X-RAY STUDIES,ELECTRICAL,OPTICAL AND DIELECTRIC STUDIES OF PbI2x A_{1-x}CdI2x A_{1-x}

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The phenomenon of polyypism has been regarded as he existence of an element or compound in two or more structures, which have same chemical composition but differ in manner of stacking of layers. The crystals of polytypic materials usually consist of closed packed layers. From the applied aspect polytypes have great potential, since the different polytypes of a material are crystallographically different, so their structure sensitive properties must also be different. Hence different polytypes may serve as effective substitutes for materials having specific physical properties. The investigation of physical properties f polytypes is thus of obvious significance.

Both CdI_2 and PbI_2 are layered structure compounds with hexagonal unit cell, in which each Cd or Pb atom is sandwiched between two I atoms .The stacking of these three sandwiched sheets forms the three dimensional compound. The possibility of different stacking sequences of three layer sandwiches along the third direction due to weak bonding between layers leads to polytypic structure. Cadmium iodide and lead iodide has been the subject of many investigations in the view of their potential as device materials.

Chapter first and second of thesis provides the necessary background to the present investigation. The chapter-1 commenced with crystal imperfections, polytypism and polymorphism .Polytypic formation, phase transformation from ordered to ordered and ordered to disordered polytypes by various researchers is also explained . In chapter second different types of close packings , voids in close packing ,different polytypic notations and their conversion is explained . e.g. conversion of notations used to denote SiC polytype is given below .

SiC I (Old notation)

15R (Ramsdell notation)

ABCBACABACBCACB (Classical notation)

$(+ + - - -)_3$ (Hagg notation)

$(\blacktriangledown\blacktriangledown D\ D\ D)_3$ (Nabarro Frank symbol)

$(23)_3$ (Zhdanov symbol)

$(hchcc)_3$ (Pauling, Wyckoff and Jogodzinski Notation)

In the chapter third some of these notations are used for the evaluation of fault order.

In chapter third the phase transformation energy of 3C ordered to 2H ordered polytype, Structural entropy for most disordered polytypes and stacking fault energy of most probable disordered polytypes of ZnS was calculated. The resulting value of stacking fault energy calculated by Maxwell Boltzmann relation is 0.592 kcal /mol and 0.4474 kcal/ mol for Lennard- Jones potential method.The phase transformation energy for ordered to ordered polytypes is 9.69 kcal / mol, i.e. below this value of energy formation of disordered polytype will take place.

In chapter four, we explained the growth and characterization technique. Zone refining under the zone melting technique process was employed to purify the crystal because under this technique growth of single crystals take place itself.

In chapter fifth, we studied electrical, optical, dielectric and X-ray properties of pure and doped CdI_2 material. The material is purified using the zone refining technique. Pure crystals are extremely soft and silver white in color. After purification pure CdI_2 crystal was doped with Sn, KH_2PO_4 and $K_2Cr_2O_7$. Tin was doped 0.1% and 0.2% .The impurity of KH_2PO_4 and $K_2Cr_2O_7$ was doped 0.1 % , 0.5% but no significant changes were observed. Then 1% and 2% w/w KH_2PO_4 and $K_2Cr_2O_7$ was doped by using the above said technique. Doped crystal was found to be harder than undoped crystal, this is due to occupancy of normally octahedral voids.

The electrical conductivity of pure crystal is of order of 10^{-10} $(W - cm)^{-1}$. After doping with 0.1% Sn,1% KH_2PO_4 and $K_2Cr_2O_7$, conductivity is increased but order remains same. For 0.2% Sn,2% KH_2PO_4 and $K_2Cr_2O_7$ doped CdI_2 crystal conductivity is of order of $10^{-9}(W - cm)^{-1}$, this is due to occupation of large number of voids. For the same reason dielectric constant and optical band gap is reduced after doping.

Oscillation photograph of pure crystal after twenty five-zone pass about a-axis taken over a 15° range revealed that only reflections of 4H polytype are obtained. X-ray diffraction pattern for pure and doped material was carried out in powdered form. All structural peaks appear at same 2q value, i.e. no shifting of peaks take place . It means after doping no new polytypic formation take place, because the random stacking faults fail to arrange themselves in a regular fashion. Only a systematic movements of the partials, which may possibly be governed by the thermodynamic considerations will introduce the stacking faults at regular intervals in the structure, lead the formation of a polytype

In chapter sixth we studied electrical, optical, dielectric and X-ray properties of pure and doped PbI_2 material. The material is purified using the zone refining technique. Pure

crystals are soft (but harder than CdI_2 crytals) and yellowish (transparent) in color. After purification pure PbI_2 crystal was doped with Sn , KH_2PO_4 and $K_2Cr_2O_7$. Tin was doped . 1% and .2% .The impurity of KH_2PO_4 and $K_2Cr_2O_7$ was doped .1 % , .5% but no significant change was observed . Then 1% and 2% w/w KH_2PO_4 and $K_2Cr_2O_7$ was doped by using the above said technique. Doped crystal was found to be harder than undoped crystal. This is due to production of local internal stress .

The electrical conductivity of pure crystal is of order of $10^{-8}(W - cm)^{-1}$. After doping with 0.1% Sn,1% KH_2PO_4 and $K_2Cr_2O_7$ conductivity is increased but order remains same.For 0.2% Sn, 2% KH_2PO_4 and $K_2Cr_2O_7$ doped PbI_2 crystal conductivity is of order of $10^{-7}(W - cm)^{-1}$, this is due to occupation of large number of voids the electronic component in total energy of the structure is increased , so dielectric constant and band gap is reduced . Zone refined pure crystal was subjected to 15° a-axis oscillation photograph and exclusively showed the reflections of 4H+12R polytypes. Diffractograms of pure and doped material carried out by using X-ray powder diffractometer (PW -1830 generator) reveal that, no shifting of peak are taking place, i.e it indicate the absence of new polytypes (other than 4H+12R). The absence of other polytypes suggests that in the doped crystals, the random stacking faults fail to arrange themselves in a regular fashion.