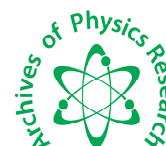




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On the phase transitions between 2H and 4H polytypes of cadmium iodide

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ABSTRACT

Lot of experimental work has been done on the polytypism of CdI₂ and a vast structural data is now available, but the phenomenon of polytypism is yet to be completely understood. It is a fact that all polytypes consist of basic structures 2H and 4H. In this paper it has been established that phase transformation 4H → 2H is hindered by the impurities present in the starting material. Further, it is suggested that vacancies also play a role in the formation of polytypes.

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

INTRODUCTION

Cadmium iodide is a layered structure [1] and has some characteristic features. One of the important factors is the existence of large number of polytypic modifications (several hundred in number). Although satisfying results have been obtained in some theoretical and experimental studies but understanding of the origin of polytypes is yet to be achieved. Having a direct energy gap of 3.8 eV, CdI₂ has relevance from the industrial point of view as a prospective scintillator material with sub nano-second luminescence decay time for use in electromagnetic calorimeters. [2]. Recently some work has been done on the nanostructures formed in the doped CdI₂ crystals under irradiation [3] and has been shown that they exhibit distinct properties which are different than pure crystals.

In the past, lot of work has been done on the growth and structure of polytypes [4,5,6]. Further Chaudhary and Trigunayat [7] 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 differed w.r.t. the crystals grown from unpurified material grown under identical conditions.

Considering a vast data available on polytypes of CdI₂, I review the basic properties of CdI₂ and discuss the statistics of occurrence of 2H and 4H polytypes in the light of STGR model [8]. Broadly, it suggests that all the polytypes are formed by combinations of small period polytypes 2H, 4H and 12R. Further it is submitted that in all the studies made on polytypism so far the presence of vacancies have not been considered in experimental or theoretical work. With the availability of most advanced computer software's available; one can revisit the above subject and make subtle differences in various structures clearer.

2. Basic structure of CdI₂

The CdI₂ structure consists of various stackings of CdI₂ sandwiches in each of which a layer of Cd ions is sandwiched between two close packed layers of iodine ions.

I-Cd-I sandwich being the repeat unit and each Cd atom is surrounded by 6 I atoms forming a near octahedral $[\text{CdI}_6]^{4-}$. The interlayer interactions are more covalent than ionic and the electron density between the sandwiches is very low that results in weak van der-Waals interactions between the sandwiches [9] of the type

$$U(R) = -d/R^6 + be^{-aR}$$

R is the separation between the atoms.

a, b and d are constants characteristics of atoms.

In the case of CdI_2 the relative bond strengths between iodine atoms within a sandwich and iodine atoms between adjacent sandwich have been estimated around 125 [9]. This results in many polytypes and complicated phase changes amongst different polytypes. As 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 the two dimensional graphene where charge carrier dynamics involving direction perpendicular to the layers of carbon atoms can be pinned to the ground state.

3. Energy difference between basic polytypes 2H and 4H

As stated earlier, the Statistical Thermodynamics and Growth Restriction (STGR) model suggests that simultaneous occurrence of basic phases 2H and 4H under similar growth conditions is possible because of very close free energies of various phases [8].

Mathematically one can express it as

$$NH = n_1 \times 2H + n_2 \times 4H + \dots$$

Where N is the identity period of polytype.

n_1 , n_2 and n_3 are number of units of basic phases.

Further STGR model suggests that if there are X% of 2H basic phase then the participation of 4H basic phase would be (100-X) %. The energy difference between these phases can be computed using the following relation

$$(100-X)/X = \exp(\Delta E/kT)$$

Table 1. shows the experimental energy difference between these basic phases as calculated from the work done by various workers [11].

Table 1. Experimental energy difference between basic phases.

Reference	Temp.($^{\circ}\text{C}$)	2H%	4H%	ΔE kcal/mol
Palosz	5	09.00	91.00	1.266
Palosz	25	17.00	83.00	0.949
Mitchell	Room Tem.	07.69	92.31	1.480
Trig.and Verma	Room Tem.	24.13	75.87	0.683
Jain and Trig.	20	26.94	73.06	0.594
Jain and Trig.	30	25.19	74.81	0.647
Jain and Trig.	40	15.40	84.59	1.060
Minagawa	Room Tem.	15.78	84.21	0.998
Chaud. and Trig.	Room Tem.	12.90	87.09	1.330

It is clear from the above table that crystals have been grown by different workers at different temperatures ranging from 5°C to 40°C and there is no consistency between the variation of temperature and the value of energy difference. Not only that, even the value of energy difference is quite different for the crystals grown at the same temperature by various workers. There is more than 100% variation in the values of energy difference, minimum value being 0.594kcal/mol and maximum 1.480kcal/mol. It clearly shows that the value of ΔE is independent of the temperature at which the crystals have been grown. It is worth-noting that all the crystals have been grown from solution. In the literature, from the year 1956 to 1983 over a period of 25 years we find no discussion of impurities present in the starting material. It is but natural that different workers might be using cadmium iodide with different

degree of impurities in the starting material. The above fact seems to be spoiling the data giving different percentages of 2H and 4H structures in different sets of experimental studies and that is giving rise to 100% variation in the values of ΔE .

An observation made by Chaudhary and Trigunayat[7] on the number of polytypes observed in the crystals grown from raw and purified material is presented in Table 2.

Table. 2 Frequencies of occurrence of various cadmium iodide polytypes in solution grown crystals from raw and purified material

TOTAL NUMBER OF CRYSTALS	POLYTYPES			
	2H	4H	Higher	Unidentified
(Raw material) 90	1	97	39	57
(Purified material) 90	7	54	43	96

Momeen et al. have used the results from Table.2 for calculation of ΔE only from the category of purified material. The value of ΔE (1.330kcal/mol) for the crystals grown from purified material somehow matches with the work of earlier workers. They have not presented the calculated value of ΔE for the crystals grown from the raw material. It is clear from the Table.2 that only one 2H polytype has been observed and the number of 4H polytypes is 97, the corresponding value of ΔE comes to ~ 2.8 kcal/mol which is quite large as compared to the various values of ΔE calculated by Momeen et al. [11] in Table 1.

CONCLUSION

From the above observation we conclude that

1. Impurities present in the raw material support the formation of polytype 4H.
2. It is not easy to transform crystal structure 4H to 2H during growth because impurities present in the raw material hinder the movement of dislocations and in turn the phase transformation $4H \rightarrow 2H$. The calculated value of ΔE being very high ~ 2.8 kcal/mol.

The above conclusion is supported by the fact that a polytypic transformation $4H \rightarrow 8H$ is easier than $4H \rightarrow 2H$ as earlier involves only the translational displacement of one molecular sandwich whereas the later involves translational displacement as well 60° rotation of the same sandwich in succession [9]. The above conclusion is also substantiated by the observation that the number of 2H polytypes in all the above studies is small.

In most of the earlier studies made on CdI_2 , PbI_2 and other polytypic crystals the role played by the vacancies is being ignored. The degree and the distribution of vacancies is also an important parameter to be looked for the understanding of polytypism and fabrication of devices from polytypic crystals. Some experimental work is also being done on the similar polytypic crystals PbI_2 [10].

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