

## CHAPTER III

### RESEARCH METHODOLOGY

#### 3.1 Sample preparation

##### 3.1.1 Preparation of Dy<sub>2</sub>O<sub>3</sub> doped (host glass)

The traditional melt quench method was utilized in the production of gadolinium borate glasses that had been doped with Dy<sup>3+</sup>. The chemical composition of these glasses was 27.5Gd<sub>2</sub>O<sub>3</sub>-(72.5-x) B<sub>2</sub>O<sub>3</sub>-xDy<sub>2</sub>O<sub>3</sub>, with the value of x ranging from 0.05, 0.10, 0.50, 1.00, and 1.50 mol%. As starting compounds, laboratory grades of the chemicals H<sub>3</sub>BO<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, and Dy<sub>2</sub>O<sub>3</sub> were utilized to produce this glass system. In an alumina crucible, melting was done in batches of roughly 15 grams each. (see Table 3.1)

**Table 3.1** Chemical composition of GdBdY glass.

Sample name	X (mol%)	Composition (mol%)
GdB0.05Dy	0.05	27.5Gd <sub>2</sub> O <sub>3</sub> -(72.5-0.05) B <sub>2</sub> O <sub>3</sub> -0.05Dy <sub>2</sub> O <sub>3</sub>
GdB0.10Dy	0.10	27.5Gd <sub>2</sub> O <sub>3</sub> -(72.5-0.10) B <sub>2</sub> O <sub>3</sub> -0.10Dy <sub>2</sub> O <sub>3</sub>
GdB0.50Dy	0.50	27.5Gd <sub>2</sub> O <sub>3</sub> -(72.5-0.50) B <sub>2</sub> O <sub>3</sub> -0.50Dy <sub>2</sub> O <sub>3</sub>
GdB1.00Dy	1.00	27.5Gd <sub>2</sub> O <sub>3</sub> -(72.5-1.00) B <sub>2</sub> O <sub>3</sub> -1.00Dy <sub>2</sub> O <sub>3</sub>
GdB1.50Dy	1.50	27.5Gd <sub>2</sub> O <sub>3</sub> -(72.5-1.50) B <sub>2</sub> O <sub>3</sub> -1.50Dy <sub>2</sub> O <sub>3</sub>

In an electrical furnace, the powder was heated to a temperature of 1400 °C Celsius for 3 hours. After that, the molten glass was spread out over a graphite plate, annealed at a temperature of 500 °C for three hours to remove thermal stress, and then cooled gradually to room temperature before being placed onto the polishers (1.00 × 1.50 × 0.30 cm<sup>3</sup>) to obtain a transparent sample with a thickness that was consistent throughout. The density of glass was initially determined using the Archimedes method, which involved the room-temperature immersion of water as the liquid medium.

After that, molar amounts were determined with the help of a sensitive microbalance with four digits (AND, HR 200). The glass sample's refractive index ( $n$ ) was determined with the assistance of an Abbe refractometer, a monobromonaphthalene ( $C_{10}H_7Br$ ) solution, and a sodium-vapor lamp serving as the light source. The FTIR spectrometer, model number Agilent-630, was used to research the chemical bonding within the glass matrix. A Shimadzu UV-3600 spectrophotometer is used to analyze the optical absorption spectra of polished samples between the wavelength ranges of 200 and 2000 nm. The photoluminescence (PL) spectra were acquired in the wavelength range of 200–800 nm and recorded at room temperature using a spectrofluorometer (Cary-Eclipse). The excitation light source was a xenon flashlight.

## 3.2 Physical properties

### 3.2.1 The density & Molar volumes

The density ( $\rho$ ) of the glasses, denoted by the symbol, was ascertained using Archimedes' method, in which water was taken to represent the immersion liquid. The apparatus for measuring density is depicted in Figure 3.1. This apparatus has a precision of 0.0001g. At room temperature, the sample was weighed using a balance in both air ( $W_a$ ) and water ( $W_w$ ), and the density was calculated using Equation (3.1).

$$\rho = \left[ \frac{W_a}{W_a - W_w} \right] \times \rho_b \quad (3.1)$$

Where  $W_a$  is the weight in the air,  $W_w$  is the weight in water and  $\rho_b$  is the density of water ( $\rho_b = 1 \text{ g/cm}^3$ ). The molar volume ( $V_m$ ) of glasses was computed with the help of density values that were brought in.

$$V_M = \frac{M_T}{\rho} \quad (3.2)$$

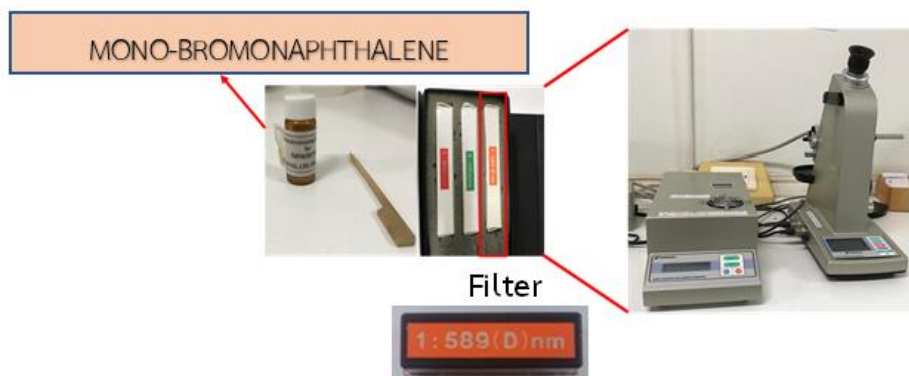
Where  $M_T$  is the glass's total molecular weight.



**Figure 3.1** Densitometer (Dietheim Limited, HR-200).

### 3.2.2 Refractive index

At a wavelength of 589.3 nm using a sodium lamp as a source and monobromonaphthalene as a contact liquid between the glass and the prism of the refractometer, the refractive indices ( $n$ ) of the glasses were determined with an Abbe refractometer with a measuring accuracy of 0.0001, as shown in figure 3.2. The accuracy of the measurement was shown to be 0.0001.



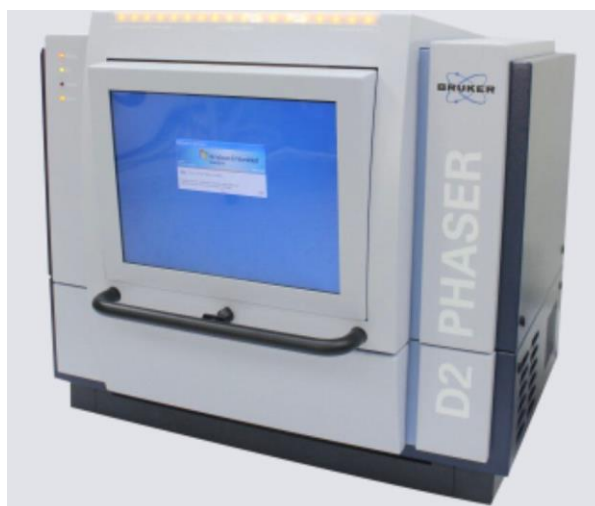
**Figure 3.2** A sodium vapor lamp was used as the light source for the Abbe refractometer (ATAGO), which had a wavelength of 589.3 nm (D line), and monobromonaphthalen was used as the contact layer.

### 3.3 Structural properties

Discovering the structure of glass samples is the focus of this dissertation, which uses X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray absorption spectroscopy.

#### 3.3.1 X-ray diffraction

X-ray diffraction is an established method for characterizing materials and obtaining microstructural data for crystalline and non-crystalline materials. Information on crystal structure, lattice parameters, crystal size, composition, etc., might be obtained using this non-destructive technology and helpful for studying ceramics, metal alloys, semiconductors, polymers, and nanomaterials. To examine the glass structure, this experiment used a D2 Advance Bruker with Cu  $K\alpha$  and  $\lambda = 0.15406$  nm. The XRD patterns in the two ranges of  $10^\circ$  to  $80^\circ$  were recorded using a step size of  $0.02$  and a step time of  $0.4$ . The primary method for identifying the phase of a crystalline material and figuring out the size of a unit cell is X-ray diffraction (XRD). The crystalline sample affects X-ray diffraction, and X-ray tubes generate constructive interference of X-rays. Once it has been filtered to produce monochromatic X-rays, the model is the only object directed at—positive interference results from the sample's interaction with the incident radiation. W.L. Bragg provided the geometrical explanation of the XRD phenomena (constructive interferences). A photograph of an X-ray diffractometer can be found in figure 3.3.



**Figure 3.3** Powder X-ray Diffraction (Bruker D2 PHASER).

## 3.4 Optical and spectral properties

### 3.4.1 Fourier-transform infrared spectroscopy

Infrared analysis using the Fourier transform was performed on glasses to determine the contributions to the spectra made by each structural component and to emphasize the function of the lanthanide ions contained within the glass network. The Fourier transform infrared spectroscopy is one of the helpful technologies that can be used to resolve the structure of the local groupings in glasses. These non-destructive methods provide a comprehensive characterization of the structure as well as the vibrational properties of glasses. It has been discussed how to quantitatively interpret the absorption bands of an IR spectrum by using the value of the stretching force constant and the reduced mass of the vibrating cation-anion. The analysis of the IR absorption curves suggests that the coordination number is the most critical factor in determining the characteristics of the spectra. Infrared spectroscopy uses the fact that different types of molecules can absorb different frequencies due to the differences in their structures. These absorptions have resonance frequencies, which means that the frequency of the absorbed radiation is identical to that of the bond or group that is vibrating. The energies are affected in various ways, including by the masses of the atoms, the associated vibronic coupling, and the geometry of the molecular potential energy surfaces. When a harmonic oscillator can approximate the molecular Hamiltonian that corresponds to the electronic ground state near the equilibrium molecular geometry, the resonant frequencies in the Born-Oppenheimer and harmonic approximations are determined by the usual modes that correspond to the possible energy surface of the molecular electronic ground state. In particular, this is the case when a harmonic oscillator can approximate the molecular Hamiltonian corresponding to the electronic ground state. The first method, on the other hand, establishes a relationship between the resonant frequencies, the degree to which the connection is vital, and the mass of the atoms on each end of the association. Consequently, one particular bond form can be linked to a specific vibrational frequency.



**Figure 3.4** Picture of Agilent Cary 630 FTIR Spectrometer.

### 3.4.2 UV-Visible spectrophotometer

The absorption spectra were obtained by utilizing an ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer (Shimadzu, UV-3600) at room temperature to record spectra in the range of 200 nm to 2500 nm with a spectral resolution of 1 nm (figure 3.5). The spectrophotometer has three different types of excitation sources: a photomultiplier tube (PMT) for the ultraviolet (UV) region, a photomultiplier tube with an indium gallium arsenide (InGaAs) detector for the visible region, and an indium gallium arsenide (PbS) detector for the infrared (NIR) regions. Eq. (3.3) is the formula that Tauc proposed, and it may be used to theoretically predict the optical band gap and the direct and indirect transitions.

$$(\epsilon hv) = C(hv - E_g)^n \quad (3.3)$$

where C is a constant,  $\epsilon$  is molar extinction coefficient,  $E_g$  is the average band gap of the material and n depend on the type of transition. For  $n = 1/2$ ,  $E_g$  in equation (3.3) is direct allowed band gap (Tauc, J. et al., 1972).

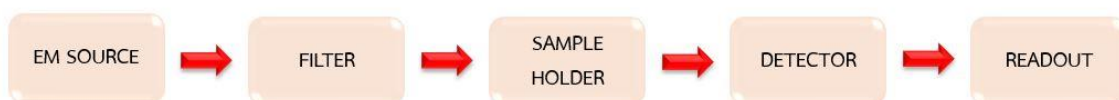


Figure 3.5(a) Block diagram of the UV-Vis NIR spectrometer.



Figure 3.5(b) Picture of UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600).

### 3.4.3 Photoluminescence technique

The emission, excitation and photoluminescence decay time of glass samples were recorded on a fluorescence spectrophotometer (Cary Eclipse) with Xe lamps as excitation sources and the block diagram of the luminescence spectrometer is displayed as shown in figure 3.6(a) and 3.6(b). The excitation and emission wavelength were monitored in region 200-1000 nm, performing the strongest emitting, were chosen to set value instrument for decay curve study. The strongest emission spectrum of each doped glass series was taken to analyze the emitting color via CIE 1931 chromaticity.

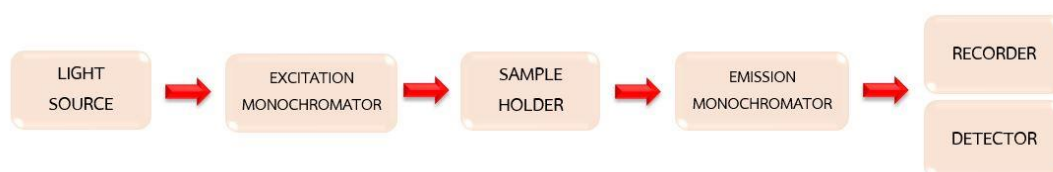


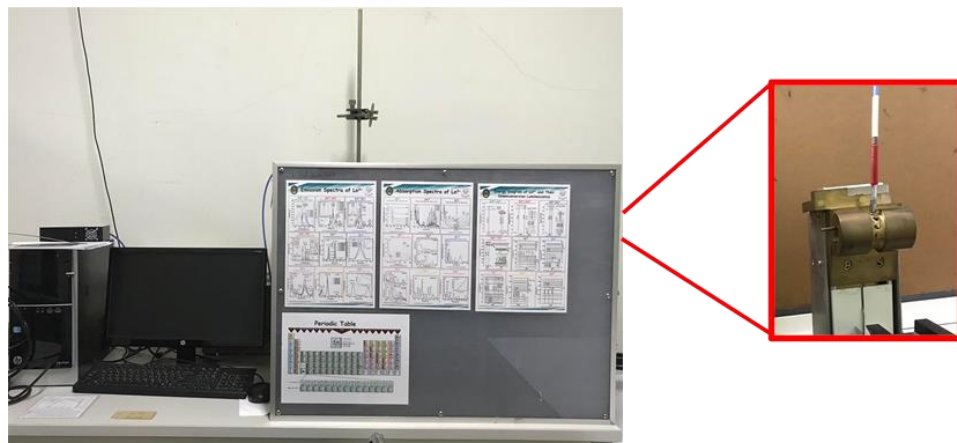
Figure 3.6(a) Block diagram of the PL process.



**Figure 3.6(b)** Picture of fluorescence spectrometer (Agilent technology Cary Eclipse).

#### 3.4.4 X-ray induced luminescence technique

The radioluminescence of the glass samples, also known as X-ray-generated optical luminescence, was also investigated at Nakhon Pathom Rajabhat University using a configuration of instruments specially designed for the purpose (figure 3.7). This apparatus includes a Cu target X-ray generator (Inel, RG3D), whose X-ray source was 50 kV and 30 mA, and a spectrometer (QE65 Pro, Ocean Optics) with an optical fiber to detect the emission spectra. The spectrometer was designed to detect the emission spectra.



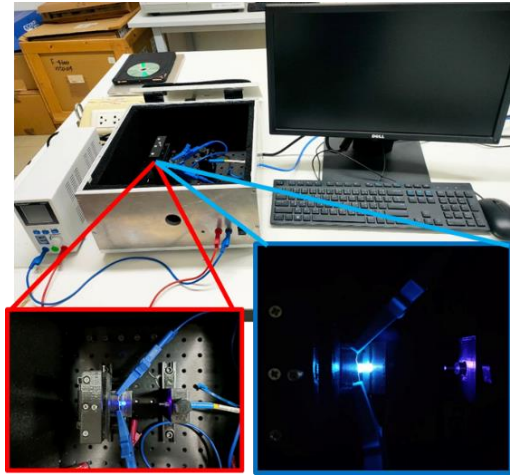
**Figure 3.7** X-ray induced luminescence.

#### 3.4.5 Electroluminescent

The light intensity emitted by the LEDs using the electroluminescent (Ocean Optics QE65 Pro spectrometer) is based on the specially designed instrumental setup in Nakhon Pathom Rajabhat University (figure 16). The principle of operation of the



machine is that when electricity is supplied from the power supply to the sample LEDs, the signal detector is checked and passed to the amplifier from will be processed and displayed on the computer.



**Figure 3.8** Electroluminescent (Ocean Optics QE65 Pro spectrometer).