PHOTOLUMINESCENCE AND CATHODOLUMINESCENCE OF
UNDOPED AND CERIUM DOPED YAG SINGLE CRYSTALS

by

CHON MENG WONG

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FOR THE DEGREES OF
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and
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May, 1982

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CHON MENG WONG

Submitted to the Department of Electrical Engineering on May 24, 1982 in partial fulfillment of the requirements for the Degrees of Master of Science and Electrical Engineer in Electrical Engineering

ABSTRACT

The problems which arise in using Ce:YAG as a laser material motivate us to study the energy transfer mechanisms in this material. Both Cathodoluminescent (CL) and Photoluminescent (PL) processes are used as probes to investigate the energy transfer mechanisms to the cerium ion. The CL and PL spectra of this material show both cerium and defect emission bands. The defect emission band is believed to be due to defect states that are found in the YAG lattice. The role of defect states in the energy transfer process to cerium ions under CL and PL excitation is studied. Excitation spectra of both of the emission bands are obtained experimentally. These spectra are utilized in conjunction with group theory to develop an energy level diagram for Ce in YAG. The material is further characterized in terms of its fluorescence decay times and emission spectra at 77 and 300 °K. The effects of an external electric field and varying electron beam current density on the crystal sample are also studied. Our results are consistent with those obtained by previous investigators. We even attempt to explain some of the unexplained phenomena mentioned by previous researchers.

Thesis Supervisor: Dr. Cardinal Warde
Title: Associate Professor of Electrical Engineering
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The author wishes to his sincere appreciation to Professor Cardinal Warde who has been an extraordinary thesis supervisor throughout the year. In addition, the author also thank Professor D. J. Epstein for lending his ears whenever the author came across new findings.

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The author appreciates having Stanley Rotman as a partner during the second period of research. The author expresses his thanks to Mr. Elias Towe who assisted the author in proof reading the thesis.

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DEDICATION

This thesis is dedicated to my wife Hong Teng and our parents for giving me moral support throughout my life.
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CHON MENG WONG

BODY OF THESIS
1.1 Introduction

Rare-earth doped dielectric crystals are known to be good laser materials. D. J. Ehrlich et al. (32) have shown that cerium doped Yttrium Fluoride (Ce:YLF) media can be used in designing a tunable UV solid-state laser. It would be desirable to design a similar tunable solid-state laser for visible operation. We are also exploring the possibility of developing an electron beam pumped laser. Cerium doped Yttrium Aluminum Garnet (Ce:YAG) being an efficient phosphor, has a broad band emission from 450 to 700 nm. This makes it a promising candidate for both electron beam pumped and UV operation. However, preliminary experimental work done by Jacobs et al. (48) and Miniscalco et al. (57) indicate the presence of excited-state absorption (ESA) losses when pumping Ce:YAG optically. This would jeopardize the laser by not giving enough gain within the cavity of the laser. In order to solve this problem we ask the basic question: how does the energy get transferred to the cerium ions? The cerium ion being a multivalent ion favors the generation of oxygen vacancies (lattice defects) in YAG. However, these lattice defects have been found to influence important parameters (63,65,75,79) such as energy transfer, fluorescence lifetimes (65,75). In addition the triply
ionized cerium in YAG has only a single 4f electron (13) available for excitation thereby making the system easier to analyse. We have also confined our investigation to single crystals as opposed to powders to avoid the complication of studying surface effects which makes the study of energy transfer mechanisms a little easier.

The principal goal of this research is therefore to determine the energy transfer mechanisms in Ce:YAG from both energetic electrons and photons to the excited state of cerium ions. Cathodoluminescence (CL) and photoluminescence (PL) are tools used to probe these energy transfer mechanisms in Ce:YAG. In PL, optical sources are easily available in the energy range of 1 to 7 eV and therefore has the advantage of exciting the Ce:YAG within its band gap (6.5 eV). In particular, it is used to excite the near band edge defect states which we believe to play an important role in the energy transfer process. In general CL sources are much more energetic than PL sources and therefore excite Ce:YAG above its bandgap.

In this research we also looked into the recent experimental models of energy transfer mechanisms, ESA loss and color centers in YAG. An investigation of the ESA loss mechanisms (48,57,60) show that this loss is due to defect states in the lattice rather than the excited states of cerium. This implies laser operation is still possible when quenching mechanisms due to higher excited states of cerium are absent (removal of
color centers). Color centers (a general term for defect states) are numerous in YAG and their participation in energy transfer processes make them even more important in our research.

In the course of this research, we have been able to a) understand the relationship between the absorption, excitation and emission spectra of both undoped and cerium doped YAG, b) characterise the materials from both the decay time and emission spectra intensity measurements, (including its dependence on temperature, electric field, and electron beam current density.) c) determine the energy levels diagram of cerium ions in YAG.

A potential practical application of Ce:YAG is the development of an efficient high intensity phosphor for the TV industries which is being discussed in the next section.

1.2 Phosphors for TV and flying spot scanners

Phosphors intended for use in color TV picture tubes and for FLYING SPOT SCANNERS (See Appendix 1) should ideally possess the following properties:

a) Short decay time (\( \tau < 100 \text{ ns} \)),

b) Emission in the visible part of the spectrum covering the three primary colors, red, green and blue. By mixing the three colors according to the color co-ordinates of the
CHROMATICITY DIAGRAM (See Appendix 2) nearly all colors in the visible spectrum can be reproduced faithfully,
c) High RADIANT EFFICIENCY,
d) Radiant efficiency independent of phosphor environment (e.g. temperature),
e) Low vapor pressure so that it would not affect the good vacuum required in all Cathode Ray Tubes, and
f) Good resistance against degradation due to electron beam bombardment (Good phosphors do not suffer ION BURN easily).

Rare earth doped dielectric crystals are potentially good phosphors since they allow high packing density of luminescent centers which are required for high radiant intensity and still possess good vacuum properties. Such materials belong to the class of phosphors known as host with activators (13). The host material is usually an ionic insulating crystal and the objective is to replace some of the cations of comparable size and charge by certain foreign ions which form luminescent centers. Such centers are referred to as activator ions. An ideal host lattice in the absence of such activator ions does not emit radiation upon excitation. Sometimes an additional ion is present in the host lattice which serves as an alternate path to channel excitation energy to the activator ion, thereby improving radiant efficiency. Such an ion is referred to as a sensitizer ion which itself may radiate light and heat upon excitation. In some cases the host lattice itself plays the role of the sensitizer.
The requirement that the decay time for flying spot scanner phosphor be less than 100 ns comes from a simple picture element count. If a well-defined picture of 525 lines is to be transmitted at a rate of 30 complete images per second, then the number of picture elements equivalently transmitted per second would be \(525 \times 525 \times 30 = 8.27\) million elements. Therefore the required decay time of the phosphor used must be less than less than 100 nanoseconds, otherwise, a blurred image is obtained which means poor signal-to-noise ratio. There are techniques available to correct the effect of long afterglow with RC networks but it is done at the expense of a lower transmission bandwidth. (17)

The two current \(\text{Ce}^{3+}\) phosphors in use for flying-spot scanner are \(\text{Ce:YAG (P46 phosphor)}\) and \(\text{Ce}_{x}: \text{Y}_{2-x}\text{SiO}_5\). The two phosphors cover the spectra range of 450 to 700 nm with a peak at 550 nm and 350 to 550 nm with a peak at 415 nm respectively. The decay times for these phosphors are 70 and 30 ns respectively. These phosphors are used in Philips tubes Q13-110 GU (15). It has been proven that these tubes have much better signal-to-noise ratio than the \(\text{ZnO tubes (15,18,19,36,37)}\). Hence the \(\text{Ce:YAG is appears to be an ideal candidate for both a laser media and a flying-spot scanner phosphor.}\)
1.3 Electronic structure of rare-earth ions

Rare-earth ions are usually selected as activator ions for present-day phosphors. It is because they involve transitions of the 4f levels of the N-shell which is not completely filled with electrons. The 5s and 5p levels of the O-shell are completely filled with electrons which screen the 4f electrons from the environment and therefore insensitive to temperature fluctuations.

The 4f shell may contain up to 14 electrons. Table 1.1 shows the most common valencies of the rare-earth ions and the number of 4f electrons in the ground state of the relevant ions.


**TABLE 1.1**

The ions of the rare-earth metals and the number of 4f electrons in their respective ground states.

<table>
<thead>
<tr>
<th>Z</th>
<th>ION</th>
<th>NUMBER</th>
<th>Z</th>
<th>ION</th>
<th>NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>La</td>
<td>0</td>
<td>64</td>
<td>Gd</td>
<td>7</td>
</tr>
<tr>
<td>58</td>
<td>Ce</td>
<td>1</td>
<td>65</td>
<td>Tb</td>
<td>8</td>
</tr>
<tr>
<td>58</td>
<td>Ce</td>
<td>0</td>
<td>65</td>
<td>Tb</td>
<td>7</td>
</tr>
<tr>
<td>59</td>
<td>Pr</td>
<td>2</td>
<td>66</td>
<td>Dy</td>
<td>9</td>
</tr>
<tr>
<td>60</td>
<td>Nd</td>
<td>3</td>
<td>67</td>
<td>Ho</td>
<td>10</td>
</tr>
<tr>
<td>61</td>
<td>Pm</td>
<td>4</td>
<td>68</td>
<td>Er</td>
<td>11</td>
</tr>
<tr>
<td>62</td>
<td>Sm</td>
<td>6</td>
<td>69</td>
<td>Tm</td>
<td>12</td>
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<tr>
<td>62</td>
<td>Sm</td>
<td>5</td>
<td>70</td>
<td>Yb</td>
<td>14</td>
</tr>
<tr>
<td>63</td>
<td>Eu</td>
<td>7</td>
<td>70</td>
<td>Yb</td>
<td>13</td>
</tr>
<tr>
<td>63</td>
<td>Eu</td>
<td>6</td>
<td>71</td>
<td>Lu</td>
<td>14</td>
</tr>
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</table>
1.4 The $\text{Ce}^{3+}$ ion

The triply ionized Ce ion has only one 4f electron and this gives rise to two energy levels, namely, the $^{2}F_{7/2}$ state in which the orbital and spin moments of the electron are parallel, and the other $^{2}F_{5/2}$ state in which the orbital and spin moments are anti-parallel. (See Figure 1) As the number of 4f electrons increases, the number of possible energy levels correspondingly increases. In general, the presence of the crystal lattice scarcely affects the locations of these discrete energy levels, thereby retaining its resemblance to that of the free ion.

The next excited state for the Ce$^{3+}$ ion is associated with the 5d level. The 5d state lies at the surface of the ion and therefore being subjected to strong crystal field influence from the lattice. In Ce:YAG, the Ce$^{3+}$ ions replace some of the Y$^{3+}$ ions. The 5d electron wavefunction interacts with the neighboring electron wavefunctions of the YAG lattice producing broad absorption and emission bands. In wave mechanics, it is said that the wavefunction of the excited cerium 5d electron partially overlaps the wavefunctions of the neighboring electrons of the other ions.

Table 1.2 shows that cerium can also attain a valency of four, forming a Ce$^{4+}$ ion. This is achieved by removing an additional 4f electron from the Ce$^{3+}$ ion and transferring it to the
surrounding ions of the lattice. This process involves a transfer of charge and hence is referred to as a Charge-Transfer state. The energy band diagram of such an ion differs from the Ce$^{3+}$ ion. Since Ce$^{4+}$ ion has a core configuration similar to that of Xenon, the Ce$^{4+}$ state is more stable than the Ce$^{3+}$ state. However, in YAG the strong ionic character of the lattice restricts the cerium ion from attaining the Ce$^{4+}$ state because it occupies the yttrium, Y$^{3+}$ site.
FIG. 1 Energy Level Diagram of Ce$^{3+}$
(Ref 30)
## Table 1.2

Electronic configuration of the Cerium atom and ions

<table>
<thead>
<tr>
<th>SHELLS</th>
<th>ORBITALS</th>
<th>Ce</th>
<th>Ce</th>
<th>Ce</th>
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<tbody>
<tr>
<td>K</td>
<td>1s</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2s</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>L</td>
<td>2p</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>3s</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>M</td>
<td>3p</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>3d</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>4s</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>4p</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>N</td>
<td>4d</td>
<td>10</td>
<td>10</td>
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</tr>
<tr>
<td></td>
<td>4f</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5s</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>O</td>
<td>5p</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>5d</td>
<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td>5f</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P</td>
<td>6s</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The parity for the 5d state is even since the orbital angular momentum quantum number (l=2) has an even value.

\( Y_{nlm}(r,\phi,\theta) = (-1)^l Y_{nlm}(r,\theta,\phi) \)

The 4f state is odd since \( l=3 \) is odd. The 5d \( \rightarrow \) 4f transition is therefore an allowed electric-dipole transition. The emission due to such transitions is expected to have a very short lifetime of order nanoseconds. Indeed cerium activated phosphors have long been recognized as very fast phosphors. (2,11,12,15-20,36,37,68)

1.5 Cathodoluminescence experiments

Cathodoluminescence is the generation of light in a material under electron beam excitation. Materials exhibiting cathodoluminescence are known as phosphors. It is appropriate to study the properties of phosphors under the same form of excitation as in their actual application. In this thesis, an electron beam with a kinetic energy of 17 KeV is used to study the properties of Ce:YAG. Since the bandgap of YAG is about 6.5 eV, electron beam excitation would excite the host easily. In a lightly doped sample, the probability of excitation of the dopants is insignificant compared to the host lattice. It is therefore important to understand how the lattice transfers its energy to the activator ions. In such cases the host lattice participates as a sensitizer. Unfortunately, such above bandgap excitation involves very complex energy mechanisms, thereby making analysis of any single event difficult. General analyses on electron excitation of solids have been
done (31,34) However, established theories on this subject are still far from being able to estimate the optimum value for phosphor radiant efficiency. This thesis attempts to understand some of the energy transfer mechanisms which in turn provide a better framework within which the problem posed above can be understood.

1.6 **Photoluminescence experiments**

Photoluminescence (PL) is the generation of light in a material upon excitation with light of a shorter wavelength. The principal advantage in this form of excitation is its ability to isolate complex above bandgap mechanisms like plasma oscillations, secondary ionizations and Auger transitions. Only electric-dipole allowed transitions are involved in PL experiments. Ideal luminescent centers emit the wavelength they absorb. Therefore radiationless processes are not involved and the quantum efficiency is high. However, real host materials are not ideal and they absorb a portion of the excitation energy to support non-radiative processes. Some activator ions too lose energy non-radiatively causing Stokes shifted emission. All these events only lower the quantum efficiency of the phosphor.

PL is a photon probe which allows between bandgap energy transfer mechanisms to be analysed. Q-switched lasers with nanosecond pulses can be used to measure fluorescence life-
times of both defect states and activator ions. A pulsed tunable UV laser from the MIT Regional Laser Center was used in our PL experiments.

1.7 Thesis outline

Chapter 1 outlines the theme of studying the energy transfer mechanisms in Ce:YAG. Then applications of this material to lasers, TV screens and flying spot scanners are mentioned. The latter part of this chapter discusses the nature of the Cerium free ion and the various tools used in studying the problem.

Chapter 2 emphasizes the electronic structure of Ce ion in YAG and how the lattice crystal field affects the energy levels of Cerium. A quantitative description is given for the derivation of the energy level diagram for Ce:YAG. Then the absorption, emission, and excitation spectra are presented to support this derivation.

Chapter 3 informs the reader on recent CL and PL models and experiments. In particular the Exciton-Impurity model is discussed because of the success in applying simple ideas to predict phosphor efficiencies in rare-earth doped YAG. Previous CL and PL experimental works indicate that the defect states in YAG participate in the energy transfer mechanisms. Therefore this introduces the motive to determine both the nature and
type of color centers (a general term for defect states) found in YAG.

Chapter 4 then studies these color centers from understanding the previous work done by other investigators. The excited state absorption experiments mentioned in the early part of the chapter also relate back to the problem of color centers in YAG.

Chapter 5 describes the setup for both CL and PL experiments performed in the Crystal Physics laboratory and the MIT Regional Laser Center. The various techniques used to measure the emission spectra and the decay times in YAG are also discussed.

Chapter 6 solely concerns with the experimental results which support our views concerning energy transfering processes. The corresponding relationships between the CL and PL parameters are also discussed. The excitation spectra is then used in explaining these relationships. A summary of conclusions is also included in this chapter.
Chapter 2

CHAPTER 2

ELECTRONIC STRUCTURE OF CE$^{3+}$ ION IN YAG AND SPECTRA

2.1 The 4f electron

Table 1.1 showed that the triply positively ionized cerium ion has a single 4f electron. An electron in its stationary orbit around the atom can be fully described by a wavefunction satisfying the time-independent Schroedinger Equation (SE).

$$\frac{-\hbar^2}{2m} \nabla^2 \Psi(x, y, z) + V(x, y, z)\Psi(x, y, z) = E\Psi(x, y, z) \quad \text{Eqn 2.1}$$

This wavefunction $\Psi(x, y, z)$ is also known as an eigenfunction of the SE.

The eigenfunction depends on three important parameters, the quantum numbers $n$, $l$ and $j$. Given the quantum numbers, the wavefunction specifies uniquely the state of the electron. This is commonly referred to as an eigenstate, which may or may not be occupied. However, many different eigenstates can have the same total energy or eigenvalue when occupied. These eigenstates are said to be degenerate.

For the one-electron case, the relative orientation of the orbital angular momentum $\vec{l}$ and the spin moment $\vec{s}$ of the electron determine the total electronic angular momentum $\vec{j}$ of
the atom (i.e. \( j = l + s \)). Only open shell electrons are being considered since the closed shell electrons have their spin moments paired. A spinning electron experiences a torque due to the effective magnetic field produced by its orbital motion and also the other unpaired electrons orbital motion. Such interaction involving the spin magnetic dipole moment and the orbital motion is known as the spin-orbit interaction.

In cerium, the \( l \) and \( s \) values are 3 and \( \pm 1/2 \) respectively. The possible \( j \) values are then 7/2 and 5/2. The Russell-Saunders notation for these two eigenstates are given as \( ^2F_{7/2} \) and \( ^2F_{5/2} \). The cerium ion ground state configuration is said to be split into \( ^2F_{7/2} \) and \( ^2F_{5/2} \) states by the spin-orbit interaction. Since the eigenstate \( ^2F_{7/2} \) has a larger total angular momentum than the \( ^2F_{5/2} \) state, therefore the \( ^2F_{7/2} \) state has a larger eigenvalue. In the free ion case, this splitting is approximately 2000 \( \text{cm}^{-1} \).
2.2 The energy level diagram for Ce:YAG

The energy level diagram for Ce:YAG is derived here in this section. The crystal field splitting parameters are obtained from our experiments on the excitation spectra of cerium, emission spectra of cerium at 300 & 77 °K and the approximate value for energy separation between the 5d band and the 4f levels of the Ce free ion (26,30). The fourth and fifth 5d bands of cerium in YAG are found to be above the bandgap of the lattice (6.5eV). Therefore these bands are not observable from absorption spectra.

YAG crystal has a unit cube edge of 12.01 ± 0.02 Å and the space group Ia3d (Oh) (80,81). The atomic positions are:

Al in 16(a) 0 0 0

Y in 24(c) 1/8 1/8 0

Al in 24(d) 1/4 3/8 0

O in 96(h) x y z

where x, y and z are 0.04, 0.055 and 0.64 respectively. The cubic unit cell contains 8 units of $\text{Y}_3\text{Al}_2(\text{AlO}_4) = \text{Y}_3\text{Al}_5\text{O}_{12}$. The yttrium is in eight fold co-ordination; the aluminum is in both four and six fold co-ordination (33,35,77,80,81).
FIG. 2.1 a) Ce$^{3+}$ ion at center of cube
0$^{2-}$ ion at each cube corner
b) & c) Boundary surfaces of
5d orbitals of Eg group
FIG. 2.1 d, e, & f Boundary surfaces of 5d orbitals of T₂g group
The dopant, Ce$^{3+}$, substitutes for some of the Y$^{3+}$ ions at the Yttrium site. If the center of the cube is the yttrium site, then the eight oxygen ions are positioned at the eight corners of a heavily distorted cube as shown in figure 2.1a. The four edges of each face on the cube have unequal length. The edges may differ in length by more than 10%. Since the wavefunction of the 5d state is spatially extended, the crystal field affects strongly the position of the 5d levels. To a first approximation, the crystal field may be regarded as a cubic field. It is well established that a cubic field splits the five degenerate 5d states into a triplet, $T_{2g}$, and a doublet, $E_g$ (14, 21, 45, 46, 62). The doublet, $E_g$, has an energy lower than the triplet, $T_{2g}$, in a cubic field because the charge cloud of the doublet is pointing in the directions between the negatively charged oxygen ions (See figures 2.1b & c). Whereas the triplet charge cloud is pointed closer to the oxygen ions than the doublet case.

The heavily distorted crystal field experienced by the cerium ion must be taken into account. It is known that distortions split both the doublet and triplet into five singlets as shown in figure 2.2. The spin-orbit interaction for the 5d electron is small compared to the crystal field splittings and is ignored here. However, the 4f electron has a much stronger spin-orbit interaction than the crystal field splitting which in this case is ignored.
Fig. 2.2 Energy level diagram of Ce:YAG
The parameters on the energy values of crystal field splittings are obtained experimentally. Our excitation spectra for cerium emission shows that there are three 5d bands located at 223 nm, 340nm, and 460 nm. A free cerium ion is known to have an energy separation for the 5d ---→ 4f levels of $\Delta_1 = 53,000$ cm$^{-1}$. The energy separation between the 4f levels obtained experimentally from the emission spectra of Ce:YAG is found to be 2000 cm$^{-1}$. (See chapter 6)

Applying the center of gravity rule for energy level splittings, we obtain $\Delta_5 = \Delta_6$ and $2\Delta_8 = 3\Delta_9$. Therefore the rest of the splittings are calculated as follows:

$$\Delta_7 = 10^7((1/340\text{nm}) - (1/460\text{nm})) = 7,673 \text{ cm}^{-1},$$

$$\Delta_3 = (10^7/460\text{nm}) + (\Delta_7/2) = 25,576 \text{ cm}^{-1},$$

$$\Delta_8 = \Delta_1 - (\Delta_4/2) - (\Delta_3) = 26,425 \text{ cm}^{-1},$$

$$\Delta_9 = 2/3 \text{ of } \Delta_8 = 17,616 \text{ cm}^{-1},$$

$$\Delta_2 = \Delta_1 + \Delta_9 = 70,616 \text{ cm}^{-1},$$

$$\Delta_5 = \Delta_6 = \Delta_2 - (\Delta_4/2) - (10^7/223\text{nm}) = 24,773 \text{ cm}^{-1}.$$}

The crystal field parameters are given in Table 2.1.
Teruhiko Hoshina (45) theoretically calculated the energy level diagram of Ce ion in a cubic field (Note: His calculation is for face centered cube but our's is for body centered cube). He also pointed out that the energy separation for the two groups, $T_{2g}$ and $E_g$ must be larger than $10^4$ cm$^{-1}$. Our calculations showed that this value is given by $\Delta_2 - \Delta_1 = 17,616$ cm$^{-1}$. It is therefore in close agreement with Hoshina's theoretical calculations.
TABLE 2.1

Energy separation values for the Ce:YAG band diagram

\[ \Delta_1 = 53,000 \text{ cm}^{-1} \]
\[ \Delta_2 = 70,616 \text{ cm}^{-1} \]
\[ \Delta_3 = 25,576 \text{ cm}^{-1} \]
\[ \Delta_4 = 2,000 \text{ cm}^{-1} \]
\[ \Delta_5 = 24,773 \text{ cm}^{-1} \]
\[ \Delta_6 = 24,773 \text{ cm}^{-1} \]
\[ \Delta_7 = 7,673 \text{ cm}^{-1} \]
\[ \Delta_8 = 26,424 \text{ cm}^{-1} \]
\[ \Delta_9 = 17,616 \text{ cm}^{-1} \]

\[ d_1 = 460.0 \text{ nm (2.70 eV)} \]
\[ d_2 = 340.0 \text{ nm (3.65 eV)} \]
\[ d_3 = 223.0 \text{ nm (5.56 eV)} \]
\[ d_4 = 143.6 \text{ nm (8.64 eV)} \]
\[ d_5 = 104.8 \text{ nm (11.83 eV)} \]
Chapter 2

a) Undoped YAG at 300°C
Thickness 1.66 mm (002u)

b) Ce-YAG (0.05% At Wt.) at 300°C
Thickness 1.52 mm (002d)

FIG. 2.3 Absorption Spectra of YAG
2.3 Absorption spectra

Figures 2.3a and b show the absorption spectra of nominally undoped YAG and cerium doped YAG at 300 °K. The y-axes are plotted in terms of optical density and the x-axes the wavelength in nm. Two significant broadband absorption peaks are observed at 340 and 460 nm which correspond to the $5d \rightarrow 4f$ transitions of cerium. Additional absorption peaks are found near the fundamental absorption edge of the lattice. The distinction between cerium peaks and other absorption processes can be obtained from the cerium excitation spectra given in section 2.5.

Glen A. Slack et al. (74) studied the fundamental absorption edge in the region $30,000 < \nu < 55,000$ cm$^{-1}$ in single crystals of YAG grown under various conditions. The steepest absorption edge was obtained in a stoichiometric sample of YAG grown in Argon and 0.1% Oxygen atmosphere. (Figure 2.4)
FIG. 2-4 Optical-absorption coefficient, $\alpha$, vs. photon wave number for several single crystals of $Y_3Al_5O_{12}$ at 300 K. (REF. 74)
Single crystals of $Y_3Al_5O_{12}$ used in the study of the optical absorption in the ultraviolet region, $30,000\ cm^{-1}$. SRF = standard radio-frequency heating conditions, in which a thick-wall (0.15 cm) iridium crucible is directly heated with a 450 kHz rf generator. SM = stoichiometric melt of $3.000\ Y_2O_3 + 5.000\ Al_2O_3$. Linde = crystal obtained from Union Carbide Corporation in 1965. The other crystals were grown in Slack's laboratory between Oct. 1966 and March 1968.

<table>
<thead>
<tr>
<th>Crystal number</th>
<th>Atmosphere during growth</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B26</td>
<td>Helium</td>
<td>tungsten susceptor - Ir crucible, SM</td>
</tr>
<tr>
<td>Linde</td>
<td>?</td>
<td>Ir crucible</td>
</tr>
<tr>
<td>M4</td>
<td>Argon</td>
<td>tungsten susceptor - Ir crucible, SM</td>
</tr>
<tr>
<td>M9</td>
<td>A + 0.2% $O_2$</td>
<td>SRF, SM</td>
</tr>
<tr>
<td>M12</td>
<td>A + 0.5% $O_2$</td>
<td>SRF, SM</td>
</tr>
<tr>
<td>M15</td>
<td>A + 0.5% $O_2$</td>
<td>SRF, $3.000\ Y_2O_3 + 5.002\ Al_2O_3$ melt</td>
</tr>
<tr>
<td>M18</td>
<td>A + 0.5% $O_2$</td>
<td>SRF, $3.005\ Y_2O_3 + 5.000\ Al_2O_3$ melt</td>
</tr>
<tr>
<td>M28</td>
<td>A + 0.1% $O_2$</td>
<td>SRF, SM</td>
</tr>
</tbody>
</table>

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2.4 Emission spectra

Since the energy separation between the ground state and the lowest 5d state is large and also the transitions are electric-dipole allowed. The decay from the lowest 5d level state is therefore primarily radiative. Thus, exciting any of the upper d bands results in fluorescence from the lowest 5d level with near unity quantum efficiency. At 300 °K, the fluorescence appears as a broadband extending from 450 nm to beyond 700 nm with a peak at 550 nm corresponding to the $^2F_{5/2}$ terminal state and a gentle slope to the red side due to the transition to the $^2F_{7/2}$ state. G. Blasse and A. Bril (12) reported that two visible emission bands of Ce:YAG are located at 19,000 cm$^{-1}$ (523.56 nm) and 17,400 cm$^{-1}$ (574.71 nm) at 4.2 °K. At 300 °K, the emission spectra can be regarded as two gaussian bands of approximately equal magnitude superimposed to obtain the peak at 18,250 cm$^{-1}$ (547.95 nm). Our experiments confirm the emission spectra cerium peak to be at 550 nm. (See Figure 2.5)

The displacement of emission to a longer wavelength with respect to absorption is known as a Stokes shift. When the emission wavelength coincides with the absorption wavelength, there is no indirect transition and the particular wavelength is referred to as the Zero Phonon Line (ZPL). D. J. Robbins (62) reported the ZPL in Ce:YAG to be at 489.16 nm. (Figure 2.6)
Our emission spectra at 77 °K from both CL and PL experiments show that there is a prominent cerium peak at 523 nm. This value is in agreement with G. Blasse and A. Bril (12).
Pump Laser set at 266 nm, 1 mW, 10 Hz
Spot diameter 2 mm Slit width 500 μm
10 ns gate, 20 ns away from Laser rising edge
(Nov/An-H2 Ce/300-S10)

FIG. 2.5 Photoluminescence Spectrum of H2 annealed Ce=YAG at 300 °K
FIG 2.6  Zero phonon line found at 489.16 nm from absorption and emission spectrum of Ce:YAG at 4.2 K: absorption (solid line), emission (broken line).

(REF. 62)
2.5 Excitation spectra

An excitation spectrum is an emission intensity measurement at a particular emission wavelength when the excitation source of constant intensity is swept in wavelength. An excitation spectrum is used to identify all wavelengths that excite a particular emission wavelength. The 5d → 4f transition bands of the cerium can be obtained in an excitation spectrum at 550 nm. Figures 2.7 & 2.8 show the excitation spectra of three different samples at 300 and 77 °K respectively. W. J. Miniscalco et al. (57) believed that four of the five 5d levels are observed before the onset of YAG intrinsic absorption as shown in Figure 2.9. However, our excitation spectra showed that the third peak seen by W. J. Miniscalco is not associated with cerium. Our data suggests that the three cerium peaks are at 223, 340 and 460 nm. Furthermore, the room temperature excitation measurements showed that the peaks at 223 and 340 nm are relatively stronger at 300 than 77 °K. The absorption is measured in terms of its absorption co-efficient which is defined as $\alpha$ in the equation:

$$ I = I_0 e^{-\alpha x} \ldots \ldots \ldots \text{Eqn 2.2} $$

where $I_0$ is the incident photon flux,

$I$ is the photon flux passing through a material of thickness, $x$. 

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FIG. 2.7 Excitation Spectra of Ce:YAG at 300 °K
(This was done at GTE Laboratories)
FIG. 2.8 Excited Spectra of Ce: YAG at 77 °K
(This was done at GTE Laboratories)
FIG. 2.9 The optical absorption coefficient $\alpha$ versus photon wavelength $\lambda$ for Ce:YAG at 300 °K. Arrows indicate the four observed absorption lines attributed to 5d levels. (Reference 57)
2.6 Phonon spectra

The study of optical phonon spectra in Ce:YAG is important since the phonons do contribute significantly to the energy transfer mechanism. The strong ion-lattice coupling enables the phosphor system to have a large Stokes shift (53,73,78). Energy band gap information is available from the excitation spectrum. At 77 °K, the energy gaps between the 5d bands are 4,475 cm⁻¹(2,235 nm) and 8,750 cm⁻¹(1,143 nm) respectively. As temperature increases the bandwidths increase reducing the effective band gaps. Glen A. Slack et al. (74) performed optical absorption measurements on YAG from 10 to 55,000 cm⁻¹. His results show that there exists a highly absorbing region, 100 < ν < 860 cm⁻¹, which is noted as a single photon process region. The two-photon process region is from 860 < ν < 1,700 cm⁻¹ and the three-phonons process region from 1,700 < ν < 2,400 cm⁻¹. Figure 2.10 shows the optical absorption coefficient, α, verses photon wave-number, ν for YAG at 300 K in the infrared region.

J. P. Hurrell and S. P. S. Porto (47) have done a factor group analysis of YAG space group and showed that there are 18 \( T_{lu} \) IR-active modes, and 3 \( A_{1g} \), 8 \( E_g \) and 14 \( T_{2g} \) Raman-active modes. The IR data obtained from experiments were interpreted by a Kramers Kronig transformation (51) to yield values of the complex dielectric constant and the frequencies of the longitudinal and transverse long wavelength \( T_{lu} \) modes. With one \( T_{lu} \)
mode constituting the acoustic branch, 17 optic modes are present in the spectrum. Although Hurrell and co-worker (47) did not find two of the 17 optic modes, there is an agreement with Glen A. Slack's results (74) that the 17 optic modes lie in the region $120 < \nu < 830 \text{ cm}^{-1}$. 
FIG. 2.10 The optical absorption coefficient $\alpha$ versus photon wave number $\nu$ for YAG at 300 °K.
(Reference 74)
Glen A. Slack (74) specifically states that the multiphonon lattice absorption bands extend upward to 2,400 cm\(^{-1}\) wave-numbers. Beyond 2,400 cm\(^{-1}\) the crystal is transparent with an absorption coefficient, \(\alpha = 0.1\) cm\(^{-1}\) up to \(\nu = 30,000\) cm\(^{-1}\) (74). From 30,000 to 52,000 cm\(^{-1}\) Slack found a variation in the absorption coefficient from sample to sample, therefore Slack believed that absorption was caused by impurities with a concentration in the range of 10 to 100 ppm. There were two absorption bands centered about \(\nu = 39,000\) cm\(^{-1}\) (256.4 nm) and \(\nu = 45,000\) cm\(^{-1}\) (222.2 nm) which Slack associated with impurities.

The optical absorption increases rapidly for wavenumbers above \(\nu = 52,000\) cm\(^{-1}\) (192.3 nm) and reaches an absorption coefficient of \(\alpha = 1,000\) cm\(^{-1}\) at 54,300 cm\(^{-1}\) (6.73 eV or 184.2 nm). This steeply rising absorption edge is the fundamental absorption edge or the conduction band edge.

2.7 A simple model for a luminescent center (13, 28, 53)

With the aid of a simple model given in Figure 2.11 (the Mott-Seitz model) we attempt to explain:

a) The broad-band character of the emission and absorption of the cerium activator ion, and

b) The Stokes shift of the emission.
At 0 °K the luminescent center will occupy the lowest vibrational level of the ground state. The ions surrounding the central ion vibrate about their equilibrium positions situated at a distance $r_0$ from the central ion. At higher temperature, higher vibrational levels may be occupied. In Figure 2.11, the horizontal lines represent vibrational states. Due to the absorption of radiation of appropriate wavelength, the center is raised to an excited state. Since the equilibrium distance $r_e$ of the excited state will not in general be equal to that of the ground state, and since the center may be at different vibrational levels, this transition will correspond to a fairly broad absorption band.

Once in an excited state, the system will relax towards the equilibrium state (of the excited level) by dissipation of phonons (heat). Since a number of the vibrational levels in the excited state are occupied, the emission is therefore broad. Line emission is only found under very exceptional condition where the configurational co-ordinate curves are identical in shape and have the same equilibrium distance, as for example the $F \rightarrow I$ transitions in Neodymium doped YAG (26,30). Figure 2.12 shows a Cathodoluminescence spectra of Thullium doped YAG obtained from our experiments which shows also a line spectra. The entire process must satisfy the conservation of energy and crystal momentum. The photon wave vectors inside the crystal differ from the free space values by a factor of the index of refraction of the crystal $\eta$ (since
the frequencies in the crystal are unchanged, and the velocity is given by $c/n$.

If the free space wave vectors of the incident and emitting photons are $\vec{q}$ and $\vec{q}'$, and the corresponding angular frequencies are $\omega$ and $\omega'$, then the conservation laws require that

$$h \omega = h \omega' + h \omega_1(k) + h \omega_2(k)$$

$$\hbar \vec{q} = \hbar \vec{q}' + \hbar \vec{k}_1 + \hbar \vec{k}_2 + \hbar \vec{K}$$

where $\omega_1$ is the angular frequency of the 1st phonon, $\omega_2$ is the angular frequency of the 2nd phonon, $\vec{k}_1$ is the phonon (1) wave vector, $\vec{k}_2$ is the phonon (2) wave vector, and $\vec{K}$ is the reciprocal lattice vector.

Since there are phonons emitted in Stokes shifted emission, energy from the incident photon excites several normal lattice modes (optical phonons) such as the 17 possible optic $T_{lu}$ modes. Hence the emission always lies at a lower energy than the absorption.

Multiphonon relaxation processes can take place between two levels whose energy difference is greater than the greatest energy of the available phonons. The calculations of the transition probabilities of radiationless multiphonon processes is extremely complicated. It may, however, be safely assumed that these processes are less probable the larger the number of emitted phonons, namely, the greater is the energy gap of the two levels involved in the transition.
When competing with the radiative decay process the radiationless processes represent a serious loss in a fluorescent system, especially when a large output of radiation is desired. It is important to note that radiationless processes are fast if there is a crossing between the upper and lower parabola energy levels (This is the point S in Figure 2.11). In Ce:YAG the upper 5d bands decay to the lowest 5d band in less than 2 ns through nonradiative processes. This decay measurement was performed by M. J. Weber (78).
FIG. 2.11 Configurational-coordinate diagram of a luminescent center. The potential energy $E$ of the center in the lattice is plotted as a function of the configurational coordinate $r$ for the ground state and the first excited state. In practice $r$ is identified with the distance between the central cation and the surrounding anions. Vibrational states are represented schematically by horizontal lines in the parabolae. The excitation and emission transitions correspond to vertical transitions between the two curves. (Reference 13)
FIG. 2.12  CL spectrum for Tm$^{3+}$ in YAG at 300 $^\circ$K
3.1 **Excitation produced by fast electrons**

An electron with a kinetic energy in the 20 KeV range upon entering a solid loses energy by collision to both the bound and the valence electrons in the material, but is not energetic enough to displace the nuclei from their lattice sites. Since there are more inner shell electrons than valence shell electrons, the former accounts for the major part of the energy loss. Thus the major primary excitation produced by a fast electron are excited ions and fast secondaries due to ionization. The energy loss from the primary electron beam is characterized by its specific energy loss, \( \frac{dE_p}{dx} \), where \( E_p \) is the residual primary electron energy at penetration depth, \( x \). The specific energy loss relation is given by: (34,82)

\[
\frac{dE_p}{dx} = -\pi \frac{N_{\text{eff}}}{Z} e^+ \ln\left(\frac{E_p}{E_{\text{eff}}}\right) / (4 \pi \varepsilon_0) E_p \quad \text{Eqn 3.1}
\]

where \( N_{\text{eff}} \) is the effective number of atoms per unit volume participating the collision event, \( Z \) is the average atomic number of the solid, \( E_p \) is the primary electron energy at penetration depth, \( x \), \( E_{\text{eff}} \) is the average value of electron binding energy overall shells, and \( \varepsilon_0 \) is the permittivity of free space.
The excited ions lose energy by Auger transitions in which an electron is emitted. A fraction of the incident primary electrons and their secondaries leave the solid, resulting in a back-scattering loss which typically amounts to about 10% of the energy of the primaries. In addition, a small fraction of order 1% (34) of the excitation is lost by X-ray emission.

Residual secondary electrons set up plasma oscillation and this reduces their energy in integral multiples of the plasmon energy. The entire valence electron sea oscillates back and forth with respect to the ion cores at the plasma frequency given by:

$$\omega_p = \left[ \frac{(4\pi n_e^2)/m^*e}{m^*e} \right]^{1/2}$$

Eqn 3.2

where \( n \) is the valence electron density, \( m^*e \) is the effective mass of the electron.

There are losses to this plasma resonance system which allow the important energy transfer to the lattice states and activator ion states. At high temperatures, thermalization occurs and allow transfer of the lattice defect states which indirectly feed the activator ions.

From the above complex events, it is therefore difficult to calculate theoretically the efficiency of cathode-ray phosphors. A vast amount of literature exists on this subject.
Recent CL and PL models and experiments (13,52,55,56,63,64) but there is little agreement between theoretical and experimental values for existing theories.

3.2 Energy transfer models

The problem of doped impurities in semiconductors is handled by treating the perturbing impurity potential in the effective mass approximation whereby the periodic potential is replaced by an effective Hamiltonian based on the $E(k)$ relations for the perfect crystal (41,42,43). The assumption is that the wavefunction $\psi n(\mathbf{r},t)$ can be expressed as an expansion of Bloch states. However, this approach is not acceptable for our phosphor system, Ce:YAG, because the impurity ions, Ce$^{3+}$, are very localized and therefore cannot be expressed in terms of Bloch states.

D. J. Robbins et al. (67) suggested an Exciton-Impurity model which predicts the quantum efficiency of a phosphor from the core structure of the activator ion. He believed that the nature of impurity core determines ultimately the efficiency in energy transfer from the lattice to the activator ion. The sequence of energy transfer events to activator ion is shown in Figure 3.1.
Chapter 3

IONIZING RADIATION

FORMATION OF FREE EXCITATION (FE)

IMPURITY POTENTIAL CAPTURES FREE EXCITON

TO FORM BOUND EXCITON STATE (BES)

FE & BES INTERACTS WITH IMPURITY ION

CORE ELECTRONS PRODUCING EXCITED STATE

\[ \text{RADIATES} \]

RETURN TO GROUND STATE

Figure 3.1 Energy Transfer Processes Representation
If the level of doping is low, the impurity ions can be considered isolated. The electron-hole pair (exciton) which wanders in the crystal can be treated as a pair of effective mass like particles. When an exciton passes near the impurity ion, coulomb interaction between the exciton and the impurity core occurs thereby forming an excited ion. Figure 3.2 gives a pictorial representation of such an event. Hence the degree of interaction determines the effectiveness of such an energy transfer.

Robbins et al. (67) further derived the above process quantum mechanically. The details of this derivation is not shown here. The calculated interaction matrix demands two conditions to be satisfied for an effective energy transfer. The conditions are given below:

(a) The impurity should have electric-dipole transitions quasi-resonant with the lattice absorption edge, and
(b) these quasi-resonant impurity transitions should be relatively strongly coupled to the lattice phonons.
Chapter 3

An Exciton (Treated as Effective Mass like particles)

Core Electrons of an impurity ion

FIG. 3.2 A MODEL OF AN EXCITON IN THE VICINITY OF A STRUCTURED IMPURITY CENTER (REF. 67)
To achieve high luminescence efficiency, the phonon coupling between the lattice states and the impurity ion should not be so strong that excited core electrons decay non-radiatively through multiphonon emission. In the case of Ce:YAG, this condition is satisfied since the 5d excited state is spatially extended and strongly affected by crystal field. The result of this lattice activator coupling gives rise to large Stokes shift observed for cerium emission.

D. J. Robbins et al. (67) have also experimentally determined the relative quantum efficiency of four different rare-earth impurities in YAG. The four phosphors have their corresponding absorption spectra shown in Figure 3.3. All these impurity ions show localized atomic absorption bands below the lattice absorption edge, which lies at approximately 195 nm, they are to be considered as iso-electronic structured impurities in the YAG lattice. It is noticed that Ce$^{3+}$ and Tb$^{3+}$ show strong inter-configurational $f \rightarrow d$ transitions near the lattice absorption edge and is hole-attractive. Eu$^{3+}$ shows a charge-transfer transition and should be electron attractive. Gd$^{3+}$ may not form a thermally stable bound state. Energy transfer from any exciton localized near the impurities to the core excitations should be efficient for Ce$^{3+}$, Eu$^{3+}$ and Tb$^{3+}$, all of which possesses strong and relatively broad dipolar transitions quasi-resonant with the lattice excitons. The energy transfer to Gd$^{3+}$ should be much weaker.
The prediction of poor quantum efficiency for Gd$^{3+}$ in YAG from the Exciton-Impurity theory is confirmed experimentally as shown in Figure 3.4. (A plot of relative quantum intensities against activator concentration) Therefore the presence of strong activator induced absorption bands near the lattice absorption edge does indeed correlate with a high quantum efficiency for CL in YAG. The similarity in the behavior of Ce$^{3+}$, Eu$^{3+}$ and Tb$^{3+}$ suggests that at 300 °K, the lattice-impurity coupling is not sensitive to detailed interaction mechanism when the general conditions for efficient transfer are satisfied. The relative inefficiency in Gd$^{3+}$ as an activator may result from thermal instability of any bound exciton state, and/or form weak coupling between the carrier recombination and quasi-resonant, parity forbidden core excitations.

The general success of these simple ideas in describing the properties of garnet phosphors encourages further study of absorption band edge of the lattice and the impurity ion bands near to this edge. In our experiments on excitation of the 290 nm emission, we showed that the absorption lattice edge of YAG is responsible for this emission. In addition our excitation spectra for the 550 nm cerium emission shows a third 5d cerium band which overlaps the extended absorption lattice edge of YAG.
Fig. 3.3 Absorption spectra of RE ions in YAG crystals at 300°C. The YAG lattice absorption edge rises rapidly below 200 nm. (REF. 67)
Fig. 3.4  CL quantum efficiency at 300°K as a function of activator concentration for the YAG:RE$^{3+}$ phosphors. The ions Ce$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, which all have strong absorption bands near the (REF. 67)
D. J. Robbins et al. (65) found that the Ce$^{3+}$ luminescence at 540 nm in Ce:YAG can be resolved into two exponential decay regions, A (fast) and B (slow). The fast components are of the order of hundredths of nanoseconds and the slow components are in the region of microseconds. The slow decay component suggests an energy storage mechanism which feed the cerium ions. A possible candidate for such energy storage system is the lattice defect states. In addition, a broad band emission in the UV range 200 to 450 nm was observed in the nominally pure YAG under CL excitation. The peak of this UV emission shifts (65) from 330 to 270 nm when the temperature is lowered from 445 to 120 K. This UV emission band is also observed in the Ce:YAG sample.

D. J. Robbins et al. (65) also obtained a thermoluminescence spectra (TL) which showed three prominent peaks in both undoped (See figure 3.5a) and Cerium doped YAG (See figure 3.5b) with the exception of a small peak at 310 °K. This additional small peak is assumed to be cerium induced. Table 3.1 gives the values of the thermalization activation energies for the lattice defect states. The activation energy is the amount of energy required by a trapped carrier in a trap site to be released. The probability for releasing the trapped carrier is proportional to $\exp(-E_a/kT)$, where $E_a$ is the activation energy, $k$ is the Boltzmann constant and $T$ is the absolute temperature.
TABLE 3.1 (Ref 65)

Thermalization activation energies for defect centers in YAG

<table>
<thead>
<tr>
<th>CENTER</th>
<th>THERMALIZATION RANGE (°K)</th>
<th>ACTIVATION ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>50 to 220</td>
<td>16 meV</td>
</tr>
<tr>
<td>D2</td>
<td>220 to 300</td>
<td>130 meV</td>
</tr>
<tr>
<td>D3</td>
<td>&gt; 300</td>
<td>450 meV</td>
</tr>
</tbody>
</table>

**Fig. 3.5** THERMOLUMINESCENCE SPECTRA OF UNDOPED AND Ce³⁺: YAG (REF. 65)
3.3 The Kinetic model

A kinetic model has been developed (65) based upon the thermalization processes in the TL spectra of the Undoped and Cerium doped YAG. The three prominent defect centers D1, D2, D3 and the cerium emission band, are shown in Figure 3.6. The activation energies are given by E1, E2, E3 respectively. Each center is characterized by three rate processes, namely, c for capture rates, e for rate of thermal re-emission to lattice band states, and f for an effective recombination rate which is not simply of a radiative type. The rate, f should be the slowest process in the recombination of effective mass like particles, electrons and holes. This can be confirmed by the long emission lifetime obtained from both the cerium emission band and defect emission band.
Fig. 3.6 Kinetic Model

(Ref. 65)
Such a model is useful in treating the interactions between centers in a solid but suffers from a lack of knowledge of the physics of the mechanisms involved. Rate equations can be written with the capture and thermal emission rates defined as:

\[ C_i = \sigma_i \nu N_i \quad \text{Eqn 3.3} \]
\[ E_i = N_b \sigma_i \nu \exp\left(-\frac{E_i}{kT}\right) \quad \text{Eqn 3.4} \]

where \( \sigma_i \) is the capture cross-section for one quantum of excitation propagating in the lattice, \( N_i \) is the concentration of unexcited centers \( i \) in lattice, \( N_b \) is the effective density of lattice band states into which the excitation can be emitted, and \( \nu \) is the thermal velocity associated with the quantum of lattice of excitation.
3.4 Introduction to photoluminescence

Photoluminescence (PL) refers to the luminescence observed in materials due to excitation by an electromagnetic radiation source. For most phosphors, the luminescence characteristics are, to a good approximation, independent of the type of excitation. In other words, the emission spectrum is independent of whether the excitation is from ultraviolet radiation, gamma radiation, and cathode rays. The reason being that there exists only one equilibrium configuration for the relaxation of the activator ion. However, if the equilibrium configuration changes due to excitation (e.g. because of charge built-up or significant rise in temperature changing the active phonon modes in the lattice) the corresponding emission spectra from different excitation could then differ. There are also cases where the configuration of the host is altered while under excitation; for example, the generation of permanent or transient color centers under strong gamma radiation. Transient color centers in YAG have been observed by Bass and Paladino (3), Katsumi Mori (58, 59), K. Cermak and A. Linka (22-25).

W. Hayes and D. J. Robbins (44) have reported that a UV broad band emission with its peak at 270 nm was observed in undoped YAG under X-rays at 4 °K. This UV emission is also observed by us at 77 °K under electron bombardment. There-
Recent CL and PL models and experiments

before this observation proved that there is only one equilibrium configuration even for the defect states.

3.5 Previous work on photoluminescence

A. Bril (11-13) excited Ce:YAG with 254 nm radiation and obtained a cerium emission identical to both of our CL and PL spectra of Ce:YAG. However, the UV emission had a peak at 350 nm and a magnitude of about half of the cerium emission intensity at 550 nm. He found a decay time of $\tau$ (1/e) = 55 ns for Ce:YAG with UV excitation at 254 nm. He also noticed a non-exponential decay of $\tau = 70$ ns when excited by a 20 KeV electron beam. The cerium concentration in Bril's sample was about 1 to 2%. He specifically stated that the UV emission observed was weak under cathodoluminescence.

There are three important questions to Bril's experimental results. Firstly, why did he obtain the intrinsic cerium decay time under CL excitation? Secondly, why was the UV emission intensity of the same order of magnitude as the cerium 550 nm emission peak under PL excitation? Thirdly, why the UV emission band was so weak under CL excitation? According to D. J. Robbins' observation (65) the intrinsic cerium decay cannot be observed because the defect states which have a longer lifetime than cerium, transfer their energy into the cerium, thereby increasing the decay time under CL excitation. We have a suggestion that because the
cerium concentration in Bril's sample is particularly high compared to D. J. Robbins' sample, the intrinsic cerium decay time may still dominate due to strong direct excitation of the cerium ions. The non exponential decay reported does support the evidence that an indirect transfer process to cerium ions exists. We have no good explanation for the second question. The third question may be answered the following way. In our CL experiments we found that the current density of the electron beam has an effect on increasing or decreasing the UV emission peak intensity as compared to the cerium 550 nm emission peak. Bril might be exciting the sample with high current density thereby enhancing the cerium emission peak far beyond the UV emission peak. In our defect excitation spectra on both doped and undoped YAG, the shorter wavelengths are more efficient in exciting the defect emission. In fact we expected Bril's UV emission peak to be also very weak.

D. J. Robbins (63) mentioned that the excitation of the defect absorption band at about 260 nm gives a lower quantum yield (This is interpreted as a quantity proportional to quantum efficiency) for cerium emission for the oxygen annealed sample than the unannealed sample. He found the quantum yield remains fairly constant regardless of the oxygen annealing process or cerium doping level when excited directly into the second 5d cerium band by a 340 nm radiation. Our interpretation is that there is little
Recent CL and PL models and experiments

excitation of the defect band at 340 nm and therefore the cerium ions are directly excited without any energy transferred from the defect bands. Hence the quantum yield is not affected.

N. S. Rooze and N. A. Anisimov (69) measured the absorption, emission and luminescence excitation spectra in nominally undoped YAG single crystals grown by Czochralski method. They found an absorption band with a peak at 5.45 eV or 227.9 nm even for their most pure crystal sample. This absorption band is observed by us too. They also found that excitation of the YAG crystal at room temperature by UV light with $h\nu > 6.3$ eV (197 nm) gives an additional emission band with a peak at 315 nm. This emission band shifts to 265 nm when cooled to 77 °K. It appears to us that this UV emission band is the same as our defect emission band. They believed that the UV emission belongs to the anionic complexes $\text{AlO}_4^{5-}$. The complex anions in YAG are the $\text{AlO}_4^{5-}$ ions whose intramolecular vibrations give rise to absorption peaks in the region $620 < \nu < 860$ cm$^{-1}$ wavenumbers (47, 69, 74). The distance between the $\text{Al}^{3+}$ and $\text{O}^{2-}$ ions in these complexes has the smallest value, 1.76 Å. Rooze (69) suggested that the luminescence at 315 nm which has a large Stokes shift of 2.5 eV, satisfies the requirement that the interactions between the separate complexes to be small. However, no explanation was given for the shift in emission peak when the crystal is cooled. Figure 3.7 shows the
excitation spectra of YAG at 300 and 77 °K and the luminescence spectra of YAG at 300, 180 and 77 °K.
FIG. 3.7 Excitation spectra of intrinsic luminescence of YAG at $T = 300 \, ^\circ\text{K}$ (1) and $77 \, ^\circ\text{K}$ (2); intrinsic luminescence spectra of YAG at $T = 300 \, ^\circ\text{K}$ (3), $180 \, ^\circ\text{K}$ (4), and $77 \, ^\circ\text{K}$ (5).

(Reference 69)
EXCITED STATE ABSORPTION AND COLOR CENTERS

4.1 Excited state absorption

Excited state absorption (ESA) refers to absorption that arise from further excitation of excited states. This is a widely used technique to obtain the positions of higher energy levels in a level diagram. There have been a number of researchers (48,57,60,78) interested in searching for the third, fourth and fifth 5d cerium energy bands in YAG. The energy band diagram is used to determine which wavelengths are good for optical pumping so that the Ce:YAG can be used as a tunable wavelength solid state laser. The energy transfer mechanism in Ce:YAG may be obtained as a consequence.

The general experimental setup for ESA involves a strong laser beam and a weak tunable probe beam. The strong laser beam is intended to lift all electrons above their ground states. While the electrons are still in their excited states, a probe beam is used to excite these excited electrons to an even higher energy level state. Since optical excitation requires electric-dipole allowed transitions, the higher 5d cerium bands may not be obtained from this technique because all the 5d cerium bands are of the same parity. There are three important papers (48,57,60) written on this topic and unexpected
Excited state absorption and color centers

results were obtained. The next section is dedicated to highlight some of these important findings which would help us to understand the energy transfer mechanisms of Ce:YAG.

4.2 Previous work on ESA of Ce:YAG

Owen et al. (60) used a 337 nm pulsed nitrogen laser beam as a pump beam and a tunable pulsed dye laser beam as a probe beam. The probe beam lags the pump beam by 3 ns in time. The time dependent phenomena on the magnitude of ESA at 77 °K was studied with a 640 nm probe beam. Figure 4.1 shows the magnitude of ESA increases to a plateau for 0 < t < B while the crystal Ce:YAG sample was exposed to the 337 nm pump beam pulsed at 30 Hz. Owen believed that his 3ns pump beam successfully excited the ground electrons into the second 5d cerium band. Using the experimental evidence on the non-radiative decay time for the higher 5d bands (60) to the lowest 5d cerium band, he argued that the cerium ions are in the lowest 5d excited states before the arrival of the probe beam pulse. Since the ESA events are repeated for each cycle of a pump beam pulse followed by a probe beam pulse, the magnitude of ESA should remain constant if there were no other processes involved. Instead there is a slow rise in magnitude of ESA which then implies that additional absorption other than cerium is involved. At t = B, the pump beam is removed and the ESA falls to an intermediate value with a long relaxation time. Yellow fluorescence, presumably from the Ce$^{3+}$ excited ions is
observed in region C where the probe beam is the only energy source pumping the sample. This phosphorescence decay was measured at 499 nm and observed to have at least two lifetimes, namely, 165 secs and 11 mins. Warming the crystal slowly produced thermoluminescence peaks at 97, 130, and 161 °K, similar to the results obtained by D. J. Robbins (65).

Owen et al. believed that this broadband absorption in region C is due to a stable trap induced by the 337 nm pump beam. Figure 4.2 shows the ESA transmission curves for Ce in YAG at 77 °K before and after irradiation with the 337 nm pump beam. He further attributed the absorption spectrum of his stable trap to be the difference between the two transmission curves. He also noticed that the absorption due to the stable trap could be bleached with a tungsten lamp, but no decay was observed if the probe beam has a wavelength greater than 600 nm.
FIG. 4.1 The time dependence of the intensity of excited-state absorption for Ce in YAG at 77 °K with $\lambda_{\text{probe}} = 640 \text{ nm}$ (Reference 60)

FIG. 4.2 The transmission curves for Ce in YAG at 77 °K before and after irradiation with nitrogen laser at 337 nm. Shown in the inset is the difference in transmission, which corresponds to absorption by a stable trap. (Reference 60)
This is an important experiment because the yellow phosphorescence observed by Owen must be cerium. In addition, his thermoluminescence peaks agree with D. J. Robbins' thermoluminescence peaks. This implies that the defect bands reported by D. J. Robbins are related to Owen's stable trap which is capable of transferring its energy to cerium. It appears that Owen did excite the defect states from the 5d cerium bands. The coupling between the cerium 5d bands and the defect states seem to be electric dipole allowed. Owen further reported that bleaching occurs when excited sample is irradiated with light of energy exceeding 16,000 cm. Our interpretation of Owen's bleaching effect is that the trapped carriers are released to the cerium ions in a more direct way after bleaching. This effect can be correlated with K. Mori's (58) bleaching effect on his traps. In the case of K. Mori the traps are only bleached by raising temperature because he studied the effect in undoped YAG where a direct path to cerium cannot be obtained to drain away the trapped carriers.

Owen et al. also attempt to construct an energy level diagram for Ce:YAG based on his ESA experiments. Figure 4.3 shows his proposed energy band diagram. In chapter 2, our experimental data on excitation spectra on cerium 550 nm emission and the absorption spectra of Ce:YAG indicates that the third 5d cerium band in Ce:YAG is located at 223 nm and is below the YAG lattice conduction band. Therefore the conduction band
Excited state absorption and color centers

position in Owen band diagram is inconsistent with our experimental data.
FIG 4.3 An energy-level diagram for Ce$^{3+}$ in YAG at 77 K. The energies are given relative to the conduction band at 0 cm$^{-1}$.

(Reference 60)
W. J. Miniscalco et al. (57) also performed ESA in Ce:YAG with a 337 nm pulsed pump beam and a CW probe beam. The ESA coefficient was measured from 480 to 680 nm. Again a sharp rise in ESA was observed at about 15,000 cm⁻¹ (57) which the author believed to be a transition between the first and third 5d cerium bands. In addition to this sharp feature, a strong background absorption was observed. His ESA results are consistent with Owen ESA results. Our interpretation is the same as for the case of Owen where traps are responsible for all his observations. Miniscalco et al. have also proposed an energy level diagram which is base upon his ESA results and the absorption spectrum. He took the shoulders at the extended band edge to be the cerium third and fourth 5d bands. This is a dangerous assumption because the shoulders may originate from the nature of the YAG lattice band edge. Our excitation spectrum for cerium 550 nm emission showed that only the third 5d cerium band is within the YAG band gap and it has a band peak at 223 nm. Therefore our data disagree with Miniscalco's et al. band diagram. (Figure 4.4)
FIG. 4.4 Energy levels for Ce$^{3+}$:YAG. Inset shows the cross section for ESA as it varies with photon energy, relative to the lowest excited state. Lined region around 19,000 cm$^{-1}$ corresponds to the fluorescence photon energy. (Reference 57)
Ralph R. Jacobs et al. (48) also performed ESA in Ce:YAG. A XeF laser was used to pump the Ce:YAG at 351 nm and 353 nm. A tunable CW probe beam (550 to 610 nm) is used to measure the ESA. Measurements were made with the sample at room temperature and cooled to 250 °K. The fluorescence intensities and decay rates at the two crystal temperatures 295 and < 250 °K were identical to the lifetime of 75 ± 5 ns. This lifetime is the intrinsic value for cerium emission in YAG and is measured by us too. However, the optical probe transmission oscillograms at 590 nm for the above two crystal temperatures are different. (See Figure 4.5 and Table 4.1) A monotonic decrease in loss was observed as the crystal temperature was reduced from 295 to < 250 °K. The transient absorption was resolved into two time components one with lifetime 75 ns and a second, shown in detail on the right-hand side of figure 4.5, with a lifetime of 400 ↔ 800 ns. The agreement of the short lifetime with fluorescence decay time of the lowest 5d level indicates the optical loss originates from this level.

Jacobs et al. (48) attribute the longer-lived response to one of the following reasons:

a) Population buildup in the \( ^2F_{7/2} \) state from fluorescence terminating at this level. This population, and its associated probe beam loss, relaxes by phonon-assisted non-radiative decay to the \( ^2F_{5/2} \) ground state.
b) Two-pump-photon excitation of high lying Ce³⁺ metastable levels that absorb at the probe wavelengths and decay non-radiatively at these longer times. This mechanism was discounted on the basis that the loss amplitude is linearly proportional to XeF laser pump intensity. At two-pump-photon processes is expected to have a square law dependence on the pump intensity.

c) One can consider the probe beam absorption by transient color centers in the Ce:YAG formed by the pump photons.

The first reason was excluded because measurements on Nd:YAG indicate the multiphonon decay times for comparable energy gaps to be shorter. Hence the last reason is the best explanation and it agrees well with Owen et al. and Miniscalo’s et al. experimental data.
Excited state absorption and color centers

Figure 4.5 (Reference 48)
Oscillograms of optical probe transmission at 590 nm for YAG:Ce$^{3+}$ following excitation by XeF laser radiation at 351/353 nm: (a) $T = 295 \, ^{\circ}$K; (b) $T \leq 250 \, ^{\circ}$K. Indicated are the zero and peak probe beam amplitudes with no excitation.

<table>
<thead>
<tr>
<th>Probe wavelength (nm)</th>
<th>550</th>
<th>560</th>
<th>570</th>
<th>580</th>
<th>590</th>
<th>600</th>
<th>610</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \chi^* \ (\times 10^3)$</td>
<td>0.75</td>
<td>0.85</td>
<td>0.80</td>
<td>0.95</td>
<td>1.0</td>
<td>1.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

TABLE 4.1 Maximum net excited-state-absorption coefficients $\Delta \chi^* \ (\text{cm}^{-3})$ for $Y_2Al_5O_{12}:Ce^{3+}$ at 295 $^{\circ}$K. (Ref.48)
4.3 Color centers in YAG

The thermoluminescence experiments mentioned in Chapter 3 support the idea that trapped carriers do participate in the energy transfer mechanism in Ce:YAG. Therefore it is important to investigate the types of defect states that are present in YAG which are present in YAG which are responsible for trapping carriers. "Color centers" is a more general term used to describe all the defect states. If the color centers responsible for energy transfer in YAG are found, then a more exact model can be developed to quantify the energy transfer processes. In addition, we can even predict and control these energy transfer mechanisms thereby determining the efficiency of a phosphor.

However, there are a variety of color centers in YAG. Often color centers show up in the absorption spectrum. In undoped YAG, significant absorption is found for wavenumbers \( \nu > 30,000 \text{ cm}^{-1} \), thereby giving a very extended YAG lattice band edge appearance. In general, the undoped YAG crystal is transparent in the visible region. However, a slight tint of blackness is observed for the hydrogen annealed sample which is particularly transparent compared to all other undoped samples.
4.4 The extended absorption edge of YAG lattice

Glen A. Slack (74) did a detailed study on the extended absorption edge at 300 °K. He prepared many different different YAG crystals grown both stoichiometrically and non-stoichiometrically and in different atmospheres. A particular sample, crystal M28, had the lowest absorption coefficient in this region (See Figure 2.4). He reported this sample to be particularly transparent and free from Tyndall scattering centers in the visible part of the spectrum, where $15,000 < \nu < 20,000 \text{ cm}^{-1}$. He believed the residual optical absorption with the two absorption bands centered about $\nu = 39,000 \text{ cm}^{-1}$ (256 nm) and $45,000 \text{ cm}^{-1}$ (222 nm) to be due to impurities with concentration in the range 10 to 100 ppm. However, no specific impurities were identified to be responsible.
Color Centers in the visible region

Bass and Paladino (3) reported an absorption band in YAG from 300 to 600 nm peaking at 330 nm after irradiation with radiation at wavelengths between 200 and 400 nm. The absorption spectra is shown in Figure 4.6.
FIG. 4.6 The optical density of the indicated YAG sample minus that of the sample before irradiation is plotted against wavelength. Curve A: after 100 flashes, Curve B: after 100 flashes through the 7-54 filter. Curve C: after 100 flashes through the 7-51 filter. (Reference 3)
Willis and Dixon (79) found a brown color center related to quenching of YAG crystals from 1500 °C. The absorption spectrum of such sample was found to have peaks at 330 and 450 nm. However, the 450 nm band can be bleached by annealing the sample at 600 °C in air. They further found that exposing crystal samples to UV light causes an additional absorption band peaking at 625 nm which disappears upon removal of UV source. Figure 4.7 shows the absorption bands of such color centers.
FIG. 4.7 Absorption spectra of color center effect in Nd:YAG (the sharp neodymium absorption lines have been eliminated for clarity). (a) After anneal at 600 °C; (b) after heat treatment at 1500 °C and fast cool; (c) during UV irradiation at 3000 °A. (Reference 79)
K. Mori (58,59) studied the color centers by first reducing the YAG samples using metallic aluminum heated to 1150 °C for about 3 hours and then bleaching the color centers by reheating crystals in an oxygen atmosphere. The discoloration depth was found to decrease exponentially with annealing temperature. The absorption spectra of the UV irradiated undoped YAG sample was found to decrease in magnitude when heated to a higher temperature and cooled to 87 °K (See Figure 4.8). It is evident these color centers have certain activation energies. K. Mori fitted three distinct absorption bands from the absorption spectrum of these color centers. Then he performed an Electron Spin Resonance experiments on these color centers at various temperatures. The effective frequency of the phonon that couples with the color center is given by the relationship (53) \[ \omega^{1/2} = A \left( \coth \left( \frac{h \nu}{2kT} \right) \right), \] where \( \omega \) is the width at half maximum of the absorption band of the color center, \( A \) is a constant, \( \nu \) is the effective frequency phonon coupled with the color center. The effective phonon frequency which coupled to the color center was found to be 7.2 x 10^{12} Hz. He found the \( g \) factor (which is the ratio of spin magnetic moment, \( \vec{\beta} \), to spin angular momentum, \( \vec{s} \), divided by orbital magnetic moment, \( \vec{m} \), to orbital angular momentum, \( \vec{p} \)). For the color center to be 1.995 ± 0.002. This \( g \) value is below the free spin value of an electron, 2.0023. The effective \( g \) value can differ from the free spin value because of spin orbit interaction.
FIG. 4.8 Optical absorption spectra of UV irradiated undoped YAG crystals after heating to indicated temperatures and recooling to 87 °K. 
(1) T at 87 °K, (2) 141 °K, (3) 166 °K, 
(4) 202 °K. (Reference 58)
K. Mori suggested the color center to be due to an electron trapped in an oxygen vacancy based upon the fact that F center has an effective $g$-value lower than $2.0023$ (1, 61).

W. Hayes et al. (44) also employed the Electron Paramagnetic Resonance (EPR)(1, 61) technique to study the color centers. He looked at the color centers which emit at 270 nm at 4 °K. His EPR results suggested three types of color centers, namely, a) an excited triplet of $O^{2-}$ associated with a vacant $Al^{3+}$ in the octahedral site (a-site), b) $O^{2-}$ associated with a vacant $Al^{3+}$ in the tetrahedral site (d-site), c) $O^{2-}$ associated with a vacant a vacant $Y^{3+}$ site (h-site).

4.5 Color centers due to polarons in YAG

K. Cermak, A. Linka, (22-25) and H. J. Bernhardt (4-10) reported that polarons are responsible for the color centers which absorb in the visible region in YAG. In the next section we introduce the concept of a polaron so that the following experimental evidence supporting the presence of polarons in YAG may be understood.

4.6 Polarons and their transport phenomena

When a slow conduction carrier, either electron or hole is present in a polar crystal, it polarizes and distorts the ion lattice in its neighborhood. The polarization, in turn, acts on
the carrier and lowers its energy. As the carrier moves through the crystal, it takes along the distortion of the lattice. The carrier together with the accompanying self-consistent polarization field can be thought of as a quasi-particle, and this quasi-particle is called a Polaron. Its effective mass is larger than that of a Bloch carrier. The polaron in YAG is classified as small because the associated lattice distortion is limited to less than a lattice constant. A small polaron spends most of its time trapped on a single ion. This is known as "self-trapping" phenomenon. At high temperatures, carrier moves from site to site by thermally activated hopping. At low temperatures, the carrier tunnels slowly through the crystal as if it is in a band of large effective mass. The strength of the carrier-lattice interaction is measured by a dimensionless coupling constant \( \alpha \) given by \( \frac{1}{2} \alpha = \text{deformation energy} / \hbar \omega \), where \( \omega \) is the longitudinal optical phonon frequency near zero wave-vector. It is believed that the activated hopping process gives rise to absorption bands which are responsible for the observed color centers. (72)

4.7 Experimental evidence for polarons in YAG

K. Cermak and A. Linka (22-25) found an absorption band peaking at 525 nm after illuminating the Nd:YAG sample with UV light source. The absorption coefficient was further found to decrease with increasing temperatures for all samples in the temperature range, 20 °C to 70 °C.
In K. Cermak's paper (24) on optical polaron absorption, he reported that the decomposition of color centers gives rise to two hyperbolic recombination constants with two values for their activation energies. At lower temperatures, the process with activation energy $\Delta E_1 = 0.92$ eV dominates. At high temperatures, the process with activation energy $\Delta E_2 = 1.22$ eV dominates.

K. Cermak explained that the absorption band arises from the hole transfer from one $O^{2-}$ anion into another equivalent $O^-$ anion in the vicinity of the cation vacancy. Such a hopping process gives rise to absorption band consisting of single bands of Gauss form which are separated from one another by resonance splitting and should differ from each other in their polarization. If resonance splitting of the excited states is neglected, the shape of the absorption band is given by (24,72)

$$I(\text{absorption}) = \hbar \omega \sqrt{W} \exp \left[ -W \left( \frac{\hbar \omega}{2W} - 2.67 \right)^2 \right] \quad \text{Eqn 4.1}$$

where $W = \left( \frac{5.33 E_{JT} \hbar \omega }{\coth \left( \frac{\hbar \omega}{2kT} \right)} \right)^{-1} \quad \text{Eqn 4.2}$

which gives the steepness of the quasi-Gauss form.

$E_{JT}$ is the quasi Jahn-Teller energy giving the stabilization energy gained by the carrier capture. The position of the absorption peak is determined by $2.67 E_{JT}$. He calculated the color center parameters to be as follows:

$\hbar \omega_0 = 0.073$ eV, $E_0 = 0.885$ eV, $E_{JT} = 2.36$ eV, $\tan \alpha = 1.7$, $W$ at half width $E_{1/2} = 0.98$ eV is $2.89$ eV.
The value for $\hbar \omega_c$ (0.073 eV or 589 cm) is a reasonable value for the LO phonon mode in YAG. The ratio $E_{JT}/\hbar \omega = 12$ is a measure of the coupling constant and is evidently a strong vibronic coupling. The quasi Jahn-Teller energy value $E_{JT} = 0.885$ eV which represents the stabilization energy due to carrier capture is in close agreement with the experimental value for activation energy at low temperatures, $\Delta E_l = 0.92$ eV. K. Cermak therefore concluded that the optical absorption is due to small bound polaron phenomena.

H. J. Bernhardt (4-10) also use the polaron model to explain all the visible color centers in YAG. In particular he modelled the polaron problem in YAG to be the case of an electron trapped between two oxygen ions. This model predicts the energy levels of the polaron in YAG. He then compared the theoretical values with the experimental absorption peaks with the assumption that $\hbar \nu = 0.275$ eV.

Similar color centers in YAG have been observed by other researchers (38-40, 49, 50, 54, 55, 70). The references given are mainly work done by the Soviet scientists. They were interested in the UV color centers in YAG. Their thermoluminescence spectra for the color centers in YAG are consistent with D. J. Robbins TL spectra (65).

In conclusion we believe that the major color centers are those found in the band edge of YAG lattice. The exciton model
is applicable for the color centers found near the band edge. Since both electron and photon excitation generate electron hole pairs, excitons are more likely to form than polarons. Polarons being involved with single carrier type are considered secondary in nature. Hence the visible part of the spectrum tend to be dominated more by the polaron effects. In both models, the presence of anion and cation vacancies is acceptable. Therefore, the color centers in YAG include all these defect states. The energy transfer mechanism to Cerium is expected to have close relationship with the excitons since they are the most abundant followed immediately by an excitation.
5.1 CL spectrum measurements

a) General description

The entire system used in our CL experiments can be divided into five basic units as follows: a) the electron gun, b) the vacuum system, c) the cryogenic sample holder, d) the electronics, and e) the collection optics.

The block diagram (Figure 5.1) shows how these units were configured to perform CL experiments. The electron gun (Model 5-448 M from Electroscan) was attached to the sample chamber via an isolation gate valve. The electron gun and the ion pump were connected to the sample chamber through a gate valve so that the sample chamber could be raised to atmospheric pressure in the event of changing samples but keeping the electron gun under vacuum. This is an important measure against oxidation of the cathode which reduces the lifetime and performance of the cathode of the electron gun. The electron gun was connected electrically to a high voltage supply which established the required electric field to focus the electron beam on the sample. The sample was fixed on a demountable copper sample holder which was kept electrically isolated from the cryogenic unit. Such an arrangement allows an electrometer to measure the
electron beam current passing through the sample. Additional information on the sample surface current could be obtained by coating the parallel faces of the sample with evaporated aluminum.
FIG. 5.1 Block Diagram for Cathodoluminescence Experiments
In order to eliminate the background noise in the system, a pulsed technique was employed to improve the signal-to-noise performance ratio. The cathode of the electron gun was modulated through a video coupling amplifier which was kept at the potential of the high voltage supply. A modulating signal was then applied to the coupling amplifier via a variable pulse generator. The pulsed electron beam bombarded the sample thereby generating fluorescence. The luminescence was passed through the quartz window of the sample chamber and then collected by the UV clear optics. Finally, the light was focused in into the slit of a half meter Jarrell Ash scanning spectrometer, which scanned the emission spectrum. A photomultiplier tube was attached to the output slit of the spectrometer thereby converting the optical signals to electrical signals. A lock-in amplifier was used to sample the modulated signal. Synchronization was achieved by taking the reference signal from the same signal source that pulsed the electron gun. In addition a strip chart recorder was used to record the CL emission spectrum obtained from the output of the lock-in amplifier.

5.2 The electron gun

The 5-448M electron gun had an oxide cathode. The electric field potential in the gun was established by three grid controls. Grid G1 served as an aperture control for the electron beam. Grid G2 being an accelerating grid was used to set the
electron beam intensity. Grid G4 was the electrostatic focusing grid for controlling the spot size on the target. Vertical and horizontal magnetic deflection was employed. A μ metal cap was used to screen the stray magnetic fields near the electron gun. All grid voltages were measured with reference to the cathode potential, which was also stated as "the floating ground" for the signal paths in the system. The sample and its chamber were maintained at real earth potential thereby requiring the cathode be set negative with respect to the actual ground. (Earth potential)

Cathode modulation was employed in place of the usual grid G1 modulation. The grid G1 was set at a fixed potential and the cathode was modulated. The modulated cathode potential was screened beyond the control grid G1. Although the electron gun was designed to have a maximum of -30 KV for its anode to cathode voltage, a limit of -22 KV was set in all experiments as to avoid arcing problems. Hence a maximum voltage on the energy of the electron beam was set.

Figure 5.2 shows the grid control arrangement and dimensions. Grids G1 and G2 were controlled by the high voltage coupling amplifier which was floated at cathode potential. A separate variable 0 to 5 KV floating supply was used for focusing control. The anode was detached from the electron gun assembly to achieve a long focusing path (In our case 13
inches) thereby giving a better spot size control. (approximately 5 mils)
FIG. 5.2 Pin Configuration, Dimensions and Materials of Electron Gun 5-448M

Top View
Base Bl2-244
Glass Type: 0120
Both coupling amplifier and focusing supply derived their power from an isolation transformer capable of taking 50 KV across the primary and secondary windings. This arrangement allowed the focusing supply and the coupling amplifier to be floated and their circuits to work at relatively low voltages.

The electron gun ratings are given as follows:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
<th>Nominal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode-Cathode</td>
<td>0 to -22 KV</td>
<td>-17 KV</td>
</tr>
<tr>
<td>Grid G1</td>
<td>-105 to -170 V</td>
<td>-140 V</td>
</tr>
<tr>
<td>(cut-off range at G2 = 600 V)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grid G2</td>
<td>460 to 740 V</td>
<td>600 V</td>
</tr>
<tr>
<td>Grid G4</td>
<td>1.5 to 3.5 KV</td>
<td>2.2 KV</td>
</tr>
<tr>
<td>Beam current</td>
<td>0 to 2.0 mA</td>
<td>100 microamps</td>
</tr>
<tr>
<td>Vacuum</td>
<td>10^-7 Torr</td>
<td></td>
</tr>
<tr>
<td>Heater current</td>
<td>1.0 A (Max)</td>
<td>600 mA at 6.3 V</td>
</tr>
</tbody>
</table>

The cathode will generally age because of contamination from impurities of the system. However, it can be revived several times through the burning in process.
5.3 The vacuum system

The vacuum system was supported by a diffusion pump and an ion pump. The diffusion pump being a more powerful pump ensured a good vacuum of $10^{-7}$ Torr in the sample chamber. The ion pump was used to improve the pressure of the electron gun region during operation and to maintain a high vacuum when the isolation gate valve was closed. The isolation gate valve was only opened when the sample chamber pressure fell below 10 Torr. At all times the electron gun was kept in high vacuum. The gate valve seal was made with an O-ring.

5.4 The cryogenic sample holder

Figure 5.3 illustrates the cryogenic sample holder which had a demountable copper piece. The copper piece was electrically isolated from its socket by a teflon cover and a mica sheet placed between the copper thermal bath and the socket. Two stainless steel tubes were used to flow cooled nitrogen gas or liquid nitrogen into the copper block. Stainless steel has low thermal conductivity and therefore being used to maintain a large thermal difference between the copper block and the flange. These tubes were welded onto a 2.5 inch stainless steel flange. The entire cryogenic unit was then lowered into the sample chamber from a back port opening situated at the top of the sample chamber.
FIG 5.3 THE CRYOGENIC SAMPLE HOLDER
5.5 The electronics

The electronics here refers to two parts, namely, the high voltage power supply and the signal processing electronics.

The basic blocks of the high voltage supply can be seen in Figure 5.4. The idea was to use an isolation transformer to power both high voltage coupling amplifier and the homemade focusing power supply. The Litton Industries high voltage coupling amplifier, (model 1067-03) had another video isolation transformer for its signal path isolation. All circuitry details were given in the manual provided.

The signal processing electronics referred here consists of the photomultiplier assembly, the lock-in amplifier, electrometers and a strip chart recorder. A homemade biasing network was used for the photomultiplier tube, Hamamatsu R955. This photomultiplier tube was selected for its fairly flat, wide spectral response (185 to 900 nm) and had a very fast response time which was then used for decay-time measurements. The fast system response enabled the cerium emission decay of 70 ns to be measured fairly accurately. However, the response rate was critically dependent on the choice of load resistor value. In emission spectral measurements where a large output voltage was required, a 1 megaohm resistor was used. On the other hand a 50 ohm termination was used in every decay time measurement.
A Princeton Applied Research JB4 lock-in amplifier was used to sample electrical signals from the photomultiplier assembly. A very selective high Q filter was employed at its input stage so as to eliminate noise. Therefore only the signal frequency corresponding to the fundamental frequency of the reference signal can be picked up. In addition a low pass filter was placed at the lock-in amplifier output so as to reduce the jitter of the strip chart recorder pen. A full scale of 10 V output signal from the lock-in amplifier was available to drive the Hewlett Packard HP7132A strip chart recorder. The pulse period of the signal source must be set longer than the longest emission decay. Otherwise, the CL emission spectra recorded would be convoluted in time.
FIG. 5.4 HIGH VOLTAGE SUPPLY FOR ELECTRON GUN
5.6 The collection optics

The entire optical path involved a front surface coated spherical mirror, a UV clear quartz lens and a Jarrell Ash half meter scanning spectrometer. A spherical mirror was used to convert an optical point source into a slightly curved line image which fitted the input slit geometry of the spectrometer. The mirror was positioned such that the incident ray and the reflected made an approximate angle of 45 degrees. (See Figure 5.5)

The YAG crystal sample was tilted at an angle of 45 degrees with respect to the electron beam so that the front surface emission was observed through the side quartz window of the sample chamber.

The spherical mirror was held by an xz translator bolted down to the table outside the quartz window. The UV lens was mounted on an optical rail placed between the spectrometer and the spherical mirror.

A 1800 lines per millimeter grating blazed at 2750 Å was used in the scanning spectrometer. The scanning range with this grating was 1600 to 9000 Å. A filter was used outside the spectrometer input slit as to avoid second order diffraction.
Alignment was achieved with the aid of a Helium Neon laser. During alignment, the photomultiplier tube was removed and the Helium Neon laser beam ran backward from the output of the spectrometer. The mirror was used to adjust the laser beam so as to hit the crystal sample. Scattering from the crystal allowed the laser spot to be seen. The electron beam was then magnetically deflected so that luminescence of sample coincided with the laser spot. Alignment was then achieved.
FIG. 5.5 Optical Diagram for Cathodoluminescence Experiments
5.7 Calibration of system response

The entire system has its unique spectral response. All the emission spectra measured can be corrected if the system spectra response is found. A standard 150 W Oriel Xenon Arc Lamp of known emission spectra was used as a source for calibration. The entire set-up was copied except for the sample chamber. An iris was used in place of the sample position. The lamp was then placed 50 cm away from this iris. The emission spectra for this lamp was then recorded by our system. A filter was used only when the second order of the grating was observed. The filter was selected to give 100% transmission at the beginning of the second order (400 nm). Any wavelength below 400 nm was cut-off. The system spectra response was obtained by dividing the actual lamp emission spectra values by the corresponding measured spectra values obtained by our system.

5.8 Time resolved mesurements

Decay time measurements with the CL apparatus were more difficult than the PL apparatus because the CL pulses were longer than the cerium decay time in YAG, whereas the laser pulses in PL were short. The simplest method is to record the decay on a fast oscilloscope and take pictures of the scope display.
In the PL apparatus, a boxcar integrator with a 2ns gate width was used to scan through the decay times. A typical decay curve is shown in Figure 5.6.
Unannealed Ce-YAG at 300°K (Nov/Un-Ce/6/300°K)

$\lambda_{Ce} = 550$ nm  

Pump Laser 1.0 mW at 266 nm

Spot 2.0 mm diameter  

Slit 100 $\mu$m

$\tau_{Ce} \approx 70$ ns

FIG. 5/6 Photoluminescence Cerium Time Constant Measurements
5.9 PL spectra measurements

The general setup differed greatly from CL experimental setup. Figure 5.7 shows the block diagram for the PL experimental setup. The basic blocks for PL experiments used are as follows: a) lasers, b) cryogenic sample holder, c) the electronics, and d) the collection optics.

A Neodymium doped YAG laser was used as the prime source of photons. Two KDP crystals were used as doublers to obtain the fourth harmonic 266 nm. The laser was Q switched and produced approximately 10 ns laser pulses with a repetition rate of 10 Hz and an average power density of 0.1 W/cm².

The laser beam was focused onto the sample with a 23 cm focal length UV clear lens. In order for consistency in the sample environment, the sample was held in place by a tightly secured cryogenic sample holder for both room and liquid nitrogen temperature measurements. The cryogenic sample holder used was an Air Product liquid nitrogen insert holder. The vacuum in this insert holder was maintained by a cryogenic adsorption pump. The collection optics were identical to CL experimental setup except for a Schott filter, WG305, which was placed in front of the spectrometer input slit. This filter would block off any remaining UV laser beam entering the spectrometer. A Hamamatsu photomultiplier tube, R955, was used to collect the optical signal from the spectrometer output. A Lecroy
wideband preamplifier was attached to the PMT assembly which amplified the signal ten times. The signal was then fed through a very long doubly shielded coaxial cable to an EG and G Boxcar integrator. The long cable had a 100 ns reflection time so that the 70 ns seconds decay time of cerium would be clearly distinguished. The decay time measurements were made using the scanning property of the gate whereas the spectra measurements used only the fixed gate option. Sometimes the fixed gate position was delayed with respect to the laser pulse so that time-resolved spectra can be obtained. All measurements were recorded by the HP chart recorder. The entire system was designed to resolve a decay with an accuracy of ± 5 ns.
Fig. 5.7 Block Diagram for Photoluminescence Experiments
EXPERIMENTAL RESULTS AND CONCLUSIONS

This chapter is divided into two main sections, namely, the cathodoluminescence and photoluminescence experimental results.

6.1 CL parameters as a function of position on the crystal

A well polished Ce:YAG crystal was used to study the CL intensity, sample current and the ratio of defect to cerium emission peak as a function of position of the crystal. (See figure 6.1) Results showed CL intensity in the range of 3.5 to 8.8 arbitrary units of intensity. The ratio of defect to cerium emission peak in the range of 1.46 to 2.63. The sample current was in the range of 1.2 to 2.4 μA. The upper portion of the crystal had approximately doubled the sample current as compared to the lower portion of the crystal. Each spot was repeated for at least two runs for their CL emission spectrum. The results in figure 6.1 show that the CL properties of Ce:YAG sample are reproducible and is fairly uniform over the entire sample.
Chapter 6

All measurements are made at 300 °K

Figure 6.1 CL intensity, sample current and defect to cerium emission intensity as a function of position of beam spot
6.2 CL 'burning' effect experiment

Prolonged electron beam bombardment on Ce:YAG was observed to have a 'burning' effect on the sample. The crystal surface darkened and the CL emission spectra became distorted. This is illustrated in figure 6.2. Both the cerium and defect emission bands were affected. The darkening of the sample may be explained by the formation of color centers. It is possible for electron bombardment to remove certain ions from the crystal surface and create color centers. However, the darkened surface did not bleach after exposing to air and daylight over long periods.
FIG. 6.2 CATHODOLUMINESCENCE SPECTRUM OF A BURNT Ce:YAG SAMPLE
6.3 Relationship between CL intensity and e-beam current density

In our CL experiments on e-beam current density, an approximate linear relationship was found for both defect and cerium emission. A metal mask with a hole was used to limit the area of the e-beam on the target. Both sample current and metal mask current were measured and plotted as shown in figure 6.3. The linear relationship between current on metal mask and crystal sample current indicates no change in the e-beam diameter with increasing current. Therefore the current density on crystal can be measured. Figure 6.4 shows plots of CL intensity against sample current density for both defect and cerium emissions. These plots are found to be fairly linear. However, the defect emission band appears to saturate at about 2 mA/cm with an e-beam energy of about 17 KeV.

When the e-beam current density falls below 0.1 mA/cm the defect emission intensity is larger than the cerium intensity as seen in figure 6.5. Van der Weg (65) has reported that CL intensity for his sample Ce_{0.02}:Y_{2.99}Al_{0.1}O_2 is linearly proportional to incident e-beam current density up to a power density of 10 Watts/m.
Current on metal mask

$\mu A$

FIG. 6.3 MASK CURRENT Vs CRYSTAL CURRENT
Experimental results and conclusions

FIG. 6.4 GRAPH OF CL INTENSITY Vs CURRENT DENSITY

CL INTENSITY (mV)

290nm

550nm

Current Density

mA/cm²
FIG. 6.5 CL SPECTRA AT TWO CURRENT DENSITIES

CL Intensity
mV

0.1 mA/cm²

0.07 mA/cm²

300 400 500 600 700 nm
6.4 Electric field effects on CL intensity

An aluminum mask with finger electrodes of the shape as shown in figure 6.6 was deposited on the front surface of the Ce:YAG crystal sample. Five masks were used on the same sample with each mask rotated 45° from each other to cover a total angle of 180°. Since the application of a dc voltage across the electrodes a and b, the electric field alternates between each adjacent pair of fingers. The results of the lateral electric field experiments were negative. This result is not surprising because YAG crystallographic group is cubic and therefore inversion symmetry prevents electro-optic effects. Hence the CL parameters are independent of crystal orientation.

Longitudinal electric field experiments were also performed on the crystal sample. The application of an electric field of order 1.5 KV/mm across the crystal sample in the same direction of the electron beam impinging upon the sample suppressed a small fraction of the CL intensity in both the defect and cerium emission bands. The biasing scheme used for this case is illustrated in figures 6.7a and b where the front surface electrode was grounded so that the incoming electrons cannot see the electric field in the crystal sample.
FIG. 6.6 Aluminum mask with finger electrodes
Experimental results and conclusions

FIG. 6.7a Longitudinal e-field in \( \hat{x} \) direction

FIG. 6.7b Longitudinal e-field \(-\hat{x}\) direction
550nm Emission
Sample thickness 1.6 mm

FIG. 6.3 GRAPH OF CHANGE IN CL INTENSITY wrt ELECTRIC FIELD

Applied Voltage with electric field in the direction of electron beam
When the direction of the applied electric field was reversed (See figure 6.7b) an enhancement of the CL intensity was observed. Figure 6.8 shows the plot of change in CL intensity before and after electric field is applied against the applied voltage.

Saturation of a CL intensity was observed due to longitudinal electric field applied. This is seen in figure 6.8.

This effect can perhaps be understood in the following way. W Ehrenberg et al. (31) have shown that the luminescence profiles in various materials excited by electron beam depends on the primary electron penetration depths. The application of longitudinal electric field in the crystal either increases or decreases the penetration depth and hence determines the profile of luminescence.

In our case there is a limit to which the electrons can be stopped by the electric field. The electron beam can always remain at the interface x = 0, if the electric field opposes penetration. In this case the value of \( I_0 \) would be the luminescence intensity due to surface cerium ions being excited. \( I_0 \) therefore depends only on the surface density of the cerium ions. On the other hand the luminescence intensity also saturates when penetration depth is very deep. The luminescence profile for deep electron penetration appears like a tear drop with a long tail as shown in figures 6.9a and
b. It should be noticed that the effective volume of luminescence does not increase significantly for increasing penetration depth after a tear profile is observed. Therefore the luminescence intensity observed would be solely dependent on the number of secondary electrons found in the tear drop. Such electric field effects have been observed by many researchers, such as D. W. Satchell (71). There is also a limit to which an electric field can be applied since dielectric breakdown will ultimately set in.
Experimental results and conclusions

Fig. 6.9 LUMINESCENCE PROFILES OF DEEP ELECTRON PENETRATION.
6.5 PL spectra measurements

a) General

The PL spectra of both undoped and Ce:YAG are quite similar to their counterparts CL spectra. However, the intensity of the defect emission was always much smaller than the cerium emission in the case of PL. A Schott WG305 filter was used in front of the spectrometer slit in all PL experiments for $\lambda$ greater than 310 nm. This is essential to keep any scattered 266 nm laser beam out of the spectrometer. Therefore the PL spectra are good only for $\lambda$ greater 310 nm.

b) Self induced absorption in Ce:YAG

A few features about PL spectra are noteworthy. In the Ce:YAG sample, there was a dip at 340 nm in the PL spectra (See figure 6.10) which was not observed in the CL spectra. This is because under PL, emission takes place all along the beam path throughout the bulk of the Ce:YAG sample, and the emission can be absorbed by the second 5d cerium band before it exits the crystal. This effect is known as self induced absorption. This effect was not observed in CL spectra because CL is truly a surface phenomenon.
Pump Laser set at 266 nm, 1 mW, 10 Hz
Spot diameter 2 mm Slit width 500 μm
10 ns gate, 20 ns away from Laser rising edge
(Nov/An-H₂ Ce/300-SiO)

340 nm dip Sensitivity 500 mV
PMT -1000 V
(483 x 5)

Sensitivity
2.5 V
PMT -600 V

FIG. 6.10 Photoluminescence Spectrum of H₂ annealed Ce-YAG at 300 °K
c) The defect emission peak shift

A shift of the emission peak to a shorter wavelength was observed for both cerium band and the defect band when the samples were cooled to 77 °K. Our explanation for the defect band shift when cooled to 77 °K is that the defect band is formed by a number of defect states with different activation energies. Activation energy is the excess energy over the ground state which must be acquired by an electron to re-emit. Once the electron is freed from its trapping site, it can reach for the conduction band, or move to another neighboring site for recombination. Radiative recombination of the depopulated electron produces the observed defect emission. Different defect states have different activation energies and they are located at different sites in the crystal. Therefore at lower temperatures only those defect states with lower activation energies would have a chance to depopulate. The probability for such an event is given by $A \exp \left(-\frac{E_a}{kT}\right)$ where $A$ is a constant and $E_a$ the activation energy of the trap. The lower activation energy traps are assumed to be associated with shorter emission wavelength for their radiative recombination. Hence the effective emission band peak shifts to a shorter wavelength at lower temperature.

d) The cerium emission peak shift

At 300 °K, the Ce:YAG CL or PL emission spectra show a peak at 550 nm. However, this peak is shifted to 523 nm (See figure
6.11) when cooled to 77 °K. This shift in peak may be attributed to a change in the matrix element for the allowed electric dipole transition 5d $\rightarrow$ $^2F_{7/2}$ with the temperature. The broad band emission peak at 550 nm is most probably the result of superposition of two equally strong emission bands situated on both sides of the 550 nm wavelength. These two emission bands correspond to the two electric dipole allowed transitions 5d $\rightarrow$ $^2F_{7/2}$ and 5d $\rightarrow$ $^2F_{5/2}$.

The $^2F_{7/2}$ state decays non-radiatively to the $^2F_{5/2}$ state because they are of the same parity. The non-radiative decay involves phonon emission. Di Bartolo (29) shows that the probability of emission of phonons has a temperature dependent factor given by $1/[1 - \exp(-\hbar \omega /kT)]$. At low temperatures the probability of emission of phonons decreases. Therefore the decay rate in relation also decreases. The occupancy of the $^2F_{7/2}$ level increases at low temperature. The matrix element for the 5d $\rightarrow$ $^2F_{7/2}$ transition decreases since there are less unoccupied $^2F_{7/2}$ state available. The emission band arises from the 5d $\rightarrow$ $^2F_{7/2}$ transition begins to saturate. As a result an apparent shift in the emission band peak to 523 nm at 77 °K is observed. The emission band peak due to 5d $\rightarrow$ $^2F_{7/2}$ transition is expected to be located at $1/\lambda = (2/550 \text{ nm}) - (1/523 \text{ nm})$ where $\lambda$ is found to be 580 nm.

The related energy split between the 4f levels is therefore

$$10^7 ((1/523 \text{ nm}) - (1/580 \text{ nm})) = 1900 \text{ cm}^{-1}.$$ A rounded value of
2000 cm\(^{-1}\) was used in the crystal field calculations. In addition the investigation of A. Bril (12) at 4.2 °K revealed emission band peaks of Ce:YAG to be located at 19,100 cm\(^{-1}\) (523.56 nm) and 17,400 cm\(^{-1}\) (574.71 nm) which is in close agreement with our results.

From the excitation and emission spectra we conclude that the cerium bands are located as shown in the energy level diagram, Figure 5.12.
Pump Laser set at 266nm, 1mW, 10Hz
Spot diameter 2mm Slit width 110/500 μm PMT -1000V
10ns gate, 20ns away from Laser rising edge
(Nov/An-H₂ Ce/77-Si4) Sensitivity 2.5V

FIG. 6.11 Photoluminescence Spectrum of H₂ annealed Ce:YAG at 77°K

340 nm dip

x39
Chapter 6

Energy Level Band Diagram for Ce: YAG

FIG. 6.12
e) Relationship between PL and CL intensity of defect bands

The PL intensity of the defect band is much weaker than the CL intensity of the defect band. This significant difference in intensity can be explained from observing the excitation band for the 290 nm emission (See figure 6.13 for the undoped YAG sample). In PL experiments the 266 nm laser excite at the long wavelength part of the excitation spectra. The excitations at shorter wavelengths are much more effective than at long wavelengths. Since the CL excitation is an above bandgap excitation, therefore CL would be more effective than the PL 266 nm excitation.
FIG. 6.13

EXCITATION SPECTRUM OF UNANNEALED CE:YAG  T = 300 K
EMISSION WAVELENGTH: 290NM
XX316 XX317

NORMALIZED INTENSITY

50
40
30
20
10
0

200 210 220 230 240 250 260 270 280
EXCITATION WAVELENGTH (NM)
f) Annealing effects on excitation spectra

The 290 nm excitation spectra for the different annealed samples are quite similar except in the region of 205 nm. The results are not conclusive as far as indentifying peaks related to oxygen vacancies or interstitials.

However, the excitation spectra for the 550 nm emission includes some differences due to the annealing processes. The annealed samples have a lower 460 nm excitation value than the as-grown sample at 300 °K. (See figures 6.14-8) However, at 77 °K the reverse is true. Annealing in different atmospheres also affect the ratios among the 223 nm, 340 nm and 460 nm excitation. At 77 °K both ratios (Intensity at 223 nm/Intensity at 460 nm), (Intensity at 340 nm/Intensity at 460 nm) are relatively weaker than the 300 °K values. This change in ratios with respect to temperature should be related to the change in absorption spectra peak ratios as observed by D. J. Robbins (64).

Note: The excitation spectra for the 290 nm emission are the same for both undoped and cerium doped YAG samples. Compare figure 6.18 with figure 6.13. This implies that the excitation mechanisms are the same for both type of samples.
Excitation spectra of CE:YAG at 300°K
Emission wavelength: 550 nm

Uncorrected for system response
ANNEALING DATA

---

NONE XX342KR
IN H2 XX343KR
IN O2 XX344KR

EXCITATION SPECTRUM OF CE:YAG AT 77K
EMISSION WAVELENGTH: 550 NM

UNCORRECTED FOR SYSTEM RESPONSE
FIG 6.16

EXCITATION SPECTRUM OF UNANNEALED CE:YAG
EMISSION WAVELENGTH: 550 NM
KEREX X342 X297

DOTS: \( T = 77^\circ\text{K} \)
LINE: \( T = 300^\circ\text{K} \)

CORRECTED FOR
SYSTEM RESPONSE
Excitation Spectrum of Ce:YAG $T = 300\, K$
Emission Wavelength: 550 NM
Kerex X297, X306, X307

Corrected for system response

Unannealed
H2 Annealed
O2 Annealed

Intensity

Wavelength (NM)
FIG 6.18
EXCITATION SPECTRUM OF UNANNEALED CE:YAG  T = 300 K
EMISSION WAVELENGTH: 290NM
XX316 XX317
Experimental results and conclusions

6.5 PL DECAY TIME MEASUREMENTS

PL decay measurements were made on six YAG samples as listed below:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Undoped YAG</th>
<th>Ce:YAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>H-annleled</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>O-annleled</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Using the setup as shown in Figure 5.7, decay times were measured in two ways: (a) A direct measurement at fixed emission wavelength as a function of time, (Fig. 5.6) (b) An indirect decay measurement can also be obtained from the time resolved emission spectra. The time resolved spectra gives a complete picture of decay times for a continuous band of wavelengths during a discrete decay time interval.

The specific wavelengths selected in direct measurement are 290 nm, 320 nm, 340 nm, 370 nm, 460 nm, and 550 nm. PL emission decay tables are given in Tables 6.1-5. In addition graphical plots for both cerium and defect decay for the samples are given in figure 6.19-21.
### TABLE 6.1 DECAY PARAMETERS FROM SPECTRA FOR UNDOPED YAG

The table provides decay parameters from spectra for undoped YAG. The abbreviations used in the table are as follows:

- **D** - Gate Delay Time
- **G** - Gate Width
- **W** - Band Width
- **I_t** - Defect Intensity at 320 nm
- **I_c** - Cerium Intensity at 550 nm

<table>
<thead>
<tr>
<th>T(K)</th>
<th>UNANNEALED</th>
<th>H₂ ANNEALED</th>
<th>O₂ ANNEALED</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>ns</td>
<td>mv</td>
<td>nm</td>
</tr>
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<td></td>
<td>D</td>
<td>G</td>
<td>I_t</td>
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<td>77</td>
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<td>0.05</td>
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### TABLE 6.2 DECAY TIMES AT GIVEN WAVELENGTH FOR UNDOPED YAG.

<table>
<thead>
<tr>
<th>℃ (°K)</th>
<th>λ (nm)</th>
<th>τ₁</th>
<th>τ₁₀</th>
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<th>τₚ</th>
<th>τ₁</th>
<th>τ₁₀</th>
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<th>τₚ</th>
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<th>τ₁₀</th>
<th>τ₂</th>
<th>τₚ</th>
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<td>290</td>
<td>-</td>
<td>1.32</td>
<td>0.64</td>
<td>5.5</td>
<td>-</td>
<td>1.5</td>
<td>0.64</td>
<td>5.5</td>
<td>-</td>
<td>1.5</td>
<td>0.91</td>
<td>3.6</td>
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<tr>
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<td>-</td>
<td>8.0</td>
<td>3.7</td>
<td>10.0</td>
<td>24</td>
<td>5.2</td>
<td>2.18</td>
<td>10.0</td>
<td>-</td>
<td>9.0</td>
<td>1.28</td>
<td>9.0</td>
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<tr>
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<td>320</td>
<td>-</td>
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<td>0.79</td>
<td>5.0</td>
<td>58</td>
<td>1.6</td>
<td>0.79</td>
<td>5.0</td>
<td>-</td>
<td>2.0</td>
<td>0.80</td>
<td>5.0</td>
</tr>
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<td>320</td>
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- **τ₁**: Short Decay (1⁄2 Value) Time
- **τ₁₀**: 10% to 90% Decay Time
- **τ₂**: Long Decay Time (1⁄2 Value)
- **τₚ**: Persistence Time

**UNDOPED YAG**


### Table 6.3 Decay Parameters from Spectra Measurements and Decay Times for Unannealed Ce : YAG

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### Ce : YAG

**$H_2$ ANNEALED**

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**Table 6.4: Decay Parameters from Spectra Measurements and Decay Times for $H_2$ Annealed Ce : YAG**
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FIG. 6.19 PL Decay plot of As Grown samples of YAG

As Grown

DOPED

Cerium 550nm emission

Defect 320nm emission

UNDOPED-Defect 320nm emission

Ce~7Ons

PL Intensity

PMT Voltage (mV)

0 500 1000 1500 2000 2500

TIME in ns

0 0.04 0.1 0.4 1

300°K 77°K

* K

Experimental results and conclusions

page 160
FIG. 6.20 PL Decay plot of H$_2$ annealed samples of YAG

- **H$_2$ Annealed**
  - Cerium: 550nm emission
  - Defect: 320nm emission

- **300°C**
  - ×
  - ○

- **77°C**
  - △
  - ⊙

Ce ~ 70ns
FIG. 6.21 PL Decay plot of O$_2$ annealed samples of YAG

Experimental results and conclusions
The following conclusions are observed from decay measurements:

a) All the cerium doped YAG samples give a strong 550 nm cerium emission with two decay times. The short decay of 70 ns dominates the long decay of 800 ns in intensity for \( t < 400 \) ns. The reverse is true for \( t > 400 \) ns.

b) The short decay component of 70 ns is associated with the cerium intrinsic lifetime. Therefore this decay must be a direct process. The weak long decay components of 800 ns implies that the energy transfer mechanism to cerium is an indirect process.

c) At 300 °K, the defect emission at 320 nm for the six samples has a decay time about 800 ns. This decay time matches that of the long decay component of cerium.

d) Assuming the ratio of intensity due to a direct process to the intensity due to the indirect process of the cerium emission to be equal to the ratio of intensity of cerium emission at 550 nm (I\(_c\)) to intensity of defect emission at 320 nm (I\(_t\)). Let the cerium short decay component be represented by A exp (-t/70 ns) and the long decay component of cerium be represented by B exp (-t/800 ns). The first assumption says that A/B = I\(_c\)/I\(_t\) = exp(1/70 ns - 1/80 ns)t = exp(t/76.71)ns. Therefore the 'breakpoint' at which the indirect process becomes signif-
Experimental results and conclusions

icant is given by $t = 76.71 \ln (Ic/It)$ ns. The values of breakpoints for the six cases are:

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<td>Un-Ce 77</td>
<td>$t = 76.71 \ln 185 = 400$ ns</td>
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<tr>
<td>O-Ce 77</td>
<td>$t = 76.71 \ln 90 = 345$ ns</td>
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The breakpoint analysis gives a value of about 400 ns which is in close agreement to the value given in part (a). This calculation supports the evidence of a relationship between the 320 nm emission and the long decay cerium emission.

e) At 77 °K, decay times of defect emission at 320 nm increases in all six samples. This effect can be observed as the slopes of the lines from figure 6.19-21

f) Short decay times are found in the defect emission of most samples but they are generally very weak. At 77 °K, the undoped hydrogen annealed sample gives a very strong, short decay time emission with its peak at 460 nm. The emission intensity peak at 460 nm is roughly equal to that at 320 nm. However, the decay time at 460 nm is only about 12 ns. We therefore believe that this emission bears no relationship to the 320 nm emission. The emission spectra for this short decay emission is identical to that obtained by K. Mori (58). According to K. Mori, this
emission is due to electrons trapped at oxygen vacancy sites. Since this sample is annealed in hydrogen, oxygen vacancies are very likely. However, at 300 °K, the emission is absent which probably could imply instability of trap at high temperatures.

6.6 summary of conclusions

Our CL experiments suggest that CL emission intensity and spectra can be utilized to characterize properties of Ce:YAG so long as precautions are taken against the 'burning' process under prolonged electron beam exposure.

A linear relationship between CL intensity and beam current density is found for both cerium and defect emission.

Lateral electric surface fields do not affect both CL intensity and spectra. However, longitudinal electric field does affect CL intensity and its relationship is believed to be related to an alteration of penetration depth of electrons in the material.

The great difference in ratio of defect emission to cerium emission between CL and PL experiments have been explained with the aid of the excitation spectra for emission at 290 nm. Wave-lengths shorter than 266 nm excite the 290 nm defect emission band much more efficiently than longer wavelengths.
Experimental results and conclusions

An energy level diagram for Ce:YAG was derived and the crystal field splitting parameters were determined.

The shift in cerium emission emission with respect to temperature is explained in terms of saturation of the $^{2}F_{7/2}$ state.

Decay times for various emission wavelengths were determined. These times support the evidence of energy transfer from defect states to the cerium ions.

In addition we have found that the optical absorption of Ce:YAG below the bandgap can be resolved into a component associated with lattice defects and a component associated with direct absorption by cerium ions.
FLYING SPOT SCANNER

A flying spot scanner is used for production of TV video signals from films or transparencies by scanning the photographic image with a 'flying spot' light source of constant intensity, developed on the face of a cathode-ray tube with a short persistence phosphor. The spot of light is made to follow the conventional raster pattern so that a phototube receiving transmitted or reflected light from the subject will have a signal output proportional to the subject brightness and the subject position as required.
FIG. APPI-1  TELEVISING A COLOR FILM WITH FLYING SPOT SCANNER
APPENDIX 2

CHROMATICITY DIAGRAM

It is a plane diagram, as shown in Figure App2-1, formed by plotting one of the three chromaticity co-ordinates against another. Nearly all colors in the visible spectrum can be faithfully reproduced on the screen of a color television tube. The principle of color reproduction is to mix three primary colors, red, green and blue in intensity ratios determined from the color co-ordinates of the desired color TV, three distinct color spots are produced accordingly in close proximity. The human eye being unable to resolve the colors perform mixing which gives the apparent desired color. An example to illustrate the application of chromaticity diagram is to calculate the intensity ratios required for color mixing. This example is described as follows:

There are three phosphors with color co-ordinates of values R, G and B as shown in figure App2-1. These phosphors are to be mixed in a particular intensity ratio so that it is perceived as white light having the color co-ordinates given by point W. The three points R, G, and B form three vertices of a triangle. Any color having color co-ordinates enclosed by this triangle can be produced by these three phosphors. Two lines BX and RY are drawn from two of the three vertices through point W. Applying the lever principle to the pivot points X, Y on the
Appendix 2

APPENDIX 2

CHROMATICITY DIAGRAM

lines RG and GB, the color intensity ratios for the three phosphors can be derived as follows:

RED/GREEN = GX/RX and BLUE/GREEN = GY/BY

which can be expressed alternatively as

RED:GREEN:BLUE = BY.GX:BY.RX:GY.RX
CHROMATICITY DIAGRAM

 Δ Color co-ordinates for blue phosphor - B
 o Color co-ordinates for green phosphor - G
 x Color co-ordinates for red phosphor - R
 W is the desired white point in the locus of black body radiation at temperature 6000 °K

 Locus of Black Body Radiation at various temperature

 FIG. APP-2-1  CHROMATICITY DIAGRAM
REFERENCES


REFERENCES


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