CHAPTER 3 MATERIALS AND METHODS

3.1 Materials Preparation

The soda-lime silicate glass doped with MnO_2 were prepared in composition (65-x)SiO_2: 10CaO: 25Na_2O: xMnO_2 (where x is 0.00, 0.10, 0.20, 0.30, 0.40 and 0.50 mol%). Analytical reagent grade chemicals used in the present study consisted of SiO_2 (Fluka, 99.99%), Na_2O (Riedel – de Haen, 99.99%), CaO (Riedel – de Haen, 99.99%) and MnO_2 (Unilab, 99.50%) are shown in Figure 3.1. All chemical composition was finely powder and then mixed in whole of composite. Batches for producing 30 g of glass were melted in high purity alumina crucibles in a laboratory electric furnace at 1200, 1300, 1400 and 1500°C with soaking time for 3 h. Afterwards, the melts were quickly poured onto a preheated stainless steel mould, annealed at 500°C for 3 hours, and cooled down to room temperature, respectively. Finally, the as-prepared glass samples were cut and then finely polished to a dimension of 1.0cm x 1.5cm x 0.3cm. The glasses preparation procedure is shown in Figure 3.2. The chemical compositions of the glasses are summarized in Table 3.1. The high temperature electrical furnace for glass melting and annealing are shown in Figure 3.3 to 3.4, respectively.

Table 3.1 Chemical compositions of the glasses.

MnO_2 (mol%)	Glass composition (mol%)
0.00	65.0SiO_2: 10.0CaO: 25.0Na_2O
0.10	64.9SiO_2: 10.0CaO: 25.0Na_2O: 0.10MnO_2
0.20	64.8SiO_2: 10.0CaO: 25.0Na_2O: 0.20MnO_2
0.30	64.7SiO_2: 10.0CaO: 25.0Na_2O: 0.30MnO_2
0.40	64.6SiO_2: 10.0CaO: 25.0Na_2O: 0.40MnO_2
0.50	64.5SiO_2: 10.0CaO: 25.0Na_2O: 0.50MnO_2

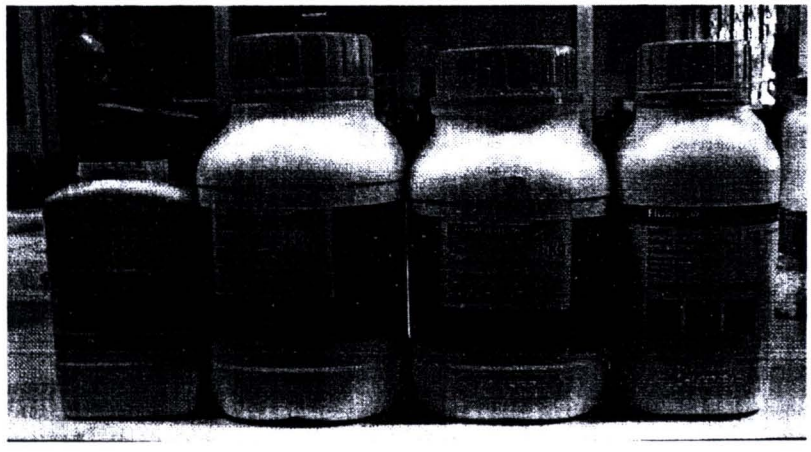

Figure 3.1 The reagent grade chemicals.

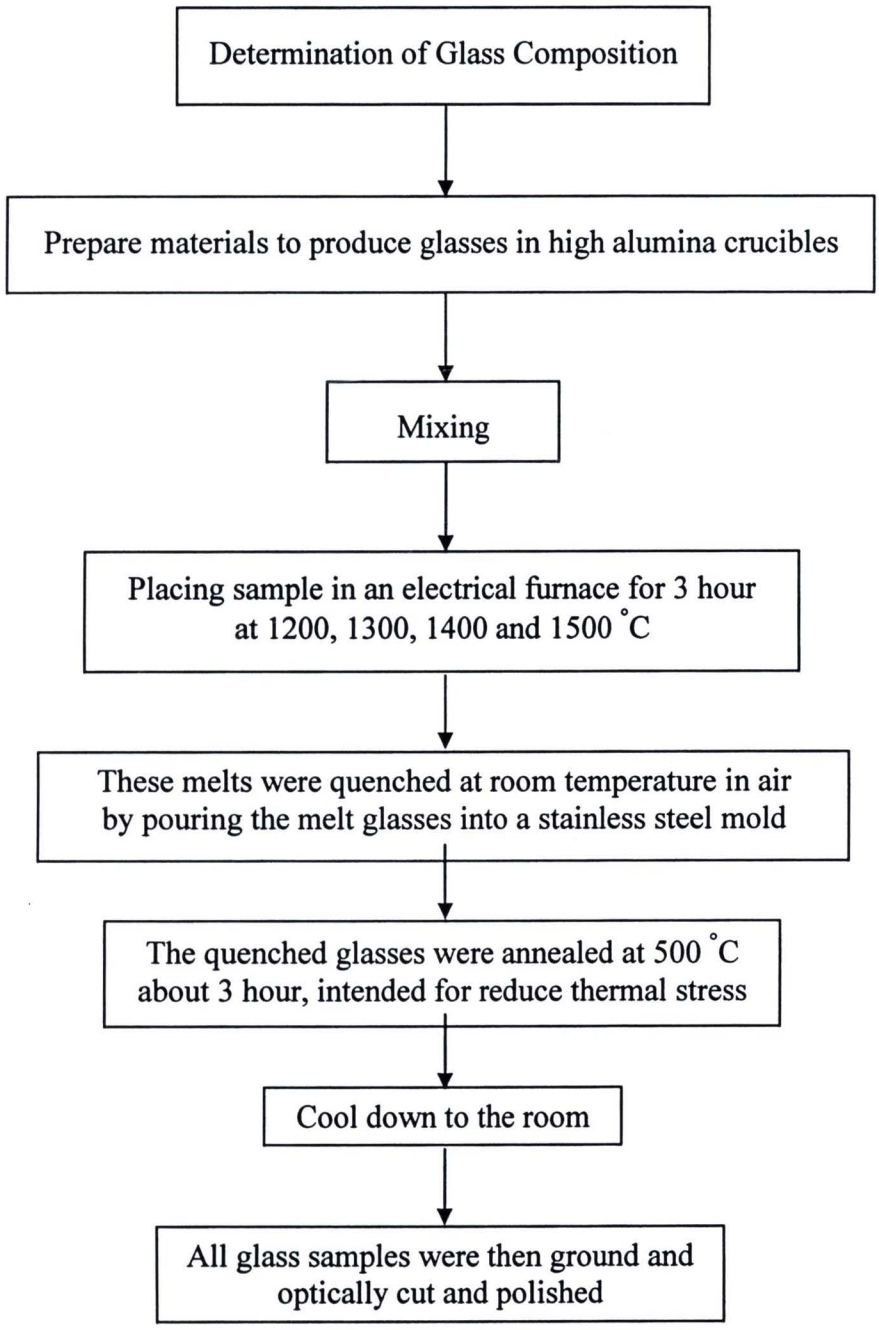

Figure 3.2 Flow sheet of preparation the glass samples.

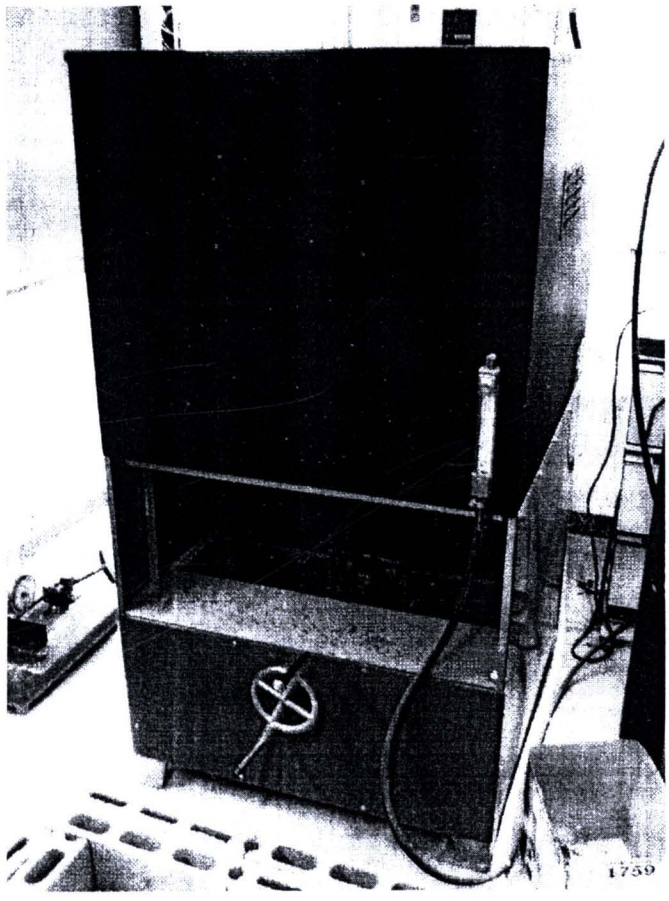

Figure 3.3 High temperature electrical furnace for melting glass.

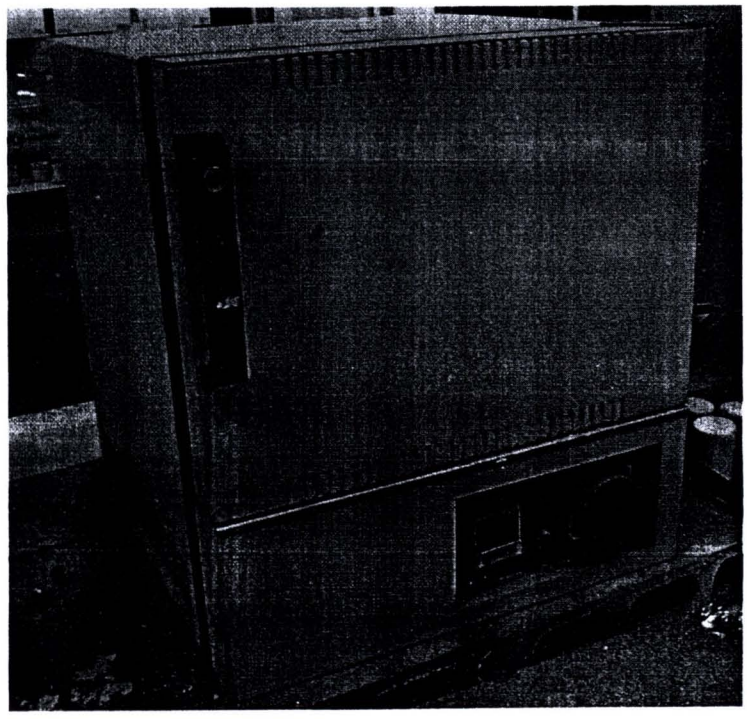

Figure 3.4 High temperature electrical furnace for annealing glass.

3.2 Material Characterization

The properties of samples were characterized using the various techniques, i.e. density measurement, UV-Visible spectrophotometer, refractive index measurement, Theoretical optical basicity, and electronic polarizability. The procedures are shown in Figure 3.5.

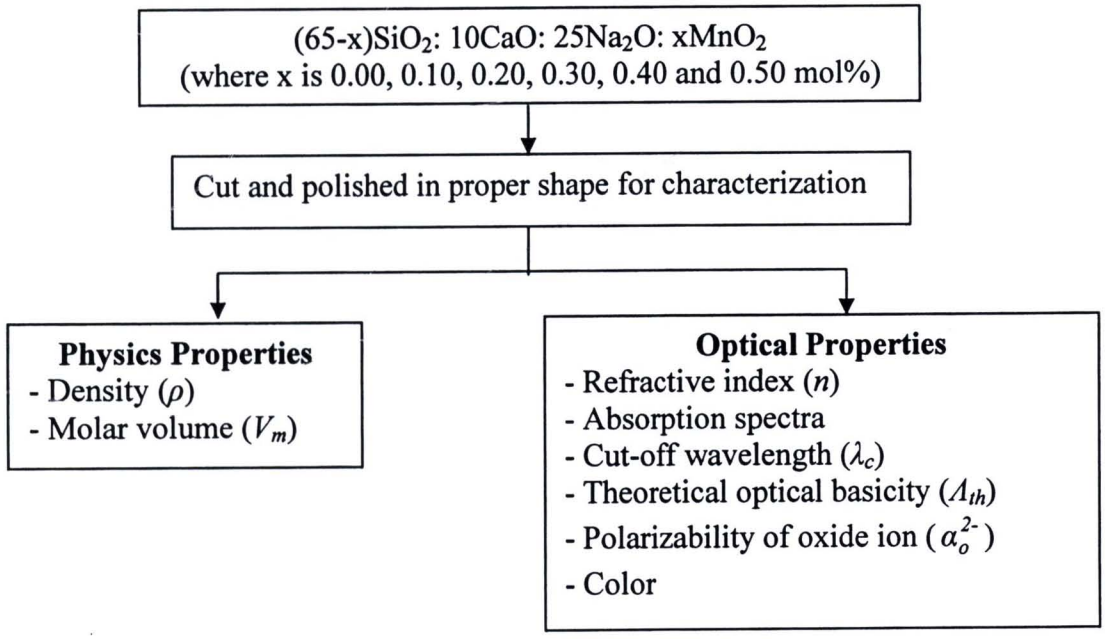

Figure 3.5 The diagram shows the steps of preparation and characterization of glass samples.

3.2.1 Density Measurement

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

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

where W_a and W_b is the weight of glass in air and xylene, respectively, and ρ_b is the density of xylene (ρ_b = 0.863 g/cm^3). All weight measurements were used a 4 – digit sensitive microbalance (Denver, Pb214), as shown in Figure 3.6.

The molar volume (V_m) of the glass samples was 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 the total molecular weight of the multi-component glass system given by

$$M_T = x_{SiO_2} Z_{SiO_2} + x_{Na_2O} Z_{Na_2O} + x_{CaO} Z_{CaO} + x_{MnO_2} Z_{MnO_2} \quad (3.3)$$

where x_{SiO_2}, x_{Na_2O}, x_{CaO} and x_{MnO_2} are the mole fractions of the constituent oxides, and Z_{SiO_2}, Z_{Na_2O}, Z_{CaO} and Z_{MnO_2} are the molecular weights of the constituent oxides.

Figure 3.6 The sensitive microbalance for density determination.

3.2.2 Refractive index, electronic polarizability and optical basicity measurements

The refractive index were measured by using an Abbe refractometer (ATAGO) with a sodium vapor lamp as the light source emitting the light at a wavelength, λ, of 589.3 nm (D line) and having mono-bromonaphthalene as the contact layer between the sample and prism of the refractometer. The Abbe refractometer is shown in Figure 3.7

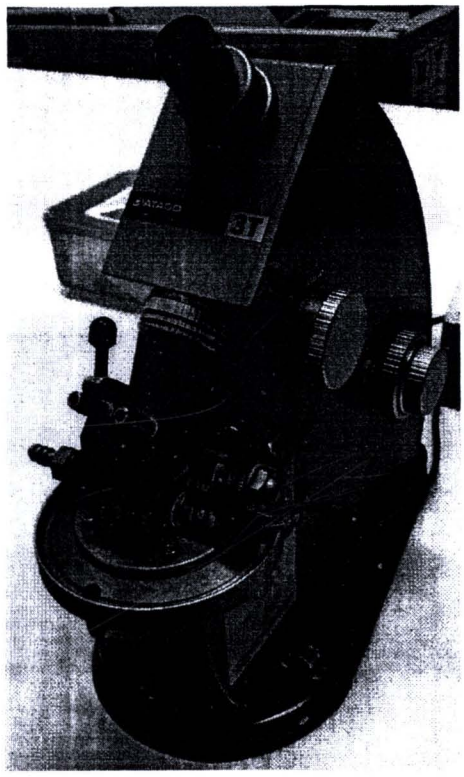

Figure 3.7 The Abbe refractometer (ATAGO).

Then, the refractive index was used to calculate the molar refraction (R_m) by using the well-known Volf, Lorentz and Lorenz [4] formula

$$R_m = \frac{(n^2 - 1)}{(n^2 + 2)}\left(\frac{M}{\rho}\right) \tag{3.4}$$

where n is the refractive index at wavelength, λ = 589.3 nm, ρ is the density and M is the molecular weight of the glass samples. M/ρ is called molar volume, V_M, and $R = \frac{(n^2 - 1)}{(n^2 + 2)}$ is known as the refraction loss.

The molar polarizability is proportional to the molar refraction of the material according to the relation [4]

$$\alpha_m = \left(\frac{3}{4\pi N}\right)R_m \tag{3.5}$$

where N is the number of polarizable ions per mole and is assumed to be equal to the Avogadro's number N_A. The value $4\pi/3$ is known as a constant in Lorentz function. With α_m in (Å^3), Eq. (3.5) can be transformed to $R_m = 2.52\alpha_m$.

The optical basicity (Λ) of an oxide medium is the average electron donor power of all the oxide atoms comprise in the medium. The polarizability of oxide ions is closely related to the optical basicity of oxide materials. The optical basicity could be predicted from the composition of the glass and the basicity moderating parameters of the various

cations present. Theoretical optical basicity (Λ_{th}) is calculated using the following expression proposed by Duffy and Ingram [7]

$$\Lambda_{th} = \sum_i x_i \Lambda_i \tag{3.6}$$

where $x_1, x_2, \ldots, x_n$ are equivalent fractions based on the amount of oxygen each oxide contributes to the overall material stoichiometry and $\Lambda_1, \Lambda_2, \ldots, \Lambda_n$ are optical basicity values assigned to the individual oxides. The values optical basicity in this glass are $\Lambda_{SiO_2} = 0.50$, $\Lambda_{Na_2O} = 1.15$, $\Lambda_{CaO} = 1.00$ and $\Lambda_{MnO_2} = 0.88$, respectively [7,58,59].

The average polarizability of oxide ions is also interpreted in terms of optical basicity. The optical basicity value of an oxide medium is a numerical expression of the average electron donor power of the oxide species constituting the medium so that it is used as a measure of the acid-base properties of oxides, glass, alloys, etc. The optical basicity of glasses can be obtained experimentally by several methods including measurements of frequency shifts in the $^1S_0$-$^3P_1$ band UV spectra of metal ion probes, e.g. Tl^+ or Pb^{2+} and changes in oxygen 1s binding energy. On the basis of refractive data Duffy has established that an intrinsic relationship exists between the electronic polarizability of oxide ion, α_O^{2-} and the optical basicity of oxide ions medium (Λ_{th}), by the following correlation [7].

$$\Lambda_{th} = 1.67\left(1 - \frac{1}{\alpha_O^{2-}}\right) \tag{3.7}$$

The theoretical optical basicity for this glass system under study can be calculated using Eq. (3.7).

3.2.3 Ultraviolet-Visible Spectrophotometer

To study of the optical absorption edge in UV-Visible 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. In this work, the optical absorption spectra were recorded at room temperature using a UV-visible spectrophotometer (Hitachi, U-1800), as shown in Figure 3.8, working in 300-1100 nm. The absorption coefficient, α(ν), was calculated for each sample at different photon energies by the relation

$$\alpha(\nu) = \left(\frac{1}{d}\right) ln\left(\frac{I_o}{I}\right) \tag{3.8}$$

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

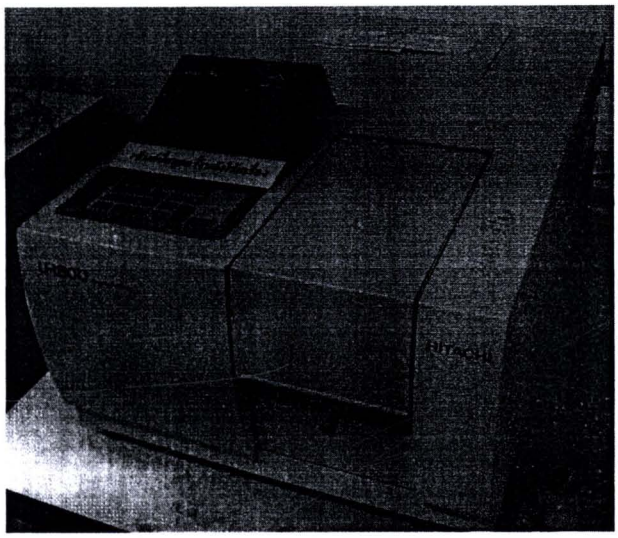

Figure 3.8 UV-visible spectrophotometer (Hitachi, U-1800).

3.2.4 Color Index Measurements

The glasses color was measured by spectrophotometer using colorimeter (Varian, CARY 50) Color analysis (Figure 3.9). CIE L*a*b* (CIELAB) color space were indicated glasses color in this work. The CIELAB color scale is an approximately uniform color scale. In a uniform color scale, the differences between points plotted in the color space correspond to visual difference between the colors plotted. The CIELAB color space is organized in cube form. The L* axis runs from top to bottom. The maximum for L* is 100, which represents a perfect reflecting diffuser. The minimum for L* is zero, which represents black. The a* and b* are the chromaticity coordinates that indicate color directions, a* and b* axes have no specific numerical limits. Positive a* is red direction. Negative a* is green direction. Positive b* is yellow direction. Negative b* is blue direction.

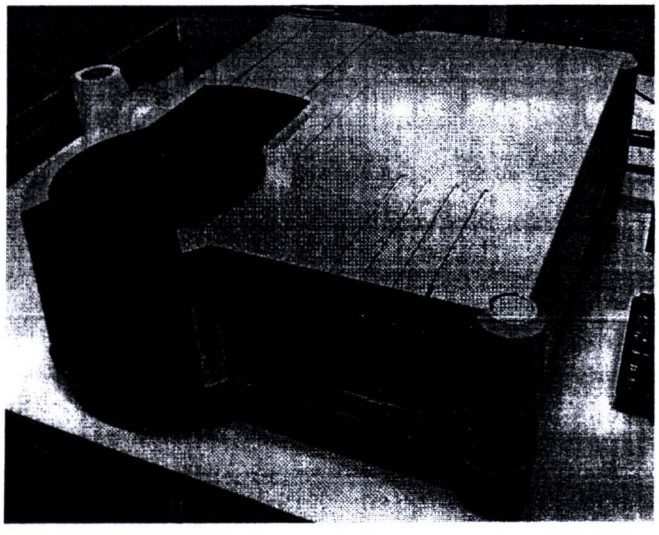

Figure 3.9 Colorimeter (Varian, CARY 50).

3.3 Batch Calculations [1]

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 molar composition. Begin by multiplying the mole fraction of each component by the molecular weight of that component. Next, total these contributions to determine the molecular weight of the glass, and then divide each individual contribution by the molecular weight of the glass to determine the weight fraction of each component. 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. Use of raw materials which supply more than one batch component requires additional calculations.

In this work soda-lime silicate glass doped with MnO_2 were prepared in composition $(65\text{-}x)SiO_2$: $10CaO$: $25Na_2O$: $xMnO_2$ (where x is 0.00, 0.10, 0.20, 0.30, 0.40 and 0.50 mol%).

Glass composition: $64.9SiO_2$: $10CaO$: $25Na_2O$: $0.1MnO_2$
Molecular weights of components (in $g \cdot mol^{-1}$):

SiO_2 = 60.09
CaO = 56.08
Na_2O = 61.98
MnO_2 = 86.94

Molecular weights of glass:

$(0.649 \times 60.09) + (0.10 \times 56.08) + (0.25 \times 61.98) + (0.001 \times 86.94) = 60.1858\ g \cdot mol^{-1}$

Weight fraction of each component:

SiO_2 = (0.649 x 60.09)/60.1858 = 0.6479
CaO = (0.10 x 56.08)/60.1858 = 0.0932
Na_2O = (0.25 x 61.98)/60.1858 = 0.2575
MnO_2 = (0.001 x 86.94)/60.1858 = 0.0014

For 30 grams of glass:

SiO_2 = 0.6479 × 30 = 19.4377 g
CaO = 0.0932 × 30 = 2.7953 g
Na_2O = 0.2575 × 30 = 7.7236 g

MnO_2 = 0.0014 × 30 = 0.0433 g

If we use Na_2CO_3 as the source of Na_2O, Using the gravimetric factors for Na_2CO_3 is 1.71, we will require 7.7236 × 1.71 = 13.2073 g of Na_2CO_3.
Final Batch:

SiO_2 = 19.4377 g
CaO = 2.7953 g
Na_2O = 13.2073 g
MnO_2 = 0.0433 g