

CHAPTER 4 RESULTS AND DISCUSSION

The soda lime silicate glasses doped with MnO_2 were prepared in composition $(65-x)\text{SiO}_2: 10\text{CaO}: 25\text{Na}_2\text{O}: x\text{MnO}_2$ (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_2CO_3 (Riedel – de Haen, 99.99%), CaO (Riedel – de Haen, 99.99%) and MnO_2 (Unilab, 99.50%). 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 $1.0 \times 0.5 \times 0.3 \text{ cm}^3$. The chemical compositions of the glasses are summarized in Table 4.1. The glass samples with different melting temperature are illustrated in Figure. 4.1. The color of the transparent Mn^{3+} doped soda-lime silicate glasses changes with increasing of MnO_2 content between colorless and dark violet.

Table 4.1 The chemical compositions of the glasses.

MnO_2 (mol %)	Glass composition (mol%)
0.00	65.00 SiO_2 : 10.0 CaO : 25.0 Na_2O
0.10	64.90 SiO_2 : 10.0 CaO : 25.0 Na_2O : 0.10 MnO_2
0.20	64.80 SiO_2 : 10.0 CaO : 25.0 Na_2O : 0.20 MnO_2
0.30	64.70 SiO_2 : 10.0 CaO : 25.0 Na_2O : 0.30 MnO_2
0.40	64.60 SiO_2 : 10.0 CaO : 25.0 Na_2O : 0.40 MnO_2
0.50	64.50 SiO_2 : 10.0 CaO : 25.0 Na_2O : 0.50 MnO_2

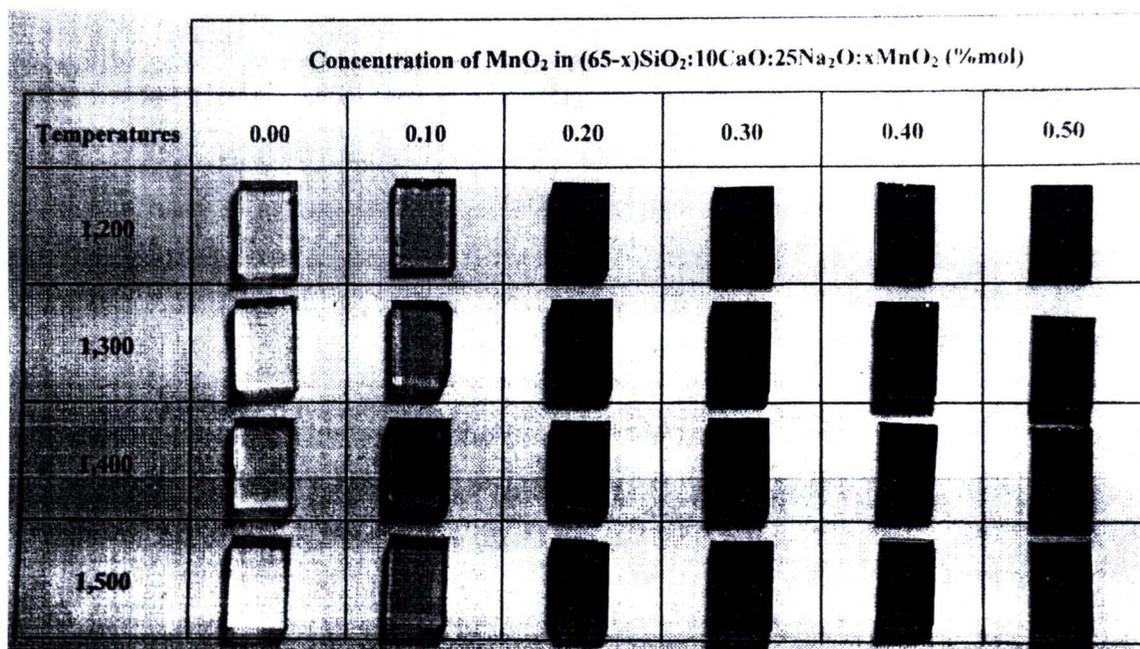


Figure 4.1 Soda lime silicate glasses doped with MnO_2 with different melting temperature.

4.1 Effect of MnO₂ Concentration

4.1.1 Density and Molar Volume

The measured density of Mn-ions doped soda lime silicate glass samples for different MnO₂ concentrations. The variation of the density with MnO₂ concentration of Mn-ions doped soda lime silicate glass samples is shown in Figure. 4.2. As can be seen that, the density increases when increases MnO₂ concentration, indicates that replacing SiO₂ by addition of a small amount of MnO₂ results in the increase of the average molecular weight of oxide ions in the glass due to MnO₂ has a higher relative molecular mass than that of SiO₂.

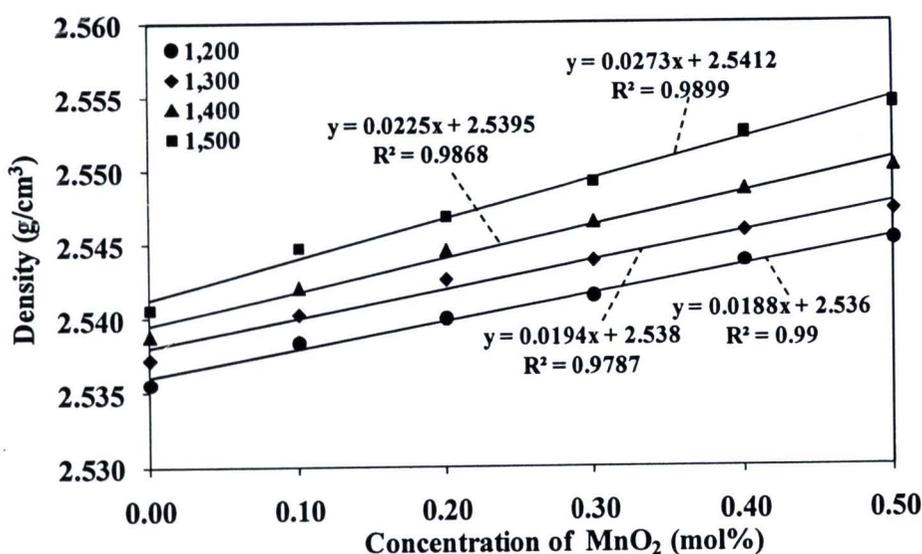


Figure 4.2 Variations of the density with MnO₂ concentration on difference melting temperature in soda lime silicate glasses.

The glass molar volume shows an opposite trend to the density for all glass samples. The molar volume depends on both the rates of change of density and molecular weight. However, the molar volume decreases when MnO₂ concentration is increased due to the decrease in the bond length or inter-atomic spacing between the atoms which may be attributed to the increase in the stretching force constants of the bonds inside the glass network. This indicates that the structure becomes more compacted (Figure 4.3).

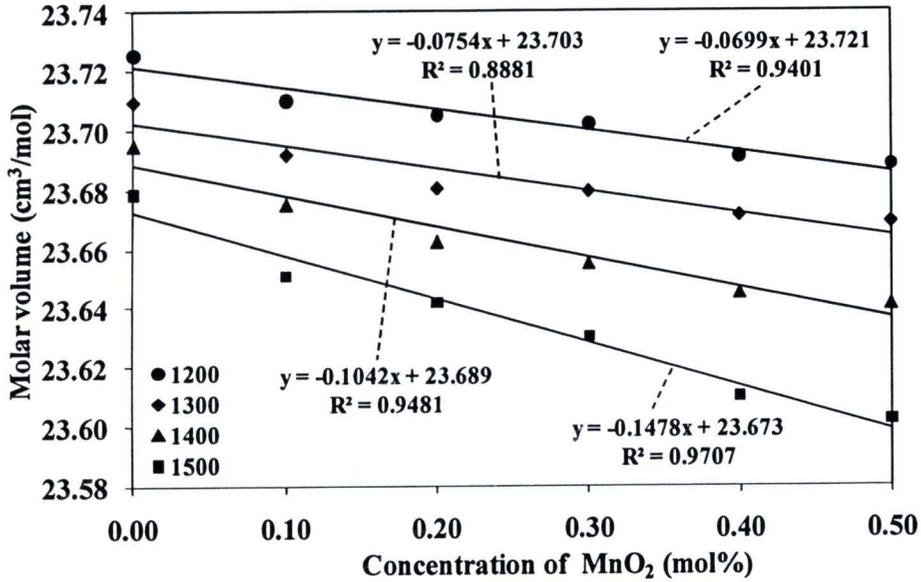


Figure 4.3 Variations of the molar volume with MnO₂ concentration on difference melting temperature in soda lime silicate glasses.

Based on the measured density the Mn-ion concentration and other related physical properties, i.e. polaron radius, inter nuclear distance and field strength can be determined using equation (4.1)-(4.4) [4]:

$$N (\text{ion}/\text{cm}^3) = (\% \text{mol of RE}) \times \frac{(\text{Avogadro's number})(\text{glass density})}{(\text{glass average molecular weight})} \quad (4.1)$$

Polaron radius:
$$r_p (A^\circ) = \left(\frac{1}{2} \right) \left(\frac{\pi}{6N} \right)^{1/3} \quad (4.2)$$

Inter nuclear distance:
$$r_i (A^\circ) = \left(\frac{1}{N} \right)^{1/3} \quad (4.3)$$

Field strength:
$$F (\text{cm}^2) = \left(\frac{Z}{r_p^2} \right) \quad (4.4)$$

From the Table 4.2, found that the polaron radius and inter nuclear distance have been decreased due to the decrease in the bond length or inter-atomic spacing between the atoms which may be attributed to the increase in the stretching force constants of the bonds inside the glass network.

Table 4.2 The value of polaron radius, inter nuclear distance and field strength of glass samples.

Melting Temperature		MnO ₂ concentration (mol%)					
		0.0	0.1	0.2	0.3	0.4	0.5
Polaron radius, r_p (Å)	1200	-	13.7132	10.8834	9.5072	8.6365	8.0171
	1300	-	13.7097	10.8797	9.5042	8.6341	8.0149
	1400	-	13.7065	10.8769	9.5009	8.6309	8.0118
	1500	-	13.7018	10.8737	9.4975	8.6266	8.0074
Interionic distance, r_i (Å)	1200	-	34.0234	27.0025	23.5879	21.4277	19.8910
	1300	-	34.0148	26.9933	23.5805	21.4218	19.8856
	1400	-	34.0068	26.9864	23.5724	21.4139	19.8778
	1500	-	33.9951	26.9784	23.5641	21.4032	19.8668
Field Strength, F ($\times 10^{15}$ cm ⁻²)	1200	-	0.2127	0.3377	0.4425	0.5363	0.6223
	1300	-	0.2128	0.3379	0.4428	0.5366	0.6227
	1400	-	0.2129	0.3381	0.4431	0.5370	0.6232
	1500	-	0.2131	0.3383	0.4434	0.5375	0.6239

4.1.2 UV-Visible Absorption Study

In soda lime silicate glasses, the optical absorption measurements of glass samples were made at room temperature in the wavelength region 300–900 nm. The absorption bands are observed in the spectrum with peaks at 495 nm (Figure. 4.4). This absorption band is assigned to a single allowed ${}^5E_g \rightarrow {}^5T_{2g}$ transition which it arises from the manganic ions ($3d^4$ configuration) in octahedral symmetry [35]. However, it is known that the most common manganese ions found in oxide glasses are manganous and manganic ions. In these absorption spectra, it cannot observe the band for the manganous ions at room temperature. Because the manganous ions have a $3d^5$ configuration and all transitions are spin-forbidden and therefore give a low intensity compared with that of the manganic ions [25].

From Figure 4.1, the color of a manganese containing glass will be determined by the equilibrium between the purple – generating Mn^{3+} form and the essentially non-coloring Mn^{2+} form. In soda lime silicate glasses, the manganese ion gives a purple coloration due to the absorption spectrum shows a single broad band at 495 nm (Figure. 4.5) [24].

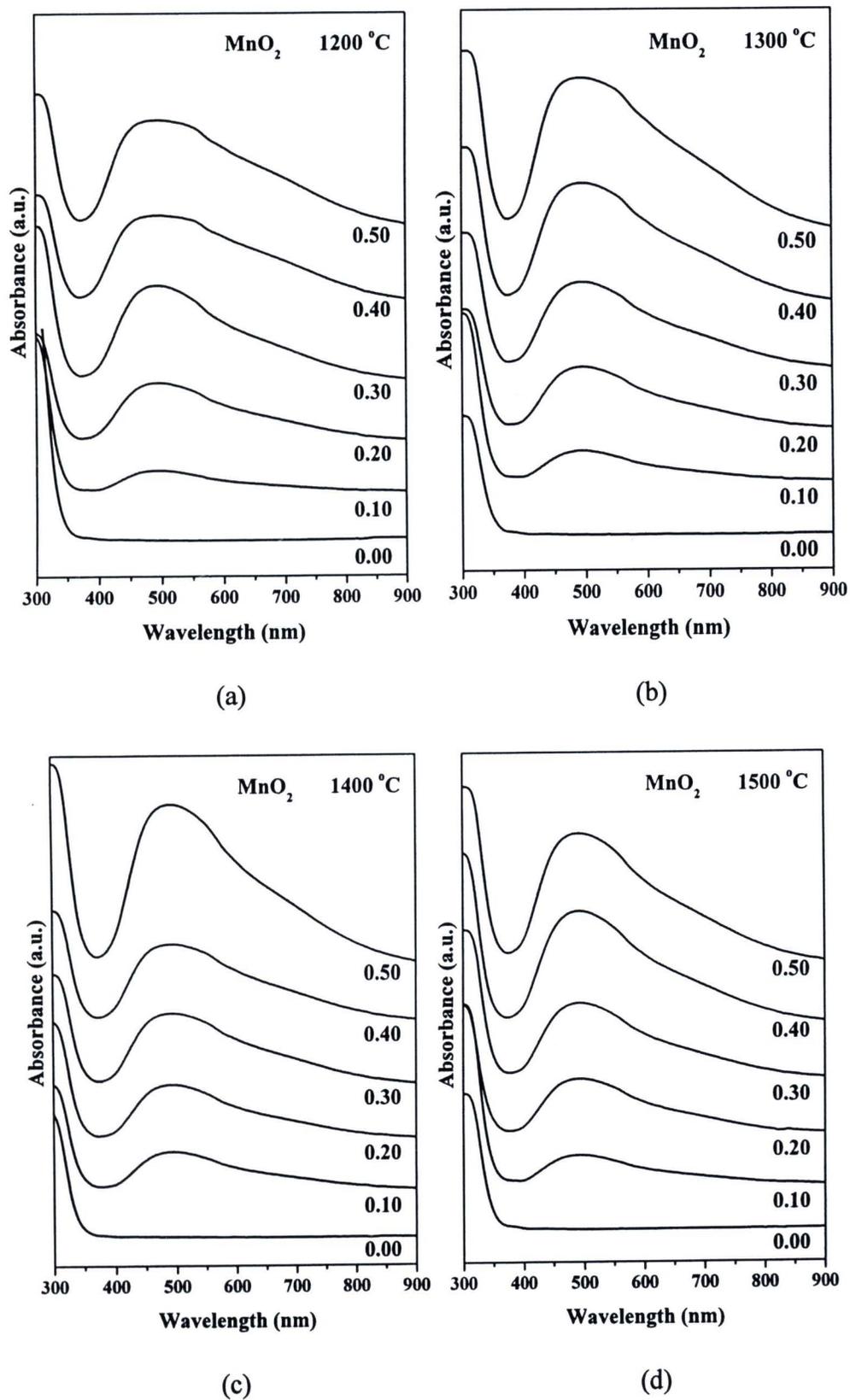


Figure 4.4 The absorption spectra of Mn³⁺ doped soda lime silicate glasses at melting temperature (a) 1200 °C, (b) 1300 °C, (c) 1400 °C and (d) 1500 °C.

4.1.3 CIE L* a* b* Color Index Measurements

The undoped glass sample was colorless while the MnO₂ doped glasses were color change. They have yellowish at low MnO₂ concentration and change to dark purple color in soda lime silicate glasses. The color changes were almost linearly. The brightness, L* or the reflective values were decrease when the concentration of MnO₂ doping increase (Table 4.3 – 4.6).

To determine the effect of MnO₂ concentration on the color of Mn³⁺ doped soda-lime silicate glasses, their transmittance (%T) within the range of 360 to 860 nm were measure by UV/VIS spectrophotometer with an integrating sphere accessory evaluated by COLOR software developed by Variant. The CIE L* a* b* color index of six samples of undoped and doped glasses were calculated by using the white color plate of BaSO₄ as a reference. These calculations were performed by the CIE 1931 standard colorimetric method with the illuminant D65. The changes in color of each sample are listed in Table 4.3 – 4.6 and the graphics of undoped and doped glass samples are shown in Figure 4.5 – 4.8.



Table 4.3 CIE L*a*b* color scale of Mn³⁺ doped in soda lime silicate glasses at 1200 °C.

MnO ₂ concentration (mol%)	Soda-lime-silicate		
	L*	a*	b*
0.00	84.9508	0.1239	1.2817
0.10	80.5530	6.0205	0.9354
0.20	59.1783	20.1357	-0.5367
0.30	52.3612	25.0491	-1.3202
0.40	31.9540	29.4208	-2.1864
0.50	35.2807	32.3377	-3.2660

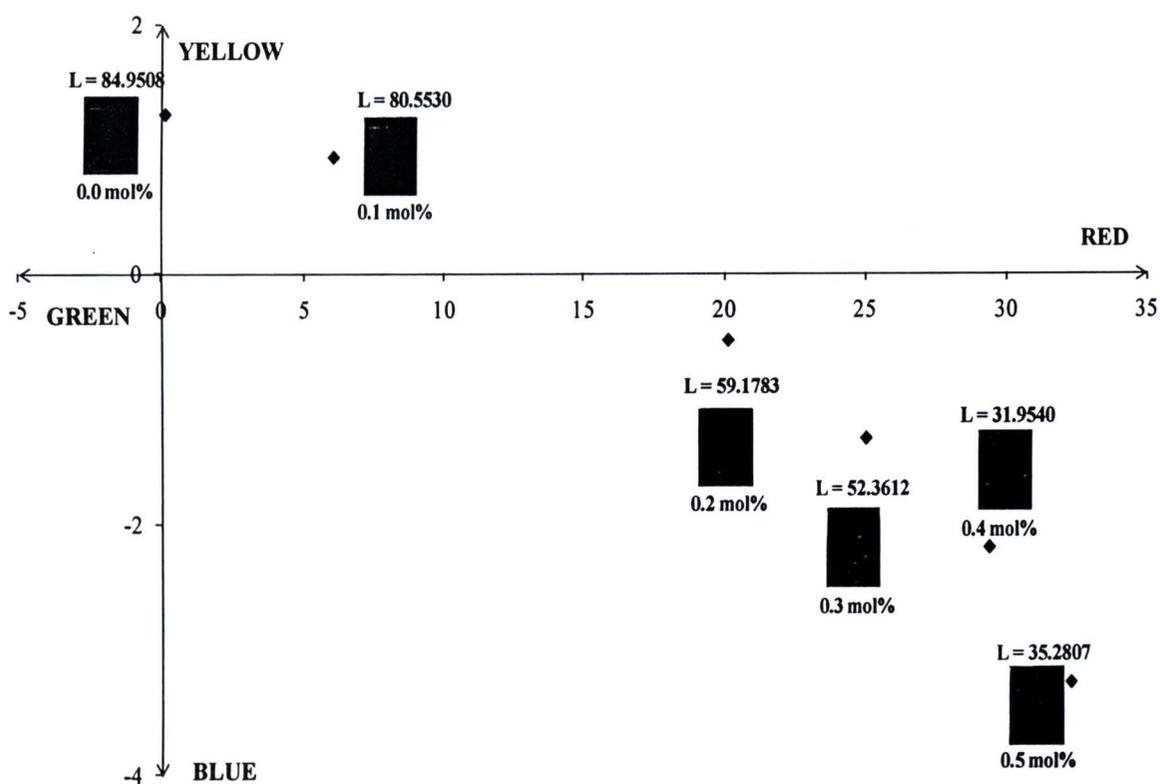


Figure 4.5 Variation of the color scale of glass samples with increasing MnO₂ concentration of 1200 °C.

Table 4.4 CIE $L^*a^*b^*$ color scale of Mn^{3+} doped in soda lime silicate glasses at $1300\text{ }^\circ\text{C}$.

MnO₂ concentration (mol%)	Soda-lime-silicate		
	L*	a*	b*
0.00	81.4291	-0.1095	1.8754
0.10	79.7981	7.9331	1.4460
0.20	60.5890	20.1082	-0.0479
0.30	55.7025	25.7377	-0.4226
0.40	40.7132	30.3125	-1.9214
0.50	33.5644	33.7171	-2.5124

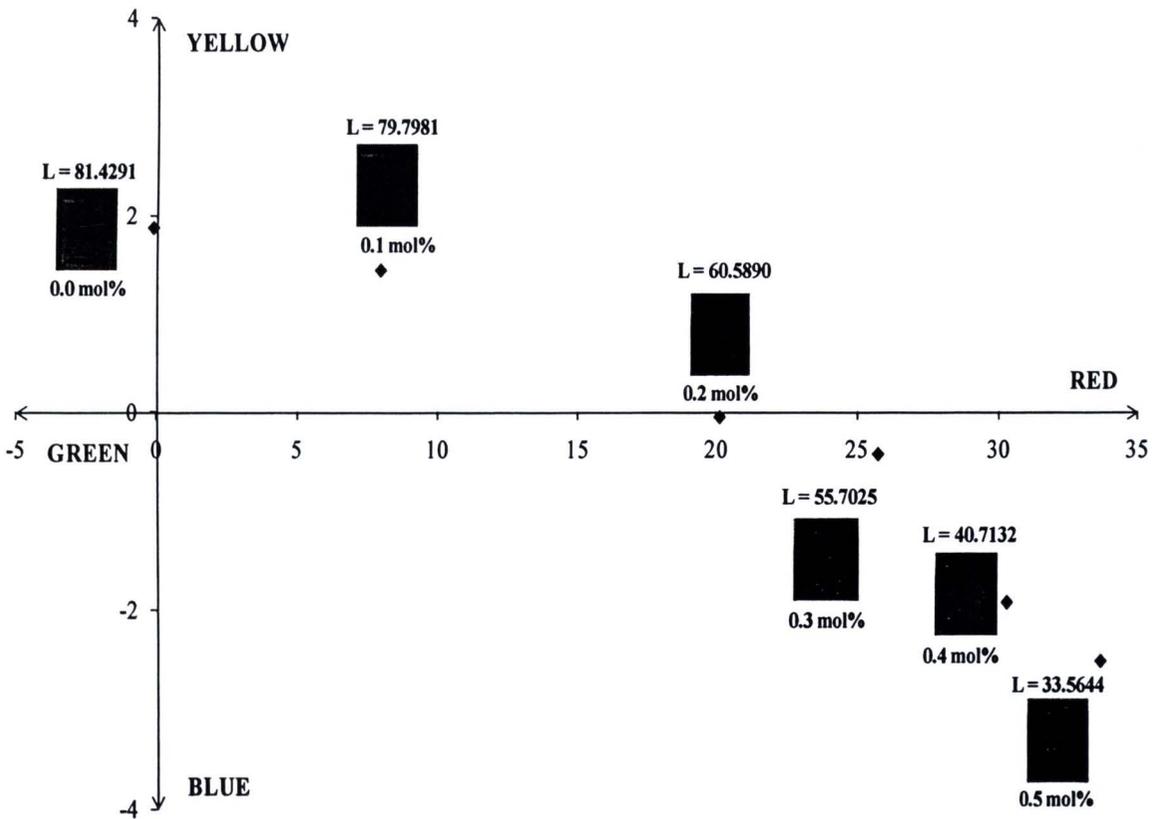


Figure 4.6 Variation of the color scale of glass samples with increasing MnO_2 concentration at $1300\text{ }^\circ\text{C}$.

Table 4.5 CIE $L^*a^*b^*$ color scale of Mn^{3+} doped in soda lime silicate glasses at 1400 °C.

MnO ₂ concentration (mol%)	Soda-lime-silicate		
	L*	a*	b*
0.00	81.5388	0.1784	2.6707
0.10	72.4716	13.3250	0.3106
0.20	66.9582	17.6721	0.7097
0.30	51.6975	25.0050	-0.5401
0.40	49.5418	26.7231	0.0129
0.50	37.8600	31.2111	-1.7912

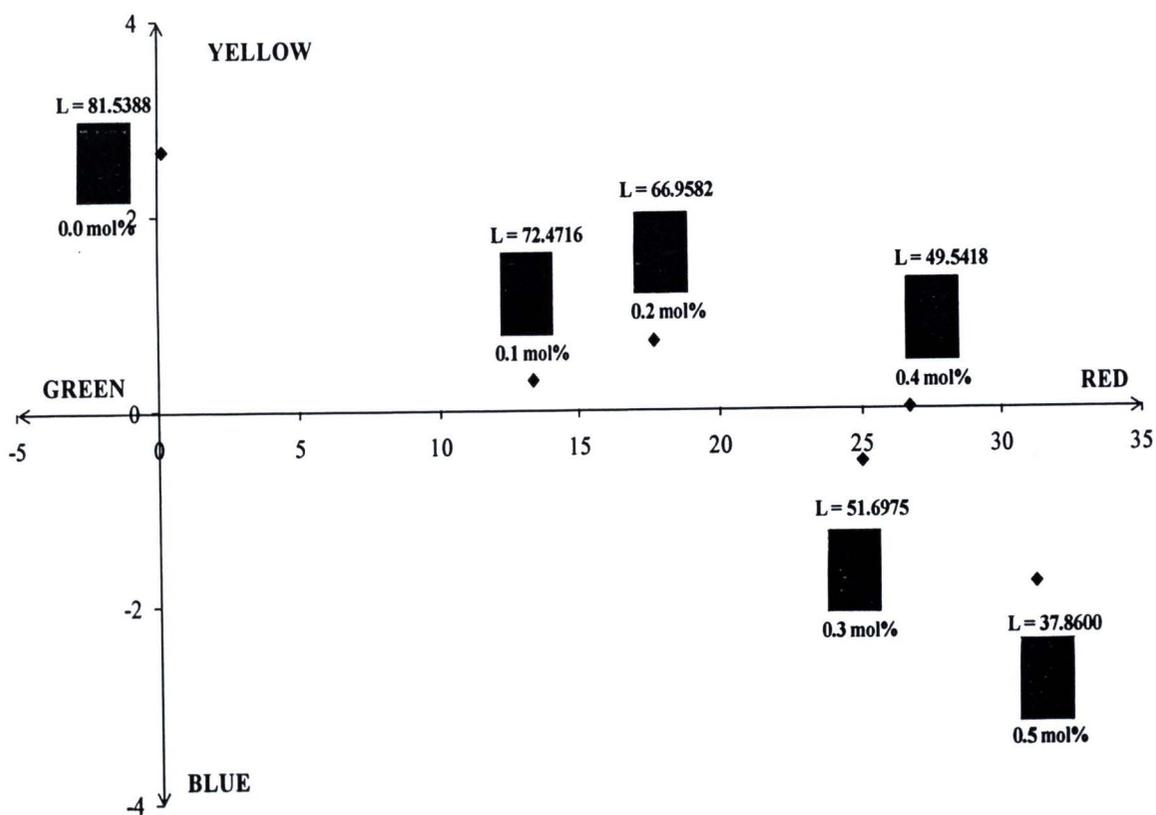


Figure 4.7 Variation of the color scale of glass samples with increasing MnO₂ concentration at 1400 °C.

Table 4.6 CIE L*a*b* color scale of Mn³⁺ doped in soda lime silicate glasses at 1500 °C.

MnO ₂ concentration (mol%)	Soda-lime-silicate		
	L*	a*	b*
0.00	88.9247	-0.1455	1.3944
0.10	79.7234	7.9651	1.0758
0.20	66.0706	16.6776	0.9830
0.30	61.3341	21.5880	0.0194
0.40	49.8286	26.6743	0.1481
0.50	42.3934	29.7320	-0.4715

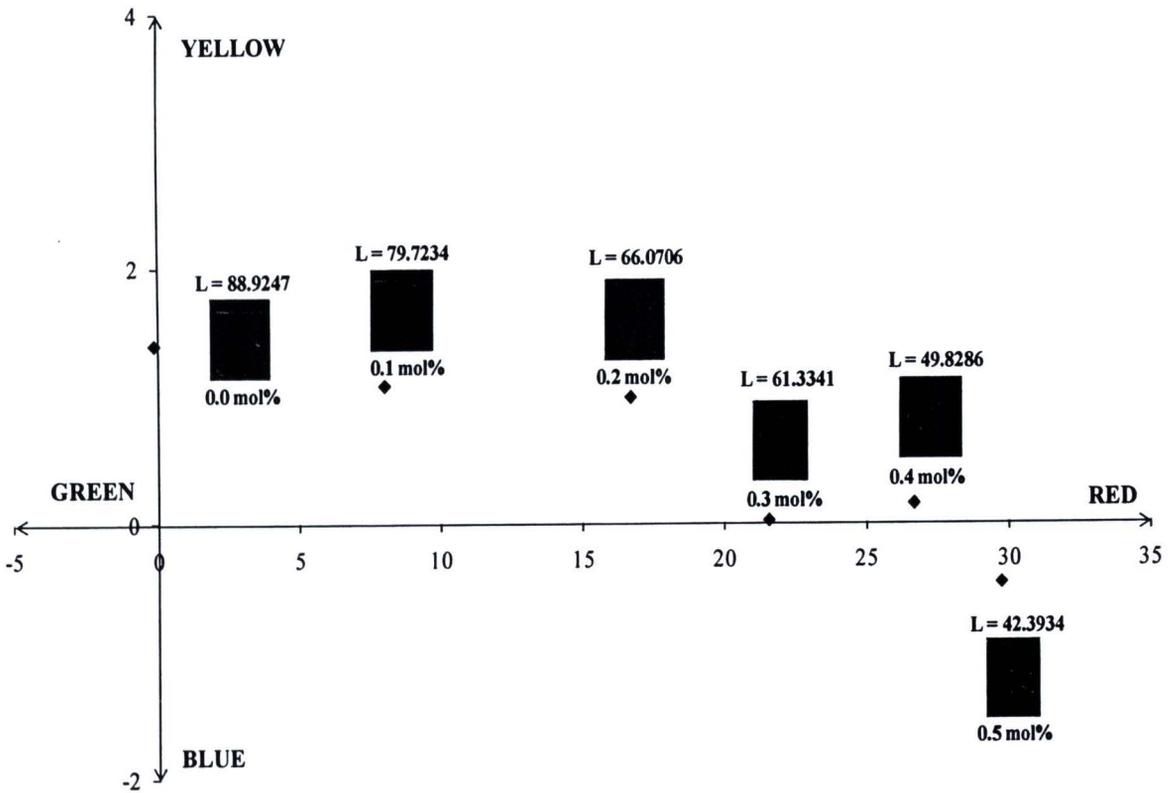


Figure 4.8 Variation of the color scale of glass samples with increasing MnO₂ concentration at 1500 °C.

4.1.4 Results on refractive index, molar polarizability and optical basicity

The refractive index (Figure 4.9) was measured by an Abbe refractometer, which permits the measurement of refractive indices up to 1.7 with an accuracy of 0.0002. It is observed that the refractive index increases with increasing MnO₂ concentration. According to the classical dielectric theory, the refractive index depend on density and on polarisabilities of the atom in a given materials. So, when density increased, the refractive index increased. These density results are corresponding with refractive index values [62].

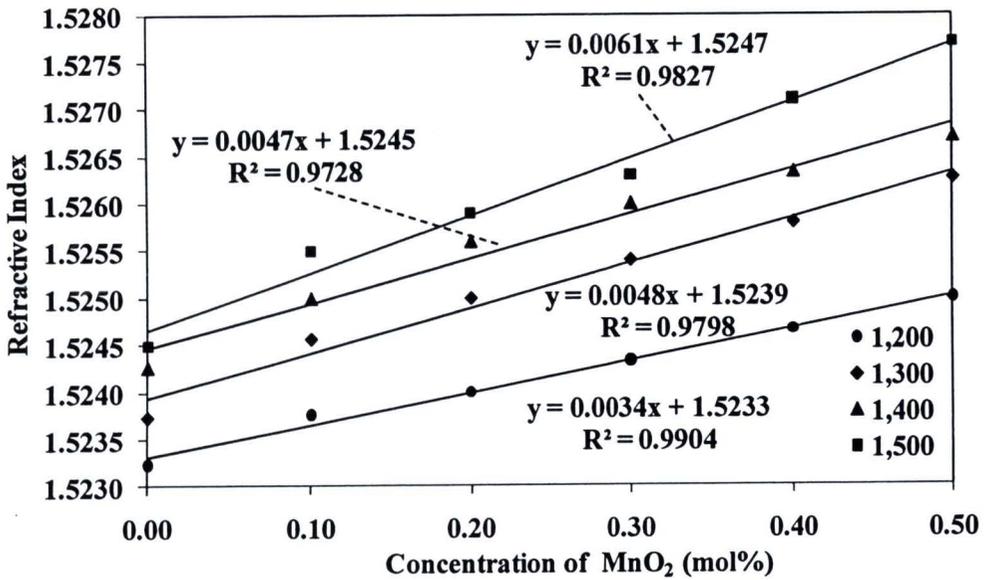


Figure 4.9 Variation of the refractive index with increasing melting temperature in soda lime silicate glasses.

The measured refractive indices are will be used for the determination of molar polarizability and optical basicity.

The dielectric constant (ϵ) was calculated from the refractive index of the glass using [4]:

$$\epsilon = n_o^2 \quad (4.5)$$

The optical dielectric constant ($\frac{P\partial t}{\partial P}$) was calculated from the measured refractive index at 589.3 nm using the formula [4]:

$$\frac{P\partial t}{\partial P} = \epsilon - 1 = n_o^2 - 1 \quad (4.6)$$

The molar refraction (R_m), derived by Volf, Lorentz and Lorenz [4] is given by Eq. (3.4). The molar refraction and the reflection loss depend on both the rates of change of

density and refractive index. In soda lime silicate glasses, the dielectric constant, optical dielectric constant, molar refraction and the reflection loss are increases with increasing MnO_2 concentration (Figure 4.10 – 4.13).

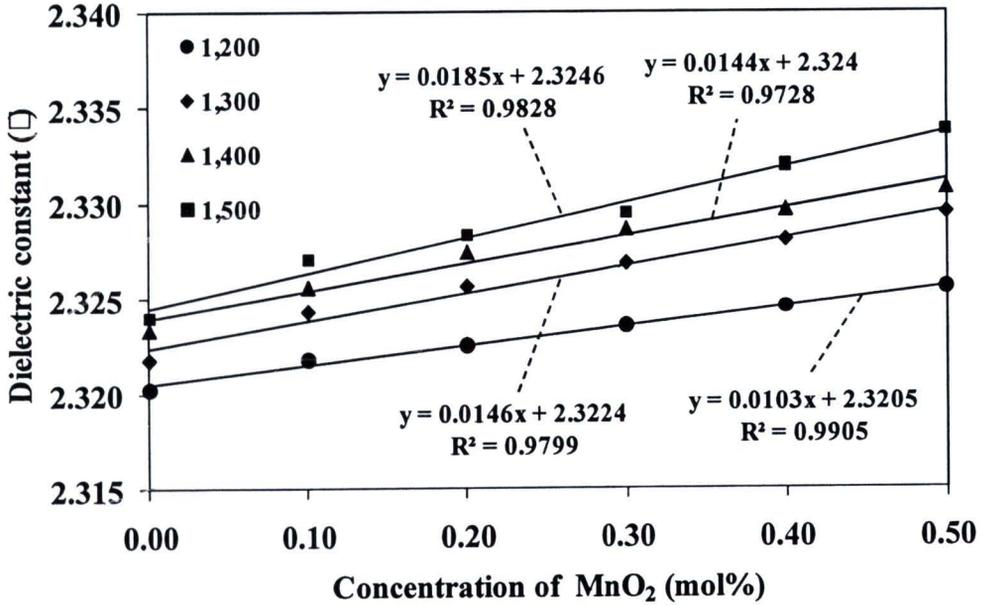


Figure 4.10 Variations of the dielectric constant with MnO_2 concentration in soda lime silicate glasses.

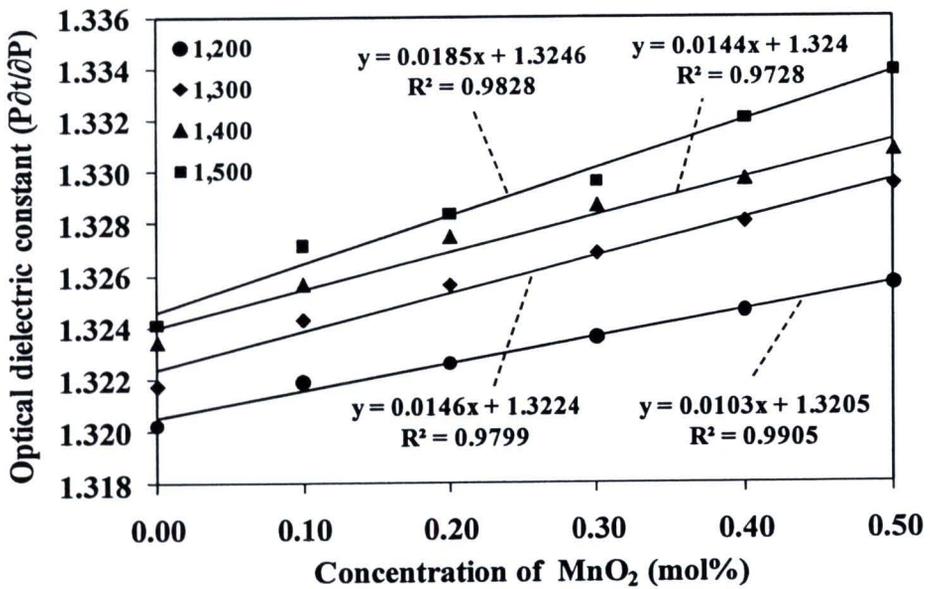


Figure 4.11 Variations of the optical dielectric constant with MnO_2 concentration in soda lime silicate glasses.

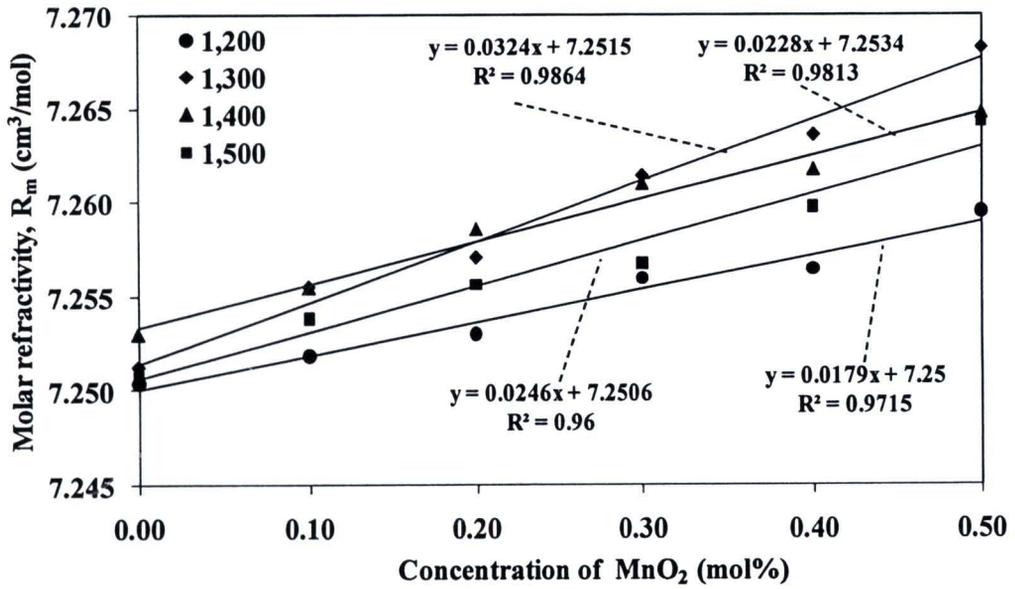


Figure 4.12 Variations of the molar refraction with MnO₂ concentration in soda lime silicate glasses.

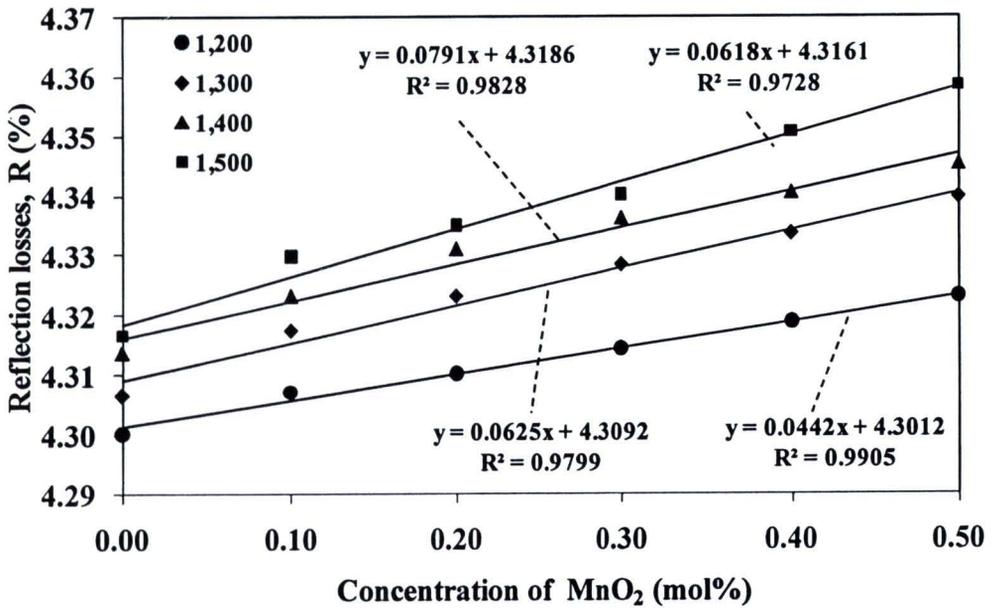


Figure 4.13 Variations of the reflection loss with MnO₂ concentration in soda lime silicate glasses.

The molar refraction is related to the structure of the glass and it is proportional to the molar polarizability of the material, α_m (in $\text{cm}^3 \times 10^{-24}$), which can be determined using Eq. (3.5). It is calculated that the molar polarizability increases with increasing MnO₂ concentration (Figure 4.14).

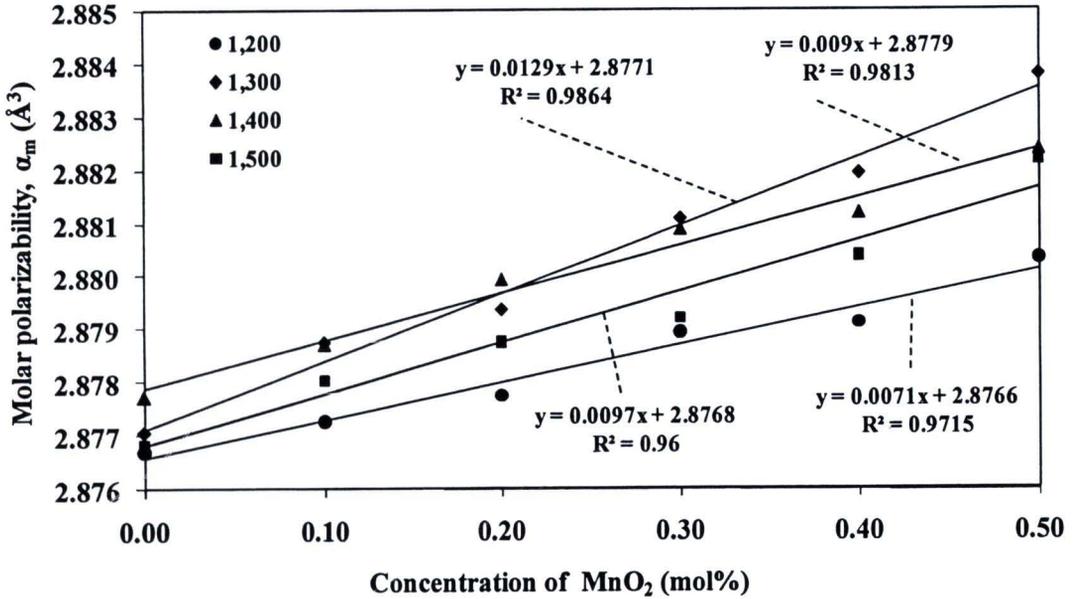


Figure 4.14 Variations of the molar polarizability with MnO₂ concentration in soda lime silicate glasses.

In addition, the molar polarizability have results are similar with density and refractive index of glass samples. The results show that the refractive index of the glass does not only depends on the density but also the electronic polarizability of the glass [7, 14, 59]. The polarizability of oxide ions was plotted as shown in Figure 4.15 - 4.18 as a function of density and refractive index at 1200, 1300, 1400 and 1500 °C, respectively.

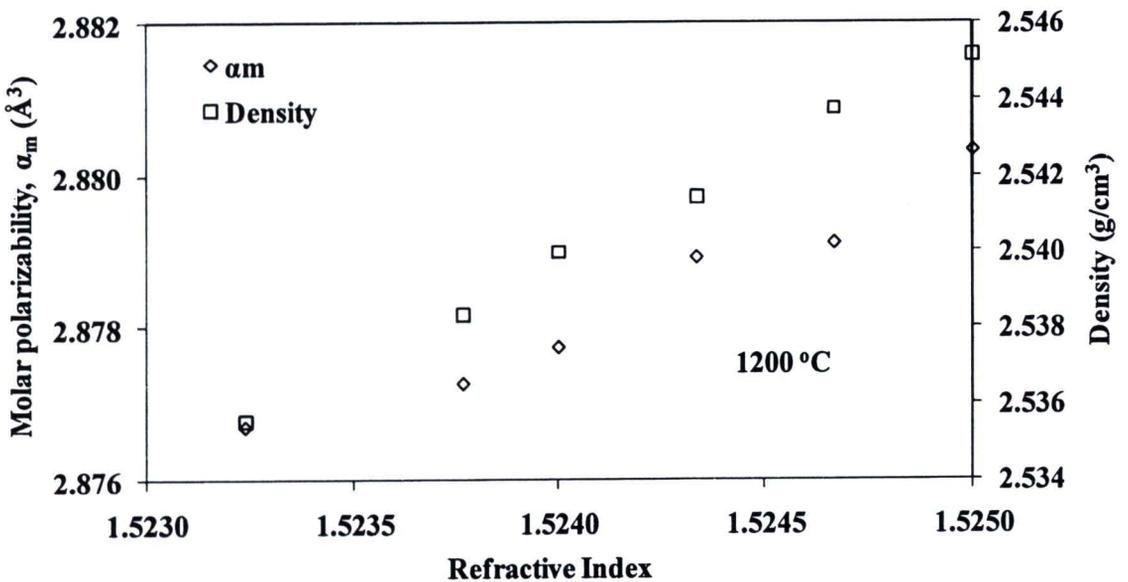


Figure 4.15 The relation between molar polarizability, density and refractive index in soda lime silicate glasses at 1200 °C.

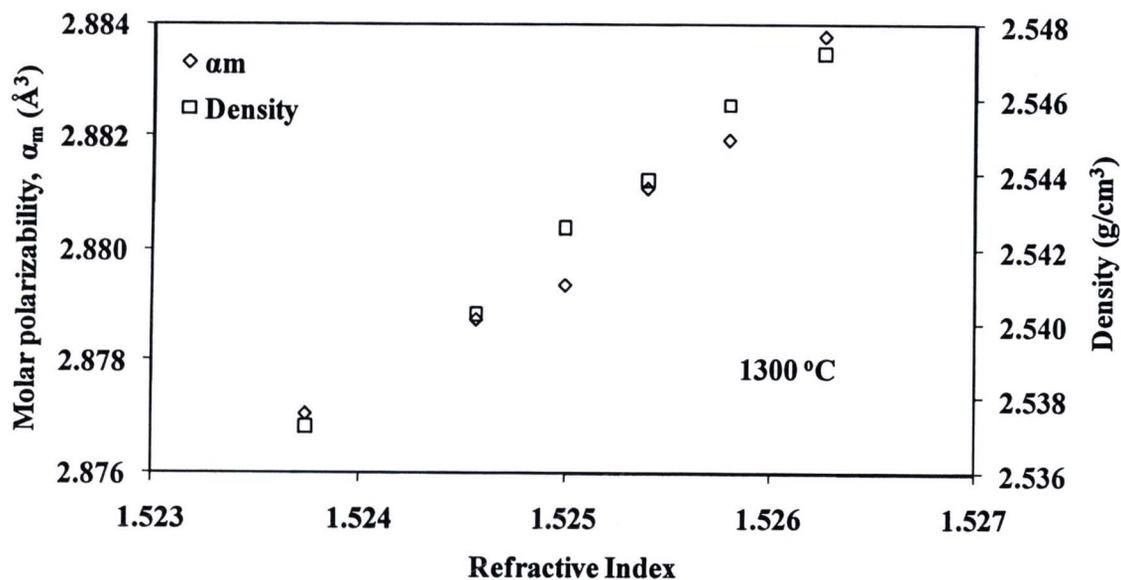


Figure 4.16 The relation between molar polarizability, density and refractive index in soda lime silicate glasses at 1300 °C.

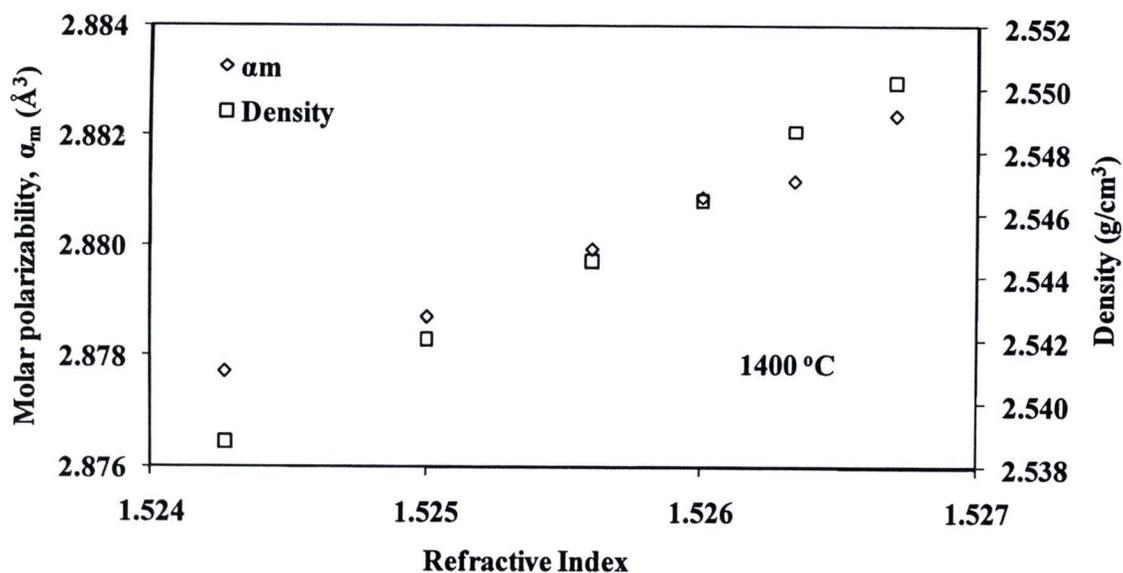


Figure 4.17 The relation between molar polarizability, density and refractive index in soda lime silicate glasses at 1400 °C.

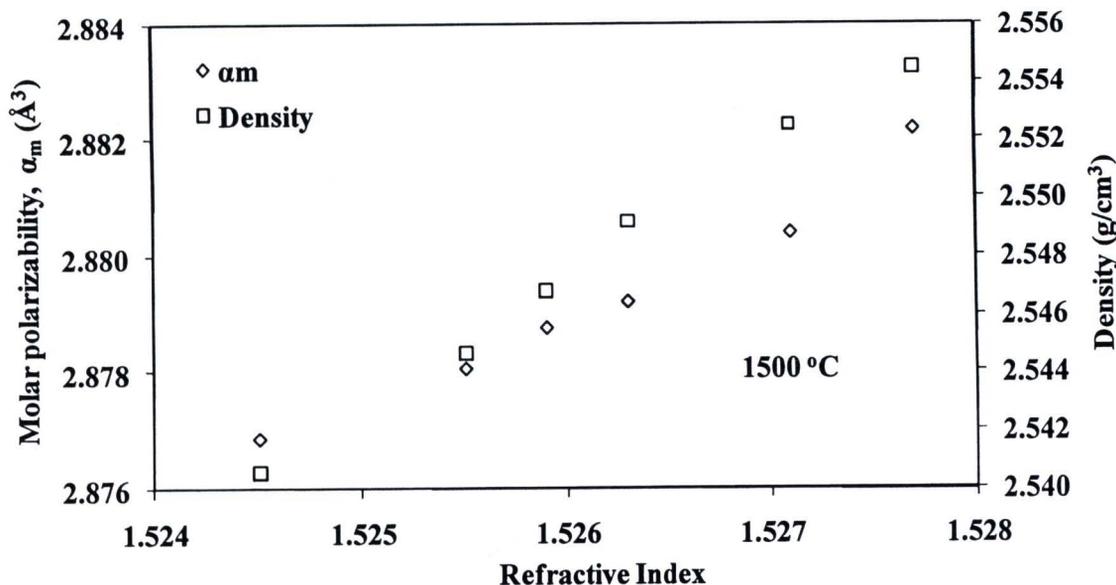


Figure 4.18 The relation between molar polarizability, density and refractive index in soda lime silicate glasses at 1500 °C.

The optical basicity of an oxide glass will reflect the ability of the glass to donate negative charge to the probe ion. Duffy and Ingram reported that the optical basicity can be predicted from the composition of the glass and the basicity moderating parameters of the various cations present. In multi-component oxide glasses, the theoretical basicity, A_{th} , was calculated based on the basis of the equation proposed by Duffy and Ingram [7] as given by

$$A_{th} = x_1 A_1 + x_2 A_2 + x_3 A_3 + \dots \quad (4.7)$$

where A_1 , A_2 and A_3 are basicities of the oxide components, and x_1 , x_2 and x_3 are their equivalent fractions (fraction of the total oxygen provided by the component oxide glass). In context of modification, therefore, we may note the following: modifier oxides should be more basic than the glass forming oxides. When modifier oxides are added to glass-forming oxides, the resulting modification reaction is like acid-base reaction in which the sites in the acidic (glass forming) oxide are approached by the oxide ion (of the modifier) in the order of decreasing acidities. It can be used to classify the covalent/ionic character of the glasses since an increasing A_{th} indicates decreasing covalence.

The optical basicity for the glass systems in present study was calculated using relation [7]:

$$A_{th} = x_{SiO_2} A(SiO_2) + x_{Na_2O} A(Na_2O) + x_{CaO} A(CaO) + x_{MnO_2} A(MnO_2) \quad (4.8)$$

where $A(SiO_2)$, $A(Na_2O)$, $A(CaO)$ and $A(MnO_2)$ are optical basicity values assigned to the constitute oxides, and x_{SiO_2} , x_{Na_2O} , x_{CaO} and x_{MnO_2} are the equivalent fractions of the different oxides, i.e., the proportion of oxide atoms they contribute to the glass system. Here the values of $A(SiO_2) = 0.50$, $A(Na_2O) = 1.15$, $A(CaO) = 1.0$ and $A(MnO_2)$

= 0.88 were obtained from the literature [57,59]. The values of basicity assigned to transition metals oxide (MnO_2) are greater than that of SiO_2 , but the proportion of MnO_2 oxide ion is very small as compared to those of alkaline earth oxides. However the overall result is an increase in the basicity are shown in Figure 4.19.

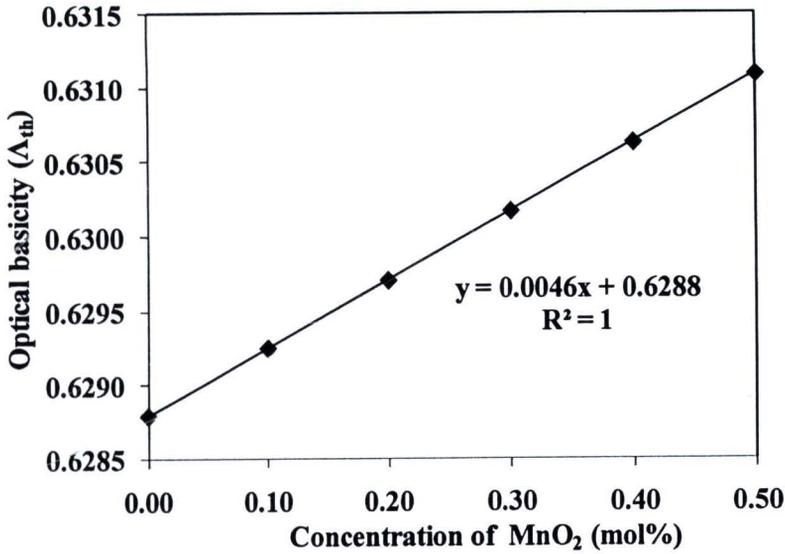


Figure 4.19 The optical basicity as a function of concentration of MnO_2 .

It is clearly observed from Figure 4.19 that the optical basicity increases when SiO_2 is replaced by one of the metal manganese oxide. The increase of optical basicity in this work means the higher ability of oxide ions to transfer electrons to the surrounding cations [34]. Since the polarizability of oxide ions is closely related to the optical basicity of oxide materials. The result shows that the increase of polarizability results in the increase of optical basicity and consequently the refractive index. A higher optical basicity of MnO_2 than that of SiO_2 , the doped glass is expected to possess higher refractive indices. The correlation between optical basicity and molar polarizability of melting temperature at 1200, 1300, 1400 and 1500 °C are shown in Figure 4.20-4.23, respectively. The figure shows almost a linear distribution of optical basicity with respect to molar polarizability. The results revealed that the optical basicity is correlated to molar polarizability.

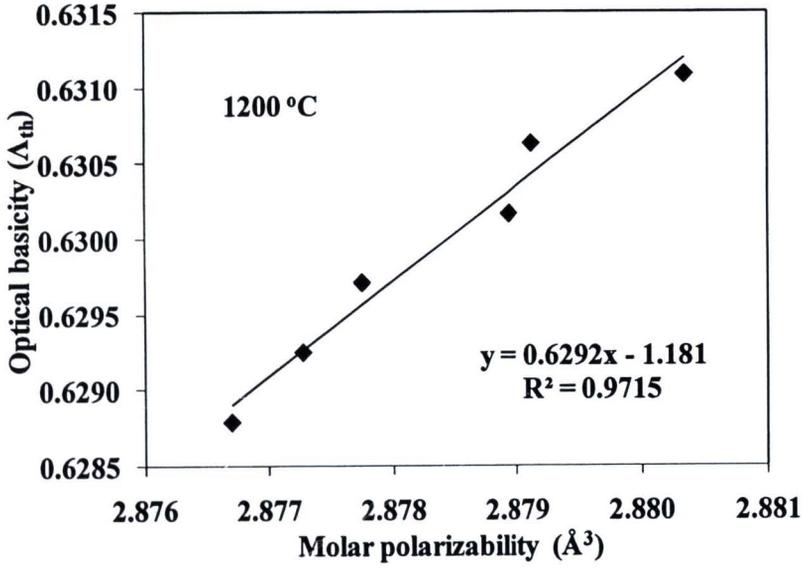


Figure 4.20 The correlation between optical basicity and molar polarizability at 1200 °C.

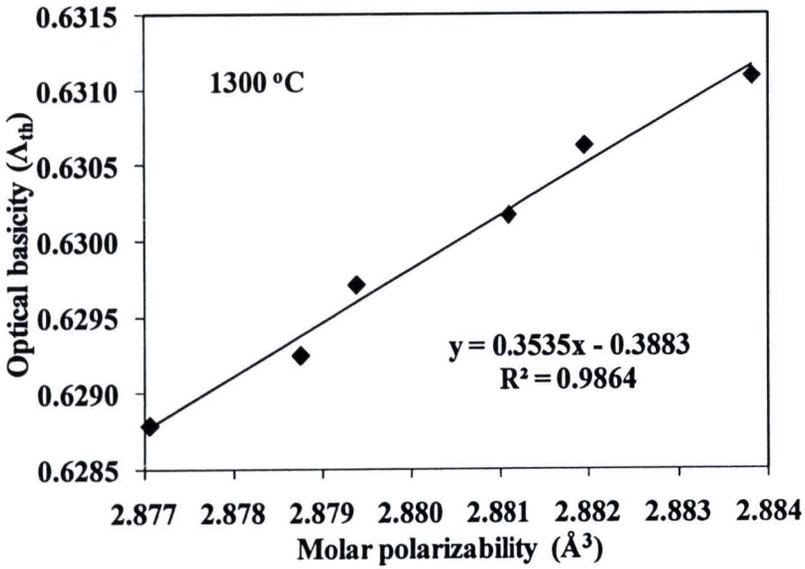


Figure 4.21 The correlation between optical basicity and molar polarizability at 1300 °C.

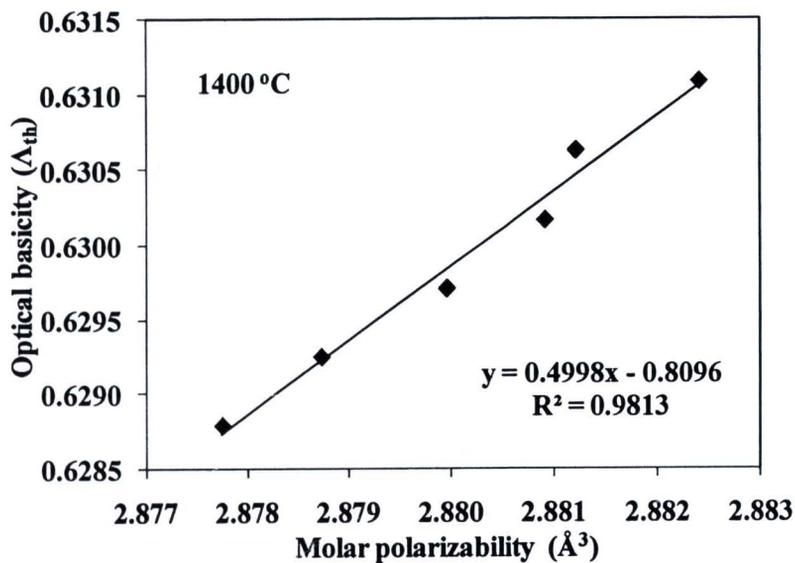


Figure 4.22 The correlation between optical basicity and molar polarizability at 1400 °C.

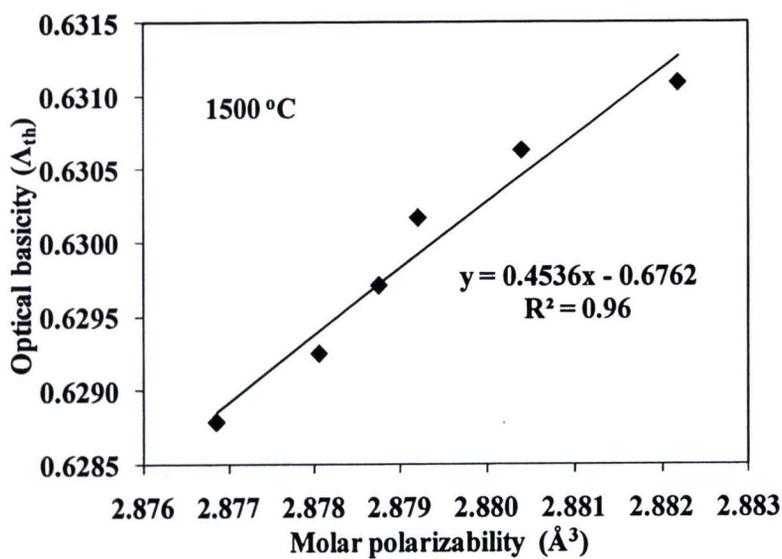


Figure 4.23 The correlation between optical basicity and molar polarizability at 1500 °C.

4.2 Effect of Melting Temperature

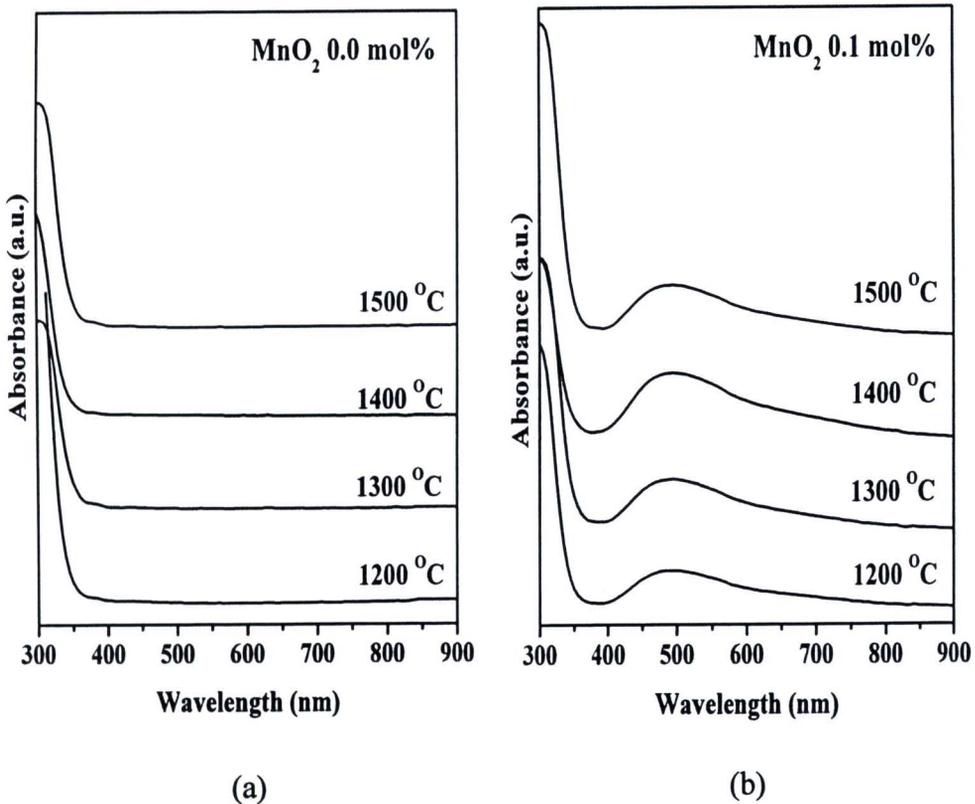
4.2.1 Density and Molar Volume

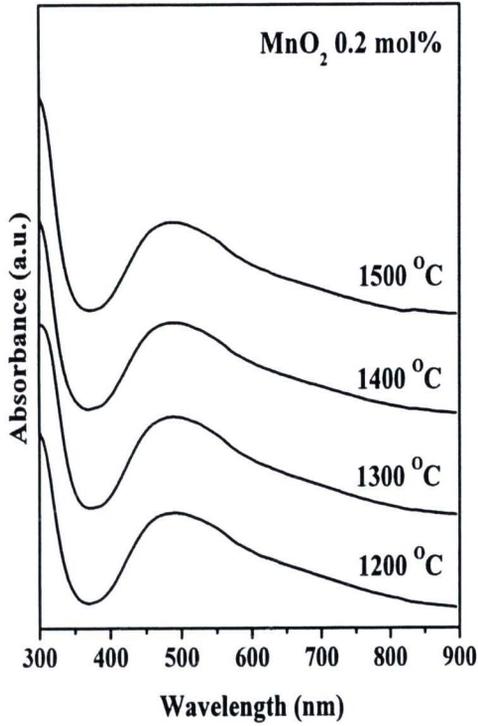
In the soda lime silicate glasses, the density of the glass samples as a function of the melting temperature and concentration of MnO_2 content in the glasses. It is observed that the density increases with increasing melting temperature is shown in Figure. 4.2.

The molar volume shows an opposite trend to the density for all glass samples. The molar volume decreases when increases melting temperature due to the decrease air bubble in glass structure which the density increases (Figure 4.3).

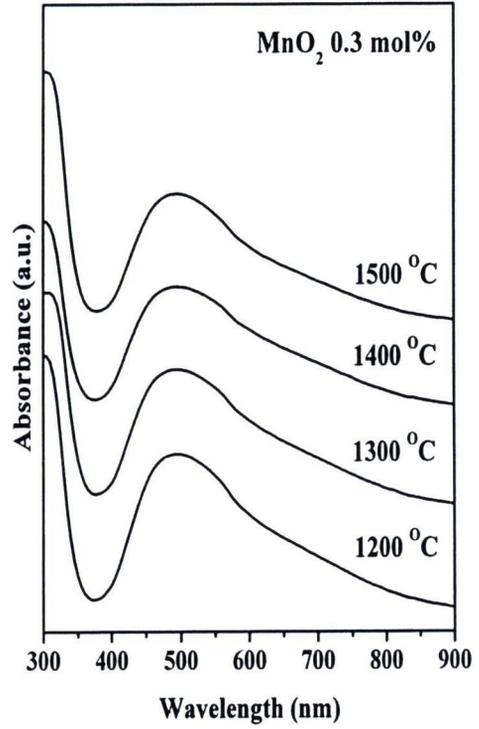
4.2.2 UV-Visible Absorption Study

Typical spectra of different MnO_2 concentration in soda lime silicate glasses at different melting temperature are shown in Figure 4.24. The absorption bands are observed in the spectrum with peaks at 495 nm. This absorption band is assigned to a single allowed ${}^5E_g \rightarrow {}^5T_{2g}$ transition which it arises from the manganic ions ($3d^4$ configuration) in octahedral symmetry.

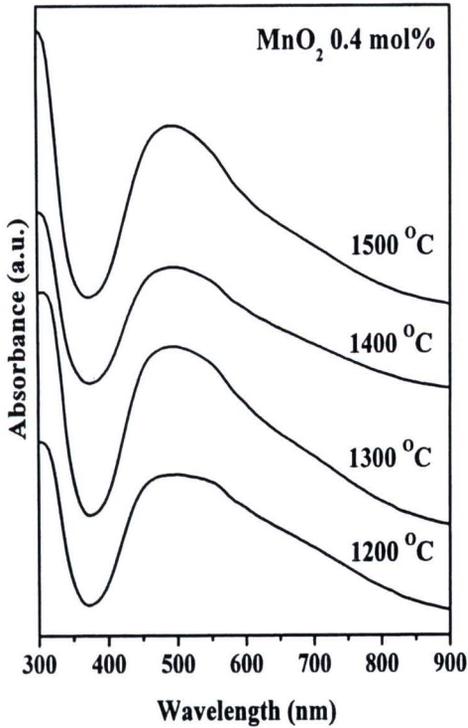




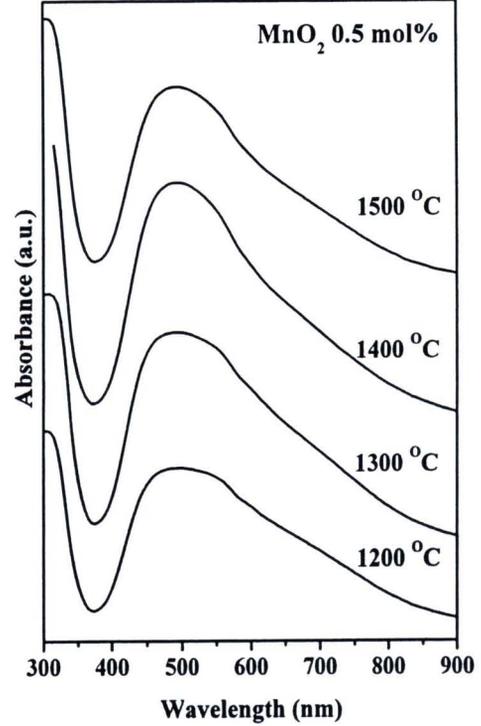
(c)



(d)



(e)

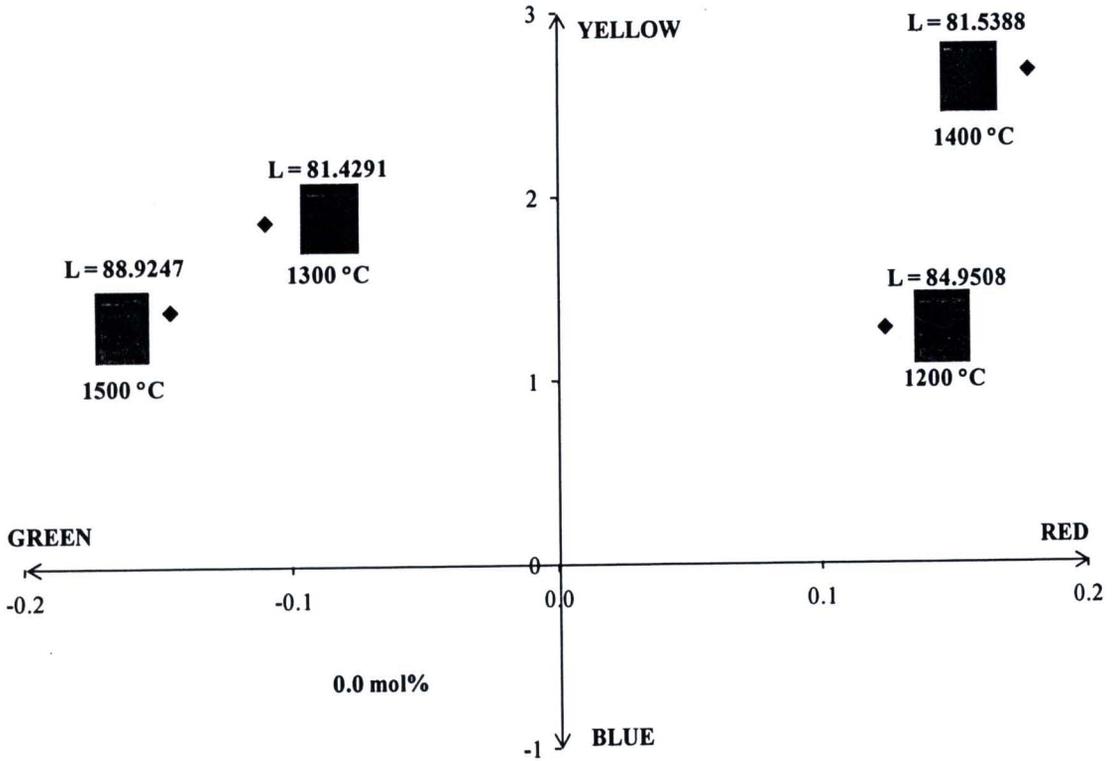


(f)

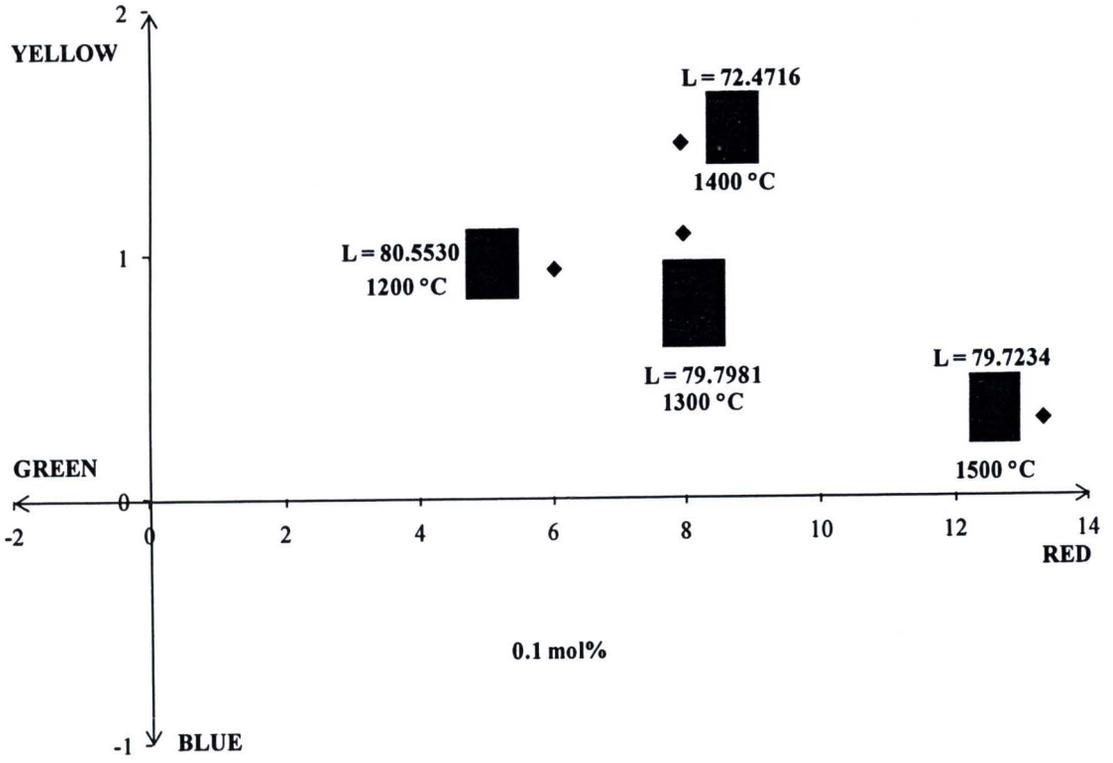
Figure 4.24 Variation of the optical absorption spectra of glass samples with increasing melting temperature a) 0.0 mol%, b) 0.1 mol%, c) 0.2 mol%, d) 0.3 mol%, e) 0.4 mol% and f) 0.5 mol%.

4.2.3 CIE L* a* b* Color Index Measurements

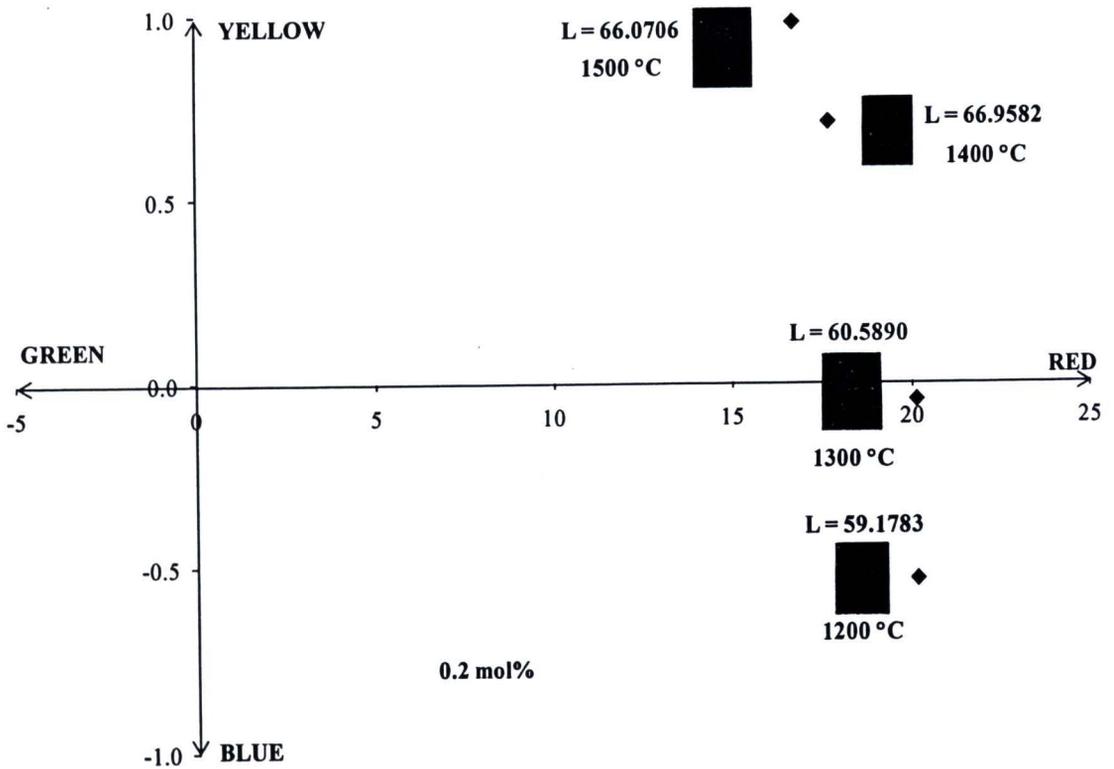
The relations between color of glass sample and melting temperature have not significant, which correspond to optical absorption spectra of glass samples every MnO_2 concentration as shows in Figure 4.25.



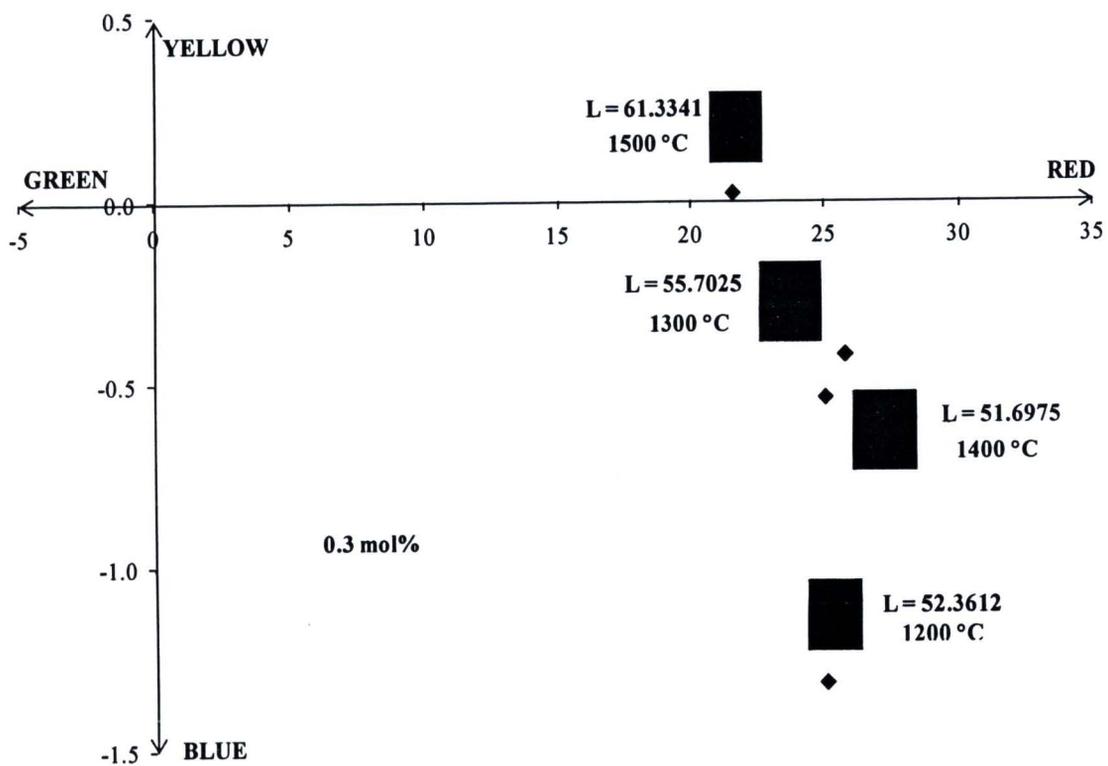
(a)



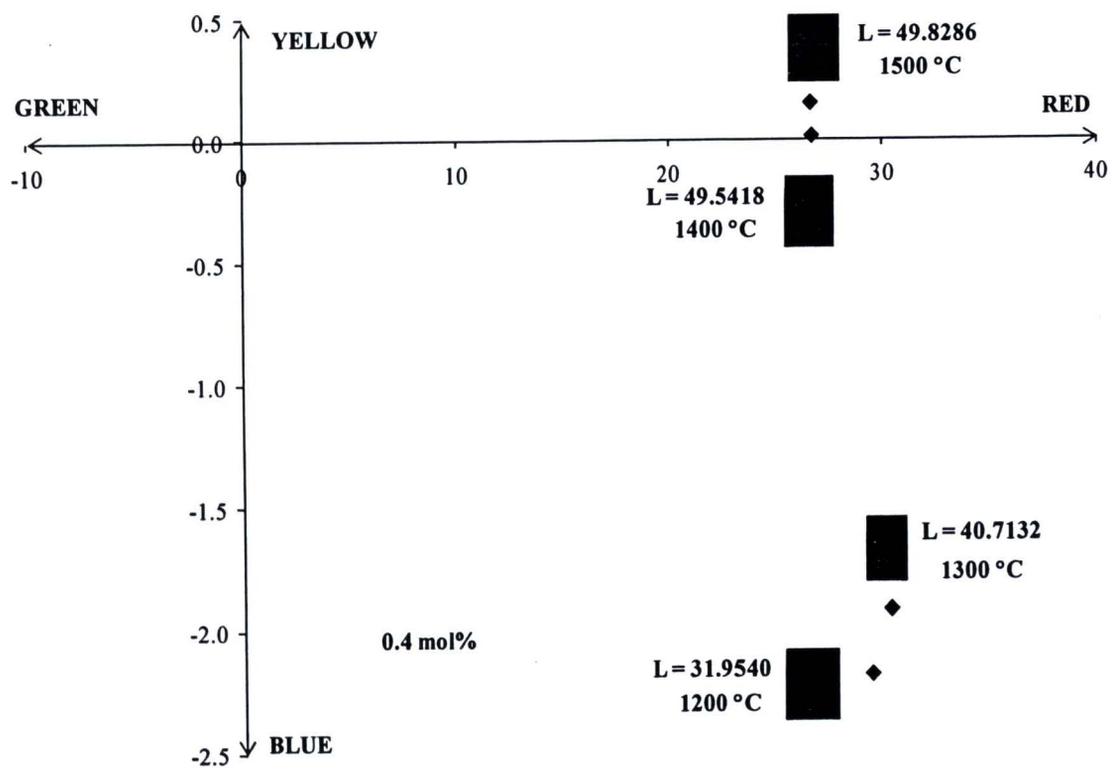
(b)



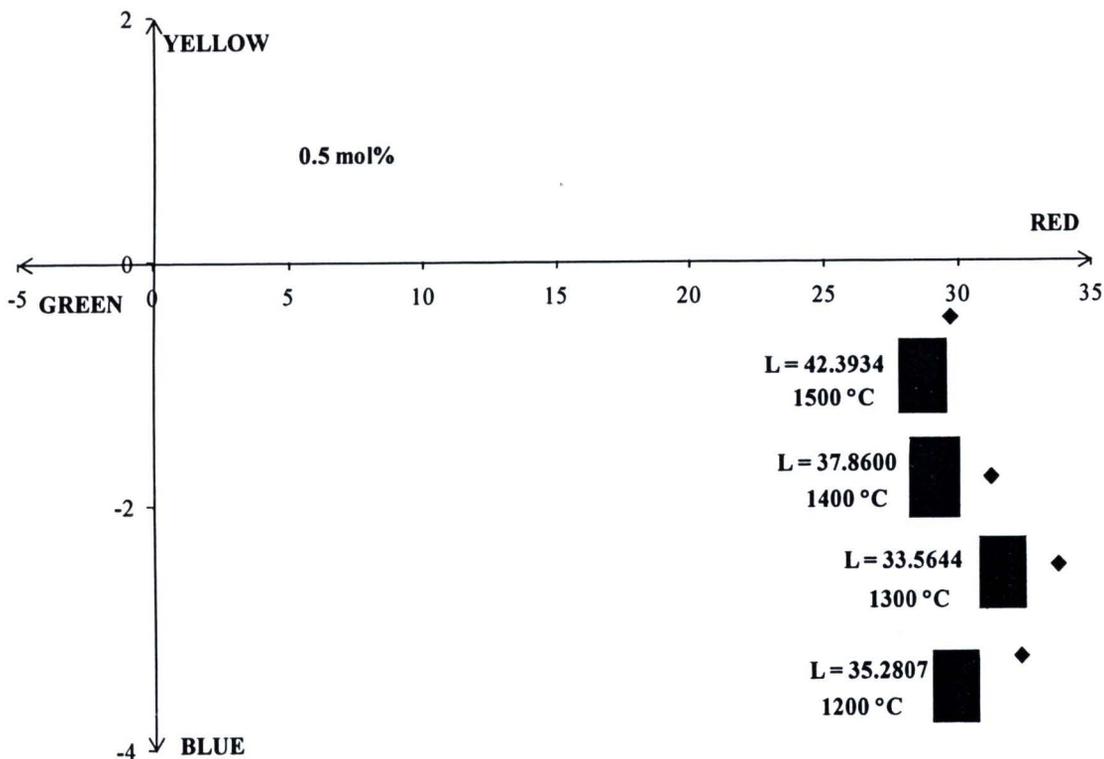
(c)



(d)



(e)



(f)

Figure 4.25 Variation of the color scale of glass samples with increasing melting temperature a) 0.0 mol%, b) 0.1 mol%, c) 0.2 mol%, d) 0.3 mol%, e) 0.4 mol% and f) 0.5 mol%.

4.2.4 Results on refractive index, molar polarizability and optical basicity

The refractive index depend on density and on polarisabilities of the atom in a given materials. Thus, the refractive index will be increased with increase of the melting temperature. That result from the decrease air bubble in glass structure which the density increases is shown in Figure. 4.9.

The molar refraction and the reflection loss depend on both the rates of change of density and refractive index. Thus, when the melting temperature increases, the dielectric constant, optical dielectric constant and the reflection loss are increasing but the relation between molar refraction and melting temperature have not significant (Figure 4.10 – 4.13).

The molar refraction is related to the structure of the glass and it is proportional to the molar polarizability of the material. It is calculated that the relation between molar polarizability and melting temperature have not significant (Figure 4.14).

The optical basicity can be calculated from Equation 4.9, which showed that the optical basicity is not dependent on the melting temperature.