

## Polytypism and Related Phenomena in CdBr<sub>2</sub>-Doped Dendritic Single Crystals of Cadmium Iodide

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### Abstract

Dendritic single crystals of CdI<sub>2</sub>, doped with 3% CdBr<sub>2</sub>, were grown from vapour phase in vacuum. The crystals exhibited well developed dendritic morphology. They were characterized by X-ray diffraction for their polytypism and related phenomena of streaking and arcing. The CdI<sub>2</sub> common polytype 4H was found to occur exclusively in 28% of cases and in combination with the polytype 12R in the rest of the cases. The frequency of occurrence of streaking and arcing were found to be rather high, viz 47 and 25%, respectively. The results point to a large-scale formation of dislocations and the consequent stacking faults inside the crystals, presumably created due to stresses produced in the host structure by the introduction of doped ions. Optical and scanning electron-microscopic study of the surface features shows a well developed dendritic morphology conforming with the hexagonal symmetry of the crystals.

### 1. Introduction

Impurities are known to play an important role in the growth of polytypes (Trigunayat, 1991). Of late, Jain and Trigunayat (Jain, 1996; Jain & Trigunayat, 1996) have studied the role of specific cations, viz cadmium, bismuth, tin, zinc and silver on the growth of polytypism in vapour-grown PbI<sub>2</sub> crystals. The formation of polytypes is also known to be influenced by crystal habit. For instance, only needle-shaped GaSe crystals display polytypism, although they grow in other habits too, viz plates, thin ribbons, prisms *etc.* (Terhell, 1983). Similarly, out of various possible habits (hexagonal plates, prisms *etc.*), only needle-shaped crystals of AgI show polytypism (Prager, 1983; Cochrane, 1967). During the last four decades, a great deal of work has been done on the polytypism of the MX<sub>2</sub>-type compounds CdI<sub>2</sub>, PbI<sub>2</sub> and CdBr<sub>2</sub>, almost all of which have been carried out on platy crystals (Trigunayat, 1991). For the first time, dendritic crystals of the richly polytypic materials CdI<sub>2</sub> and PbI<sub>2</sub> were grown from the vapour phase by Kumar & Trigunayat (1991a,b) and the effect of growth conditions on their polytypism was reported. The work was extended to study the effect of impurities on the formation of polytypes of CdI<sub>2</sub>, employing PbI<sub>2</sub> as the

dopant (Kumar & Trigunayat, 1993a,b). The effect was found to be different from that on the crystals with platy habit. The doping resulted in the replacement of the cation in the host structure. The present work involves a similar study with a dopant that could replace the anions in the host structure. The choice of the dopant, viz cadmium bromide, has been based on the consideration of the relevant factors like valency, electronegativity, ionic radius *etc.*, *vis-a-vis* the host structure. The doped crystals were characterized for their polytypism and related behaviour by X-ray diffraction. Their surface features were also studied, employing optical and scanning electron microscopy. The experimental results have been analyzed to assess the effect of doping.

### 2. Experimental

Analar grade CdI<sub>2</sub> and CdBr<sub>2</sub> (initial purity >99.9%) were highly purified by the method of zone refining. Cadmium iodide was purified by a horizontal zone-refining process, the experimental details of which have been reported earlier (Kumar & Trigunayat, 1991a). CdBr<sub>2</sub> could not be purified by this set-up owing to its high vapour pressure (nearly five times greater than that of CdI<sub>2</sub>), which caused rapid evaporation during zone melting. The difficulty was overcome by employing a vertical zone-refining set-up (Singh & Trigunayat, 1989), with some modifications. A high-pressure inert atmosphere of argon was created on the free surface of CdBr<sub>2</sub> to prevent its fast evaporation.

The purified CdI<sub>2</sub> and CdBr<sub>2</sub> (3% wt/wt) were thoroughly mixed and placed in a small quartz cup, which was dried in an oven at nearly 330 K for 2 h and then placed midway inside the growth tube. The tube was inserted inside a cylindrical furnace such that the charge occupied the central region of the furnace. It was evacuated up to 0.1 Pa, after which the temperature at the centre of the furnace was increased to 850 K. Within 6 to 7 h, dendritic crystals were found to grow nearly 10 cm away on either side of the charge. They grew in a small region measuring nearly 2 cm along the length of the tube, with the temperature at the ends of the region measured as nearly 600 and 620 K (Fig. 1). The appropriate temperature profile for crystal growth was obtained by adjusting the power in the two heating coils

of the furnace. Subsequently, the temperature was lowered and the crystals were collected on soft tissue paper.

The polytypes residing in the crystals were identified through their X-ray photographs, taken by oscillating the crystals about their *a* axis such that the angle between the *c* axis and the incident beam varied between 25 and 40°. This range of oscillation enables the recording of a large succession of *10.l* reflections, which are especially helpful in a quick identification of the polytypes. For each crystal, two or three different regions on either face were exposed to X-rays, since it is known that different portions of CdI<sub>2</sub> crystal may exhibit different polytypes (referred to as 'parallel growth' of polytypes).

**3. Results and discussion**

Most of the crystals exhibited well defined dendritic morphology, with well developed stems, branches and subbranches. They were fairly transparent with shining surfaces. Their lateral size varied between 9 × 3 and 3 × 1 mm and their thickness was of the order of 100 μm. A full dendritic single crystal is shown in Fig. 2. On the whole, it presents a platy appearance.

The X-ray diffraction studies revealed that the basal faces of a crystal lie in the *ab* plane (*i.e.* the *c* axis is perpendicular to the faces), with the stem directed along the *a* (or *b*) axis. In spite of unevenness of the surface and irregularity in shape, different portions of a dendrite, *viz* stem, primary arms and secondary arms, were crystallographically similarly oriented. This fact considerably helped in 'setting' the crystals for oscillation photographs.

The information gathered from the oscillation photographs of the crystals is summarized below:

Number of crystals studied	: 20
No. of X-ray photographs taken	: 103

Break-up of X-ray photographs in respect of various polytypes:

4 <i>H</i>	: 30 (29%)
4 <i>H</i> + 12 <i>R</i>	: 36 (35%)
4 <i>H</i> + 12 <i>R<sub>R</sub></i> + 12 <i>R<sub>0</sub></i>	: 30 (29%)
4 <i>H</i> + 12 <i>R</i> + 24 <i>R</i>	: 1 (1%)
4 <i>H</i> + unidentified	: 6 (6%)
Photographs showing streaking	: 48 (47%)
Photographs showing arcing	: 26 (25%)

A salient feature is the growth of polytype 12*R* in as many as 64% cases. A typical photograph of the mixture (4*H* + 12*R*) is shown in Fig. 3. This is in contrast with the earlier results of undoped CdI<sub>2</sub> dendritic crystals which had been found to exclusively consist of the common CdI<sub>2</sub> polytype 4*H* (Kumar & Trigunayat, 1991*b*). It is obvious that the formation of 12*R* and other polytypes arises from the doping of CdBr<sub>2</sub> in cadmium iodide. Presumably, the stable phase 4*H* is first formed during crystal growth and the formation of 12*R* results from the entry of large-sized Br ions in the host 4*H* structure, leading to the creation of stacking faults that subsequently arrange themselves as follows. The CdI<sub>2</sub> and CdBr<sub>2</sub> crystals are compatible in respect of crystal structure and valency but differ in regard to ionic radius and electronegativity. In the CdI<sub>2</sub> structure, the radius of an octahedral void is 0.89 Å and the radius of an I ion is 2.16 Å. The radius of a Br ion is 1.95 Å. Consequently, a dopant Br ion has little chance of occupying an octahedral void in the structure but it may replace an I ion in the structure, particularly as it has a higher electronegativity than the I ion, leading to the formation of a substitutional solid solution of cadmium bromide in cadmium iodide. The insertion of the Br ions in the I positions produces local distortions, which build up strong local internal stresses in the structure. These stresses are relieved by mutual slippage of the molecular layers I–Cd–I, which are bound together by weak van der Waals forces of attraction and so are prone to slip easily with respect to one another. This leads to the

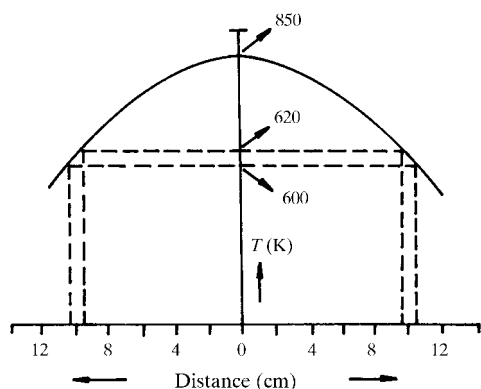


Fig. 1. Temperature profile of the furnace used in crystal growth.

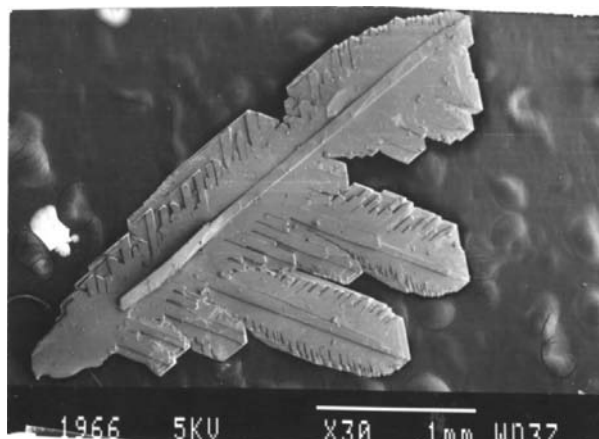
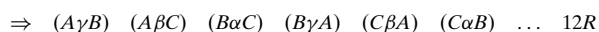
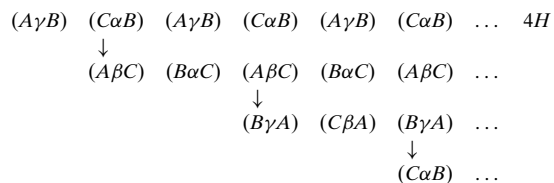


Fig. 2. Scanning electron micrograph of a CdBr<sub>2</sub>-doped cadmium iodide dendritic single crystal.

generation of both unit edge dislocations and partial edge dislocations in the structure. The latter lead to the creation of stacking faults, which under favourable thermodynamic conditions arrange themselves in a regular fashion to produce a well defined polytype. The formation of the 12R polytype in the host 4H structure may take place by suitable layer displacements, as shown below through extended layer sequences:



The arrows indicate the positions of the layer displacement, *i.e.* fault positions. Such a 4H → 12R transformation is highly probable as it involves just three stages of layer displacement.

It is noteworthy that the lead-doped (3% doping) dendritic single crystals of CdI<sub>2</sub>, too, had been found to show the formation of the rhombohedral polytype 12R (Kumar & Trigunayat, 1991a). The percentage of occurrence was found to be 49%, as compared with 64% in the present case of bromine doping. It implies that the creation of stacking faults should have been higher in the present case, which can be understood as follows. For the lead doping, the difference in the ionic radii of Pb<sup>2+</sup> (1.20 Å) and Cd<sup>2+</sup> (0.89 Å) is 24%, while for the bromine doping the difference in the ionic radii of Br (1.95 Å) and I (2.16 Å) is 12%. Consequently, the chances of insertion of the Br ions into the host structure are higher compared with the Pb<sup>2+</sup> ions, leading to a larger number of positions of local internal stresses in the structure and consequently increased creation of dislocations and stacking faults.

The increased creation of dislocations and stacking faults is reflected in the greater incidence of streaking and arcing in the present case of Br doping. The phenomena of streaking and arcing arise from (i) the

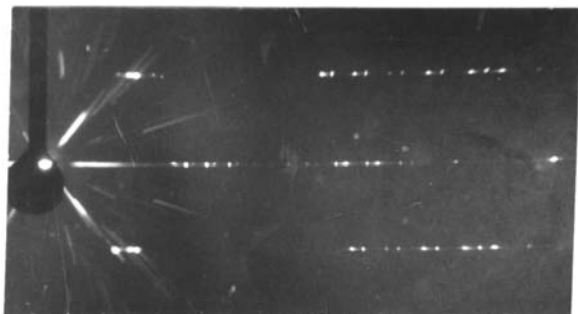


Fig. 3. An *a*-axis 15° oscillation photograph of a crystal showing reflections of the polytype mixture (4H + 12R). Camera radius 3 cm; Cu K $\alpha$  radiation.

presence of random stacking faults in the crystal and (ii) arrangement of edge dislocations into small-angle tilt boundaries in the crystal, respectively (Trigunayat, 1966). If a large number of faults is created in the Br-doped crystals, a large fraction of them is also expected to remain randomly distributed in the structure, after their possible rearrangement into a polytype structure, which agrees with the observation, *viz* the figures for the occurrence of streaking are 47, 11 and 0% (nil), for the Br-doped, the Pb-doped and the undoped crystals, respectively (Kumar & Trigunayat, 1993a,b, 1991b). Similarly, because of the large creation of dislocations in them, the Br-doped crystals are also expected to have the highest incidence of arcing in them, which also agrees with observation, *viz* 25, 7 and 0% (nil) arcing for the Br-doped, the Pb-doped and the undoped CdI<sub>2</sub> crystals, respectively.

A significant observation is that all the oscillation photographs contain reflections of the common polytype 4H, either exclusively or in association with those of other polytypes. Since the polytype 4H is known to be the thermodynamically most stable configuration of cadmium iodide, both at room temperature and at high temperatures, its observed wide occurrence in all the crystals is naturally expected, particularly as the bulk of the material in the crystal is cadmium iodide, with the doping of CdBr<sub>2</sub> being just 3%.

In the study of surface features, the crystals showed well developed dendritic morphology. A well defined stem was seen to run in the middle of a crystal, as clearly seen in Fig. 2. This feature is also present in the primary arms (Fig. 4). In most of the cases, the stem looked straight. The branching out of the arms from the stem along crystallographic direction could be seen frequently. The terminal parts of the tip of the dendrite and the primary and secondary arms were mostly seen to be hexagonal, in conformity with the hexagonal symmetry of the CdI<sub>2</sub> structure. Only in some cases

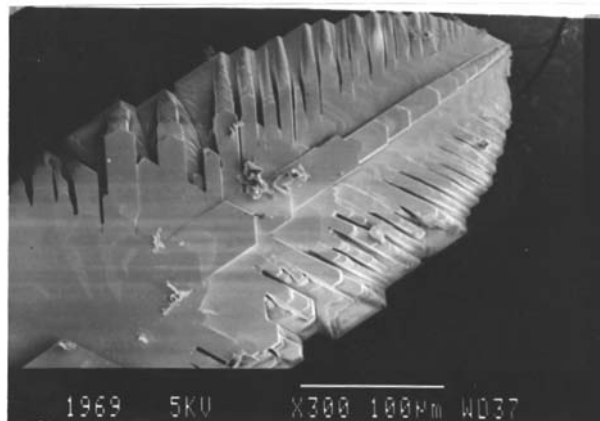


Fig. 4. Scanning electron micrograph of a primary arm. The stem, secondary arms and various layers having hexagonal and curved edges, both on the stem and the secondary arms, are seen.

(nearly 10%) were they found to be curved. A representative photograph depicting the coexistence of both hexagonal and curved terminals is shown in Fig. 5. The gaps between the various primary arms were found to be unfilled in most of the cases as seen in Figs. 2 and 5. However, no such gap existed between adjacent secondary arms. The observed existence of gaps between the primary arms indicates that the growth rate

is high along the direction of primary arms while along the secondary arms it is relatively low.

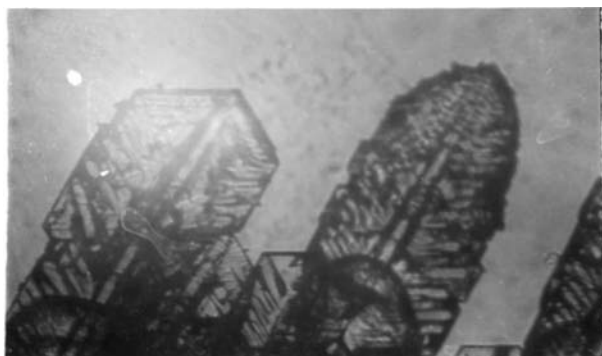


Fig. 5. An optical micrograph showing two primary arms of a dendrite. The terminal point of one of the arms is hexagonal while that of the other is angular.  $\times 210$ .

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