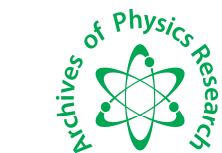




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Mechanism of phase transformations due to impurities in cadmium iodide crystals

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ABSTRACT

Cadmium iodide is an important inorganic solid for fundamental scientific research. The structure is a simple I-Cd-I layered structure with $[\text{CdI}_6]^{4-}$ octahedron being the basic building block. There are many ways of stacking the layers which result in many polytypes. Till now several hundreds of polytypes have been reported. Taking into account some known structures of CdI_2 worked out earlier and work done on the purification of material it is noted that the presence of impurities in the starting material distorts the $[\text{CdI}_6]^{4-}$ octahedron, which in turn give rise to formation of polytypes.

Key words: cadmium iodide, polytypism, impurities, phase transformations, crystal structure.

INTRODUCTION

Cadmium iodide belongs to the class having layered structure [1]. The crystals of cadmium iodide are considered to be a two dimensional system and it is important to study their physical properties as it belongs to one of the promising materials for scintillator with sub nanosecond luminescence decay time for use in electromagnetic calorimeters [2].

Till date several hundreds of CdI_2 polytypes have been discovered and all of which involve I-Cd-I sandwiches stacked in a variety of ways. Although satisfying results have been obtained in some aspects of polytypes, but systematic understanding of the origin of polytypes is yet to be achieved. Recently some work has been done on nanostructures formed in the doped CdI_2 crystals under irradiation [3, 4] and it is reported that these crystals show distinct properties which are different than that of pure crystals. Initially Jain and Trigunayat [5] have studied the effect of impurities on the nature of growth of polytypes in crystals of cadmium iodide grown from solution in a qualitative way. Further, Chaudhary and Kaur [6] have reported 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 to how their polytypism is different w.r.t. the crystals grown from unpurified material grown under identical conditions.

Considering some known structures of CdI_2 from Inorganic Crystallographic Structure Database (ICSD) [7], a mechanism of phase transformations in cadmium iodide due to the presence of impurities, using movement of dislocations and distortion of $[\text{CdI}_6]^{4-}$ octahedron has been presented (not suggested earlier in literature). It is further suggested that vacancies also play a major role in the formation of polytypes.

2. Formation of polytypes due to impurities

The CdI_2 structure consists of various stackings of CdI_2 sandwiches in each of which a layer of Cd ions is sandwiched between two close packed layers of iodine ions. I-Cd-I sandwich is considered as the structure unit of

crystal and each Cd atom is surrounded by 6 I atoms forming a near octahedral $[\text{CdI}_6]^{4-}$. The binding within a molecular sandwich, believed to be largely ionic, is quite strong but two adjacent sandwiches are bonded together with weak van der Waals forces which bring about an ideal cleavage of CdI_2 along (0001) basal planes. The I-Cd-I sandwich contains three layers of atoms and charge carrier dynamics perpendicular to these layers have several quantum states. This is in contrast to two dimensional graphene where charge carrier dynamics involving direction perpendicular to the layers of carbon atoms. Wahab and Trigunayat [8] 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. Shukla and Trigunayat [9] in their study of defects in cadmium iodide crystals have frequently observed the slip lines and slip bands on their basal faces using electron microscopy.

The details of some of the CdI_2 structures worked out earlier are given (Table 1). Here, θ characterizes the maximum departure from ideal octahedral $[\text{Cd}_6]^{4-}$. It is clear from the table that various polytypes have different departure from octahedral $[\text{Cd}_6]^{4-}$ arrangement. The relation between departure from exact octahedron and the polytype is an important part of structure but has not been discussed in the literature. It so appears that earlier pioneers might not have taken into account the presence of impurities in the starting material as there is no discussion about it in their work. One such distorted octahedron with a single Cd-I distance is shown in the figure 1.

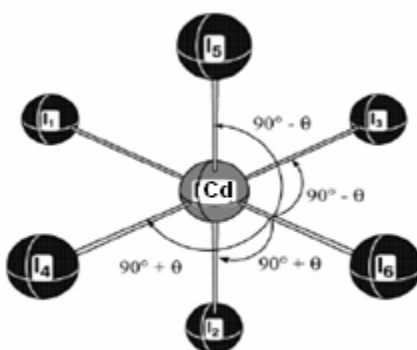


Fig.1 The near octahedral $[\text{CdI}_6]^{4-}$. It has six equal Cd-I distances, six I-Cd-I angles that are smaller than 90° by θ , and six I-Cd-I angles that are larger than 90° by the same deviation. The angle θ is a measure of deviation from octahedral symmetry. I_1, I_2 and I_3 are in one plane (Towards the viewer) of I-Cd-I sandwich and $\text{I}_4, \text{I}_5, \text{I}_6$ are in the other plane (away from the viewer)

Departure from exact octahedral structure (all values of θ are zero for a perfect octahedron) could be due to presence of impurities inside the sandwich. If the cadmium atoms (anions) are not situated at the centre of symmetry of the octahedron, the angular distortion of octahedron will take place due to the existence of static dipoles arising from the anisotropic polarization of the iodine atoms. Similarly if the Cd^{2+} ions are replaced by the impurity atoms (as in CdI_2 crystal structure half of the octahedral voids are unoccupied) or impurity atoms settles somewhere else in the available voids in molecular I-Cd-I sandwich, then the interaction of impurities with the host lattice will also lead to the distortion of exact $[\text{CdI}_6]^{4-}$ octahedron which in turn will disturb the iodine planes and all the atoms of iodine layers may not be in same plane in the same sandwich.

Table 1 Some CdI_2 Polytypes with known structures.

($a=b=4.24 \text{ \AA}$ for all polytypes)

S.No.	Ref.	Year	θ ($^\circ$)	Polytype	$C(\text{\AA})$	Space Group
1	19	1980	0.51	6H	20.50	P3M1
2	19	1980	0.51	12H	41.01	P3M1
3	19	1980	0.52	14H	47.84	P3M1
4	20	1982	0.52	14H	47.84	P3M1
5	21	1978	0.51	14H	47.85	P3M1
6	19	1980	0.50	20H	68.35	P3M1
7	22	1970	0.61	24R	82.02	R3MH
8	23	1971	0.56	12H	41.01	P3M1

Taking into account the above fact it is permissible to say that iodine layers of adjacent sandwiches will not be as close packed as should have been in the absence of impurities. Consequently local internal stresses will be built up in the structure around the position of these ions. The stresses are relieved by mutual slippage of the sandwiches

(The slip should most favorably occur along (0001) basal planes and in $\langle 11\bar{2}0 \rangle$ direction as it is the most closely packed direction in CdI_2) as these sandwiches are prone to translation/rotation due to weak binding [10] and are responsible for the formation of polytypes and complicated phase changes amongst different polytypes (unidentified polytypes). We find no discussion about the mechanism of polytype formation due to deviation from ideal octahedron anywhere but it becomes important when there is very little electron density between the sandwiches and sandwich-sandwich interaction is of van der Waals type. Undoubtedly the localization of impurities in the voids causes significant changes in structure as well as physical properties.

An interesting example of structural transformation in CdI_2 crystals is shown by Trigunayat [11] when stored for three to four years at room temperature. In such cases the stresses available are due to impurities (of the order few ppm) which are very small and the phase transformation takes as long as years.

3. Formation of polytypes due to other factors

A large number of studies are of the opinion that thermodynamic considerations also do hold for the formation of polytypes. For example, till now an attempt to convert a polytypic 4H structure of CdI_2 into any other structure has completely failed. (4H being stable structure when grown at room temperature or at high temperature) whereas for polytypic lead iodide crystals grown at room temperature, structure 2H is formed and when grown at high temperature (from melt) structure 12R dominates even though both CdI_2 and PbI_2 are isostructural in nature [12].

Under the ideal conditions of close- packing the energy of the crystal does not depend upon stacking order and any arrangement is equally probable. According to Helmholtz concept of free energy, we know that $F = U - TS$. For F to be minimum, S should be maximum i.e. maximum disorder state of the system. Our experimental observations made earlier are in agreement with the above as the number of unidentified polytypes (disordered) in the crystals grown from pure material (nearly ideal system) is 93 whereas it is 58 in the case of crystals grown from raw material (non-ideal system) out of 180 polytypes studied and reverse is the case for number of 4H structures observed [6]. It is necessary to point out that 4H is the most stable polytype of cadmium iodide and from above one can conclude that the presence of impurities in the starting material stabilizes the 4H polytype in cadmium iodide crystals.

Not only thermodynamic, polytype formation and phase transitions can be substantially aided by other factors in polytypic materials. The interesting $4H \rightarrow 2H$ transformation observed in the crystals of PbI_2 upon irradiation to Ruby Laser pulse is noteworthy [13]. It is believed to result from weakening of interlayer bonds by excitation of electronic sub systems in the structure. In this case, the governing factor has been the external pulsed laser radiation.

Till now the role of concentration of vacancies in the material for their polytypism has only been studied by Palosz et al [14]. It is reported that the vacancies in 2H and 4H structures can take up 15-20 % of the sites and can change the crystal structure. The role of vacancies becomes very important when one goes for the fabrication of devices and semiconducting properties of materials [15]. Further in a theoretical investigation, Ito et al [16] using ab initio pseudo potential approach have calculated that in the case of polytypic SiC with Si vacancy, crystals prefer 6H structure and 4H structure is favored in C vacancy condition. Thus concluding that vacancy formation in SiC plays an important role to stabilize a certain structure amongst various metastable structures. Similar calculations have also been made on ZnS polytypic crystals [17]. Some experimental work is Also being done on polytypic lead iodide crystals [18].

CONCLUSION

Cadmium iodide is theoretically interesting and an important pseudo two-dimensional material. Considering the existing Database of some known crystal structures and departure of $[\text{CdI}_6]^{4-}$ from a perfect octahedron arrangement a mechanism of phase transformations in cadmium iodide due to impurities has been suggested. Finally the role of vacancies in polytype formation can not be ruled out and is a new problem of interest.

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