CHAPTER 3 MATERIALS AND METHODS

The wide variability of bismuth borate glass chemistry allows the creation of very different structure types of glasses. The aim of this research was to develop, prepare, produce, and analyze the bismuth borate glass system doped with rare-earth (dysprosium) in the form of chemical compound oxides (Dy_2O_3). Dysprosium is present in rare-earth in lanthanide groups. Optical absorption spectra were used to determine the energy level of glasses. Photoluminescence, x-ray luminescence and proton luminescence or scintillation were studied for emission peak characterization from energy level transitions.

3.1 Materials Preparation

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.

Bismuth borate glass combined with 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 bismuth borate glass system doping was dysprosium (Dy) in the form of chemical compound Dy_2O_3.

Batch calculations of glass samples (Bi_2O_3-B_2O_3) were doped with the rare-earth (dysprosium, Dy) by the formula of glass composition $30Bi_2O_3 : (70-x)B_2O_3 : xDy_2O_3$. 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 (regent 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.

Sample of batch calculation

Glass composition:

$30Bi_2O_3 : 69.5B_2O_3 : 0.5Dy_2O_3$

Molecular weights of components (g/mol)

Bi_2O_3 = 465.92 g/mol, B_2O3 = 69.62 g/mol and Dy_2O_3 = 373 g/mol

Molecular weights of glass (0.5 mol% of Dy_2O_3 doped):

(0.3)(465.92) + (0.695)(69.62) + (0.005)(373) = 190.0269 g/mol

Weight fraction of each component:

Bi_2O_3 = (0.3)(465.92)/190.0269 = 0.7356
B_2O_3 = (0.695)(69.62)/190.0269 = 0.2546
Dy_2O_3 = (0.005)(373)/190.0269 = 0.0098

For 30 grams weight of glass mixture:

Bi_2O_3 = (0.7356)(30 g) = 22.068 g
B_2O_3 = (0.2546)(30 g) = 7.638 g
Dy_2O_3= (0.0098)(30 g) = 0.294 g

3.2 Experimental Methodology

The preparation of glass samples (bismuth borate, Bi_2O_3-B_2O_3) were doped with the Dy_2O_3 base using the formula $30Bi_2O$: (70-x)B_2O_3: xDy_2O_3. The percentage of molecular weight of Dy_2O_2 varies between x = 0 - 2.5 mol% (see Table 3.1). All component powder of chemical weight 30 g of glass samples were mixed finely by hand milling for each batch for homogenous being. Glass samples were melted in alumina crucibles in an electrical furnace for 3 hours, at temperature 1,100 ^{0}C by the use of normal quenching technique. These melting components were quenched between two stainless steel plates. These glasses thus obtained were all annealed at temperature 500 ^{0}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 3.1 Fractional doping of Dy_2O_3 in bismuth borate glasses.

Samples no.	Dy_2O_3 (mol%)	Glass formula
1	0.00	$30Bi_2O_3$- $70B_2O_3$
2	0.50	$30Bi_2O_3$- $69.5B_2O_3$- $0.5Dy_2O_3$
3	1.00	$30Bi_2O_3$- $69.0B_2O_3$- $1.0Dy_2O_3$
4	1.50	$30Bi_2O_3$- $68.5B_2O_3$- $1.5Dy_2O_3$
5	2.00	$30Bi_2O_3$- $68.0B_2O_3$- $2.0Dy_2O_3$
6	2.50	$30Bi_2O_3$- $67.5B_2O_3$- $2.5Dy_2O_3$

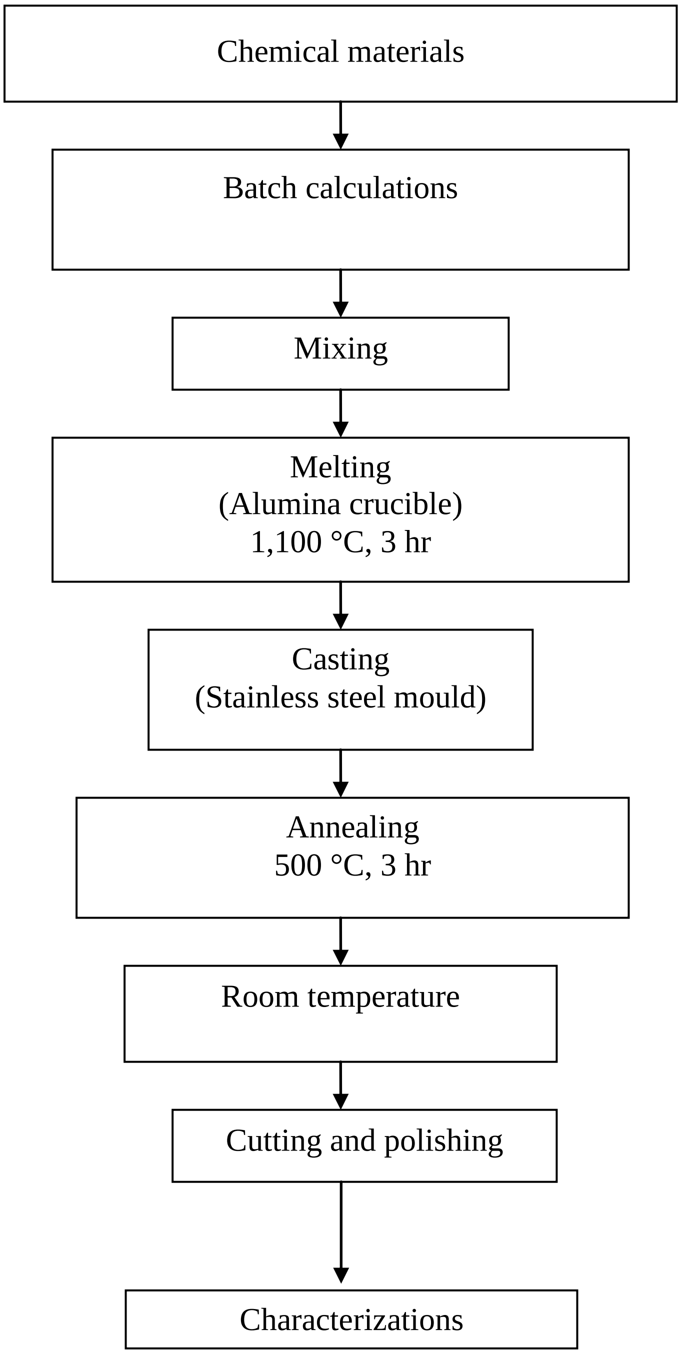

Figure 3.1 Flow chart of the glass sample prepared process.

3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) 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 $K_{\alpha1}$ and $K_{\alpha2}$. $K_{\alpha1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha2}$. 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. $K_{\alpha1}$ and $K_{\alpha2}$ 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 (XRD) (Bruker D8 Advanced). Figure 3.2 shows x-ray diffractometer for confirms amorphous nature of glass samples in this research.

Figure 3.2 X-ray diffractometer.

3.2.2 Density Measurement

According to Archimedes' principle, the densities of glass samples can be determined by weight measurement in air and liquid, and then multiplied with the density of liquid (xylene). The equation to calculate glass samples density is

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

where W_a and W_b is the weight of glass samples in air and xylene, respectively. ρ_b is xylene density (ρ_b = 0.863 g/cm^3). All weight measurements were used a 4 - digit sensitive microbalance (AND, HR-200) some time call dense meter, shown as Figure 3.3.

Figure 3.3 Dense meter.

Molar volume (V_M) of glass samples were calculated using the molecular weight (M_T) and density (ρ) with the following relation,

$$V_M = M_T/\rho \tag{3.2}$$

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

$$\mathrm{M_T} = \mathrm{x_{Bi_2O_3} Z_{Bi_2O_3} + x_{B_2O_3} Z_{B_2O_3} + x_{Dy_2O_3} Z_{Dy_2O_3}} \tag{3.3}$$

where $x_{Bi_2O_3}, x_{B_2O_3}$ and $x_{Dy_2O_3}$ are mole fraction oxides of bismuth, borate and dysprosium, respectively.

$Z_{Bi_2O_3}, Z_{B_2O_3}$ and $Z_{Dy_2O_3}$ are the molecular weight oxide of bismuth, borate and dysprosium, respectively.

3.2.3 UV-VIS-NIR Spectrophotometer

To study of the optical absorption edge in Ultraviolet-Visible-Near infrared (UV-VIS-NIR) region has proved to be very useful method for clarification of optical transition and electronic band structure of the materials. It is possible to determine direct and indirect transition occurring in band gap by optical spectra at the fundamental absorption edge of the materials. In both case, electromagnetic waves interact with the electrons in the valance band, which are raised across the fundamental gap to the conduction band. In amorphous materials a different type of optical absorption edge is observed. This research, the optical absorption spectra were recorded at room temperature using a UV-VIS-NIR spectrophotometer (Shimadzu UV-3100, Japan), as shown in Figure 3.4, working in 200 - 2,000 nm. The absorption coefficient, α(ν), was calculated for each samples at different photon energies by the relation

$$\alpha(\nu) = \left(\frac{1}{d}\right) ln\left(\frac{I_o}{I}\right) \tag{3.4}$$

where d is the thickness of the samples, and I_o and I are the intensities of incident and transmitted radiations, respectively.

Figure 3.4 UV-VIS-NIR spectrophotometer (Shimadzu UV-3100, Japan).

3.2.4 Photoluminescence

Figure 3.5 Spectrofluorophotometer (Shimadzu RF-5301PC, Japan).

The spectrofluorometer is an instrument which takes advantage of photoluminescence property of some compounds in order to provide information regarding their concentration and chemical environment in a sample. A certain excitation wavelength is selected, and the emission is observed either at a single wavelength or a scan is performed to record the intensity versus wavelength also called an emission spectra. This research, the emission spectra were recorded at room temperature using a Spectrofluorophotometer (Shimadzu RF-5301PC, Japan), as shown in Figure 3.5. Specifications of spectrofluorophotometer in this research are shown in Table 3.2.

Table 3.2 Some specification of spectrofluorophotometer.

Light Source	150 W Xenon lamp
Excitation and emission Monochromators	Concave, blazed holographic grating
Wavelength scale	220 - 900 nm
Spectral bandwidth	6-step selection of 1.5, 3, 5, 10, 15 and 20 nm
Wavelength accuracy	±1.5 nm
Wavelength scanning	7-step selection of Survey (about 5500 nm/min), Super (about 3,000 nm/min), Very Fast, Fast, Medium, Slow and Very Slow
Response	8-step selection of 0.02, 0.03, 0.1, 0.25, 0.5, 2, 4, and 8 seconds
Sensitivity selection	2-steps of HIGH and LOW (The sensitivity at HIGH is about 50 times that of LOW)
Weight	43 kg
Operational temperature range	15 - 35 ^{0}C
Operational humidity range	40 - 80%

3.2.5 X-ray Luminescence

In this work, the luminescence excited by x-rays (x-ray luminescence or radio luminescence) of the Dy_2O_3 doped bismuth borate glasses were measured at Radiation Science Research Institute (RSRI), Kyungpook National University (KNU), Daegu 702-701, Korea, 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-ray 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-ray luminescence setup and diagram are shown in Figure 3.6 and Figure 3.7, respectively.

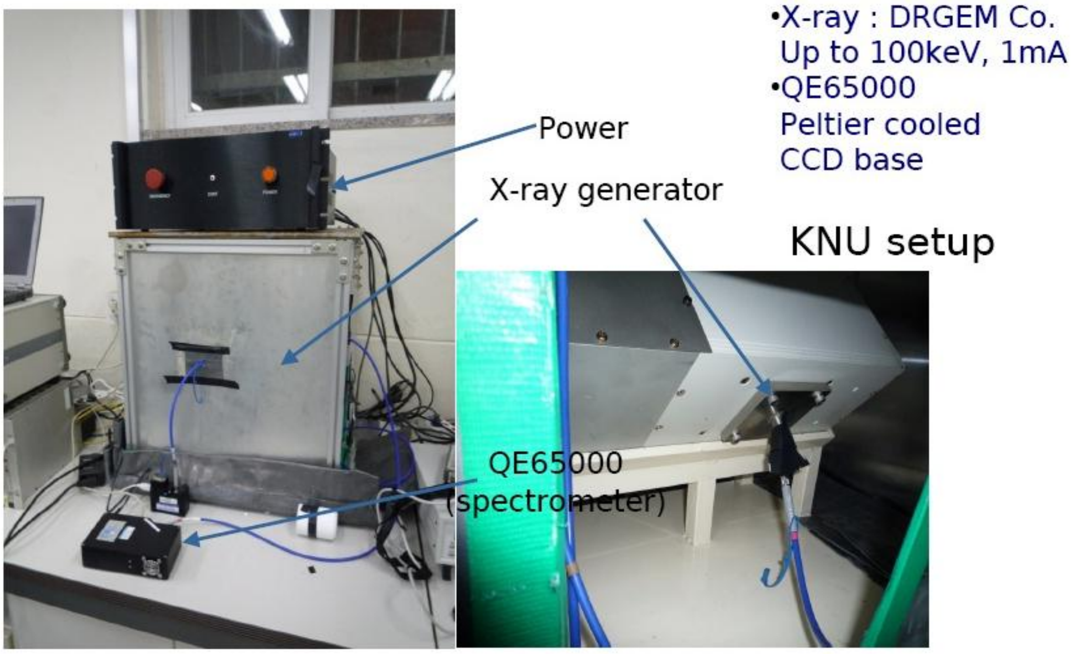

Figure 3.6 Experimental setup of x-ray luminescence measurement.

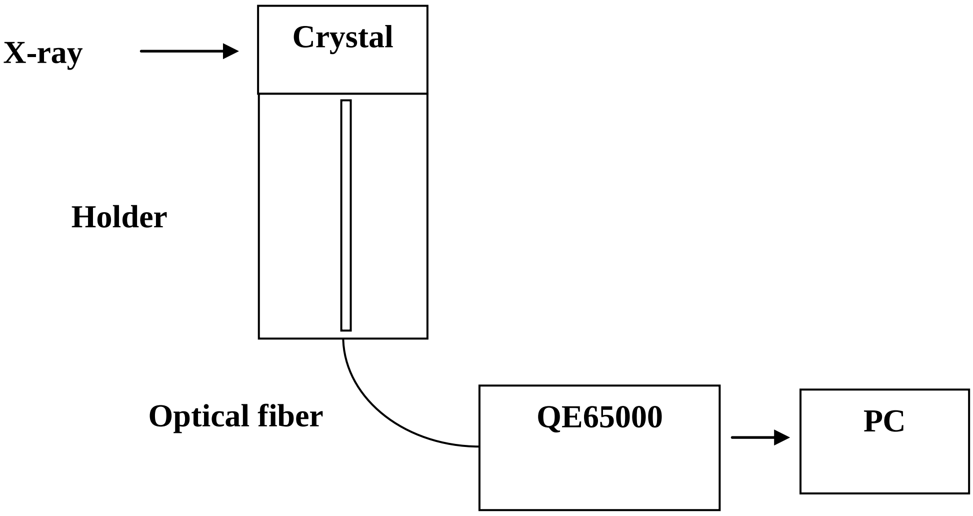

Figure 3.7 Diagram of x-ray luminescence measurement.

3.2.6 Proton Luminescence

The 50 MeV proton beam test facility at the MC-50 Cyclotron of KIRAMS (Korea Institute of Radiological & Medical Sciences) was established by PEFP (Proton beam Engineering Frontier Project) of the Korea Atomic Energy Research Institute (KAERI). This facility will be used for pilot studies of the PEFP, especially, for studies using a very low proton beam flux, $10^4 \sim 10^{10}/cm^2$-sec. The beam line is composed of a collimator, a Faraday cup, a vacuum tube for beam drift, bellows for easy alignment, a BPM (beam profile monitor), an exit window for an external beam, a phosphor screen, a scattering foil, an energy degrader, a target stage, an irradiation uniformity measurement system, a dose measurement system, an energy measurement system, etc. The 45 MeV incoming proton beam passes through a 0.2 cm of thick aluminum window capping the beam pipe with 10 cm of air and loses energy down to 38 MeV. Proton beam current of 10 nA for 10 seconds was used for this study.

Signal from the Dy_2O_3 doped in bismuth borate glass samples by the 38 MeV proton beam irradiation was transmitted through an optical fiber to the USB 4000 spectrometer produced by Ocean Optics Co. Ltd. The picture of proton luminescence setup and diagram are shown in Figure 3.8 and Figure 3.9, respectively. In this work, only 2.0 mol% of Dy_2O_3 sample was measured, for check scintillation properties of glass sample.

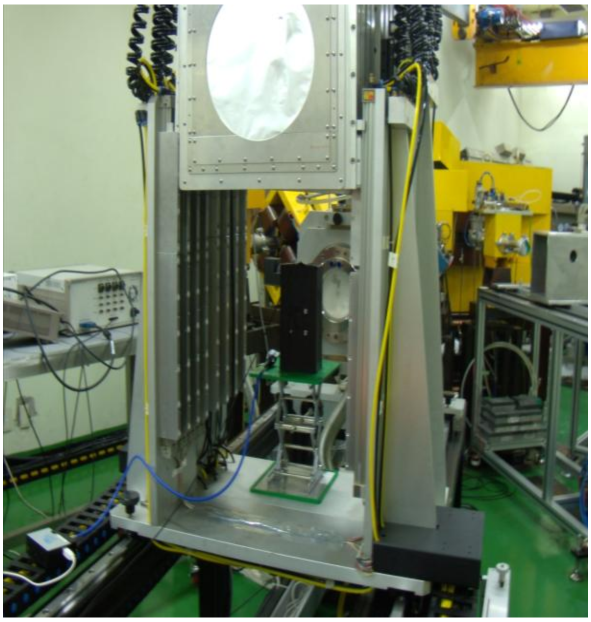

Figure 3.8 Photograph of an exit window in the proton beam line with a sample glass sample attached to the sample holder.

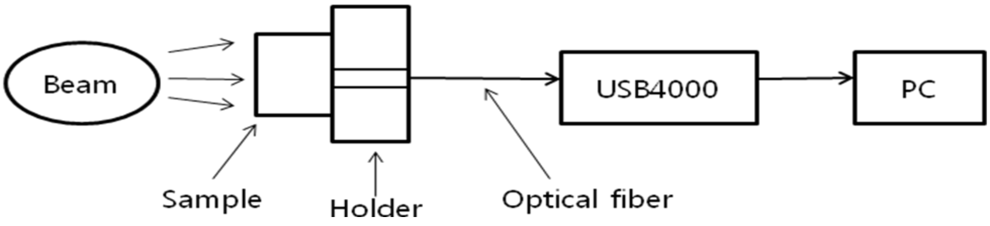

Figure 3.9 Diagram of proton luminescence measurement.

3.3 Material Characterization

The procedure of characterizations is shown as Figure 3.10.

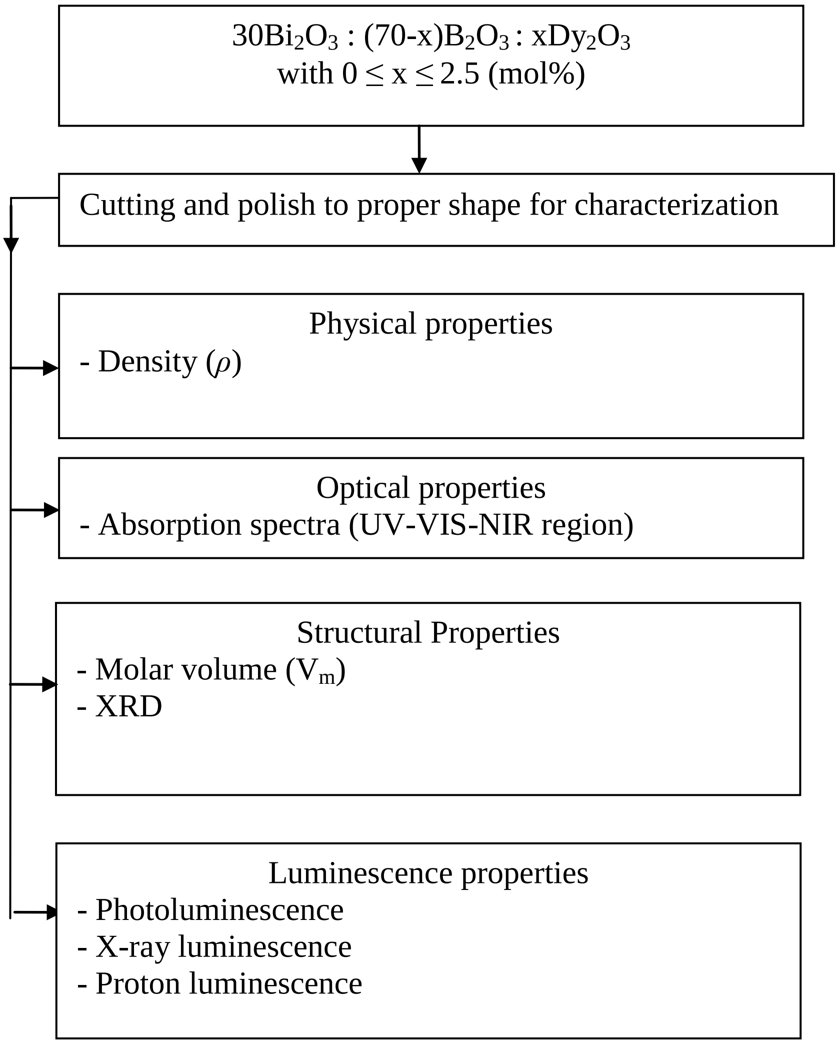

Figure 3.10 Diagram of glass samples characterizations.