

## Challenges in the study of polytypism in $\text{MX}_2$ compounds

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### ABSTRACT

*Lot of experimental work has been done on the polytypism of cadmium iodide and lead iodide crystals and enough data is available. In addition, a number of theories have been put forward from time to time but the origin of polytypism is not yet clear. After going through the data on the subject, a number of unanswered problems have been presented in this paper and it is suggested that with advancement of experimental facilities and computational systems both experimentalists and theorists should look into the phenomenon of polytypism again.*

**Key words:** cadmium iodide, lead iodide, polytypism, phase transformations, Inorganic crystal structure

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### INTRODUCTION

Lot of work has been done during last few decades on the polytypism of  $\text{MX}_2$  compounds. The research has been mainly concentrated on structure determination of cadmium iodide and lead iodide and enough data is available for the above two compounds [1]. More than 250 polytypes have been identified in the case of cadmium iodide and nearly 200 structures worked out. Similarly 50 polytypes have been identified in the case of lead iodide and complete crystal structures have been determined for 20 polytypes.

In spite of having so much data, the problem is yet to be completely understood. Till date, after a long experimental work one is not in a position to grow the polytype of one's choice. The above data can be of interest to the theoretical researchers.

### MATERIALS AND METHODS

#### **Importance of $\text{CdI}_2$ and $\text{PbI}_2$**

$\text{CdI}_2$  is high energy gap (~3.8 eV) material and finds applications as scintillation material with characteristic time ~ several nano seconds. Due to second order non linear effects observed [2],  $\text{CdI}_2$  is a promising material for producing UV detectors. Further, some work has also been done on the studies of nanostructures that are formed in doped  $\text{CdI}_2$  crystals under radiations [3].

$\text{PbI}_2$  is also a high energy gap material (~ 2.3eV) and it is a potential candidate for future nuclear radiation detector that can work at room temperature and do not require cryogenic cooling. Further, it has other medical and scientific applications as imaging system, X-ray and gamma ray detection [4].  $\text{PbI}_2$  is also used to study the films of various molecules that can be placed between the layers [5]. It is used for making nanobelt bundles [6]. and for construction of quantum wells of different sizes [7]. The synthesis and characterization of  $\text{PbI}_2$  nanoparticles have also been reported.

### Basic structure of CdI<sub>2</sub> and PbI<sub>2</sub>

The structure of PbI<sub>2</sub> and CdI<sub>2</sub> consists of a layer of Pb/Cd atoms sandwiched between two close packed layers of I atoms. Each Pb/Cd atom is surrounded by 6 I atoms forming a nearly octahedron [PbI<sub>6</sub>]<sup>4-</sup>. The adjacent sandwiches are bound by weak Vander walls forces [8] 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.

Thus the structure consists of extended molecular sheets stacked on top of one another. The basic structural difference between CdI<sub>2</sub> and PbI<sub>2</sub> is shown in the figure [1]. The distance between adjacent sandwiches is 0.5c in the case of CdI<sub>2</sub> whereas it is 0.47c in the case of lead iodide. Therefore displacement between sandwiches in CdI<sub>2</sub> is easier than in PbI<sub>2</sub>. That is the reason CdI<sub>2</sub> has more number of polytypes.

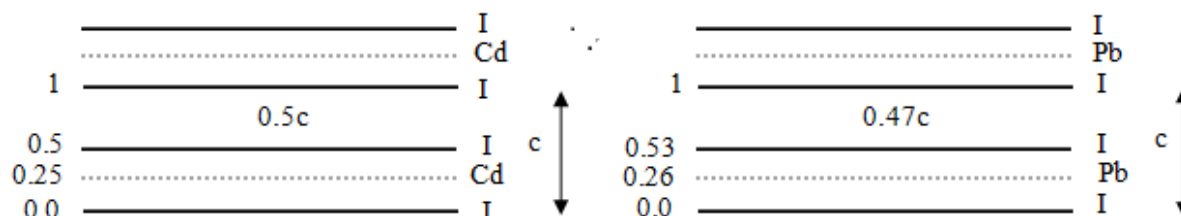


Fig.1 Spacing in the molecular sheets of cadmium iodide and lead iodide

## RESULTS AND DISCUSSION

### Challenges

#### Variation in c- value

In the case of lead iodide, on heating at 415K, as reported by Salje [9], there was sudden change of 0.0685% in c- value i.e. periodicity of iodine layers along c-axis suddenly changes, otherwise c increased linearly with temperature, but with different slopes on the two sides of the transition point. No difference between a and b was found.(indicating that two lattices are identical w.r.t. their basal planes)

Similarly Wahab and Trigunayat [10] using least square method has reported a linear behavior between iodine layers for the case of CdI<sub>2</sub>.

The above difference in the nature of variation in c-axis in the case of CdI<sub>2</sub> and PbI<sub>2</sub> is yet to be explained.

In addition, Bolesta et.al.[11] have investigated the dependence of lattice parameter c of CdI<sub>2</sub>. With increase in Cd concentration, at a certain value of Cd, there is an abrupt change in c- value of 4H polytype. Further increase in Cd concentration causes much less enhancement of lattice parameter.

### Method of growth

As stated earlier in the case of CdI<sub>2</sub>, a large number of crystal structures have been reported. It is to be noted in almost all the cases, crystals have been grown from solution. When crystals are grown from solution, the growth rate is quite high and there is random motion of molecules and statically there is every possibility of random structure (higher and disordered polytype) to be formed.

On the other hand lead iodide crystals reported have been mainly grown from gel where growth rate is quite small and therefore due to slow movement of molecules they find enough time to settle and only very few higher polytypes have been observed.

Very few higher polytypes have been reported when the crystals are grown at high temperature i.e. from vapor and melt. In the case of CdI<sub>2</sub> the crystal structure have been reported as 4H whereas 12R in the case of PbI<sub>2</sub>.

Further, it is yet to be answered that 4H is stable at both low and high temperature in CdI<sub>2</sub> whereas, in the case of PbI<sub>2</sub>, 2H is low temperature modification and 12R is high temperature modification. Though they are similar structured materials.

### Impurities

Though a very large number of structures of CdI<sub>2</sub> and PbI<sub>2</sub> have been reported and their structures worked out over a long span of 30 years. Nobody has reported the contents of impurities present in the starting material. How the impurities existing in the polytypic material can influence the formation of polytypes, is reported by Chaudhary and Trigunayat [12] in melt grown crystals of CdI<sub>2</sub>, PbI<sub>2</sub> and CdBr<sub>2</sub>. In the case of CdI<sub>2</sub>, all the crystals show common polytype 4H. In the case of PbI<sub>2</sub>, the crystals were found to be 12R and 4H and phase transition 12R → 2H was observed when crystals stored for few months.

The above studies show only qualitative information because exact nature and amount of the impurities in the material usually remain unknown. However some work has been carried out on three MX<sub>2</sub> compounds CdI<sub>2</sub>, PbI<sub>2</sub> and CdBr<sub>2</sub> [13]. The following dopants Bi, Pb, Sn and Zn were used for CdI<sub>2</sub>; Bi, Cd, Sn and Zn for PbI<sub>2</sub> and Zn for CdBr<sub>2</sub>. All the doped crystals of CdI<sub>2</sub> and CdBr<sub>2</sub> showed the most common polytype 4H and 6R. The PbI<sub>2</sub> crystals doped with Bi, Cd and Sn has structure 4H and (4H+12R). For all the materials a significant increase in the D.C. conductivity was observed. The above work is again qualitative in nature.

### Deviation from stoichiometry

Again it is out of place to mention that in spite of immense work done on the polytypism of CdI<sub>2</sub> and PbI<sub>2</sub> the effect of deviation from stoichiometry on polytypism has not been reported. Deviation from stoichiometry might be contributing towards formation of polytypes. In the case of Ti-S the polytypism has been exhibited only by Ti<sub>1.2</sub>S<sub>2</sub>. The reason of origin of polytypism for just one composition viz. Ti<sub>1.2</sub>S<sub>2</sub> is yet to be understood [14]. Recently in a theoretical investigation for the polytypism in SiC and ZnS, it has been reported that vacancy formation plays an important role in the formation of polytypes [15].

## CONCLUSION

Taking into account the above factors and with the availability of very sophisticated instrumentation and computational methods available these days it calls for the work on polytypism with pure materials and in the clean space so that phenomenon could be better understood.

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