

A new Rhombohedral Polytype, 12R, of Cadmium Iodide

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The crystal structure of a new rhombohedral polytype of cadmium iodide has been determined. It is the first rhombohedral type discovered in solution-grown crystals and has a 12-layered cell. The structure is $[13]_3$ in Zhdanov's notation with space group $R3m$. The crystals, three in all, show interesting coalescences. Their mode of formation is discussed.

More than 80 hexagonal polytypes of cadmium iodide, grown from solution and vapour, have been reported so far by various workers. Recently two rhombohedral types, *viz.* 30R and 42R, grown from the vapour phase, were reported by Chadha & Trigunayat (1967). We have now found a new rhombohedral polytype, 12R, in the crystals grown from solution. Three crystals of this type have been encountered, showing the same intensity sequence and spacing of X-ray reflexions. All these occurred in syntactic coalescence with other polytypes. One of them was chosen for detailed structure determination.

The crystal was oscillated about the *a* axis in the range 25–40° (*i.e.* the angle between the incident X-ray beam and the *c* axis varied between 25° and 40°), which is particularly suited for the identification of polytypes occurring in syntactic coalescence with others (Chadha & Trigunayat, 1967). Fig. 1 is the oscillation photograph taken so that surface reflexions from the upper part alone of the crystal, as picked up from the crystallizing dish, are obtained, identifying it as the type 12R. A zero layer *a*-axis normal beam Weissenberg photograph (Fig. 2) was taken for the structure work. The oscillation photograph, not reproduced here, taken to record surface reflexions from the lower part alone, identified it as the common type 4H.

There are two possible ways in which the atoms can be arranged to form a 12-layered rhombohedral structure. These are:

- (a) $[31]_3$
(b) $[13]_3$.

The intensity calculations for these cases were made for 10.*l* and 10. \bar{l} reflexions, *l* varying from 0 to 24, and were compared with those observed on the Weissenberg photograph (Fig. 2). As the spots in the 10. $\bar{24}$ to 10.24 range are not visible due to absorption, the comparison was made for the reflexions 10.24 to 10.48 and 10.24 to 10.48. The calculated and observed intensities differed widely for the structure (a) but were found to be in excellent agreement with each other for the structure (b). These values are listed in Table 1.

The detailed structure of 12R is therefore as follows:
Space group $R3m$

Zhdanov symbol $[13]_3$

ABC-sequence: $(A\beta C)(A\gamma B)(C\alpha B)(C\beta A)(B\gamma A)(B\alpha C)$
 $a=b=4.24 \text{ \AA}$, $c=41.01 \text{ \AA}$ (hexagonal indexing).

Table 1. *Calculated and observed relative intensities for the structure 12R*

(10. <i>l</i>)	$I_{\text{calculated}}$		I_{obs}^*
	$[31]_3$	$[13]_3$	
10.1	24.0	92.7	w†
4	178.1	68.8	vw†
7	1000.0	1000.0	vs
10	231.2	896.1	s
13	157.4	45.2	w
16	0.2	340.9	s
19	50.5	378.0	s
22	8.6	0	a
10. $\bar{2}$	81.2	0.5	a
5	331.1	1000.0	vs
8	0.9	581.8	s
11	416.1	47.3	w
14	372.2	575.7	s
17	1000.0	398.4	s
20	116.1	17.3	vw
23	10.7	17.3	vw

* As mentioned in the text, the observed intensities were actually taken from the series 10.24 to 10.48. This series has the same intensity sequence as 10.0 to 10.24.

† As can be seen in Fig. 2, the absorption is abnormally high for these reflexions because of the plate-like shape of the crystal.

Chadha & Trigunayat (1967) have pointed out that the formation of rhombohedral polytypes can be explained by the layer-transposition mechanism of Jagodzinski (1954). It is observed on the oscillation photograph (Fig. 1) that each diffraction spot is spread into a small arc. This arcing phenomenon has been explained by the authors (Agrawal & Trigunayat, 1967) in terms of tilt boundaries formed by the arrangements of edge dislocations lying in the different basal planes of the crystal. As these dislocations are created by the mutual slippage of the layers, their existence goes to show that layer displacements have taken place quite copiously inside the crystal during growth. Then the formation of the polytype can be easily explained as follows. As already mentioned, the type 12R (upper part) was syntactically coalesced with the common type 4H (lower part) in the crystal. On examining the ABC-sequence of 12R it is seen that its unit cell contains three 4H units, each shifted horizontally to a neighbouring orientation with respect to its predecessor in an anticyclic manner $[(A\gamma B)(C\alpha B) \rightarrow (C\beta A)(B\gamma A) \rightarrow (B\alpha C)(A\beta C)]$, which

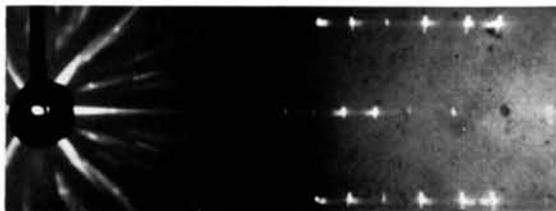


Fig. 1. X-ray oscillation photograph of polytype 12R; $\alpha - 15^\circ$ oscillation, Cu $K\alpha$ radiation, 3 cm camera radius.

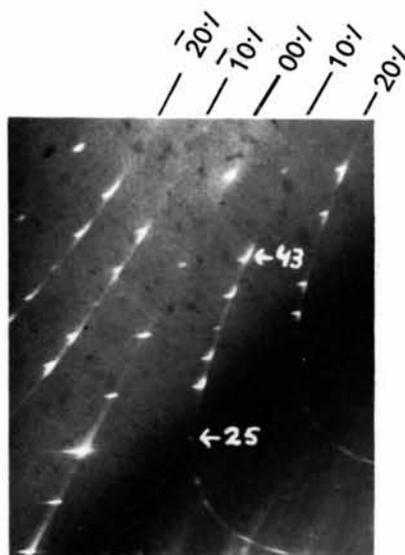


Fig. 2. Zero-layer a -axis Weissenberg photograph of polytype 12R; Cu $K\alpha$ radiation, camera diameter 5.73 cm; the festoons corresponding to $10.l$ and $\bar{1}0.l$ rows of spots are recorded on the right and left side, respectively, of the straight row of $00.l$ spots. The arrow marks indicate the l -values of the reflexions on the $10.l$ festoon.

indicates that the type 4H must have been formed in the initial stages of crystal growth and later transformed into the rhombohedral polytype 12R owing to layer displacements. This explanation is supported by the X-ray photographs of the second crystal, which was similarly found to be a mixture of type 12R (upper part) and 4H (lower part) in syntactic coalescence with each other. The arcing was found to be present to an even greater degree. The third crystal was identified as a mixture of 12R and 16H in syntactic coalescence with each other. It could not be ascertained in this case which of these belonged to the upper or lower part, respectively, of the crystal. However, the formation of a type 12R from 16H, or *vice versa*, can, in principle, be understood on the basis of layer-transposition mechanism.

Out of the two possible structures of 12R, the formation of structure (a) is less probable than the structure (b) theoretically also. The structure (b) is formed by slip between the molecular sheets themselves which are held together by weak van der Waals forces of attraction and can therefore easily slip with respect to one another under a small stress. The creation of

structure (a) will need the mutual displacements of layers within a molecular sheet itself, which is highly unlikely as the forces within a sheet are purely ionic in nature giving rise to a strong binding.

The type 12R, because it can be generated from the common type 4H, should be expected to occur more frequently than any other rhombohedral polytype of cadmium iodide. This conclusion is substantiated by the observation of three crystals of this type.

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The Crystal Structure of Pyroaurite*

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Rhombohedral pyroaurite ($R\bar{3}m$, $a=3.1094 \pm 2$, $c=23.4117 \pm 9$ Å, at 21°) consists, like hexagonal sjögrenite ($P6/mmc$, $a=3.113 \pm 3$, $c=15.61 \pm 1$ Å), of positively charged brucite-like layers $[\text{Mg}_6\text{Fe}_2^{\text{III}}(\text{OH})_{16}]^{2+}$ alternating with disordered negatively charged interlayers $[\text{CO}_3 \cdot 4\text{H}_2\text{O}]^{2-}$ ($Z=\frac{2}{3}$ for pyroaurite). Mg and Fe are randomly distributed among the octahedral positions. The OH layer sequence in pyroaurite is $-BC-CA-AB-BC-$. The water molecules of the (liquid-like) interlayer prefer positions about 0.56 Å off the threefold axis connecting two OH groups of adjacent brucite-like layers. The following distances were found: Me-OH 2.06, OH-OH 2.72 (3×) and 3.11 (6×), OH-H₂O 2.93 Å; \angle OH-H₂O-OH 158°. During the refinement with 283 reflections the residual dropped to $R=6.1\%$. The interlayer only contributes to the 00 l and 10 l reflections.

Introduction

The carbonate-hydroxides $\text{Mg}_6\text{M}_2^{\text{III}}(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ($\text{M}^{\text{III}}=\text{Fe}$, Al, or Cr) are known to occur in two dimorphic forms: the hexagonal sjögrenite group has $a \sim 3.1$ and $c \sim 15.5$ Å; the rhombohedral pyroaurite group has the same a value but c is about 23.2 Å (Aminoff & Broomé, 1930; Frondel, 1941). The two forms are very similar in their physical properties and are therefore nearly indistinguishable without the help of X-rays. According to Frondel (1941) the species in this group of minerals are the following:

M^{III}	Space group $R\bar{3}m$	Space group $P6/mmc$
Fe	Pyroaurite	Sjögrenite
Al	Hydrotalcite	Manasseite
Cr	Stichtite	Barbertonite

The best single crystals are available for the iron compounds sjögrenite and pyroaurite. The crystal structure of the hexagonal sjögrenite has already been reported (Allmann & Lohse, 1966: $a=3.113 \pm 3$, $c=15.61 \pm 1$ Å). It consists of positively charged brucite-like layers $[\text{Mg}_6\text{Fe}_2(\text{OH})_{16}]^{2+}$ and negatively charged interlayers $[\text{CO}_3 \cdot 4\text{H}_2\text{O}]^{2-}$. Since it consists of two kinds of layer this structure has been called a *hybrid layer structure* (Evans & Allmann, 1967). The brucite-like layers are stacked very regularly and form the backbone of the structure. These layers are separated by

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