JOURNAL OF SOLID STATE CHEMISTRY 5, 71–74 (1972)

The Synthesis and Properties of Cd_2P_3Cl, Cd_2P_3Br, and Cd_2P_3I*

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Received September 27, 1971

The new compounds Cd_2P_3X where X = Cl, Br, or I were prepared by chemical transport. They are isotypic, monoclinic, with space group $C2/c$, and cell dimensions: Cd_2P_3Cl, $a = 7.988 \pm 0.001$ Å, $b = 8.988 \pm 0.001$ Å, $c = 7.555 \pm 0.001$ Å, $\beta = 100.91 \pm 0.05°$; Cd_2P_3Br, $a = 8.089 \pm 0.001$ Å, $b = 9.089 \pm 0.001$ Å, $c = 7.535 \pm 0.001$ Å, $\beta = 100.36 \pm 0.05°$; Cd_2P_3I, $a = 8.255 \pm 0.001$ Å, $b = 9.304 \pm 0.001$ Å, $c = 7.514 \pm 0.001$ Å, $\beta = 99.66 \pm 0.05°$. They range in color from red for X = Cl to black for X = I and are semiconductors. They are hydrolytically stable but undergo an unusual reaction in conc HCl in which bubbles are evolved leaving an orange, flaky, amorphous form of P. Solid solutions of these compounds were prepared. The relationship of semiconducting properties to crystal structure is discussed.

Introduction

Group IIB elements form many pnictide halides and polyphosphides. $Cd_4Y_2X_3$, where X represents Cl, Br, and I, and Y represents P or As, are semiconductors and range in color from yellow to deep red (*1*). Preparation and cell dimensions have been reported for $Cd_4As_2Cl_3$, $Hg_4As_2X_3$ (X = Cl, Br, I) Cd_2AsCl_3, Hg_2AsCl_2, Cd_2AsCl_2, Hg_2SbBr_2, and Cd_4AsCl_3 (*2*, *3*). They are all transparent colored materials and undoubtedly semiconductors. Their complex formulas and semiconductivity indicate that simple valency, e.g., P^{3-}, As^{3-}, cannot apply and some form of complex anions must be present. The complex anions may be like polyphosphide ions such as occur in ZnP_2 (red form) (*4*) in which polyanions comprised of $(P)_n$ chains are present. If a valence of −1 for each P is assumed, the semiconductivity may be accounted for since each Zn is divalent and all valence electrons occupy bonding orbitals. The synthesis and properties of the new series Cd_2P_3X where X = Cl, Br, and I is reported in this study, and the relation between properties and structure is briefly discussed. Details of the structure are given elsewhere (*5*).

Experimental Methods

Cd_2P_3Cl and Cd_2P_3Br were prepared according to the equation

$$6Cd + PX_3 + 8P \rightarrow 3Cd_2P_3X \text{ where X = Cl, Br,}$$

from high purity Cd, P, and PX_3 (freshly opened), sealed in near-stoichiometric quantities in evacuated, silica tubes. A small excess of PX_3 and P was often used to enhance chemical transport. Heavy-walled silica (16 mm o.d., 10 mm i.d. by 7–8 in.) was used to contain high pressures generated during reactions in a two-zone tube furnace or a tube furnace with a natural gradient. Tubes were initially heated slowly with the end containing the reactants finally held at about 700°C, the other end at about 300°C for 1 or 2 days. Polycrystalline films with some crystals measuring about 1 mm on an edge were deposited from the vapor at about 400°C. Often, traces of CdP_4 or $CdCl_2$ were also present.

Cd_2P_3I was prepared from the elements with a small excess of I and P, to enhance chemical

* Contribution no. 1708.

TABLE I

X-RAY POWDER DIFFRACTION PATTERNS OF Cd_2P_3X, X = Cl, Br, I

Cd_2P_3Cl				Cd_2P_3Br				Cd_2P_3I			
I/I_0	$h\,k\,l$	D(obs)	D(calc)	I/I_0	$h\,k\,l$	D(obs)	D(calc)	I/I_0	$h\,k\,l$	D(obs)	D(calc)
20	1 1 0	5.9139	5.9099	25	−1 1 1	4.9998	4.9998	10	1 1 0	6.1221	6.1255
10	−1 1 1	4.9859	4.9816	5	0 2 0	4.5455	4.5445	30	−1 1 1	5.0409	5.0438
10	0 2 0	4.4959	4.4939	20	2 0 0	3.9769	3.9783	2	2 0 0	4.0647	4.0692
10	1 1 1	4.3311	4.3312	45	0 2 1	3.8749	3.8742	10	0 2 1	3.9381	3.9395
50	2 0 0	3.9224	3.9220	85	0 0 2	3.7048	3.7058	85	0 0 2	3.7027	3.7039
75	0 2 1	3.8448	3.8437	15	2 2 0	2.9929	2.9933	10	−1 1 2	3.3616	3.3631
80	0 0 2	3.7112	3.7093		−2 0 2		2.9935	2	2 2 0	3.0660	3.0628
2	−1 1 2	3.3628	3.3653	55	1 1 2	2.9756	2.9758	60	1 1 2	3.0050	3.0059
15	−2 0 2	2.9926	2.9925	100	−2 2 1	2.9170	2.9160	100	−2 2 1	2.9651	2.9657
45	1 1 2	2.9581	2.9576	35	0 2 2	2.8720	2.8720	30	0 2 2	2.8973	2.8976
100	−2 2 1	2.8911	2.8906	5	1 3 0	2.8326	2.8314	10	−1 3 1	2.7546	2.7552
45	0 2 2	2.8615	2.8607	5	−1 3 1	2.7037	2.7033	70	2 2 1	2.7116	2.7120
2	1 3 0	2.7993	2.7987	75	2 2 1	2.6537	2.6536	10	1 3 1	2.6460	2.6457
70	2 2 1	2.6203	2.6197	5	1 3 1	2.5911	2.5902	10	3 1 0	2.6035	2.6044
5	1 3 1	2.5631	2.5621	5	3 1 0	2.5458	2.5460	2	2 0 2	2.5348	2.5355
10	−3 1 1	2.5209	2.5213		−3 1 1		2.5468	2	−2 2 2	2.5200	2.5219
5	3 1 0	2.5099	2.5106	10	2 0 2	2.4967	2.4968	30	−1 1 3	2.3973	2.3976
5	−2 2 2	2.4895	2.4908		−2 2 2		2.4999	10	3 1 1	2.3415	2.3417
20	2 0 2	2.4718	2.4715	25	−1 1 3	2.4009	2.4012	30	0 4 0	2.3259	2.3259
25	−1 1 3	2.4067	2.4067	10	−1 3 2	2.3233	2.3227	5	−3 1 2	2.3096	2.3129
20	−1 3 2	2.3106	2.3104	10	3 1 1	2.2897	2.2894	5	1 3 2	2.2169	2.2189
20	0 4 0	2.2469	2.2469	25	0 4 0	2.2731	2.2723		0 4 1		2.2191
20	1 1 3	2.1731	2.1735	5	2 2 2	2.1894	2.1883	2	0 2 3	2.1811	2.1810
20	0 2 3	2.1667	2.1665	15	1 1 3	2.1824	2.1819	40	−2 2 3	2.0533	2.0532
10	0 4 1	2.1503	2.1505	15	0 4 1	2.1724	2.1724	20	4 0 0	2.0343	2.0346
25	−2 2 3	2.0455	2.0455	35	−2 2 3	2.0462	2.0462		−3 3 1		2.0354
15	4 0 0	1.9607	1.9610	25	3 3 0	1.9936	1.9956	2	2 4 0	2.0192	2.0193
30	2 4 0	1.9489	1.9497		−3 3 1		1.9960	2	−2 4 1	1.9932	1.9907
10	−2 4 1	1.9302	1.9308	25	4 0 0	1.9892	1.9891	35	0 4 2	1.9702	1.9697
30	0 4 2	1.9217	1.9218	10	2 4 0	1.9738	1.9731	20	−1 3 3	1.9378	1.9375
25	−4 0 2	1.8873	1.8876	15	−3 1 3	1.9494	1.9492	30	−4 0 2	1.9249	1.9248
30	−3 3 2	1.8536	1.8527	35	0 4 2	1.9375	1.9371	20	2 4 1	1.9085	1.9083
30	2 4 1	1.8436	1.8435	20	−1 3 3	1.9239	1.9235		3 3 1		1.9077
20	−4 2 1	1.8201	1.8206	35	−4 0 2	1.9006	1.9009	10	−3 3 2	1.8921	1.8920
20	4 2 0	1.7972	1.7973	35	2 4 1	1.8660	1.8657	10	4 2 0	1.8639	1.8641
	−2 4 2		1.7968		−3 3 2		1.8656	30	0 0 4	1.8521	1.8519
25	2 2 3	1.7761	1.7759	20	0 0 4	1.8529	1.8529	40	1 5 0	1.8141	1.8139
2	1 5 0	1.7521	1.7521	10	−4 2 1	1.8414	1.8413		2 2 3		1.8137
10	−1 5 1	1.7216	1.7216	10	4 2 0	1.8222	1.8222	5	−1 5 1	1.7776	1.7773
2	1 1 4	1.7030	1.7016	5	−2 4 2	1.8099	1.8099		−4 2 2		1.7785
10	4 2 1	1.6816	1.6813	25	2 2 3	1.7902	1.7091	2	1 1 4	1.7136	1.7138
5	0 4 3	1.6634	1.6630	5	1 5 0	1.7731	1.7721		2 4 2		1.7140
	2 4 2		1.6626	5	−1 5 1	1.7401	1.7394	10	4 0 2	1.6694	1.6690
10	−3 1 4	1.6412	1.6411	5	4 2 1	1.7055	1.7055	2	−1 5 2	1.6539	1.6537
15	4 0 2	1.6121	1.6121		1 1 4		1.7060	10	−3 1 4	1.6393	1.6391
10	−2 4 3	1.6063	1.6063	2	−2 2 4	1.6813	1.6806	2	−2 4 3	1.6310	1.6311
10	−1 3 4	1.5968	1.5970		2 4 2		1.6805	2	−5 1 1	1.6235	1.6235
2	−5 1 2	1.5310	1.5316	15	−3 1 4	1.6384	1.6389	5	−1 3 4	1.6048	1.6046
10	1 3 4	1.4993	1.5001	15	4 0 2	1.6349	1.6343		1 5 2		1.6055
10	−1 1 5	1.4901	1.4901	5	−2 4 3	1.6141	1.6135		5 1 0		1.6033
	−4 4 1		1.4903	5	−4 2 3	1.5978	1.5977	20	−3 5 1	1.5316	1.5317
15	4 4 0	1.4778	1.4775		−1 3 4		1.5980		4 4 0		1.5314
2	0 6 1	1.4682	1.4683	10	1 5 2	1.5730	1.5744	10	1 3 4	1.5198	1.5198
					2 0 4		1.5747		0 6 1		1.5177
								5	−4 0 4	1.5005	1.5006
									2 2 4		1.5029

transport in an evacuated silica tube as described above.

Solid solutions were prepared similarly using mixtures of PCl_3, PBr_3, and I.

Guinier X-ray powder photographs at 25°C with KCl as internal standard were made of all products. Cell dimensions were refined using a computerized least-squares technique. Powder patterns are shown in Table I.

Electrical measurements were made on single crystals by a four-probe technique (*6*) from room temperature to 4.2 K.

Cd_2P_3Cl

Crystals of Cd_2P_3Cl deposited as a wine-red crystalline film. Composition was determined by chemical analysis. Anal. calcd. for Cd_2P_3Cl: Cd, 63.65; P, 26.30; Cl, 10.04; found: Cd, 62.70; P, 26.16; Cl, 10.34. Lattice constants and space group were determined using Buerger precession camera techniques. Refined cell constants are: $a = 7.988 \pm 0.001$ Å, $b = 8.988 \pm 0.001$ Å, $c = 7.555 \pm 0.001$ Å, $\beta = 100.91 \pm 0.05°$. The space group is $C2/c$. Density was measured by a technique using displacement in bromoform. Anal. calcd. for $4(Cd_2P_3Cl)$ 4.40 g/cm$_3$; found $\rho = 4.31$ g/cm^3. Electrical measurements show semiconductivity: $\rho_{298°K} = 10^7$ ohm cm, $E_a = 0.6$ eV. The analysis for Cd is low, which may indicate nonstoichiometry or experimental error. The density would seem to indicate nonstoichiometry, however, the crystals show internal reflection of light from planes or lamella. Internal cracks could lead to a low observed density. The structure determination from single crystal data (*5*) showed no evidence for fractional site occupancy.

The compound is stable in water and 1:1 HCl. In concentrated HCl, bubbles are evolved without flame and the crystals are transformed to an orange flaky material having the same general shape as the original crystal. The flakes showed no X-ray pattern, and X-ray fluorescence analysis indicates pure P. The weight of the flakes indicates that they are comprised of $\frac{1}{3}$ of the original P in the crystal.

Cd_2P_3Br

Crystals formed as a red-brown polycrystalline film. Cell constants are $a = 8.089 \pm 0.001$ Å, $b = 9.089 \pm 0.001$ Å, $c = 7.535 \pm 0.001$ Å, $\beta = 100.36 \pm 0.05°$. The composition was established by chemical analysis: Anal. calcd. for Cd_2P_3Br: Cd, 56.51; Br, 20.1; P, 23.36; found: Cd, 56.11; Br, 20.65; P, 22.80. The deviations are probably due to experimental error.

Resistivity measurements show semiconductivity: $\rho_{298°K} = 1.0 \times 10^5$ ohm cm, $E_a = 0.7$ eV.

The material reacts in conc HCl as does Cd_2P_3Cl; yielding a similar product.

Cd_2P_3I

Cd_2P_3I deposits as a black polycrystalline film. Its composition was assumed by analogy since the crystal structure is isotypic with cell dimensions: $a = 8.255 \pm 0.001$ Å, $b = 9.304 \pm 0.001$ Å, $c = 7.514 \pm 0.001$ Å, $\beta = 99.66 \pm 0.05°$. It is also a semiconductor, $\rho_{298°K} = 10^7$ ohm cm (2 probe), $E_a = 0.2$ eV; and in conc HCl, it reacts like the others.

Solid solutions in the system Cd_2P_3(Cl,Br,I) were prepared; and a complete range of solid solubility is suggested.

Discussion

Group IIB elements seem to be unique in their ability to form pnictide halides, whose unusual formulas suggest the presence of polyanions. Their structures must be known if the type of bonding and its relationship to the semiconductivity is to be understood. The crystal structure of Cd_2P_3Cl has been solved and will soon be published (*5*). The P atoms form a zigzag, chain-like polyanion running in the c^* axis direction. Cl atoms bridge two Cd atoms in a direction perpendicular to the $(P)_n$ chains. The Cd atoms are bonded tetrahedrally to one Cl and three P atoms. The saturated valency leading to semiconductivity may be described by assignment $(Cd^{2+})_2(P^{1-})_3Cl^-$.

For these compounds, the c axis decreases on going from Cl to I while the volume increases. Thus the chain-like polyanion is a limiting structural feature, not tolerating expansion.

The chemical reaction of these compounds in HCl is interesting and suggests a covalent framework of P in the structure. The crystal structure does not indicate the presence of the sheet-like material that is produced; so presumably, there is a constructive rearrangement of the undissolved P during reaction.

Acknowledgments

The following people are thanked for their assistance: Mrs. C. M. Foris for determination of lattice constants and space group, Miss M. S. Licis for Guinier camera

techniques. Mr. J. L. Gillson for measurement of resistivity and Mr. W. H. O'Connor for sample preparation.

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