

Transformation Characteristics of 6*H*-Based Cadmium Iodide Polytypes

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Transformation characteristics of two cadmium iodide polytypes, 18*H*₆ and 20*H*₉, have been studied. Like other polytypes, these are not based on the most commonly found basic 4*H* structure; instead they are based on the low-periodicity structure 6*H*. On vacuum annealing, they transform according to the schemes 18*H*₆ → 4*H* and 20*H*₉ → 4*H*. An analysis of these transformations reveals that the growth and transformation processes need not necessarily be complementary. In order to determine a feasible transformation mechanism, the atomic structures (layer sequences) of the polytypes have been evaluated. These correspond to (2211)₂1122 for 18*H*₆ and (2211)₂(11)₄ for 20*H*₉. The schematic transformation mechanism has been elucidated.

Introduction

Polytypism is now known to be a widely occurring phenomenon although previously only the inorganic materials SiC, ZnS, CdI₂ etc., were found to display it. At present, however, polytypism is found in a large number of materials, the most recent examples being tin sulphide (Mitchell, Fuziki & Ishizawa, 1974) and gallium selenide (Terhell & Van der Vleuten, 1976). It is now well known that different polytypes of the same chemical compound have different physical properties and hence correspond to different materials. For example, different silicon carbide polytypes have been found to have different energy band gaps (Knippenberg, 1963) and in the case of cadmium iodide they have different dielectric constants (Fernandez & Srivastava, 1975). From the applied point of view the transformations are important since they represent the easiest way of preparing different polytypes in a controlled way. Recently some work has been done on the phase transformation in polytypic materials (Krishna & Marshall, 1971; Minagawa, 1975; Baars & Brandt, 1973; Steinberger, Kiflawi, Kalman & Mardix, 1973). To date, the most extensive studies of transformations have been made on CdI₂ polytypes (Lal & Trigunayat, 1974; Tiwari & Srivastava, 1973). In order to unravel the general principles which govern the transformation, it is essential that the layer sequences of the polytypes – the initial as well as the transformed ones – be determined and analysed in the light of the most feasible transformation mechanism. With this in view, we have studied polytypic transformations in cadmium iodide crystals. Particular emphasis has been put on the determination of the layer sequences and also on the analysis of these sequences in the light of the possible transformation modes. In this paper the transformation characteristics of the polytypes 18*H*₆ and 20*H*₉ are described. These polytypes are interesting since in contrast to usual behaviour they are not based on the most stable basic structure, 4*H*. As evidenced by the intensity distribution of the X-ray diffraction spots, both of these are based on a 6*H*

structure. The detailed layer sequences (atomic structures) of these polytypes have been determined and these have been analysed to elucidate the transformation criterion. It has been shown that although these polytypes originate from a 6*H* structure, they do not revert to this after the transformation, but transform to the most stable structure, 4*H*. These transformations reveal that regardless of the structure from which a polytype has originated, the transformation is such that it always leads to the conversion of the polytype into the basic 4*H* structure.

Experimental methods

Crystals of cadmium iodide were grown as described by Mitchell (1956). For the characterization of the polytypes, *a*-axis oscillation photographs were taken with an oscillation range starting from the position where the *c* axis (perpendicular to the crystal platelet) made an angle of 25° with the incident X-ray beam and continuing up to the position (25+15)=40°. This range was found to be most convenient for the identification of the polytypes since it records a large number of 10.*l* spots. The phase transformations were induced by controlled annealing of the polytypic crystals. From several trial runs, it was found that for the interpolytypic transformation, the best results were obtained by annealing the crystal to a temperature of 285 ± 10° for about 4 h, under a vacuum of 10⁻⁴ torr.

Experimental results

Fig. 1 (*a*) represents a 15° *a*-axis single-crystal oscillation photograph of a polytypic crystal. The polytype exhibited by Fig. 1 (*a*) was identified as 18*H* by the usual method of identification (Trigunayat & Chadha, 1971). The crystal corresponding to Fig. 1 (*a*) was heated for about 4 h at 285 ± 10°C in a vacuum of 10⁻⁴ torr. Fig. 1 (*b*) represents the oscillation photograph of the crystal after annealing. A comparison of Fig. 1 (*a*) and (*b*) reveals that a phase transformation has taken place. The transformed structure was iden-

tified as the basic 4H structure. It should be noted that there is no streak connecting the 10.l spots (the various spots of the first layer line) in Fig. 1 (b). This indicates that the transformed structure is an ordered one. Among the 18 layered hexagonal polytypes of cadmium iodide five different structures have been reported (Jain & Trigunayat, 1975). After determining the layer sequence of this polytype by actually calculating the atomic structure, we found that this is a new polytype (unknown prior to this study) and therefore it has been designated as 18H₆. Fig. 1 (c) represents a 15° a-axis single-crystal oscillation photograph of another polytypic crystal. This polytype was identified as 20H. The crystal corresponding to Fig. 1 (c) was annealed under the same conditions as stated before. Fig. 1 (d) represents an oscillation photograph of the crystal after annealing. As for the case shown in Fig. 1 (b), this transformed structure is also an ordered one. For reasons similar to those for the 18H polytype, the present polytype has been designated as 20H₉. It should be mentioned that both transformations 18H₆ → 4H and 20H₉ → 4H are irreversible. The transformed 4H structure does not change to any other structure on annealing.

Since one of the aims of the present study is to analyse the transformations in terms of the known layer sequences of the polytypes, the detailed atomic structures of the polytypes 18H₆ and 20H₉ have been evaluated. A close inspection of the intensity sequence of 10.l spots of the polytype 18H₆ corresponding to Fig. 1 (a) reveals that the spots lying near 6H positions are the most outstanding in intensity. Thus the structure of 18H₆ should be based on the low-period polytype 6H having the structure 2211. Therefore, several (2211) units should be present in the Zhdanov sequence of this polytype. Based on this criterion, several probable structures were postulated. These are as follows.

- (i) (2211)₂1122
- (ii) (2211)₂1221
- (iii) (2211)₂(11)₃
- (iv) 22111122(11)₃.

The intensities were calculated on an IBM 7044 computer for various 10.l reflexions for these structures and were compared with those obtained on the oscillation photograph. A satisfactory match (Table 1) between the calculated and observed intensities was obtained only for (i). For the other structures the agreement was found to be poor. This shows that the proposed structure represents the correct atomic structure of the polytype.

The structure of the 20H₉ polytype was determined in a similar way (Table 2) to the 18H₆ polytype, since, as is evident from Fig. 1(c), this polytype is also based on the 6H structure. The details, including the structures of the polytypes, are as follows.

Atomic structure of 18H₆: space group P_{3m1}, Zhdanov sequence (2211)₂1122, ABC sequence:

Table 1. *Observed and calculated relative intensities for 10.l reflexions of polytype 18H₆*

	Observed	Calculated		Observed	Calculated
36		4.9	55	w	38.3
37		0.4	56	s	122.5
38		5.1	57	s	196.1
39	*	18.4	58	s	233.2
40		40.8	59	s	239.7
41		63.5	60	s	163.6
42		69.8	61	ms	81.4
43		40.2	62	vw	23.1
44	vw	10.8	63	vs	1925.1
45	vs	1000.0	64	vw	7.8
46	w	24.2	65	w	35.5
47	vw	10.0	66	w	51.4
48	s	163.5	67	w	47.4
49	s	243.4	68	w	34.8
50	s	270.8	69	w	15.9
51	s	230.8	70		3.2
52	ms	112.7	71	†	0.2
53	w	38.1	72		3.8
54	s	684.8			

* The absorption is abnormally high for these reflexions because of the plate-like shape of the crystal.

† Not recorded on the X-ray film in the chosen range of oscillation.

Table 2. *Observed and calculated relative intensities for 10.l reflexions of polytype 20H₉*

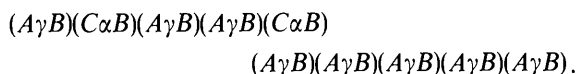
	Observed	Calculated		Observed	Calculated
40	vw	10.6	61	s	128.7
41	a	1.5	62	w	29.9
42	a	0.8	63	vw*	304.7
43	w	21.3	64	vw*	187.4
44	w	26.6	65	a	1.0
45	a	0.0	66	s	165.8
46	ms	56.4	67	s	183.2
47	ms	90.1	68	w	24.0
48	vw	9.8	69	w	51.0
49	ms	49.0	70	vs	3461.4
50	vs	1000.0	71	w	40.7
51	ms	62.1	72	w	6.3
52	w	25.0	73	ms	78.5
53	s	236.4	74		43.6
54	s	178.2	75		0.0
55	a	0.1	76		21.3
56	s	208.1	77	†	13.4
57	s	288.3	78		0.5
58	w	32.6	79		1.0
59	s	130.8	80		7.9
60	vs	1427.8			

* The absorption is very high for these reflexions because of the plate-like shape of the crystal.

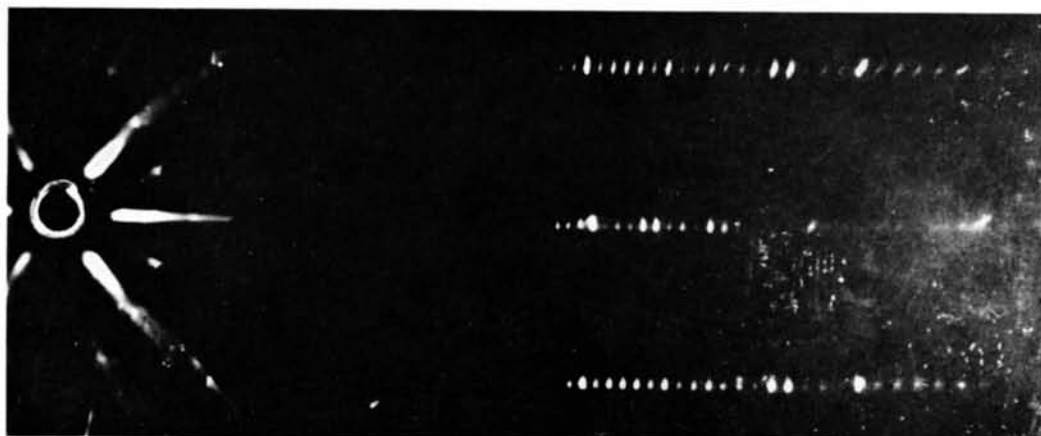
† Not recorded on the X-ray film in the chosen range of oscillation.



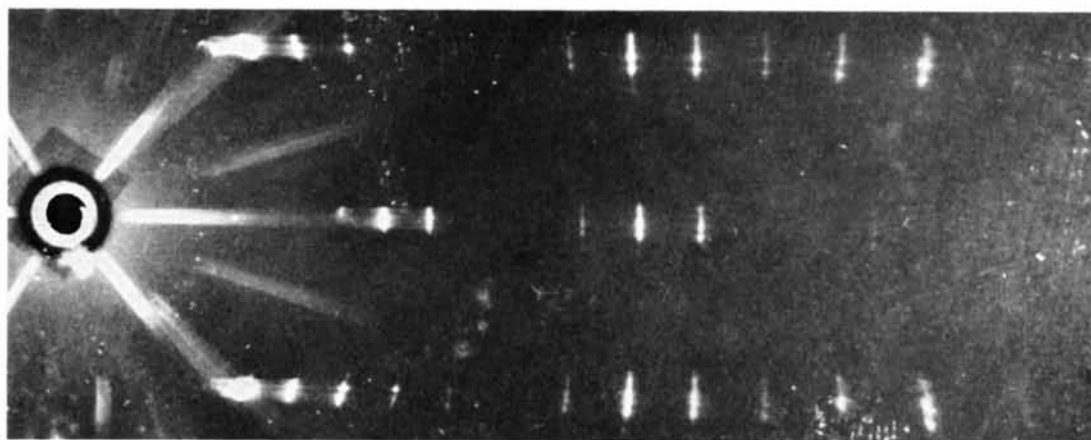
Atomic structure of 20H₉: space group P_{3m1}, Zhdanov sequence (2211)₂(11)₄, ABC sequence:



In the above, the capital letters denote the posi-

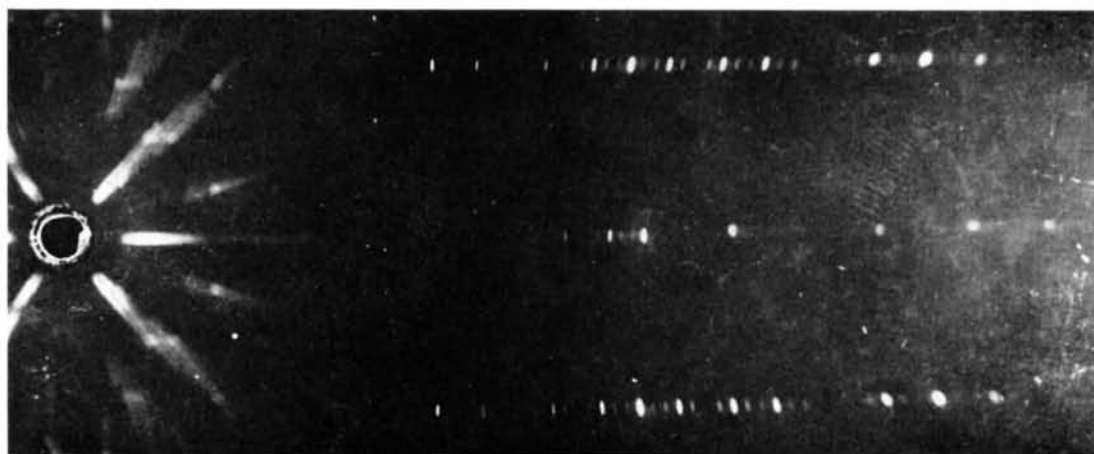


(a)

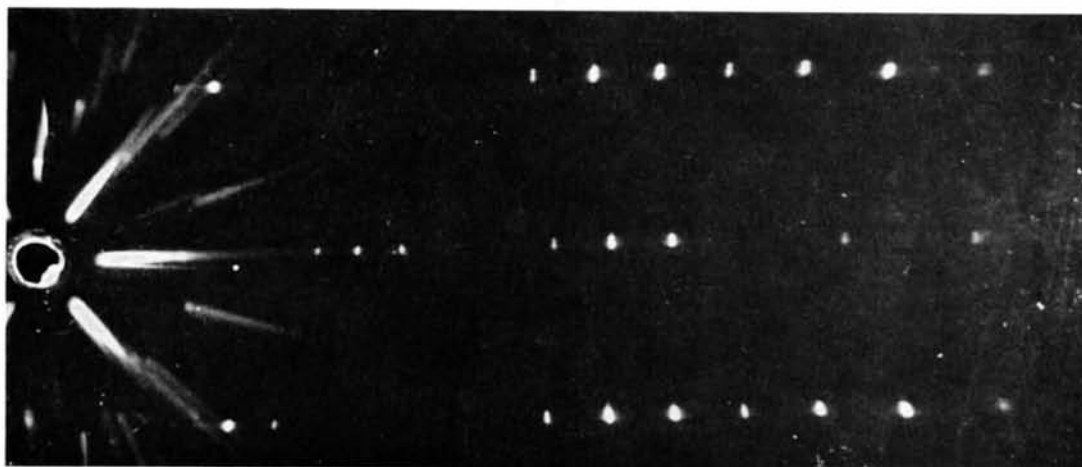


(b)

Fig. 1. (a) A 15° a -axis oscillation photograph of the $18H_6$ polytype of cadmium iodide with Cu $K\alpha$ radiation on a camera of radius 3 cm. The first, most intense spot outwards from the centre on the $10.l$ row (the first layer line) corresponds to 10.45. (b) A 15° a -axis oscillation photograph of the crystal corresponding to (a) after annealing, showing the basic $4H$ structure. There is no streak connecting the $10.l$ spots.



(c)



(d)

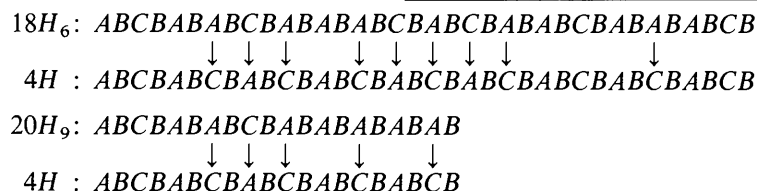
Fig. 1. (cont.) (c) A 15° a -axis oscillation photograph of the $20H_9$ polytype of cadmium iodide; other conditions as in (a). The most intense spot outwards from the centre on the $10.l$ row (the first layer line) corresponds to 10.50 . (d) A 15° a -axis oscillation photograph of the crystal corresponding to (c) after annealing, showing the basic $4H$ structure. There is no streak connecting the $10.l$ spot.

tions of the iodine atoms while the Greek letters denote the positions of the cadmium atoms. Only the atomic layer sequence has been given. The atomic coordinates can easily be derived from the given atomic sequences (Mitchell, 1956).

Discussion and conclusion

It is generally believed that a polytype originates as a result of the creation and ordering of stacking faults in any of the basic structures (Prasad & Srivastava, 1971; Gyaneshwar, Chadha & Trigunayat, 1973). Based on this, the polytypes $18H_6$ and $20H_9$ would result because of the occurrence of ordered stacking faults in the $6H$ basic structure. It should be mentioned that the origin and role of stacking faults in the growth and transformation of polytypes are now well established (Jagodzinski, 1971). This being the case, based on the previously determined criterion of transformation in cadmium iodide polytypes (Tiwari & Srivastava, 1973; Rai & Srivastava, 1974), the two polytypes should transform to their base structure, $6H$. However, as described in the previous section the present polytypes did not transform to $6H$, but to the most stable structure, $4H$. The present transformations are thus curious in character and they illustrate that regardless of the basic structure from which the polytype has resulted, the transformation by-product is always the most stable basic structure, $4H$. This may be understood in the light of the fact that $6H$ is the metastable modification and may be taken to result from the basic $4H$ structure (Trigunayat & Chadha, 1971). Thus, during growth, if the metastable modification has nucleated, the polytypic structure may result through the creation of ordered stacking faults. On transformation, however, the intermediate metastable modification $6H$ may not be achieved and the most stable $4H$ structure is likely to result. This is actually the case observed in the present transformations. We discuss below the scheme of this curious transformation process.

It is generally taken that the transformation proceeds through nucleation and propagation of newly created stacking faults or through the rearrangement of the initial stacking fault sequences in the ordered or disordered modes (Tiwari & Srivastava, 1973; Rai & Srivastava, 1974). Since in the present case the transformation leads to the ordered $4H$ structure, the first possibility can be ruled out. The transformation characteristics can best be understood by invoking the rearrangement of existing stacking faults in an ordered way. The schematic transformation process involving this is shown below.



As can be seen from the above, while postulating the transformation we have considered two unit cells for the $18H_6$ structure and one unit cell for the $20H_9$ structure. This is because the periodicity of the former structure is not a multiple of $4H$. In this case, therefore, for a conservative stacking-fault-induced transformation, two unit cells would have to be involved at the microscopic level. The eventual result of the transformation is again the formation of the $4H$ structure.

To summarize, the present investigation reveals that the growth and the transformation processes are not necessarily complementary. The base structure during growth may be different from the most stable $4H$ structure (for example the $6H$ structure in the present case). On the other hand, on transformation the polytypic structures always change to the most stable $4H$ structure. This is evidenced by the $18H_6 \rightarrow 4H$ and $20H_9 \rightarrow 4H$ transformations observed in the present investigation.

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