1.2 Aim of the Present Work

— To grow good quality single crystals of red mercuric iodide by three different techniques :

i. Hydration of DMSO–MeOH–α-HgI_2 saturated solution,

ii. Solvent evaporation from THF–α-HgI_2 saturated solution and

iii. Polymer controlled growth (PCG) technique in vapour phase.

— To study the photoconducting properties of the grown crystals and hence to determine the mobilities, effective lifetimes and surface recombination velocities of electron and hole in these crystals,

— To study the thermally stimulated currents (TSC), photon stimulated currents (PSC) and isothermal currents in all the three types of crystals in order to uniquely characterize the trapping levels present in these crystals.

— To develope a Monte Carlo simulation algorithm in order to simulate the performance of x-ray and γ-ray detectors fabricated out of these three types of α-HgI_2 single crystals.

1.3 An Overview of the Present Work

— **Chapter 2** presents a brief review of the purification and crystal growth techniques. It also presents a detailed description of the present purification and crystal growth techniques.

Commercially available red mercuric iodide powder (E-MERCK : 98% assay) was purified by repeated sublimation followed by repeated crystallization. The purified material was examined by ICP-AES and infrared spectrophotometer to determine the impurity content. The purity level of the crystals was found to be comparable with that of the crystals grown in other laboratories all over the world.

Using this purified material, single crystals of α-HgI_2 were grown by hydration of α-HgI_2–Dimethyl Sulphoxide–Methanol saturated solution, solvent evaporation from α-HgI_2–Tetrahydrofurane saturated solution and by polymer controlled growth (PCG) technique in vapour phase.

Single crystallinity of the as-grown crystals was confirmed by Laue photography. Room temperature band-gap energies for these crystals were determined by optical absorption studies. The band gap energy thus determined was 2.12 eV for the solution grown crystals and 2.15 eV for the crystals grown by polymer controlled growth technique. These values match quite well with those reported in the literature [27,31].

— **Chapter 3** presents the study of the dark conductivity as well as photoconductivity in the as-grown crystals. This is probably the first study of photoconductivity in crystals grown by solvent evaporation from THF–α-HgI_2 saturated solution (THF crystal) and by polymer controlled growth technique in vapour phase (PCG crystal). The dark resistivity at room temperature was of the order of 10^{12} ohm-cm for solution grown crystals and 10^{13} ohm-cm for PCG crystals. These values match well with those reported in the literature [31,41].

Spectral response of photoconductivity in these crystals was studied in the wavelength region 450–700 nm at different temperatures ranging from 80–300 K. The photoconductivity spectra, obatained in the present study, can be divided into three spectral regions : weakly absorbed region (700–600 nm), peak region (600–550 nm) and strongly absorbed region (550–450 nm). From the peak position in the spectra, the band gap energy for all the three types of crystals were determined at different temperatures. The temperature coefficient of the band gap energy was (-3.4×10^{-4}) eV/K for DMSO crystals, (-2.12×10^{-4}) eV/K for THF crystals and (-4.2×10^{-4}) eV/K for PCG crystals. These values match well with the reported values [27,42].

In general, photoconductivity in the weakly absorbed region (*i.e.* the region with energies less than the band gap energy) is analysed by assuming uniform charge carrier generation in the bulk. This assumption is valid only when the absorption in this region is very low. In the present instance, the optical absorption studies indicated that the above mentioned assumption is not valid for α-HgI_2 single crystals. Thus, in the present study, more generalized equations have been employed to analyze the photoconductivity spectra of α-HgI_2 single crystals in order to determine the mobilities, effective lifetimes and surface recombination velocities of the charge carriers in these crystals. First, a theoretical photoconductivity spectrum was generated with the help of the generalized equations and then the values of the above mentioned parameters were optimized in such a manner that the experimentally obtained spectrum was superposed on the theoretical spectrum. The whole analysis was done using Apollo Domain 3000 computer. A comparative study of these of these parameters for the three types of crystals show that PCG crystals are of much superior quality as compared with the solution grown crystals. DMSO and THF crystals are of almost same quality as far as their photoconducting properties are concerned. Though the PCG crystals are of much better quality, it is difficult to use these crystals as photodetectors due to their small volumes. On the other hand, the solution grown crystals do not suffer from this constraint.

— **Chapter 4** describes the characterization of trapping levels in all the three types of crystals.

i. *Section 4.1* presents a brief introduction to this chapter.

ii. *Section 4.2* presents a brief review of the studies on the thermally stimulated currents (TSC) in red mercuric iodide single crystals of varied origin. It also describes the present experiment and results of TSC measurements on the three types of crystals. This is probably the first such study on THF crystals as well as on PCG crystals. The peak positions in the TSC spectra match reasonably well with those reported in the literature. The energies of different trapping levels were evaluated using Bube's model and Grossweiner's model. The capture cross sections were then determined using Bube's model and Grosswweriner's model. The trap densities were determined roughly from the area under the corresponding TSC peaks. For each of the TSC peaks, the values of the energy and capture cross section, determined using the above mentioned models, were quite different from each other. This ambiguity is also quite apparent in the previous literatures. This shows that the analysis of TSC measurements is quite model dependent and hence no trapping level can be assigned with a unique value of activation energy and capture cross section. Thus, in the present work, photon stimulated current (PSC) studies were performed on red mercuric iodide single crystals in order to uniquely characterize the trapping levels.

iii. *Section 4.3* presents a detailed theory of photon stimulated currents (PSC). The method of analyzing the PSC measurements is also described in detail.

The PSC meaurements were performed on all the three types of crystals grown in the present work. The trapping level energies were determined from the peak positions in the PSC spectra of these crystals. It was observed that the

DMSO crystals and the THF crystals, in general, possess six and seven trapping levels respectively. On the other hand, the PCG crystals possess only four trapping levels. The nature (electron or hole trap) of the trapping levels was also determined using PSC measurements.

For determining the density and capture cross section of any particular trapping level in PCG crystals, at liquid nitrogen temperature the crystal was excited for some definite trap-filling time. After stopping the trap-filling excitation, the sample current was allowed to decay to its value in the dark and then the current-time transient curve was obtained by emptying the traps with the help of a constant intensity monochromatic infrared light of wavelength corresponding to the concerned trapping level. For each of the trapping levels, a set of transient curves was obtained by varying the initial trap-filling times. Thus, for each of the trapping levels in the PCG crystal, a set of current-time transient curves was obtained. These curves were then analyzed using the model developed in the present study. The analysis provides the values of the capture cross section, density and type of all the trapping levels present in PCG crystals.

iv. *Section 4.4* presents the isothermal current (IC) decay measurements performed on the PCG crystals. The detrapping times, corresponding to all the trapping levels present in these crystals were directly determined by IC measurements at different temperatures in the range 80–230 K. These measurements also helped in evaluation of the energies, capture cross sections and densities of the trapping levels present in PCG crystals. The values of these parameters match very well with those obtained from the PSC studies.

v. *Section 4.5* describes how it is possible to find out the unique values of the energy and capture cross section of all the trapping levels in the solution grown crystals by a combined study of TSC and PSC in these crystals. Considering the energies obtained from PSC spectra to be accurate, each TSC peak was assigned with a unique value of activation energy by comparing the different energies obtained using different models for TSC analysis with the energy obtained from PSC spectra. The unique values of capture cross sections were then determined using the corresponding models.

vi. *Section 4.6* describes how the detrapping times corresponding to each trapping level in all the three types of crystals were evaluated using the values of the energies and the capture cross sections determined in the above mentioned manner. The possible effects of these trapping levels on the performance of the detectors fabricated from these crystals have also been discussed in this section.

— **Chapter 5** presents the development of a Monte-Carlo algorithm to simulate and predict the efficiencies (detection efficiency and full energy peak efficiency) and response of α-HgI_2 detectors to x- and γ-rays. This simulation program was written in PASCAL language and was run in Apollo Super Domain 10000 computer. Using the values of mobilities, lifetimes, surface recombination velocities and trapping times for PCG crystals, determined in the present work, spectra were generated for ^{241}Am and ^{137}Cs sources for different thicknesses of α-HgI_2 detectors. The simulated spectrum of ^{241}Am match quite well with the experimental spectra reported in the literature.

— **Chapter 6** summarizes the present work and suggests the scope for future work.

1.4 Salient Features of the Present Work

i. The electronic and optoelectronic properties of the crystals grown by polymer controlled growth technique have been studied for the first time.

ii. For the first time, α-HgI_2 single crystals grown from THF–α-HgI_2 solution have been studied for their electronic and optoelectronic properties.

iii. A very general approach has been undertaken to analyse the photoconductivity spectra in order to determine the mobility, effective lifetime and surface recombination velocity of the charge carriers in all the three types of crystals.

iv. For the first time, Photon Stimulated Current (PSC) measurements were performed on α-HgI_2 single crystals of any origin. These measurements helped in unambiguous determination of the energies and nature (electron or hole trap) of different trapping levels present in the three types of crystals.

v. A detailed methodology for analysing the PSC measurements has been developed. This analysis was used for the complete characterization of the trapping levels (*i.e.*, the determination of energy, capture cross section, density and nature) present in the crstals grown by polymer controlled growth technique.

vi. In the present study, attempt has been made to carry out a comparative study of the three types of crystals on the basis of their optoelectronic properties.