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**Atomic structures of three new rhombohedral polytypes of lead iodide.** By MAHESH CHAND and G. C. TRIGUNAYAT, *Department of Physics and Astrophysics, University of Delhi, Delhi-110007, India*

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The complete atomic structures of three new  $\text{PbI}_2$  polytypes,  $12R_2$ ,  $18R_1$  and  $18R_2$ , grown by the silica-gel method, have been determined. They are  $[13]_3$ ,  $[1311]_3$  and  $[(21)_2]_3$  respectively, in Zhdanov notation and belong to the space group  $R3m$ . The cell dimensions are  $a=b=4.56$  Å, for all of them, and  $c=41.87$  and  $62.81$  Å for the 12-layered and 18-layered polytypes respectively. All three polytypes have been found to be syntactically coalesced with the common  $\text{PbI}_2$  polytype  $2H$ , thus showing a transformation of structure during crystal growth. The mode of transformation is discussed.

### Introduction

To date about 40 polytypes of lead iodide have been reported, of which the complete crystal structures of only eight have been determined by various workers. They include seven hexagonal polytypes (Terpstra & Westbrink, 1926; Mitchell, 1959; Agrawal, Chadha & Trigunayat, 1970; Mahesh & Trigunayat, 1974) and one rhombohedral polytype (Mitchell, 1959). During the course of a study on cleavage of  $\text{PbI}_2$  crystals, grown by the gel method (Henisch, 1970), we have discovered several new polytypes, of which it has been possible to determine the crystal structures of one 12-layered and two 18-layered rhombohedral polytypes. Each of these polytypes has been found to be syntactically coalesced with the common  $\text{PbI}_2$  type  $2H$ , thus showing a transformation of crystal structure during growth. The structure determination is described in the following and the possible modes of transformation are discussed.

### Structure of polytypes

The usual method of structure determination of  $\text{PbI}_2$  polytypes was used, *viz.* calculating intensities for 10.1 reflexions for all possible structures and comparing them against the observed intensities.

#### (i) Polytype $12R_2^*$

There are only two possible ways in which 12 layers can stack together to form a rhombohedral polytype: (a)  $(31)_3$ , (b)  $(13)_3$ . As shown in Table 1, the calculated and observed

intensities are in excellent agreement for the structure (b).

Since the polytype with structure (a) was reported earlier by Mitchell (1959), the present polytype was designated as  $12R_2$ . The detailed structure of  $12R_2$  is therefore as follows: space group  $R3m$ , Zhdanov symbol  $(13)_3$ ,  $a=b=4.56$ ,  $c=41.87$  Å (hexagonal indexing).

#### (ii) Polytypes $18R_1$ and $18R_2$

These two polytypes have the same  $c$  dimension but different crystal structures were found coexisting in a parallel orientation on the same face of the crystal, along with the polytype  $6H$ , having crystal structure  $(2211)$  (Mitchell, 1959). Two eighteen-layered rhombohedral polytypes of lead iodide have already been reported by Hanoka & Vand (1968), but neither have their crystal structures been determined nor have their X-ray photographs been reproduced. Hence the present polytypes, designated as  $18R_1$  and  $18R_2$ , could not be compared with them.

With no assumptions, there are  $2^5$  possible ways of arranging the atoms in the unit cell of  $18R$ . However, most of the known polytypic structures of  $\text{CdI}_2$  and  $\text{PbI}_2$ , which are isostructural, have been found to have only the Zhdanov numbers 1, 2 and 3 in their stacking sequences. Making use of this clue and of the condition for a rhombohedral structure that the stacking sequence should necessarily end with  $\nabla$ , if started with  $\Delta$ , we reduced the possible arrangements to the following: (1)  $(3111)_3$ , (2)  $(1311)_3$ , (3)  $(1131)_3$ , (4)  $(1113)_3$ , (5)  $(1212)_3$ , (6)  $(2121)_3$ . Of these, the calculated intensities for (2) and (6) were found to be in excellent agreement with the observed values for the polytypes  $18R_1$  and  $18R_2$ , respectively (Table 1). The detailed structure of  $18R_1$  is: space group  $R3m$ , Zhdanov symbol  $[1311]_3$ ,  $a=b=4.56$ ,  $c=62.81$  Å (hexagonal indexing). The detailed structure of  $18R_2$  is: space group  $R3m$ , Zhdanov symbol  $(2121)_3$ ,  $a=b=4.56$ ,  $c=62.81$  Å (hexagonal indexing).

\* The polytype notation in this paper follows the scheme suggested by Trigunayat & Chadha (1971).

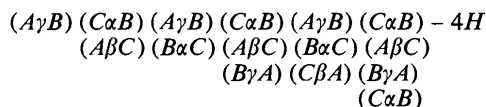
Table 1. Calculated and observed relative intensities for 10.1 reflexions of  $\text{PbI}_2$  polytypes  $12R_2$ ,  $18R_1$  and  $18R_2$

$12R_2(13)_3$			$18R_1(1311)_3$			$18R_2(2121)_3$		
Reflexion	Observed intensity	Calculated intensity	Reflexion	Observed intensity	Calculated intensity	Reflexion	Observed intensity	Calculated intensity
10.23	<i>uvw</i>	1.5	10.35	( <i>w</i> )*	12.6	10.37	( <i>s</i> )*	56.1
26	<i>s</i>	47.4	38	( <i>ms</i> )*	39.7	40	<i>a</i>	1.6
29	<i>vs</i>	98.5	41	<i>a</i>	2.4	43	<i>vs</i>	105.4
32	<i>vvs</i>	176.3	44	<i>vvs</i>	140.7	46	<i>vvs</i>	112.6
35	<i>mw</i>	5.8	47	<i>vvs</i>	132.7	49	<i>ms</i>	27.4
38	<i>vs</i>	96.0	50	<i>ms</i>	30.0	52	<i>vvs</i>	110.1
			53	<i>a</i>	0.4	55	<i>mw</i>	3.9
			56	<i>s</i>	56.8	58	<i>ms</i>	31.7
			59	<i>ms</i>	27.0			

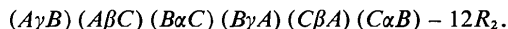
\* These reflexions lie in the absorption region, so their intensities are not reliable.

## Discussion

(i) The energy considerations (Mahesh & Trigunayat, 1974) suggest that the polytype  $12R_2$  has possibly been formed by the introduction of stacking faults into the corresponding hexagonal structure  $4H$ , according to the following scheme of successive cyclic layer displacements:



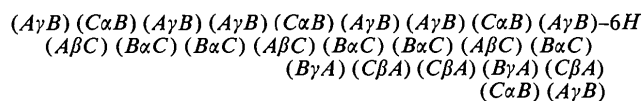
Thus one finally obtains the following structure:



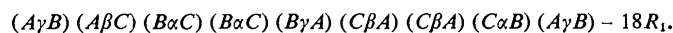
Of the two possible crystal structures for a 12-layered rhombohedral polytype of lead iodide, *viz.*  $12R_1$  ( $31$ )<sub>3</sub> and  $12R_2$  ( $13$ )<sub>3</sub>, the former has been reported (Mitchell, 1959), but we failed to encounter it at all in our present investigations, whereas we have encountered the latter 15 times. According to the above scheme of derivation, the  $12R_2$  structure is formed by a slip between molecular sheets,  $(A\gamma B)$ ,  $(C\alpha B)$  etc., which is very much easier than the slip between the layers within a molecular sheet itself, as is involved in the creation of polytype  $12R_1$ . Thus the large difference observed in the frequencies of occurrence of the two types is theoretically justified.

(ii) Polytypes  $18R_1$  and  $18R_2$ : Most probably, these types should have resulted from the accompanying type  $6H$ , according to the following schemes (involving cyclic and anticyclic shifts respectively).

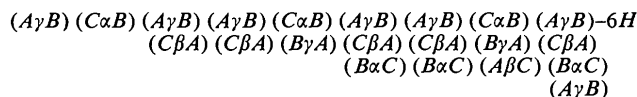
(a) Polytype  $18R_1$



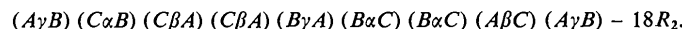
Thus one finally obtains the structure:



(b) Polytype  $18R_2$



Thus the final structure is:



Two different mechanisms have been suggested for bringing about the ordering and perpetuation of the stacking faults, once they have been created. According to the first, the vibration entropy helps towards this end by lowering the free energy of the crystal in the expression  $F = E - TS$  where  $E$  is the internal energy,  $S$  is the entropy, and  $T$  is the temperature (Jagodzinski, 1954). However, for the  $PbI_2$  crystals growing at room temperature, the product  $TS$  is likely to be too small to affect the value of  $F$  appreci-

ably. In the second mechanism, proposed for  $ZnS$  polytypes, the same result is achieved through a screw-dislocation controlled expansion of stacking faults in the crystal (Alexander, Kalman, Mardix & Steinberger, 1970). Since the  $PbI_2$  crystals frequently show growth spirals, centred on large screw dislocations, this mechanism is most likely operative during crystal growth in the creation of the  $PbI_2$  polytypes also.

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