Absorption and Emission Spectroscopy of a Lasing Material: Ruby

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Ruby is a crystalline material of great historical importance since it was used as the active medium to create the first laser *(1).* Advanced courses in the areas of materials science and laser principles and applications are becoming of increasing importance in modern chemistry curricula, thus making it desirable to develop experimental activities related to the mentioned topics. The study of the photophysical properties of ruby establishes a useful connection between materials science and lasers. In addition, it allows one to elucidate some basic concepts of inorganic chemistry, photochemistry, and kinetics. An experiment on the temperature dependence of the decay of ruby luminescence is described by Shoemaker, Garland, and Nibler *(2),* where a frequency doubled, pulsed Nd:YAG laser is used as fast optical pump. This article describes a technically and conceptually simpler experiment that can be considered as an introduction to the more advanced experiment by Shoemaker, Garland, and Nibler *(2).* It consists of the study of the absorption and emission spectra of ruby and in the determination of the room-temperature lifetime of the luminescent excited state. A description of a similar laboratory experiment can be found on the Web *(3).* Education literature on photoluminescent solids is not widely represented *(4–8),* and the present article provides a further contribution to this field. This experiment allows the students to directly obtain precise knowledge of the radiative properties of ruby and also to acquire technical abilities in performing spectroscopic measurements on solids. Each group of students can usually perform the set of measurements in one hour of laboratory time.

Energy Levels and Electronic Transitions of Cr^{3+} in Ruby

Ruby is crystalline Al_2O_3 (corundum) in which a small percentage of Al^{3+} ions are substituted by Cr^{3+} ions. In the corundum crystalline host, each Cr^{3+} ion is at the center of a distorted octahedral site whose vertices are occupied by O^{2-} ions. Cr^{3+} has three electrons in its 3d valence shell, and its electronic ground state corresponds to a $(t_{2g})^3$ configuration where all electrons have parallel spins, thus producing the quartet state $^4A_2$. Three further electronic states derive from the $(t_{2g})^3$ configuration, but they correspond to doublet states and are designated as ^2E, $^2T_1$, and $^2T_2$, respectively. Several electronic states are also produced by the excited electronic configuration $(t_{2g})^2\,(e_g)^1$, two of which are quartet states designated as $^4T_1$ and $^4T_2$, respectively *(9, 10).* Electronic transitions between the ground $^4A_2$ state and the $^4T_1$ and $^4T_2$ excited states produce the main absorption features of ruby in the visible region. When the population of the $^4T_1$ and $^4T_2$ excited states is increased upon irradiation, a subsequent fast nonradiative decay first brings population to the metastable, low-energy ^2E excited state, from which the final relaxation takes places radiatively, through the spin-forbidden electronic transition $^2E \rightarrow {}^4A_2$. This transition is responsible for the deep-red emission of ruby when excited by shorter wavelengths, and it was exploited to produce the first laser emission *(1).*

Experimental Details

Disks of industrial ruby were purchased from Swiss Jewel. These disks have polished surfaces, and the Cr^{3+} concentration is around 2%. Students record the absorption spectrum of ruby in the visible region using a Cary 1E spectrophotometer (Varian), whereas emission spectra (including time resolved spectra) are collected using a Cary Eclipse spectrofluorometer (Varian). Both absorption and emission spectra can be recorded using standard cuvettes as sample holders, without the need of any solid-state accessory. (More experimental details are available in the Supplemental Material.[W])

Hazards

No significant hazards are associated with this experiment.

Results

Absorption Spectrum

Figure 1 shows the absorption spectrum of ruby recorded in the visible region. It is dominated by two broad absorption bands peaked at 407 nm ($^4T_1 \leftarrow {}^4A_2$) and 551 nm ($^4T_2 \leftarrow {}^4A_2$), respectively. Some other very weak and sharp absorption bands are detectable in the spectrum: they correspond to spin-forbidden transitions between the ground electronic state and doublet excited states arising from the same $(t_{2g})^3$ configuration that become weakly allowed because of spin–orbit coupling. The weak band occurring at the longer wavelength (694 nm) corresponds to the $^2E \leftarrow {}^4A_2$ transition. This band is actually made of two closely spaced components (additional information in the Supplemental Material[W]), as it can be seen from the inset of Figure 1, which shows the recording of the 694 nm band made with 0.2 nm resolution.

Emission Spectrum

Figure 2 shows the fluorescence spectrum of ruby recorded in the visible region using 407 nm excitation. A sharp emission is present in the red region, at 694.2 nm, which the students can immediately assign to the spin-forbidden $^2E \rightarrow {}^4A_2$ electronic transition. By collecting the excitation spectrum, students can verify that the red luminescence of ruby can actually be excited by any radiation in the violet to yellow range.

Radiative Decay

Having identified the exact position of the emission peak, students can measure the lifetime of the emitting ^2E state. Figure 3 shows the decay curve of the 694.2 nm fluorescence signal, excited with 407 nm radiation. Students analyze the decay curve using Origin graphics software (Microcal). A mono-exponential decay function of the type

$$I = I_0 \, e^{-t/\tau}$$

(where I is the emission intensity and τ the lifetime of the ^2E state) can be fitted to the observed curve, which indicates that this radiative decay follows a first-order kinetic law. The nonlinear least-squares analysis of the decay curve reported in Figure 3 yields the lifetime $\tau = 4.268 \pm 0.006$ ms.

Discussion

This article describes a laboratory experiment that allows the students to characterize the main photophysical properties of ruby. The absorption spectrum indicates that ruby efficiently absorbs most of the visible light with $\lambda < 600$ nm. The fluorescence and excitation spectra demonstrate that any radiation absorbed in the wavelength range between 400 and 600 nm is converted into a narrow emission in the red region. This allows the students to understand why a broadband flashlamp was used by Maiman as the pumping device to obtain stimulated emission from a ruby rod *(1)* and also why a ruby laser is an untunable laser source. The red fluorescence is peaked exactly at the same wavelength as the $^2E \leftarrow {}^4A_2$ absorption band. This makes clear that the final state of the emission is the ground electronic state of Cr^{3+} ions, so that a population inversion between the excited ^2E state and the ground $^4A_2$ state must be achieved to produce laser action at 694.2 nm, on the basis of a three-level laser scheme *(11)*. The study of the radiative decay from the ^2E state shows that a simple first-order kinetic model reproduces the observed curve. This means that the processes that bring population from the optically pumped $^4T_1$ and $^4T_2$ states to the metastable ^2E state are much faster than the subsequent radiative decay. The analysis of the decay curve allows the students to determine the exceptionally long lifetime of the ^2E state. This property is of fundamental importance to permit laser action in ruby because it makes it possible to accumulate population in the ^2E state until the condition of inverted population with respect to the ground electronic state is achieved.

This laboratory experiment has been designed to provide new experimental activities to courses that include topics related to lasers' operation and properties of crystalline materials, but more general courses of inorganic chemistry, photochemistry, and even chemical kinetics could also include this instrumental experiment in the respective laboratory activities. Ruby is an exotic, but well known material, and this stimulates students' interest towards the study of its spectroscopic properties.

Acknowledgment

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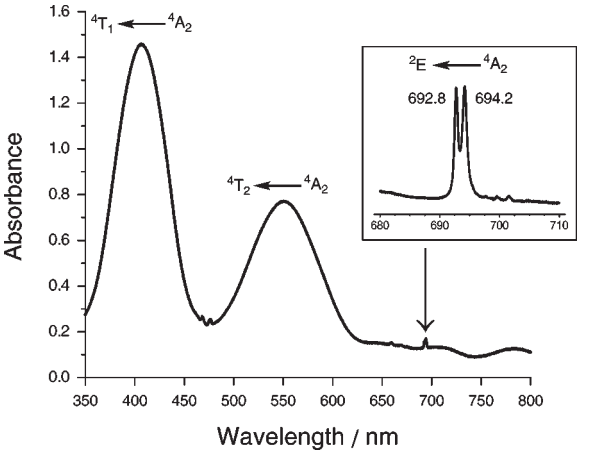

Figure 1. The absorption spectrum of ruby in the visible region.

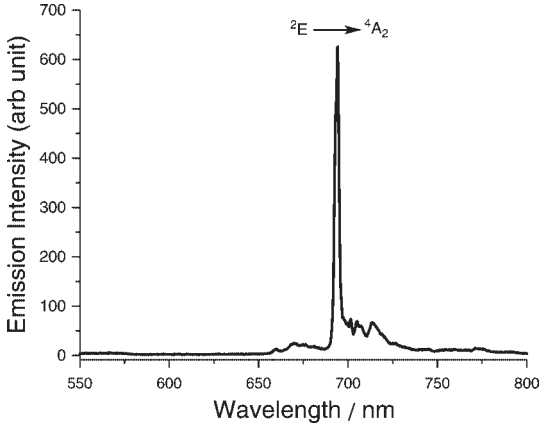

Figure 2. The fluorescence spectrum of ruby. Excitation wavelength is 407 nm.

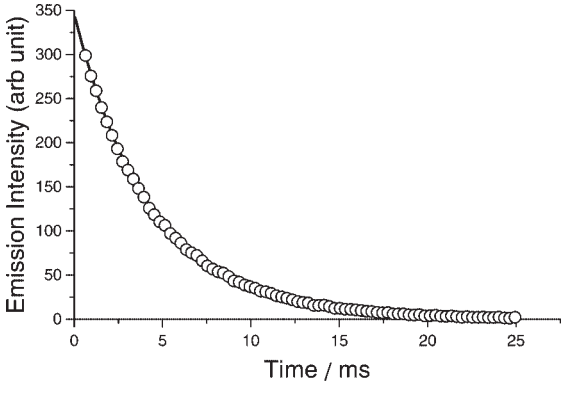

Figure 3. Radiative decay of the ^2E state. Emission wavelength 694.2 nm. Circles indicate experimental points (1/10 of the total number), whereas the continuous line corresponds to the fitted mono-exponential decay function.

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[W]Supplemental Material

More theoretical and experimental details concerning the study of the photophysical properties of ruby are available in this issue of *JCE Online*. An ASCII file (spectra.txt) containing the spectra collected for this experiment is provided. It can be downloaded and used to prepare slides for classroom lessons.

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