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Common Polytypes of PbI₂ at Low and High Temperatures and the 2*H*-12*R* Transformation

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PbI_2 single crystals grown in gel and grown from vapour were studied by X-ray diffraction. The structure analysis of the type 2*H* with space group $P\bar{3}m1$ has revealed that the *z* coordinate of the I ion is 0·268 and the thermal vibration of the Pb ion in its own layer is considerably smaller as compared with that perpendicular to the layer. From the dependence of the frequencies of types 2*H* and $12R[13]_3$ on temperature of crystal growth, it has been shown that type 2*H* is the most common type at room temperature and type $12R[13]_3$ the most common type at high temperatures. Observations on the 2*H*–12*R* transformation by annealing have revealed that this transformation is reversible.

Introduction

The 2*H* structure of PbI_2 has the hexagonal space group $P\bar{3}m1$ and the lattice constants are $a=4{\cdot}557$ and $c=6{\cdot}979$ Å (Swanson, Gilfrich & Ugrinic, 1955). The coordinates of the ions are:

1 Pb at 000
2 I at $\frac{2}{3}\frac{1}{3}\bar{z}$; $\frac{1}{3}\frac{2}{3}z$.

The value of *z* was determined to lie between 0·26 and 0·27 by Pinsker, Tatarinova & Novikova (1943). Mitchell (1959) used the average value, 0·265. In the present study a single crystal of type 2*H* grown in gel was investigated by X-ray diffraction, and the value of *z* and the thermal parameters of the Pb and I ions were determined.

The frequency distribution of the polytypes was investigated by Mitchell (1959) on many crystals grown in gel at room temperature and, later, by Hanoka & Vand (1968) on those grown in the same way at various temperatures ranging from 23° to 83 °C. Prasad & Srivastava (1974) reported the transformation, $2H \rightarrow 4H+$disorder $\rightarrow 12R$(order) $\rightarrow 18R$(order), by repeated annealing of a 2*H* crystal under a vacuum of 10^{-3} to 10^{-4} torr. In the present study the frequencies of types 2*H* and 12*R* were also investigated by growing crystals at room temperature (gel growth) and at high temperatures (vapour growth), and the 2*H*–12*R* transformation by annealing was studied.

X-ray measurements

All polytypes were examined using Weissenberg photographs. The 2*H* crystal used for intensity measurement was a hexagonal flat plate 480 μm across and 9 μm thick. With Cu *Kα* radiation, intensity data were recorded on multiple-film zero-layer integrated Weissenberg photographs about **b**. The intensities were estimated visually by comparing with a standard scale. The number of reflexions measured was 53. The observed intensities were corrected for the Lorentz–polarization effect, spot size and absorption ($\mu=1623$ for Cu *Kα*). The absorption factor was obtained by applying to a hexagonal plate the formulae given by Takaki, Sakata & Watanabé (1961), who derived absorption factors for a right-prismatic crystal by dividing the rectangular cross section into triangular and parallelogram-shaped areas.

Type 2*H*

Crystals were grown at room temperature by the gel method described by Mitchell (1959), except that ethyl silicate was used in place of water glass. Crystals were hexagonal or trigonal thin plates. All ten crystals examined were found to be of type 2*H*. One of them was selected for intensity measurement. The atomic scattering factors used for calculating the structure factors were those of Cromer & Waber (1965) for Pb^{2+} and those of Doyle & Turner (1968) for I^-. Anisotropic thermal parameters for *h*0*l* reflexions of the form, $\exp[-(B_1s_1^2+B_3s_3^2)]$ with $s_1^2=h^2/3a^2$ and $s_3^2=l^2/4c^2$, were used for both ions. The observed and calculated structure factors showed a good agreement when $z=0{\cdot}268$, $B_1=0{\cdot}7$ and $B_3=3{\cdot}0$ for the Pb ion, and $B_1=B_3=2{\cdot}0$ for the I ion. The *R* index was 0·113. F_o's and F_c's are given in Table 1.

Table 1. *Observed and calculated structure factors of type* 2*H*

Each group of three columns contains, from left to right, the index *l*, F_o and F_c.

	0 0 L		2	114	120	4	40.4	38.7	2	10.6	2.0
			1	7.0	1.2	3	18.4	5.5	3	60.8	55.6
2	27.5	16.6	0	33.8	28.6	2	84.6	74.9	4	79.5	69.0
3	92.1	85.1	-1	126	153	1	109	123			
4	105	106	-2	90.6	89.1	0	31.6	28.6		4 0 L	
5	9.8	11.4	-3	22.8	11.3	-1	3.0	7.4			
6	8.0	2.5	-4	42.9	43.2	-2	106	99.2	3	56.2	50.3
7	46.8	47.3	-5	87.5	87.4	-3	95.2	86.5	2	59.2	56.3
8	31.8	33.5	-6	20.3	23.5	-4	4.6	1.6	1	6.4	10.8
			-7	12.2	8.6	-5	8.5	15.2	0	16.4	21.3
	1 0 L		-8	27.7	26.0	-6	60.4	59.1	-1	63.0	67.3
						-7	25.4	27.8	-2	45.4	44.1
8	11.2	8.5		2 0 L		-8	10.4	6.3	-3	4.0	3.3
7	28.6	30.7									
6	66.7	67.3	8	24.9	23.6		3 0 L				
5	10.9	15.2	7	10.5	6.0						
4	7.6	1.6	6	19.6	21.8	0	82.4	100			
3	100	102	5	78.7	75.8	1	47.5	44.5			

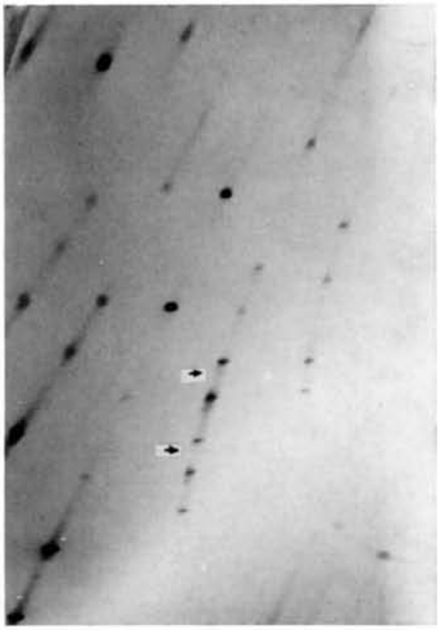

Fig. 1. A Weissenberg photograph of a faulted 12*R* crystal coalesced with small amounts of 2*H* and unidentified types. Intense spots are the reflexions of the faulted 12*R* structure and those marked with arrows are the reflexions of 2*H*.

Fig. 2. A Weissenberg photograph of a 2*H* crystal coalesced with small amounts of a faulted 12*R* structure and unidentified types. Intense spots are the reflexions of 2*H* and those marked with arrows are the reflexions of the faulted 12*R* structure.

Fig. 3. A Weissenberg photograph of the ordered 12*R* structure (obverse and reverse) coalesced with 4*H*. Plate-like, intense spots are the reflexions of 12*R* (obverse), those marked with arrows are the reflexions of 4*H* and the remaining ones are the reflexions of 12*R* (reverse).

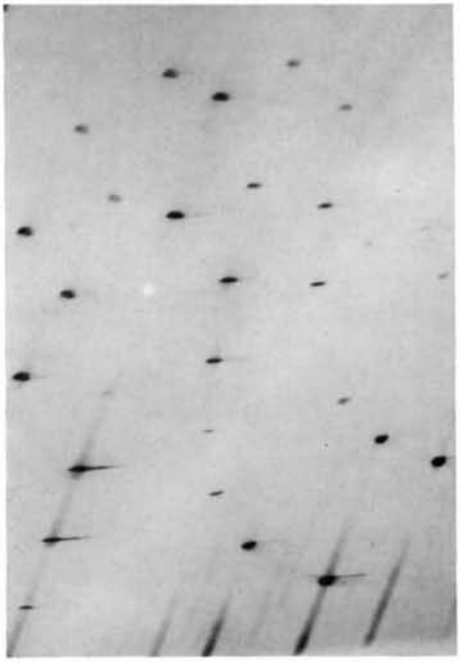

Fig. 4. A Weissenberg photograph of a 2*H* crystal.

Type $12R[13]_3$

Crystals were grown from vapour. PbI_2 powder was sealed in a glass tube under a vacuum of 10^{-3} to 10^{-4} torr; one end containing the powder was heated up to about 400 °C in an electric furnace and a temperature gradient was given near the other end along a length of a few cm. About the middle of this portion, thin plate-like crystals of suitable size were formed after a day. All ten crystals examined were found to be of type 12*R* and three of them contained a small amount of type 4*H*. Type 2*H* was not observed. One face of a crystal plate was formed of 12*R* (obverse) and the other face 12*R* (reverse), and no single crystal of 12*R* was obtained. From a rough estimation of the intensities, these 12*R* structures were all found to be $[13]_3$: $(A\gamma B)$ $(A\beta C)$ $(B\alpha C)$ $(B\gamma A)$ $(C\beta A)$ $(C\alpha B)$.

Mitchell (1959) reported that, out of 100 crystals grown in gel at room temperature, 93 were of pure 2*H* while only one was of type $12R[13]_3$ coalesced with 4*H* and 2*H*. Hanoka & Vand (1968) also reported that, out of 650 crystals grown in gel at various temperatures ranging from 23° to 83 °C, 373 were of 2*H*, 120 were of $12R[13]_3$* and a common sort of syntactic coalescence was the combination, 12*R* (in obverse position)–4*H*–12*R* (reverse). From a comparison between these reports and the present observations, it may be concluded that in PbI_2 the type 2*H* is the most common type at room temperature and the type $12R[13]_3$ the most common type at high temperatures.

2*H*–$12R[13]_3$ transformation

The transformation between types 2*H* and $12R[13]_3$ was investigated by annealing crystals in air. The results can be summarized as follows:

(i) Six 2*H* crystals grown in gel transformed into faulted 12*R* crystals after annealing at 150 °C for five days. Fig. 1 shows a typical Weissenberg photograph of a faulted 12*R* crystal coalesced with small amounts of 2*H* and unidentified types.

(ii) Four out of six faulted 12*R* crystals obtained in (i) changed back again into 2*H* crystals after being left at room temperature for about a month. Fig. 2 shows that the crystal in Fig. 1 has changed back again into a 2*H* crystal coalesced with small amounts of the faulted 12*R* and unidentified types.

(iii) Three out of four vapour-growth crystals of ordered 12*R* (obverse and reverse), one of which contains a small amount of 4*H* (Fig. 3), transformed into 2*H* crystals after being left at room temperature for about a month and a half (Fig. 4). From a comparison between Figs. 3 and 4, which were obtained from the same crystal, it is seen that not only type 12*R* but also type 4*H* has changed into type 2*H*.

(iv) Three 2*H* crystals obtained in (iii) changed back again into 12*R* crystals after annealing at 200 °C for two days.

(v) Faulted 12*R* and ordered 12*R* crystals showed no change after each cycle of several times of annealing at 300 °C for a day.

Observations (i) and (iv) show that 2*H* transforms into $12R[13]_3$ at high temperatures as reported by Prasad & Srivastava (1974). Observations (ii) and (iii) show that faulted 12*R* and ordered $12R[13]_3$ structures transform into 2*H* at room temperature. Observation (v) shows that type $12R[13]_3$ is the high-temperature form. Finally, observations (i) and (ii) and observations (iii) and (iv) show that the transformation 2*H*–12*R* is reversible.

In connexion with the above observations, the following two remarks are to be added. Firstly, as to (i), out of eight 2*H* crystals examined, two changed into faulted 4*H* crystals when subjected to the same treatment as in (i) and transformed into 12*R* crystals after further annealing at 300 °C for a day. Secondly, two faulted 12*R* crystals obtained in (i) and one remaining ordered 12*R* crystal referred to in (iii) did not transform into 2*H* after being left at room temperature for two months.

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* Although they did not determine the structure of these 12*R* crystals, the structure may be concluded to be $[13]_3$ from their photographs.