Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2012, 3 (6):436-440
(http://scholarsresearchlibrary.com/archive.html)

Archives of Physics Research
Scholars Research Library
ISSN : 0976-0970
CODEN (USA): APRRC7

Present status of polytypism in cadmium iodide crystals

S. K. Chaudhary

Department of Physics, M.D. University, Rohtak-124001 (India)

ABSTRACT

Polytypism has been observed in a large number of materials where the nearest neighbor relationship between identical two-dimensional layers of atoms can be satisfied in more than one way. Cadmium iodide structure is a simple I-Cd-I layered structure with $[CdI_6]^{4-}$ octahedron being the basic building block. Due to presence of overstoichiometric cadmium atoms during crystal growth and impurities in the starting material, the layers can be stacked in many ways. Taking into account some known structures of CdI_2, work done on the overstoichiometric Cd atoms and purification of cadmium iodide it is noted that the presence of impurities in the starting material and excess cadmium atoms distorts the $[CdI_6]^{4-}$ octahedron, which in turn give rise to formation of polytypes.

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

INTRODUCTION

The phenomenon of polytypism has been engaging the attention of both physicists and mineralogists for long. Of late, it has further attracted the attention of solid state physicists by virtue of the fact that various polytypic modifications of the same substance have been found to possess different dielectric, semi conducting, and photovoltaic properties [1]. Having a direct energy gap of 3.8 eV, CdI_2 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] .The specific properties of closed cage /nanotubular structures formed under electron beam irradiation in CdI_2 [3] determine the importance of the material in the field of nanotechnology. The effect of co-existence of various polytypes due to impurities in the materials of technological interest has recently become important (controversial) issue. Such problems are frequently encountered in pharmaceutical applications where polymorphism in a solid drug affects chemical reactivity and patient intake safety [4].

Till date, nearly 200 structures have been worked out, all of which involve I-Cd-I sandwiches stacked in a variety of ways. Although satisfactory results have been obtained in some aspects of polytypes, but systematic understanding of the origin of polytypes is yet to be achieved. 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 were 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 in a qualitative way.

The characteristic feature of CdI_2 consists in the formation of overstoichiometric cadmium atom during the crystal growth. Preliminary studies indicated that the excess stoichiometric cadmium atoms in CdI_2 or impurities in the starting material may occupy different crystallographic positions. They are predominantly localized between the neighboring iodine planes of I-Cd-I layers i.e. in the tetrahedral or octahedral voids existing in the van der Waals

gap of layered crystals and can also exist inside I-Cd-I layers. Therefore Cd atoms give rise to the change in c lattice parameter and that can influence the optical and luminescence properties [8].

Taking into account some known structures of CdI_2 from Inorganic Crystallographic Structure Database (ICSD) [9], the mode of phase transitions in cadmium iodide due to the presence of excess cadmium atoms and the impurities, using movement of dislocations and distortion of $[CdI_6]^{4-}$ octahedron has been presented. Further, the role of vacancies in the formation of polytypes can not be ruled out

2. Polytype formation when impurities lie between neighboring sandwiches

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 being the repeat unit and each Cd atom is surrounded by 6 I atoms forming a near octahedral $[CdI_6]^{4-}$. 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 walls forces. Wahab and Trigunayat [10] 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. (Fig.1).With the help of a suitable van der Waals potential a quantitative estimate of interlayer equilibrium separation I-I in CdI_2 was made by them and it was found to be 4.22 Å. This value represents the distance at which two molecular sandwiches will tend to glide past one another, if necessary driving force is available and this will bring about a change in the structure. Incidentally the estimated equilibrium separation of 4.22 Å well corresponds with value 4.23 Å of I-I separation in CdI_2 at room temperature.

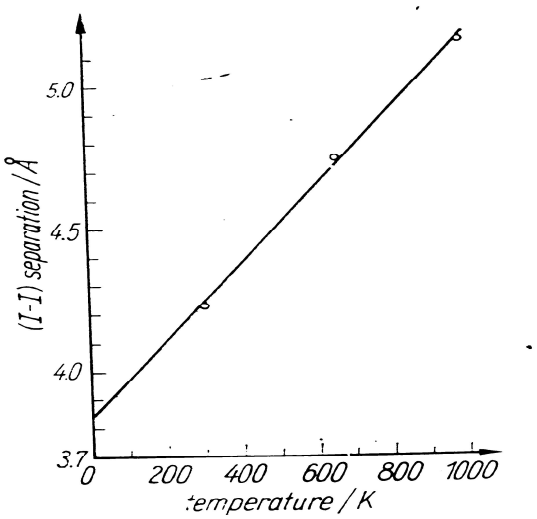

Fig. 1 Increase in I-I distance with temperature

The above calculation supports the observation made by Trigunayat [13]. When CdI_2 crystals were stored for three to four years at room temperature, all the crystals got transformed to other structures. In such case 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.

In the case of crystals of CdI_2 when the impurities are localized between the neighboring sandwiches i.e. in the tetrahedral or octahedral voids, plays a dual role, creation of dislocation and hindering their movement. The slip due to impurity should most favorably occur along (0001) basal planes and in $<11\bar{2}0>$ direction as it is the most closely packed direction in CdI_2. The slip in the crystal can lead to the formation of linear rows of edge dislocations. If these planer groups of dislocations are obstructed or forced against some impurity particles and the particle is hard in the sense that its resistance to the slip is high, the piling of dislocations and hence local stress may be generated in the vicinity of the impurity particle (Figure 2). These stresses are relieved by mutual slippage of the sandwiches that can lead to the creation of nucleation centre for the formation of new polytypic structure. Earlier Shukla and Trigunayat [11] in their study of structural defects in melt grown cadmium iodide crystals have frequently observed the patterns of slip lines and slip bands on their basal faces using electron microscopy.

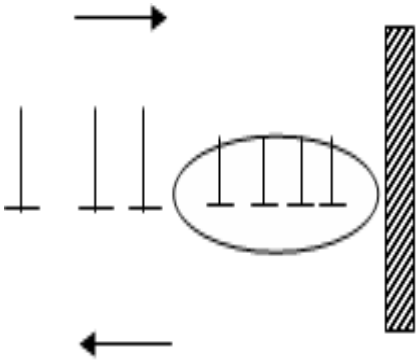

Fig. 2 Formation of nucleation centre due to obstruction of edge dislocations by an impurity particle.

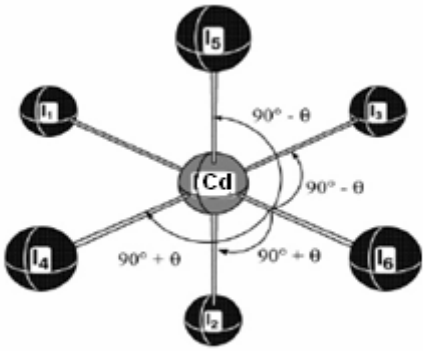

Fig. 3 The near octahedral $[CdI_6]^{4-}$. It has six equal CdI distances, six I-Cd-I angles that are smaller than 90° by θ, and six 1-Cd-1 angles that are larger than 90° by the same deviation. The angle θ is a measure of deviation from octahedral symmetry.

3. Polytype formation when impurities lie inside the sandwich

Some of the CdI_2 structures worked out earlier are given in Table1. Here, θ characterizes the maximum departure from ideal octahedral $[CdI_6]^{4-}$. It is clear from the table that various polytypes have different departure from octahedral $[CdI_6]^{4-}$ 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 and excess cadmium atoms during crystal growth 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 3. 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 sit 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 $[CdI_6]^{4-}$ 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 Å for all polytypes)

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

Considering 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 as these sandwiches are prone to translation/rotation due to weak binding [12] and are responsible for formation of polytypes and complicated phase changes amongst different polytypes (unidentified polytypes). We find no discussion of the 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. Further it is necessary to mention that Bolesta et. al have studied the variation in c dimension of a 4H polytype with variation in concentration of cadmium atoms [8] and it is reported that there is an abrupt change in c parameter at concentration of 3.10^{18} cm^{-3} from 13.720 Å to13.724 Å.

DISCUSSION

Cadmium iodide being a layered structure and assuming that all atomic plane displacements have the time dependence e^{-iwt} the solution of equation of motion of phonons is obtained as

$$-Mw^2Us = \sum Cp\ (Us+p - Us)$$

Where M is the phonon mass, Us and Us+p are the displacements of the atomic planes s and s+p and Cp is the force constant between planes mutually removed by p [14].

On left hand side w^2 has positive value for both + and – sign of w. However since physically a phonon must have positive value of energy it is both suitable and conventional to take w as positive. Yet it is possible that at some instant of time the crystal structure is rendered unstable due to unusual dependence of force constants on the presence of impurities that will make w^2 negative. Then w becomes imaginary. However, since the corresponding structural mode is unstable, the crystal will spontaneously tend to transform into a stable structure because energy of phonons must be positive. Only a quasi-stable structure is likely to be formed and phase transformation can take place by suitable impurity and/or time effects, even long after crystal growth.

A 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 [15].

Polytype formation and phase transitions can be substantially aided by other factors in polytypic materials. The interesting 4H→2H transformation observed in the crystals of PbI_2 upon irradiation to Ruby Laser pulse in noteworthy [16]. 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.

The crystals in general 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 cell heights up to thousands of angstrom units implies certain external agencies like (dust particles, lattice vibrations, vibration entropy, electron density) are also operational in their creation.

In most of the earlier studies made on CdI_2 crystals the role played by the vacancies was being ignored. The degree and the distribution of vacancies is also an important parameter to be looked for the fabrication of devices from CdI_2 crystals. It is expected that atoms surrounded by a large number of vacancies should be considered to be more mobile than others along the layers as well as in the direction perpendicular to them. In a recent theoretical investigation, Ito et. al [17] 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 in stabilizing a certain structure amongst various metastable structures. Similar calculations have also been made on ZnS polytypic crystals [18].Some experimental work is being done on the polytypic crystals PbI_2 [19].

REFERENCES

[1] Y.M. Tairov and V.F. Tsvetkov, in: edited by P. Krishna Crystal growth and Characterization of polytype structures. (Pergamon Press, oxford, **1983**) p.111
[2] G.I.Britvich, A.I.Peresypkin, V.G. Vasil chenko, E.A.krivandina, B.P.Sobolev, E.G.Devitsin, Yu.I Hovsepyan, V.A.Kozlov and T.V.Uvarova *Nucl. Instrum. Methods* A **1991**, 308**,** 509.
[3] N.Sallacan, R.Popovitz-Biro, and R.Tenne *Solid State Sci*. **2003**,5,905.
[4] A.S.Raw, M.S.Furness, D.S.Gill, R.C.Adams, F.O.Holcombe Jr and L.X.Yu *Adv.Drug Delivery Rev*. **2004**, 56,397
[5] R.Singh, S.B.Samanta, A.V.Narlikar and G.C.Trigunayat, *Bull. Mater. Sci*.**2000,** 23, No 2, 131.
[6] S.Kumar, X-Ray Studies, Electrical, optical and Dielectric studies of PbI_2xA_1-$xCdI_2xA_1$-x, PhD Theses, Jamia Milia Islamia (New Delhi, INDIA, **2004**).
[7] P.C.Jain and G.C.Trigunayat, *J.Crystal Growth***.1980,** 48, 107.
[8] I.M.Bolesta, V.Kityk, V.I.Kovalisko and R.M.Turchak. *Ferroelectrics.* **1997**,192,107.
[9] ICSD http://icsdweb.fiz-karlsruhe.de/.
[10] M.A. Wahab and G.C.Trigunayat, *Cryst.Res.Technol*.**1989,** 24, 355.

[11] N. Shukla and G.C. Trigunayat, *phys. stat. sol*.**1987**, 103 337.
[12] M.A. Wahab and G.C.Trigunayat, *Solid State Communications*.**1981**, 36, 885.
[13] G.C.Trigunayat, Phys. stat. sol. (a) **1971**, 4, 281.
[14] C.Kittle, Introduction to Solid State Physics Ed. 7 (John Wiley,New York, **1996**) 104
[15] G.C.Trigunayat, *Phase Transitions*.**1989,** 16/17, 509.
[16] V.A. Bibik, I.V. Blonskii, M.S. Brodin and N.A. Davydova, *Phys. Stat. Sol*. (a)**1995** 90, K 11.
[17] T. Ito, T. Kondo, T. Akiyama and K. Nakamura, *Physica Status Sol*. C, **2011**, 8, 583 .
[18] T. Ito, T. Kondo, T. Akiyama and K. Nakamura, *Journal of Crystal Growth*, **2011** 318, 141.
[19] D.S.Bhavsar, *Archieves of PhysicsResearch*, **2011**,3(2), 146.
[20] B.Palosz, *Z.fuer Krist* **1980**, 153, 51.
[21] B.Palosz, *Acta Cryst.* C, **1982**, 38, 3001.
[22] P.C.Jain and G.C.Trigunayat, *Acta Cryst.B* **1978**, 34, 2677.
[23] R.K.Jain, G.K.Chadha and G.C.Trigunayat, *Acta Cryst.* B**1970**, 26, 1785.
[24] V.K.Agrawal, G.K.Chadha and G.C.Trigunayat, *Z.Kristallogr*.**1971**, 134, 161.