22	32.11	2.55	62.23	$CdBr_2 \cdot 3CH_3OH$
6	55.12	7.00	37.88	2.08	67.29	$CdBr_2 \cdot 3CH_3OH$ + $CdBr_2 \cdot CS(NH_2)_2$
7	55.99	8.10	35.91	18.31	63.98	$CdBr_2 \cdot CS(NH_2)_2$
8	58.01	7.65	34.34	13.94	51.52	$CdBr_2 \cdot CS(NH_2)_2$
9	61.10	7.47	31.43	16.90	61.41	$CdBr_2 \cdot CS(NH_2)_2$
10	61.40	7.60	31.00	22.65	58.14	$CdBr_2 \cdot CS(NH_2)_2$ + $CdBr_2 \cdot CS(NH_2)_2$
11	66.00	6.50	27.50	29.50	54.50	$CdBr_2 \cdot 2CS(NH_2)_2$
12	73.96	6.85	19.19	31.00	57.15	$CdBr_2 \cdot 2CS(NH_2)_2$
13	79.08	7.20	13.72	29.02	54.50	$CdBr_2 \cdot 2CS(NH_2)_2$
14	80.47	6.82	12.71	31.93	60.85	$CdBr_2 \cdot 2CS(NH_2)_2$
15	73.75	12.36	13.89	31.85	59.88	$CdBr_2 \cdot 2CS(NH_2)_2$
16	70.09	14.30	15.61	33.21	60.09	$CdBr_2 \cdot 2CS(NH_2)_2$
17	65.41	17.28	17.31	33.50	59.53	$CdBr_2 \cdot 2CS(NH_2)_2$
18	62.24	19.62	18.14	29.30	53.52	$CdBr_2 \cdot 2CS(NH_2)_2$
19	58.87	21.90	19.23	35.02	63.14	$CdBr_2 \cdot 2CS(NH_2)_2$
20	52.98	24.81	21.21	33.63	58.49	$CdBr_2 \cdot 2CS(NH_2)_2$
21	50.92	27.49	21.59	62.38	17.70	$CdBr_2 \cdot 2CS(NH_2)_2$ + $CS(NH_2)_2$
22	51.85	27.07	21.08	79.16	5.44	$CS(NH_2)_2$
23	51.79	27.76	20.45	62.72	9.15	$CS(NH_2)_2$

(*continued*)

Table 1. (*continued*)

No.	Liquid phase (mass %)			Wet residue (mass %)		Equil. sol. phase
24	56.12	24.53	19.35	79.21	4.22	$CS(NH_2)_2$
25	59.24	24.28	16.48	72.98	5.73	$CS(NH_2)_2$
26	64.37	21.00	14.63	75.48	3.42	$CS(NH_2)_2$
27	67.91	20.42	11.67	77.73	2.80	$CS(NH_2)_2$
28	70.22	18.98	10.80	74.03	2.74	$CS(NH_2)_2$
29	74.00	17.30	8.70	82.22	1.30	$CS(NH_2)_2$
30	88.05	11.95	0.00	–	–	$CS(NH_2)_2$
CdI_2-$CS(NH_2)_2$-CH_3OH						
1	38.89	0.00	61.11	–	–	CdI_2
2	38.71	0.29	61.00	0.05	82.20	CdI_2
3	35.99	2.65	61.36	0.47	84.06	CdI_2
4	31.04	6.58	62.38	3.35	80.23	CdI_2
5	27.23	9.63	63.14	4.17	81.37	CdI_2
6	25.50	10.70	63.80	14.36	72.30	$CdI_2 + CdI_2 \cdot 2CS(NH_2)_2$
7	24.46	12.22	61.32	20.28	65.08	$CdI_2 \cdot 2CS(NH_2)_2$
8	27.37	12.58	60.05	21.53	65.17	$CdI_2 \cdot 2CS(NH_2)_2$
9	29.96	13.76	56.28	22.17	63.64	$CdI_2 \cdot 2CS(NH_2)_2$
10	32.32	13.48	54.20	20.00	59.65	$CdI_2 \cdot 2CS(NH_2)_2$
11	34.69	15.26	50.05	21.52	58.82	$CdI_2 \cdot 2CS(NH_2)_2$
12	34.74	18.34	46.92	25.97	61.37	$CdI_2 \cdot 2CS(NH_2)_2$
13	31.60	21.63	46.77	26.88	58.48	$CdI_2 \cdot 2CS(NH_2)_2$
14	30.81	25.85	43.34	27.54	56.13	$CdI_2 \cdot 2CS(NH_2)_2$
15	26.29	30.11	43.60	51.29	36.25	$CdI_2 \cdot 2CS(NH_2)_2 + CS(NH_2)_2$
16	31.79	27.06	41.15	34.00	37.29	$CS(NH_2)_2$
17	33.84	25.86	40.30	91.40	5.52	$CS(NH_2)_2$
18	39.90	23.60	36.50	61.07	19.54	$CS(NH_2)_2$
19	47.11	22.59	30.30	65.27	14.61	$CS(NH_2)_2$
20	56.17	20.58	23.58	83.23	4.80	$CS(NH_2)_2$
21	71.79	16.00	12.21	63.53	6.00	$CS(NH_2)_2$
22	88.05	11.95	0.00	–	–	$CS(NH_2)_2$

Preparation of CdS from double salts and saturated solutions

The double salts obtained from the systems under consideration were subjected to DTA and TG analyses. Figure 4 presents the DTA curves of the double salts and thiourea, while the thermal data are given in Table 2. Rising the temperature up to 180 °C causes the double salts and thiourea to melt. The DTA curve of $CdI_2 \cdot 2CS(NH_2)_2$ exhibits an endothermic effect at 140 °C which is due to a phase transition of the double salt. At 230 °C the thiourea decomposes, producing an endothermic effect, whereas an exothermic effect is observed with the double salts. Further increase of temperature leads to endothermic effects due to the dissociation of the thiourea and the double salts, as a result of which CdS appears at 400 °C. The complete decomposition of thiourea occurs at 620 °C, while thiourea existing as a double salt decomposes at 400 °C. As a result of the thermal dissociation of the

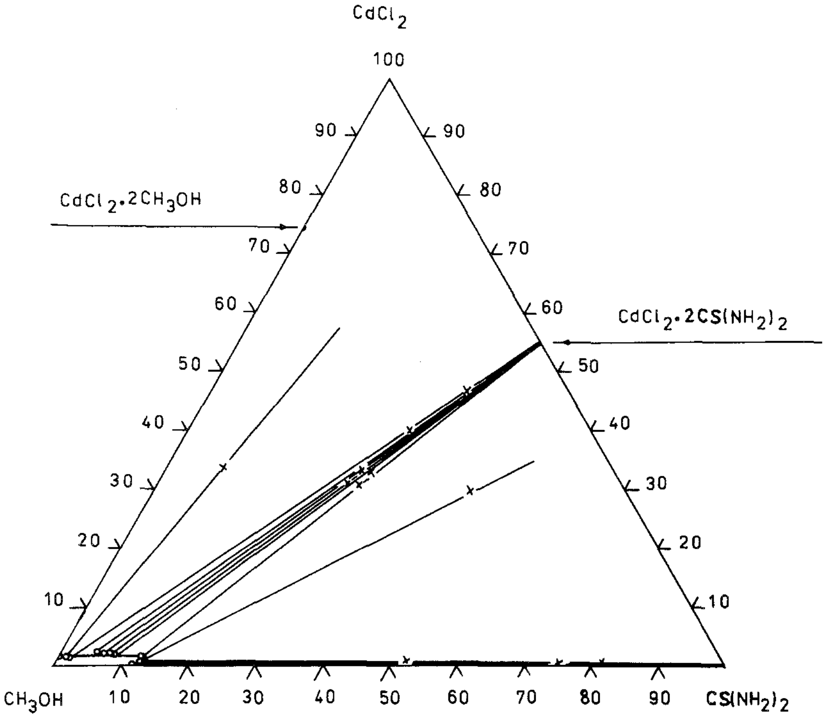

Fig. 1. Solubility isotherm for the $CdCl_2$-$CS(NH_2)_2$-CH_3OH System at 25 °C

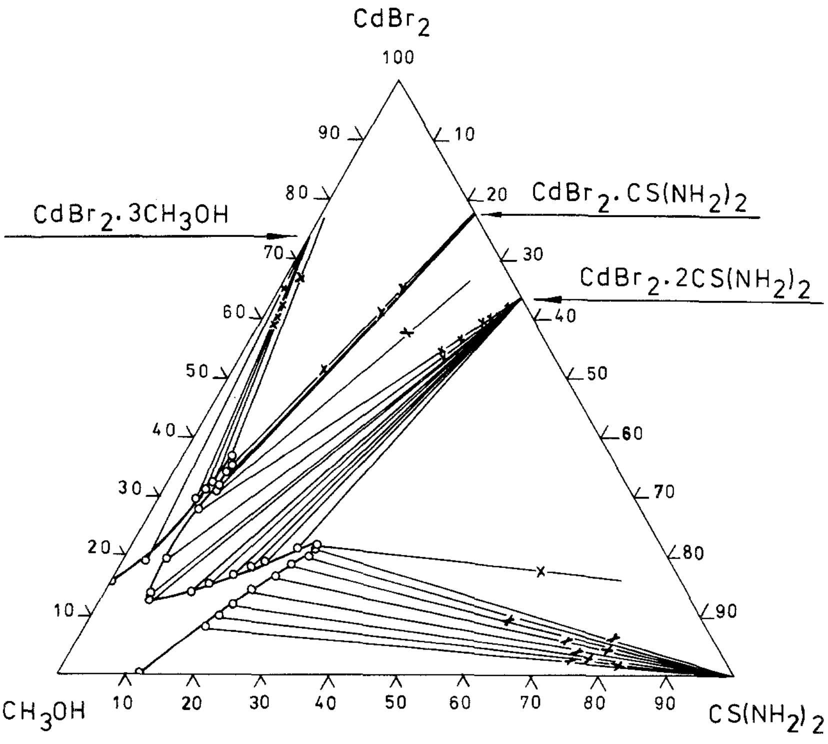

Fig. 2. Solubility isotherm for the $CdBr_2$-$CS(NH_2)_2$-CH_3OH System at 25 °C

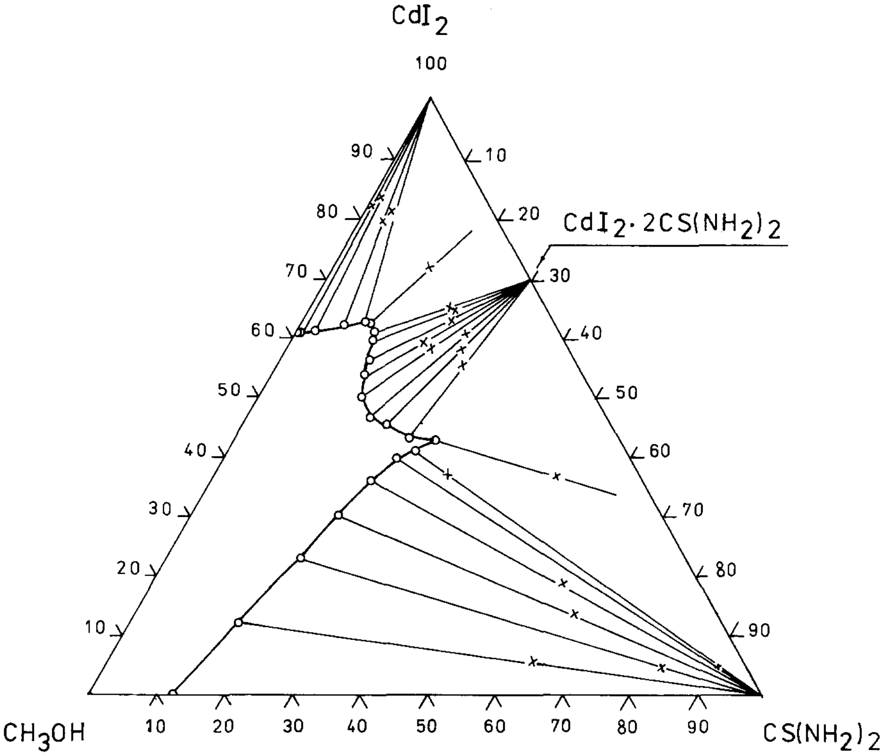

Fig. 3. Solubility isotherm for the CdI$_2$-CS(NH$_2$)$_2$-CH$_3$OH System at 25 °C

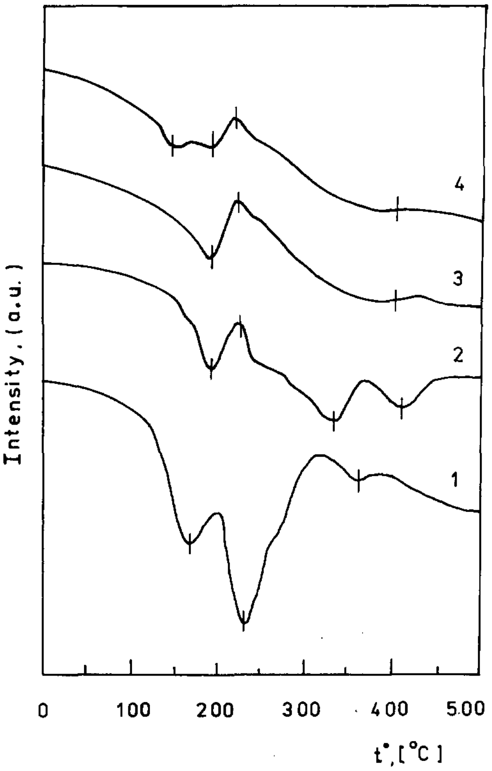

Fig. 4. DTA curves of the samples:
1 – CS(NH$_2$)$_2$, 670 mg
2 – CdCl$_2$·2CS(NH$_2$)$_2$, 770 mg
3 – CdBr$_2$·2CS(NH$_2$)$_2$, 350 mg
4 – CdI$_2$·2CS(NH$_2$)$_2$, 540 mg

Table 2. Thermal data obtained from T, DTA, DTG, and TG curves

Sample	Melting (°C)	Dissociation (°C)	Exper. found weight losses up to 400 °C (mass %)	Theoret. values of $CS(NH_2)_2$ (mass %)
$CS(NH_2)_2$	170	230, 370	83.58	100.00
$CdCl_2 \cdot 2CS(NH_2)_2$	180	230, 340, 410	44.45	45.33
$CdBr_2 \cdot 2CS(NH_2)_2$	180	230, 400	34.28	35.83
$CdI_2 \cdot 2CS(NH_2)_2$	140, 180	220, 400	29.63	29.33

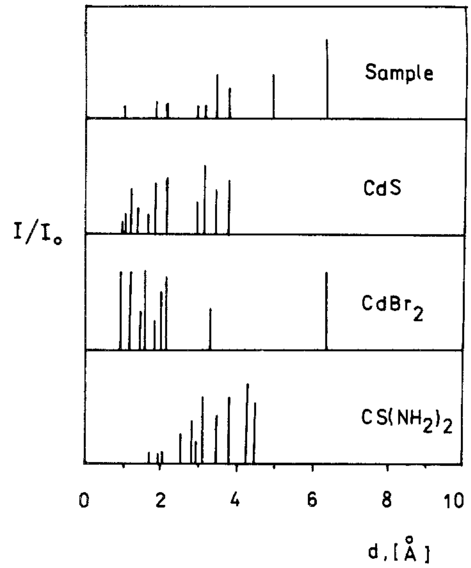

Fig. 5. X-ray analyses of the sample (CdS prepared by dip technique, heating at 400 °C, 5 min in the air atmosphere) from $CdBr_2$-$CS(NH_2)_2$-CH_3OH system

double salt, CdS and anhydrous cadmium halides are formed. The CdS obtained easily sublimates and is oxidized by the oxygen in the air at temperatures above 400 °C. Glass substrates were placed in the saturated solutions of the double salts of the above systems. When the substrates were pulled slowly out of the solutions, the methyl alcohol evaporated and a film of the congruently soluble double salts remained on the substrate surface. The layers obtained by this dip technique were calcined under air in a furnace at 400 °C for 5 min. The X-ray data of the CdS formed are shown in Fig. 5. The anhydrous cadmium halides are dissociated at temperatures much higher than 400 °C due to the fact that the halide X = Cl, Br and I is strongly bound in a CdX_2 compond. This is the reason for contamination of the CdS layer by anhydrous cadmium halides when the preparation from double salts and saturated solutions is achieved by a thermal process.

Conclusions

The anhydrous salts $CdCl_2$ and $CdBr_2$ in the systems $CdCl_2(CdBr_2)$-$CS(NH_2)_2$-CH_3OH are solvated with methanol, forming the crystalline solvates $CdCl_2 \cdot 2CH_3OH$

and $CdBr_2 \cdot 3CH_3OH$, while CdI_2 and $CS(NH_2)_2$ remain unsolvated in the ternary systems.

The double salts $CdCl_2 \cdot 2CS(NH_2)_2$, $CdBr_2 \cdot 2CS(NH_2)_2$ and $CdI_2 \cdot 2CS(NH_2)_2$ are congruently soluble and can be isolated from the saturated solutions by isothermal evaporation of methanol.

Thermal dissociation of the double salts of the systems investigated and application of the dip technique allow preparation of CdS from the saturated solutions.

Acknowledgements

Thanks are due to the Bulgarian Ministry of Science and Education for the financial support under Project X-81.

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Received July 6, 1993. Accepted July 28, 1993