Study of cracks and phase transitions in cadmium iodide crystals using X-Ray diffraction

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Abstract. Polytypism has been observed in a large number of materials where the nearest neighbour relationship between identical two-dimensional layers of atoms can be satisfied in more than one way. The phenomenon has posed interesting problem for the Scientists, since the nature of force that causes ordering over the scale ranging from few angstrom to few thousands of angstrom units is not known. The Cadmium iodide has been purified and single crystal grown using a zone-refining system. The frequent appearance of cracks in the grown crystals when exposed to N$_2$ laser at room temperature has been explained on the structural considerations of CdI$_2$. The crystals of cadmium iodide have also been grown from solution in two batches using unpurified and purified material. A comparative study has been made on these batches for polytypism using x-ray diffraction technique. Formation of small period polytype 2H is governed by both temperature and impurities contained in the starting material. 4H is the most stable polytype. Higher occurrence of unidentified polytype in crystals of purified material has been attributed to free movement of edge dislocations during growth. The results have been examined, keeping in view the empirical considerations of earlier investigations.

1. Introduction
There are many physical factors associated with the growth of polytypes and a number of solutions have been put forward by the researchers to account for the phenomenon. These have been based on considerations like temperature; rate of crystallization and presence of impurities. Of these the presence of impurities is prominent one. Salje [1] in his large and wide studies has emphasized that the polytype growth is kinetic in nature and supports nucleation and growth mechanism of polytypes. While some specific studies on the effect of impurities on polytype formation have been carried out on SiC, ZnS, and PbI$_2$ crystals [2, 3, and 4]. Little work has been done on CdI$_2$ that are richly polytypic in nature. Till date, several hundreds of CdI$_2$ polytypes have been discovered and nearly 200 structures have been worked out. In a combined optical, SEM and STM study of cadmium iodide, precise information about the growth features on the crystal surface and mode of growth of polytype 4H by screw dislocation have been reported [5]. Further, Kumar has studied the electrical, optical and dielectric properties of pure and doped melt grown CdI$_2$ and PbI$_2$ crystals. In the doped crystals no new polytypes have been observed and were found to be harder than the undoped ones [6]. Earlier Jain and Trigunayat [7] have studied the effect of impurities on the nature of growth of polytypes in solution grown crystals of cadmium iodide. Since the zone-refining enables one to exercise control on the degree of purification, so it was hoped that this effect could be better studied in a semi-quantitative
way by growing crystals of cadmium iodide under controlled conditions of temperature and humidity using purified material and to examine as how their polytypism differed w.r.t. the crystals of unpurified material grown under identical conditions.

2. Experimental details
The cadmium iodide has been purified by using zone refining technique and crystals have been grown by two methods.

2.1. From melt (using zone refining system)
The details of purification of material and growth of crystals from melt have been described earlier [8]. The complete purification necessitates 20 zone passes (manufacturers of Analar grade cadmium iodide have mentioned the presence of alkalis in the raw material. Atomic absorption spectroscopy tests show only 1ppm of K and Na.). The grown ingot measured nearly 10 cms in length and 0.5 cm in thickness. Small pieces were cleaved from the ingot for the study of X-Ray diffraction and exposure to laser beam.

2.2. From solution
The crystals have been grown by simple method [9] of slow evaporation of aqueous solution of cadmium iodide. For controlling the conditions of growth, a humidity cabinet was employed in which humidity and temperature could be separately controlled. The door of the cabinet had a glass window through which the crystals could be observed during the growth.

10 grams of analar grade/purified cadmium iodide was dissolved in 20 cc of doubly distilled water and filtered through a fine quality filter paper. The filtered solution was transferred into a well-cleaned shallow flat-bottomed crystallizing dish that was kept in humidity cabinet. The values of humidity and temperature were maintained at 70% and 38ºC respectively. The dish was kept inside the humidity cabinet until a number of well-developed platy crystals were formed. The crystals were hexagonal in shape and measured nearly 1-3 mm across and 50-500 micrometer thickness with shining (0001) basal faces.

The crystals were carefully transferred to a well-cleaned microscope slide for the optical examination. The perfect ones were chosen for further investigation. The well-developed morphology of the crystals helped in mounting them in a desired orientation on the X-ray camera. 15º oscillation photographs of the crystals were taken with crystal so positioned that a long succession of 10.1 reflections, that are suited for the polytypic identification were recorded on zero layer line.

From the viewpoint of obtaining reliable statistical results it was proposed to carry out the X-ray diffraction study of nearly 90 crystals each of
(1) Crystals grown from the raw material.
(2) Crystals grown from the purified material.
Separate X-Ray diffraction photographs were obtained from the faces of each crystal.

3. Results and Discussion

3.1. Melt grown crystals
All the crystals grown by zone refining system have the structure 4H. In the melt growth, the temperature of growing crystal is just below the melting point of the substance and any metastable structure, if at all formed must transform into a structure which has minimum energy configuration at that temperature which in fact is 4H (Figure 1)
3.2. Cracking under laser and storage

During the optical gain studies of perfect cadmium iodide crystals with N₂ laser at room temperature, some cracks were observed in the crystals. [10]

Further it is to be reported that when the crystals of cadmium iodide (Figure 2) were stored in an isolated place for a long period (~ 5 years) cracks and many defects appeared on the crystals and transparency also decreased considerably as shown in Figure 3. Similar is the situation for another crystal (Figure 4, Figure 5)

![Figure 1](image1.png)

**Figure 1.** An a-axis 15°-oscillation photograph of a CdI₂ crystal, showing the reflections of most common polytype 4H. CuKα radiation; 3 cm camera

![Figure 2](image2.png)

**Figure 2.** Photograph showing a CdI₂ Crystal cleaved from the ingot.

![Figure 3](image3.png)

**Figure 3.** Same crystal (as in Fig.2) after Being stored for a period of ~ 5 years.

![Figure 4](image4.png)

**Figure 4.** A CdI₂ crystal mounted on the glass fiber with one crack only.

![Figure 5](image5.png)

**Figure 5.** Same crystal (as in Figure 4) after being stored for a period of ~5 years. (Many a cracks are visible)
The CdI$_2$ structure consists of various stackings of CdI$_2$ sheets in each of which a layer of Cd ions is sandwiched between two close packed layers of iodine ions. The binding within a molecular sheet, believed to be largely ionic, is quite strong but two adjacent sheets are bonded together with weak van der walls forces. Wahab and Trigunayat [11] have shown that there is an increase in I-I separation of CdI$_2$ molecules with rise in temperature, thus implying the weakening of I-I bonds.

When exposed to N$_2$ laser, the necessary energy for the formation of cracks is provided by the laser pulse. The laser pulse has enough energy to weaken the bonding between various sandwiches, leading to appearance of cracks. The appearance of cracks has been explained in terms of movement of edge dislocations and their obstruction against some impurity particle. It may be added here that during purification by zone-refining system, the impurities with $K_0 = (C_s/C_I) < 1$ can be removed. The role of impurities with $K_0 > 1$ is passive as these impurities are to be accommodated by the host lattice.

The steady state dislocation velocity in a material is usually related to the net shear stress acting on the dislocation $\sigma_d$ by a power law equation of the form $V_{ss} \propto \sigma_d^m$ where $m$ varies between 5-40 for metals but for ionic compounds like CdI$_2$ the dislocation velocity is approximately proportional to the stress i.e. $m=1$ [12]. From the above fact it is very clear that when exposed to the laser, there is a very strong stress due to thermal heating and very fast movement of dislocations that leads to formation of cracks instantaneously. Whereas, in the case of CdI$_2$ stored for longer times the stresses available are due to impurities (of the order of few ppm) which are very small and development of cracks takes as long as many years. However a detailed microscopic work would be considered.

3.3. Solution grown crystals

Table 1 shows the frequency of occurrence of various polytypes in solution grown crystals from raw and purified material. It is clear that the most common polytype 4H has a dominating occurrence viz. nearly 50% of the total in the case of raw material and 32% in the case of purified material. The percentage of disordered or unidentified structures is 32% of the total in the raw material and nearly 51% in the case of purified material.

| TOTAL NUMBER OF CRYSTALS | POLYTOPES | 2H | 4H | Higher | Unidentified |
|--------------------------|-----------|----|----|--------|--------------|
| (Raw material) 90        |           | 1  | 90 | 46     | 58           |
| (Purified material) 90   |           | 7  | 57 | 43     | 93           |

The higher occurrence of 4H in raw material may be attributed to the fact that the presence of impurities play a dual role in the case of polytypic crystals: (!) producing local stresses in the crystal structure leading to generation of dislocations and stacking faults (!!) providing hindrance to the movement of dislocations and consequent reduction/elimination of stacking faults[13].

In the case of 4H, nuclei preferably are formed around some impurity particle for subsequent growth of 4H. Since the crystals of above category have the maximum impurities, they have the
highest percentage of 4H in them. The dislocations originating during the crystal growth are hindered due to the presence of impurities thus eliminating the stacking faults, pinning down transformation front for other structures and leading to the formation of 4H polytype. By the same token, the lesser percentage of 4H in the pure material can be attributed to the fact that in this case the dislocations can move relatively more freely and there are greater chances of creation of random stacking faults leading to lesser incidence of 4H type. The above discussion also explains the lesser frequency of occurrence of the unidentified in the raw material and higher occurrence in the purified material.

In the present work the number of higher polytypes obtained in the crystals grown from both pure and raw material are nearly equal.

The polytype 2H has been observed only once in the crystals grown from raw material whereas in the case of crystals grown from pure material it has been observed 7 times. Earlier Jain and Trigunayat [7] have reported that temperature of growth has marked effect on the formation of 2H. Higher the temperature, lower is the frequency of 2H and it comes down to naught at 40°C. In our case all the crystals have been grown at 38°C indicating that it is not only the temperature that affects the formation of 2H but also the impurities contained in the starting material.

The crystals in general largely owe the regularity of their internal structure to the existence of atomic forces of attraction and repulsion, which exercise their influence over a short range ≈20 Å. The observed higher polytypes with cell heights up to thousands of angstrom units implies certain external agencies like (dust particles, lattice vibrations, vibrational entropy, electron density) are also operational in their creation.

The frequency of occurrence of 2H only once in the crystals grown from raw material and 7 times in the crystals grown from pure material indicates that action of atomic forces dominates in the case of formation of 2H in the purified material.

From the above discussion it becomes an open question and interesting problem that if 2H polytype will have the highest probability of occurrence when grown from the pure material under dust free atmosphere?

In the above studies only some specific conclusions could be made for only small period polytypes. However to study the effect of purification/impurities on the distribution of higher polytypes we need to study a very large number of crystals.

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