

Photoluminescence

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Photoluminescence is an emission of light with a specific wavelength by a matter when the matter absorbs photons. The characteristics of emitted light depend on the electronic structure of the matter. In this experiment, the photoluminescences of rhodamine 590 (an organic molecule) and ruby crystal (an inorganic crystal) were measured and analyzed with proper fitting techniques. Two photoluminescence spectra of each matter were compared and contrasted. Also, the photoluminescence of ruby was observed in the low-temperature regime. The photoluminescence of rhodamine 590 around 567 nm consisted of two broad peaks with little wavelength difference, which represents fluorescence and phosphorescence, respectively. The photoluminescence of ruby showed relatively sharp and separated peaks compared to that of rhodamine 590. For ruby, peaks were broadened and their intensities changed as the temperature increased. The temperature dependence of the properties of peaks was analyzed.

I. INTRODUCTION

Luminescence is the emission of photons by a matter when the electron in the matter is excited. The emitted photon by luminescence has a unique wavelength that does not depend on the black-body radiation. Therefore, electronic structures and other properties of the matter can be determined by luminescence. Especially, if the excitation of electrons occurs by light, it is termed photoluminescence. In this experiment, the photoluminescence of Rhodamine 590, which is an organic compound used as a dye, and ruby, which is a chromium-doped alumina crystal, was analyzed. The photoluminescence at room temperature was analyzed first, and then the photoluminescence by ruby was analyzed at a low temperature of about 10 K.

A. Background: Rhodamine

Rhodamine is an organic molecule that is used as a dye and ink. The core structure of rhodamine is shown in FIG. 1. The properties of rhodamine can be tuned by changing the functional group. [1] In this experiment, the

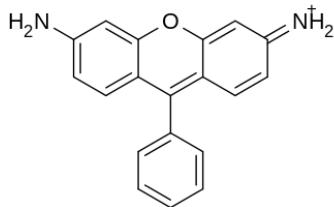


FIG. 1. The core structure of a rhodamine molecule.

photoluminescence of rhodamine 590 was analyzed. Rhodamine 590 has two ethyl groups ($-\text{CH}_2\text{CH}_3$) attached to two nitrogens, and one carboethoxy group ($-\text{COOCH}_3$) attached to the ortho-position of the separated benzene ring. The variations of rhodamine-based compounds including rhodamine 590 are shown in FIG. 2. [2]

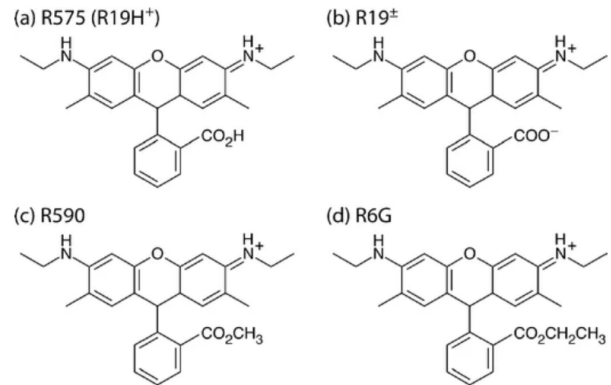


FIG. 2. Some variations of rhodamine-based compounds. [2]

In an organic molecule, the energy of molecular orbitals determines the wavelength of emitted photons. Especially, the energy difference between a HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) is significant. Though electrons may excite to the state whose energy is higher than LUMO, the electrons immediately drop to the LUMO due to the short lifetime of the state. Then, the electron falls from LUMO to HOMO. Therefore, the predominant energy of emitted photons is the energy difference between the LUMO and the HOMO. This empirical tendency is termed Kasha's rule. [3]

In an organic molecule, molecular orbitals can be simplified to the wave function of an infinite potential well. When double bonds and single bonds are alternatingly

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connected, the π orbitals of atoms are arranged in the same orientation. This structure can be approximated to an infinite potential well. As more atoms are connected with alternating double and single bonds, the length of the well increases. The structure in which double bonds and single bonds alternate is termed conjugation. Conjugation structure and the length enable the organic molecule to emit photons with a certain wavelength. [4]

The electronic structures of rhodamine-based molecules have already been investigated by computational methods such as Density Functional Theory (DFT). The energy diagram of rhodamine 6G's molecular orbitals is shown in FIG. 3. [5] Rhodamine 590 and Rhodamine 6G have slightly different structures, as shown in FIG. 2.

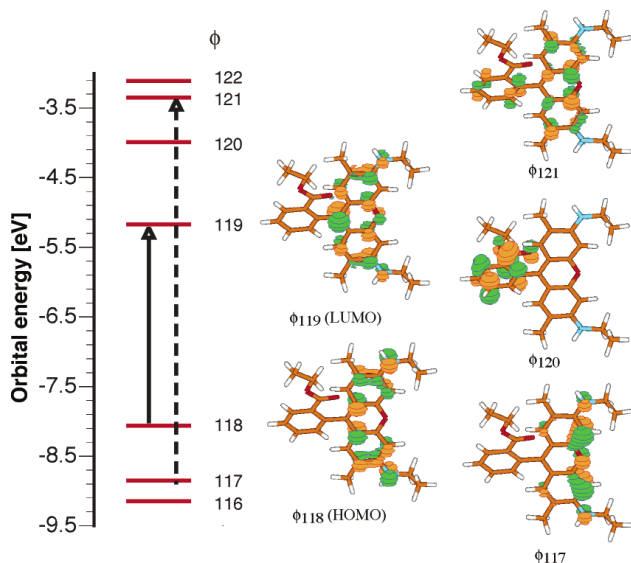


FIG. 3. Molecular orbital structures of rhodamine 6G and their energy diagram. [5]

B. Background: Ruby

Ruby is Al_2O_3 based crystal with chromium impurity. The photoluminescence of a ruby crystal is different from that of organic molecules. Ruby crystal consists of numerous atoms with spatial periodicity. By quantum mechanical effect, the atoms construct continuous energy levels, which are termed bands. The photoluminescence of ruby occurs due to the electron transition between two bands. The energy difference of two bands is termed a band gap.

Without any impurities, the band gap of Al_2O_3 is over 7.0 eV. [6] With this wide band gap, the crystal does not absorb and emit visible rays. However, with an appropriate concentration of chromium impurity, the electronic structure of the crystal changes, and it can emit a visible ray. Especially, the energy level of chromium mainly con-

tributes to the photoluminescence of ruby. The energy diagram of chromium impurities in the Al_2O_3 crystal is shown in FIG. 4. As shown in FIG. 4, the incident light excites the electron of chromium, which is labeled as 'excited states'. Given that these states have a relatively short lifetime, the electrons in these states transit to the metastable state that has lower energy. The lifetime of the metastable state is relatively longer than other excited states. Therefore, the electrons are accumulated in the metastable state. They spontaneously transit to the ground state and then emit photons with a certain wavelength. The ray is termed the R-line, which is the major peak of photoluminescence in ruby. The wavelength of the R-line is known to be about 690 nm, which is visible light with red color. [7]

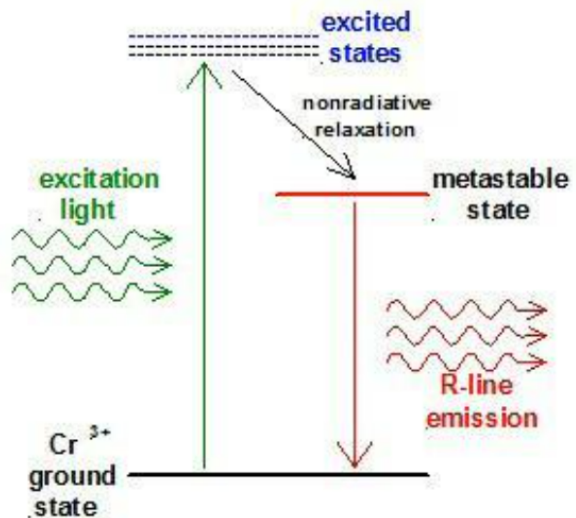


FIG. 4. Energy diagram of chromium impurities in the Al_2O_3 crystal.

II. MATERIALS AND METHODS

A. Apparatus Setup

To measure photoluminescence, some optical apparatus and their good alignment are required. The overall setup of the optical system in this experiment is shown in FIG. 5. The path of LASER was shown as green lines; the path of photoluminescence was shown as red lines.

The LASER was SLD (Super-Luminescent Diode) with a wavelength of 532 nm (SLD-532-070T, Anritsu Cooperation, inc.). The LASER beam is aligned by lenses and then passes through the dichroic filter. The dichroic filter reflects the LASER beam to the sample. For the rhodamine 590, the solution was contained in a sealed vial. The vial was located in an appropriate position to absorb the incident beam well. Meanwhile, the ruby sample was located in the cryostat where a rotary pump

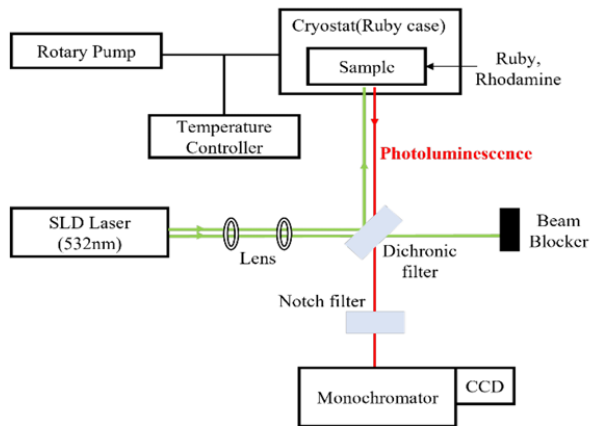


FIG. 5. The schematic diagram of the apparatus.

and a temperature controller are attached. The locations of the two samples were set well to make them absorb the incident beam from the LASER. The photoluminescence light emitted from the sample consecutively passes through the dichroic filter and the notch filter. Finally, the CCD (DU401A-BVF, Andor, Inc.) with a monochromator (DM500i, DXG, inc.) receives the photoluminescence light to analyze the spectrum. The dichroic filter and the notch filter block the incident LASER beam in front of the CCD since the CCD might be broken when it is exposed to high-intensity light.

B. Photoluminescence of Rhodamine 590

The photoluminescence of rhodamine 590 was analyzed at room temperature. To obtain the spectrum of the photoluminescence, Andor Solis software (Andor, Inc.) was applied. First, the temperature of CCD was set to be -35°C and stabilized. Then, the central wavelength to measure was set to be 567 nm. The exposure time of each measurement and the number of measurements were set to be 0.1s and 10, respectively. These parameters were tuned to improve the result, which will be shown in the following section. The background signal without photoluminescence, the total signal with photoluminescence, and the difference between the two signals were all obtained during the spectrum measurement.

C. Photoluminescence of Ruby

The photoluminescence of ruby was analyzed at various temperatures. The measurement was conducted between 10°C and 290°C , with an interval of 10°C . To obtain the low temperature, the helium compressor and the rotary pump was applied. The helium compressor can maintain extremely low temperatures of about 5 K. Since the helium compressor must function at a

low pressure, the vacuum was maintained by a rotary pump. Otherwise, the air will liquefy inside the helium compressor. After reaching the temperature low enough, a temperature controller (331 temperature controller, Lakeshore, Inc.) was turned on to obtain the set temperature. When the temperature was stabilized, the spectrum measurement was performed. Note that the central wavelength for ruby was set to be 690 nm. The obtained spectrum was analyzed with an appropriate fitting technique, which will be explained in the following section. Also, the temperature dependence of the photoluminescence spectrum was analyzed.

III. RESULT

A. Photoluminescence of Rhodamine 590

The photoluminescence spectrum of rhodamine 590 is shown in FIG. 6 with a black solid line. The overall form of the spectrum shows a broad peak with a center located in about 2.2 eV. Since the spectrum seems to have a single peak, the single Gaussian fitting was tried first, as shown in 6 with a red dotted line. The position and intensity of the peak and RMSE (Root-Mean-Square Error) of the fitting were shown.

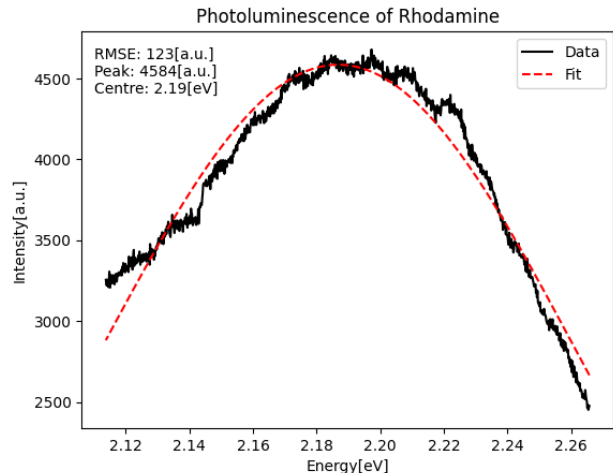


FIG. 6. The photoluminescence spectrum of rhodamine 590 with a single Gaussian fitting.

However, the fitting result seems to deviate from the experimental spectrum. To fit the experimental spectrum, the double Lorentzian fitting was conducted. The double peaks were assumed because rhodamine 590 is known to show both fluorescence (photoluminescence due to the electron transition from a singlet state to a singlet state) and phosphorescence (photoluminescence due to the electron transition from a triplet state to a singlet state). Note that the wavelengths of the two peaks due to fluorescence and phosphorescence are too small to distinguish them with a naive observation of the spectrum.

[8] The result is shown in FIG. 7.

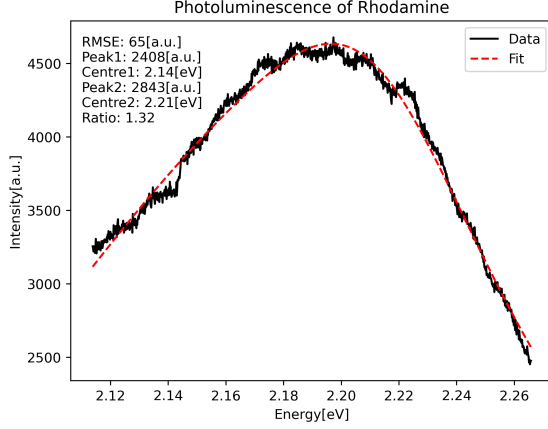


FIG. 7. The photoluminescence spectrum of rhodamine 590 with a double Lorentzian fitting.

As shown in FIG. 7, the root mean square error (RMSE) of the fitting was decreased from 123 to 65, where the improved one is almost half of the previous one. From the improved RMSE, the double-peak model seems to be plausible. According to the fitting, the position of the first peak was 2.14 eV (579.4 nm), and the position of the second peak was 2.21 eV (561.1 nm). Each peak corresponds to the phosphorescence and the fluorescence, respectively. [8]

B. Photoluminescence of Ruby

The photoluminescence of ruby was measured from 10 K to 290 K, with an interval of 10 K. The photoluminescence spectrum of ruby at 10 K (which represents the low-temperature limit) and at 290 K (which represents the room-temperature result) are shown in FIG. 8a and 8b, respectively. The measured spectrum was shown with solid black lines. Since there were two major peaks in the spectrum, the double Lorentzian fitting was conducted, as done in FIG. 7. The fitting function was shown with dotted red lines.

As shown in FIG. 8a and 8b, there are two peaks in the photoluminescence spectrum of ruby. The result seems to be consistent with the preceding research. The preceding research reported two peaks for the photoluminescence of ruby as well as their broadening effect by temperature increase. [9] The properties of peaks such as intensity or width significantly changed depending on the temperature. The temperature dependence of the parameters that describe the peak shape is shown in FIG. 9. With regard to the temperature dependence, further discussion will be conducted in the following section.

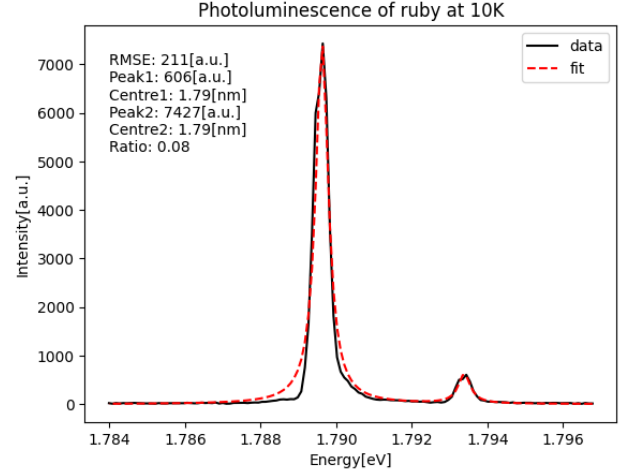


FIG. 8a. Photoluminescence spectrum of ruby at 10 K.

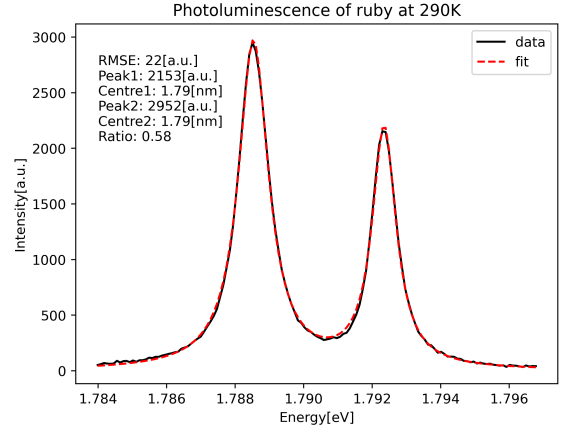


FIG. 8b. Photoluminescence spectrum of ruby at 290 K.

IV. DISCUSSION

A. Comparison of Rhodamine 590 and Ruby

Comparing the photoluminescence spectra of rhodamine 590 and ruby, their shape is quite different. The major difference between the two spectra is the width of the peaks. In rhodamine 590, the widths of the two peaks were too large (Full Width at Half Maximum (FWHM): 0.101 eV and 0.064 eV respectively) to distinguish them, as shown in FIG. 7. As a result, the overall spectrum of rhodamine 590 was unimodal around 2.20 eV (563.6 nm). On the contrary, ruby showed a very sharp peak (FWHM: 0.054 eV and 0.041 eV respectively at 290 K) that is enough to be distinguished. As a result, the overall spectrum of ruby was bimodal around 1.790 eV (692.7 nm).

Broad peaks imply that the energy fluctuation of the states is large. Therefore, the broadness of peaks is an

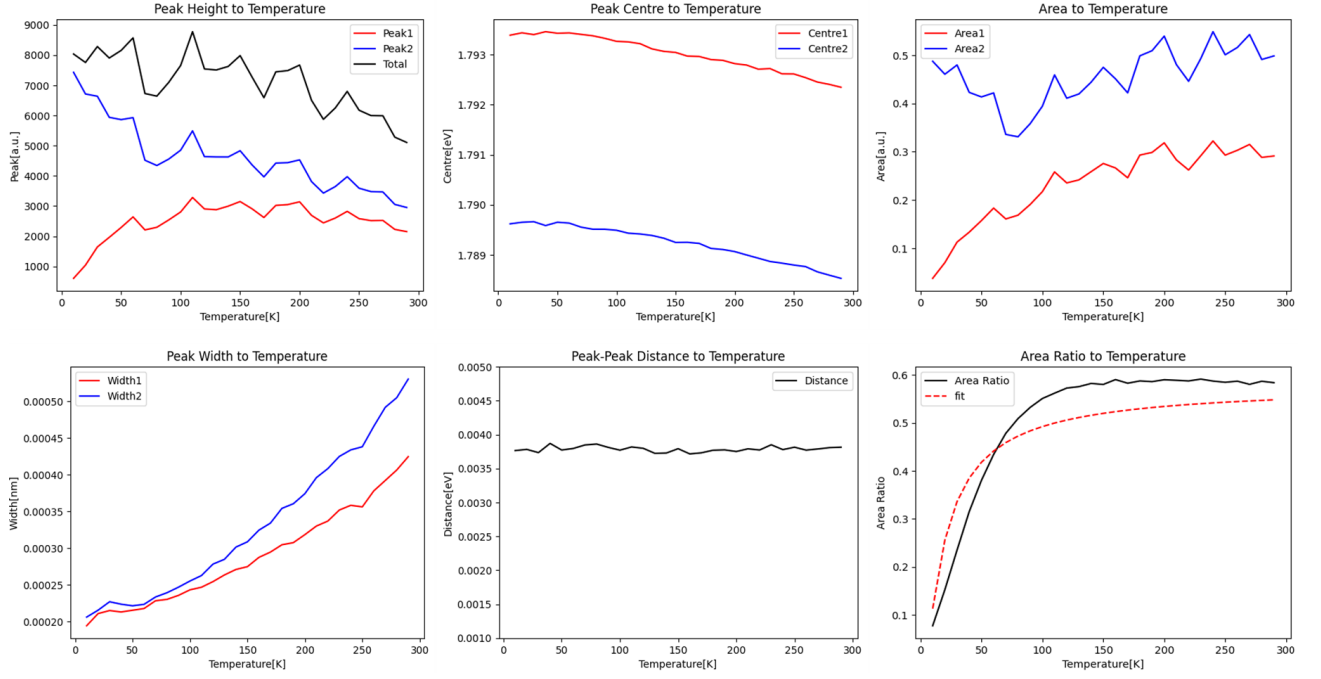


FIG. 9. The temperature dependence of photoluminescence spectrum in ruby. The temperature dependence of peak heights (top left), peak widths (bottom left), peak centers (top middle), peak-peak distance (bottom middle), peak areas (top right), and area ratio (bottom right) were shown.

indicator of the magnitude of energy fluctuation for each state in the system. In rhodamine 590, the energy states of the molecule may fluctuate due to its vibration, rotation, or interaction with a solvent. On the contrary, ruby does not show such behavior. Though there is a lattice vibration in the ruby crystal, the positions of atoms in ruby are more constrained than in rhodamine 590. Namely, the bulkiness of ruby crystal constrains the fluctuation of energy states and shows sharp peaks, while relatively flexible rhodamine 590 shows broad peaks.

B. Temperature Dependence of Photoluminescence in Ruby

As explained in the above section, the temperature dependence of the photoluminescence spectrum in ruby is a meaningful topic to discuss in detail. The temperature dependence of the spectrum can be separated into mainly three parts as follows: 1) peak broadening, 2) peak shift, and 3) peak area change.

1. Peak broadening

The heights and widths of the two peaks depending on the temperature are shown on the left side of FIG. 9. As the temperature increases, the widths of both peaks increase while the heights decrease. Though there is a little fluctuation in the height decrease, the overall tendency

can be checked in the upper left side of FIG. 9. Namely, the peaks are broadened as the temperature increases.

As mentioned in the previous subsection, the peak broadening implies an increase in energy level fluctuation. In ruby, the energy level might fluctuate due to a thermal fluctuation. The magnitude of thermal fluctuation can be briefly represented as $k_B T$, where k_B is a Boltzmann constant. Therefore, the thermal fluctuation contributes more to the peak broadening as the temperature increases. The quantitative relationship between the temperature and the peak broadening effect must be proposed based on the theory and a proper model.

2. Peak shift

The positions of the two peaks and their difference depending on the temperature are shown in the middle of FIG. 9. As the temperature increases, the two peaks are shifted to the long wavelength side (i.e. low energy side). The magnitude of the shift for the two peaks is almost identical, as shown in the bottom middle of FIG. 9. This result matches well with the preceding literature. The result obtained from the literature is shown in FIG. 10. In the literature, the photoluminescence spectra of ruby at -140°C , -90°C , and 0°C were reported. Referring to FIG. 10, both peaks are shifted to the long wavelength side as the temperature increases with a similar magnitude of shifts.

In FIG. 10, 4A_2 state is a ground state. Above it,

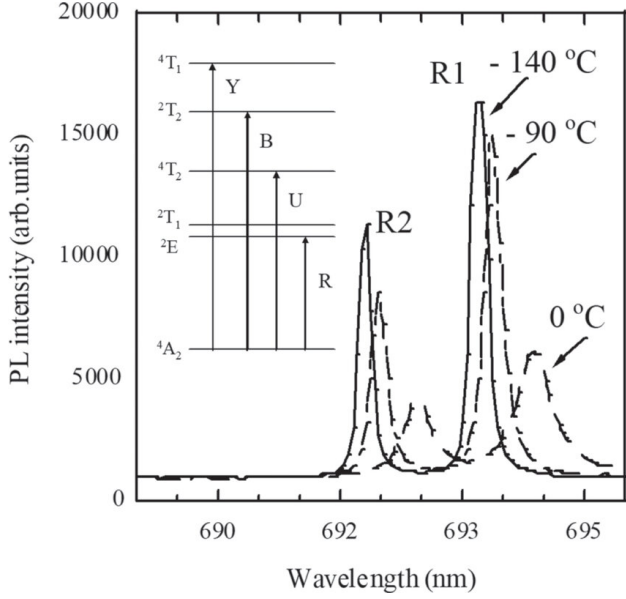


FIG. 10. The temperature-dependent photoluminescence spectra of ruby from the literature. [9]

there are a couple of excited states with a slight energy difference. The lower one is 2E state, whose spin state is a triplet state. The upper one is 2T_1 state, whose spin state is a singlet state. The R1 peak accounts for the transition from 2E to 4A_2 , while the R2 peak accounts for the transition from 2T_1 to 4A_2 .

In the same logic as the peak broadening effect, the thermal fluctuation accounts for the peak shift. When the temperature increases, the energy level of the 4A_2 state increases due to the thermal fluctuation. Therefore, the energy differences between the 4A_2 state and other states decrease. This accounts for the overall peak shift. However, the distance between the two peaks was maintained static. It is because the distance depends on the energy difference between the 2T_1 state and the 2E state, which is the singlet-triplet conversion energy. Since the spin state is not affected by temperature change, the energy difference of the 2T_1 state and the 2E state remains static. As a result, the peak-peak distance is not affected by the temperature change.

3. peak area change

The area of each peak was calculated by the product of its FWHM and height. The temperature dependence of the area and area ratio are shown on the right of FIG. 10. The area of each peak does not have a clear temperature dependence, since the area was calculated by the product of the FWHM and the height which show the opposite temperature dependence. However, the area ratio of the two peaks showed a clear temperature dependence. The result can be analyzed briefly based on the Boltzmann distribution. According to the Boltzmann distribution,

the probability p_i that an electron possesses the state of energy E_i is written as follows. k_B is a Boltzmann constant.

$$p_i \propto \exp\left(-\frac{E_i}{k_B T}\right) \quad (1)$$

If electrons are assumed to be distributed with the Boltzmann distribution in the 2T_1 and 2E states, the ratio of electron in two states are described as follows.

$$\frac{N_T}{N_E} = \exp\left(-\frac{E_T - E_E}{k_B T}\right) \quad (2)$$

If the area of the photoluminescence peak is proportional to the number of electrons in the excited state, the ratio in 2 is identical to the area ratio. To confirm this, the exponential fitting with a fitting parameter a was conducted. The fitting function is given below.

$$f(T; a) = \exp\left(-\frac{a}{k_B T}\right) \quad (3)$$

The optimized fitting function is shown in the bottom right of FIG. 10 with a red dotted line. The fitting gave the parameter a to be 0.002304 eV. As shown in FIG. 10, the fitting function does not match the experimental result perfectly. Also, the optimized parameter a , which represents the peak-peak distance, slightly deviates from the experimental value (i.e. about 0.0037 eV, according to the bottom middle of FIG. 10). This mismatch implies that the Boltzmann distribution is not enough to perfectly account for the temperature dependence of the area ratio. Nevertheless, with the Boltzmann distribution, it is possible to roughly follow the curve and approximate the energy difference of the two states. To predict the temperature dependence more accurately, quantum mechanical theory and knowledge from solid-state physics are necessary, which is out of the scope of this experiment.

C. Further Discussions

In this experiment, a darkroom or a blind to screen the external light source was not prepared due to a technical issue. Because of the external light source that is not screened, the CCD may count not only the photoluminescence signal but also the signal by the external light source. Therefore, to improve the experiment, all of the apparatus must be located in a darkroom to screen the external light.

The temperature controller is the other major drawback of this experiment. During the experiment, obtaining a perfectly stable temperature was almost impossible. Despite the heater being turned on at a specific temperature for a long time, a significant temperature fluctuation remained. Furthermore, the temperature displayed in the temperature controller might not be equal to that of the ruby sample. Since the inner structure of the cryostat is

unknown, the thermal equilibrium between the cryostat and the ruby cannot be ensured. To resolve the problem, the temperature of ruby needs to be measured directly. The detailed method to measure the temperature is a technical part, which is beyond the scope of this experiment.

V. CONCLUSION

The photoluminescence of rhodamine 590 and ruby crystal was measured and analyzed. An appropriate curve fitting such as a double Lorentzian fitting was conducted to interpret the result of the measurement properly. The photoluminescence spectra of rhodamine 590 and ruby were compared, where the peaks of rhodamine 590 were found to be much broader than

those of ruby. The broader peaks of rhodamine 590 stem from the flexibility of rhodamine 590 molecule which can vibrate or rotate more freely than ruby. Also, the temperature dependence of the photoluminescence spectra in ruby was analyzed. Peak broadening, peak shift, and peak area change were mainly studied, and a qualitative explanation for each phenomenon was proposed. Most of the phenomena were found to occur by thermal fluctuation, whose magnitude is proportional to the temperature.

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