Chapter Three

Optical Amplification In CdI$_2$ and CsI:In(Tl) Ionic Crystals

Ever since the discovery of optical amplification a lot of efforts have been done by scientists to reveal this phenomenon in a variety of optical materials. Since optical amplification is a fundamental process behind laser action a lot of theoretical as well as experimental investigations have been carried out in this field over the past few decades. The results of all these investigations helped in the design and development of a lot of laser materials. Nowadays, a lot of materials are found to exhibit laser action in the solid, liquid and gaseous state. Solid state laser materials can be either crystalline or amorphous in nature. An important condition for laser action in any material is the existence of a number of states whose mean lifetimes are relatively long so that it will be possible to pile up a considerable amount of energy in the excited state. Higher values of cross section, long lifetime of the levels and the sharpness of the spectral line are the characteristic features of a good optical (laser) material. However, on the other hand, optical materials having short lived excited states are found to be good laser materials because of the fact that the stored energy should be released in the shortest possible interval realising high optical gain. Among the crystalline laser materials, rare earth doped crystals, colour centre laser crystals and semiconductors are of special interest. This chapter deals with the spectroscopic investigations on the optical amplification of
CdI$_2$ and CsI:In(Tl) single crystals using time resolved spectroscopy (TRS) and optical gain spectroscopy (OGS).

3.1 Introduction

In the last few decades an increasing amount of research has been carried out on CdI$_2$, particularly on their interesting anisotropic optical and electrical properties.$^1$ Cadmium iodide is a typical layer structured ionic crystal. The basic structural unit is a sandwich consisting of two layers of iodine ions with one layer of cadmium ions between them. All good ionic crystals are transparent over a broad region of the spectrum centred in the near infra-red which is bounded on the long-wave side by the lattice absorption, and on the short-wave side by the onset of electronic absorption corresponding to exciton or interband transitions across the energy gap. The onset of electronic absorption is marked by the fundamental absorption edge. Studies of the optical and electrical processes based on the illumination at the fundamental absorption edge give valuable information on the exciton structure, effective masses, carrier mobilities, phonons and trapping states.$^1$

Optical absorption and luminescence studies of CdI$_2$ single crystals have been made by several workers.$^{1-3}$ The phenomenon of Raman scattering in CdI$_2$ was extensively studied by Hayashi et al.$^4$ Optical gain measurements in CdI$_2$ under high power laser excitation was conducted by Nakagawa et al.$^5$ These workers observed stimulated emission in CdI$_2$ and suggested that the amplification is due to the formation of self-trapped bi-excitons. In addition to this, being a very good photoconductor, a lot of investigations have been done on the non-linear photoconductivity mechanisms and optoelectronic behaviour of CdI$_2$ under laser excitation.$^6,7$ In the present work an attempt has been made to investigate the optical properties of the melt grown CdI$_2$ single crystal with special emphasis on time resolved emission spectrum, relaxation process, stimulated emission, and optical gain.
Tunable lasers in a wide range of optical spectrum are of great interest for research in linear and non-linear spectroscopy and for applications in many fields, such as remote detection and photochemistry.\textsuperscript{8} At present in the visible region wideband tunable lasers are realised by means of organic dyes but for some applications, the photochemical degradation of these materials (bleaching) reduces their efficiency to some extent. On the other hand, the ultraviolet region is covered essentially by lasers operating in the second or third harmonic or by frequency mixing with a large loss in intensity.\textsuperscript{9,10} Excimer lasers can extensively be used in the UV region but it lacks tunability.

During the last 10-15 years much effort has been devoted to the search for new tunable solid state laser (TuSSL) materials. Among the systems investigated impurity centres represent a very attractive class of active media due to their luminescent characteristics in a very wide spectral range from UV to the IR. The importance of colour centre lasers is due to their features of tunability, output power up to about 100 MW in pulsed mode (PM), while in continuous wave mode (CW) output power up to 60 W with flash lamp pumping or 600 mW with ion-laser pumping and narrow laser-line width due to the stability of the active medium. The active medium of these solid state lasers is a monocystal (sometimes containing lattice defects) doped with a suitable impurity which gives rise to absorption bands in the transparent region of the pure crystal. The possibility of obtaining laser action in IR region (2.6–2.8 \textmu m) in alkali-halide crystals containing $F_A$ centres was demonstrated by Mollenauer and Olson.\textsuperscript{11} At present such a possibility has been extended in the range of 0.8–4 \textmu m with a suitable selection of the material. Recently, the possibility of obtaining optical amplification in UV region with $F^+$ centres in CaO was shown by Duran et al.\textsuperscript{12} extending the possibility of employing such materials in another spectral region.

An important set of colour centres emitting in the UV/VIS region is represented by the $Tl^+$-like impurities in alkali-halide crystals whose luminescent features have been investigated for a long time.\textsuperscript{13} The first attempt made in this field was that on KCl:Tl crystals, pumped by an excimer (KrF) laser. But this
crystal showed the difficulty of obtaining optical amplification due to the presence of an additive colouration and is attributed to the formation of $\text{TI}^{++} \rightarrow \text{TI}^+$ pairs. The aim of the present investigation is to study the possibilities offered by alkali-halide crystals in getting optical amplification. Earlier Fabeni et al. measured the lifetime of the luminescent band in CsI:In(Tl) due to the excitation by 337 nm wavelength. Its time resolved spectra clearly indicate the presence of two prominent bands appearing at $\sim$ 430 nm and 540 nm, former being the faster component having lifetime in the 10 ns range. As such, this is the component important for gain studies. The other component lying in the 1 $\mu$s range is of little importance from that point of view. These investigators have also studied the impact of nitrogen laser pulses in the development of colour centres. In the beginning, when one or two pulses fall on the crystal, both the faster as well as the slower component appear. The relative intensity of the slower component drops down to almost zero value when the number of shots becomes something of the order of 70 pulses or more. With the repetition rate of around 50 pulses used in the present case, one can very easily expect the total domination of the slow component, irrelevant from the point of view of the gain studies. Fabeni et al. have used double beam technique for optical gain measurement. In this case the emission intensity, for two values of the pump power as a function of the pumped length is recorded using a boxcar averager. The ratio of these two curves is used to eliminate the uncertainties induced due to the beam inhomogeneity and pulse-to-pulse variation. The gain coefficient measured by these investigators varies in the range 0.8–1.1 dB/cm, and hence the uncertainty in using CsI:In(Tl) as a probable tunable laser material. The present chapter also describes the time resolved spectroscopic and optical gain measurements of CsI:In(Tl) single crystals.
3.2 Growth and characterisation of CdI₂ single crystal

3.2.1 Preparation of CdI₂ single crystal

The CdI₂ single crystals were grown and purified by employing the method of horizontal zone melting. The method of horizontal zone melting has been found to be an elegant and simple technique for obtaining single crystals of high optical quality.\textsuperscript{16} The central idea involved in this method is that of purifying the crystal after melting. Here crystal growth is achieved by horizontal zone melting and purification by repeated zone passes after melting. This is effected by adopting different viable set-ups.\textsuperscript{17} One of the most common set-ups is to have a movable heating arrangement with the material held in a container and kept at rest. However, most of these systems are bulky and expensive in their design aspects. In addition to this they lack precision in their pulling arrangement and temperature measurements. In view of this, we have designed and developed a horizontal zone melting system for growing single crystals in the laboratory. The system incorporates a temperature controller and speed controlling facilities for the heater. The design and technical aspects, circuit description of the temperature controller cum recorder and its performance and application are described here.

3.2.2 Design and techniques

The apparatus fabricated here is a simplified version of the one developed by Pfann and Olsen.\textsuperscript{18} Figure 3.1 shows the apparatus with the associated electrical circuitry. 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. The travelling arrangement consists of a synchronous motor (1 or 10 rpm) coupled with a gear box, which helps to reduce the speed further. The gear system is specially designed to have the required speed. The circular heater consists of a coil of Kanthal (A1 grade, temperature range 1150–1375°C). To avoid heat loss
the coil is surrounded by a thick package of fire-brick silica (working temperature 1100°C, melting point 1710°C). The width of the heating element is about 4 cm and can be further reduced depending upon the temperature required. The filament is also covered with a sillimanite (Al₂O₃-SiO₂) tube (maximum working temperature 1500°C, melting point 1710°C). This helps to provide a uniform heating region at the centre of the heater. In addition to this, it avoids any thermal shocks during crystal growth. 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 and the power to the system was stabilised using servo stabiliser (230 V, 2 kVA). The system was also provided with an automatic stopping arrangement after each zone pass.

![Diagram](image)

**Figure 3.1** The horizontal zone refining system for the growth of CdI₂ 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.
Figure 3.2  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 convertor (ADC, IC7107); 7. seven segment decoder; 8. seven segment driver; 9. digital display.

3.2.3 Circuit description of the temperature controller cum recorder

Figure 3.2 shows the block diagram of the temperature controller cum recorder. The thermocouple used here is of chromel-alumel (Cr-Al) type, which can be effectively used to sense temperatures in the range 1100-1200°C. The output of the thermocouple is calibrated to 0.04 mV°C⁻¹ and is fed directly to the comparator circuit as shown in the block diagram. 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.

The analogue signal from the thermocouple is converted to a digital one with the help of an A/D converter. Here we are using a three-digit single-chip
A/D converter IC 7107 (Intersil) having high accuracy. This A/D converter provides a built-in seven segment decoder and driver. Thus by using four seven-segment display units the temperature can be displayed digitally. This temperature recorder can record temperature up to a maximum of about 1200°C. 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. As a result, a temperature gradient is set up along the axis of the moving zone. The leading edge of the temperature profile follows a near-Gaussian shape as reported elsewhere. This is the determining factor in specifying the maximum temperature of the melting zone. A photograph of the crystal growth system is given in Figure 3.3.

Figure 3.3 Photograph of the fabricated crystal growth system.
3.2.4 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 coaxial quartz tube arranged as shown in Figure 3.1. 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 (CdI$_2$ 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 the prow of a sailing ship. The heating zone is produced by a coaxial circular heater of length approximately 4 cm. The power to the heater was fed through a servo stabiliser (230 V, 2 kVA). The heater is mounted on wheels and carriage and could be pulled along the rails at the desired speed using a synchronous motor.

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. A satisfactorily good single crystal could be grown in about 10-20 zone passes. 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 3.4 shows the photograph of the CdI$_2$ single crystals grown by employing the present zone refining system.
3.2.5 Performance of the system

As a test performance the set-up has been employed to grow single crystals of compounds of layered structure. Initially it was planned to purify the material in vacuum to avoid oxidation but during the process of purification most of the material is evaporated and got deposited on the walls of the growth chamber. To suppress evaporation and at the same time to avoid oxidation it was proposed to purify the material in the presence of argon gas. The system performance is found to be satisfactory when one grows the crystal in the presence of an argon (inert gas) atmosphere. After every zone pass the heater can be stopped by the automatic stopping arrangement associated with the instrument. Another important feature is that the temperature at the centre of the heater is made steady by using a silimanite tube. This also helps to avoid thermal shocks that may occur during crystal growth. The performance of the temperature controller depends on several factors like the thermal coupling between the sensor and heater, the rate of heat loss from the molten zone and the temperature distribution over the zone. The present controller uses sensor of
fairly good sensitivity and thus avoids the problem of noise and drift during crystal growth. Also it has low nonlinearity, which permits easy temperature calibration. The performance of the controller has been monitored and it is found that the temperature is steady to within ± 0.08°C, at the melting temperature of the crystal. The speed of the moving arrangement is found to be the critical parameter. Higher speeds (3 cm h⁻¹ or more) tend to form polycrystalline samples whereas lower speeds (1.2 cm h⁻¹ or less) do not exhibit any remarkable improvement in crystal growth. The material is found to have the tendency of producing single crystals in this range of speeds. Therefore, after many trials, an optimum speed of 1.8 cm h⁻¹ is maintained and a satisfactorily 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 ~0.5 mm and having length ~6.8 mm were obtained from the grown ingot for the experimental measurements. The surfaces 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.

3.2.6 Experimental details

(i) Optical absorption and time resolved emission measurements

The room temperature absorption spectra for Cdl₂ will not give any informations regarding the lattice processes occurring in the crystal. On the other hand the low temperature absorption spectra are found to yield a wealth of informations about the exciton transitions in the crystal. The

![Figure 3.5](image)

Figure 3.5 Low temperature absorption spectra of Cdl₂ (After Takemura et al., Ref. 20). A at 2 K, B at 16 K, C at 31 K, and D at 48 K.
low temperature absorption spectra of CdI₂ recorded by Takenuara et al.²⁰ in the range 2.48 K are given in Figure 3.5.

For recording the time resolved emission spectra the experimental arrangement described in Chapter 1 was employed. The sample crystal was mounted on the copper sample holder of the cryostat and was then cooled down to liquid nitrogen temperature (77°K). Pressure in the cryostat was kept less than $5 \times 10^{-6}$ Torr. Since the wavelength of N\textsubscript{2} laser (337.1 nm = 3.68 eV) lies in the excitonic absorption region (3.5 eV) of CdI₂ crystal, the 337.1 nm light pulses with pulse duration of about 10 ns from a high power N\textsubscript{2}-gas laser was used for the high density excitation. The exciting light pulse was irradiated in the direction parallel to the crystal c-axis and focused with a quartz lens on the crystal surface perpendicular to the c-axis. The degree of focusing was adjusted by changing the position of the lens with respect to the crystal surface. The luminescence was focused with another quartz lens and monochromatised with a monochromator through a cut-off filter and detected with a photomultiplier (Philips XP 2020). The output signals were finally displayed on a microcomputer, which give the time resolved emission spectra.

While the multichannel analyser (MCA) oscilloscope screen shows a histogram of the accumulated counts which is equivalent to the fluorescence decay curve. The time resolved emission spectra of CdI₂ crystal recorded at LNT are shown in Figure 3.6. In Figure 3.7 the oscilloscope traces of the 2.37 eV emission of CdI₂ under N₂-laser excitation is given and in Figure 3.8 the corresponding fluorescence decay curve is shown.

![Figure 3.6. Time resolved emission spectrum of CdI₂ crystal recorded at LNT.](image-url)
Figure 3.7  Oscilloscope traces of the 2.37 eV emission of Cdl₂ under N₂ laser excitation: (a) slow component and (b) fast component.

Figure 3.8  Fluorescence decay curve of the 2.37 eV emission of Cdl₂ under N₂-laser excitation.

(ii) Optical gain measurements

In order to measure the optical gain of Cdl₂ corresponding to a particular emission, the intensity of luminescence is measured as a function of the excitation length. The experimental details for the gain measurements are discussed in Chapter 2. From the linear dependence of the luminous intensity upon the excitation length, the gain value can be calculated. Figure 3.9 shows the plot of the luminous intensity vs excitation length.
3.2.7 Results and discussion

(ii) Analysis of optical absorption and time resolved emission spectra

The low temperature absorption spectra show that the absorption edge of CdI$_2$ is around 3.2 eV. From the absorption spectra it is clear that, the low temperature spectra show some well defined structures. These structures are found to be the characteristics of the intrinsic absorption edge of CdI$_2$.\textsuperscript{21}

The low density excitation in the excitonic absorption edge region (3.5 eV) give rise to two emission bands at LNT, the green (G) emission (at 2.44 eV) and the yellow (Y) emission (at 2.15 eV). These emissions are supposed to be intrinsic (spontaneous) ones\textsuperscript{22} since they are strongly stimulated only in the fundamental absorption region and highly reproducible for every sample. When exciting the crystal strongly with N$_2$-laser, the new emission bands appear at the low energy sides of the usual G and Y emission bands (at 2.37 eV and 2.0 eV, respectively) and are rather sharp compared to the intrinsic emission bands (Figure 3.6). It was found that at LNT the intensity of the G-emission is larger
than that of the Y-emission. This is contrary to the case of the intrinsic emission spectra of CdI$_2$. It is supposed that these spectra consist of two components, that is, the usual intrinsic emission spectra and the new emissions characteristic of the strong excitation.

In order to calculate the decay time of the 2.37 eV emission, the fluorescence emission is recorded on the multichannel analyser (MCA) of the detection system and is shown in Figure 3.8. It was found that each curve consists of two components, the fast and slow ones. The slow component (Figure 3.7a) decays with a time constant of about 4.3 µs and is mainly due to the spontaneous emission process. The fast component which is given by the curve b in Figure 3.7 decays with a time constant of 81.21 ns. This component can be attributed to the new emission characteristics of the strong excitation. By analysing the decay curves at various emission energies between 2.0 and 3.5 eV the stimulated luminescence spectrum of CdI$_2$ crystal at LNT can be obtained. For this each decay curve was decomposed into two components, the fast and slow ones and then subtract the slow component from the observed decay curve. The stimulated emission spectrum thus obtained is shown in Figure 3.10.

![Stimulated emission spectrum of CdI$_2$ at LNT.](image)

**Figure 3.10.** Stimulated emission spectrum of CdI$_2$ at LNT.
The stimulated emission spectrum is different from the usual spontaneous emission spectrum which gives a broad emission band in the yellow and green region at LNT. It was observed that the stimulated emission spectrum consists of eight fine-structures, namely, three in the region of the V-emission ($V_1$, $V_2$, $V_3$) three in the region of the G-emission ($G_1$, $G_2$, $G_3$) and two in the region of the Y-emission ($Y_1$, $Y_2$). These structures are considered as the fine-structures of the self trapped exciton (STE) states in the CdI$_2$ crystal.

In CdI$_2$ crystal the excitons have a strong interaction with the crystal lattice and are considered as the trapped excitons. The trapped excitons relax the lattice nearly and become quasi-stable relaxed excitons. These relaxed excitons may be localised in the crystals. The long lifetimes of the emission are attributed to the emission from relaxed excitons. The relaxed excitonic states in CdI$_2$ can be approximated by the excited states of the $[\text{Cd}^{2+}X^-]^{4+}$ complex molecular ions where $X^-$ is a halogen ion.$^{23,24}$ This consists of a central cadmium ion which is surrounded by six halogen ions. The schematic energy diagram of this complex ions in $D_{4h}$ symmetry field is shown in Figure 3.11. In the left column are given possible combinations of orbitals of a hole and an electron which compose a relaxed exciton. Central column shows opposite states derived from the combination of such a hole and an electron in the octahedral symmetry. The G-emission,
which is dominant in CdI$_2$ at low temperature, can be assigned to a transition from E$_g$ (T$_{1g}$) to A$_{1g}$. The transition from E$_g$(E$_g$) to A$_{1g}$ is identified to be responsible for the Y-emission. The V-emission corresponds to the parity forbidden transition from A$_{2g}$(A$_{2g}$), A$_g$(E$_g$) and B$_g$(E$_g$) to A$_{1g}$(A$_{1g}$).

(ii) Analysis of optical gain

It was found that the G-emission (stimulated emission of CdI$_2$) in CdI$_2$, under strong excitation coincides with the maximum gain peak (2.37 eV) of the optical gain spectrum obtained at LNT. The optical gain corresponding to this emission can be obtained by measuring the slope of the linear region of the semilog plot of (ΔI/Δl) vs the excitation length (l) (For details see Chapter 2). From Figure 3.9 the slope of the linear region is found to be 1.4 x 10$^4$ cm$^{-1}$ and this gives the optical gain coefficient. Knowing the length of the exciting region the optical gain can be obtained by using the equation G = exp (αL). The values of the optical gain and stimulated emission cross section for the G, Y and V emission from CdI$_2$ are given in Table 3.1.

Table 3.1.

<table>
<thead>
<tr>
<th>Emission component</th>
<th>Photon energy (eV)</th>
<th>Gain coefficient (10$^4$ cm$^{-1}$)</th>
<th>Excited state (5pl, 5s Cd) population (ions/cm$^3$)</th>
<th>Stimulated emission cross section (10$^{17}$ cm$^2$)</th>
<th>Gain (G) (dB cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>2.37</td>
<td>1.4</td>
<td>2.2 x 10$^{20}$</td>
<td>6.36</td>
<td>18.23</td>
</tr>
<tr>
<td>Y</td>
<td>2.15</td>
<td>0.9</td>
<td>2.2 x 10$^{20}$</td>
<td>4.09</td>
<td>11.70</td>
</tr>
<tr>
<td>V</td>
<td>2.90</td>
<td>0.2</td>
<td>2.2 x 10$^{20}$</td>
<td>0.90</td>
<td>2.55</td>
</tr>
</tbody>
</table>

The existence of the large value of optical gain demonstrates that the amplification process is much dominant under strong excitation. Our experimental results show that three different optical transitions with a high
optical gain contribute to the optical amplification process in CdI₂. Contrary to previous observations,⁵ it seems more reasonable that the mechanism observed for CdI₂ are consistent with the general scheme of four level laser proposed for selftrapped excitons in ionic crystals.²⁵

3.4 Characterisation of CsI:In(Tl) single crystal

3.4.1 Experimental details

(i) Optical absorption and time resolved emission measurements

CsI:In(Tl) crystals were supplied by G. P. Pazzi, Institute di Ricerca Sulle Onde Electromagnetiche del CNR, Firenze, Italy. The concentrations of both impurities (Cs and Tl) were estimated to be roughly 0.002 mol% in the melt.

The room temperature absorption spectrum of CsI:In(Tl) crystal taken on a spectrophotometer (Hitachi U 3410) is given in Figure 3.12. In order to record the time resolved emission spectra, the time resolved experimental set-up, the details of which are given in Chapter 1 has been employed. The present method removes the extraneous contributions due to the pump source and therefore, has excellent sensitivity and good time resolution. The time resolved spectra of CsI:In(Tl) recorded in the range from 300 nm (4.1 eV) to 700 nm (1.7 eV) is shown in Figure 3.13. In order to get the lifetime value of the components present (fast or slow) in the emission spectra, fluorescence decay histograms are recorded on the multichannel analyser (MCA) screen of the detection system as discussed in Chapter 1. A typical time calibration of MCA has been shown in Figure 3.14. The recorded data are printed out and within experimental error, the decay is found to follow simple exponential curve. The lifetime is estimated by fitting the decay curve to a straight line on a semilog plot of luminescence intensity vs time and is shown in Figure 3.15. A convolution-deconvolution method was also applied to extract the lifetime.
(ii) **Optical gain measurements**

The amplified spontaneous emission (ASE) technique\textsuperscript{13,15,26} has been employed to measure the optical gain of the crystal. The detailed theoretical aspects of the technique has been described earlier in Chapter 2. It involves the comparison of the fluorescence intensity from the entire length (L) and one-half of the length (L/2) of the crystal. It is done by masking the pumping beam with a shutter. However, in the case of marginal gain, the effect of shot-to-shot fluctuations and inhomogeneity of the beam has to be eliminated before coming to any conclusion. It may be mentioned here that the nitrogen laser beam, which is most commonly used as a pumping source in gain studies, does not have the entire beam of the same intensity distribution. The peripheral part of this beam is of very low intensity while the central portion is quite intense. In spite of this drawback, the nitrogen laser does not have a substitute, so one has to go for the modifications in the method of measurement. We have used a technique in which the output intensity is recorded in the different quadrants of the multichannel analyser in order to avoid any overlap of emission intensity from two discrete pump lengths. This technique serves the dual purpose of elimination of both the effects of the pump beam mentioned above. The shot-to-shot fluctuations are averaged over a large number of shots for various pump intensities and pumped length of the crystal. The oscilloscope traces corresponding to the fluorescence intensity from the entire length (L) and half length (L/2) of the crystal are shown in Figure 3.16. It is assumed in the present case that the colour centres developed due to the nitrogen laser shots become stable after few seconds. Knowing the values of the fluorescence intensity at full length (I\textsubscript{L}) and half length (I\textsubscript{L/2}) the gain coefficient (\(\alpha\)) and the gain (G) can be evaluated.
Figure 3.12  Room temperature absorption spectrum of CsI:In(Tl).

Figure 3.13  Time resolved emission spectrum of CsI:In(Tl).
**Figure 3.14** Time calibration of multichannel analyser (Calibration = 750 ps/channel)

**Figure 3.15** Semilogarithmic plot of luminescence intensity vs time for CsI:In(Tl) crystal.
Figure 3.16 Oscilloscope traces of CsI:In(Tl) fluorescence intensity from (top) full length (L) and (bottom) half length (L/2). Time scale 0.2 μs/div.
3.4.2 Results and discussion

(i) Analysis of optical absorption spectra

Alkali halide crystals have large band gap and the pure crystals are therefore transparent over a wide frequency range that includes the visible, near infrared (NIR) and near ultra-violet (NUV) regions of the spectrum. The presence of impurity ions with the ns\(^2\) ground state configurations (In\(^+\), Tl\(^+\), Ga\(^+\), etc.) induces new absorption bands on the long-wavelength side of the UV-absorption edge, which is associated with the exciton production in the crystal. The newly originated bands are usually denoted by A, B, C, D\(_1\), D\(_2\) bands\(^27\) in order of increasing photon energy. In CsI:In(Tl) the room temperature absorption spectra shows three bands, namely, the A, B bands of In\(^+\) and A band of Tl\(^+\). These three bands appear at 294 nm (4.2 eV), 274 nm (4.5 eV), 260 nm (4.7 eV), respectively. The formation of these bands can be explained by analysing the energy level diagram\(^27\) of the impurity ion in the alkali halide crystal. The A, B bands are due to electronic excitations of In\(^+\) and Tl\(^+\) ions from their ns\(^2\) (5s\(^2\), 6s\(^2\)) ground state to the nsnp (5s5p, 6s6p) configuration. A free ion with the configuration ns\(^2\) has the electronic ground state \(^1\)S\(_0\). The first excited configuration is nsnp and this gives rise to the states \(^1\)P\(_1\), \(^3\)P\(_2\), \(^3\)P\(_1\), and \(^3\)P\(_0\) in Russell-Saunders (RS) coupling. However, it was found that RS coupling is an improper approximation for large n value. Hence to find the energy levels, one has to take into account the electron-electron (e-e) and spin-orbit (S-L) interactions. From theoretical spectroscopic analysis it can be seen that the effect of spin-orbit interaction is to separate the degenerate 3P levels and also to mix the \(^3\)P\(_1\) and \(^1\)P\(_1\) states. These effects are shown in Figure 3.17. In a cubic crystal field the \(^3\)P\(_2\) state is split into few closely-spaced states \(^3\)E\(_U\) and \(^3\)T\(_{2U}\). Also \(^3\)P\(_0\) becomes \(^3\)A\(_{1U}\), whereas the \(^3\)P\(_1\) and \(^1\)P\(_1\) states become linear combinations of \(^1\)T\(_{1U}\) and \(^3\)T\(_{1U}\). The A band corresponds to the spin-orbit allowed A\(_{1g} \rightarrow\)T\(_{1U}\) (\(^1\)S\(_0\) \rightarrow \(^3\)P\(_1\)) transition, the B band to the vibration-induced A\(_{1g} \rightarrow\)E\(_U\) and T\(_{2U}\) (\(^1\)S\(_0\) \rightarrow \(^3\)P\(_2\)) transition and the C band corresponds to the dipole allowed A\(_{1g} \rightarrow\)T\(_{1U}\) (\(^1\)S\(_0\) \rightarrow \(^1\)P\(_1\)) transition.
Figure 3.17  Energy level diagram for an impurity with ns\(^2\) ground state electronic configuration.

(ii) **Analysis of time resolved emission and optical gain**

In the time resolved emission spectra of CsI:In(Tl) crystal (Figure 3.13) two components are observed: one in the indigo blue region (~430 nm), the fast component and the other in the green region (~540 nm), the slower one. Many authors have held different view points regarding the origin of these emission bands. Fukuda et al.\(^{28}\) assuming the Ti\(^+\) ions to be in the cation sublattice (Seitz Centre) have attributed these bands to the transitions from the first relaxed excited \(3P_1\) level (this level splits into two levels due to the Jahn-Teller effect) to the \(1S_0\) ground level. Another interpretation associates the bands to single and paired activator ions.\(^{29}\) A third explanation\(^{30,31}\) supports the model of Fukuda et al. for the 430 nm band while the 540 nm band is assumed to arise from the D exciton produced by the photothermal excitation of Ti\(^+\). Also Gutan et al.\(^{32}\) held the fast \(3P_1 - 1S_0\) transition in the Seitz centres responsible for the 430 nm band.

With heavily concentrated crystals containing 0.1-4 mol\% Ti\(^+\) ions, Fontana et al.\(^{29}\) relate the longer wavelength emission to paired activator ions. However, at relatively low concentration of 0.002 mol\% used in the present study, the formation of pair activator ions is unlikely and hence the pair ions can
be excluded as a source of the 530 nm band. The quantitative estimate of the fluorescence lifetime and the optical gain, the two relevant optical parameters, gives experimental evidence about optical amplification in the crystal. The lifetime of the fast component (∼430 nm) is measured to be 10.17 ± 0.01 ns using the semilogarithmic plot. While the convolution-deconvolution technique of the experimental data yields a value of 9.52 ± 0.01 ns. The pump source has pulse energy 2 mJ, pulse duration 10 ns and repetition rate 50 Hz. The size of the pumping spot was 1 cm long and 0.02 cm wide. Using the pump source, the optical intensity gain coefficient (α) is measured as 1.17 cm⁻¹. This gives an optical gain of 8.63 dB cm⁻¹ and the stimulated emission cross section corresponding to this transition is calculated to be 1.17 x 10⁻¹⁶ cm². This is surely due to the Ti⁺ impurities, because a test performed on CsI crystal doped with only In⁺ shows a gain much smaller than unity. The remarkable feature however, is the fact that codoping with traces of In⁺ yields a better result than obtained with single Ti⁺ as dopant. In fact, fluorescence lifetime and optical gain are directly influenced by a possible reabsorption effect popularly known as excited state absorption. However, the fast relaxation time and a positive gain value suggest that this effect is weak. Further, the value of these parameters substantiates the well known fact that the stored energy should be released within a short time to have appreciable amplification. The aforesaid experimental findings provide support to the energy level model of Fukuda et al., where some specific energy level combination do not foster reabsorption processes, yielding a positive gain.

In conclusion the crystal shows strong radiative transition, strong coupling between electronic levels and lattice leading to wide emission bands and is almost free from excited state absorption. Further, the high stability of Ti⁺ ions together with high durability of the host material against radiation damage makes it a suitable amplifying medium. Thus, these significant features and the results of optical amplification reveal the potentiality of the crystal as a candidate for stimulated emission in the visible region at room temperature.
References

Chapter Four

Spectroscopic Investigations of \( \text{Nd}^{3+} \) and \( \text{Pr}^{3+} \) Ions in Glassy Matrices

In the development of optically pumped solid state lasers the rare earth materials, play a very important role. This is because of the multitude of energy levels possessed by these ions when doped into a solid state matrix. A lot of rare earth doped materials can be suitably processed so as to get the laser action in the entire visible and ultraviolet region. Efforts are being made to discover new laser materials for various applications and thus laser action has been observed in a large number of crystalline and amorphous media doped with rare earth ions. Out of all the rare earth ions, the most extensively used activator ion is the trivalent neodymium. In the second place is Holmium followed by Erbium and Thulium. In solid state rare earth doped lasers, several energy levels capable of producing stimulated emission in the wavelength range 500-3000 nm have been found amongst the rare earth ions.

The fluorescence efficiency of an active ion in a material depends on various spectroscopic parameters such as the absorption and emission cross-sections, transition probabilities, lifetimes of the metastable levels, concentration of the dopant ions, and also the effect of ligand field on them. A lot of theoretical as well as experimental spectroscopic techniques are available to obtain these parameters for a particular rare earth ion. In this chapter a detailed spectroscopic investigations of trivalent neodymium and praseodymium ions in