CHAPTER 4
NONLINEAR OPTOELECTRONIC
PROPERTIES OF PbI₂

4.1 Introduction

High power lasers with its salient features have become an indispensable instrument in nonlinear spectroscopy. With the availability of nonlinear experimental techniques, it is now possible to investigate the optical and electronic properties of crystalline solids. In the context of multiphoton spectroscopic studies in various crystalline media, effects are being made to extend the spectroscopic region of operation with tunable solid state laser sources.

The nonlinear photoconductivity technique (NLP) allows the quantitative determination of multiphoton absorption coefficient with required sensitivity and allows the quantitative measurement of optical properties in an indirect way [1]. Baltog et al. [2] studied the influence of gap localised levels on the luminescence and photoconductivity in pure and doped PbI₂ arising due to one photon absorption using a dye laser. Cingolani et al. [3] have studied the behaviour of the cooperative fluorescence emission from PbI₂ at 80 K at high exciton density by means of a tunable high intensity dye laser pumping. The spectral response for the two photon photoelectric effect has been measured in PbI₂ in the temperature range from 110 K to 300 K by Atsuo Kasuya et al. [4]. Pollini et al. [5] and Tubbs [6] gave the detailed band structure calculations of PbI₂. Adducci et al. [7] have measured the 2PA coefficient using nonlinear transmittance (NLT) method and Catalano et al. [8] obtained the 3PA coefficient of PbI₂ grown by Bridgeman
technique using nonlinear luminescence (NLL) method. In the present work, we have investigated the nonlinear absorption in the layered semiconductor PbI$_2$ grown by zone refining method in our laboratory at neodymium and ruby laser wavelengths. The 2PA coefficient $\beta$ has been measured by the nonlinear transmittance method. By means of two and three photon comparative photoconductivity measurements, the 3PA coefficient $\gamma$ is determined.

Earlier studies [9,10] on the spectral dependence of 2PA coefficients in semiconductors have shown that the lack of agreement between theoretical and experimental results is due to the factors, namely, (a) the square of the dipole matrix elements, (b) the transition mechanism actually involved and (c) the density of states. Further, experiments on the 2PA line shapes have shown that the 2PA dominant mechanism changes in the same material when the excitation energy is varied [9]. In particular, in direct gap semiconductors transitions are of the allowed-allowed type near the energy gap and become of the allowed-forbidden type far from it. In the present work, we reconsider this problem in PbI$_2$ semiconductor in order to analyse the transition mechanism actually involved. Similarly, the 3PA spectra have been experimentally investigated for a large excitation energy range above the energy gap. The 3PA coefficient spectral behaviour has been demonstrated to be described by a parametric formula containing a varying number of different terms. Also a comparison between experimental and theoretical line shapes has been carried out.

4.2 Theories for NLP and NLT

In the case of short laser pulses with very high photon density of the order of $10^{26}$ photons/cm$^2$/sec or more, one usually measures the total charge $Q$ induced by the laser pulse across a condenser C as shown in Figure 4.1.
The time constant $RC$ of the integration circuit is kept larger in comparison to the expected lifetime of the charge carriers. From the electrical circuit of the system, one can correlate the charge $Q$ with the photoconductance $G(t)$ induced by the laser pulse as

$$\frac{1}{C} [V - V_0(t)] G(t) = \frac{V_0(t)}{RC} + \frac{dV_0(t)}{dt}$$  \hspace{1cm} (1)

Since the time constant $RC$ is much larger than the characteristic time of $G(t)$, integration of equation (1) gives [assuming also $V \gg V_0(t)$]

$$V_0(t) = \exp\left(\frac{-t}{RC}\right) \frac{V}{C} \int_{-\tau_1}^{t} G(t') \exp[t'/RC] dt'$$

$$\approx \exp\left(\frac{-t}{RC}\right) \frac{V}{C} \int_{-\tau_1}^{\infty} G(t') dt'$$

$$= \frac{V}{C} C_0 \exp\left(\frac{-t}{RC}\right)$$  \hspace{1cm} (2)

where $\tau_1$ is the laser pulse width. Using equation (2) $C_0$ may be correlated to the total charge $Q$ induced by the light pulse, as

$$Q = V_0 \max C_0 = VC_0$$  \hspace{1cm} (3)
It has already been shown [11] that $C_0$ is quite insensitive to such parameters as the diffusion constant and recombination rate. Therefore, the measurement of $Q$ allows the determination of the nonlinear cross section.

The nonlinear photoconductivity method basically involves a $Q^{(n)}$ vs. $I$ measurement, where $Q^{(n)}$ is the total charge generated by a single laser pulse and $I$ is the incident photon flux (corrected by reflection losses). For an $n$-photon process:

$$Q^{(n)} = K \frac{\sigma^{(n)}}{n-1} I^{(n)}$$

(4)

where the "constant" $K$ depends, among other things, on the transport parameters of the crystal and its geometrical characteristics and $\sigma_n$ is the $n$-photon absorption cross section. The analytical expression of $K$ has been calculated in [12].

In the nonlinear transmittance technique, we consider the variation of the intensity of light $I$ of the plane wave as it passes through the sample with linear absorption coefficient $\alpha$ and $N$-photon absorption coefficient $\beta$ ($N = 2, 3, \ldots$), which is given by

$$\frac{dI}{dx} = -\alpha I - \beta I^N$$

(5)

when free carrier absorption is negligible.

The solution of (5) has the form [13]

$$I = I_0 e^{-\alpha x} \left( 1 + \frac{2\beta}{\alpha} I_0^{N-1} \left( 1 - e^{(-1-N)\alpha x} \right) \right)^{1/N}$$

(6)

when the reflectivity $R$ at the wavelength of the incident radiation is taken to be minimum. It follows from (6) that the wave intensity does not depend on $I_0$ when

$$I_0^{N-1} \approx \frac{\alpha}{2\beta} [1-e^{(-1-N)\alpha x}]$$

The limiting level is determined by the expression

$$I_{max} = e^{-\alpha x} \left[ \frac{2\beta}{\alpha} \left( 1 - e^{(-1-N)\alpha x} \right) \right]^{1/N}$$

(7)
If the linear absorption is small, so that $\alpha x \ll 1$ (the material is transparent in the ordinary sense), then

$$I_{\text{max}} \approx \left[(N-1)2\beta x\right]^{-\frac{1}{2}}$$

and in two photon absorption,

$$I_{\text{max}} \approx \frac{1}{2\beta x}$$

To determine $\beta$ the energy of the incident pulse and of the pulse transmitted through the specimen was measured with power meters. The linear and two photon absorption coefficients of the crystals were determined from the experimental relationships $I(I_0)$ using the following expression obtained from (6) for $N=2$.

$$T = \frac{I}{I_0} = \frac{\exp(-\alpha x)}{1 + 2\beta I_0[1 - \exp(-\alpha x)]/\alpha}$$

where $x$ is the thickness of the sample. The reciprocal two photon transmittance formula is therefore obtained as

$$\frac{I_0}{I} = e^{\alpha x} + \frac{2\beta}{\alpha} I_0 (e^{\alpha x} - 1)$$

### 4.3 Preparation of PbI$_2$ single crystal

The PbI$_2$ crystals were grown and purified by zone refining technique [14]. In the zone melting method, if we have a rod of polycrystalline material and melt a part of it i.e., a ‘zone’, we can sweep this zone down the length and eventually melt and freeze all the rod. We have to induce a ‘seed’ to form the single crystal. In the forward direction of travel, the zone is melting whereas at the back of the zone, freezing occurs. If we can induce the back part to freeze as single crystal, then we can transform the whole rod. This means that we can start with polycrystalline material and end up with a single crystal via powder $\rightarrow$ polycrystalline $\rightarrow$ single crystal.

The horizontal zone melting system for growing single crystals that we have in our laboratory incorporates a temperature controller and speed controlling facilities for the heater. A brief report of the design and technical aspects, circuit
description of the temperature controller cum recorder and its performance are given below.

4.3.1 Design and techniques

The apparatus with the associated electrical circuitry is shown in Figure 4.2. The most important parts of the system are (1) a circular heater of required temperature; (2) a travelling arrangement of the heater; (3) the growth chamber; and (4) the temperature controller cum recorder. In order to provide a uniform heating region at the centre of the heater and to avoid the thermal shocks during the crystal growth, the heating filament is covered with a sillimanite tube. The heater is also provided with two gun metal sliders, which can move freely over two rails, and is connected to the travelling arrangement through iron rods. The temperature of the heater can be controlled and recorded by a digital temperature controller cum recorder. The system was also provided with an automatic arrangement after each zone pass.

Figure 4.2. The horizontal zone refining system for the growth of PbI₂ single crystal: 1, quartz growth tube; 2, sample container (boat); 3, circular heater; 4, rotary inlet; 5, argon outlet; 6, quartz coupling tube; 7, argon inlet; 8, gearbox; 9, brass strip with wooden edge; 10 and 11, iron rods (rails); 13, servo stabilizer (230 kVA); 14, temperature controller cum recorder; 15, motor switch; 16, leads to thermocouple; 17, leads to the heater; 18, chromel-alumel thermocouple; and 19, wooden support.
4.3.2 Circuit description of the temperature controller cum recorder

Figure 4.3 shows the block diagram of the temperature controller cum recorder. By adjusting the hysteresis loop of the comparator using a hysteresis voltage regulator one can control the set (on) and re-set (off) voltage for the relay switch. The voltage corresponding to the setting temperature had already been referenced by the comparator. The circular heater is connected through the relay switch and the power to the heater and thereby the temperature was controlled by the comparator circuitry.

![Block diagram of the temperature controller cum recorder](image)

Figure 4.3. Block diagram of the temperature controller cum recorder: 1, power supply; 2, voltage regulator; 3, relay switch; 4, load (heater coil); 5, comparator (IC LN324); 6, analog-to-digital converter (ADC, IC7107); 7, seven segment decoder; 8, seven segment driver; 9, digital display.

The analogue signal from the thermocouple is converted to a digital one with the help of an A/D converter. Depending upon the melting point of the sample, the required temperature can be set by tuning the arrangement of the system. When the temperature reaches the melting point of the sample the heater cuts off automatically by the action of the relay switch. After a few seconds the heater is again switched on and the process is repeated, thus maintaining a constant temperature. A photograph of the crystal growth system is given in Figure 4.4.
4.3.3 Working of the system

The most important part of the apparatus is the quartz growth tube of length 50 cm and diameter nearly 2.8 cm. One end of the tube is connected to an argon gas cylinder and the other end is connected to another co-axial quartz tube arranged as shown in Figure 4.2. The open end is connected to a rubber tube which was dipped in water from where argon gas could escape. The side tube is for a rotary or diffusion pump inlet. The boat containing the material (PbI₂ powder) was inserted into the growth chamber through the wider end. The boat is also made up of quartz, having diameter 1.8 cm and length 10 cm or more. To enable nucleation of a single crystal one end of the boat was shaped like a prow of a sailing ship.

The boat containing powdered sample was placed in the central portion of the growth chamber. After providing the necessary vacuum using a rotary or diffusion pump, argon gas was made to flow slowly through the system to prevent...
oxidation of the material during crystal growth. The heater is switched on and the temperature is set to nearly the melting point of the sample. Now the driving motor is also switched on and the speed of movement was maintained at 2 cm h\(^{-1}\). At the end of each zone pass the heater was quickly returned to its initial position by manual operation and the process repeated. In the final pass the crystal was allowed to cool slowly. While growing crystals in this way one should take care of the speed of movement of the zone, as higher speeds tend to form polycrystalline masses. Figure 4.5 shows the photograph of the PbI\(_2\) single crystals grown by employing the present zone refining system.

![Figure 4.5](image)

Figure 4.5. Photograph of PbI\(_2\) single crystals grown by using the fabricated zone refining system. The intense reflections are from the perfectly plane portions of the surface of the crystal.

4.3.4 Performance of the system

The system performance is found to be satisfactory when one grows the crystal in the presence of an argon (insert gas) atmosphere. The use of silmanite
tube maintains a steady temperature at the centre of heater and avoids thermal shocks that may occur during crystal growth. After many trials, an optimum speed of 18 cm h\(^{-1}\) is maintained and a satisfactory good single crystal could be grown in about 8-10 zone passes. The crystallinity of the grown sample was confirmed by analysing the XRD pattern. Crystals of thickness \(\sim 0.5\) mm and having length \(\sim 6-8\) mm were obtained from the grown ingot for experimental measurements. The surface of the crystal perpendicular to the c-axis were obtained by cleaving, and the surfaces parallel to the axis were cut and polished with ethyl alcohol.

4.4 Experimental details

The PbI\(_2\) samples were cleaved from single crystal ingots grown by horizontal zone melting and refining system. The crystals were rectangular in shape with typical dimension 6 x 5 x 2.5 mm\(^3\). Good quality crystals were selected to use maximum power density for excitation without crystal damage and photodecomposition. Silver paint contacts on the two opposite faces of the crystal were used for photoconductivity measurements. The two and three photon photoconductivity were excited by a Q-switched ruby laser (\(2\hbar\omega = 3.56\) eV, peak power = 40 MW) and a Nd:YAG laser (\(3\hbar\omega = 3.51\) eV, peak power = 100 MW) respectively. Both the lasers (IMPULSPHYSK) have 7 ns pulse duration. The intensity of the lasers were changed using neutral density filters. All measurements were carried out it liquid nitrogen temperature with proper correction for reflection losses.

The 2PA spectrum was obtained by a Molecron dye laser (Pulse duration 5 ns maximum peak power \(\equiv 30\) MW/cm\(^2\) for Rhodamine 6G) pumped by the second harmonic of the Nd:YAG laser. The spectral dependence of 2PA coefficient has been measured near and far from the energy gap (5 meV \(\leq 2\hbar\omega - \text{Eg} \leq 1800\) meV). While the 3PA spectrum was obtained by means of the same dye laser with excitation energy in the range 50 meV \(\leq 3\hbar\omega - \text{Eg} \leq 2100\) meV. Different dyes were used to have the appropriate excitation energy values and the beam was focused to have the required power.
4.5 Results and discussion

4.5.1 Nonlinear studies in PbI$_2$

The fundamental direct energy gap of PbI$_2$ is 2.5 eV at 80 K and consequently two photon interband direct absorption can be observed by the ruby laser. The NLT method gives directly the two photon absorption coefficient $\beta$ by measuring the reciprocal transmittance $I_0/I$ (equation 10). The plot of $I_0/I$ vs. $I_0$ is shown in Figure 4.6.

![Figure 4.6. Reciprocal transmittance vs. incident power](image-url)
The linear dependence is good in agreement with equation (10). The Y-intercept gives the value of the one photon absorption coefficient as 4.65 cm\(^{-1}\). The \(\beta\)-value has been evaluated to be \(2.8 \times 10^{-1}\) cm/MW from the slope of the straight line. Figure 4.7 shows the emission spectrum of PbI\(_2\) under ruby laser excitation. The emission peak is centred at 502 nm (2.47 eV) and shows a long wavelength tail. It's half width is \(\approx 40\) meV. The peak intensity of the 502 nm emission has a quadratic dependence on the laser intensity followed by saturation effects (Figure 4.8). This clearly establishes the fact that the emission is essentially a spontaneous one below the pump intensity of \(\approx 2\) MW/cm\(^2\). Above this threshold intensity, saturation effects set in because of the saturating tendency of the gap energy levels involved in the recombination processes. This clearly substantiates the results obtained under one photon pumping by earlier workers [2].

![Emission spectrum of PbI\(_2\) at LNT](image)

**Figure 4.7.** Emission spectrum of PbI\(_2\) at LNT
The charge versus intensity characteristics were obtained for two different photon energies by using the most sensitive method based on NLP [1]. This involves a $Q$ vs. $I$ measurement (equation 4). Figure 4.9 shows the dependence of the charge on the exciting intensities $I_{Rb}$ and $I_{Nd}$. Each experimental point is obtained by averaging over several measurements. In the case of neodymium excitation the straight line has a slope of three which is consistent with a three photon absorption processes. On the other hand, the slope of two obtained for ruby excitation is an evidence of a two photon process. Moreover, the dependencies are found to give an almost invariant slope with applied voltage under band to band excitation uninfluenced by localised gap levels [15].
Figure 4.9. Charge vs. laser input power: (a) Ruby laser; (b) Neodymium laser
From the experimental results it is possible to determine the ratio between $\sigma_3$ and $\sigma_2$. In fact, assuming a constant charge efficiency, the charges are equal when

$$\frac{Q^{(3)}}{Q^{(2)}} = 1 = \frac{\sigma_3}{2\sigma_2} \frac{I_{Nd}^3}{I_{Rb}^2}$$

\hspace{1cm} (11)

where $Q^{(3)}$ and $Q^{(2)}$ are three and two photon generated charges.

One gets, then from Figure 4.9,

$$\frac{\sigma_3}{\sigma_2} = \frac{2I_{Rb}^2}{I_{Nd}^3} = 4.9 \times 10^{-33} \text{ cm}^2 \text{ sec}$$

\hspace{1cm} (12)

The $\beta$-value of $2.8 \times 10^{-1}$ cm/MW obtained from the NLT method translates to a value of $1.25 \times 10^{-38}$ cm$^4$ sec for the two photon absorption cross section $\sigma_2$ [16]. Knowing $\sigma_2$, one can deduce the three photon absorption cross section $\sigma_3 = 6.13 \times 10^{-41}$ cm$^6$ sec$^2$ which is equivalent to $1.05 \times 10^{-2}$ cm$^3$/GW$^2$ for the $\gamma$ coefficient [16].

The $\beta$ and $\gamma$ coefficients determined during this study are compared with the theoretical predictions and the previous experimental data (Table 4.1). Theoretical values have been computed following the methods discussed in Chapters 2 and 3. The agreement between the $\beta$-value obtained from the perturbative method and the experimental one may be considered quite good, while the nonperturbative method underestimates the value by three orders of magnitude. The perturbative treatment underestimates the $\gamma$-value by an order of magnitude only while, the nonperturbative case greatly underestimates the experimental result. The inconsistency of the values of the coefficients in the case of the nonperturbative model with the experimental ones is a direct consequence of the approximations adopted in the model. However, the experimental results are found to be quite consistent with the previously observed values. The study confirms the usefulness of the nonlinear techniques for the analysis of nonlinear processes of order higher...
than two. Moreover, one concludes that higher order optical nonlinearities can be probed by well characterised lasers and crystals and choosing the proper range of laser powers.

### Table 4.1. Comparison of theoretical and experimental values of $\beta$(cm/MW) and $\gamma$ (cm$^3$/GW$^2$).

<table>
<thead>
<tr>
<th>Absorption coefficient</th>
<th>Perturbative method</th>
<th>Nonperturbative method</th>
<th>Experimental results</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>$1.32 \times 10^{-1}$</td>
<td>$2.47 \times 10^{-4}$</td>
<td>$2.50 \times 10^{-1}$ [7]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2.80 \times 10^{-1}$ [present work]</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$3.25 \times 10^{-1}$</td>
<td>$1.73 \times 10^{-9}$</td>
<td>$1.53 \times 10^{-2}$ [8]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.05 \times 10^{-2}$ [present work]</td>
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</table>

#### 4.5.2 Spectral dependence of 2PA and 3PA coefficients

Figure 4.10 shows the spectral dependence (dots) of the 2PA coefficient for PbI$_2$. In this figure the full line is related to the three band model (Chapter 2; allowed-allowed transition and nonparabolic approximation). In the region near the direct gap $50 \text{ meV} \leq 2 \hbar \omega - E_g \leq 140 \text{ meV}$ the experimental points well fit the curve related to the perturbative three band model characterised by a spectral dependence roughly equal to $(2 \hbar \omega - E_g)^{3/2}$. Beyond 140 meV, above the band gap, $\beta$ value shows a spectral dependence approximately equal to $(2 \hbar \omega - E_g)^{3/2}$ consistent with an allowed-forbidden type transitions. These results show that for PbI$_2$ allowed-allowed transition dominate 2PA processes near the energy gap while allowed-forbidden transition are predominant well above the energy gap and confirm the previously obtained results for other direct gap semiconductors [9,10].
Figure 4.10. Two photon absorption coefficient vs. \((2 \hbar \omega - E_g)\) for PbI₂

As regards interband transitions, the 3PA coefficient line shape measured over a large excitation energy range can be fully described by the parametric equation

\[
\gamma = \sum_{n=0}^{3} C_n (3\hbar \omega - E_g)^{n+1}.
\]  

(13)

containing four different terms and their energy dependences being predicted by the 3PA selection rules. In particular, the \((3\hbar \omega - E_g)^1\), \((3\hbar \omega - E_g)^3\), \((3\hbar \omega - E_g)^5\) and \((3\hbar \omega - E_g)^7\) dependences correspond to allowed-allowed-allowed (a-a-a), allowed-allowed-forbidden (a-a-f), allowed-forbidden-forbidden (a-f-f) and forbidden-forbidden-forbidden (f-f-f) type respectively [17,18]. The 3PA line shape (dots) of PbI₂ versus \((3\hbar \omega - E_g)\) has been reported in Figure 4.11. The experimental line shape has been fitted with equation (13). The agreement is good as shown by the \(\chi^2\) value for degree of freedom equal to 0.24 and by the fit probability equal to 0.994.
Moreover, the $C_n$ coefficient values have been reported in Table 4.2. The results of these fittings show that all the terms of equation play a part in the 3PA spectral dependence and therefore all four 3PA mechanisms already stated depending on the selection rules contribute simultaneously to 3PA interband transition amplitude.

**Table 4.2.** Values of the parameter formula $C_n$ coefficients for PbI$_2$. $C_n$ dimensions are cm$^3$ GW$^{-2}$ meV$^{(n-1)}$ for $n = 0, 1, 2, 3$.

<table>
<thead>
<tr>
<th></th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2.6 \times 10^{-4}$</td>
<td>$5.9 \times 10^{-7}$</td>
<td>$2.6 \times 10^{-10}$</td>
<td>$1.8 \times 10^{13}$</td>
</tr>
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</table>
The 3PA line shapes are found to be in reasonably good agreement with theoretical ones of the allowed type near the energy gap of ionic crystals in a qualitative way [18]. For confirming this in the case of PbI$_2$ a comparison between theoretical and experimental line shapes have been made (Figure 4.12). In particular curve A comes from a perturbative approach which assumes a four band model and curve B is obtained from a nonperturbative approach (Chapter 3). It is evident that in the energy range $50 \text{ meV} \leq (3 \hbar \omega - E_g) \leq 300 \text{ meV}$ only a satisfactory qualitative agreement between the experimental line shape and the perturbative one is obtained. On the contrary in this range the experimental data are underestimated by the nonperturbative one. Beyond 300 meV the experimental and theoretical line shapes do not agree at all. The mismatching of the experimental line shape and the perturbative one in the lower energy side can be ascribed to the excitonic effects [19]. Also even the parametric approach of Wherret [20] to multiphoton absorption does not give more satisfactory results.

Thus one finds that the 2PA results allow one to affirm that in direct gap semiconductors the dominant mechanism depends more on the frequency than on material parameters. In the higher energy range the role of the density of states has to be reckoned with while considering the actual transition mechanisms involved. The 3PA results can be both qualitatively and quantitatively described by a parametric equation which considers all the four type of transitions. Further, only the more realistic perturbative approach gives a satisfactory qualitative agreement with the experimental data near the energy gap.
Figure 4.12. Quantitative comparison between the $\gamma$ experimental (dots) and theoretical (solid lines) line shapes for PbI$_2$. Solid lines A and B correspond to perturbative and nonperturbative models.
References