CHAPTER 3 MATERIALS AND METHODS

3.1 Zinc Bismuth Borate Glass System

3.1.1 Material Preparation

The preparation of glass samples ZnO - Bi_2O_3 - B_2O_3 based on formula 10ZnO : xBi_2O_3 : (90-x)B_2O_3 (where x = 15, 20, 25 and 30 mol %) were prepared by the melt quenching technique. All chemicals; ZnO, Bi_2O_3 and H_3BO_3, used in the present work were of high purity (Fluka, 99.99 %). Appropriate amounts of the raw materials were thoroughly mixed and ground in a pestle and mortar for half an hour. The prepared mixture was then heated in a high purity alumina crucible at 1,100 °C inside an electric furnace for about 3 hours to ensure complete melting of all components. The melt was then quickly poured into a preheated stainless steel mold and annealed at 500 °C for 3 hours before left it to cool down slowly to room temperature. The amount of the glass batch is about 30 g/melts. Finally, the glass samples were cut and then finely polished to a dimension of 1.0 cm × 1.5 cm × 0.3 cm. The glasses preparation procedure is shown in Figure 3.1. The chemical compositions of the glasses, prepared in the present work, are summarized in Table 3.1.

Table 3.1 Chemical compositions of the glasses (in mol %).

Samples no.	Bi_2O_3 (mol%)	Glass formula
1	15	10ZnO:15Bi_2O_3:75B_2O_3
2	20	10ZnO:20Bi_2O_3:70B_2O_3
3	25	10ZnO:25Bi_2O_3:65B_2O_3
4	30	10ZnO:30Bi_2O_3:60B_2O_3

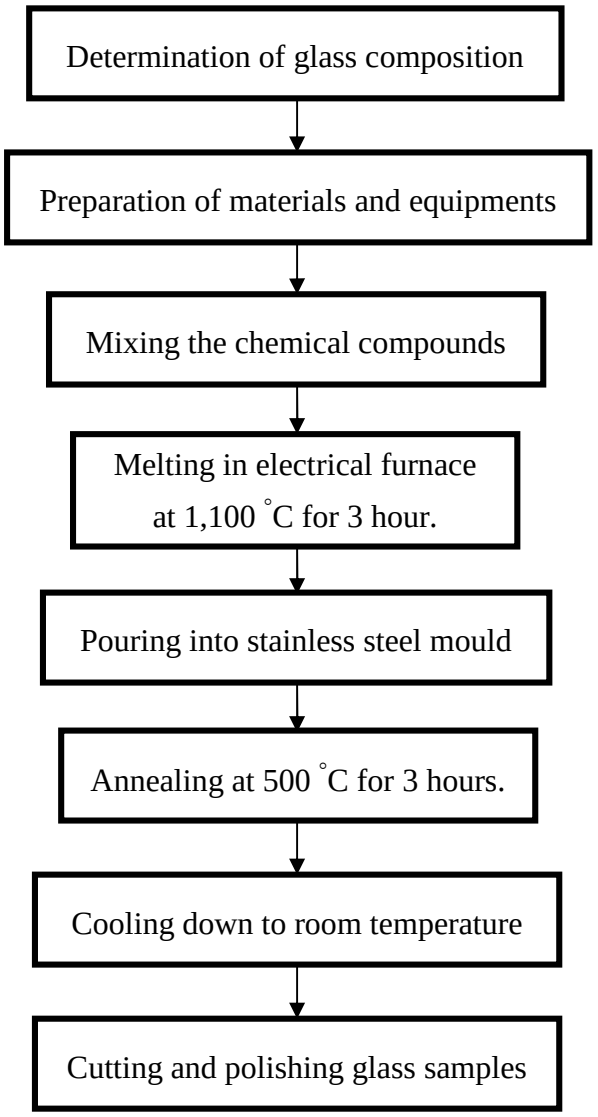

Figure 3.1 The preparation process of glass samples.

From Table 3.1 weights of glass mixture for each formula of glass component. Mixing and milling in high alumina crucible shown in Figure 3.2.

Figure 3.2 High alumina crucible.

After that, melting at 1,100 °C for 3 hours with electrical furnaces are shown in Figures 3.3 and 3.4.

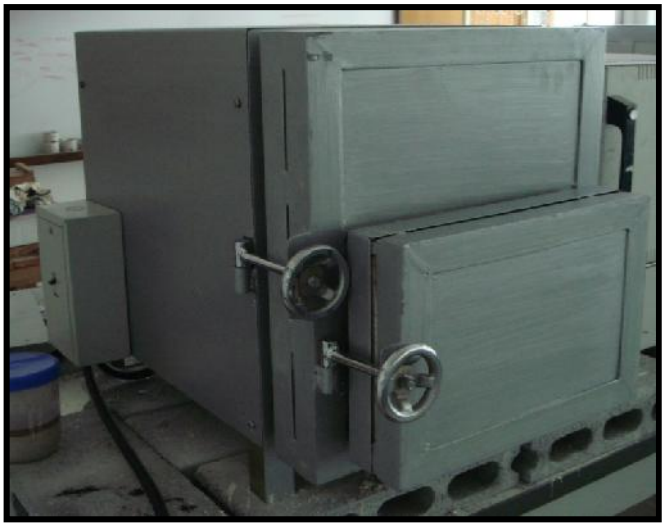

Figure 3.3 High temperature electrical furnaces for glass melting.

Figure 3.4 Melting at 1,100 °C.

Casting in stainless steel mould is shown in Figures 3.5 and 3.6

Figure 3.5 Stainless steel moulds.

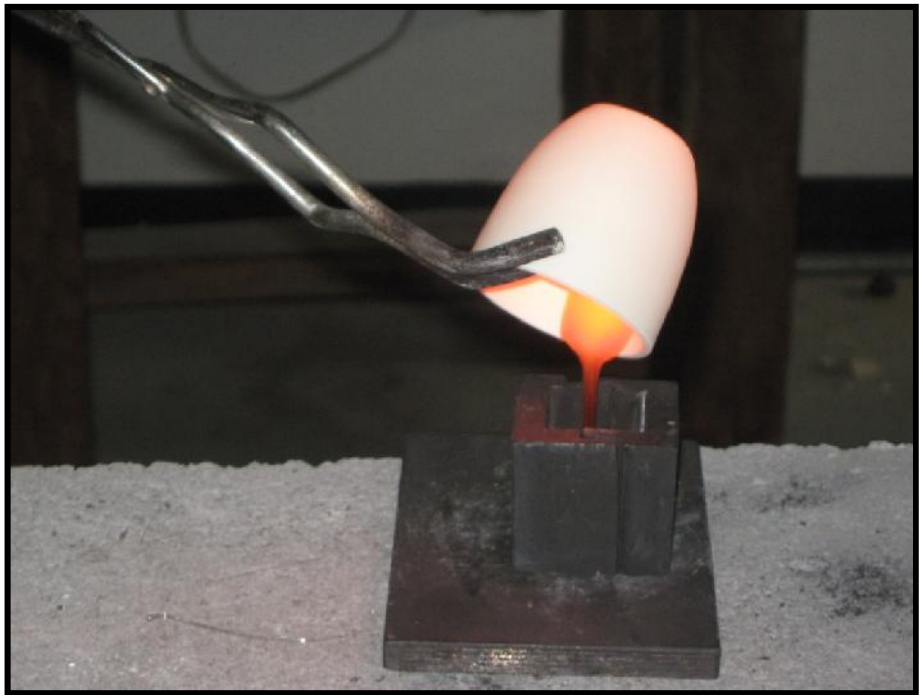

Figure 3.6 Casting melt glass in stainless steel mould.

Then, annealing glass at 500 °C, for 3 hours with electrical furnaces for glass annealing and cooling down at room temperature as shown in Figures 3.7 and 3.8.

Figure 3.7 Glasses in stainless steel mould.

Figure 3.8 High temperature electrical furnaces for glass annealing.

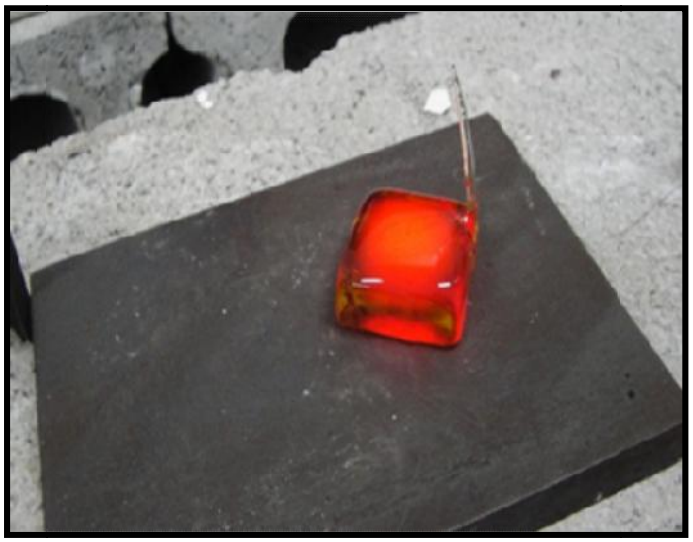

Figure 3.9 Glass before cut and polish.

3.1.2 WinXCom Program [91-92]

Study of the scattering and absorption of gamma and neutron radiations in shielding materials has been an important subject in the field of radiation physics. In order to design the protective shielding around the nuclear reactor, accelerators and high radiation region, the knowledge of the attenuation of high energy X - rays in shielding materials is very essential.

Photon attenuation coefficient is an important parameter used in characterization the penetration and diffusion of X - ray and gamma-rays in the multi-element materials. The scattering and absorption of gamma radiations are related to density and effective atomic numbers of material; knowledge of the mass attenuation coefficients is of prime importance. However, the linear attenuation, μ (cm^{-1}) or mass attenuation, $\mu/°$ (cm^2g^{-1}) coefficient, which are defined as the probability of all possible interactions between gamma-rays and atomic nuclei, has been described to investigate the radiation shielding properties of any shielding materials. These attenuation coefficients depend on the incident photon energy and the chemical composition of the absorbing materials' parameters such as their types, thickness and densities. The accurate values of mass attenuation coefficients of gamma - rays in several materials are of great importance for industrial, biological, agricultural and medical studies. A number of related parameters can be derived from mass attenuation coefficient such as mass energy - absorption coefficient, the total interactions cross - section, the molar extinction coefficient, the effective atomic number and the electron density.

An alternative or convenient method to experimental determination of mass attenuations coefficients is theoretical or manual calculations using tabulated data that is generated using a computer program. For this purpose, Berger and Hubbell [94] developed a computer program called XCOM, a database which can be used to calculated cross-sections and attenuation coefficients for any element, compound or mixture, at energies from 1 keV to 100 GeV. Afterwards, a well-known program was updated and transformed to Windows operating system and Windows version is being called Win X Com [91-92].

Figure 3.10 The front page of WinXCom program.

3.1.3 Material Characterization

The ZBB glasses of chemical composition (in mol %) 10ZnO : xBi_2O_3 : $(90 - x)B_2O_3$ (where x = 15, 20, 25 and 30 mol %). The densities (ρ) were measured by using the Archimedes method using distilled water as an immersion liquid. The Vickers micro hardness (HV) of the glasses was measured using a Digital Micro Vickers Hardness Tester (DHV - 1000) (Enkay enterprises). Infrared spectra of the glass samples were recorded at room temperature in the range 650 - 3000 cm^{-1} using an Agilent - Cary - 630 FT - IR spectrometer. The optical absorption spectra of the glasses sample were recorded in the UV- visible regions in the range of 300 - 1,100 nm using a Varian Cary 50 UV - VIS spectrophotometer. The photoluminescence spectra and lifetime measurements were carried out using Cary Eclipse Fluorescence Spectrophotometer with 302 nm excitation wavelength of xenon flash lamp.The procedures are shown in Figure 3.11.

The radiation shielding properties of the as-prepared glass samples were characterized using the Compton scattering technique. The schematic of the Compton scattering technique for mass attenuation coefficient measurement is shown in Figures 3.12. The source system was mounted on a composite of adjustable stands. This setup can move in the transverse direction for proper beam alignment. The ^{137}Cs radioactive source of 15 mCi (555 MBq) strength was obtained from the Office of Atom for Peace (OAP), Thailand. The aluminum rod was used as the scattering rod. The Compton scattered γ - rays were measured on a rotatable 2″×2″ NaI(Tl) scintillator detector in the scattering plane having an energy resolution of 8 % at 662 keV (BICRON model 2M2/2), with CANBERRA photomultiplier tube base model 802-5. The optimum set up distances between the source to the scatterer and from scatterer and detector were found equally at 20 cm. The spectra were recorded using a CANBERRA PC-based multi-channel analyzer (MCA). The spectrum on the MCA of detector gave instance counts in

each of 1024 bins divided by voltage. To measure the angular dependence of Compton scattering, we first performed a calibration on the relating channel number of the MCA spectrum with the known energy of gamma-ray sources and varied the angle of the scatter detector. The scattering angles (θ) were used to produce gamma ray of different energies [95]. J. Kaewkhao et. al, [96] was the first group to apply the Compton scattering technique for measuring mass attenuation coefficient and has confirmed the validity and energy calibration of the system. The procedure for measuring mass attenuation coefficients of glass samples at different gamma ray energies are described in our previous work [95-96].

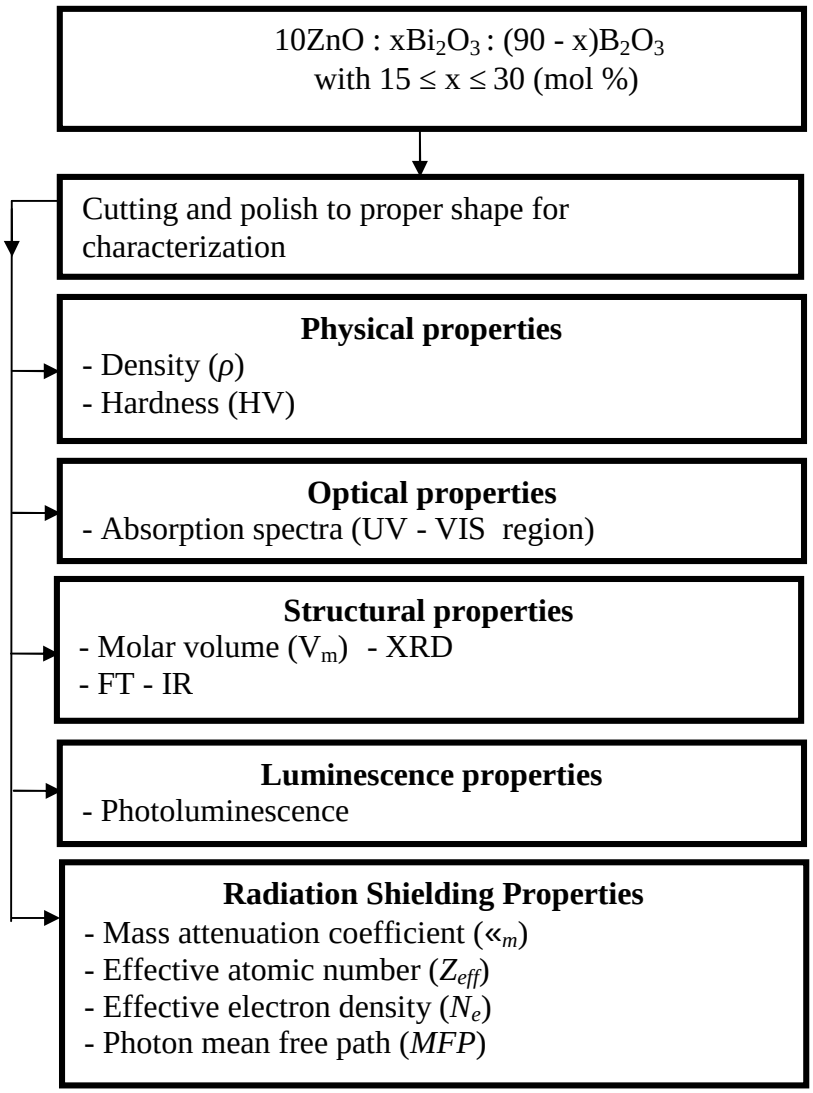

Figure 3.11 The process of characterization.

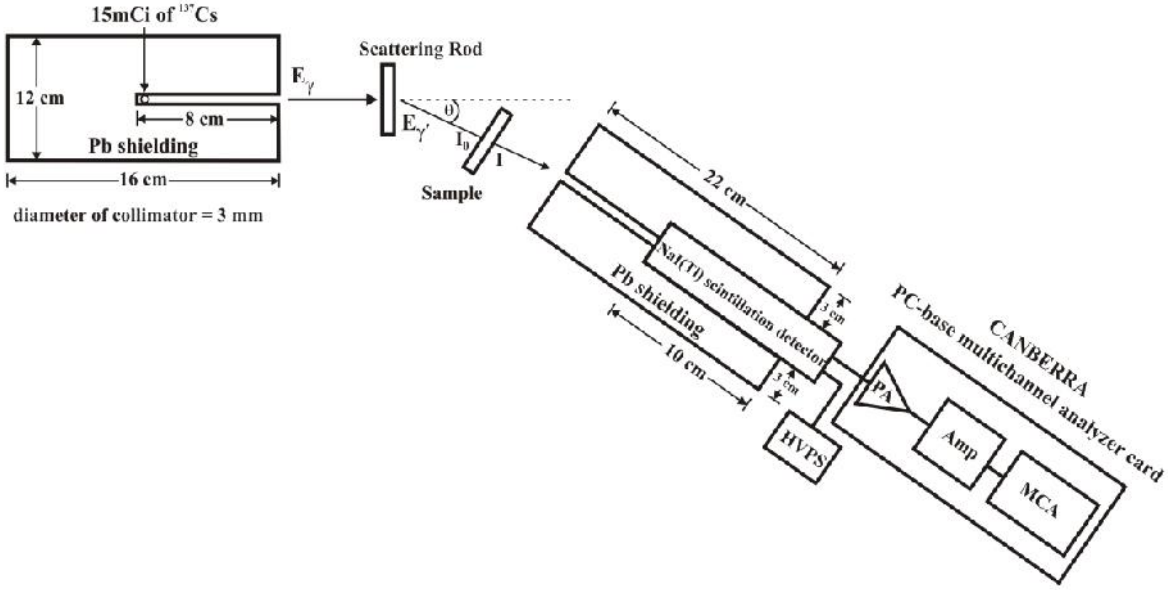

Figure 3.12 Schematic of the Compton scattering technique for mass attenuation coefficient measurement.

3.1.4 Density and Molar Volume Measurement

The densities of glass samples were determined by the Archimedes principle using xylene as an immersion liquid at room temperature. The density (ρ) was then calculated from the following equation :

$$\rho = \frac{W_a}{W_a - W_b} \cdot \rho_b \tag{3.1}$$

where W_a, W_b are the weights of glass in air and xylene, respectively. ρ_b is the density of xylene (ρ_b = 0.863 g/cm^3).

Figure 3.13 The sensitive microbalance for density determination.

The molar volume V_m is calculated with the relation

$$V_m = \frac{molar\ wt.}{density} = \frac{M_T}{\circ} \tag{3.2}$$

where M_T is the total molecular weight of the multi - component glass system

$$M_T = x_{Bi_2O_3} Z_{Bi_2O_3} + x_{B_2O_3} Z_{B_2O_3} + x_{ZnO} Z_{ZnO} + x_{Eu_2O_3} Z_{Eu_2O_3} \tag{3.3}$$

where $x_{Bi_2O_3}$, $x_{B_2O_3}$, x_{ZnO} and $x_{Eu_2O_3}$ are mole fraction oxides of bismuth, borate, zinc and europium, respectively.
$Z_{Bi_2O_3}$, $Z_{B_2O_3}$, Z_{ZnO} and $Z_{Eu_2O_3}$ are the molecular weight oxide of bismuth, borate, zinc and europium, respectively.

3.1.5 Vicker's Hardness Test

The Vicker's hardness test method consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a load of 1 to 100 kgf. The full load is normally applied for 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their average calculated. The area of the sloping surface of the indentation is calculated. The Vicker's hardness is the quotient obtained by dividing the kgf load by the square mm area of indentation.

$$VHN = \frac{2F \sin\frac{136^\circ}{2}}{D^2} \tag{3.4}$$

$$VHN = \frac{18.19F}{D^2} \tag{3.5}$$

When F is the load in kgf and D is the arithmetic mean of the two diagonals, D_1 and D_2 in mm

3.1.6 X-ray Diffractometer (XRD)

X - ray diffractometer is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. X - ray diffractometer consist of three basic components: X - ray tube, a sample holder, and X - ray detector. X - rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward to a target by applying a voltage, and bombarding the target material with electron beam. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X - ray spectra are produced. These spectra consist of several components, the most common being K_{α} and K_{β}. K_{α} consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, and Cr). Filtering, by foils or crystal monochrometer, is required to produce monochromatic X - ray needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. These X - rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X - ray is recorded. When the geometry of the incident X - rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X - ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. In this research, the x-rays diffraction patterns were recorded at room temperature using a X - ray diffractometer (Bruker D8 Advanced). Figure 3.14 shows X - ray diffractometer for confirms amorphous nature of glass samples in this research.

Figure 3.14 X - ray diffractometer.

3.1.7 FTIR Transmission Spectra

The FTIR vibration spectra of the present glasses were recorded at room temperature in the wavenumber range 650 - 3,000 cm^{-1} using an Agilent - Cary 630 FT - IR spectrometer, as shown in Figure 3.15, which has a resolution of 1 cm^{-1}

Figure 3.15 Agilent Cary - 630 FTIR spectrometer.

3.1.8 UV-Visible Spectrophotometer

The optical measurement were performed at room temperature using UV - Visible spectrophotometer (Varian, Cary50), together with a dual light source capable of outputting ultraviolet as well as visible light, as shown in Figure 3.16.

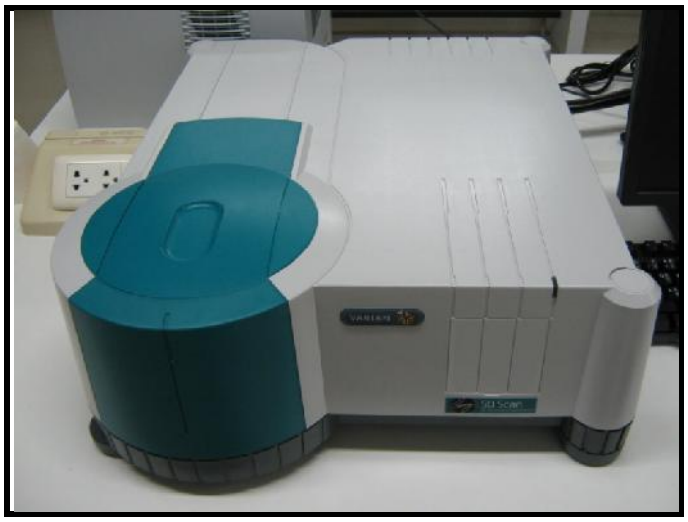

Figure 3.16 UV - Visible spectrophotometer (Varian, Cary50).

3.1.9 Ultraviolet-Visible-NIR Spectrophotometer

The optical transmission spectrum in UV - VIS - NIR range was measured by UV - VIS - NIR spectrophotometer (UV - 3600, Shimadzu), as shown in Figure 3.17, with a measurement wavelength range of 300 - 1,800 nm. The obtained glass was cut and finely polished into a size of 1.0 cm × 1.5 cm × 0.3 cm.

Figure 3.17 UV – VIS - NIR spectrophotometer (UV - 3600, Shimadzu).

3.1.10 Photoluminescence

For photoluminescence study, the emission spectra measurement was performed at room temperature using a Spectrophotometer with the analysis based on the principle of absorption and emission of light from the sample when the excitation light (Cary Eclipse Fluorescence Spectrophotometer), as show in Figure 3.18 has xenon lamp as a light source.

Figure 3.18 Fluorescence Spectrophotometer (Cary Eclipse, Agilent).

3.2 Eu^{3+} Ion Doped in Zinc Bismuth Borate Glasses

The wide variability of zinc bismuth borate glass chemistry allows the creation of very different structure types of glasses. The aim of this research is to develop, prepare, produce, and analyze the zinc bismuth borate glass system doped with rare - earth (europium) in the form of chemical compound oxides (Eu_2O_3). Europium is present in rare - earth in lanthanide groups. Optical absorption spectra were used to determine the energy level of glasses. Photoluminescence and X - rays luminescence properties were studied for emission peak characterization due to energy level transitions.

Production of glasses by melting involves four steps: batching, batch melting, fining, and homogenization. Batching involves selection of raw materials, calculation of concentrations of each material, weighing, and mixing of powders, and occasionally, etc. Batch melting involves the decomposition of the raw materials to form the initial melt, and control of temperature and atmosphere during the time of formation of the liquid. Glass batch calculations can range from very simple to very complex, as a function of the complexity of the composition and the raw material used to prepare the mixture.

Zinc bismuth borate glass combined with zinc oxide (ZnO), bismuth oxide (Bi_2O_3) and boric oxide (B_2O_3) resulted in high viscosity and thus allowed for tuning or modifying the physical and optical properties in a wide range depending on its composition. Rare-earth atoms are divided into two classes. The first one is lanthanides with atomic number 57 through 71 and the second is actinides with atomic number 89 through 103. Rare-earth (RE) ions (4f electronic configuration) doped glasses has previously been studied, and results applied for different objectives and many potential uses. In this research, one specific rare-earth for zinc bismuth borate glass system doping was europium (Eu) in the form of chemical compound Eu_2O_3.

Batch calculations of glass samples (ZnO - Bi_2O_3 - B_2O_3) were doped with the rare-earth (Europium, Eu) by the formula of glass composition $30Bi_2O_3$: (60 - x) B_2O_3 : 10ZnO : xEu_2O_3. Batches containing only oxides in their exact state as express by the glass formula. This glass sample preparation was used as the function of composition and the raw materials to prepare the chemical mixtures (reagent grade). Batches containing only oxides in their exact state were expressed by the glass formula. All batch calculations were figured by determining the weight fraction of each component required to produce the desired molar composition and began with multiplying the mole fraction of each component by the molecular weight of sample component. These total contributions determined the molecular weight of the glass, and then divided each individual contribution by the molecular weight of the glass to determine the weight fraction of each component. Multiplying the weight fraction of each component by the amount of glass produced the batch weight of any component which decomposes during melting and was adjusted by multiplying the weight fraction of that component to the appropriate factor for the raw material actually used in the batch. The use of raw materials which supply more than one batch component requires additional calculations.

Example of batch calculation

Glass composition :

$30Bi_2O_3 : (60\text{-}x)B_2O_3 : 10ZnO : xEu_2O_3$

Molecular weights of components (g/mol)

Bi_2O_3 = 465.92 g/mol, B_2O_3 = 69.62 g/mol, ZnO = 81.39 g/mol

and Eu_2O_3 = 351.92 g/mol

Molecular weights of glass (0.2 mol% of Eu_2O_3 doped):

(0.3)(465.92) + (0.598)(69.62) + (0.1)(81.39) + (0.002)(351.92) = 190.26 g/mol

Weight fraction of each component:

Bi_2O_3 = (0.3)(465.92)/190.26 = 0.7347

B_2O_3 = (0.598)(69.62)/190.26 = 0.2188

ZnO = (0.1)(81.39)/190.26 = 0.0428

Eu_2O_3 = (0.002)(351.92)/190.26 = 0.0037

For 30 grams weight of glass mixture:

Bi_2O_3 = (0.7347)(30 g) = 22.041 g

B_2O_3 = (0.2188)(30 g) = 6.564 g

ZnO = (0.0428)(30 g) = 1.284 g

Eu_2O_3= (0.0037)(30 g) = 0.111 g

3.2.1 Material Preparation

The preparation of glass samples (zinc bismuth borate, ZnO - Bi_2O_3 - B_2O_3) were doped with the Eu_2O_3 base using the formula $30Bi_2O$: (60 - x)B_2O_3 :10ZnO: xEu_2O_3. The percentage of molecular weight of Eu_2O_3 varies between x = 0.0 - 1.0 mol% (see Table 3.2). All component powder of chemical weight 30 g of the raw materials were thoroughly mixed and ground in a pestle and mortar for half an hour. Glass samples were melted in alumina crucibles in an electrical furnace for 3 hours, at temperature 1,100 $^{\circ}$C by the use of melt quenching technique. These melting components were quenched between two stainless steel plates. These glasses thus obtained were all annealed at temperature 500 $^{\circ}$C for 3 hours before cooled down to room temperature to remove thermal strains in the glass samples. Finally, glass samples were cut and finely polish to a dimension of 1.0 cm x 1.5 cm x 0.3 cm. Flow chart of the glass samples preparation and experimental methodology were show as Figure 3.1.

Table 3.2 Fractional doping of Eu_2O_3 for zinc bismuth borate glass.

Samples no.	Eu_2O_3 (mol%)	Glass formula
1	0.0	$30Bi_2O_3$-$60.0B_2O_3$-10ZnO
2	0.2	$30Bi_2O_3$-$59.8B_2O_3$ -10ZnO-$0.2Eu_2O_3$
3	0.4	$30Bi_2O_3$-$59.6B_2O_3$ -10ZnO-$0.4Eu_2O_3$
4	0.6	$30Bi_2O_3$-$59.4B_2O_3$ -10ZnO-$0.6Eu_2O_3$
5	0.8	$30Bi_2O_3$-$59.2B_2O_3$ -10ZnO-$0.8Eu_2O_3$
6	1.0	$30Bi_2O_3$-$59.0B_2O_3$ -10ZnO-$1.0Eu_2O_3$

3.2.2 Material Characterization

The Eu^{3+} : ZBB glasses of chemical composition (in mol %) (60 - x)B_2O_3 : $30Bi_2O_3$: 10ZnO : xEu_2O_3 (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 mol %). The densities (ρ) were measured by using the Archimedes method using distilled water as an immersion liquid. The Vickers micro hardness (HV) of the glasses was measured using a Digital Micro Vickers Hardness Tester (DHV - 1000) (Enkay enterprises). Infrared spectra of the glass samples were recorded at room temperature in the range 650 - 3,000 cm^{-1} using an Agilent - Cary - 630 FT - IR spectrometer. The optical absorption spectra of the glasses sample were recorded in the NIR regions in the range of 1,800 - 2,400 nm using a UV - 3600 Shimadzu UV - VIS - NIR spectrophotometer. The emission spectra and lifetime measurements were carried out using Cary Eclipse Fluorescence Spectrophotometer with 465 nm excitation of xenon flash lamp.

3.2.3 X-Rays Luminescence

In this work, the luminescence excited by X - rays (X - rays luminescence or Radioluminescence) of the Eu_2O_3 doped zinc - bismuth - borate glasses were measured at Radiation Science Research Institute (RSRI), National KyungPook University, South Korea (KNU) by using an X - ray tube (DRGEM Co.). The glasses were wrapped with several layers of teflon tapes except the one for attachment with an optical fiber. To avoid the light loss when the glasses were attached to the optical fiber, a holder with a hole at its center was made from the teflon material. Scintillation light from the glass by the X - rays irradiation was transmitted through the optical fiber to the QE65000 spectrometer (Ocean Optics Co.). The spectrometer was cooled down at -15 degree to reduce thermal noise in CCD. The windows based software provided by the manufacturer of the spectrometer was used for plotting the X - ray emission spectrum of the sample. The picture of X - rays luminescence setup and diagram are shown in Figures 3.19 and 3.20, respectively.

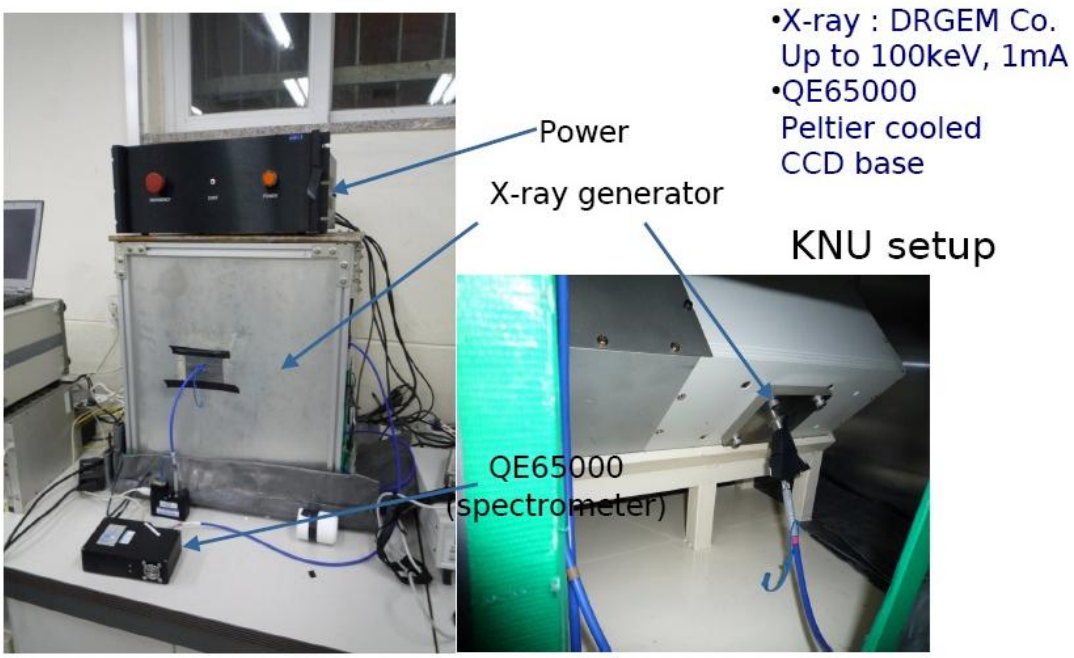

Figure 3.19 Experimental setup of X - rays luminescence measurement.

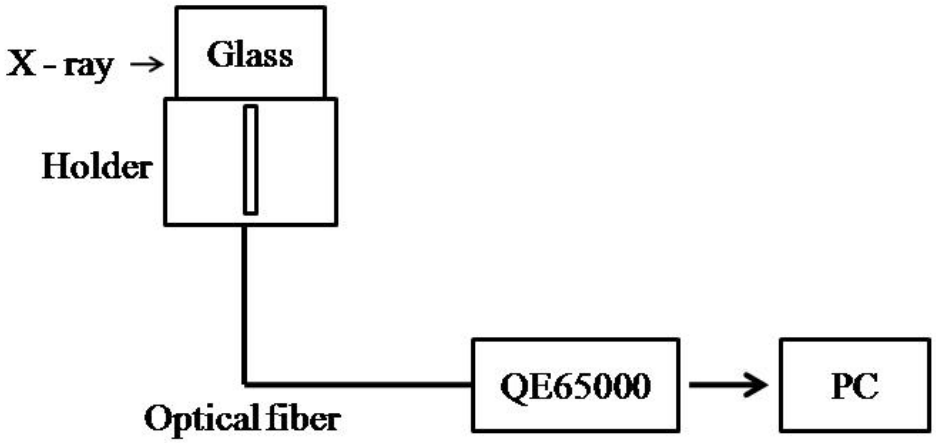

Figure 3.20 Diagram of X - rays luminescence measurement.