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X-Ray Induced Luminescence of Sapphire and Ruby

Ivan Collier Jr.

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X-RAY-INDUCED LUMINESCENCE OF SAPPHIRE
AND RUBY

A Thesis

Presented to

the Faculty of the Department of
Physics and Astronomy
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Ivan E. Collier, jr.

August 1970

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X-RAY INDUCED LUMINESCENCE OF SAPPHIRE
AND RUBY

APPROVED Sept 3, 1971;
(date)

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INTRODUCTION

Over the past decade the luminescence properties of sapphire ($\alpha\text{-Al}_2\text{O}_3$) and ruby ($\text{Al}_2\text{O}_3:\text{Cr}_2\text{O}_3$) have been the subject of many investigations because of their importance in materials technology. Sapphire and ruby are at present used as lasing materials, radiation dosimeters, and as optical windows. In order that these operations may be made more efficient, and that other useful luminescent properties may be systematically explored and developed, much attention has been given to understanding the luminescent mechanisms from the standpoint of the physics of the solid state. However, mechanisms have not yet been proposed that describe in detail the known luminescent properties of sapphire and ruby.

The luminescence experiments which have been previously reported in the literature on sapphire and ruby fall into two classes: experiments in which the exciting energy is stored in the crystal by some defect mechanism and subsequently released by perturbing the crystal, and experiments in which the luminescence is observed while the crystals are being excited. Thermoluminescence, in which energy is stored in the crystal by exposing it to ionizing radiation and subsequently released by raising the temperature of the crystal, is the most extensively used technique of the former class. The facts concerning the thermoluminescence of sapphire and ruby are well documented. (11, 12) Numerous experiments in the latter class have been reported in which the exciting radiation was in the visible or ultraviolet energy region. (16, 17) These latter experiments have a disadvantage; the amount of exciting energy absorbed is not independent of two important parameters, temperature and chromium concentration.

It was the primary intent of these investigations to resolve the difficulty of the dependence of the absorbed energy by exciting sapphire and ruby crystals with x-rays. Because the energy of the x-ray photons incident on and within the crystal is more than an order

of magnitude more energetic than is necessary to produce highly mobile or free electrons within the crystal, the number of such electrons produced is independent of the temperature and chromium concentration over the range that these parameters were varied.

The program of experiments reported herein was designed to answer the following questions: (1) How does the intensity of the total luminescence depend on the temperature? (2) How does the emission spectrum depend on temperature and chromium concentration? (3) How does the luminescence yield depend on temperature? The answers to these questions were obtained by observing the luminescence of sapphire and ruby, subjected to continuous x-ray excitation, as a function of temperature and chromium concentration. The total x-ray-induced luminescence and emission spectra of two crystals, one nominally pure sapphire and the other sapphire containing 0.005% Cr_2O_3 , were observed as the temperature of the crystals was raised and lowered between 25°C and 400°C . The results for other chromium concentrations (0.05% and 0.5% Cr_2O_3) may be found in Mr. Wayne Cooke's masters' thesis.⁽²¹⁾ The thermoluminescence total emission and emission spectra were observed between 25°C and 400°C after x-ray exposure at room temperature.

It should be noted that there is one experiment in the literature in which the x-ray-induced luminescence of ruby was observed as a function of temperature.⁽¹⁹⁾ The investigators observed the luminescence as the temperature increased; hence, much of the emission was thermoluminescence. The experiments described in this report overcome the difficulty by observing the emission as the temperature decreases because the energy stored in a crystal at a particular temperature has a decreasing probability of being released at lower temperatures.

CHAPTER I

LITERATURE REVIEW

Introductory Comment

Many of the properties of solids, such as x-ray and electron diffraction, and macroscopic shape, may be explained in terms of the spatial periodicity of their constituent atoms; however, many other solid state properties such as x-ray diffraction intensities, mechanical properties, color, and electrical conductivity cannot be explained quantitatively in terms of the periodic or lattice structure alone.⁽¹⁾ One of the predominant features of solid state physics is that it explains the properties of solids in terms of both the lattice and defect structure, or deviations from periodicity, of solids.

Solid state luminescence, which is defined in accordance with Leverenz⁽²⁾ as "a process whereby matter generates non-thermal radiation which is characteristic of the particular luminescent material", is typical in that the theoretical explanation involves the periodic structure - defect structure dichotomy. The theory of solid state luminescence may thus be divided into two parts, lattice luminescence and defect luminescence.

The Sapphire Lattice and Its Electronic Structure

The Crystal Structure of Sapphire (α - Al_2O_3) - The most important feature of the crystal structure of sapphire for these investigations is the anisotropy of its optical and luminescent properties with respect to direction in the lattice. It is well known that ruby and sapphire have an axis of three fold symmetry (C-Axis) and that the optical absorption and polarization of the luminescent emission are different when observed parallel and perpendicular to this axis. Thus, the importance of this subsection is the identification of the C-Axis.

Bartram et. al. (3) report that the structure of $\alpha\text{-Al}_2\text{O}_3$ can be viewed as a slightly distorted hexagonal close packing of O^{2-} ions with two out of three of the interstices of that structure filled with Al^{3+} ions. When the distortion, which is a deviation of the angles between the oxygen atoms from that of true close packing, is taken into account, the primitive cell of sapphire is trigonal. The angle between any two of the primitive translation vectors is $55^\circ 17'$ and the magnitude of the vectors is 5.124\AA (3). The C-Axis passes through the origin of the trigonal cell and is perpendicular to a plane with Miller indices (1,1,1). The origin of the cell is centered on either a chromium ion or a void in the crystal. Laurance et. al. (4) include two good drawings of the sapphire structure showing the lattice and the position of the C-Axis. The Electronic Structure of Sapphire - Nominally pure sapphire is a good insulator and, unless the crystal has been exposed to large amounts of ionizing radiation, appears to the eye to pass light of all wavelengths. Hence, one would expect that the outermost energy band for electrons in the sapphire lattice is sparsely populated, that the next lowest energy band is quite heavily populated, and that the forbidden gap between them is of the order of several electron-volts.

Indeed, the previous observations are the case. Measurements of the fundamental optical absorption of sapphire and conductivity versus temperature reveal a band gap of between eight and nine electron-volts. Dunkelmann et. al. (5) report an absorption edge at 8.66eV. The Linde Company (6) reports an absorption edge at 8.55 electron-volts. Measurements of conductivity versus temperature by Harrop and Creamor (7) lead to a calculated width of the forbidden gap of 9.28eV.

The luminescence due to the recombination of an electron in the conduction band with a hole in the valence band has not been observed with certainty. Runciman (8) has observed the x-ray-induced luminescence at 4°K and 77°K of nominally pure Linde sapphire. He observed a 1650\AA band with a temperature independent half-width of .8eV and a broad 2000\AA to 3500\AA band whose shape was temperature dependent. Because of the temperature dependence of the peak height of the 1650\AA band, Runciman concluded that this might be recombination luminescence, and that the longer wavelength band was due to an impurity, possibly iron. Lehman and Gunthard (9) studied the luminescence of nominally pure sapphire with flash light excitation. These

researchers report a luminescent emission band with a peak at 3300\AA . By limiting the pass band of the exciting light, the emission at 3300\AA was related to an absorption peak at 2060\AA , well above the onset of charge transfer absorption in the sapphire lattice which should occur at wavelengths below 1450\AA .⁽⁹⁾

Defects in The Sapphire Lattice - Defects in the sapphire lattice make their existence manifest in several ways. They are the principal cause of optical absorption and luminescence in the visible and ultra-violet energy regions. However, the mechanism of absorption and luminescence is not well known and in this section, four types of defects which have been proposed in the literature will be discussed.

Gamble et. al.⁽¹⁰⁾ have observed in single crystal sapphire a gamma radiation induced electron spin resonance (ESR) line. The ESR line which was observed at 77°K could be removed by raising the temperature of the sample. A stepwise annealing process showed an abrupt change in the number of spins/ cm^3 after a 150°C anneal. The abrupt change at 150°C suggests a correlation between a thermoluminescence glow peak in sapphire reported by Rieke and Daniels⁽¹¹⁾ at 164°C , by Sujak and Niklas⁽¹²⁾ at 143°C , and observed by the author of this report at 150°C .

Gamble et. al.⁽¹⁰⁾ have proposed trapped hole and electron centers to explain the ESR line. Initially present as defects in the Al_2O_3 lattice are charge deficient cation sites compensated for by an anion vacancies. The charge deficient cation site is either a vacancy, or a divalent or monovalent substitutional impurity. Radiation induced electrons become trapped at anion vacancies and the holes become trapped at charge deficient cation sites, but are localized near an anion so that the trapped hole can be visualized as an O^- defect.

Bartram et. al.⁽³⁾ have made crystal field calculations of the energy levels of an O^- ion near a charge deficient cation using the charge deficiency as a variable parameter. The investigators found the best agreement with the ESR experiment mentioned in the previous paragraph by assuming a cation vacancy rather than a monovalent or divalent impurity.

The addition of chromium as an impurity to Al_2O_3 is thought to create in sapphire at least three different types of defects, the relative number of which depends on the chromium concentration and the

history of the crystal. Chromium enters the sapphire lattice in substitution for aluminum ions and for the most part is in the triply oxidized state. It is the Cr^{+3} which is responsible for the characteristic red color of ruby crystals. There is good evidence of the existence of doubly and quadruply ionized states of the chromium ion. (14)

In two papers on the color centers of ruby, Arkhangelskii et al. (14, 15) have observed the ESR, the luminescence quantum yield, and the additional absorption of ruby crystals colored by x-, γ -, and intense optical radiation. From the studies of the ESR of colored crystals, (14) it was concluded that the decrease in the number of Cr^{+3} ions was concurrent with the coloration of the crystal. When the crystals were colored with optical radiation, the decrease was 5% and when α -rays were used, the decrease was 20%. (15) Arkhangelskii and his colleagues concluded that the Cr^{+3} center was acting as a trap for both electrons and holes generated by the radiation. Additional absorption bands also appeared in these crystals after exposure to the radiation. (14)

Arkhangelskii and his colleagues studied the luminescence quantum yield of the crystals (15) and found that the additional bands were either active or inactive; that is, when colored crystals were exposed to light corresponding to the wavelengths of absorption, the active bands produced luminescence in the R-line region while the inactive bands produced comparatively little luminescence. It was concluded that the active bands were due to Cr^{+2} ions, whose excited states lie in the conduction band. Hence, absorption by these centers produces a conduction electron which can recombine to produce luminescence. The inactive bands are attributed to Cr^{+4} centers since it is unlikely that this ion could lose another electron. It was observed that active bands were thermally bleached, along with luminescence in the R-line region, at 300°C. A thermal energy of activation of 1.5eV was calculated for this process.

Hoskins and Soffer (24) have grown chromium doped sapphire crystals using methods that would favor the formation of Cr^{+4} rather than Cr^{+3} . Nitrides were added to the materials from which the crystals were grown in order to produce N^{-3} in the crystal to compensate for the extra charge on the Cr^{+4} ion. The concentration of chromium without regard to oxidation state was measured by emission spectroscopy, and the concentration of Cr^{+3} was measured by ESR methods.

The difference in the two concentration measurements was taken as the concentration of Cr^{+4} . An electron spin resonance was observed which was not previously reported for Cr^{+3} and was attributed to Cr^{+4} . The crystals showed only a small amount of red luminescence when excited by mercury vapor lamp.

Luminescence and (Exo) Electron Emission Studies

Luminescence Studies - A number of luminescence studies have been performed on sapphire and ruby which were not discussed in the section on defects. These articles were for the most part experimental in nature and offer little discussion of the theory of defect centers. These articles are discussed in the following paragraphs.

The long wavelength (6500 \AA -8200 \AA) emission spectra of Al_2O_3 doped with chromium has been observed by both Tolstoi et. al. (16), and Powell et. al. (17). Tolstoi and his colleagues observed the luminescence of ruby crystals varying in chromium concentration from .055% to 8% Cr_2O_3 by weight. The crystals were excited by visible light from a mercury vapor lamp and the observations were carried out at -180°C . In the lightly doped chromium sample, only the doublet lines of chromium (known as the R-lines: R1, 6943 \AA ; and R2, 6929 \AA) were observed. (23) As the chromium concentration was increased, a diffuse band with a peak at about 7750 \AA and two other lines appeared in the spectrum at about 7010 \AA and 7050 \AA . It was concluded that the diffuse band and the short wavelength doublet were due to single chromium ions and that the longer wavelength pair were due to interacting chromium ion pairs.

Powell and his colleagues (17) studied the fluorescence of two ruby samples (2.1% and .94% by weight Cr_2O_3) at temperatures ranging from 15°K to 700°K . The crystals were excited by light from a mercury vapor lamp. The emission spectra consisted of four temperature dependent lines and one temperature dependent band. The observed lines were the R-lines of the single chromium ion, and the N_1 and N_2 lines (7041 \AA and 7099 \AA) of exchange coupled chromium ion pairs. These lines are due entirely to electronic transitions in the crystal. The N_1 and N_2 lines were most intense at low temperatures and the high chromium concentration. The R-lines were most intense at the low

chromium concentration and room temperature. In the temperature range from 15^oK to 300^oK, the diffuse band had an intensity maximum at about 7750Å and was structured. Above 300^oK, the low energy tail of this band extended below 6500Å, the band showed little structure, and its peak was positioned at 7100Å. The diffuse band was attributed to vibrationally assisted electronic transitions known as vibronic sidebands.

The x-ray-induced luminescence of ruby has been observed by both W. Low⁽¹⁸⁾, and Niklas and Sujak⁽¹⁹⁾. Low exposed ruby crystals to x-rays and observed luminescence in the R-line region and in two bands at 6560Å and 6650Å. When the excitation ceased, phosphorescence with a temperature dependent half-life was observed. The chromium concentration of the crystals and the temperatures at which the measurements were made were not mentioned in the article.

Niklas and Sujak⁽¹⁹⁾ observed the x-ray induced luminescence of ruby single crystals (.1% by weight Cr₂O₃) as the samples were heated under continuous x-irradiation. The temperature range was 305^oK to 705^oK. The emission as monitored with a photomultiplier tube, showed a peak at about 600^oK which correlated with a peak at 600^oK in the thermoluminescence glow. The emission spectra, reported for 300^oK and 615^oK, showed emission in the R-line region and a band at 6700Å for the low temperature. At the high temperature, the R-line was reduced in intensity and the 6700Å band increased in intensity.

Thermoluminescence Studies - Niklas and Sujak⁽¹²⁾ have also measured the thermoluminescence and thermostimulated (EXO) electron emission from sapphire and ruby samples. These observations were made on x-irradiated nominally pure sapphire and ruby (.08% and .1% by weight Cr₂O₃) crystals with a linear heating rate between 300^oK and 660^oK. In the sapphire samples, three EXO-electron emission glow peaks were observed at 463^oK, 563^oK, and 626^oK. Three thermoluminescence glow peaks were observed at the same temperature. In the ruby crystals, one main peak in the electron emission glow curve was observed at 663^oK. A thermoluminescence glow peak was observed at the same temperature. The authors concluded that the thermoluminescence mechanism involves electron and not hole transitions in sapphire and ruby.

The Theory of Glow Curves

The method of initial rise was used to calculate the trap depth of the energy levels responsible for the thermoluminescence observed in the experiments reported in this thesis. For this reason, the theory of glow curves is discussed. The discussion presented here is that of Randall and Wilkins. (20)

If an electron is trapped in a metastable energy level below the conduction band of a phosphor, then the probability of its release is a function of temperature and may be written quantitatively as:

$$P = Se^{-E/KT}$$

Where P is the probability of release per unit time, E is the depth of the energy level below the conduction band, K is Boltzman's constant T is the absolute temperature, and S is a constant. It is assumed that there is only one trap depth, E, as distinguished from a distribution of depths. Further it is assumed that the electron, once released from the trap, recombines at a luminescence center and is not re-trapped.

If N is the number of trapped electrons at any time t, then the rate of detrapping is from the definition of P

$$\frac{dN}{dt} = -NP = -NSe^{-E/KT}$$

This equation may be transposed into:

$$(1) \quad \frac{dN}{N} = -Se^{-E/KT} dt$$

And now if the temperature is increased linearly with time, we can write $dT = \beta dt$, where β is a constant. By putting $\frac{dT}{\beta}$ into (1) for dt we have:

$$\int_{N_0}^N \frac{dN}{N} = -\frac{S}{\beta} \int_{T_0}^T e^{-E/KT} dT$$

which may be integrated to obtain

$$N = N_0 e^{-S/\beta} \int_{T_0}^T e^{-E/KT} dT$$

Now the intensity of the glow is proportional to N , so by calculating the derivative of the above equation, we have

$$(2) \quad I = N_0 C S e^{-E/KT} e^{-S/\beta} \int_{T_0}^T e^{E/KT} dT$$

where C is a constant.

For sufficiently small T , equation (2) is dominated by the exponential term $e^{-E/KT}$. Hence, a semilog plot of the luminescence intensity versus reciprocal of the absolute temperature should be initially a straight line with slope E/K . This method of determining E is called the method of initial rise.

CHAPTER II

EXPERIMENTAL APPARATUS

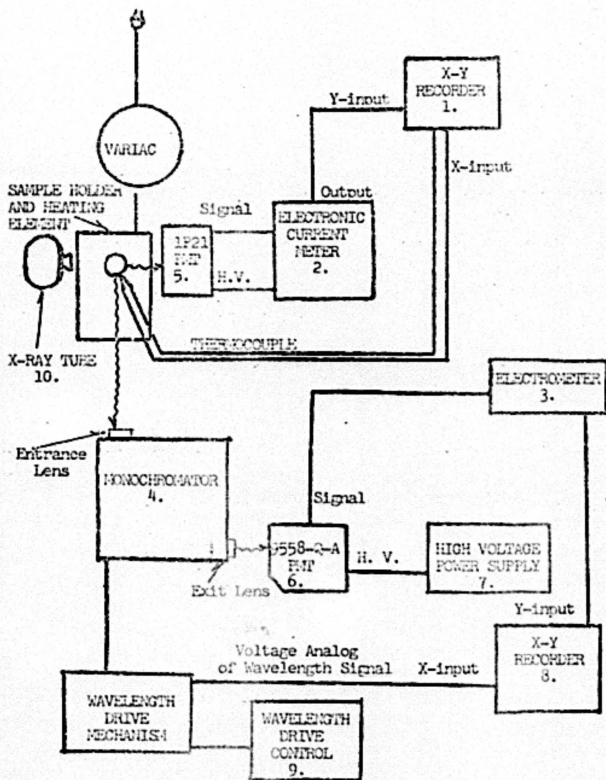
Introductory Comment

The questions which this investigation proposed to answer required the construction of an experimental apparatus that would simultaneously allow the crystals to be heated and exposed to x-rays, and both the total emission and the emission spectra to be observed. This problem was solved by constructing a spectrophotometer to scan the emission spectra, a photomultiplier tube set-up to monitor the total light, and a crystal holder mounted on a soldering iron to raise the temperature of the crystals. A mobile medical x-ray unit (150 KVP) was obtained to provide the excitation for the crystals.

Construction of Apparatus

The components used to construct the apparatus are shown schematically in figure 2-1. Light enters the monochromator through the entrance lens and is dispersed by the grating. Light leaves the monochromator through the exit lens and excites a photomultiplier tube. The photomultiplier tube current is measured by an electrometer, the output of which is used to drive the y-axis of an x-y recorder. The wavelength axis, or x-axis, is driven by the voltage drop across a ten-turn precision variable resistor. The shaft of the resistor is connected to the lead screw of the wavelength drive of the monochromator by a set of reduction gears.

The total emission of the samples was observed with an RCA 1P21 photomultiplier tube. The 1P21 photomultiplier tube (hereafter called PMT) current was measured with an electronic current meter, the output of which was used to drive the y-axis of an x-y recorder. The temperature axis, or x-axis, was driven by the voltage across a chromel-alumel thermocouple.



Schematic Diagram of Apparatus

Figure 2-1

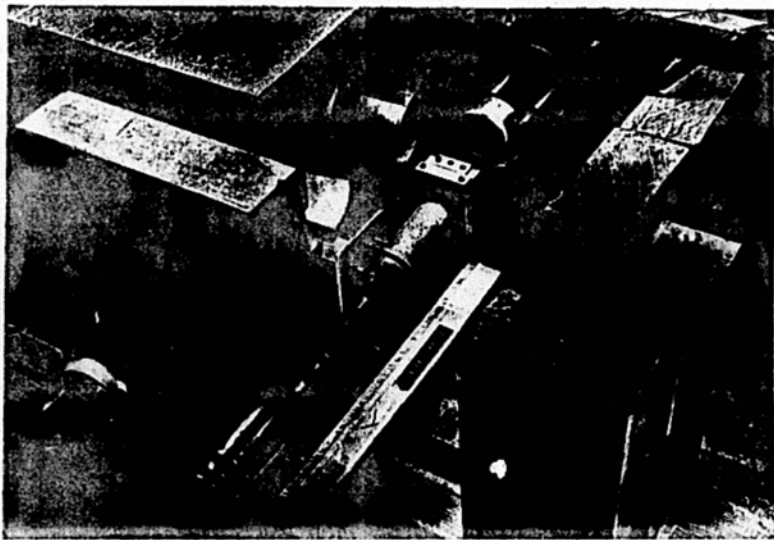
The sample holder and heating element were constructed using a 1.3 cm x 3.1 cm aluminum block, a soldering iron and a rotary table. A hole was drilled in the block and a soldering iron was fitted into the hole. The soldering iron was connected to the rotary table, the top of which slides on two ways and the position of which can be adjusted in the horizontal plane by means of two mutually perpendicular lead screws. Thus, the sample's position can be continuously adjusted with respect to the entrance lens of the monochromator. The sample is placed on top of the aluminum block and is held in place by means of a clamp. A small hole in the block, 1/16 inch below where the sample is mounted, provides a location for mounting the thermocouple. The temperatures reported in this thesis were measured by the thermocouple in this position.

Figure 2-2, a close up picture of the entrance lens, PMT, and sample holder, shows the geometric relationship of the two light collectors to the sample holder. The photograph differs from the operating conditions only in that the x-ray tube holder is lowered so that its distance from the sample holder is approximately 13 cm. An overall view of the apparatus is shown in figure 2-3.

The manufacturer and model numbers of all instruments are listed in Appendix 1. Each instrument in the list that is represented in the schematic diagram (Figure 2-1) is given a number in the schematic diagram which corresponds to that instrument's number in the list.

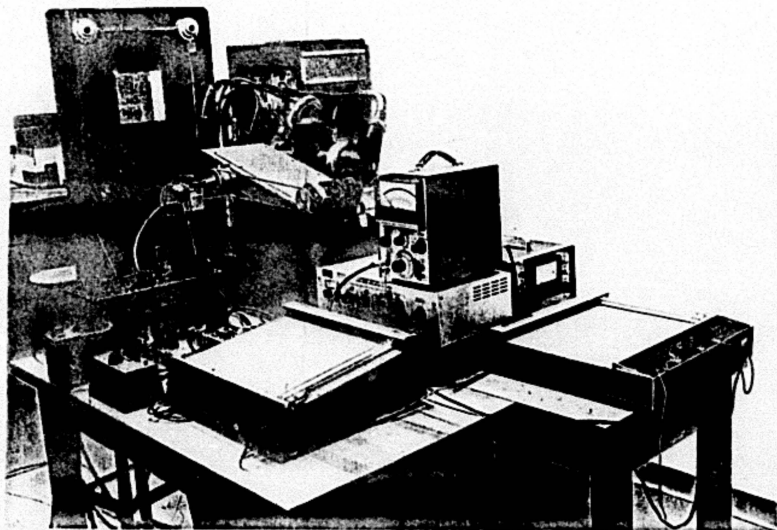
Calibration and Measurement of Parameters

Determination of the Heating Rate - To obtain a linear temperature rate over the range from 25°C to 400°C using a Variac to power the soldering iron, it was found necessary to make six voltage changes at particular temperatures as the temperature was increasing. This was determined by observing the thermocouple voltage at one minute intervals (determined by the sweep hand of a wrist watch) and trying different voltages at different temperatures until by trial and error the voltage changes and temperatures were found which produced a heating rate of near 10°C per minute. A least squares line was fitted to the temperature versus time data, and it was found that the slope of the line was 10.30°C per minute with standard deviation of 0.26°C per minute.



Close Up View of Entrance Lens and Sample Holder

Figure 2-2



Overall View of Apparatus

Figure 2.3

Determination of the Response of the Spectrophotometer - The relative spectral response of the spectrophotometer was determined using a calibrated Eppley tungsten halogen light source. The spectral irradiance of this lamp at a distance of forty centimeters has been calibrated traceable to the National Bureau of Standards. The procedure used was to take an emission spectrum of the standard lamp and calculate the number of μA of PMT current produced per unit of spectral irradiance at each of the calibrated wavelengths. Several difficulties complicated this procedure.

First, the Eppley standard is a high intensity standard, and its intensity had to be reduced in order that the emission of the lamp could be observed without over-driving the 9558-Q-A PMT. The intensity was reduced by moving the lamp as far away from the entrance lens as laboratory space allowed (eight meters) and by reducing the high voltage on the PMT from -1000V, the voltage at which the data was taken, to -580V.

Second, it was determined after the emission spectrum of the lamp was observed that two Wood grating anomalies⁽¹³⁾ existed at 5400 \AA and 6050 \AA . Since there was an emission band in the spectrum of sapphire and ruby near the second of these two anomalies, it was decided that the response of the instrument should be calibrated at intervals of 100 \AA between 5500 \AA and 7000 \AA . The data which was sent from the Eppley Company with the lamp listed calibration points at intervals of only 500 \AA . Hence it was necessary to interpolate between the 500 \AA points. It was found that for the region of interest the data of spectral irradiance versus wavelength could be fitted using the least squares criterion by a curve of $Y = A e^{-E/\lambda}$, where y is the spectral irradiance, λ is the wavelength in Angstroms, and A and E are constants to be determined by the least squares fit. The least squares calculation and the calculation of the spectral irradiance at 100 \AA intervals were done on a digital computer. The reader is referred to Appendix 2 for a description of the computer and the programming techniques used.

Using the emission spectrum of the lamp obtained with the spectrophotometer and the interpolated spectral irradiance data, a response curve was calculated in the following manner. At each wavelength for which the spectral irradiance of the lamp had been calculated, the PMT current was obtained from the emission spectrum of the lamp.

The PMT current at each wavelength was then divided by the spectral irradiance. Because the response obtained was only relative, the data was normalized by dividing the response at each wavelength by the smallest value of the response. Hence, after normalization, the maximum response was 1.0. Figure 2-4 shows a graph of the reciprocal of response versus wavelength. The response was determined for the region between 3000Å and 7250Å only.

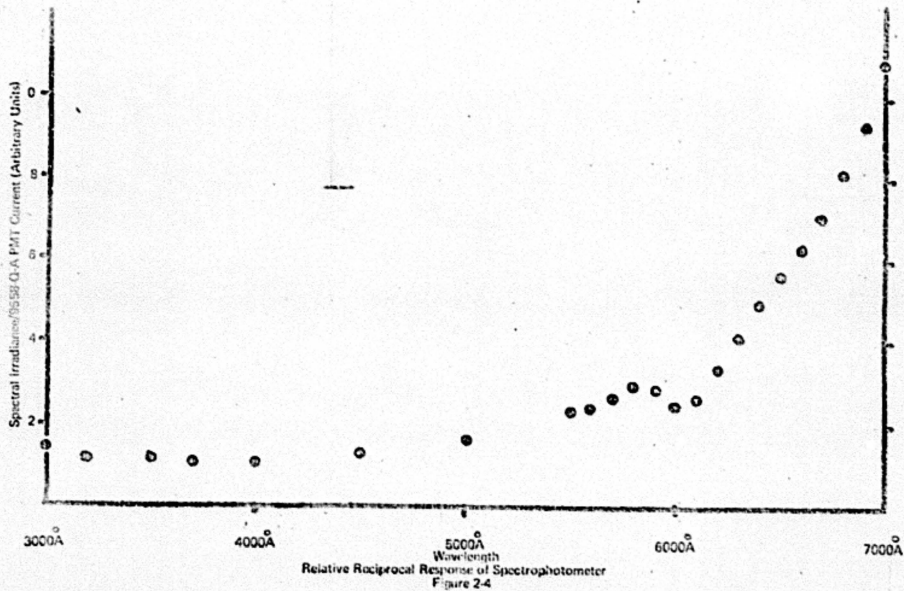
Determination of the Temperature Gradient Across the Samples - The temperature gradient across the samples was determined by placing a second chromel-alumel thermocouple between the sample and the clamp used to hold the sample in place. The top thermocouple was connected to the y-axis of an x-y recorder and the bottom thermocouple was connected to the x-axis of the same recorder. The sample was then heated up with a 10°C per minute heating rate. Every two minutes a mark was placed on the graph being traced by the x-y recorder to indicate the position of the pen with respect to time. The results of this experiment for both the two millimeter and four millimeter thick samples are shown in figure 2-5.

Determination of the Half-Value Layer of the X-ray Beam - The half-value layer was determined by placing various thicknesses of aluminum between the x-ray beam and the R-chambers, used to measure the intensity, until that thickness of aluminum was found that reduced the intensity by one half. The half-value layer was found to be 1.5mm of aluminum.

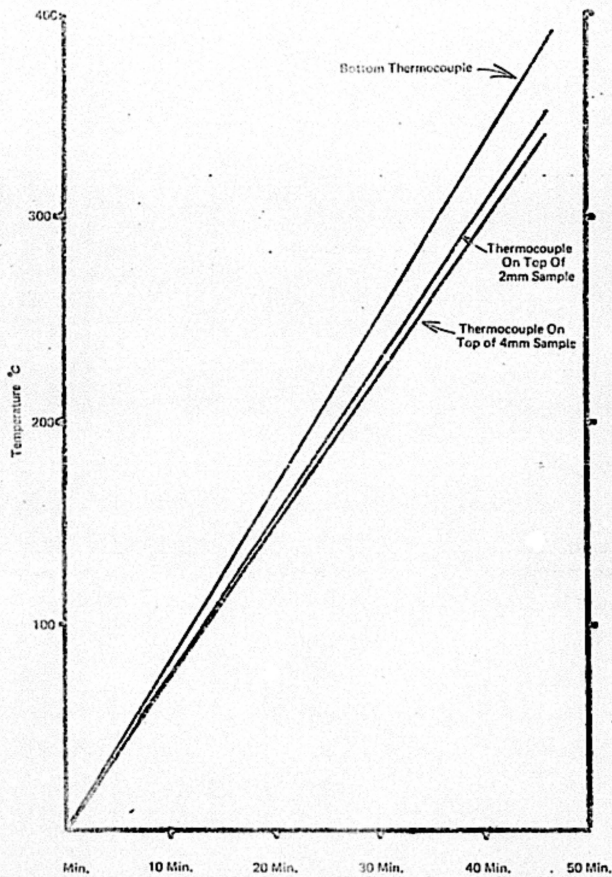
Sapphire and Ruby Samples

One nominally pure sapphire sample and one ruby sample (0.005% by weight Cr_2O_3), referred to as sapphire number one and ruby number three, were used in these investigations. The samples were obtained on loan from the laser laboratory of the Physics Department of North Carolina State University and were manufactured by the Linde Corporation. The chromium concentration reported for the ruby was obtained from the supplier. The samples were in the form of discs with radii five millimeters, and thicknesses of two millimeters for the ruby sample and four millimeters for the sapphire sample.

The C-axis of the samples was located by Laue back scatter x-ray diffraction. The C-axis of the ruby was found to be co-linear with



Relative Reciprocal Response of Spectrophotometer
Figure 2-4



Time
Sample Temperature Gradients
Figure 2-5

the axis of the disc. The C-axis of the sapphire sample was found to be perpendicular to the axis of the disc. The location of the C-axis in the sapphire was marked for future reference in performing the experiments.

Experimental Procedure

There were several steps in the procedure of the experiments which affect the conclusions of this investigation. First, each sample was aligned with the entrance lens of the monochromator when it was placed in the sample holder. The alignment was accomplished at room temperature by turning on the x-ray beam, adjusting the monochromator to a peak in the emission spectrum of the sample and then adjusting the sample position by means of the rotary table to give a maximum deflection of the electrometer. The procedure usually took from two to three minutes.

Second, the sample was exposed to x-rays for fifteen minutes (including the two to three minute adjustment period) before the first part of the experiment was performed. The first part was to heat the samples with a 10°C per minute heating rate and observe the luminescence while the sample was being continuously exposed to the x-ray beam.

Third, when the sample temperature reached the maximum temperature of interest (which depended on the sample) the x-rays were turned off, the sample temperature was allowed to get about 10°C higher, and the sample was held at this temperature for about five minutes. The x-ray beam was then turned on and while the sample temperature was held constant, and the luminescence was observed. When the luminescence as measured by the 1P21 PMT current or the 9558-Q-A (depending on which experiment was being run) PMT current reached a steady value, the sample was allowed to cool, and the luminescence was observed.

When the sample had cooled to room temperature while being continuously exposed, the x-rays were turned off and the sample was annealed. The sapphire sample was annealed to 270°C and the ruby to 400°C . The thermoluminescence glow was observed during the annealing, but the total exposure of the sample was not accurately known. After the sample was annealed and had cooled to room temperature,

it was given a known exposure and the thermoluminescence glow was observed again.

It should be noted that the emission spectra measurements and the measurements made with the 1P21 PMT were made at different times on sapphire. The emission spectra and 1P21 measurements of the luminescence of ruby were made simultaneously.

CHAPTER III

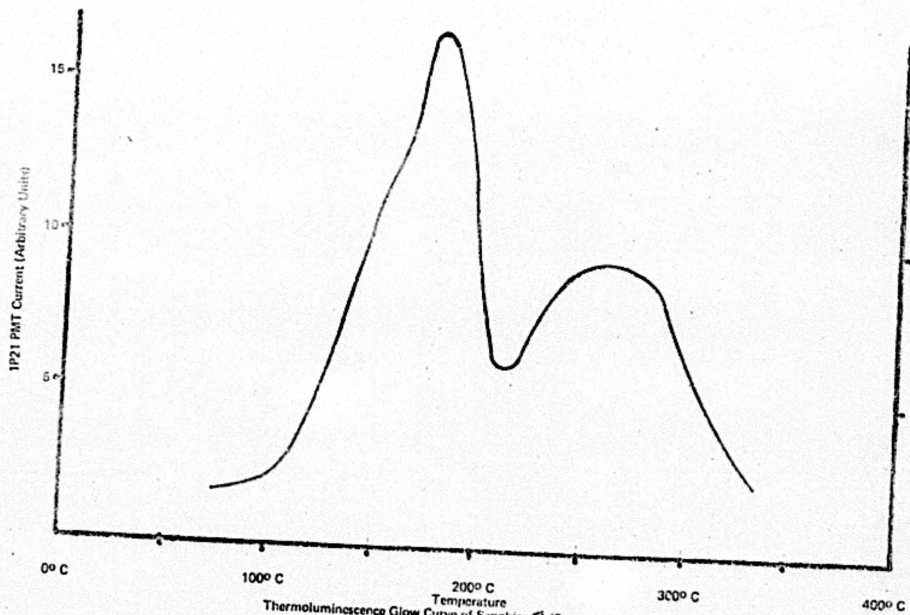
RESULTS, AND DISCUSSION

Thermoluminescence Studies

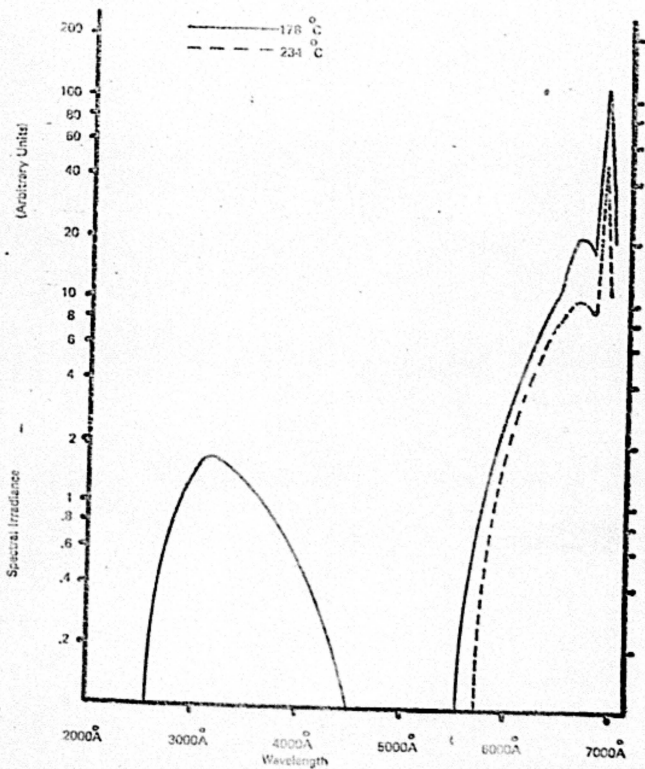
The thermoluminescence glow and thermoluminescence emission spectra of sapphire #1 and ruby #3 were observed for emission perpendicular and parallel to the C-axis of the sapphire and ruby samples (hereafter called the perpendicular and parallel orientation respectively). The thermoluminescence glow curve of sapphire #1, observed in the perpendicular orientation after exposing the sample to 1000R of x-rays, is seen in figure 3-1. One well resolved glow peak was observed at 179°C, and another broad peak was observed at 263°C. An unresolved peak or shoulder was observed at 144°C. Glow curves observed at higher but unknown exposures resolved the broad peak at 263°C into one peak at 256°C and a shoulder at 280°C.

The emission spectra of the thermoluminescence glow at two different temperatures in the perpendicular orientation are shown in figure 3-2. The exposure was not accurately known but was in excess of 1000R. The broad regions of emission, as can be seen from the graph, consisted of a band with a peak at 6700Å, a band with a peak at 3200Å, and an emission line at 6940Å. The 6700Å band can be identified with the vibronic sidebands of the chromium ion (17) which, even though a trace impurity in the nominally pure sapphire, has a great effect on the luminescence of sapphire. The emission line can be identified with the R-line emission of triply ionized chromium in the sapphire lattice. From these emission spectra, it can be seen that light emitted from the 179°C glow peak contained emission from all three of the regions just described, while light from the 263°C glow peak contained emission in the vibronic side bands and R-line region.

The thermoluminescence of sapphire #1 observed in the parallel orientation after exposing the sample to 1000R of x-rays is



Temperature
Thermoluminescence Glow Curve of Sapphire #1 (Perpendicular Orientation)
Figure 3-1



Thermoluminescence Emission Spectra of Sapphire #1 (Perpendicular Orientation)

Figure 3-2

shown in figure 3-3. Glow peaks were observed at 182°C and 263°C. A shoulder was observed at 149°C. Two emission spectra, taken at different temperatures, of the thermoluminescence in this orientation are shown in figure 3-4. The spectra were obtained after an exposure in excess of 1000R. The same regions of emission were observed in this orientation as in the previous one.

The thermoluminescence glow of ruby #3 was observed in the perpendicular orientation. The glow curve obtained after exposing the crystal to 18.5 minutes of x-radiation at 1200R per hour is shown in figure 3-5. A single peak was observed at 346°C. The emission spectrum associated with this peak is shown in figure 3-6. Emission was detected in vibronic side band and R-line region only.

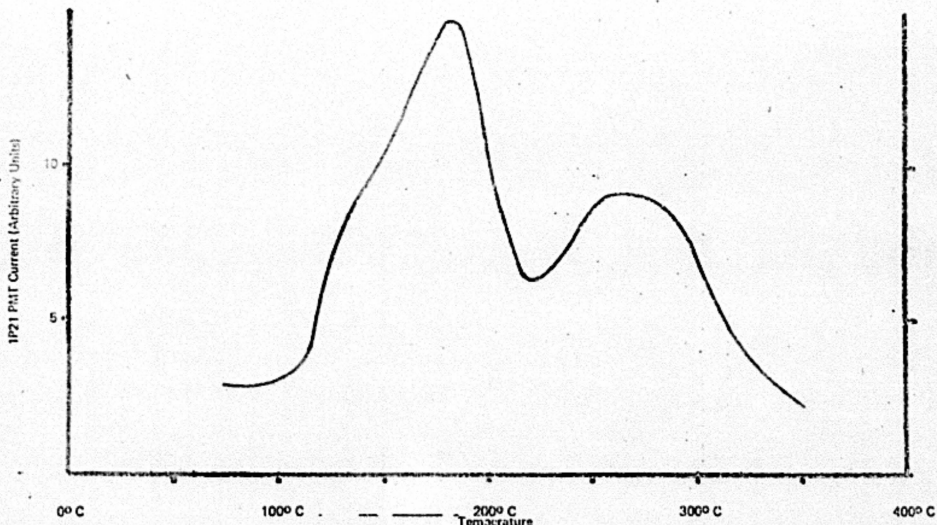
An attempt was made to calculate the energy of activation for the 179°C (figure 3-1) and the 182°C glow peak (figure 3-3) in sapphire and the 346°C glow peak in ruby. The calculation was made using the initial rise method. Because of several factors, the nature of the assumptions associated with the method, the approximate nature of the calculation, and the fact that no step annealing was done, the energies of activation reported are no more than crude estimates. Table 1 is a list of the glow peaks and the energies of activation that were calculated.

X-Ray-Induced Luminescence Studies

Studies with the 1P21 PMT - The x-ray-induced luminescence of sapphire #1 in both the perpendicular and parallel orientation and ruby #3 in the perpendicular orientation was observed with the 1P21 PMT as the samples were heated from room temperature to about 400°C (hereafter called the heating cycle), and as the samples were cooled from about 400°C to near room temperature (hereafter called the cooling cycle). These results are reported in the following paragraphs.

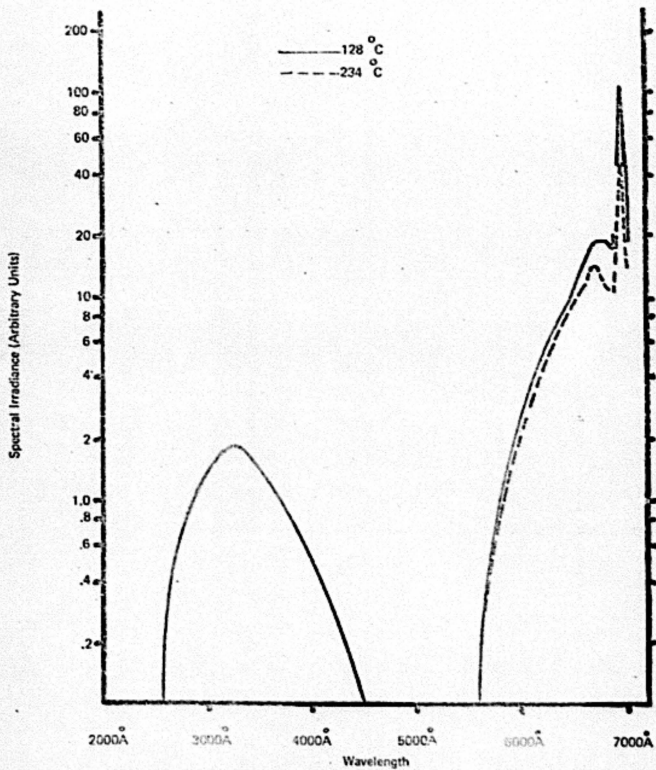
The x-ray-induced luminescence of sapphire during the cooling cycle for the perpendicular orientation is shown in figure 3-7. The light intensity, as indicated by the PMT current, had a maximum at 319°C, a minimum at 204°C, and increased from 204°C to room temperature. The x-ray intensity was 2400R per hour.

The x-ray-induced luminescence of the sapphire sample in the heating cycle for the perpendicular orientation is shown in figure



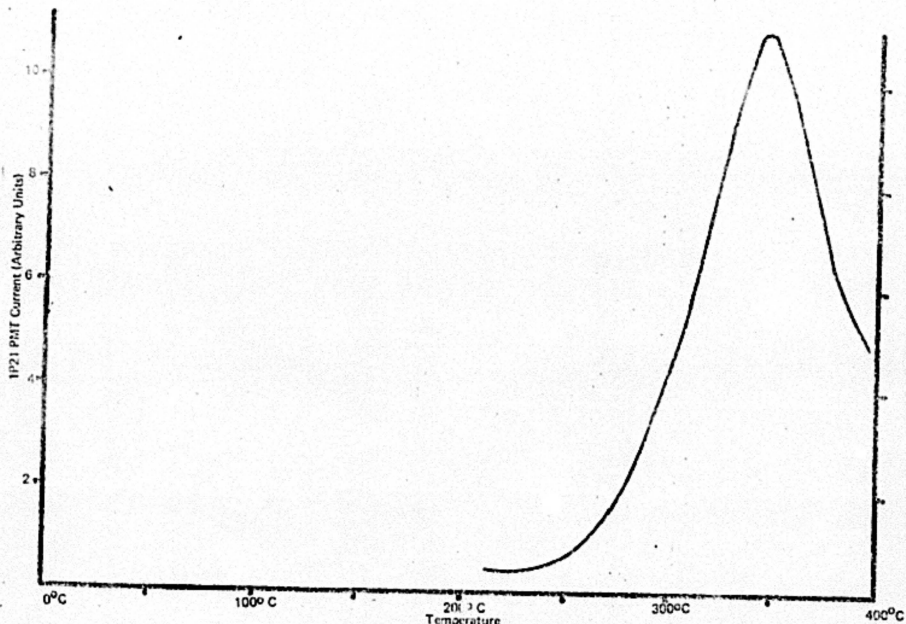
Thermoluminescence Glow Curve of Sapphire #1 (Parallel Orientation)

Figure 3-3



Thermoluminescence Emission Spectra of Sapphire 1 (Parallel Orientation)

Figure 3-4



Thermoluminescence Glow Curve of Ruby//F3 (Perpendicular Orientation)

Figure 3-5

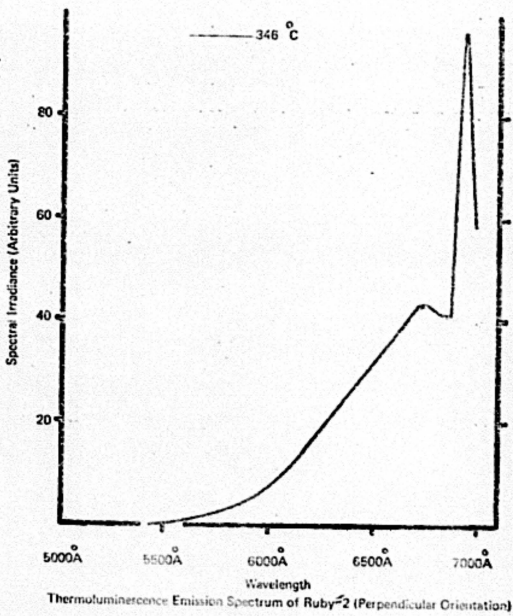
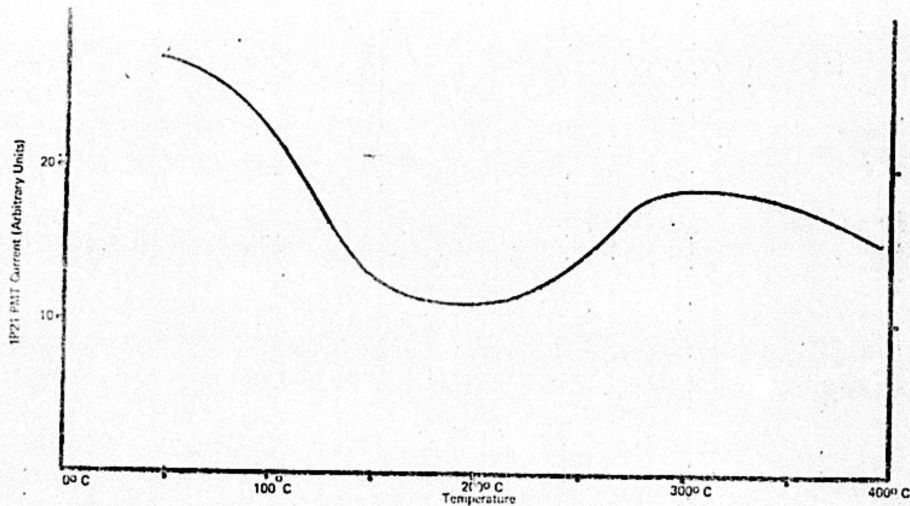


Figure 3-6

TABLE 1

ENERGIES OF ACTIVATION

SAMPLE	PEAK	ORIENTATION	ENERGY OF ACTIVATION
Sapphire #1	179°C	Perpendicular	.5eV
Sapphire #1	182°C	Parallel	.5eV
Ruby #3	346°C	Perpendicular	1.6eV



X-Ray-Induced Luminescence of Sapphire ⁴⁶¹ (Perpendicular Orientation) Decreasing Temperature
Figure 3-7

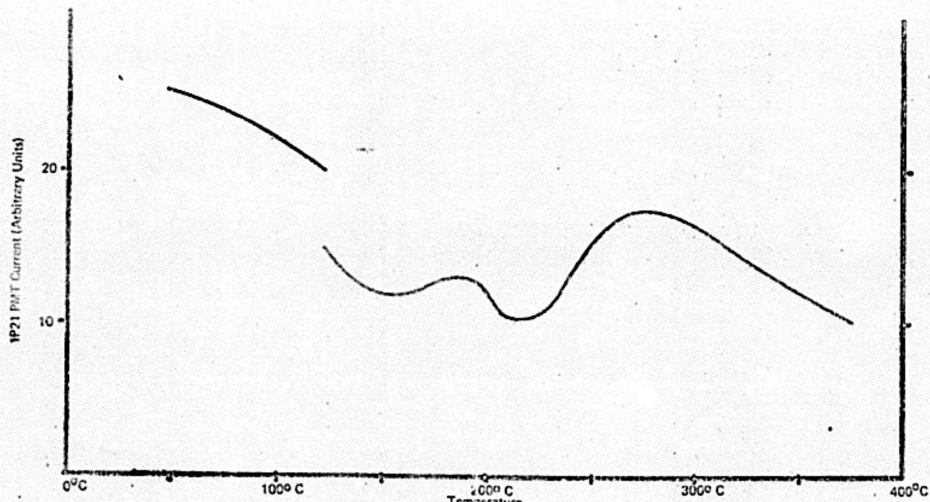
3-8. The x-ray intensity during the experiment was 2400R per hour, and the sample received a fifteen minute exposure prior to the experiment. There is a discontinuity in the intensity curve at approximately 115°C . The reason for the discontinuity is as follows: the sample was heated to approximately 115°C , the x-rays were turned off, and the sample was annealed by heating it to 260°C . The sample was allowed to cool to about 115°C , whereupon the heating element was turned on. When the sample temperature began to rise, the x-rays were turned on, and the experiment was continued. The annealing step allows a crude estimate of the amount of the luminescence that was due to thermoluminescence. The experiment showed that the induced luminescence decreased from 40°C to 150°C , had two peaks, one at 190°C and another at 280°C , and decreased from 280°C to 400°C . The peaks in the induced luminescence correlate with observed thermoluminescence.

The observation of the x-ray-induced luminescence for ruby #3 in the cooling cycle for the perpendicular orientation is shown in figure 3-9. The x-ray intensity during the experiment was 1200R per hour. The experiment indicated that there was a peak in the luminescence at 375°C , a minimum at 275°C , and a slight, but almost linear, increase between 275°C and 50°C .

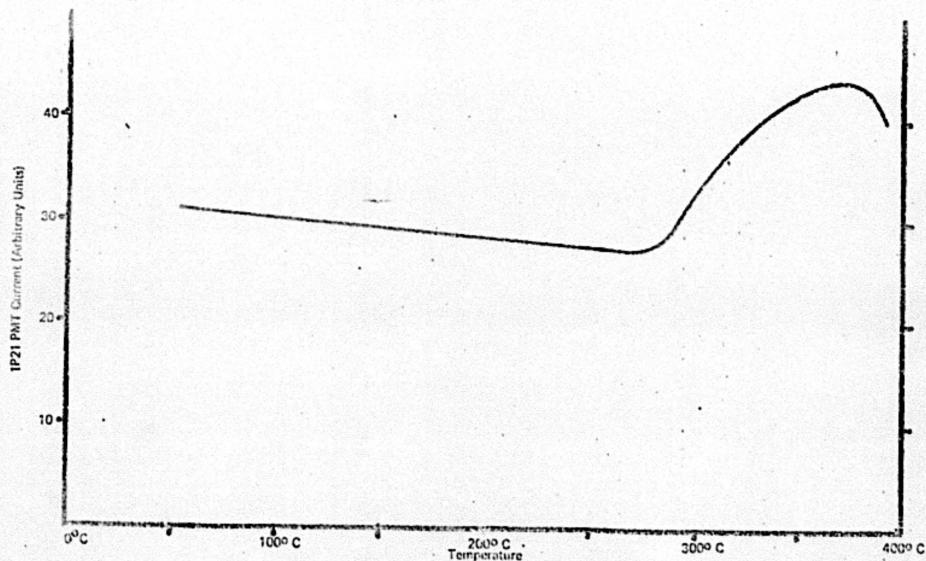
The observation of the x-ray-induced luminescence of ruby #3 in the heating cycle for the perpendicular orientation is shown in figure 3-10. The x-ray intensity was 1200R per hour, and the sample was exposed to x-rays for fifteen minutes at the same intensity before heating. The luminescence as indicated shows almost no increase between 50°C and 250°C , but after this appears to be starting over a peak. In other experiments, reported in Mr. Cooke's masters thesis (21), the peak was observed at 319°C which correlates well with the observed thermoluminescence peak.

The measurements of the x-ray-induced luminescence of sapphire #1 in the parallel orientation made with the 1P21 PMT did not differ significantly from those just reported for the perpendicular orientation.

Emission Spectra Studies - The emission spectra of the x-ray-induced luminescence of sapphire #1 in the perpendicular and parallel orientation, and ruby #3 in the perpendicular orientation were observed with the spectrophotometer described in Chapter II. Observations were made

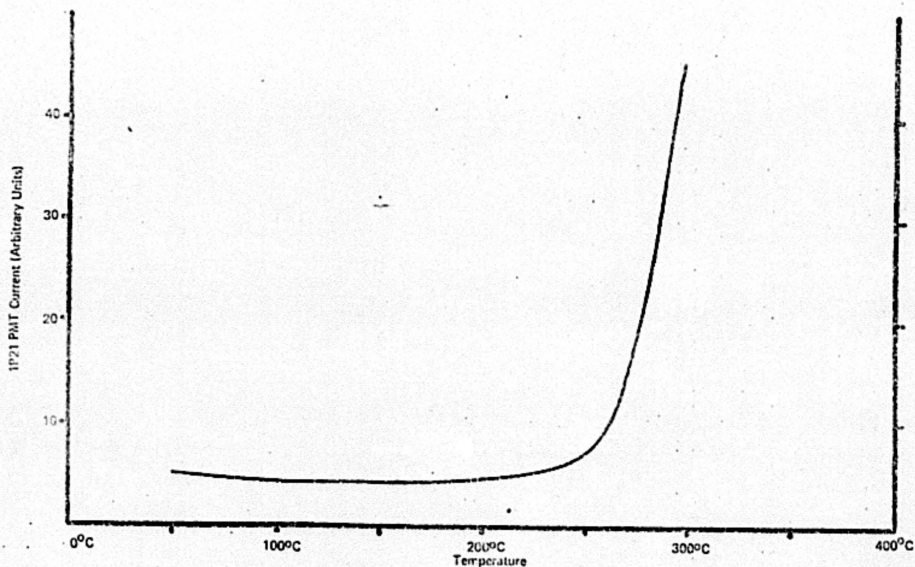


X-Ray-Induced Luminescence of Sapphire #1 (Perpendicular Orientation) Increasing Temperature
Figure 3-8



X-Ray-Induce Luminescence of Ruby #3 (Perpendicular Orientation) Decreasing Temperature

Figure 3-9



X-Ray-Induced Luminescence of Ruby #3 (Perpendicular Orientation) Increasing Temperature
Figure 3-10

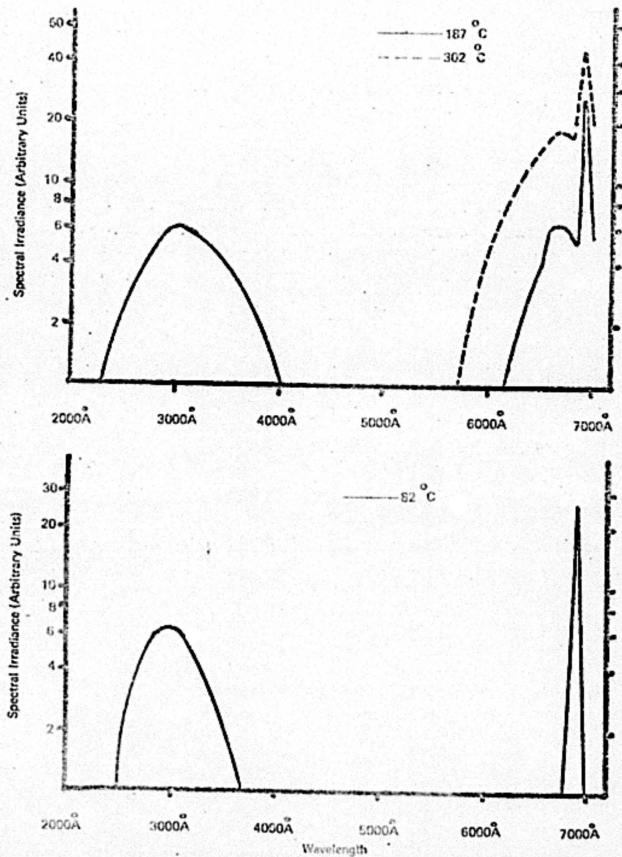
for both the heating and cooling cycles. These measurements are reported in the following paragraphs.

A large amount of data was taken in the course of the experiments and in order to report the information in as concise a manner possible, the following format was used. First, in each of the experiments, eight or nine spectra were obtained. From these spectra, three typical ones which show the various regions of emission and their shapes and intensities at different temperatures were selected and reported.

Finally, in order to summarize the results of all the spectral measurements, the data from each spectrum was compiled and plotted in the following manner. After the emission spectra were corrected for the response of the spectrophotometer, the area under each emission band was calculated. These data together with the observed R-line intensity, measured in terms of the PMT current, were plotted versus the temperature at which the measurements were made. The beginning and ending temperatures of each emission spectrum had been recorded, and this information together with the scan rate of the spectrophotometer (50°A per second) was used to calculate the temperature at which each band or line, occurring in different regions of the spectrum, was observed. The following convention was used in constructing the graphs just described.

The area under the 3000\AA band was symbolized by solid circles (e), the circles were connected by solid lines, and the value of the area is read from the left hand scale. The area under the 6700\AA band is symbolized by diamonds (\diamond), the diamonds are connected with a short broken line, and the value of the area is read from the extreme right-hand scale. The height of the R-line is symbolized by open circles (o), the circles are connected by long broken lines, and the value of the R-line height is read from the first of two right hand scales. The lines connecting the points are not fitted curves. They are drawn in order that the reader might easily separate the various data on the graph and in order to indicate the trend of the data.

Three of nine x-ray-induced luminescence emission spectra, taken during the cooling cycle for sapphire #1 in the perpendicular orientation, are shown in figure 3-11. Emission was observed in three regions. First, an emission band with a peak at 3000\AA ; second, a band



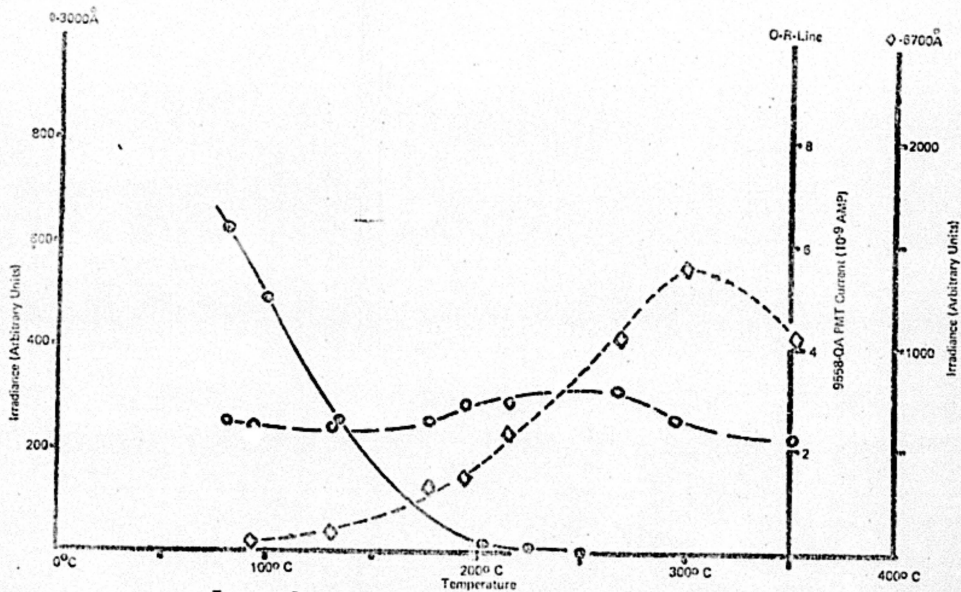
X-Ray-Induced Emission Spectra of Sapphire¹¹ (Perpendicular Orientation)

Decreasing Temperature

Figure 3-11

with a peak at 6700\AA , previously reported in the emission spectrum of thermoluminescence; third an emission line at 6940\AA , also previously reported, were observed. The results of all the emission spectra, compiled and plotted as described in the two previous paragraphs, is seen in figure 3-12. This graph shows quite clearly the temperature dependence of the emission. The 6700\AA band, while quite prominent at high temperatures, was quenched as the temperature decreased. The area under this region, which is proportional to the irradiance of that band, passed through a maximum at 300°C . The two lowest temperature values reported in figure 3-12 for the area of the 6700\AA band could not be calculated in the same manner as were the others, but are estimates based on the height of the band at those temperatures. The emission band at 3000\AA , not observed at temperatures above 250°C , increased in intensity as the temperature decreased. The R-line intensity showed a slight peak at 250°C . The x-ray intensity during the experiment was 2400R per hour.

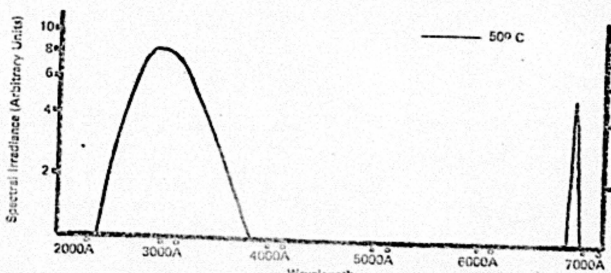
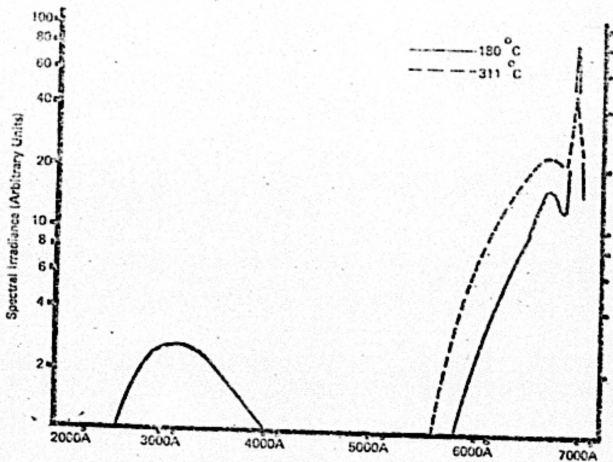
The x-ray-induced luminescence emission spectra of sapphire #1 in the perpendicular orientation was observed during the heating cycle. Three of eight emission spectra taken during the experiment are seen in figure 3-13. The x-ray intensity during the experiment was 2400R per hour. The sample was exposed for fifteen minutes at the same intensity before the heating was started. The same regions of emission were observed in this experiment as in the last. An interesting feature of this experiment is seen in the spectrum taken at 180°C . The peak of the 3000\AA band has shifted to about 3200\AA , the same peak wavelength as that observed for the band in the emission spectrum of the 179°C thermoluminescence glow peak (figures 3-1 and 3-2). At no time in any of the experiments did it appear that there was an unresolved shoulder on the 3000\AA band. The experiments always showed a band with a single peak in this region. Again the results of the remainder of the emission spectra were compiled and are displayed in figure 3-14. These data show a strong peak in the irradiance of the 6700\AA band at about 287°C . The two low temperature values for the area under this band were estimated from the height of the band at those temperatures. The R-line intensity showed a maximum between 165°C and 265°C . The irradiance of the 3000\AA band decreased from 50°C to about 300°C above which it was not observed; there was a shoulder at 175°C on the



Temperature Dependence of Emission Spectra of Sapphire⁽¹⁾ (Perpendicular Orientation)

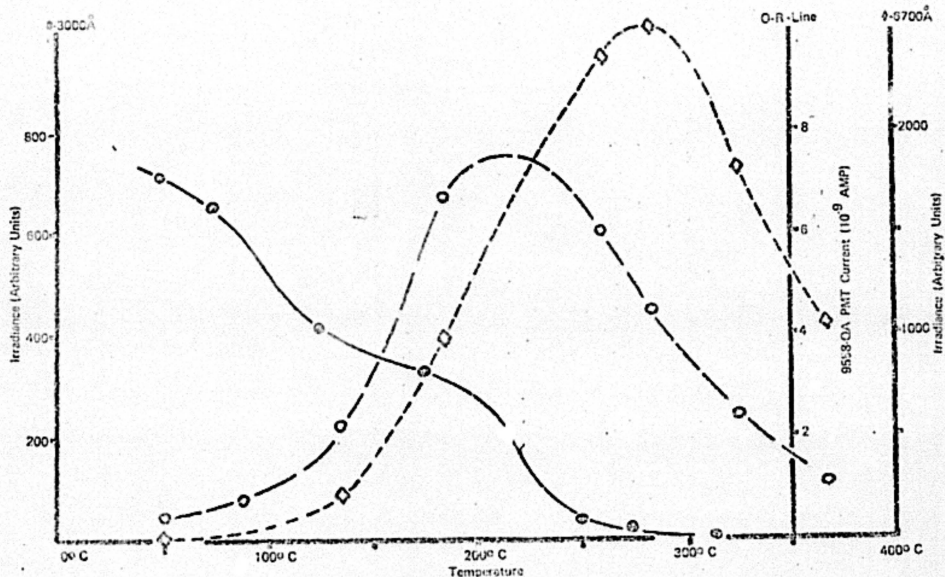
Decreasing Temperature

Figure 3-12



X-Ray-Induced Emission Spectra of Sapphire #1 (Perpendicular Orientation)
Increasing Temperature

Figure 3-13

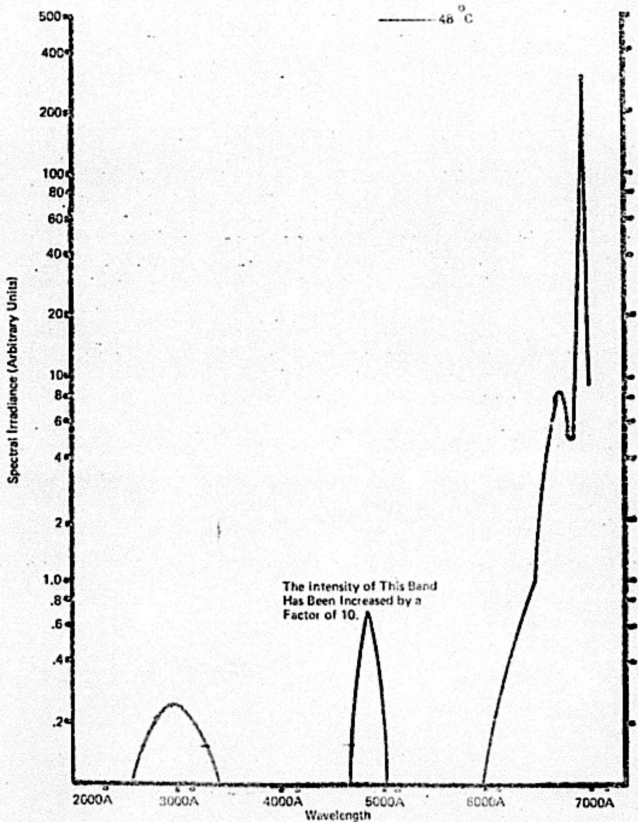


Temperature Dependence of Emission Spectra of Sapphire²¹ (Perpendicular Orientation) Increasing Temperature
 Figure 3-14

curve of the irradiance of this region. The datum which the point at 175°C represents was obtained from the emission spectrum taken at 180°C , the spectrum which showed the shift in the peak of the 3000\AA band. The shoulder at 175°C can be correlated with the thermoluminescence glow peak observed at 179°C .

The x-ray-induced luminescence emission spectra of ruby #3 was observed in the perpendicular orientation during the cooling cycle. The x-ray intensity during the experiment was 1200R per hour. Three of eight emission spectra, taken during the experiment, are shown in figures 3-15 and 3-16. The spectra show four emission regions. The emission regions are similar to those observed in sapphire. There is a band with a peak at 3000\AA (reduced in intensity by an order of magnitude compared to the corresponding region in sapphire). The 6700\AA band was observed; this band, while hardly detectable in sapphire at 50°C , was distinct at 48°C in ruby #3. The 6940\AA line was observed and was roughly an order of magnitude larger than the corresponding line in the emission spectra of sapphire. There is a band with a peak at 4800\AA which was not observed in sapphire. The results of all the spectral measurements made in this experiment were compiled and are seen in figure 3-17. The following features are indicated by the data displayed in figure 3-17. The irradiance of the 6700\AA band decreased as the sample cooled from about 375°C to about 150°C ; a slight shoulder occurred at about 165°C . From 150°C to about 45°C , the amount of light increased slightly. The 3000\AA emission, again not observed above 300°C , increased with decreasing temperature. The R-line showed radically different behavior than the corresponding experiment on sapphire; the R-line intensity increased smoothly as the temperature decreased from 375°C to 45°C .

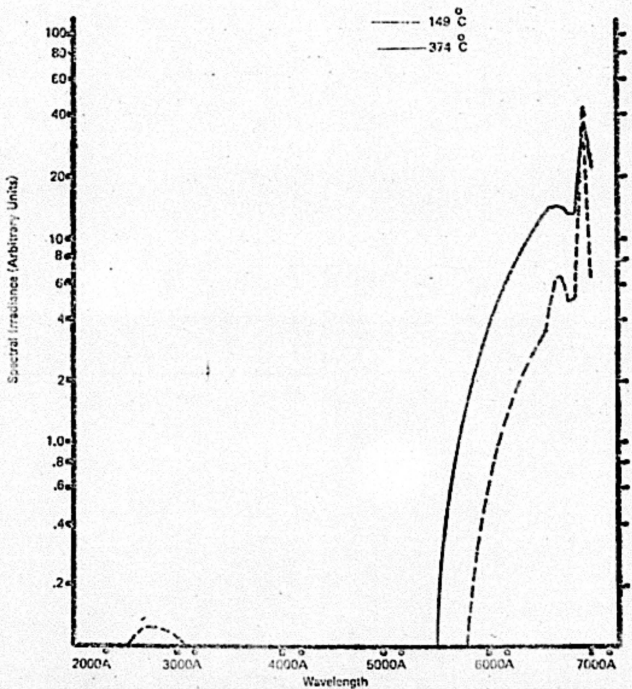
The x-ray-induced luminescence emission spectra of ruby #3 was observed in the perpendicular orientation as the crystal was heated under continuous x-ray intensity of 1200R per hour; the sample was exposed for fifteen minutes at the same intensity before the heating was started. Three of eight emission spectra taken in this experiment are shown in figures 3-18 and 3-19. It should be noted that in this experiment and the one just described, the peak of the 3000\AA band shifted to lower wavelengths as the temperature increased. For example, in figure 3-18 the emission scan taken at 47°C shows a band with a peak



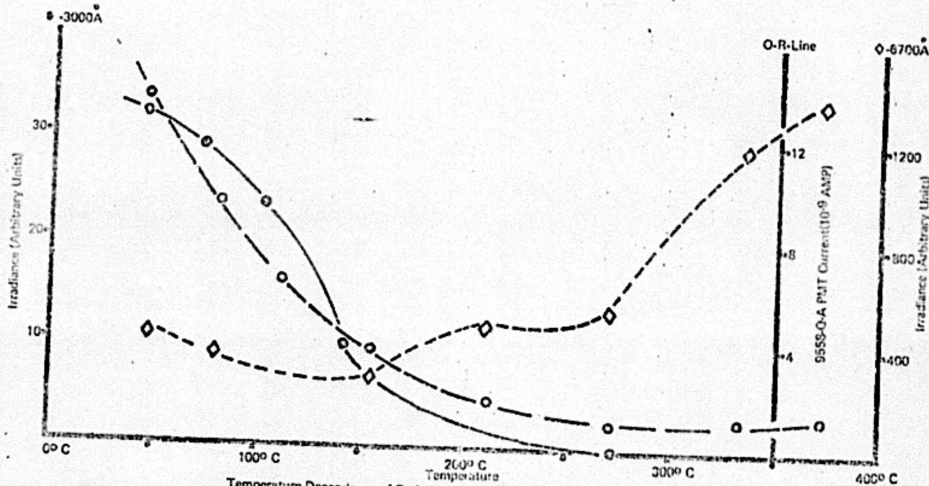
X-Ray-Induced Emission Spectrum of Ruby #3 (Perpendicular Orientation)

Decreasing Temperature

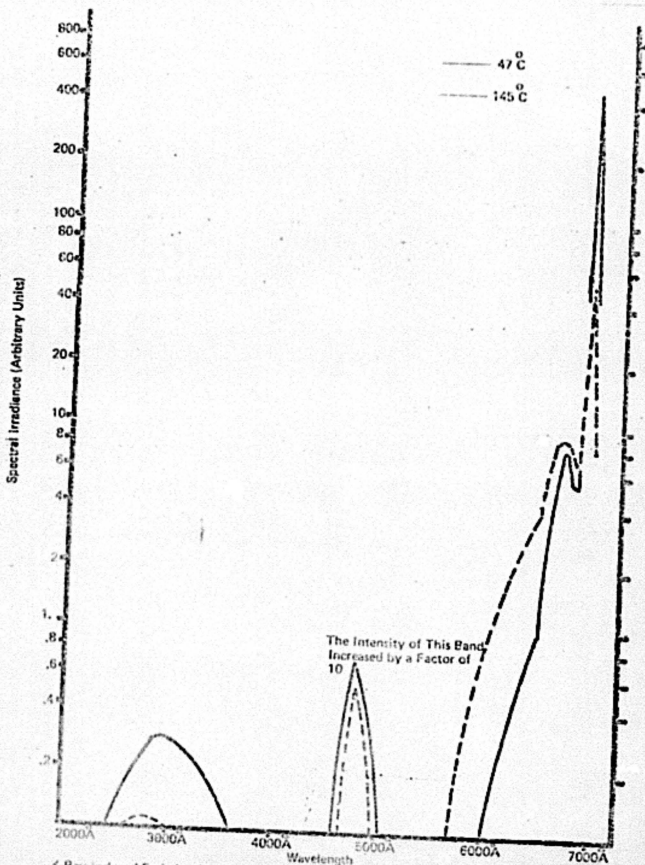
Figure 3-15



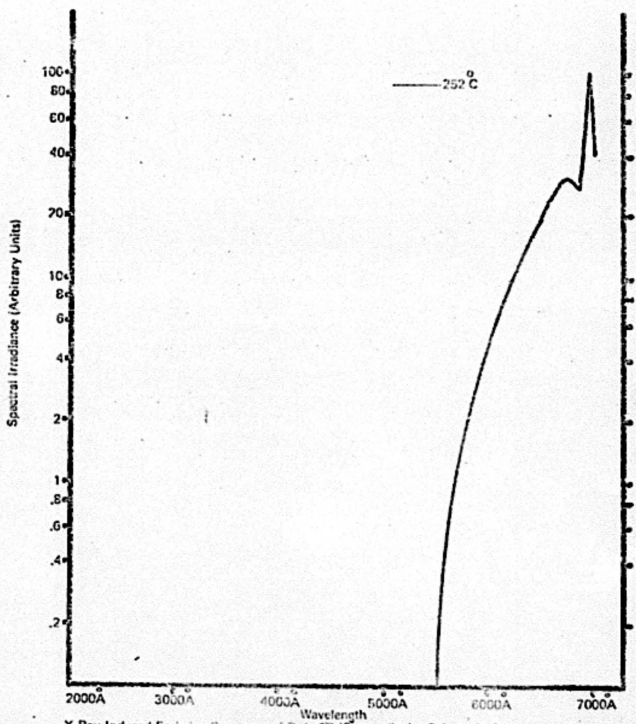
X-Ray-Induced Emission Spectra of Ruby⁷³ (Perpendicular Orientation) Decreasing Temperature
Figure 3-16



Temperature Dependence of Emission Spectra of Ruby #3 (Perpendicular Orientation)
 Decreasing Temperature
 Figure 3-17



X-Ray-induced Emission Spectra of Ruby #3 (Perpendicular Orientation) Increasing Temperature
Figure 3-13



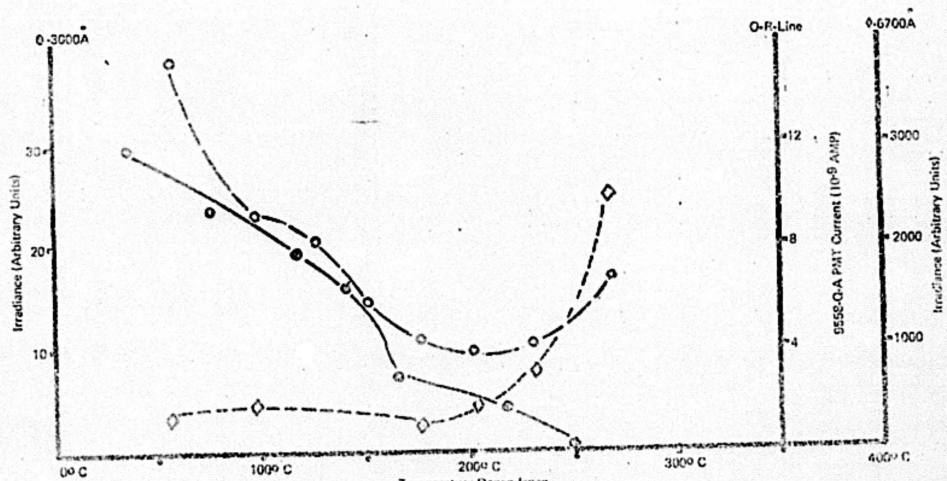
X-Ray-Induced Emission Spectrum of Ruby*3 (Perpendicular Orientation) Increasing Temperature

Figure 3-19

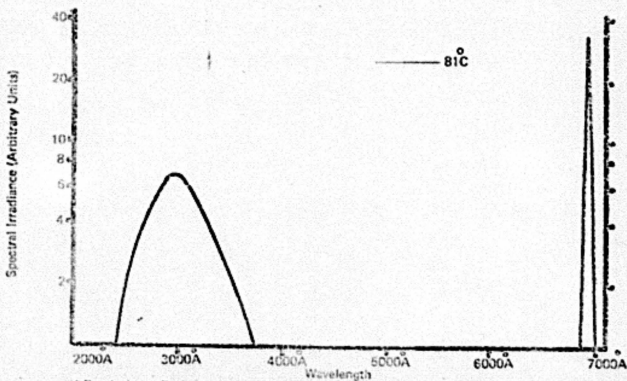
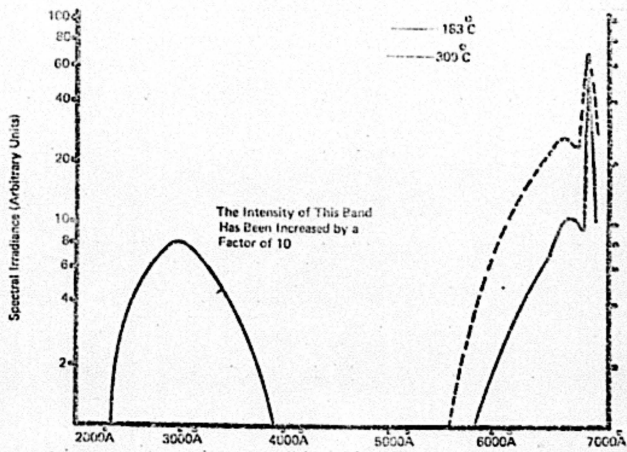
at 3000\AA while the emission scan taken at 145°C shows the peak shifted to about 2600\AA . The results of all the spectral measurements made in this experiment are graphed in figure 3-20. As can be seen in figure 3-20, the 3000\AA band was thermally quenched as the temperature increased and above 250°C was not detectable. The irradiance of the 6700\AA band increased as the temperature increased. The intensity of the 6940\AA line had a minimum at about 200°C and increased between there and about 250°C .

The x-ray-induced luminescence emission spectra was observed for sapphire #1 in the parallel orientation as the sample cooled from 358°C under a continuous exposure to x-rays at an intensity of 2400R per hour. Three of nine emission spectra are shown in figure 3-21. The most noticeable difference between the emission spectra taken in the parallel and perpendicular orientation is the height of the 6940\AA line at lower temperatures. The results of all the spectral measurements were compiled and are shown in figure 3-22. The data represented indicates that the luminescence behaved as follows: the irradiance of the 6700\AA emission region had a maximum value at about 280°C and decreased from there to room temperature. The values of area for the 6700\AA band at the two lowest temperatures reported in figure 3-22 are estimates based on the height of the 6700\AA band at those temperatures. The irradiance of the 3000\AA band decreased in value as the temperature increased. The R-line intensity had a peak at 150°C .

The emission spectra of the x-ray-induced luminescence of sapphire #1 in the parallel orientation for the heating cycle was observed. The x-ray intensity was 2400R per hour. The sample was exposed for fifteen minutes at the same intensity prior to heating. Three of eight emission spectra taken are shown in figure 3-23. The most noticeable feature of the data in this orientation is the intensity at 25°C of the 6940\AA line which was noticeably greater in this orientation. The shift in the peak of the 3000\AA band toward longer wavelengths was observed again at 182°C . The results of all the emission spectra were compiled and can be seen in figure 3-24. There is a shoulder, which was also observed in the perpendicular orientation, at 175°C on the curve representing the irradiance of the 3000\AA band. The shoulder occurred at the same temperature as the shift in wavelength with the

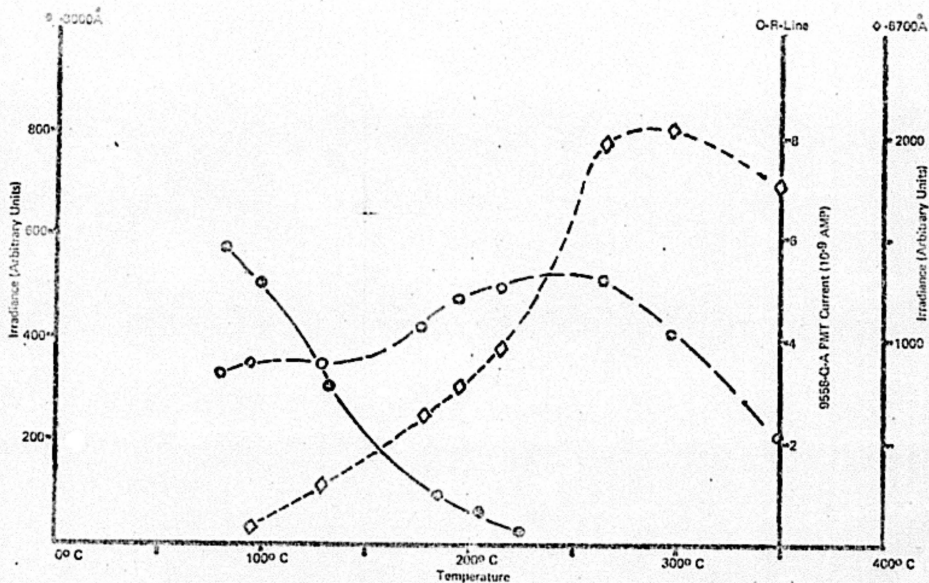


Temperature Dependence of Emission Spectra of Ruby-33 (Perpendicular Orientation) Increasing Temperature
 Figure 3-20

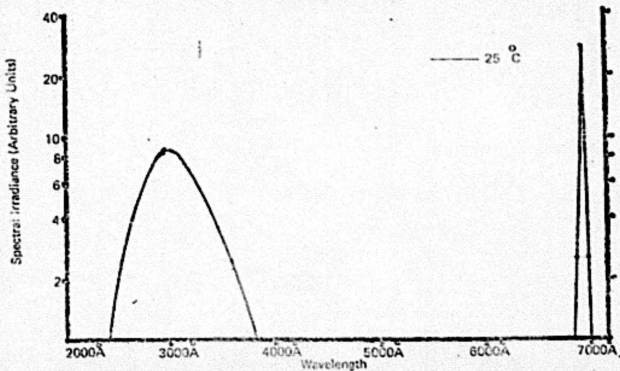
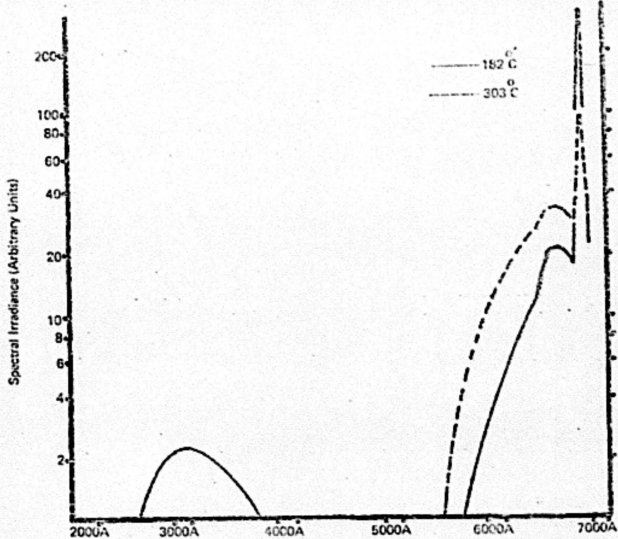


X-Ray-Induced Emission Spectra of Sapphire⁹¹ (Parallel Orientation) Decreasing Temperature

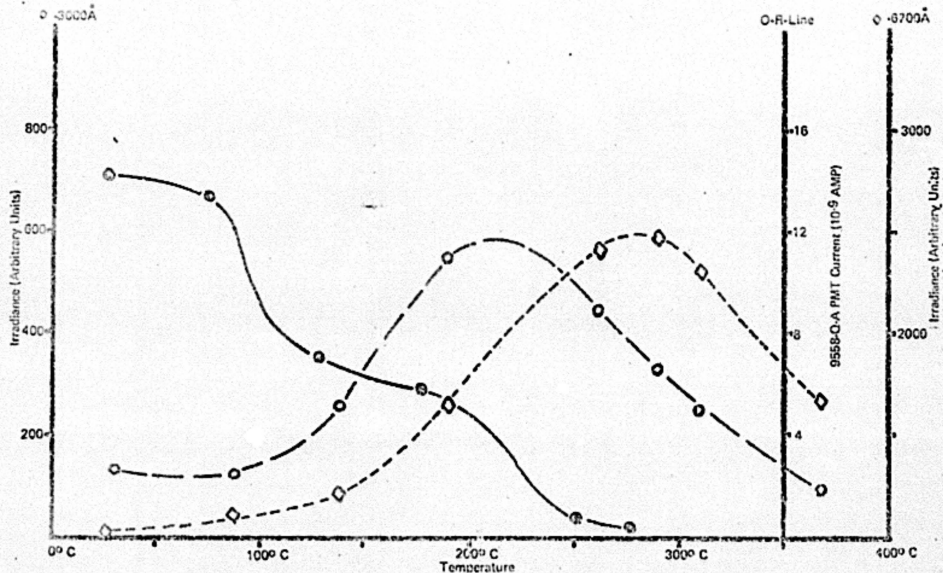
Figure 3-21



Temperature Dependence of the Emission Spectra of Sapphire[®] (Parallel Orientation) Decreasing Temperature
Figure 3-22



X-Ray-Induced Emission Spectra of Sapphire¹¹ (Parallel Orientation) Increasing Temperature
Figure 3-23



Temperature Dependence of Emission Spectra of Sapphire #1 (Parallel Orientation) Increasing Temperature
Figure 3-24

peak of the 3000\AA band. The irradiance of the 6700\AA band passed through a maximum at about 275°C . The intensity of the R-line shows a maximum between 160°C and 250°C .

Comment on Emission Spectra Studies - Three comments should be made about the emission spectra studies. First, it was discovered that the monochromator polarized light passing through it. Therefore, differences in relative intensity, such as were observed when the orientation of the crystal was changed, may be due to the fact that the emission itself is polarized, and in changing the orientation, the angle between the electric vector and the angle of polarization of the monochromator was changed, thus, causing an apparent change in the intensity of the emission.

Second, there is a shoulder on the short wavelength side of the 6700\AA band. The shoulder was at first questionable. Two Wood anomalies (13) were observed in the 1200 lines per millimeter Bausch and Lomb grating (Chapter II) at 5400\AA and 6050\AA . The latter anomaly was close enough to this aforementioned shoulder that it was thought possible that the shoulder was caused by the anomaly. However, a monochromator response curve which took into account the anomaly was used to correct the data as it appears in the graphs in this report, and still the shoulder is evident. This fact and the occurrence of a 6700\AA band (21) without such a shoulder in one of the more heavily chromium doped ruby samples (0.05%) lead this experimenter to conclude that the shoulder is truly characteristic of the emission spectra of the sample.

Finally, the 4800\AA band reported in the emission spectrum of ruby #3 is quite possibly due to the x-ray luminescence of the aluminum sample holder. The spectra of ruby #3 reported were taken under conditions of unusually low PMT dark current. The low intensity of the 4800\AA band and the good dark current conditions of the reported experiment make the possibility of an interfering spectrum hard to check. Nevertheless, there exists some evidence that this band is due to the sample holder. An emission spectrum of the empty sample holder under continuous radiation, also taken at a time of favorable dark current, showed the indication of a possible band at 4800\AA just above the PMT dark current. Because the spectrophotometer was not set for maximum sensitivity, the evidence was inconclusive.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Summary

Introductory Comment - The x-ray-induced luminescence of sapphire and lightly doped ruby (0.005% by weight Cr_2O_3) has been observed and the emission spectra of this luminescence has been found to consist of three components, a band with a peak at 3000Å, a band with a peak at 6700Å and a short wavelength shoulder, and an emission line at 6940Å. The 6700Å band is identified with the vibrationally assisted transitions in the Chromium ion ⁽¹⁷⁾ and the line at 6940Å is identified with the R-lines of chromium. ⁽²³⁾ The relative intensities of the two bands and line were observed to be temperature and chromium concentration dependent.

Temperature Dependence of the Luminescence - In both the sapphire and ruby samples, the 3000Å band was most intense at room temperature, and decreased in intensity as the temperature increased. In none of the experiments was the band observed above 300°C. In experiments performed in the cooling cycle, the intensity of the band increased monotonically as the temperature decreased. In the heating cycle, the intensity decreased as temperature increased, but there was slight shoulder on the curve at 175°C (Figures 3-24 and 3-14). The shoulder was not observed in the luminescence of ruby.

It was observed in both sapphire and ruby that as the irradiance of the 3000Å band decreased, the irradiance of the vibronic sidebands increased and vice versa. Figures 3-12, 3-14, 3-17, 3-20, 3-22, and 3-24 show clearly this relationship. It should be noted that the relative amount of power per unit area (irradiance) emitted in the vibronic sidebands is greater than that in the 3000Å band, in other words the power gained by the vibronic sidebands at high temperatures is greater than that lost by the 3000Å band. The half width of the 3000Å band

was temperature independent within the limits of observation.

Concentration Dependence of the Luminescence - Figures 3-7 and 3-8 show the luminescence intensity of sapphire and ruby respectively as measured with 1P21 PMT. These graphs show quite different shapes for the temperature dependences of the luminescence. One important difference which should be noticed is the fact that the luminescence of sapphire shows a peak (figure 3-7) at about 300°C while the luminescence of ruby (figure 3-9) shows a peak at about 350°C .

The measurements made with the 1P21 PMT do not take into account the response of the PMT (S-4) to light of different wavelengths. However, the observations made with the spectrophotometer, the results of which are shown in figures 3-12, 3-14, 3-22, and 3-24 for sapphire and figures 3-17 and 3-20 for ruby, show that the temperature relationship between the 3000\AA and the 6700\AA band is approximately the same.

The irradiance of the 3000\AA band in ruby is reduced in intensity compared to the same region in sapphire by a factor of about $1/20$. Unlike the reduction in intensity of this band due to temperature changes, a comparison of figures 3-12 and 3-17 shows that the amount of power lost by the 3000\AA band, at least at low temperatures, is within 20% to 40% equal to the amount of power gained by the 6700\AA band.

The temperature dependence of the intensity of the R-line is quite different for sapphire and ruby. At low temperatures in ruby (figures 3-17 and 3-20), the R-line is most intense and decreases as the temperature is increased. Figure 3-20 shows the R-line intensity starting to increase at about 350°C , but this is, however, due to thermoluminescence. In the luminescence of sapphire however, the R-line intensity does not change by so large a ratio except as it passes over a thermoluminescence glow peak.

Conclusions and Suggestions for Future Work

Luminescence in the 3000\AA Band - The center responsible for the emission band at 3000\AA in the x-ray-induced luminescence emission spectrum is not identified by the author of this report. However, luminescence emission in this region has been reported previously (8, 9) and, whether due to a recombination of a hole with an electron across the conduction band, a structural defect in the lattice, or a trace

impurity indigenous to the materials from which the sapphire was grown, it is characteristic of some other center than those associated with chromium in sapphire.

The peak of the 3000Å band was observed to shift to 3200Å at 175°C; after which, the peak of this band was observed to shift back to 3000Å again. The temperature, 175°C, at which this shift took place corresponds to the temperature of a thermoluminescence glow peak, and the wavelength, 3200Å, corresponds to the peak of a band in the emission spectrum of that glow peak.

Luminescence in the 6700Å Band and R-line - The luminescence observed in the 6700Å band and in the line at 6940Å is attributed to the R-line transitions and vibrationally assisted sidebands of Cr⁺³ in sapphire.

Competition Between the 6700Å and 3000Å Band - The irradiance of the 6700Å and 3000Å bands was observed to be mutually competitive with respect to both temperature and chromium concentration.

At low temperatures in sapphire, the 3000Å band was most intense and decreased at higher temperatures. As the irradiance of the 3000Å decreased, the irradiance of the 6700Å band increased. The irradiance of the 6700Å band at maximum was about 6 times larger than the irradiance of the 3000Å band at maximum.

In ruby with 0.005% Cr₂O₃, the 3000Å band was observed to be decreased in intensity by a factor of 1/20 compared to the same band in sapphire. The amount of power lost by the 3000Å band was, within the error of measurements, gained by the 6700Å band. The temperature competition was observed in the ruby sample also. In experiments performed on ruby of 0.05% and 0.5% Cr₂O₃ and reported in Mr. Cooke's masters thesis, the 3000Å band was not observed.

Suggestions for Future Work - In this report the author has observed the effects of the transition from sapphire to ruby (0.005% by weight Cr₂O₃) on the x-ray-induced luminescence of these crystals. It is apparent that there is a distinct change in the luminescence mechanism. It is necessary only to point out the changes in the thermoluminescence glow spectrum (compare graphs 3-1 and 3-5), the concentration quenching of the 3000Å band, and the change in the R-line luminescence temperature dependence to substantiate that conclusion. Yet it is not within the ability of the author to draw conclusions concerning the nature

of the mechanism of luminescence based on the information contained in this report. However some experiments which would aid in making such conclusions are discussed in the following paragraphs.

In these experiments, the distinction between fluorescence and phosphorescence was not made. Experiments to determine the lifetimes of the three regions of emission observed in the x-ray-induced emission spectra would be most useful in determining the energy levels involved in the process.

A large number of luminescence experiments have been reported in which the excitation used was ultraviolet and visible radiation from mercury vapor lamps. Experiments using this form of excitation have never been performed on the crystals used in the investigations for this thesis, and such experiments would be useful in comparing these experiments with many of those reported in the literature and could be incorporated into a larger set of experiments in the manner described as follows. First the absorption spectra of the unirradiated samples could be determined. Next, the wavelength dependence of the luminescence quantum yield could be determined over the wavelength region for which the absorption spectra were measured. Finally, photoconductivity measurements over this same wavelength region could be made. The series of experiments would allow the experimenter to determine which absorption transitions were responsible for luminescence and which of these transitions involved conduction electrons.

APPENDIX I

INSTRUMENT LIST

NUMBER

1. Hewlett-Packard 7005B, x-y Recorder.
2. Atomic Laboratories Photon Meter.
3. Keithley 610B, Electrometer.
4. Bausch and Lomb No. 45, 500mm Monochromator, 1200 lines per mm.
5. RCA 1P21 PMT, Response S-4.
6. EMI 9558-Q-A PMT, Response S-20 (Q).
7. Keithley 246, 0V-2000V Power Supply.
8. Hewlett-Packard 7000A, x-y Recorder.
9. RMS Motor Corporation, Speed Control.
10. Picker Mobile Medical X-ray Unit with a Machlett X-ray tube.

APPENDIX 2

COMPUTER TECHNIQUES AND CALCULATIONS

Computer and Programming Language Used

The computer used in performing many calculations reported in this thesis was a Digital Equipment Corporation (DEC) PDP-8/I with the following peripheral devices and accessories: 4000 bytes of extended core memory, a Dectape drive unit, an ARS teletype unit, a DEC AX08 analog to digital converter (ADC), a DEC AX08 display unit, a Hewlett-Packard 7000A x-y recorder, and a Hewlett-Packard 7005B x-y recorder. The FOCAL programming language was used exclusively. FOCAL is a proprietary language of the Digital Equipment Corporation.

Calculations Using the Least Squares Criterion

The least squares curve fitting criterion was used several times in analyzing the data. A subroutine was written to perform the least squares calculation and was incorporated into several main programs which linearized the data according to the particular type of curve to which the data was being fitted.

The least squares calculation was performed on the spectral irradiance versus wavelength data and it was found that in the wavelength region between 5500Å and 7000Å the curve reported in chapter II could be fitted to the data with a maximum deviation of about 5%.

The calculation of the energies of activation of the traps associated with the thermoluminescence was performed using the least squares criterion. The data from the thermoluminescence was plotted on semi-log paper and the region which appeared as a straight line was selected for analysis. This data was then linearized by fitting the logarithm of the PMT current to the inverse of the absolute temperature. The slope of the straight line obtained was reported as the energy of

activation of the trap.

Correction of Emission Spectra Data

In order to report the emission spectra data in the form in which it is seen in chapter III it was necessary to correct for the response of the spectrophotometer. This was done using the ADC, the two Hewlett-Packard x-y recorders, and the PDP-8/I computer with the extended memory. The emission spectra data in the form of 8"x11" graphs was digitized using the ADC. A voltage analog of the graphical data was generated using a power supply constructed out of two 1.5V dry batteries and two ten turn variable resistors. The power supply was used to position the pen of the x-y recorder on the curve of the emission spectrum. The inputs of two channels of the ADC were connected across the x and y inputs of the recorder, and the operator was able to order the analog to digital conversion under program control. In this manner, selected points on the emission spectragraphs could be digitized and stored in the computer.

Once the data was in the computer, it was corrected for spectrophotometer response, the corrected data was plotted on a second x-y recorder using the AX08 display unit, and the area under selected regions of the corrected spectrum calculated. The correction of the data was carried out using the data shown in figure 2-4. A second order polynomial was used to interpolate between the digitized data points. The La Grange interpolation formula was used ⁽²⁴⁾. The areas under the various spectral regions were calculated by evaluating exactly the areas under the interpolating polynomials. The areas under the interpolating polynomials were reproducible to 20%.

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BIOGRAPHICAL SKETCH

Ivan E. Collier, Jr. was born [REDACTED] in Evansville, Indiana and has lived for the past 21 years in Owensboro, Kentucky. He attended Owensboro High School where he was graduated in 1962.

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