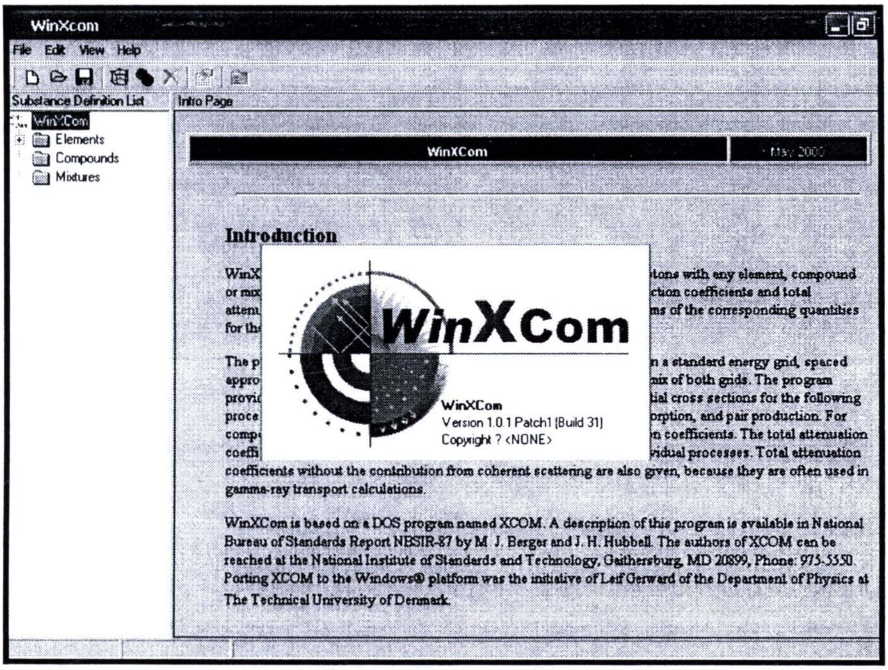
# CHAPTER 3 MATERIALS AND METHODS

## 3.1 WinXCom Program [37-38]

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 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, $\mu$ (cm$^{-1}$) or mass attenuation, $\mu/\rho$ (cm$^{2}$g$^{-1}$) 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 [36] 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 100GeV. Afterwards, a well-known program was updated and transformed to Windows operating system and Windows version is being called WinXCom [37-38].



**Introduction**

WinX … tons with any element, compound
or mix … ction coefficients and total
attenu … ms of the corresponding quantities
for th…

The p … n a standard energy grid, spaced
appro … mix of both grids. The program
provi … tial cross sections for the following
proce … orption, and pair production. For
comp … n coefficients. The total attenuation
coeffi … vidual processes. Total attenuation
coefficients without the contribution from coherent scattering are also given, because they are often used in gamma-ray transport calculations.

WinXCom is based on a DOS program named XCOM. A description of this program is available in National Bureau of Standards Report NBSIR-87 by M. J. Berger and J. H. Hubbell. The authors of XCOM can be reached at the National Institute of Standards and Technology, Gaithersburg, MD 20899, Phone: 975-5550. Porting XCOM to the Windows® platform was the initiative of Leif Gerward of the Department of Physics at The Technical University of Denmark.

WinXCom
Version 1.0.1 Patch1 (Build 31)
Copyright ? <NONE>

**Figure 3.1** The front page of WinXCom program.

## 3.2 Chemical Composition of Glass Sample [52]

In this work, the radiation shielding properties and physical properties of borate glass system with the formula $x$PbO : $(100 - x)B_2O_3$ with $x = 30, 40, 50, 60$ and 70 by wt % has been studied.

In general, glasses are either produced from high quality, chemically pure components, or from a mixture of far less pure minerals. Research specimens, optical glasses, and many glasses used for low volume, high technology applications are produced using those chemicals might routinely encounter in any chemical laboratory. Bulk commercial products, on the other hand, are produced from minerals, which typically have names and compositions which are not familiar to the novice. The names of many of these minerals and their compositions are listed in Table 3.1. Gravimetric factors, a combination of the mole ratios and the formula weights used in the stoichiometric calculation, which allow calculation of the yield of the desired glass component for each weight unit of raw material, are also listed in this table. The calculated gravimetric factor used in this work are also shown in Example 3.1

The primary glass formers in commercial oxide glasses are silica ($SiO_2$), boric oxide ($B_2O_3$), and phosphoric oxide ($P_2O_5$), which all readily form single component glasses. A large number of other compounds may act as glass formers under certain circumstances, including $GeO_2$, $Bi_2O_3$, $As_2O_3$, $Sb_2O_3$, $Te\ O_2$, $A1_2O_3$, $Ga_2O_3$, and $V_2O_5$. With the exception of $GeO_2$, these oxides do not readily form glasses by themselves unless very rapidly quenched or vapor deposited, but can serve as glass formers when mixed with other oxides. The elements S, Se, and Te act as glass formers in chalcogenide glasses. Although halide glasses can be made in many systems, with many different compounds acting as glass formers, the two most common halide glass formers are $BeF_2$ and $ZrF_4$.

**Table 3.1** Raw materials for glassmaking [52].

| Common name | Nominal composition | Gravimetric factor |
|---|---|---|
| Albite feldspar | $Na_2O$-$Al_2O_3$-$6SiO_2$ | $Na_2O = 8.46$ |
| | | $Al_2O_3 = 5.14$ |
| | | $SiO_2 = 1.45$ |
| Alumina | $Al_2O_3$ | $Al_2O_3 = 1.00$ |
| Alumina hydrate | $Al_2O_3$-$3H_2O$ | $Al_2O_3 = 1.53$ |
| Anorthite feldspar | $CaO$-$Al_2O_3$-$2SiO_2$ | $CaO = 4.96$ |
| | | $Al_2O_3 = 2.73$ |
| | | $SiO_2 = 2.32$ |
| Aragonite | $CaCO_3$ | $CaO = 1.78$ |
| Bone ash | $3CaO$-$P_2O_5$ or $Ca_3(PO_4)_2$ | $CaO = 1.84$ |
| | | $P_2O_5 = 2.19$ |
| Barite (Heavy spar) | $BaSO_4$ | $BaO = 1.52$ |
| Borax | $Na_2O$-$2B_2O_3$-$10H_2O$ | $Na_2O = 6.14$ |
| | | $B_2O_3 = 2.74$ |
| Anhydrous borax | $Na_2O$-$2B_2O_3$ | $Na_2O = 3.25$ |
| | | $B_2O_3 = 1.45$ |
| Boric acid | $B_2O_3$-$3H_2O$ | $B_2O_3 = 1.78$ |
| Burnt doromite | $CaO$-$MgO$ | $CaO = 1.72$ |
| | | $MgO = 2.39$ |
| Caustic potash | $KOH$ | $K_2O = 1.19$ |
| Caustic soda | $NaOH$ | $Na_2O = 1.29$ |
| Cryolite | $3NaF$-$AlF_3$ | $NaF = 1.67$ |
| | | $AlF_3 = 2.50$ |
| Dolomite | $CaCO_3$-$MgCO_3$ | $CaO = 3.29$ |
| | | $MgO = 4.58$ |
| Fluorspar | $CaF_2$ | $CaF_2 = 1.00$ |
| Gypsum | $CaSO_4$-$_2H_2O$ | $CaO = 3.07$ |
| Lime (quick lime or burnt lime) | $CaO$ | $CaO = 1.00$ |
| Limestone (calcite) | $CaCO_3$ | $CaO = 1.78$ |
| Litharge (yellow lead) | $PbO$ | $PbO = 1.00$ |
| Microcline | $K_2O$-$Al_2O_3$-$6SiO_2$ | $K_2O = 5.91$ |
| | | $Al_2O_3 = 5.46$ |
| | | $6SiO_2 = 1.54$ |
| Nepheline | $Na_2O$-$Al_2O_3$-$2SiO_2$ | $Na_2O = 2.84$ |
| | | $Al_2O_3 = 1.73$ |
| | | $6SiO_2 = 1.47$ |
| Niter (saltpetre) | $KNO$ | $K_2O = 2.15$ |
| Potash | $K_2O$ or $K_2O_3$ | $K_2O = 1.00$ |
| | | $K_2O = 1.47$ |
| Red lead | $Pb_2O_4$ | $PbO = 1.02$ |
| Salt cake | $Na_2SO_4$ | $Na_2O = 2.29$ |
| Sand (Glassmaker's sand) | $SiO_2$ | $SiO_2 = 1.00$ |
| Slaked lime | $CaO$-$H_2O$ or $Ca(OH)_2$ | $CaO = 1.32$ |
| Soda ash | $Na_2CO_3$ | $Na_2O = 1.71$ |
| Soda niter (Chile saltpetre) | $NaNO_3$ | $Na_2O = 2.74$ |
| Spodumene | $Li_2O$-$Al_2O_3$-$4SiO_2$ | $Li_2O = 12.46$ |
| | | $Al_2O_3 = 3.65$ |
| | | $SiO_2 = 1.55$ |
| Whiting | $CaCO_3$ | $CaO = 1.79$ |

*Quantity required to yield one weight unit of glass component.

Example 3.1: The precipitate in this work was $H_3BO_3$, which yield $B_2O_3$ according to the chemical equation:

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$$

Molecular weight of H atom = 1.00794 g/mol
Molecular weight of B atom = 10.811 g/mol
Molecular weight of O atom = 15.9994 g/mol
Molecular weight of $B_2O_3$ = (1 × 10.811) + (1 × 15.9994) = 69.6202 g/mol
Molecular weight of $H_3BO_3$ = (3 × 1.00794) + (1 × 10.811) + (3 × 15.9994)
= 61.8330 g/mol

$$\text{Gravimetric factor} = \frac{\text{Substance sought}}{\text{Substance known}}$$

$$\text{So, Gravimetric factor} = \frac{H_3BO_3}{B_2O_3} = \frac{2\times 61.8330}{1\times 69.6202} = 1.78$$

Although the number of possible glass compositions is effectively unlimited, the vast bulk of commercial glasses are based on silica as the glass former. While silica itself forms an excellent glass, with a wide range of applications, the use of pure silica glass for bottles, windows, and other bulk commercial applications would be prohibitively expensive, due to the high melting temperature (> 2000 °C) required to produce vitreous silica. Production of silicate glasses requires the addition of a flux to reduce the processing temperature to within practical limits, e.g., < 1600 °C. The most common fluxes are the alkali oxides, especially $Na_2O$ (soda) and PbO. Most commercial glasses contain soda, including those used for containers and window glasses. Potassium oxide is also used extensively in commercial glasses, while lithium oxide is used in a number of commercial glass-ceramics. Rubidium and cesium oxides are frequently used in laboratory studies of trends in behavior due to changes in the identity of the alkali oxide present in glasses, but are very rarely used in commercial products, due to their high cost. PbO, which is an excellent flux, is becoming much more limited in use due to concerns regarding toxicity of heavy metals. PbO is especially useful in dissolving any refractory or other impurity particles which might otherwise result in flaws in the final glass.

While addition of fluxes to silica lead to decreased cost of glass formation, the addition of large amounts of alkali oxides results in serious degradation in many properties. In particular, the chemical durability of silicate glasses containing large concentrations of alkali oxides is degraded to the point where they can no longer be used for containers, windows, or insulation fibers. The degradation in properties is usually countered by addition of property modifiers, which include the alkaline earth and transition metal oxides, and, most importantly, aluminum oxide (alumina). While these oxides partially counter the reduction in processing temperature obtained by addition of fluxes, they also improve many of the properties of the resulting glasses. The properties are thus modified, or adjusted, by careful control of the amount and concentration of these oxides to obtain precisely the desired results. Since many of these oxides are actually very weak fluxes for silica, and the property modifiers are usually added in lesser quantities than the fluxes, their use does not lead to excessively high processing temperatures.

Colorants are used to control the color of the final glass. In most cases, colorants are oxides of either the 3d transition metals or the 4f rare earths. Uranium oxides were once used as colorants, but their radioactivity obviously reduces their desirability for most applications. Gold and silver are also used to produce colors by formation of colloids in glasses. Colorants are only used if control of the color of the glass is desired, and are usually present in small quantities. Iron oxides, which are common impurities in the sands used to produce commercial silicate glasses, act as unintentional colorants in many products. When colorants are used to counteract the effect of other colorants to produce a slightly gray glass, they are referred to as decolorants.

Finally, fining agents are added to glass forming batches to promote the removal of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, NaCl, fluorides such as $CaF_2$, NaF, and $Na_3AlF_6$, and a number of sulfates. These materials are usually present in very small quantities (< 1 wt%), and are usually treated as if they have only minor effects on the properties of the final glasses. Their presence, however, is essential in many commercial glasses, which would be prohibitively expensive to produce without the aid of fining agents in reducing the content of unwanted bubbles in the final product.

## 3.3 Batch Calculation [52]

Glass batch calculations can range from very simple to very complex, as a function of the complexity of the composition and the raw materials used to prepare the mixture. Batches containing only oxides in their exact state as expressed by the glass formula, for example, involve very simple calculations, while batches using a number of different minerals, where a glass component may be present in two or more raw materials, require much more complicated calculations.

All batch calculations follow the same procedure. First, determine the weight fraction of each component required to produce the desired weight composition. Begin by multiplying the weight fraction of each component by the molecular weight of that component. Next, total these contributions to determine the molecular weight of the glass. Finally, multiply the weight fraction of each component by the amount of glass to be produced. The batch weight of any component which decomposes during melting is adjusted by multiplying the weight fraction of that component by the appropriate gravimetric factor for the raw material actually used in the batch (as seen in Example 3.2).

Small compositional changes are often excluded from batch calculations. For example, it is common to use a base glass of fixed composition to study effects of minor additions of other components. These additions are usually expressed as wt% additions. One might, for example, consider the effect of arsenic oxide as a fining agent by preparing the same batch containing 0, 0.1, 0.2, or 0.5 wt% additions of $As_2O$, to a base soda-lime-silicate glass composition. In reality, the actual molar composition of the glass changes as the arsenic oxide content changes. If the additions are quite small, however, the base composition is only very slightly affected by these additions, and the exact composition of each glass is usually not stated. While this procedure is pragmatically acceptable, one should be careful when the effects of the additions on the overall composition become too large to be ignored. In some cases, additions of 5 to 10 wt% of a component have been treated as negligible changes in the base composition. This is not an acceptable procedure.

Example 3.2: Lead borate with composition: 30PbO : 70$B_2O_3$ by wt%

Molecular weight of H atom = 1.00794 g/mol
Molecular weight of B atom = 10.811 g/mol
Molecular weight of O atom = 15.9994 g/mol
Molecular weight of Pb atom = 207.2 g/mol

$$\text{Weight fraction of PbO} = \frac{\text{Weigth percent of oxide}}{100} = \frac{30}{100} = 0.30$$

$$\text{Weight fraction of } B_2O_3 = \frac{\text{Weigth percent of oxide}}{100} = \frac{70}{100} = 0.70$$

Molecular weight of PbO = (1 × 207.2) + (1 × 15.9994) = 223.1994 g/mol
Molecular weight of $B_2O_3$ = (2 × 10.811) + (3 × 15.9994) = 69.6202 g/mol
Molecular weight of lead borate glass = (0.30 × 223.1994) + (0.70 × 69.6209)
= 115.6940 g/mol
For 100 grams of glass contains PbO = 0.30 × 100 g = 30 g
For 100 grams of glass contains $B_2O_3$ = 0.70 × 100 g = 70 g

Due to this work use $H_3BO_3$, which yield $B_2O_3$ after decomposition. It is necessary to multiply the desired quantity of $B_2O_3$ by the gravimetric factor for $H_3BO_3$ (1.78), to obtain the weight of $H_3BO_3$ to be used to yield the quantity of $B_2O_3$.

In this work, each batch contains chemicals 30 g,

Weight of PbO = 0.30 × 30 g = 9.00 g
Weight of $H_3BO_3$ = 0.70 × 30 g × 1.78 = 37.38 g

## 3.4 Materials Preparation

The following lead borate glass samples in the composition of $(100\text{-}x)B_2O_3 : x\text{PbO}$ with $x$ = 30, 40, 50, 60 and 70 wt% have been prepared using conventional melt-quenching technique. Analytical reagent grade chemicals used in the preparation contain PbO (UNILAB, 99.99%) and $H_3BO_3$ (UNIVAR, 99.99 %) are shown in Figure 3.2 and the chemical compositions of the glasses are enlisted in Table 3.2. Each batch weights about 30 g with the above chemicals were mixed together by grinding to obtain a fine power. The mixture was melted in a alumina crucible in an electrically heated furnace at 1100°C for an hour till a bubble free liquid was formed. After complete melting, the homogenized molten was casted in a preheated stainless steel mould and annealed at 500°C for 3 hours before cooled down to room temperature. At the last process, the prepared glass samples were cut and finely polished to a dimension of 1.0cm x 2.0cm x 0.3cm for further studies. The process of glasses preparation is shown in Figure 3.3. The high temperature electrical furnace for glass melting and annealing are shown in Figure 3.4 to Figure 3.5, respectively.

**Figure 3.2** The analytcal reagent grade of chemicals.

**Table 3.2** Chemical compositions of the prepared glasses.

| PbO (weight %) | Glass composition with following formula (weight %) |
|---|---|
| 30 | $30PbO : 70B_2O_3$ |
| 40 | $40PbO : 60B_2O_3$ |
| 50 | $50PbO : 50B_2O_3$ |
| 60 | $60PbO : 40B_2O_3$ |
| 70 | $70PbO : 30B_2O_3$ |

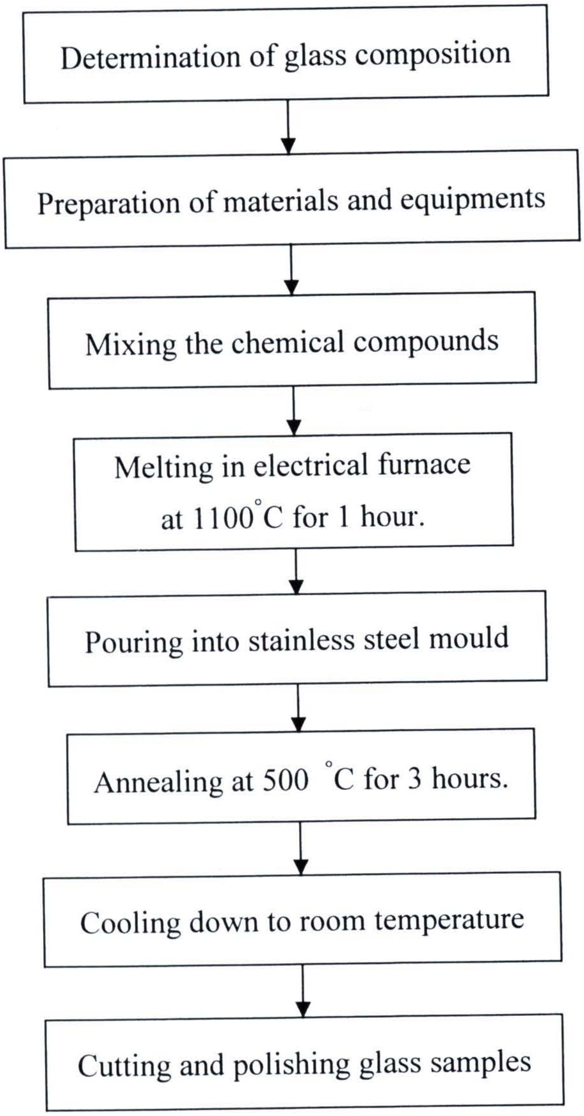


**Figure 3.3** Diagram shows the steps of the preparation process of glass samples.

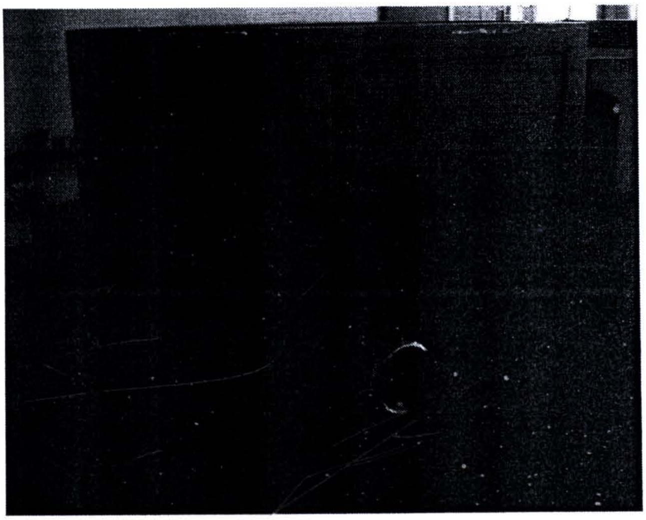


**Figure 3.4** High temperature electrical furnace for melting glass.

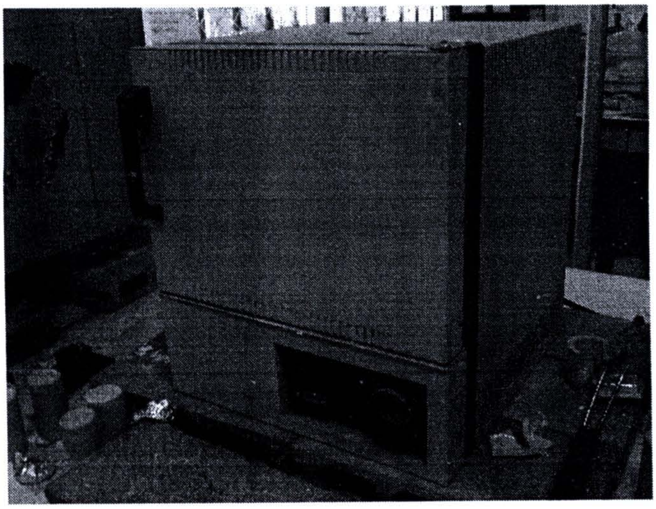


**Figure 3.5** High temperature electrical furnace for annealing glass.

## 3.5 Glass Characterization

The radiation shielding properties of the as-prepared glass samples were characterized using the gamma-ray transmission experiment. In addition, some physical and optical properties were also characterized using the various techniques, i.e. thickness, density measurement, UV-Visible spectrophotometer. The procedures are shown in Figure 3.6.

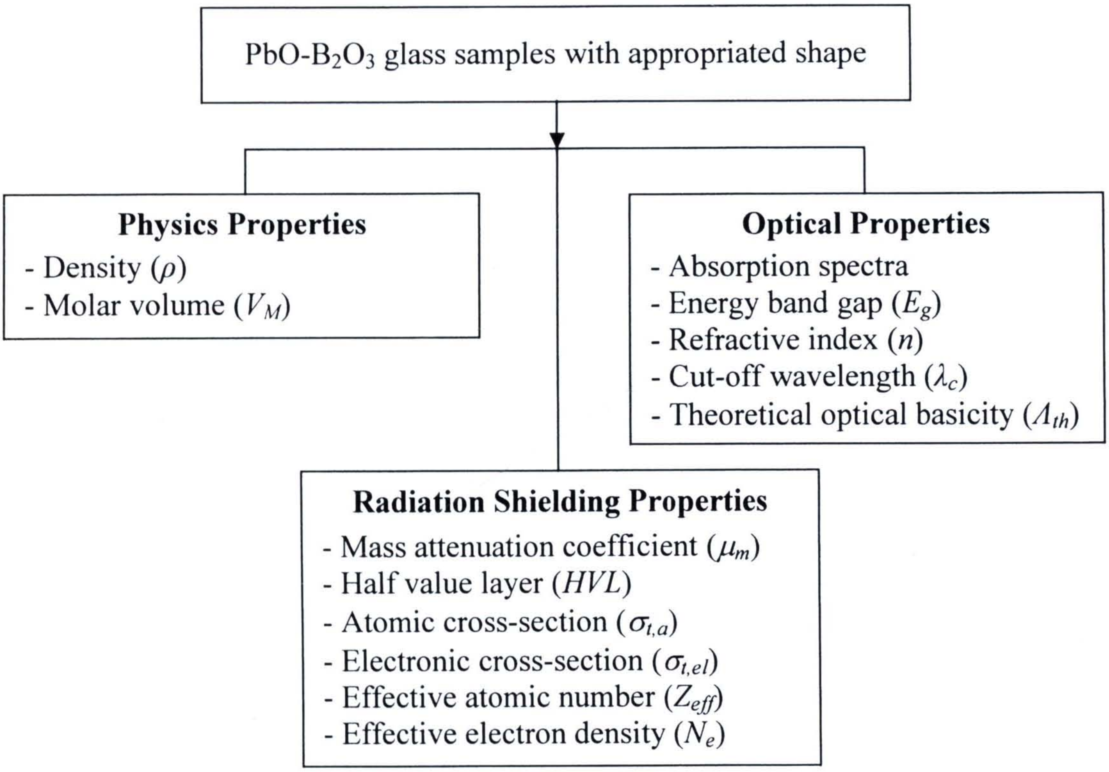


**Figure 3.6** The process of characterized parameters.

### 3.5.1 Physical Properties

#### 3.5.1.1 Density Measurement

The determined density of all glass samples was obtained by applying Archimedes principle, the weight of the prepared samples was measured in air and in working fluid, xylene, using a 4-digit sensitive microbalance (Denver, Pb214) at room temperature, as shown in Figure 3.7. Then, the density, $\rho$, was determined using the relation

$$\rho = \frac{w_a}{w_a - w_b} x\ \rho_b \tag{3.1}$$

where $w_a$ and $w_b$ are the weight of sample in air and in xylene, respectively. $\rho_b$ is the density of xylene ($\rho_b = 0.863$ g/cm$^3$).

The molar volume ($V_M$) of the glass samples was calculated using the molecular weight ($M_T$) and determined density ($\rho$) with the following relation,

$$V_M = \frac{M_T}{\rho} = \frac{\sum m_i x_i}{\rho} \tag{3.2}$$

where $m_i$ is the molar weight of oxides, $x_i$ is the molar fraction of oxides and $M_T$ is the total molecular weight of the multi-component glass system given by

$$M_T = x_{PbO} Z_{PbO} + x_{B_2O_3} Z_{B_2O_3} \tag{3.3}$$

where $x_{PbO}$ and $x_{B_2O_3}$ are the mole fractions of the constituent oxides, and $Z_{PbO}$, $Z_{B_2O_3}$ are the molecular weights of the constituent oxides.

**Figure 3.7** The sensitive microbalance for density determination.

### 3.5.2 Optical Properties

### 3.5.2.1 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 3.8.

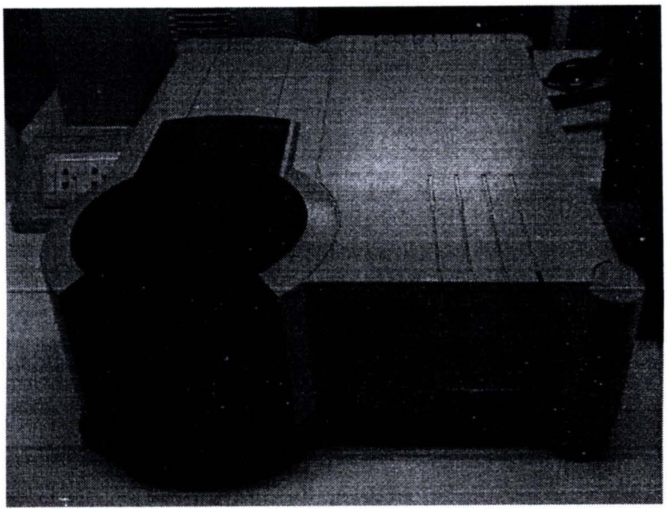


**Figure 3.8** UV-Visible spectrophotometer (Varian, Cary50).

### 3.5.3 Radiation Shielding Properties

#### 3.5.3.1 Gamma-Ray Transmission

The diagram of experimental setup for determines the total mass attenuation coefficient by using the narrow beam gamma-ray transmission technique is shown in Figure 3.9. This set up can move in the transverse direction to the incident beam for proper alignment. The radioactive source, $^{137}$Cs radioactive of 15mCi strength was acquired from the Office of Atomic for Peace (OAP), Thailand, was enclosed in lead container and was mounted on composite of adjustable stands. The incident and transmitted gamma-ray intensities were measured for a fixed preset time by recording the corresponding counts, using the 2″×2″ NaI(Tl) detector having an energy resolution of 10.2% at 662 keV (BICRON model 2M2/2), with CANBERRA photomultiplier tube base model 802-5. The dead time in this experiment was 0.73%-1.37%. The pulse shaping time was 0.5 μs. An optimum sample thickness ($0.5 \le \mu x \le 5.0$) was selected in this experiment on the basis of the Nordfors criteria [71]. The statistical error in this experiment calculated from the standard error of 3 items (i) ray-sum measurement, which calculated from experiment, the ray-sum is product of linear attenuation coefficient ($\mu$) with thickness ($x$), (ii) density measurement and (iii) thickness measurement. Finally, the total standard error has been determined by combining errors for the ray-sum measurement, density measurement and thickness measurement in quadrature. The statistical uncertainly was kept below 0.3 % by choosing the counting time so that $10^5$-$10^6$ counts were recorded in the full energy peak. All measurements were made using an ordinary counting system. The spectra were recorded using a PC-based multichannel analyzer, supplied by CANBERRA, USA.

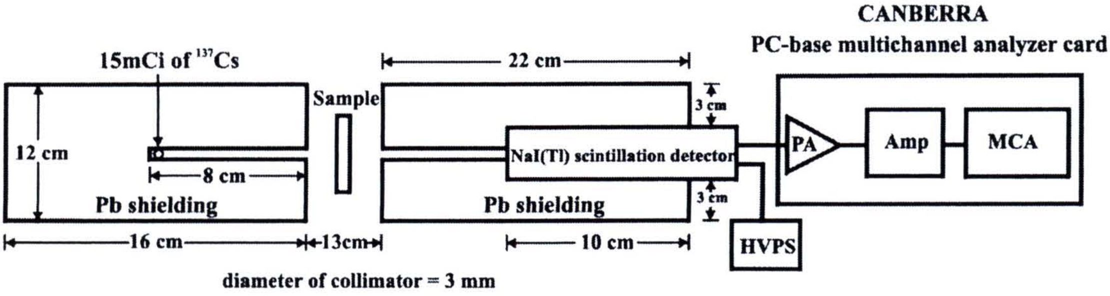


**Figure 3.9** Experimental setup of gamma-ray transmission technique.

#### 3.5.3.2 Weight fraction Calculation

To obtain the theoretical values of total mass attenuation coefficient by using the WinxCom program, it is necessary to calculate the weight fraction of constituent elements in glass compositions. The example of calculation of weight fraction was shown in Example 3.3 and also enlisted in Table 3.3.

<u>Example 3.3:</u> Weight fraction of $i^{th}$ constituent elements in the glass composition: $30PbO : 70B_2O_3$ by wt%

Molecular weight of B atom = 10.811 g/mol
Molecular weight of O atom = 15.9994 g/mol
Molecular weight of Pb atom = 207.2 g/mol
Molecular weight of PbO = (1 × 207.2) + (1 × 15.9994) = 223.1994 g/mol

Molecular weight of $B_2O_3 = (2 \times 10.811) + (3 \times 15.9994) = 69.6202$ g/mol

$$\text{Weight fraction of PbO} = \frac{\text{Weigth percent of oxide}}{100} = \frac{30}{100} = 0.30$$

$$\text{Weight fraction of } B_2O_3 = \frac{\text{Weigth percent of oxide}}{100} = \frac{70}{100} = 0.70$$

Weight fraction of element in oxide

$$= \frac{\text{Wt. fraction of element in oxide} \times \text{No. of atoms} \times \text{Molecular weight of element}}{\text{Molecular weight of oxide}}$$

$$\text{Weight fraction of Pb } = \frac{0.3 \times 1 \times 207.2}{223.1994} = 0.2785$$

$$\text{Weight fraction of B } = \frac{0.7 \times 2 \times 10.811}{69.6202} = 0.2174$$

$$\text{Weight fraction of O } = \frac{0.3 \times 1 \times 15.9994}{223.1994} + \frac{0.7 \times 3 \times 15.9994}{69.6202} = 0.5041$$

**Table 3.3** Weight fraction for each element in the as- prepared glass samples.

| Sample No. | Glass Formula (by wt%) | Glass composition (by wt%) | | Weight fraction | | |
|---|---|---|---|---|---|---|
| | | PbO | $B_2O_3$ | B | O | Pb |
| 1 | $30PbO : 70B_2O_3$ | 30 | 70 | 0.2174 | 0.5041 | 0.2785 |
| 2 | $40PbO : 60B_2O_3$ | 40 | 60 | 0.1864 | 0.4423 | 0.3713 |
| 3 | $50PbO : 50B_2O_3$ | 50 | 50 | 0.1553 | 0.3806 | 0.4641 |
| 4 | $60PbO : 40B_2O_3$ | 60 | 40 | 0.1242 | 0.3188 | 0.5570 |
| 5 | $70PbO : 30B_2O_3$ | 70 | 30 | 0.0932 | 0.2570 | 0.6498 |