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Crystal Structures of Eight New Cadmium Iodide Polytypes

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With the newly suggested refinements in the method for the structure determination of polytypes, crystal structures of eight new cadmium iodide polytypes have been derived: $18H_6$ [$2(2211)_2211$], $22H_2$ [$(22)_22112(11)_4$], $22H_3$ [$(22)_211(22)_2(11)_2$], $24H_7$ [$222112(22)_2(11)_3$], $28H_5$ [$(22)_22(11)_2222(11)_4$], $30H_5$ [$(22)_22112211(22)_2211$], $36R_3$ [$(22211121)_3$] and $36R_4$ [$(221223)_3$]. The first six polytypes belong to space group $P3m1$, the next to $R3m$ and the last to $R\bar{3}m$. The existence of the homometric counterparts $112(1122)_22$, $(11)_42112(22)_2$, $(11)_3(22)_2211222$ and $(11)_4222(11)_22(22)_2$ of the polytypes $18H_6$, $22H_2$, $24H_7$ and $28H_5$, respectively, is reported.

Introduction

In the last two decades, cadmium iodide has emerged as one of the most extensively studied and richly polytypic substances. So far, complete crystal structures of more than 80 different polytypes of this compound have been determined by various investigators and this knowledge has been helpful in several ways in understanding the mode of growth and transformations (Trigunayat & Verma, 1976) of polytypes. In order to render the method of structure determination free from discrepancies and to make it as perfect as possible, Jain & Trigunayat (1978) have indicated several refinements of the existing method.

In this paper we report the crystal structure analysis of eight new cadmium iodide polytypes using the refined method.

Experimental methods and structure determination

Crystals were grown by evaporation of an aqueous solution. Details of the growth procedure, the selection of crystals and the X-ray methods employed are available elsewhere (*e.g.* Chadha & Trigunayat, 1967). The method of structure determination together with the various refinements employed are given in Jain & Trigunayat (1978).

Crystal structures of new polytypes

Complete crystal structures of eight new CdI_2 polytypes, six hexagonal and two rhombohedral, have been determined. The polytypes, along with their structural details, are listed in Table 1. The oscillation photographs of the polytypes are reproduced in Fig. 1 and the calculated and observed intensity values of their $10.l$ reflexions are given in Tables 2 to 9.

In the structure determination of polytypes a large number of structures are usually possible for a given polytype, running into several thousands and more for large unit cells. However, experimental clues are often available which initially reduce the number of possibilities drastically. A brief description of the structure determination of the polytypes follows. The crystal

Table 1. *Detailed crystal structures of new* CdI_2 *polytypes* ($a = b = 4{\cdot}24$ Å *for all polytypes*)

No.	Polytype	Zhdanov symbol	*ABC* sequence	Space group	c (Å)
1	$18H_6$	$2(2211)_2211$	$[(A\gamma B)(C\alpha B)]_2(C\alpha B)(A\gamma B)(C\alpha B)_2(A\gamma B)$	$P3m1$	61·52
2	$22H_2$	$(22)_22112(11)_4$	$[(A\gamma B)(C\alpha B)]_3(C\alpha B)(A\gamma B)_4$	$P3m1$	75·20
3	$22H_3$	$(22)_211(22)_2(11)_2$	$[(A\gamma B)(C\alpha B)]_2(A\gamma B)[(A\gamma B)(C\alpha B)]_2(A\gamma B)_2$	$P3m1$	75·20
4	$24H_7$	$222112(22)_2(11)_3$	$[(A\gamma B)(C\alpha B)]_2[(C\alpha B)(A\gamma B)]_3(A\gamma B)_2$	$P3m1$	82·02
5	$28H_5$	$(22)_22(11)_2222(11)_4$	$[(A\gamma B)(C\alpha B)]_3(C\alpha B)(A\gamma B)(C\alpha B)(A\gamma B)_4$	$P3m1$	95·69
6	$30H_5$	$(22)_22112211(22)_2211$	$[(A\gamma B)(C\alpha B)]_3(C\alpha B)_2(A\gamma B)(C\alpha B)[(C\alpha B)(A\gamma B)]_3$	$P3m1$	102·52
7	$36R_3$	$(22211121)_3$	$[(A\gamma B)(C\alpha B)]_2(C\alpha B)(C\beta A)_2(B\gamma A)(C\beta A)(B\gamma A)_2$ $(B\alpha C)_2(A\beta C)(B\alpha C)(A\beta C)_2(A\gamma B)$	$R3m$	123·03*
8	$36R_4$	$(221223)_3$	$(A\gamma B)(C\alpha B)(A\gamma B)(A\beta C)(A\gamma B)[(A\beta C)(B\alpha C)]_2$- $(B\gamma A)(B\alpha C)[(B\gamma A)(C\beta A)]_2(C\alpha B)(C\beta A)(C\alpha B)$	$R\bar{3}m$	123·03*

* Hexagonal indexing.

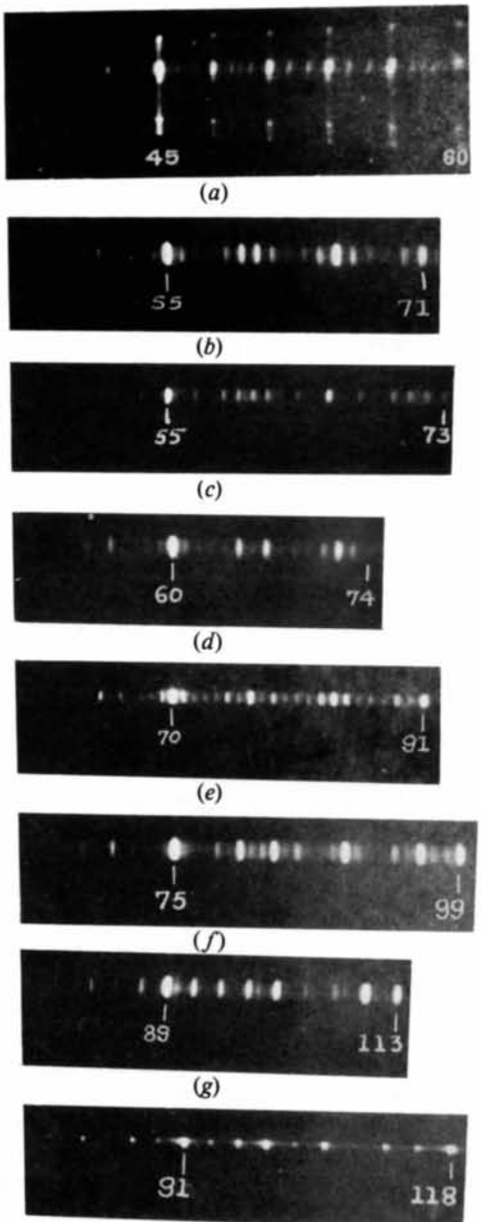

Fig. 1. 15° a-axis zero-layer oscillation photographs of the various polytypes, showing a succession of $01.l$ reflexions (×2·7) (camera diameter 60 mm, except for (c) and (e), for which it is 57·73 mm; Cu $K\alpha$ radiation).

structures finally arrived at on the basis of a satisfactory agreement between calculated and observed intensities for $10.l$ reflexions are given in Table 1. The X-ray photographs record successive $01.l$ reflexions on the zero layer lines but they have the same intensities as $10.l$ reflexions.

Polytype $18H_6$

The diffraction spots of this polytype had lateral elongation (Fig. 1*a*). The other face of the crystal showed spots of the common polytype $4H$, elongated in the same fashion, thus suggesting that the elongation was due either to an arcing effect (Agrawal & Trigunayat, 1969) or to distortion of the crystal. However, since our interest was confined to the determination of the crystal structure alone, this aspect was ignored. The photograph also shows a slight admixture of the common polytype $4H$.

The intensity distribution of the reflexions closely resembled that of the smaller polytype $6H$, which has its crystal structures represented by the Zhdanov sequence 2211. It followed that the present structure was based on $6H$. Therefore, various Zhdanov sequences predominantly consisting of 2211 units were tried; of these, the sequence $2(2211)_2211$ gave satisfactory agreement between the calculated and observed intensities (Table 2). The empirical condition derived by Jain & Trigunayat (1977*b*) for an MX_2-type structure to possess a homometric counterpart led us to conclude that $112(1122)_22$ is a homometric counterpart of the above structure. This was confirmed by a calculation of the intensities for this structure, which turned out to be the same as those for $2(2211)_2211$. Since there is no known way of distinguishing between two homometric structures, the structure in the present case is not uniquely determinable and the actual structure may be either of the two structures.

Polytypes $22H_2$ *and* $22H_3$

The strong spots lie at or near $4H$ positions (Fig. 1*b*,*c*) and the distribution of the spots is symmetric in both photographs. About 50 possibilities containing several 2's and pairs of 1's only were tried; of these, $(22)_22112(11)_4$ (Table 3) and $[(22)_211]_211$ (Table 4), respectively, provided satisfactory agreement between the calculated and observed intensities for the two

Table 2. *Calculated and observed relative intensities for* $10.l$ *reflexions of the polytype* $18H_6$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
36	0	Absent	49	39	*vw*
37	0	Absent	50	42	*vw*
38	1	Absent	51	310	*vs*
39	19	*vw*	52	46	*w*
40	5	*vvw*	53	47	*w*
41	8	*vvw*	54	332	*vs*
42	80	*ms*	55	47	*w*
43	15	*vw*	56	46	*w*
44	19	*vw*	57	315	*vs*
45	1000	*vvs*	58	43	*vw*
46	28	*vw*	59	41	*vw*
47	32	*vw*	60	264	*s*
48	252	*s*			

polytypes. In Fig. 1(*b*) the reflexions $l = 49$, 50 appear to be slightly more intense than is suggested by the calculated values; this is possibly due to a slight admixture of a polytype having the same cell dimensions as $22H_3$ but giving particularly strong reflexions for $l = 49$, 50. Further, a close examination of Fig. 1(*c*) shows the presence of three faint spots of the common type $4H$, after the spots $l = 49$, 60 and 71, respectively, of the polytype $22H_3$. However, the extremely weak intensities of these spots indicate that the admixture of $4H$ is too small to be of any consequence to the structure determination of the main polytype $22H_3$.

As for the earlier polytype $18H_6$, the empirical criteria for a homometric counterpart in the MX_2-type structures suggested that the structure $(22)_2 2112(11)_4$ should be homometric to $(11)_4 2112(22)_2$. This was verified by calculating the intensities for the two structures; these were found to be the same. Thus the crystal structure of the polytype $22H_2$ cannot be uniquely determined; it may be either $(22)_2 2112(11)_4$ or $(11)_4 2112(22)_2$.

Table 3. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $22H_2$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
44	1	Absent	58	40	*vvw*
45	1	Absent	59	110	*w*
46	2	Absent	60	203	*s*
47	2	Absent	61	215	*s*
48	10	Absent	62	131	*w*
49	27	*vw*	63	54	*vw*
50	39	*vw*	64	86	*vw*
51	31	*vvw*	65	199	*ms*
52	16	Absent	66	644	*vs*
53	31	*vvw*	67	200	*ms*
54	85	*vw*	68	87	*vw*
55	1000	*vvs*	69	55	*vw*
56	115	*w*	70	133	*w*
57	57	*vw*	71	221	*s*

Table 4. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $22H_3$

l	I_{calc}	I_{obs}		I_{calc}	I_{obs}
44	1	Absent	59	197	*s*
45	0	Absent	60	274	*s*
46	2	Absent	61	291	*s*
47	0	Absent	62	234	*s*
48	18	*vvw*	63	3	Absent
49	37	*vw*	64	130	*ms*
50	53	*w*	65	12	Absent
51	56	*w*	66	644	*vs*
52	1	Absent	67	12	Absent
53	47	*w*	68	131	*ms*
54	5	Absent	69	3	Absent
55	1000	*vvs*	70	238	*s*
56	7	Absent	71	298	*s*
57	86	*ms*	72	285	*s*
58	2	Absent	73	206	*s*

Polytype $24H_7$

The strong spots lie on or around the positions of the common type $4H$, which has the structure 22 in Zhdanov notation (Fig. 1*d*). Also, the intensity distribution of the spots is symmetric around the $4H$ positions. Consequently, nearly 100 possible sequences, mostly containing 2's and pairs of 1's, were tried; of these, the structure $222112(22)_2(11)_3$ provided satisfactory agreement between the calculated and observed intensities (Table 5).

Here, again, the structure $(11)_3(22)_2 211222$ has a homometric counterpart, *viz* $222112(22)_2(11)_3$, and hence, once again, the structure determination is not unique.

Polytype $28H_5$

Like the previous polytype $24H_7$, the intensity distribution of the reflexions is symmetric and the strong spots lie on or around $4H$ positions (Fig. 1*e*). The spots at $2H$ positions are, however, stronger than the remaining spots occupying the $4H$ positions, thus suggesting that the Zhdanov symbol of the polytype must contain an appreciable number of 11 units, in addition to 22 units. Nearly 180 such possibilities were tried; of these, the structure $(22)_2 2(11)_2 222(11)_4$ provided satisfactory agreement between the calculated and observed intensities (Table 6). Another structure, $(11)_4 222(11)_2 2(22)_2$, gave the same calculated intensities and is thus homometric to the determined structure, $(22)_2 2(11)_2 222(11)_4$. Consequently, in this case too, the structure determination has not been unique.

Polytype $30H_5$

The intensity distribution of strong spots is akin to that of the polytype $10H_1$ (222211), already reported by Mitchell (1956) (Fig. 1*f*). Also, the overall distribution of the spots is symmetric. Thus the

Table 5. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $24H_7$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
48	1	Absent	62	24	*vw*
49	1	Absent	63	26	*vw*
50	1	Absent	64	29	*vw*
51	1	Absent	65	321	*vs*
52	2	Absent	66	33	*vw*
53	37	*w*	67	357	*vs*
54	5	Absent	68	35	*w*
55	73	*ms*	69	35	*w*
56	9	*vvw*	70	37	*w*
57	11	*vvw*	71	134	*s*
58	14	*vvw*	72	494	*vs*
59	58	*w*	73	134	*s*
60	1000	*vvs*	74	38	*w*
61	76	*ms*			

Table 6. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $28H_5$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
56	1	Absent	74	20	*w*
57	1	Absent	75	86	*ms*
58	0	Absent	76	22	*w*
59	1	Absent	77	371	*vs*
60	1	Absent	78	24	*w*
61	7	*vvw*	79	103	*ms*
62	3	Absent	80	26	*w*
63	58	*ms*	81	37	*w*
64	5	*vvw*	82	27	*w*
65	25	*w*	83	202	*s*
66	7	*vvw*	84	468	*vs*
67	12	*vvw*	85	202	*s*
68	10	*vvw*	86	27	*w*
69	90	*ms*	87	37	*w*
70	1000	*vvs*	88	26	*w*
71	113	*s*	89	105	*ms*
72	17	*w*	90	25	*w*
73	25	*w*	91	382	*vs*

Table 7. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $30H_5$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
60	0	Absent	80	14	*vvw*
61	0	Absent	81	258	*vs*
62	0	Absent	82	50	*w*
63	0	Absent	83	53	*w*
64	3	Absent	84	293	*vs*
65	1	Absent	85	17	*vvw*
66	27	*vvw*	86	66	*w*
67	7	Absent	87	1	Absent
68	9	Absent	88	1	Absent
69	63	*w*	89	32	*vw*
70	4	Absent	90	342	*vs*
71	20	*vvw*	91	32	*vw*
72	0	Absent	92	1	Absent
73	0	Absent	93	1	Absent
74	14	*vvw*	94	67	*w*
75	1000	*vvs*	95	17	*vvw*
76	18	*vvw*	96	299	*vs*
77	0	Absent	97	54	*w*
78	1	Absent	98	52	*w*
79	49	*w*	99	269	*vs*

Zhdanov symbol of the polytype most probably consists of 2's and pairs of 1's only. The following possibilities containing two units of (222211) and the remainder 2's and pairs of 1's only were tried:

(1) $(22)_4 11(22)_2(11)_2$

(2) $(22)_3 211(22)_2 2(11)_2$

(3) $(22)_3 11(22)_3(11)_2$

(4) $(22)_3(211)_2(22)_2 11$

(5) $(22)_3 11211(22)_2 211$

(6) $(22)_3 112211(22)_2 11$

(7) $(22)_2 2112211(22)_2 211$

(8) $(22)_2 21122211(22)_2 11$.

Table 8. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $36R_3$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
74	1	*vvw*	95	143	*ms*
77	0	Absent	98	154	*s*
80	49	*w*	101	366	*vs*
83	26	*vw*	104	15	*vvw*
86	50	*w*	107	23	*vw*
89	1000	*vvs*	110	614	*vs*
92	214	*s*	113	266	*s*

Table 9. *Calculated and observed relative intensities for* 10.*l reflexions of the polytype* $36R_4$

l	I_{calc}	I_{obs}	l	I_{calc}	I_{obs}
73	5	Absent	97	193	*s*
76	0	Absent	100	925	*vs*
79	80	*ms*	103	22	*w*
82	20	*vw*	106	335	*s*
85	96	*ms*	109	8	Absent
88	49	*w*	112	137	*ms*
91	1000	*vs*	115	97	*ms*
94	61	*ms*	118	823	*vs*

Of these, satisfactory agreement between the calculated and observed intensities was obtained for sequence (7) (Table 7).

Polytype $36R_3$

The presence of a slight admixture of $4H$ helped to identify the rhombohedral character of the lattice of the present polytype (Fig. 1*g*). The most intense spots are found to lie near the $4H$ positions, which, coupled with the fact that the cadmium iodide polytypes mostly contain 2's and 1's in their Zhdanov sequences, led to the postulation of the following four structures:

(1) $(22212111)_3$

(2) $(22211121)_3$

(3) $(22121211)_3$

(4) $(22112121)_3$.

Of these, satisfactory agreement was found to exist between the calculated and observed intensities for sequence (2) (Table 8).

Polytype $36R_4$

Here the rhombohedral lattice was identified by the usual method of superimposing the X-ray photograph of the polytype (Fig. 1*h*) on that of the common polytype $4H$ (or polytype $12H$). The observed and the calculated intensities were compared for all 131 possibilities for a 36-layered rhombohedral polytype of cadmium iodide (Jain, 1976). Of these, only the structure $(221223)_3$ yielded satisfactory agreement (Table 9). The Zhdanov sequence of the structure is symmetric around the odd digit 1. Therefore, according to the modified condition evolved by Jain & Trigunayat (1977*a*), the space group of the polytype is $R\bar{3}m$. The use of the old condition, employed by earlier workers (*e.g.* Srivastava, 1964), would have yielded the wrong space group $R3m$.

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Structure Cristalline du Polyphosphate de Baryum γ: $Ba(PO_3)_2\gamma$

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The γ form of barium polyphosphate is monoclinic, $P2_1/n$, with $a = 9{\cdot}695$ (3), $b = 6{\cdot}906$ (3), $c = 7{\cdot}522$ (3) Å, $\beta = 94{\cdot}75$ (5)° and $Z = 4$. Polyphosphate chains run along the **b** direction with a period of four tetrahedra.

Introduction

La préparation chimique et les principales caractéristiques cristallographiques de $Ba(PO_3)_2\gamma$ ont été décrites par Grenier & Martin (1975) dans une étude d'ensemble des méta- et polyphosphates de baryum. Rappelons simplement que $Ba(PO_3)_2\gamma$ est monoclinique $P2_1/n$ avec une maille a = 9,695 (3), b = 6,906 (3), c = 7,522 (3) Å, β = 94,75 (5)° et Z = 4.

La structure d'une autre variété, $Ba(PO_3)_2\beta$, orthorhombique, a été déterminée par Grenier, Martin, Durif, Tranqui & Guitel (1967).

Détermination de la structure

1318 réflexions indépendantes ont été mesurées à l'aide d'un diffractomètre Philips PW 1100 utilisant la longueur d'onde $K\alpha$ du molybdène. Chaque réflexion était mesurée dans un domaine angulaire de 1,20° balayé à la vitesse de 0,04° s^{-1}.

Le fond continu était mesuré durant 5 s à chaque extrémité du domaine d'intégration. Le domaine de mesure s'étendait de 3 à 30° (θ). Aucune variation significative des deux réflexions de référence (600 et 331) n'a été observée durant les mesures. Malgré la géométrie peu favorable du cristal utilisé (plaquette épaisse approximativement hexagonale de $\frac{8}{100}$ à $\frac{10}{100}$ mm d'arête et de $\frac{4}{100}$ à $\frac{5}{100}$ mm d'épaisseur) aucune correction d'absorption n'a été effectuée.

La structure a été déterminée par la méthode classique de l'atome lourd: interprétation de la fonction de Patterson suivie de synthèses de Fourier. Après quelques cycles d'affinement (Prewitt, 1966), on aboutit rapidement à une valeur finale de 0,033 pour le facteur R.*

* Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope et la Fig. 3 ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 33530: 17 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

Tableau 1. *Paramètres des positions atomiques et facteurs de température équivalents dans* $Ba(PO_3)_2\gamma$

Les écarts standard sont donnés entre parenthèses.

	x	y	z	$B_{éq}$
Ba	0,32374 (4)	0,40293 (6)	0,64267 (5)	0,77
P(1)	0,4220 (2)	0,2053 (3)	0,1286 (2)	0,50
P(2)	0,1638 (2)	0,3939 (3)	0,1206 (3)	0,54
O($L2'1$)	0,3985 (5)	−0,0020 (7)	0,2166 (7)	1,01
O($L12$)	0,3146 (5)	0,3422 (7)	0,2222 (7)	0,75
O($E21$)	0,0873 (5)	0,2097 (7)	0,0848 (7)	0,97
O($E11$)	0,3721 (5)	0,1845 (7)	−0,0630 (6)	0,94
O($E2'2$)	0,3181 (6)	0,0297 (8)	0,5272 (7)	1,01
O($E1'2$)	0,0643 (5)	0,2232 (8)	0,6756 (7)	0,98