JOURNAL OF SOLID STATE CHEMISTRY **80**, 75–79 (1989)

Synthesis of a New Orthorhombic Metastable Form of CdS through Solid-State Reactions

M. KIZILYALLI,* M. BİLGİN,† AND A. USANMAZ

Middle East Technical University, Chemistry Department,
Ankara 06531, Turkey

Received October 28, 1988; in revised form January 19, 1989

CdS has been prepared through solid–gas reactions of CdO with a sulfidizing gas mixture, at 750°C for 3 hr, and slow cooling under nitrogen atmosphere. The X-ray diffraction data of the product was indexed in a hexagonal system with unit cell parameters of $a = 4.136$ and $c = 6.713$ Å, which agreed with the literature data. However, the presence of extra strong lines in the X-ray diffraction pattern and the splitting in the d-spacings showed that a new orthorhombic form of CdS was obtained. The unit cell dimensions were found to be $a = 14.315$, $b = 14.074$, and $c = 14.568$ Å and the space group was found to be *Pnnn*. The IR absorption spectrum showed the formation of pure CdS. The X-ray powder pattern of this phase which was taken after 2 years showed only the presence of the hexagonal phase reported in the literature. This proved that the orthorhombic phase is metastable.

Introduction

The stable form of CdS (greenockite, $a = 4.135$, $b = 6.712$ Å, space group $P6_3mc$) is hexagonal with a wurtzite-type structure (*1*), but in addition to this form a cubic zinc blend-type (hawleyite, $a = 5.833$ Å, space group $F43m$) and some complicated polytypes (*2*) are also known. At a pressure of about 20 kb, CdS is transferred into a rock salt type (*3*) ($a = 5.516$ Å, space group $Fm3m$). Another form of CdS was also reported by Miller *et al.* (*4*) at high temperatures and pressures.

In the literature there are numerous methods for the preparation of CdS. In addition to well-known solution reactions, solid-state and melt techniques to obtain pure CdS and thin films for solar cell applications were also reported (*5*, *6*). Novak (*7*) prepared a very pure compound by heating a LiCl, KCl melt mixture containing $CdCl_2$ at 400°C with H_2S or Na_2SO_3 and washing the reaction product with water. Lanbies and Beltran (*8*) used a thermal analysis technique and obtained hexagonal and cubic forms from a mixture of solid CdO and sulfur. The same method was used by Kornilow *et al.* (*9*), but only a wurtzite type of CdS was obtained. Photosensitive films of CdS were synthesized by Miranova and Veksina (*10*) from CdC_2O_4 and sulfur sintering reactions. Photoconductive CdS was prepared by Cannon (*11*) through sintering a cadmium salt with a sulfide powder at 450°C and then washing the product.

---

* To whom correspondence should be addressed.

† Formerly M. Çetin. Present address: Türkiye Elektrik Kurumu, Ankara, Turkey.

0022-4596/89 $3.00

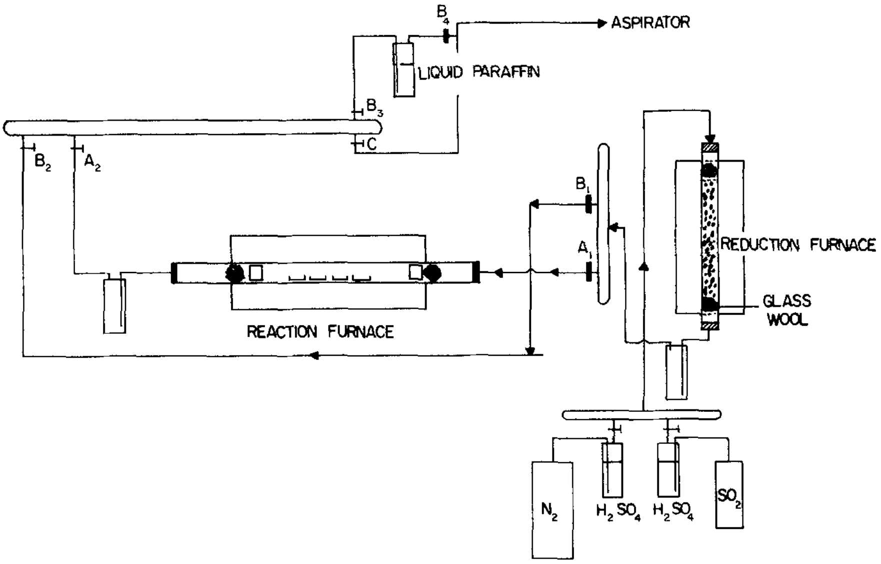

FIG. 1. The sulfidizing and reduction chambers.

On the other hand, if CdO is heated either in the flow of carbon disulfide, CS_2, carbonyl sulfide, COS vapor, or with the mixture of CO and sulfur, the solid–gas reactions are assumed to be (*12*):

$$2CdO + CS_2 \rightarrow 2CdS + CO_2$$

$$CdO + COS \rightarrow CdS + CO_2$$

$$2CdO + 2CO + S_2 \rightarrow 2CdS + 2CO_2.$$

The reducing and sulfidizing gas mixture containing CS_2, COS, CO, and small amounts of CO_2 and sulfur vapor was obtained when SO_2 was passed through activated charcoal at 1000, 1200, and 1400 K (*13*). This sulfidizing and reducing gas mixture was used to prepare bornite, Cu_5FeS_4, stoichiometric and nonstoichiometric chalcopyrites, $CuFeS_2$, and cubanite, $CuFe_2S_3$, from Fe_2O_3 and CuO (*14–16*) or iron and copper metals instead of oxides.

For the preparation of CdS, the device (*16*) used to obtain the copper–iron sulfides mentioned above was employed (Fig. 1). This paper discusses the formation conditions of a new phase of CdS and its structure as determined from powder X-ray diffraction and infrared absorption spectra.

Experimental

The starting materials were cadmium oxide (Merck analar grade) and technical-grade sulfur dioxide. SO_2 gas was bubbled through a wash bottle containing concentrated sulfuric acid, then transferred to a vertical tubular furnace filled with activated charcoal and heated at 700–850°C. The resulting sulfidizing and reducing gas mixture was passed through a horizontal tubular furnace which contained around 0.5 g of CdO in a porcelain boat inserted in the middle of a silica tube (length, 60 cm; inside diameter, 2.5 cm). The reaction temperatures employed in the different runs were 700, 750, and 800°C. While keeping the temperature constant, the reaction times were changed from 1 to 5 hr. The products obtained were cooled, weighed, and analyzed for sulfur content by oxidizing sulfide to sulfate with bromine and then by precipitating it as $BaSO_4$ (*17*).

TABLE I

X-RAY POWDER DIFFRACTION DATA OF CdS RAD. Cu$K\alpha$ (λ = 1.54178 Å)

JCPDS Card No. 6-314, hex., a = 4.136, c = 6.713 Å; space group = $P6_3mc$			Present work, orthorhombic, a = 14.315, b = 14.074, c = 14.568 Å; space group $Pnnn$			
I/I_0	d (Å)	hkl	I/I_0	d_{obs}	d_{calc}	hkl
—	—	—	55	3.641	3.641	004
75	3.58	100	65	3.578	3.578	400
—	—	—	70	3.520	3.519	040
—	—	—	40	3.408	3.404	303
60	3.36	002	45	3.363	3.373	033
—	—	—	40	3.339	3.345	330
—	—	—	40	3.303	3.308	313
—	—	—	85	3.200	3.189	420
100	3.16	101	100	3.167	3.168	042
—	—	—	100	3.153	3.158	240
—	—	—	90	3.126	3.131	412,214
—	—	—	20	2.488	2.487	305
—	—	—	28	2.475	2.475	035,441
—	—	—	35	2.467	2.466	503
25	2.45	102	40	2.447	2.456	530
—	—	—	35	2.437	2.435	053
55	2.068	110	100	2.067	2.066	444
—	—	—	100	2.062	2.060	107
—	—	—	75	1.902	1.902	037
40	1.898	103	85	1.896	1.896	722
—	—	—	25	1.792	1.791	526
18	1.791	200	25	1.789	1.789	800
45	1.761	112	80	1.762	1.763	028
—	—	—	80	1.759	1.759	080
18	1.731	201	35	1.734	1.734	820,181
—	—	—	40	1.727	1.727	464
4	1.674	004	10	1.679	1.681	437
—	—	—	10	1.5851	1.5854	084,841
8	1.581	202	10	1.5816	1.5815	663
—	—	—	10	1.5777	1.5788	480,735
2	1.520	104	5	1.5207	1.5207	664
16	1.398	203	40	1.3985	1.3977	$22\underline{10}$,419
—	—	—	20	1.3574	1.3580	491
6	1.3536	210	20	1.3533	1.3537	718
12	1.3271	211	30	1.3275	1.3277	943
—	—	—	30	1.3259	1.3260	$\underline{10}40$
8	1.3032	114	18	1.3034	1.3038	667
—	—	—	15	1.3015	1.3014	766
12	1.2572	—	36	1.2563	1.2560	196
—	—	—	30	1.2552	1.2549	874
2	1.2247	204	5	1.2255	1.2249	$3\underline{10}5$
8	1.1940	300	25	1.1931	1.1930	$\underline{12}00$
12	1.1585	213	38	1.1586	1.1580	$2\underline{12}0$
—	—	—	38	1.1593	1.1598	$5\underline{10}5$
8	1.1249	302	18	1.1252	1.1254	$\underline{10}08$
6	1.0743	205	16	1.0749	1.0751	$16\underline{12}$
—	—	—	10	1.0727	1.0733	796

The formation of a single-phase product was ascertained by X-ray powder diffraction studies using a Philips PW 1050/25, JRX-8P X-ray diffractometer and a Guinier–De Wolff Camera No. II with Cu$K\alpha$ radiation. The IR absorption spectra were obtained with a Perkin–Elmer 1430 ratio recording spectrophotometer in the range 4000–200 cm^{-1}, using KBr pellets. The IR spectrum of pure CdS from BDH (optran) was also recorded for comparison purposes.

Results and Discussion

The optimum condition for the preparation of pure CdS was found to be a 3-hr reaction at 700–750°C. Yellow, crystalline CdS (1–2 mm) was obtained by slow cooling in nitrogen atmosphere and was found to be stable in air for about 6 months. It was identified as CdS by sulfur analysis (21.8% comparable to the theoretical value of 22.2%). However, experimental and calculated weights of reaction products were different due to a sublimation of CdS toward the walls of the silica tube, in a cooler zone of about 500–600°C, in the form of very small, thin single crystals.

The X-ray powder diffraction data of CdS was compared with the literature values (*18–20*) and an exact fit was observed for the lines allowed by the hexagonal structure, as shown in Table I (*21*). However, some extra strong lines observed in this work could not be indexed with this hexagonal unit cell.

A systematic investigation of the sin$^2\theta$ values especially in the high-angle region

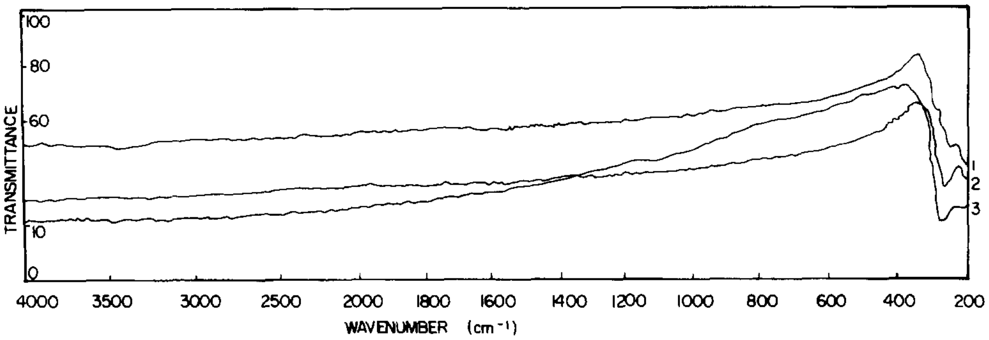

FIG. 2. IR spectrum of CdS (in KBr pellet), prepared through solid–gas reactions and from BDH (optran). Transmittance scale was chosen arbitrarily. (1) Orthorhombic form of CdS. (2) CdS from BDH (optran). (3) Hexagonal form of CdS.

indicated an orthorhombic symmetry with the unit cell parameters $a = 14.315$, $b = 14.074$, and $c = 14.568$ Å. The cell parameter relations between hexagonal and orthorhombic cells are found to be:

$$\text{(i) } a_{\text{orth}} \sim 2\sqrt{3}a_{\text{hex}}$$

$$\text{(ii) } a_{\text{orth}} \sim \frac{3}{\sqrt{2}}c_{\text{hex}}$$

$$\text{(iii) } a_{\text{hex}} \sim \frac{b_{\text{orth}}c_{\text{orth}}}{\sqrt{6(b^2_{\text{orth}}c^2_{\text{orth}})}}.$$

The systematic absences in *hkl* values (Table I) showed that the space group is *Pnnn*. The IR spectrum, which agreed with the data of Nyquist and Kagel (*22*), indicated the product is pure CdS (Fig. 2). The IR spectrum of pure CdS from BDH is identical to that of the product obtained in this work. The IR peak observed at about 280 cm^{-1} is similar to the peak reported by Mitsuishi *et al.* (*23*) for zinc and cadmium sulfide and is attributed to lattice vibrations.

The X-ray powder diffraction pattern of orthorhombic CdS, done after 2 years, showed the structural change to the hexagonal form, but no change occurred in the IR spectrum of the sample after this period.

In this work a new crystal form of CdS was prepared with larger unit cell dimensions. This new orthorhombic metastable form would be quite important for semiconducting properties and solar cell applications if it could be prepared in a stable form. More work is also needed to prepare single crystals of appreciable size to refine cell parameters and verify the space group given.

Acknowledgments

The authors thank METU Research Fund, 87-01-03-07 and university grant commission for supporting this research project.

References

1. H. Ahlburg and R. Caines, *J. Phys. Chem.* **66,** 185 (1962); JCPDS Card No. 6-314.
2. A. S. Pashinkin and L. N. Kovba, *Kristallografia* **7,** 316 (1962); *Sov. Phys. Kristallogr.* **7,** 247 (1962); JCPDS Card No. 10-454.
3. C. J. M. Roymans, *Phys. Lett.* **6,** 42 (1963).
4. R. O. Miller, F. Dachille, and R. Roy, *J. Appl. Phys.* **37,** 4913 (1966).
5. B. F. Shirreffs, C. H. Cheng, K. Geib, and K. A. Jones, *J. Electrochem. Soc.* **131**(2), 440 (1984).
6. H. P. Muruska, J. L. Sansregret, and R. A. Young, US 4, 331, 707 (Cl. 427-74 B05D1/02) 25 May (1982).
7. J. Novak, Czech. 152, 579 (Cl. COlb) 15 March (1974).
8. V. Lanbies and J. Beltran, *Rev. Acad. Cienc. Exactas Fis. Quim. Nat. Zaragoza* **32**(3–4), 169 (1977).
9. N. I. Kornilow, L. I. Sova, and V. N. Khudolozhkin, *Konf. Fiz. Khim. Ionnykh, Rasplavov Tverd. Electrol. USSR, 7th,* **1,** 128–129 (1979).

10. I. A. Miranova and N. V. Veksina, Thesis Dokt. 93, Vses Nauchno-Issled Inst. Lyuminoforov, Osoko, Chist Vesh Chestv., Stavropol (1977).
11. K. K. Cannon, Japan. Kokai Tokkyo Koho JP 57, 189, 144 (82,189,144) 20 Nov. (1982).
12. M. Çetin, "Solid State Synthesis and X-ray Diffraction Studies of CdS, Na_2S and Na_2SO_4," Ms. Thesis, Middle East Tech. Univ., Ankara (1986).
13. A. J. Owen, K. W. Sykes, and D. J. D. Thomas, *Trans. Faraday Soc.* **47,** 419 (1951).
14. A. J. E. Welch, Interim Rep. Imperial College, London (1970).
15. M. Kizilyalli, Assoc. Prof. Thesis, Middle East Tech. Univ., Ankara (1977).
16. M. Kizilyalli and H. M. Kizilyalli, "Transport in Nonstoichiometric Compounds" (G. Simkovich, Ed.), Physics Series B, Vol. 441, Plenum, New York (1985).
17. H. I. Vogel, "Textbook of Quantitative Inorganic Analysis," p. 467, Longmans, London (1961).
18. NBS Circular 529, Vol. IV, p. 16 (1956).
19. M. Traill and C. Boyle, *Amer. Miner.* **40,** 555 (1955).
20. J. Osugi, K. Shimizu, K. Inoue, and K. Yasunami, *Rev. Phys. Chem. Japan* **36,** 59 (1966).
21. M. Çetin, M. Kizilyalli, and A. Usanmaz, "Proceedings, IVth Chem. and Chem. Eng. Symp., Firat Univ., Elaziğ, Turkey, 10–12 June, 1987," Abstr. AN-3, p. 123 (1987).
22. R. A. Nyquist and R. O. Kagel, "Infrared Spectra of Inorganic Compounds," 407, Academic Press, New York (1971).
23. A. Mitsuishi, H. Yoshinaga, and S. Fujita, *J. Phys. Soc. Japan* **13,** 1235 (1958).