

# Growth Features and Characterization of Se Doped CdI<sub>2</sub> Single Crystal

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## Abstract

*Cadmium iodide is a polytypic material, more than 250 polytypes of substance have been reported. Cadmium iodide is purified, and single crystals of cadmium iodide are grown by zone refining technique. After passing thirty zones, pure crystals are grown. After purification one percent of selenium was doped in zone purified material. Resistivity, band gap, conductivity, and dielectric constant of pure and doped crystals are calculated. It is observed that after doping band gap, resistivity, and dielectric constant of single crystal decreases while conductivity increases. SEM and X-ray photograph revealed the crystalline nature of material after purification.*

## Introduction

Cadmium iodide is layer structured material with hexagonal sheets of Cd atoms sandwiched between two similar sheets of I atoms. Thus structure of cadmium iodide is hexagonal and atoms are located in layers of Cd and I perpendicular to c-axis. The sequence of layers is repeated in the units of I-Cd-I. The inter layer bonding between molecular sheets is weak vander -Wall's forces. Many of physical properties of crystals depend on the presence of defects such as foreign atoms and native point defects. In order to study the effect of these defects on the physical properties, we require the starting material in which the concentration of such defects are as low as possible. The primary problem is therefore one of purification of starting material to remove foreign atoms. Single crystal of cadmium iodide have been grown by aqueous solution, gel, melt, sublimation and chemical vapor transport. In the present work crystal is grown by melt technique (zone refining technique). The

main advantage of zone-refining technique is that single crystal growth take place during the zone-refining process itself [1]. CdI<sub>2</sub> is a well known polytypic material, more than nearly 250 polytype have been reported[2]. The reported result revealed that only pure 4H polytype was obtained for melt growth crystal [3]. X-ray studies [4], electrical and optical characterization [5], recombination process [6] of cadmium iodide have been reported. The effect of dopant (Pb,Sn,KDP etc) were studied by many researcher[2,3,4]. In the present course of investigation, we have synthesized the cadmium iodide crystals by melt technique. In this paper the purpose of our study is to check the effect of doping on resistivity, conductivity and dielectric constant and band gap of purified cadmium iodide. To check the structure SEM and X-ray photograph have been taken.

## Experimental Details

The growth of crystals from melt technique provide relatively pure crystals and also enable to exercise control on the degree of purification of the crystals. In the present work the starting material was 99.9% pure supplied by M/s CDH. Further purification was achieved by using zone refining technique. This technique is fabricated in our laboratory. Thirty zone passes were carried out to achieve maximum purity. The color of melt during zone refining was observed grey. The dark color of the melt could be due to presence of impurities which are probably removed during the zone refining technique. Flow of argon was made to avoid the decomposition. Maximum purification is achieved by thirty zone passes. The pure crystals grown by this technique are soft and white in color. Conductivity and resistivity are measured by using Kithely electrometer (Model-6517) and dielectric constant is measured by Kithely LCZ meter (Model-3330). Vacuum thermal evaporation is used for preparation of thin films. It is carried out in vacuum of 1 micron and source material is heated by an electric filament. In this technique vaporization of solid material (by heating to sufficiently high temperature) and condensing it on cooler substrate takes place to deposit the thin films. Purified cadmium iodide is placed in tungsten boat for the deposition of thin films. Thin films were deposited on the glass substrate by using vacuum coating unit (MODELEYU-3000S, VEQCO) keeping the substrate at room temperature in vacuum of  $10^{-5}$  torr. Thin films were kept inside the vacuum chamber for 15

hours. The deposition rate was slow (3-4 nm/s), as higher deposition rate led to non-uniform growth and low sticking. The optical absorption measurement were carried out in UV/VIS region by using JASCO-570 spectrometer. SEM and X-ray photographs were taken for surface morphology.

## Result and Discussion

After just one zone pass, some clearly visible black specks of impurities were found to be accumulated at far end of a boat. Impurities which are more soluble in the melt than in the host solid move in the direction of movement of molten zone and those which are less soluble in the melt move opposite to molten zone. Therefore more passes are needed to move the latter impurities. The pure crystal grown after thirty zone passes are extremely soft. In the purified material one percent selenium was doped by using the same technique (melt). For doping process ten more zone passes were required. After doping the crystal became slightly hard. Electro positivity play an important role for the case of cation substitution, but electro negativity is an important factor to reckon with anion substitution. There is small difference between electro negativity of Se and I and ionic radius of former is smaller than the latter one, therefore selenium has high probability of replacing the iodine ions in cadmium iodide structure and produce a substitutional solution. The doping results hardness of crystal. The surplus replaced atoms tend to move in to vander-waals gaps and mosaic boundaries. Differences in ionic sizes build up local internal stress in the crystal structure that are relieved by the production of dislocations and stacking

fault. It is clear from Fig.1, that with increasing the frequency dielectric constant is decreasing, because the orientation of dipoles easily changes with frequency. After doping there is reduction in dielectric constant, but this reduction does not change rapidly with the frequency, because of occupation of some of octahedral voids. The common and stable structure that  $\text{CdI}_2$  crystallizes is called 4H. For large growth rates,  $\text{CdI}_2$  exists in  $n\text{H}$  structures where  $n > 4$ . However, on heating  $n\text{H}$  structures reduce to 4H[11]. The dielectric constant of  $\text{CdI}_2$  films with  $n\text{H}$  structure lies between 60–190 (all possible structures) while the dielectric constant of the stable 4H structured films is reported to be ~15–30[12].

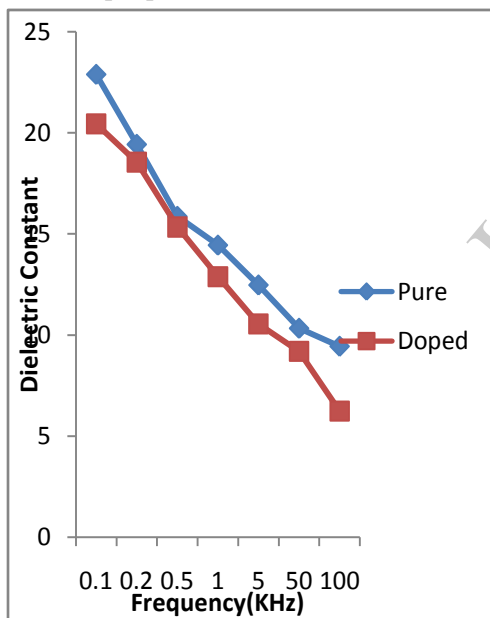


Fig.1: Variation of dielectric constant with thickness of film

The cadmium iodide is a layer structured compound (Fig-2) and dipoles are free for orientations, it is due to polar character of host material. Selenium doped cadmium iodide crystals are also

layered structure as shown in Surface Electron Microscope photograph (Fig-3).

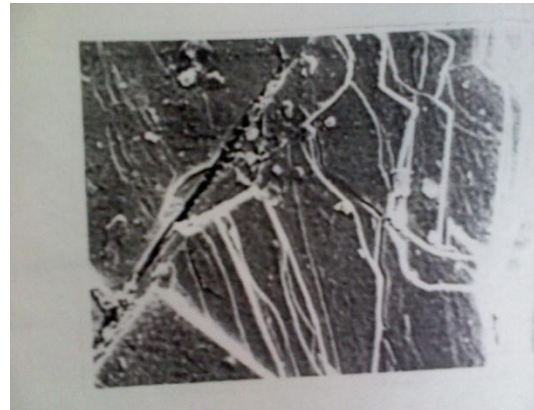


Fig.-2.SEM photograph of pure cadmium iodide

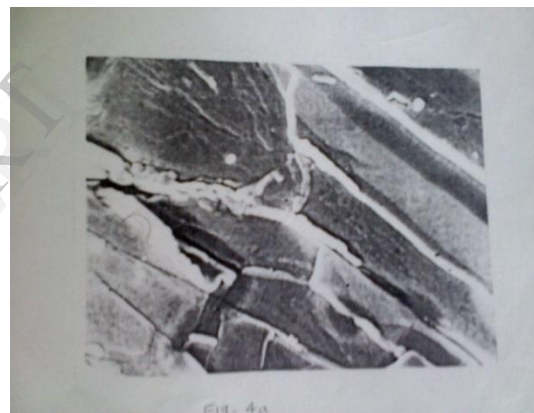


Fig.-3.SEM photograph of doped cadmium iodide

Oscillation photograph of pure(Fig.-4). and doped(Fig.-5). crystals about a-axis taken over  $0-15^\circ$  range reveal that only reflections of 4H polytype is obtained.



Fig.-4 Oscillation photograph of pure cadmium iodide crystals

Oscillation photographs of pure and KDP doped crystal were taken[2] and reported results revealed that only 4H polytypes were obtained. Using tin as dopant in  $\text{CdI}_2$  crystal oscillation photograph were also reported[7,8]. X-ray photograph revealed that after doping crystal structure remain invariant.



Fig.-5 Oscillation photograph of Se doped cadmium iodide crystal

In a crystalline or polycrystalline material both direct or indirect optical transitions are possible depending on the band structure of material[9]. Assuming parabolic bands, the relation between absorption coefficient ( $\alpha$ ) and band gap  $E_g$  for a direct transition is given by[10].

$$\alpha h\nu = \text{constant}(h\nu - E_g)^n$$

Where  $\alpha$  is absorption coefficient of material,  $h\nu$  is photon energy and  $E_g$  is band gap of material. For a direct transition  $n=1/2$  or  $3/2$  depending upon whether the transition is allowed or forbidden in quantum mechanical sense. The usual method of determining the band gap is to plot a graph between  $(\alpha h\nu)^{1/2}$  and  $h\nu$ . In the present case,  $n=1/2$  gives best graph in the band edge region. The band gap of purified material is 3.2 eV[7]. After doping of Se band gap of cadmium iodide decreases

(2.92eV), because occupancy of some octahedral voids(Fig.6).

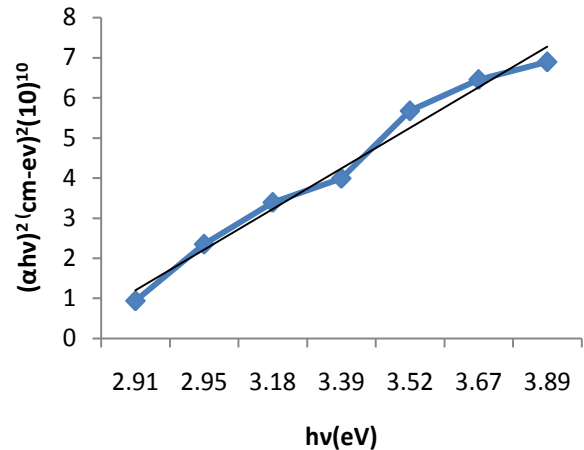


Fig6:Optical band gap of Se doped cadmium iodide crystal

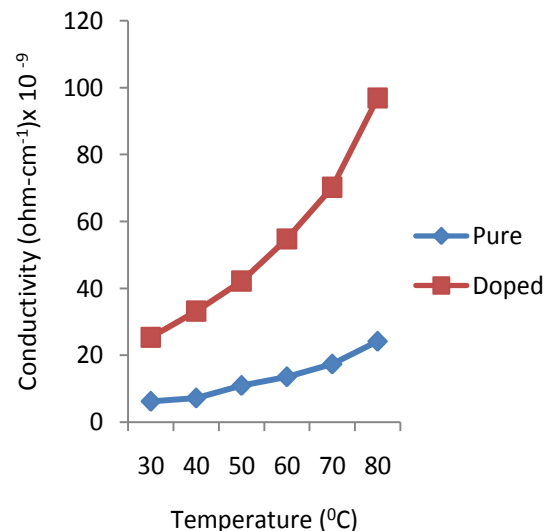


Fig. 7:Conductivity of pure and doped  $\text{CdI}_2$

Since the band gap decreases after doping, so conductivity increases

(Fig.7) and resistivity decreases because former is inverse of later one.

## Conclusion

From the present investigation it is concluded that pure and single crystal of cadmium iodide are obtained after thirty zone passes. Pure crystals are extremely soft, but doped crystals are relatively hard. After one percent selenium doping conductivity increases, while resistivity band gap and dielectric constant of cadmium iodide decreases. SEM and X-ray photograph revealed that after doping the structure of cadmium iodide remained layered structure.

## References

- [1].N. Selina, G.K. Chadha and G.C. Trigunayat, Journal of Crystal Growth, 522-52,1986, Vol 79.
- [2].D.Pandey, Phil..Mag.,1132,1975 Vol.31.
- [3].Sanjeev Kumar, Momeen and M.Y.Khan Physics of Semiconductor devices,310,2001 Vol 2.
- [4]. K.Binay and G.C. Trigunayat, Phase Transitions, 145, 1993 Vol43.
- [5].Momeen and .M.Y.Khan, Cryst. Res. And Tech.,825,1996 Vol 31,.
- [6].S.S.Novosad and V.E.Goncharuk, Journal of Applied Spectroscopy, 3 124,2009 Vol 3.
- [7].G.C.Trigunayat Solid State Ionic,48,1991 Vol.3
- [8]. G.C.Trigunayat Phase Transitions 509,1989 Vol,16.
- [9]. T.Pankaj and A.G. Vedeshwar Bull.Mater.Sc. ,297, 2001 Vol.24.
- [10].N.F. Mott and E.A.Davis Electronic Process in Non Crystalline Materials Oxford, 1, 273.1979 Vol1.
- [11] R. Coehoorn, G.A. Sawatzky, C. Haas, R.A. de Groot, Phys. Rev. (1985) 6739, Vol. B 31.
- [12] A.M. Fernandez, O.N. Srivastava, J. Appl. Crystallogr. (1977) 32, Vol 10.