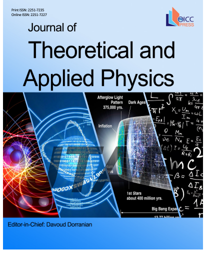

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A systematic study of polytypism in melt & solution grown crystals of cadmium iodide doped with anionic & cationic impurities

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Original Research

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Abstract:

Investigations carried out on various polytypic compounds till now have shown that the presence of impurities during the growth affects the formation of polytypes. However, this work has remained broadly qualitative. To assess the role of impurities on polytype growth in a definite manner, it was decided to systematically dope with the purified crystal of richly polytypic compound, viz., CdI_2 with cationic and anionic impurities. Such a study was conducted on both the crystals grown from melt and solution. The crystals have been characterized by X-ray diffraction and physical method such as color variation, elasticity, shape appearance and optical measurements. The results have been discussed.

Keywords: Polytypism; Doped crystals; Zone-refining; X-ray diffraction; Streaking; Arcing

1. Introduction

The growth of polytypes of a compound depends on several factors such as temperature, pressure, rate of crystallization, nature of solvent, external field, presence of impurities, etc. Out of these, the effects of temperature and rate of crystallization have been extensively studied, whereas the effects of other factors have been studied to a lesser extent. A good deal of study has been done regarding the effect of impurities on the growth of SiC polytypes [1–3]. According to them, various kinds of impurities result in the stabilization of different polytype structures. In another richly polytypic compound ZnS, it has been reported that the addition of various impurities induces structural transformation [4, 5]. X-ray diffraction (XRD) studies on well-purified crystals of cadmium iodide (CdI_2) grown from melt extensively showed the diffraction spots of most common polytype 4H [6, 7]. Even though CdI_2 has emerged as the most richly polytypic compound, the well-purified melt-grown CdI_2 crystals did not show any polytypism at all. A beginning to the study of effect of specific impurity, i.e. Sn, Pb, and PbI_2, on the polytypism of CdI_2 was also made [8–10]. In a similar study potassium dihydrogen phosphate (KDP) doped vapour-grown crystals of CdI_2 showed marked changes in the surface features as compared to the doping with PbI_2 and $CdBr_2$ [11, 12].

Recently, an analysis of the polytypism of compounds has been performed using the approach of order-disorder (OD) theory [13].

A similar theoretical study discusses the structural evolution of stacking-faulted MX_2 systems as a function of temperature and pressure, highlighting the potential for controlling composition/structure/property relationships among layered MX_2 materials [14]. Lately, structural, electronic, optical and thermal properties of undoped and metal doped [Ni, Cu and Zn] CdI_2 were also reported using a theoretical model and computational methods [15]. In a recent study on polytypism in ZnS nanowires grown by metallorganic chemical vapour deposition (MOCVD) using gold and gold gallium alloy as catalysts has thrown light on better understanding of polytypism in the semiconductor 1D nanostructures [16]. In view of the above, it was decided to carry out a quantitative study of the effect of incorporating dopants of desired category and desired amount. To this effect, only those impurities that could substitute one of the atoms of the host material were chosen, resulting in the formation of a substitutional solid solution. To give maximum possibilities for such a formation the following properties of dopants were scanned in relation to CdI_2: electropositivity, ionic radius, crystal structure of the resulting compound of the dopant and valency. Accordingly, it was decided to employ metallic gallium (Ga) and indium (In) as cationic dopants and bromide (Br_2) and chloride (Cl_2) of Cd as anionic dopants.

2. Experimental

Before carrying out the doping, the host material, i.e. CdI_2, was well purified using zone refining technique. The technique was earlier successfully used for purification of CdI_2 [6]. The so purified material was then used for doping with cationic and anionic impurities. Zone refining apparatus with a slight modification was used for the growth of single crystals doped with cationic impurities, using zone levelling techniques. On the other hand, Bridgeman-Stockbarger method was used for the growth of single crystals doped with anionic impurities.

In addition, the doped crystals were used to grow single crystals from solution. This led to an interesting study of the effect of anionic and cationic doping on the polytypism of melt and solution-grown crystals of CdI_2.

2.1 Melt growth of gallium and indium doped CdI_2 crystals

The zone levelling systems were designed to provide both forward and reverse movement of the molten zone. Both ends of the boat for holding the charge were tapered to obtain doped single crystal in the final run, irrespective of the direction of movement of the zone. The apparatus consists of an outer cylindrical jacket made of quartz, a quartz boat meant for holding the charge, and resistance heaters mounted on a trolley that can move along the rails. Zone refining of CdI_2 in air results in its oxidation .Therefore, the entire process of purification and melt growth of doped single crystals was carried out in argon gas atmosphere. Two circular heaters were mounted on the trolley for creation of two molten zones of 1 cm length each, so that one pass of trolley amounts to 2 zone passes. Up to twenty repetitive zone passes were used to purify the material. The so purified material was used for doping with Ga and In, respectively. For the purpose of doping using zone levelling technique the melting point of dopant should be less than or comparable to the melting point of CdI_2. The melting point of both Ga (29.8 °C) and In (156.4 °C) satisfies this criterion. 3% of spectroscopically pure Ga and In were individually doped in the same manner as done earlier for metallic Lead (Pb) [8].

For Ga doping, metallic Ga was placed at the initial edge of the boat containing purified CdI_2 and a molten zone of 1 cm length was created. A granule of metallic Ga was found sitting at the bottom of the zone as the density of molten Ga is higher than that of CdI_2. Soon, Ga gets dissolved in the CdI_2 and could not be seen. Ordinarily the molten zone of CdI_2 is transparent but here the starting zone was seen to be translucent. Initially, the zone containing Ga was passed through the ingot at a speed of 1.2 cm per hour. However, the shape of the interface in the initial region of the ingot was not found to be planar at this speed. In order to obtain a smooth planer solid-liquid interface the speed of the zone was reduced to 5 mm per hour. Ga rich zone was passed through the ingot at this speed fourteen times in forward and reverse direction, to achieve uniform doping by zone levelling. The upper surface of the ingot appears greyish in colour. The growth of single crystal was carried out together with zone levelling in the same boat by giving the final pass with a low temperature gradient in the solid from the side of growth interface. The entire operation was carried out in the argon gas atmosphere.

The method employed for the doping with In was the same as described above for the doping of Ga as all the properties of In including melting point of 156.4 °C satisfy the conditions required for doping using levelling technique. By trial and error, a speed of 8 mm/hr was found suitable for In zone movement in obtaining a smooth planar 1 cm solid liquid interface. The molten zone remained transparent throughout, but the colour of the zone became progressively darker. After the first zone pass, the colour of the ingot became reddish brown. The change in colour presumably occurred due to the replacement of Cd atoms in the base material by In atoms resulting in the formation of substitutional solid solution. (InI_3 has reddish colour at room temperature). To obtain better uniformity the method of repeated pass zone melting was used by giving 10 forward and backward zone passes, which resulted in attainment of near uniformity of colour in the ingot. The temperature profile during the last zone pass was shown in Fig. 1.

2.2 Melt growth of anion (Br^- and Cl^-) doped CdI_2 crystals

Our study of effect of doping with cation on the polytypic of cadmium iodide (CdI_2) encouraged us to extend the study by doping the same material with anions. For this purpose, such anions which have the tendency of replacing the existing iodine ion in the base material have been chosen so as to form substitutional solid solution. Accordingly, it was

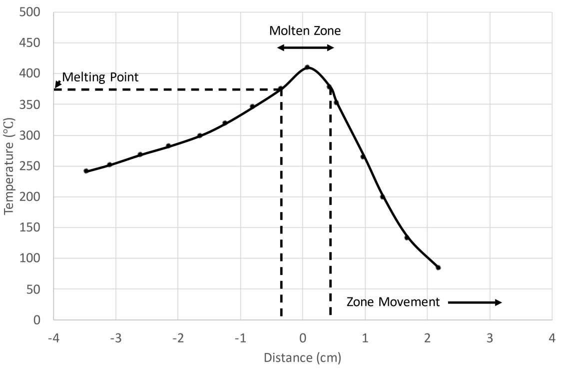

Figure 1. Temperature profile of the growth chamber for growing In and Ga-doped CdI_2 crystal by zone-melting.

decided to use $CdBr_2$ and $CdCl_2$ as dopants.

The choice of the method for the growth of doped crystals has to be consistent with the physical properties of the dopants. As the melting point of both the dopants ($CdBr_2$:567 °C; $CdCl_2$:568 °C) is much higher than the melting point of base material (CdI_2:368 °C) it was not feasible to create molten state permanently because CdI_2 largely evaporates before we could reach the melting point of each of the dopants. Also, in view of high volatility of the dopants, Bridgeman-Stockbarger technique was used for the growth of anion doped CdI_2 crystals. The apparatus used for the growth of doped crystals is shown in Fig. 2. The container for holding the charge in a quartz tube with a conical tip for crystal nucleation. $CdBr_2$ with a purity of 99.99% was first dehydrated by heating for 24 hours in vacuum at 150 °C. Then 3% of host material was added to CdI_2 and transferred to the ampule which had the shape as shown in Fig. 3.

The ampule which had internal diameter of 7 mm was thoroughly cleaned with aqua regia before using it for crystal growth. The ampule was then rinsed with the doubly ionised distilled water to remove all the traces of acid. It was then dried by keeping it in furnace at 150 °C for 1 hour. Subsequently, it was filled with the desired mixture of CdI_2 and $CdBr_2$ and then evacuated to a pressure of 10^{-5} torr with the help of a mercury diffusion pump to remove any traces of moisture and volatile impurities. The material was degassed in vacuum at 300 °C for about 5 hours and then the sample was vacuum sealed.

The sealed ampule was placed inside the Bridgeman-Stockbarger furnace the upper zone of which was maintained at a temperature of 590 °C. A synchronous motor was used for lowering the ampule into the furnace at a rate of 5 mm per hour so as to pass through a small temperature gradient. Higher rates of lowering did not produce good single crystals. The temperature profile is shown in the Fig. 4.

When the whole charge got solidified and reached a region of almost uniform temperature in the lower region of the furnace, the temperature of the furnace was reduced gradually to prevent the possible generation of stress in the crystal. The as grown crystal was taken out of the quartz container by dissolving the quartz container in hydrofluoric acid. The crystal had a cylinder shape measuring 6 cm in length and 7 mm in diameter. The method employed for Cl doped crystals was the same as the Br doped crystals. The temperature profile for the Cl doped crystals is also the same as for the Br doped crystals. These crystals measured 6.6 cm in length and 7 mm in diameter.

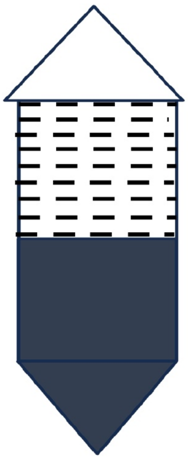

Figure 3. Depiction of crucible design for nucleating single crystals from melt using Bridgman-stockbarger.

2.3 Growth from solution

In order to make a comparative study of doping on the polytypism of crystals grown from melt and solution the melt grown doped CdI_2 was used as a raw material for growing crystals from solution. For this purpose, a solution of 40% concentration was made by dissolving 5 gram of Ga doped material in 12.5 mL of double distilled water at 75 °C. The solution was filtered through a fine quality filter paper and the filtrate was transferred to a clean flat bottom

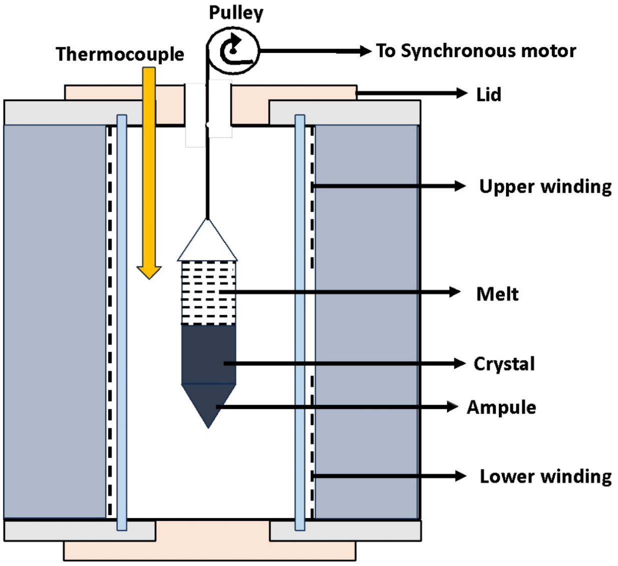

Figure 2. The schematic of growth of doped crystals.

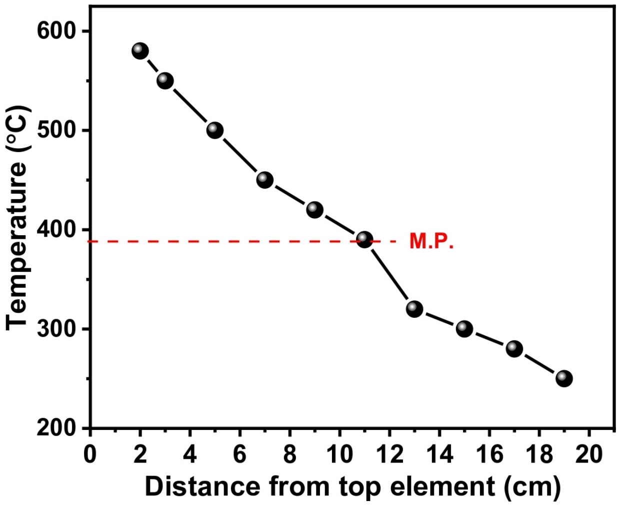

Figure 4. Temperature profile for the growth of anion doped crystals by Bridgman-Stockbarger method.

crystallizing dish. The dish was left for crystals to grow by slow evaporation at a temperature between 32 °C − 35 °C. Good numbers of crystals were seen after 60 hours, and these crystals had very fine morphology and measured 30 to 800 microns in thickness and nearly 1 − 6 mm across. The crystals were carefully removed from the solution with the help of two Celluloid splitters.

To obtain In doped solution grown crystals, 4.2 gm of melt grown CdI_2 was dissolved in 12 mm of double distilled water, a magnetic stirrer was used for dissolving the material. Unlike the Ga doped material some portion of material remain undissolved despite vigorous stirring at 80 °C. The dissolved mass consisted of some brown precipitate with reddish tints along with some tiny particles with silvery texture. The solution was filtered through a fine quality filter paper to grow crystals, as in case of Ga doped crystals. Only 8 crystals were seen nucleating in the dish after 60 hours and the experiment was repeated many times to obtain more crystals. The crystals measured 1 − 8 mm across and 100 − 400 micron in thickness.

To grow both Br and Cl doped crystals from solution, the melt grown doped CdI_2 was used as a solute to prepare aqueous solution for the growth of anion doped crystals by slow evaporation. The solution was prepared at 60 °C and no trace of undoped mass was seen in the solution. The solution with an initial concentration of 34% was prepared, filtered and left for crystallization at room temperature for about 72 hours. Unlike in cation doped crystals grown from solution, creeping of solution on the walls of the dish was observed after about 40 hours in both the cases during the growth process. Creeping was so profuse that sometimes whole of the solution crept out of the dish leaving no scope for the formation of crystals. Also, a tendency of formation of crystalline clusters adjacent to the walls of dish was observed. Owing to these difficulties the process of crystal growth had to be repeated several times to obtain adequate number of crystals for X-ray characterization. In both the cases the crystals were hexagonal in shape and measured 1 − 4 mm across with 50 to 250 microns in thickness.

3. Results and discussion

The doped crystals were characterized by XRD method and physical method such as color variation, elasticity, shape appearance and optical measurements. Their characteristics were compared with those of melt grown well purified undoped crystal of CdI_2. All the doped crystals were found to be harder compared to pure undoped crystal of CdI_2. The uniformity of doping was tested by measuring the DC conductivity of several crystal pieces from different parts of the central portion of the ingot. The values were found to be almost the same, confirming the uniform distribution of dopant in the ingot.

The optical perfection of the crystal was ensured before their X-ray studies. Small pieces having thickness nearly 0.5 mm and measuring nearly 4 × 5 mm across were cleaved along the Basal plane from different parts of the ingot. Both the Basal planes were shining in each case. The shining cleaving plane of the doped crystal were found to be perpendicular to the c-axis was as per undoped CdI_2 crystal. Also, the direction of the c-axis was found to be perpendicular to the direction of growth of the crystal. 15° oscillation photographs of the crystal about a-axis were taken. CdI_2 is known to exhibit syntactic coalescence of polytypes, X-ray photographs of two basal faces were separately taken. As the CdI_2 crystals also exhibit parallel growth of 2 or more polytypes on the same face, photographs were also taken from different parts of the same face.

In case of melt grown Ga-doped crystals a total number of 70 photographs were obtained from 10 different crystals. All the photographs showed the reflection of most common polytype 4H. One such photograph is shown in Fig. 5.

Fig. 5. depicts a-axis 15° oscillation photograph of a melt grown Ga-doped Crystal, showing reflections of the most polytype 4H. It was found that these crystals require a larger exposure time (nearly 5 times) as compared to the crystals of pure undoped CdI_2. Unlike the oscillation photograph grown from solution, all the photographs of Ga doped crystals were found to be free from “Arcing” and “Streaking”. In a similar study on Ga doped crystals grown from solution, 93 photographs were obtained from 30 different crystals and the phenomena of Arcing and Streaking was observed in 7% and 43% of the photograph, respectively.

All the photographs of In doped crystals grown from melt were devoid of ‘streaking’ and ‘Arcing’. One such photograph is shown in Fig. 6.

Fig. 6. depicts a-axis 15° oscillation photograph of a melt grown In doped crystal, showing diffused reflection of most common polytype 4H, showing absence of ‘Arcing’ and ‘Streaking’.

Similarly, study on the Br doped melt grown crystals of CdI_2 was made on 8 different pieces by taking 15° a-axis oscillation photographs with c-axis oscillating in 25° − 40° range. Unlike the melt grown crystals doped with the Ga and In, a tendency of formation of higher polytypes (that could not be identified) along with 4H was observed in 14% of the photographs. Diffraction spots on photographs were found to be diffuse in 23% of cases and comprised of streaking in 50% of the cases. One such photograph is shown in Fig. 7.

Fig. 7. depicts a-axis 15° oscillation photograph of a melt grown Br^- doped crystal, showing diffused reflection of most common polytype 4H, accompanied by streaking; some extra diffused reflections are also present. CdI_2 crystals doped with chloride ions when subjected to X-ray examination revealed streaking in 32% of cases and diffuse spots were obtained in 10% of the total number of 61 photo-

Figure 5. a-axis 15° oscillation photograph of a melt grown oscillation photograph of a melt-grown Ga-doped crystal, showing reflections of the most polytype 4H.

Figure 6. a-axis 15° oscillation photograph of a melt grown In-doped crystal showing reflections of most common polytype 4H.

graph from 12 crystal pieces. All photographs were found to be free of Arcing of reflections. Three photographs show the presence of an identified polytype along with the most common type 4H as shown in Fig. 8.

Fig. 8. depicts 15° a-axis oscillation photograph of a melt-growth Cl-doped crystals, showing reflections of the most polytype 4H, accompanied by ‘streaking’.

The results of doping of melt grown crystals are discussed in relation to the undoped crystals of CdI_2.

3.1 Doping with metallic indium

Entire Indium added to CdI_2 got dissolved during the zone levelling operations, which can be accounted for by the following considerations: In is more electropositive than Cd therefore stands a good chance for substitution for Cd in CdI_2 structure. In ions bonds with iodine ions to form InI_3 which has a hexagonal closed packed (H.C.P) structure with cations in the octahedral coordination, at room temperature. Further, like CdI_2 it has a layered structure. The In^{3+} ions, substituting for Cd^{2+} ions can easily move into the octahedral voids, because the radius of In^{3+} ions (0.81 Å) is about 10% less than that of the sphere representing octahedral void (0.89 Å). All these factors viz., electropositivity, similarity in crystal structure and ionic radius extensively favour the formation of substitutional solid solution. The process is favoured by valency considerations too. Consequently, the complete solubility of In in CdI_2 is favoured.

The observed increase in hardness can be accounted for as follows: Doping with In results in the substitution of Cd atoms by In atoms. Real crystals are always known to have mosaic blocks. Also, in CdI_2 structure half of the total number of octahedral voids formed as a result of close packing of I- ions are empty. The replaced Cd atoms can enter either into the boundary between the mosaic blocks or empty octahedral voids between I-Cd-I sandwiches. Their first choice should be the mosaic boundaries as that will neither change the dimensions of the unit cell nor the crystal structure substantially, thus producing a slight change in the energy of free crystal. They will usually enter the interstitial octahedral voids when the accommodation ceases to exist in mosaic boundaries. As a result, the bonding between the molecular sandwiches which are normally held together by week Van der Waals forces will become stronger (because now the intervening Cd atoms will be weekly attracted by the I- Ions on both the sides), resulting in the observed hardening of the Crystal. The occupancy of interstitial sites also affects the ease with which one layer may slip over another, which in turn affects the hardness, malleability and ductility of the material [17].

Figure 7. a-axis 15° oscillation photograph of a melt grown Br doped crystal, showing diffused reflection of most common polytype 4H, accompanied by streaking; some extra diffused reflections are also present.

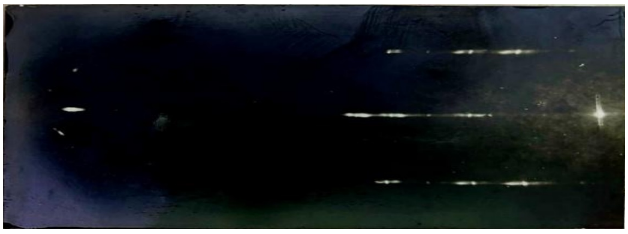

Figure 8. a-axis 15° oscillation photograph of a melt-growth Cl doped crystal, showing reflections of the most common polytype 4H, accompanied by ‘streaking’; some extra diffuse reflections are also present.

Further, In-I bond strength is 80 kcal/mol at 25 °C, which is much stronger than Cd-I bond strength (33 ± 5 kcal/mol at 25 °C. Consequently, substitution of Cd by In results in the formation of stronger bond within the molecular sandwich which will also contribute towards hardening of crystals.

3.2 Doping with metallic gallium

Like In, Ga is also trivalent. It too shows a complete solubility in CdI_2. The substitution of cadmium by gallium results in the formation of GaI_3 which has a similar structure as that of InI_3 [18, 19]. Further, Ga is more electropositive than Cd and ionic radius of Ga^{3+} ion (0.62 Å) is about 30% less than that of the sphere representing octahedral void. All these factors favour high solubility of Ga in CdI_2 as observed. Like In doped crystals, these crystals were also found to be harder than the crystals of undoped CdI_2. The underlying reason is the same as for the In doped crystal viz., due to strengthening of bond between the sandwiches. The bond strength of Ga-I is 81 kcal/mol at 25 °C [20] as compared to 33 ± 5 kcal/mol for Cd-I bond. Ga doped crystals require larger exposure time (3 to 4 hours) as compared to 1 hour for pure undoped crystals of CdI_2, for obtaining well exposed X-ray photographs. As mentioned earlier, the radius of the sphere representing octahedral void obtained as a result of closest packing of I- ion is approximately 0.9 Å. It implies that anion of radius 1 Å can enter the octahedral voids without producing any appreciable local distortions. In substitutional solid solutions local deformations are produced when solute atoms have much larger, or much smaller atomic or ionic radius as compared to that of solvent atoms. In the present case since the radius of substituting Ga^{3+} ions (0.62 Å) is much smaller than that of substituted Cd^{2+} ions (0.97 Å) by a factor of 30%. Consequently, strong local distortions will be produced in the host structure. It is known that the local displacements in a crystal structure leads to weakening of intensity of X-ray reflections [21]. Hence, the observed prolongation of exposure time is accounted for. It follows that the internal stresses arising from the local distortions are not relieved by the creation of dislocations. Instead, they remain intact within the crystal, which is substantiated by the absence of 'streaking' and 'Arcing' on the X-ray photographs.

The X-ray photographs of both In doped and Ga doped melt grown crystals revealed exclusive presence of most common CdI_2 polytype 4H. Besides no crystal has shown 'streaking' or 'arcing' on its oscillation photograph. It follows that doping with Indium or Gallium does not affect the high temperature stability of CdI_2 type 4H. Since 'streaking' arises from the existence of random stacking faults in the crystal structure, it's absence on the oscillation photograph reveals the absence of stacking faults in the crystals. Also, the absence of arcing (which arises due to arrangement of edge dislocations into tilt boundaries) indicate low density of dislocations in crystals. In short, internal stresses arising from local dislocation are not relieved by the creation of dislocations.

3.3 Doping with anions (Br^- and Cl^- ions)

Just as electropositivity was considered a crucial factor for cation substitution, electronegativity was taken into account for anion substitution. Both the anions used for doping are more electronegative compared to iodine, therefore, can favourably substitute for iodine in CdI_2. Seven X-ray photographs of the crystals doped with Br^- showed a tendency towards formation of polytypes (that could not be identified), in addition to the most common type 4H. As reported earlier, unlike the melt grown crystals of undoped cadmium iodide (CdI_2), 'streaking' and diffuse spots were seen on the photographs. Stacking faults in the structure are responsible both for the creation of higher polytypes and the presence of streaking on the oscillation photographs. The observed 'streaking' manifests the existence of random stacking faults in the crystals. The observation of the unidentified types shows that the stacking faults tend to arrange themselves with the definite periodicity but do not succeed in doing so. The appearance of diffuse spots indicates the existence of local distortions in the structure [22]. It follows that appreciable local distortions exist in the crystals doped with Br. When $CdBr_2$ is added to CdI_2 and crystallization of Br doped CdI_2 takes place, surplus ions namely Cd^{2+} ions, Br^- ions and substituted I^- ions are left in the structure. A substantial fraction of them will move to the mosaic boundaries and the rest will occupy the vacant octahedral voids between molecular I-Cd-I sandwiches. As I^- ions and Br^- ions have much larger radii (2.16 Å and 1.95 Å, respectively), they produce significant distortions upon entering the voids. Consequently, strong local stresses build up in the structure around the position of these ions. If stress attains a critical value, the structure relieves itself from such stress by nucleation of one or more dislocations. Otherwise, the local distortion stays inside the structure and manifest as diffuse XRD spots.

The observation of 'streaking' shows tendency towards formation of an identified polytypes and diffuse spots on X-ray photographs of Cl doped crystals can be explained on the same line as discussed earlier for Br doped crystals. However, the tendency towards formation of higher polytypes was observed only on three photographs. Besides, 'streaking' and diffuse spots were observed on significantly lesser number of photograph (viz. 32% and 10%, respectively). This difference may be attributed to still smaller value of Cl^- ions (1.80 Å) as compared to that of I^- ion resulting in less severe local dislocations in the structure.

The explanation of hardness in the anion doped crystal as compared to undoped crystals of CdI_2 follow on the same line as discussed earlier for cation doped crystals.

As reported in the table the relative abundance of unidentified polytypes in anion doped crystals is much more than in cation doped crystals. The cause lies in the difference between the radii of cations and anions. As mentioned earlier, the radius of dopant cations is nearly the same as that of octahedral voids formed by the close packing of iodine ions which favours the occupancy of voids between the sandwiches resulting in resisting the creation of I-I glide in the crystal. Consequently, the probability of creation of stacking faults gets reduced. On the other hand, anions with much larger radius have far less probability of entering the octahedral voids. Even if a small fraction succeeds in doing so, they cannot form a bond with neighbouring I^- ions (on account of their negative charge). Consequently, doping with anions only restraints the creation of Cd-I glides. Therefore, there is a greater possibility of creation of stacking faults in anion doped than in cation doped CdI_2, resulting in greater chances of getting an unidentified polytype in anion doped crystals as compared to cation doped crystals which agrees with the observation.

Another significant observation is the occurrence of high percentage of second most common Polytype 2H in the gallium doped crystals. This increase seems to have been achieved at the cost of 4H. Unlike the other doped crystals, the Ga doped crystals were found to be much thinner. Earlier in an extensive study of solution grown CdI_2 crystals it was reported that the crystals having Polytype 2H on both the basal faces were relatively very thin [23].

3.4 Solution grown doped single crystals

Melt grown doped material of cadmium iodide (CdI_2) was used for the growth of doped single crystals from solutions. As grown crystals were also extensively studied using XRD. In respect of polytype growth, for each doping the results have been broadly classified into four categories which are:

1. Polytype 4H
2. Polytype 2H
3. Unidentified Polytype
4. Higher order Polytype

It is evident from table that the relative abundance of most common polytype 4H is much higher in all the doped crystals than in undoped CdI_2. Further, many fold decrease in the occurrence of unidentified polytypes has been observed. It ranges from more than two-fold in anion doping to about five-fold in Indium doping. For the purpose of comparison, the results of solution grown well purified undoped crystals of cadmium iodide (CdI_2) are also present in Table 1 [7]. A

Table 1. Percentage occurrence of polytypes in solution grown crystals of CdI_2 doped with different dopants.

Dopants	Percentage occurrence of polytypes			
	4H	2H	Unidentified	Higher Order
Lead (Pb)	63	3	13	21
Tin (Sn)	70	7	5	18
Gallium (Ga)	44	20	17	19
Indium (In)	68	-	10	22
Bromine (Br)	34	6	22	38
Chlorine (Cl)	48	6	18	29
Undoped Cadmium Iodide (CdI_2)	27	4	48	21

detailed similar study on various highly polytypic materials (excluding CdI_2) conducted earlier has also been reported in Table 2 [24–29]. A quantitative study reflects that doping generally results in the stabilization of most common polytype of the material, occasionally accompanied by point defects and stacking faults.

For doping with cations the metal atoms can substitute for Cd atoms in the structure during crystallization resulting in the formation of stronger M-I Bond in the place of Cd-I bond (M stands for dopant metal atoms).The resulting stronger binding within a molecular sandwich will offer greater resistance to the creation of stacking faults associated with Cd-I glide. In addition, metal ions entering the vacant octahedral voids between the sandwiches will result in a stronger binding along with the usual weak Van der Walls binding. This will affect the ease with which a layer may slip with respect to its neighbouring layer and therefore it will resist the creation of stacking faults associated with I-I glide. Thus, the creation of stacking faults associated with both Cd-I and I-I glide gets reduced. The reduced stacking faults will increase the probability of formation of polytype 4H as observed in our study.

Similarly with regard to anion doping, both Br and Cl results in the formation of stronger bond with cadmium than the replaced iodine ion within the sandwich. As a result, the incidence of faulting goes down favouring the formation of most common type 4H and fewer occurrences of random stacking faults. Consequently, lesser formation of unidentified Polytype as compared to undoped CdI_2 is characterized either by the presence of an evenly place reflections or appreciable 'streaking' or both on oscillation photographs. The percentage of occurrence of Polytype in respective categories have been presented in Table 1.

4. Conclusion

The study of doped single crystals of CdI_2 in the present work has led to the emergence of some significant results. The results have broadly been discussed into two categories viz., melt and Solution growth. All the dopants used in the present work favour the formation of substitutional solid solutions. For all the dopants, the melt grown crystals have been found to be harder as compared to the crystals of undoped CdI_2.

The Ga doped crystals require much larger exposure time for obtaining well exposed X-ray photographs, which is attributed to the presence of local distortions in the

Table 2. Effect of various dopants on other prominent highly polytypic crystal materials.

Crystal material	Dopants	Polytypes
Silicon Carbide (SiC)	Nitrogen (N)	Promotes the stability of 4H with lattice distortions
	Aluminium (Al)	Promotes the stability of 4H and 6H
	Chromium (Cr)	Promotes the stability of 4H with unidentified polytypes. Leads to
	Titanium (Ti)	point defects and stacking faults with structural distortions
	Boron (B)	Promotes the stability of 4H and 6H
	Phosphorus (P)	Leads to the generation of localized distortions with most common
	Vanadium (V)	polytype 4H
Gallium Nitride (GaN)	Magnesium (Mg)	Leads to the stability of 4H (wurtzite structure) at low temperature
	Silicon (Si)	Increases the lattice constant along C-axis
Zinc Sulphide (ZnS)	Zinc Oxide (ZnO)	Promotes 4H (wurtzite structure) over cubic structure

structure. These distortions are created by substitution of Cd^{2+} ions by much smaller Ga^{3+} ions.

The X-ray photographs of Ga and In doped crystals have revealed the exclusive most common polytype 4H. Besides, no photograph has shown 'arching' or 'streaking' which led to the conclusion that these dopants do not affect the high temperature stability of the type 4H. The absence of 'arching' and 'streaking' further indicates a low density of dislocations and non-existence of random stacking faults in the crystals.

The X-ray photographs of crystals doped with anions (Br^- and Cl^-) show the tendency of formation of other polytypes (that could not be identified), in addition to the most common polytype 4H. These crystals also display 'streaking' on their oscillation photographs. It has been concluded that the presence of I^- ions, rendered surplus as a result of substitution of Br^- or Cl^- ions, and the presence of unused Br^- and Cl^- ions are responsible for building up of internal stresses in the crystal. The stress created by entering the octahedral voids having almost half the size of ionic radius are relieved by the production of dislocations and consequential stacking faults in the crystals.

Consequently, these crystals have a tendency of forming polytypes other than 4H. Thus, one finds that the ionic radii play a significant role in the growth of polytypes in the melt grown crystals of CdI_2.

The XRD study of crystals grown from solution (prepared by dissolving melt grown doped Crystals in water) has revealed that for all the dopants used in the present work, the relative abundance of the most common polytype 4H is much higher than in the undoped CdI_2 crystals. The relative abundance of the unidentified types has also been found to increase many folds. The results have been interpreted on the basis of the probability of creation of stacking faults associated with Cd–I and I–I glides, resulting from the doping of CdI_2 with cations or anions. It has been concluded that cation doping effects, both the Cd-I glide and I–I glide, whereas anion doping affects the Cd–I glide alone.

Authors contributions
Authors have contributed equally in preparing and writing the manuscript.

Availability of data and materials
The authors declare that the data supporting the findings of this study are available within the paper.

Conflict of interests
The authors declare no conflict of interest.

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