CHAPTER 2

EXPERIMENTAL SETUP

2.1   METHODS

The experimental methods included fluorescence excitation spectroscopy, fluorescence spectroscopy, and fluorescence transient measurements. These three methods provide complementary information on the physical processes occurring in Eu_2O_3. Excitation spectra are obtained by measuring the sample emission at a specific wavelength while the dye laser scans the wavelength of the exciting beam. Fluorescence spectra are obtained by exciting at a fixed wavelength and scanning the monochromator. Transient measurements are made with both the excitation and the emission wavelengths fixed and recording the fluorescence intensity over time. A schematic of the experimental setup is presented in Figure 4.

2.2   EXCITATION SOURCE

The excitation source was a tunable dye laser (Continuum ND60) with Coumarin 540A dye. The Coumarin 540A dye provides a scanable range of 516-590-nm with a line width of .03 nm (1 cm^{-1}). Energy output was adjustable between 2 to 400 mJ. The dye laser has one oscillator and two amplifiers.
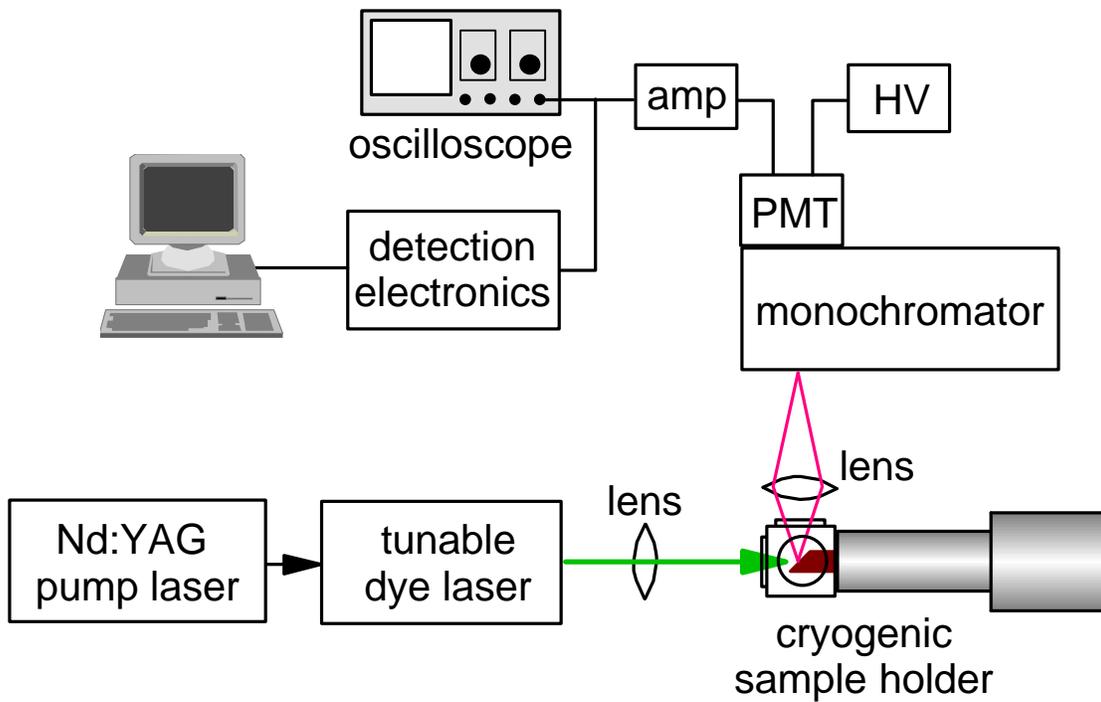
Figure 4. Experimental Setup

Wavelength selection is provided by the grazing-incidence grating method. Dye laser operation is externally controlled by a computer equipped with Continuum ND61 driver software (Version 10.1).

A 10-hertz Nd^{3+}:YAG laser (Continuum Surelite II) pumps the dye laser, which has a pulse length of 4 to 6 ns and energy stability of $\pm 4\%$. Adjusting the xenon flashlamp voltage between 1.30 kV and 1.60 kV controls laser output energy. Adjusting the Q-switch delay time also can be used to control laser energies, but in general it was kept at 200 μs for maximum efficiency. The beam from the Nd^{3+}:YAG laser is directed to the dye laser using three dichroic mirrors which are ~99.9% reflective for 355-nm radiation.

The beam exiting the dye laser is directed to the sample using a series of mirrors. The beam width is adjusted by passing through an aperture opening. In order to limit any laser fluorescence from reaching the sample or detector a LS600 cut-off filter is placed before the sample. For measurements at very low laser intensities, neutral density filters are also placed before the sample.

2.3   LASER ENERGY AND FOCUS

The laser energy of the excitation source was measured using a DigiRad R-752 Universal Radiometer. A microscope slide was placed at a 45° angle in the beam path before the sample, and 3.5% of the laser beam was reflected onto by the radiometer. This allowed continuous monitoring of laser energy during data collection.

For most experiments the laser beam was tightly focused onto the sample surface with a 6-cm focal length cylindrical lens to produce a sharp line focus. The total area excited cannot be determined exactly for powdered samples because of unavoidable variations in packing density and laser scattering of different samples. In addition, the necessary use of the high laser intensities can cause the sample packing to change during the experiment.   However, care was taken to keep the excitation focus as reproducible as possible for all experiments, and certainly a qualitative data comparison between samples is possible.

2.4   SAMPLES

All powdered samples were packed tightly into a circular depression (3-mm diameter and 3-mm deep) on a copper sample holder. A glass microscope slide cover was secured over the sample to hold it in place. Large crystal samples were affixed to the sample holder and kept in contact with thermal grease. No glass cover was used in this case. The sample holder was mounted on the cold head of a closed-cycle refrigerator (Cryomech GB15). The cooling system can maintain a temperature of approximately 11 K and was equipped with a heating unit for higher temperatures.

2.5   MONOCHROMATORS

For site specific excitation and fluorescence spectra, fluorescent emission was dispersed with a 1-meter monochromator (Spex 1000M) that was 90° from the excitation beam. The emission was focused onto the entrance slit of the monochromator using two lenses. The 1-meter monochromator has a dispersion of 0.8-nm/mm, and was normally operated with a slit width of 100-µm producing a 0.08-nm spectral bandpass.

Excitation spectra monitoring broadband emission were recorded using a ¼-m monochromator (Jarrell-Ash). The emission was focused onto the 200-µm slit of the monochromator using one lens and a turning mirror.

To avoid scattered laser light from reaching the detector two red colored filters (OG590 & OG595) were placed before the monochromator. For very strong fluorescent signals a Neutral Density filter was also placed before the monochromator.

2.6   DETECTORS

A GaAs (Cs) photomultiplier tube (HAMMAMATSU R-636-10) provided signal detection for the 1-meter monochromator. This GaAs(Cs) photocathode has a spectral response in the 185 to 930-nm range, with highest quantum efficiency in the 300 to 800-nm range. A cooled PMT housing (Amherst Scientific Corp. Model 4100) is used to maintain an operational temperature of -20° C.

The quantum efficiency of the detector refers to the number of photoelectrons emitted from the photocathode divided by the number of incident photons. In the most commonly used range of 600 to 640-nm the quantum efficiency is ~13%.

The ¼-m monochromator utilized a Sb-Cs photomultiplier tube (Hammamatsu R-636-10). It has a spectral response from 185 to 700 nm, with maximum quantum efficiency at 340 nm. Operation was conducted at room temperature.

Both photomultiplier tubes are the side-on type, and has a circular-cage type array of electron multipliers (dynodes) utilized for compactness.   The time response of the GaAs(Cs) and Sb-Cd photocathodes is 2 and 2.2 nanoseconds, respectively. The anode to cathode supply voltage is provided by a Stanford Research Systems High Voltage Power Supply (Series PS 300). The GaAs(Cs) photocathode is operated with an anode to cathode voltage of 1250(Vdc), while the Sb-Cd photocathode is operated with a voltage of 1000(Vdc).

The output current of the photomultiplier tube is converted to a voltage signal using a 100-MHz bipolar amplifier (Phillips Scientific Model 6931). The output voltage is transmitted through coaxial cable to an oscilloscope (Tektronic TDS460) and boxcar averager (Stanford SR250) and terminated with a 50-W resistor.

2.7 BOXCAR AVERAGER AND INTEGRATOR

The Stanford SR250 is well suited for recovering fast analog signals from noisy backgrounds.[1] It consists of a gate generator, a fast gated integrator, and exponential averaging circuitry. After being triggered externally by the Nd^{3+}:YAG laser, the SR250 waits a set delay time before sampling the input signal. Then the signal is integrated during the gate by the fast gated integrator. The output from the integrator is normalized to the gate width producing a voltage proportional to the input signal during the gate. Both the delay time and the gate width are varied depending on the experiment. An average of 10 samples is taken before the analog signal is sent to an analog-to-digital data-acquisition board (National Instruments Lab PC+). Following conversion the data is collected on a computer using a Lab View data acquisition program. The software collects and averages 10 data points for each data point that is displayed. After acquisition the data files are converted to ASCII format.

The signal gain of the instrument (volts out / volts in) is controlled using the sensitivity switch. The sensitivity is set from 1-V/V up to 1-V/5-mV depending on input signal strength.

2.8 OSCILLOSCOPE

The intensity decay curve after each excitation pulse is displayed on a multichannel 350-MHz digital oscilloscope (Tektronix TDS460). The signal

18

voltage from the detector is plotted against time. With the oscilloscope it is

possible to visually monitor for detector saturation or other possible problems

during excitation and fluorescence data acquisition. A gate output signal from

the SR250 and the trigger signal from the Nd^{3+}:YAG laser are also displayed on

the oscilloscope screen. Any adjustments in delay time are seen as the gate

signal is moved relative to the trigger signal.

Luminescence decay transients are recorded on the oscilloscope with the

excitation and emission set at fixed wavelengths. To limit influence from

background noise and laser jitter at least 200 decays are averaged. A decay

transient data file is then transferred to a computer hard disk via a GPIB interface

using a Lab View acquisition program. The file is stored in ASCII format.

2.9   DATA DISPLAY

The ASCII data files are imported into the Origin 4.1 (Microcal Software,

Inc.) scientific graphing program. The recorded signal voltages are displayed in

the column of a spreadsheet. If neutral density filters were placed before the

detector the recorded signal intensity is less than that actually emitted by the

sample. This is compensated for by multiplying by a factor proportional to the

amount of signal filtered. Similarly, if the emission signal strength is low the

sensitivity setting of the RS250 is increased. This results in recorded signal

intensities higher than actually emitted by the sample. In this case values are

divided by the factor of signal gain. Once adjusted for neutral density filters and

the sensitivity setting, the spectral data is plotted verses wavelength in nanometers.

For luminescent transients, signal voltages are plotted verses time. The nonlinear curve fitting function of Origin 4.1 is then used to make a best-fit approximation of the data. In most cases the decay transients can be fit with the dual exponential decay function:

$$y = y0 + A1*exp(-(x-x0)/t1) + A2*exp(-(x-x0)/t2)$$

In cases of very fast nonlinear decays the following sum of three exponential decay functions is used:

$$y = y0 + A1*exp(-(x-x0)/t1) + A2*exp(-(x-x0)/t2) + A3*exp(-(x-x0)/t3)$$

2.10   SAMPLE PREPARATION

2.10.1   CUBIC-PHASE Eu_2O_3

Cubic-phase Eu_2O_3 powder (99.99%, Aldrich) was used for characterization of micron-sized particles. The only preparation required was sintering of the powder overnight at 950° C and atmospheric pressure in a furnace. This process removes from the Eu_2O_3 powder water and any other adsorbed contaminants.

2.10.2   MONOCLINIC-PHASE Eu$_2$O$_3$

Monoclinic-phase Eu$_2$O$_3$ samples were prepared from cubic-phase Eu$_2$O$_3$ powder by heating for 4 hours at 1400° C in a tube furnace. The high temperature allows the phase transition of the oxide structure to the monoclinic form.[2] After 4 hours the heating was stopped and the sample was allowed to cool at the intrinsic rate of the furnace.

2.10.3   NANOCRYSTALS

Eu$_2$O$_3$ particles in the nanometer size range were prepared using a gas-phase condensation technique.[3] First approximately 1.0-1.2 grams of Eu$_2$O$_3$ powder (99.99%, Aldrich) was pressed into a pellet at 5000-psi for 10 minutes. Pellets were placed in an alumina boat and sintered in air overnight at 950° C. The pellets were slowly cooled to room temperature over several hours. Next a single pellet was placed on a rotating platform inside a vacuum chamber. A schematic of the chamber is presented in Figure 5. The chamber was evacuated and purged with nitrogen three times before adjusting to the desired chamber pressure. Nanocrystals were prepared at pressures of 10, 400, and 600 Torr. A ZnSe lens is used to focus a CO$_2$ laser (Synrad) beam onto a 2-mm diameter spot on the pellet. A laser power of 40 Watts was used for preparations done at 10 Torr. A laser power of 60 Watts was used for preparation at pressures of 400 and 600 Torr. The temperature of the pellet at the spot of laser focus was
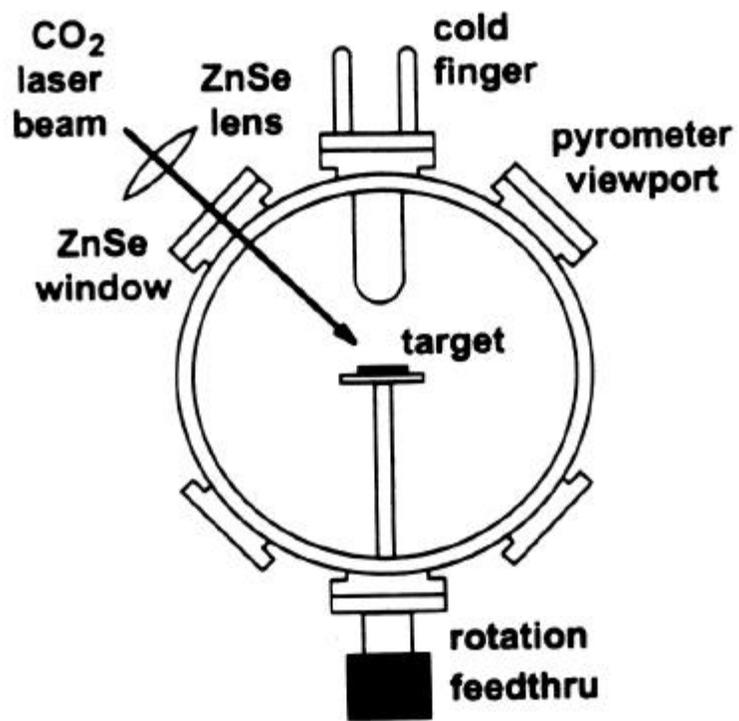
Figure 5. The nanocrystal preparation chamber.[3]

measured with a disappearing-filament optical pyrometer (Micro Optical) and was typically 2500° C. At this temperature Eu_2O_3 is vaporized, forming gas-phase clusters.[3] The nanocrystalline Eu_2O_3 particles condense on a Pyrex cold finger that reaches into the chamber 3-cm above the pellet. A stainless steel cone is attached to the base of the cold finger. This provides additional area for condensation at a uniform distance from the pellet. The cold finger is filled with distilled water, and the quenching temperature is maintained between 25-80° C. Generally 2-4 pellets are vaporized before collecting the nanoparticles from the inner cone and base of the cold finger. The rate of nanocrystal production is fairly slow, with ~50 mg per hour being produced at a pressure of 10 Torr and ~8 mg per hour being produced at 600 Torr.

2.10.4   FUSED Eu_2O_3 CRYSTAL

Preparation of a large crystal of Eu_2O_3 was carried out simultaneously with nanocrystal production. During production of nanocrystals the Eu_2O_3 pellet is melted at the point of laser focus. As the pellet is rotated its entire surface becomes fused together. The result is a rather glassy looking solid Eu_2O_3 surface, pink in color, with a thickness of approximately 0.85 mm. Luminescence spectroscopy revealed that the fused crystal, while appearing glass-like, was made almost completely of the monoclinic crystalline phase. Almost no cubic phase could be detected.

Chapter 2 References

[1]   J. D. J. Ingle, S. R. Crouch, *Spectrochemical Analysis*, Prentice-Hall,

Upper Saddle River, **1988**.

[2]   A. M. Lejus, R. Collonongues, *Current Topics in Materials Science* **1980**,

4, 481.

[3]   B. M. Tissue, B. Bipin, *J. Fluorescence* **1998**, *8*, 289.