Redox ratio and optical absorption of polyvalent ions in industrial glasses

W THIEMSORN*, K KEOWKAMNERD, P SUWANNATHADA, H HESSENKEMPER[†] and S PHANICHAPHANT

Faculty of Science, Chiang Mai University, Chiang Mai 50202, Thailand

[†]Institute of Ceramics, Glass and Cement, Freiberg University of Mining and Technology, Leipziger St. 28, 09596 Freiberg, Germany

MS received 22 September 2006; revised 13 July 2007

Abstract. The changes in glass structure and redox ratio, R (reduced ion to oxidized ion) of $\text{Mn}^{2+}\text{--Mn}^{3+}$, $\text{Cu}^+\text{--Cu}^{2+}$, $\text{Cr}^{3+}\text{--Cr}^{6+}$, $\text{Ni}^{2+}\text{--Ni}^{3+}$ and $\text{Co}^{2+}\text{--Co}^{3+}$ couples and optical absorption due to Mn^{3+} , Cu^{2+} , Cr^{3+} , Ni^{2+} and Co^{2+} ions in industrial soda–lime–silica glass were investigated as a function of Na_2O concentration in the range 11–19 mol%. With increasing Na_2O concentration in the experimental glasses, the basicity, expressed as calculated basicity, Λ_{cal} , increased. ^{29}Si NMR and X-ray diffraction were used to investigate the structural change in glasses. The NMR spectra showed high non-bridging oxygens (NBOs) when the basicity of glass was increased. The results were interpreted to be due to the tetrahedral networks; Q^4 species were depolymerized by replacing the bridging oxygens (BOs) with NBOs to Q^3 species. These results confirmed the shift of broadening peaks of XRD patterns. The redox reactions of the $\text{Mn}^{2+}\text{--Mn}^{3+}$, $\text{Cu}^+\text{--Cu}^{2+}$ and $\text{Cr}^{3+}\text{--Cr}^{6+}$ couples shifted more toward their oxidized ions due to the oxygen partial pressure, $p(\text{O}_2)$, during melting and the oxide ion activity, $a_{\text{O}^{2-}}$, increased with increasing glass basicity. These changes caused the redox ratio of these ion couples to decrease. The $\text{Ni}^{2+}\text{--Ni}^{3+}$ and $\text{Co}^{2+}\text{--Co}^{3+}$ couples were assumed to be present only in the Ni^{2+} and Co^{2+} ions in these glasses, respectively. The optical absorption bands due to Mn^{3+} , Cu^{2+} , Cr^{3+} , Ni^{2+} and Co^{2+} ions were also investigated. Their spectra occurred at constant wavelengths with different optical densities or intensities as a function of glass basicity. The increase in the intensities of the absorption bands of these absorbing ions, except for Cr^{3+} ion, at the maximum wavelength, depends not only on the ion concentration but also on the increase of polarizability of oxide (–II) species, $\alpha_{\text{oxide(–II)}}$, surrounding the ions. This value affected directly the extinction coefficients of the ions, ϵ_{ion} . The increase of ϵ_{ion} caused the colour of glasses appearing in high intensity. In the case of Cr^{3+} ion, the results were reversed such that the lower the concentration, the higher the intensities of colour.

Keywords. Calculated glass basicity; optical density; redox ratio; oxide ion activity; polarizability of oxide (–II) species.

1. Introduction

Studies of both glass structure and the incorporation of polyvalent elements into the glass are important for determining and controlling the colouring mechanism in different glass systems. For a given condition, the structure of glass depends directly on its composition where it can be represented in terms of glass basicity. Duffy (1996) defined a quantitative model to evaluate the basicity in glass. The optical or calculated basicity, Λ_{cal} , may also be calculated from the glass composition by summing terms for each cation in relation to the total number of oxygen ions. Values of Λ_{cal} are obtained using

$$\Lambda_{\text{cal}} = X_A \Lambda(A) + X_B \Lambda(B) + \dots, \quad (1)$$

where X_A , X_B , ... are the molar proportions contributed by the constituent oxides, A , B , ... to the total oxide (–II) content of the glass and $\Lambda(A)$, $\Lambda(B)$, ... are the optical basicity values of these individual oxides. Λ_{cal} is a useful index to determine the proportion of non-bridging oxygens (NBOs), oxide ion activity, $a_{\text{O}^{2-}}$ and polarizability as represented by the molar polarizability of oxide (–II) species, $\alpha_{\text{oxide(–II)}}$ (Duffy and Ingram 2002).

Manganese, copper, chromium, nickel and cobalt oxides are widely used for colour formation in glasses. When they are dissolved in a molten glass, the cations distribute into couple states such as $\text{Mn}^{2+}\text{--Mn}^{3+}$, $\text{Cu}^+\text{--Cu}^{2+}$, $\text{Cr}^{3+}\text{--Cr}^{6+}$, $\text{Ni}^{2+}\text{--Ni}^{3+}$ and $\text{Co}^{2+}\text{--Co}^{3+}$. The redox reaction of each redox couple can be investigated through the ratio of the reduced to oxidized state called as redox ratio, R . The

*Author for correspondence (worapong@chiangmai.ac.th)

change in redox depends on glass composition, melting temperature, imposed oxygen fugacity, the nature and concentration of redox couples and the presence of other redox couples (Schreiber 1986). At a given melting condition, the redox couple shifts towards the oxidized state when modifier ions or glass basicity are increased (Pyare and Nath 1982; Schreiber *et al* 1994).

When manganese oxide is dissolved in a molten glass, it transforms into Mn^{2+} and Mn^{3+} ions and generates purple colour due to Mn^{3+} ion. In soda–lime–silica glass, the Mn^{3+} band is centred around 500 nm in octahedral sites. Copper oxide distributes into Cu^+ and Cu^{2+} ions and produces sky blue to green colour due to Cu^{2+} ion which absorbed the visible spectrum at around 800 nm in octahedral sites in silicate glasses. Chromium in a silicate glass normally distributes into Cr^{3+} and Cr^{6+} ions. The Cr^{3+} ion generates green colour with three absorption peaks at around 635, 650 and 675 nm in octahedral sites. In the case of nickel and cobalt oxides dissolved in soda–lime–silica glass, which only occurs normally in the Ni^{2+} and Co^{2+} ions, produce deep brown and blue colours, respectively. The optical absorption of Ni^{2+} ion in the tetrahedral sites consists of four bands at around 450, 560, 630 and 930 nm. The absorption bands of Co^{2+} ions are centred at 540, 590 and 640 nm in tetrahedral sites (Bamford 1962, 1977).

In a particular silicate glass, the nature and intensity of colour is observed by using the following Lambert–Beer's equation (Knowles and Burgess 1984)

$$A_{\lambda_{\max}} = \varepsilon_{\text{ion}} \cdot c_{\text{ion}} \cdot d, \quad (2)$$

where $A_{\lambda_{\max}}$ is the absorbance of absorbing ion at its maximum wavelength, $\lambda_{\max}$, ε_{ion} the molar extinction coefficient of absorbing ion (l/mole.cm), c_{ion} the concentration of absorbing ion (mole/l) and d the thickness of the glass sample (cm).

According to (2), the $A_{\lambda_{\max}}/d$ is defined as the absorption density or intensity which depends directly on both the ion concentration (the redox ratio) and the extinction coefficient which are directly related to the structure of glass in a specific melting condition.

This work was designed to study the structural changes in glass, the redox ratio and the absorption colours due to polyvalent ions such as Mn^{2+} – Mn^{3+} , Cu^+ – Cu^{2+} , Cr^{3+} – Cr^{6+} , Ni^{2+} – Ni^{3+} and Co^{2+} – Co^{3+} couples over a variety of glass compositions, taking into account the effect of network modifier, Na_2O content, in industrial soda–lime–silica glass at a specific melting condition.

2. Experimental

The composition of soda–lime–silica base glass used in the present study was 66–74% SiO_2 , 11–19% Na_2O , 11% CaO , 3% MgO , 1% Al_2O_3 (in mol%) including polyvalent

metal oxides such as 0.35% MnO , 0.15% CuO , 0.07% Cr_2O_3 , 0.15% NiO and 0.04% CoO . Batches yielding 120 g of glass were made using analytical reagent grade Na_2CO_3 , CaCO_3 , Al_2O_3 , $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, MnO_2 , CuO , Cr_2O_3 , NiO and CoO together with calcined Gebaflo 10 s sand containing 0.012 wt% Fe_2O_3 . The homogenized mixtures were melted at an air atmosphere in alumina crucibles using an electric furnace held at 1450°C for 4 h. After melting, the glass was fritted by quenching in water. The dried frits were re-melted under the same conditions and were cast onto a steel mould in air at room temperature. The glasses were annealed in an electric furnace at 550°C for 15 min before cooling down to room temperature. The glass was later cut, ground and polished to dimensions required for spectroscopic analysis.

Oxygen partial pressure, $p(\text{O}_2)$, during the melting process was measured using a procedure described by Claes and Decelle (2001). Each glass compositions of 120 g were melted in alumina and heated to 1450°C in an electrical furnace. After the molten glasses were held for 5 h, electrodes were introduced into the melt in such a way that they were positioned in the middle of the sample.

The densities of the polished glass samples were determined by using Archimedes' principle at room temperature using a procedure described in the balance manual (Sartorius YDK 01, YDK 01-0D). Refractive indices of the polished glass samples were determined using Carl Zeiss DDR refractometer.

The compositions and the total MnO , CuO , Cr_2O_3 , NiO and CoO concentrations were determined using atomic emission spectroscopy with inductively coupled plasma, ARL Fisons 3410 ICP. The Mn^{3+} and Cu^{2+} ion concentrations were estimated by using their known molar extinction coefficients of soda–lime–silica glasses having similar basicity of glasses in the present work (Paul and Douglas 1995; Claes and Decelle 2001). The Cr^{3+} concentrations were determined using a procedure described by Matschat *et al* (2004).

^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were observed with a Bruker advance DPX-300 MHz NMR spectrometer operating at room temperature with 55 magic angle spinning and 300 MHz resonance frequency. All glass samples were powdered and held in ZrO_2 sample containers with 4 mm diameter. The isotropic chemical shifts (δ_{iso}) were referenced to 4,4-dimethyl 4-silapentane sodium sulfonate (DSS).

The X-ray diffraction (XRD) patterns of the glass samples were measured by using a X-ray diffractometer, Philips PW 3710 with Cu-K_α radiation in the range 10–70 of 2θ .

The UV–vis–NIR absorption spectra of the glass samples were recorded at room temperature using a double beam Perkin Elmer Spectrometer, Lambda 19, with an integration sphere detector and an optical range of 250–1500 nm. The optical observations used the transmission mode with a scan speed of 120 nm/min and a scan inter-

Table 1. Composition in mol%, density, refractive index, n_D and calculated glass basicity, Λ_{cal} , of the experimental glasses.

Sample code	Mean concentration of oxide in mol% ($\pm 5\%$)							Density (g/cm ³)	n_D	Λ_{cal}
	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	TiO ₂	K ₂ O			
1	75.30	10.24	10.83	3.03	0.43	0.02	0.01	2.481	1.518	0.557
2	73.23	10.96	10.82	3.03	1.78	0.02	0.01	2.497	1.524	0.562
3	71.03	12.83	10.80	3.02	2.14	0.02	0.01	2.521	1.527	0.571
4	69.27	14.64	10.83	3.03	2.06	0.02	0.01	2.536	1.528	0.579
5	67.11	16.29	10.81	3.03	2.59	0.02	0.01	2.552	1.530	0.587

Figure 1. The analysed Na₂O/SiO₂ ratios of the glasses compared with Na₂O/SiO₂ ratio of original compositions. The variation of chemical analysis is within $\pm 6\%$.

val of 0.5 nm using plain air as the reference. In order to calculate actual transmission values, the refraction loss of each glass sample was calculated from the refractive index. The corrected transmission values were subsequently converted into absorption (Bamford 1977).

3. Results and discussion

3.1 Compositions and calculated glass basicity, Λ_{cal}

Table 1 shows the concentration of oxide in mol% and other important properties such as density, refractive index, n_D and the calculated glass basicity, Λ_{cal} , of the glass samples. The chemical compositions in mol% of experimented glasses in which the SiO₂, Na₂O and Al₂O₃ contents varied with other components were studied. The concentrations in mol% of doped transition oxides were constant: MnO 0.35, CuO 0.14, Cr₂O₃ 0.07, NiO 0.14 and CoO 0.04. Note that the small amounts of TiO₂ and K₂O manifestation are primarily due to the impurities associated with the sand used. A slight increase in Al₂O₃ con-

tent of glass is caused by the dissolution of Al₂O₃ from the crucibles. The increased Al₂O₃ has a small effect on the basicity of glass because its optical basicity value is low at about 0.6 (Duffy and Ingram 2002). Moreover, study of effect of Al₂O₃ on redox equilibrium (Paul 1990) showed that the equilibrium changed little at low Al₂O₃ content while a maximum was seen at about 5 mol%. Thus the redox reactions of polyvalent elements are assumed to be independent on Al₂O₃ content.

Figure 1 indicates final Na₂O/SiO₂ ratios that are within $\pm 6\%$ of the batched Na₂O/SiO₂ ratio of each composition. However, it is assumed that the compositions of glasses are similar when compared with the original compositions.

The densities and refractive indices (n_D) increased with increasing Na₂O (10–16 mol%) content in the range 2.48–2.55 g/cm³ and 1.518–1.530, respectively. Λ_{cal} was obtained by using (1) as shown in table 1. The results show that the Λ_{cal} values were slightly elevated in the range 0.558–0.587 as the Na₂O content increased from 10–16 mol%. It can be argued that the proportion of non-bridging oxygens (NBOs) in glass structure as well as both the oxide ion activity, $a_{O^{2-}}$ and the molar polarizability of oxide (–II) species, $\alpha_{oxide(-II)}$, increased.

3.2 NMR studies

Examples of the ²⁹Si MAS NMR spectra from the base glasses are shown in figure 2. The spectrum of each glass contained only two isotropic peaks. One peak is centred constantly on the chemical shift, δ_{iso} at –108.5 ppm where it has been identified with silicate tetrahedral possessing four bridging oxygens (BOs) expressed in terms of Q^4 species. The other peak is varied in the range of δ_{iso} of –90.4 to –95.5 ppm for coordinating with three bridging oxygens, Q^3 species (Jones *et al* 2001). When glass basicity increased, the Q^4 peak decreased only in intensity at constant δ_{iso} whereas the Q^3 peak increased both in intensity and in δ_{iso} . The Q^3 chemical shift changes are the indicators to changes in structural parameters such as bond angles and bond lengths including with weaker ionic bonds between NBOs and the alkali cations (Zhang *et al* 1996; Jones *et al* 2001).

Table 2 lists the NBO/(BO + NBO) ratio, the δ_{iso} of Q^n species and the relative Q^n species for each composition.

Table 2. ^{29}Si MAS NMR parameters for the experimental soda–lime–silica glass with different basicities.

Λ_{cal}	NBO/(BO + NBO)	Relative Q^n species (%) ($\pm 5\%$)		Chemical shift, δ_{iso} of Q^n species (ppm)	
		Q^4	Q^3	Q^4	Q^3
0.557	0.274	32	68	-108.5	-95.5
0.562	0.282	30	70	-108.5	-93.2
0.570	0.303	24	76	-108.5	-92.5
0.578	0.330	17	83	-108.5	-91.8
0.586	0.353	12	88	-108.5	-90.4

Figure 2. ^{29}Si NMR spectra of the glass having different basicities. The spectra indicate the Q^4 and Q^3 species. The change in the chemical shift, δ_{iso} , for the Q^3 species was observed when the basicity of glass was increased.

The NBO/(BO + NBO) ratio was calculated from glass composition as described in the previous work (Jones *et al* 2001). The relative Q^n species were computed by using (3) as mentioned in previous study (Meneau *et al* 2001),

$$\frac{\text{NBO}}{\text{BO} + \text{NBO}} = \sum_{n=0}^4 \frac{8-2n}{8-n} w(Q^n), \quad (3)$$

where $w(Q^n)$ is the fraction of the respective Q species, n the number of bridging oxygens.

In all compositions, the Q^3 species were dominant and increased in the range 68–88% while that of Q^4 species decreased from 32–12% with increasing glass basicity. It can be seen that the silicate tetrahedral networks were depolymerized on replacing BOs with NBOs.

Figure 3. XRD patterns of the glass as a function of glass basicity. Fused silica glass was used as the reference.

3.3 XRD studies

Figure 3 shows the experimental XRD patterns of glass with different calculated basicities compared with a fused silica glass used as the reference. It was found that all glasses presented one broad band which could be assigned to completely amorphous phase. A fused silica has no sharp diffraction peak at 21.5 (2θ) angles corresponding to the peak of referred silica glass (Conradt 1997). This peak has been described with only presenting silicate tetrahedral, Q^4 species. However, a precise comparison between characteristics of this peak and experimental glass peaks has shown a shift to a large angle side and low intensity as well as the peaks expand as a function of increasing basicity. This change can be due to the fact that the Q^4 species decreased and changed to Q^3 species by replacing the BOs with NBOs, so this leads to the glass structure development due to high degree of depolymerization.

Table 3. The redox ion concentrations, redox ratio, R , oxygen partial pressure, $p(\text{O}_2)$ and the oxide ion activity, $a_{\text{O}^{2-}}$ of experimental soda–lime–silica glass with different basicities.

Sample code	Λ_{cal}	$a_{\text{O}^{2-}} (\times 10^{-9})$	$\log p(\text{O}_2)$ (Pa)	Mean concentration of redox ion (mol/l)			Redox ratio (R)
				Total ion	Reduced ion	Oxidized ion	
Doping with Mn							
Mn1	0.557	3.47	3.72	0.137	0.129	0.008	16.13
Mn2	0.562	4.50	3.75	0.137	0.126	0.011	11.45
Mn3	0.571	6.23	3.83	0.137	0.126	0.011	11.45
Mn4	0.579	8.16	3.91	0.137	0.126	0.011	11.45
Mn5	0.587	10.80	3.99	0.137	0.125	0.012	10.42
Doping with Cu							
Cu1	0.557	3.47	3.72	0.059	0.013	0.046	0.28
Cu2	0.562	4.50	3.75	0.059	0.013	0.046	0.28
Cu3	0.571	6.23	3.83	0.059	0.013	0.046	0.28
Cu4	0.579	8.16	3.91	0.059	0.011	0.048	0.23
Cu5	0.587	10.80	3.99	0.059	0.010	0.049	0.20
Doping with Cr							
Cr1	0.557	3.47	3.72	0.057	0.052	0.003	17.33
Cr2	0.562	4.50	3.75	0.057	0.049	0.008	6.13
Cr3	0.571	6.23	3.83	0.057	0.044	0.013	3.38
Cr4	0.579	8.16	3.91	0.057	0.042	0.015	2.80
Cr5	0.587	10.80	3.99	0.057	0.040	0.017	2.35
Doping with Ni							
Ni1	0.557	3.47	3.72	0.062	0.062	Absent	—
Ni2	0.562	4.50	3.75	0.062	0.062	Absent	—
Ni3	0.571	6.23	3.83	0.062	0.062	Absent	—
Ni4	0.579	8.16	3.91	0.062	0.062	Absent	—
Ni5	0.587	10.80	3.99	0.062	0.062	Absent	—
Doping with Co							
Co1	0.557	3.47	3.72	0.016	0.016	Absent	—
Co2	0.562	4.50	3.75	0.016	0.016	Absent	—
Co3	0.571	6.23	3.83	0.016	0.016	Absent	—
Co4	0.579	8.16	3.91	0.016	0.016	Absent	—
Co5	0.587	10.80	3.99	0.016	0.016	Absent	—

3.4 Investigation of redox ratio, R

Table 3 summarizes the concentrations of each redox couple and the redox ratio, R (reduced to oxidized state) in the experimental glass with different basicities. The results show that manganese, copper and chromium oxides dissolved and appeared in reduced and oxidized states as Mn^{2+} – Mn^{3+} , Cu^+ – Cu^{2+} and Cr^{3+} – Cr^{6+} , respectively in the glasses. Nickel and cobalt oxides were dissolved in glasses, usually as only Ni^{2+} and Co^{2+} states. Values of R decreased for manganese, copper and chromium couples at high glass basicity. It means that the Mn^{2+} – Mn^{3+} , Cu^+ – Cu^{2+} and Cr^{3+} – Cr^{6+} redox reactions shifted more toward their oxidized states with increasing glass basicity. Similar results from previous works were reported (Schreiber *et al* 1994; Müller–Simon 1996). In order to explain the effect of glass basicity on redox ratio at a given melting condition, the redox reaction can be expressed as

where x is the number of oxygens associated with the oxidized redox ion in the melt to form an oxo-anion, n the number of electrons involved in the reduction. In order to apply (4), it must be realized that $\text{MO}_{x(\text{melt})}^{(m-2x)}$ may only be used instead of the value of x which implies the relative number of oxygen associated with the oxidized ion in the melt glass with respect to the reduced ion. The activity coefficients of redox ions are not available (Schreiber 1986; Müller–Simon 1996). Therefore, the change of redox ratio in (4) depends on oxygen partial pressure, $p(\text{O}_2)$, during melting and oxide ion activity, $a_{\text{O}^{2-}}$.

The oxygen partial pressure in this study was expressed in terms of $\log p(\text{O}_2)$ as shown in table 3. The values of $\log p(\text{O}_2)$ increased in the range 3.72–3.99 Pa with increasing glass basicity. The reason for this result is that

the Mn^{2+} , Cu^+ and Cr^{3+} ions are oxidized during melting by dissolved oxygens in the glass melt causing the Mn^{3+} , Cu^{2+} and Cr^{6+} ions to increase. Another reason of redox change is due to the change of oxide ion activity, $a_{\text{O}^{2-}}$, with increasing concentration of Na_2O in glass. According to investigation on the $a_{\text{O}^{2-}}$, in the present work, it was calculated as described by Krämer (1991). The $a_{\text{O}^{2-}}$ increased between 3.40 and 11.30×10^{-9} when basicity of glass was increased as shown in table 3. It means that the

coordinating oxide species, especially on NBOs, have a greater negative charge and donate their charge clouds to redox ions until the ions become unstable. The unstable ions raise a tendency to loose the excess negative charges by going into oxidized states, as a result there is an increase in the Mn^{3+} , Cu^{2+} and Cr^{6+} ions concentration.

3.5 Optical absorption and colouration

Figure 4 shows the absorption spectra of the doped manganese with different glass basicities. The spectra due to Mn^{3+} ion had a unique and broad asymmetric band centred at about 480 nm in octahedral sites. With increasing glass basicity, the absorption density of Mn^{3+} band ($A/d_{\text{Mn}^{3+}}$ in cm^{-1}) computed by using (2) was increased at almost constant position. Similar results were found in silicate glasses with different alkali contents (Singh *et al* 2004). The increase of $A/d_{\text{Mn}^{3+}}$ caused the colour intensity of the experimental glasses to change clearly from pale purple to dark purple.

Figure 5 shows the absorption spectra of glass containing copper with different glass basicities. In general, the main broad band of Cu^{2+} ion was at 755 nm and near 800 nm in an octahedral site (Singh *et al* 2004). The figure shows raising of $A/d_{\text{Cu}^{2+}}$ due to the oxidation of some Cu^+ ions to Cu^{2+} ions. The intensity of blue colour slightly increased after increasing the basicity of glass.

In the case of glass containing chromium, the results are presented in figure 6. The absorption spectra of the green glasses showed three absorption bands due to Cr^{3+} ion at 640, 655 and 690 nm in an octahedral site. The

Figure 4. Optical absorption spectra of Mn^{3+} ion in glass having varying basicities. The λ_{max} of Mn^{3+} ion = 480 nm.

Figure 5. Optical absorption spectra of Cu^{2+} ion in glass having varying basicities. The λ_{max} of Cu^{2+} ion = 755 nm.

Figure 6. Optical absorption spectra of Cr^{3+} ion in glass having varying basicities. The λ_{max} of Cr^{3+} ion = 655 nm.

$A/d_{Cr^{3+}}$ at 655 nm slightly decreased because the Cr^{3+} ions were oxidized and shifted to the Cr^{6+} ions causing the intensity of green colour to decrease with increasing glass basicity.

For glass doped with nickel, consistently four absorption bands due to Ni^{2+} ion were observed at 450, 550, 630 and 980 nm in tetrahedral sites, as shown in figure 7. All the observed glasses containing nickel were deep brown. Glasses containing cobalt were dark blue. There were no variations in the position of bands with the change in their glass basicity as shown in figure 8. The spectra of Co^{2+} ions consist of three absorption bands at 525, 595 and 650 nm in tetrahedral site, corresponding to the one reported earlier (Bamford 1962). As an increment of glass basicity, the Ni^{2+} and Co^{2+} ion concentrations were constant and assumed to be only one state in the experimental glasses. The results, however, showed the $A/d_{Ni^{2+}}$ and $A/d_{Co^{2+}}$ values to increase when the basicity was increased from 0.557–0.587. This indicates that the A/d of Ni^{2+} and Co^{2+} ions are not affected by their concentration but depend directly on glass structure.

The wavelength maxima of Mn^{3+} , Cu^{2+} , Cr^{3+} , Ni^{2+} and Co^{2+} ion absorptions coordinated by NBOs were constant. This means that the coordination of these ions, octahedral sites for Mn^{3+} , Cu^{2+} and Cr^{3+} ions and tetrahedral sites for Ni^{2+} and Co^{2+} ions, do not change with change in the range of basicity between 0.558 and 0.587 as the Na_2O content increased from 10–16 mol%. Moreover, the ligand field strength (Dq) for these ions may be presented at high ligand field and also high stabilization energy, and/or is insensitive to given condition in this work (Singh and Kumar 1995; Dawy and Salama 2001).

The colour intensities in glasses depend not only on the absorbing ions through redox changes but also on extinction coefficients of the ion, ϵ_{ion} , which relate directly to the structure of glasses. Table 4 and figure 9 show the molar extinction coefficients of each ion at the maximum wavelength which were obtained from absorption spectra through the Lambert–Beer's relation in (2). The ϵ_{ion} values of these ions, except for the $\epsilon_{Cr^{3+}}$, shifted toward high values such as 112.50–134.17, 18.70–25.51, 44.52–56.61 and 152.50–193.13 l/mole.cm for Mn^{3+} , Cu^{2+} , Ni^{2+} and Co^{2+} ions, respectively with increasing glass basicity. The $\epsilon_{Cr^{3+}}$ value decreased a little in the range of 22.31–20.50 l/mole.cm. The behaviour of the increased ϵ_{ion} can also be evaluated through structure arguments, especially on the polarizability of the oxide (–II) species, $\alpha_{oxide(-II)}$, surrounding the absorbing ions. The $\alpha_{oxide(-II)}$ was calculated following the method described by Duffy (2002) and the results are shown in table 4. The obtained data on the $\alpha_{oxide(-II)}$ is in agreement with the previous results concerning oxide ion polarizability (Dimitrov and Komatsu 1999; Dawy and Salama 2001; Duffy 2002).

Values of the $\alpha_{oxide(-II)}$ varied from 1.573–1.608 Å³ on increasing glass basicity due to the increase of Na_2O concentration strongly affecting the electron density of the

surrounding oxide (–II) species. It means that the oxide (–II) species polarized their electron cloud to the absorbing ion causing the absorption strength of the ions to increase, as well as, the intensities of colours, especially in the cases of Ni^{2+} and Co^{2+} ions in this work.

For the $\epsilon_{Cr^{3+}}$ which varied in narrow range, i.e. the green colour intensity of Cr^{3+} ion may not be strongly affected by glass structure change but depend directly on the Cr^{3+} which is proportional to the increase of Na_2O concentration in the glasses.

Figure 7. Optical absorption spectra of Ni^{2+} ion in glass having varying basicities. The λ_{max} of Ni^{2+} ion = 450 nm.

Figure 8. Optical absorption spectra of Co^{2+} ion in glass having varying basicities. The λ_{max} of Co^{2+} ion = 595 nm.

Table 4. The optical absorption data due to Mn^{3+} , Cu^{2+} , Cr^{3+} , Ni^{2+} and Co^{2+} ions in experimental soda–lime–silica glass having different basicities.

Sample code	Λ_{cal}	$\alpha_{\text{oxide}} (-\text{II}) (\text{\AA}^3)$	Absorbing ion concentration (mol/l)	A/d at λ_{max} (cm^{-1})	ϵ_{ion} (l/mole.cm)
Mn^{3+} absorption					
Mn1	0.557	1.573	Mn^{3+} 0.008	at 480 nm 0.90	$\epsilon_{\text{Mn}^{3+}}$ 112.50
Mn2	0.562	1.585	0.011	1.25	113.64
Mn3	0.571	1.590	0.011	1.35	122.73
Mn4	0.579	1.599	0.011	1.46	132.73
Mn5	0.587	1.608	0.012	1.61	134.17
Cu^{2+} absorption					
Cu1	0.557	1.573	Cu^{2+} 0.046	at 755 nm 0.86	$\epsilon_{\text{Cu}^{2+}}$ 18.70
Cu2	0.562	1.585	0.046	0.94	20.43
Cu3	0.571	1.590	0.046	1.04	22.61
Cu4	0.579	1.599	0.048	1.11	23.13
Cu5	0.587	1.608	0.049	1.25	25.51
Cr^{3+} absorption					
Cr1	0.557	1.573	Cr^{3+} 0.052	at 655 nm 1.16	$\epsilon_{\text{Cr}^{3+}}$ 22.31
Cr2	0.562	1.585	0.049	1.04	21.22
Cr3	0.571	1.590	0.044	0.91	20.68
Cr4	0.579	1.599	0.042	0.86	20.48
Cr5	0.587	1.608	0.040	0.82	20.50
Ni^{2+} absorption					
Ni1	0.557	1.573	Ni^{2+} 0.062	at 450 nm 2.76	$\epsilon_{\text{Ni}^{2+}}$ 44.52
Ni2	0.562	1.585	0.062	2.87	46.29
Ni3	0.571	1.590	0.062	3.20	51.61
Ni4	0.579	1.599	0.062	3.30	53.23
Ni5	0.587	1.608	0.062	3.51	56.61
Co^{2+} absorption					
Co1	0.557	1.573	Co^{2+} 0.016	at 595 nm 2.44	$\epsilon_{\text{Co}^{2+}}$ 152.50
Co2	0.562	1.585	0.016	2.65	165.63
Co3	0.571	1.590	0.016	2.80	175.00
Co4	0.579	1.599	0.016	2.95	184.38
Co5	0.587	1.608	0.016	3.09	193.13

Figure 9. Maxima molar extinction coefficients of each ion in l/mole.cm at their maximum wavelength as a function of glass basicity.

4. Conclusions

The basicity of the experimental glasses increased due to increase in the Na_2O concentration. The proportion of the NBOs was obtained. The NBOs caused the Q^4 species to depolymerize and transform to Q^3 species. These results were confirmed with the shift of broadening peaks of XRD patterns. The redox ratios of the Mn^{2+} – Mn^{3+} , Cu^{+} – Cu^{2+} and Cr^{3+} – Cr^{6+} couples reduced due to the redox reactions which shifted toward their oxidized ions. While the Ni^{2+} – Ni^{3+} and Co^{2+} – Co^{3+} couples were assumed to be present only in the Ni^{2+} and Co^{2+} ions with increasing basicity in these glasses. The optical absorption bands of Mn^{3+} , Cu^{2+} , Cr^{3+} , Ni^{2+} and Co^{2+} ions occurred at constant wavelengths with different optical densities or intensities. The increase in intensities of these absorbing ions, except for Cr^{3+} ion, at the maximum wavelength was affected by the increase of ion concentration and the molar extinction coefficient. These changes were evidenced through the increase in intensities of glass colours. Whereas in the case of Cr^{3+} ion, the results were opposite as the intensities depended strongly on the decrease of concentration.

Acknowledgements

The authors gratefully acknowledge the financial support by The Commission on Higher Education, Ministry of Education, Thailand and the Graduate School, Chiang Mai University, Thailand.

References

- Bamford C R 1962 *Phys. Chem. Glasses* **3** 189
Bamford C R 1977 *Colour generation and control in glass* (New York: Elsevier Scientific Publishing Company) pp 1–16
Claes P and Decelle E 2001 *J. Non-Cryst. Solids* **288** 37
Conradt R 1997 in *Fundamentals of glass science and technology* (Glafo: The Glass Research Institute) p. 15
Dawy M and Salama A H 2001 *Mater. Chem. Phys.* **71** 137
Dimitrov V and Komatsu T 1999 *J. Non-Cryst. Solids* **249** 160
Duffy J A 1996 *J. Non-Cryst. Solids* **196** 45
Duffy J A 2002 *J. Non-Cryst. Solids* **297** 275
Duffy J A and Ingram M D 2002 *C.R. Chimie* **5** 797
Jones A R, Winter R, Greaves G N and Smith I H 2001 *J. Non-Cryst. Solids* **293–295** 87
Knowles A and Burgess C 1984 *Practical absorption spectrometry* (New York: Chapman and Hall) pp 14–16
Krämer F W 1991 *Glastech. Ber.* **64** 71
Matschat R, Dette A and Guadagnino E 2004 *Final certification report of BAM-S004* (Berlin: Federal Institute for Materials Research) pp 1–21
Meneau F, Greaves G N, Winter R and Vaills Y 2001 *J. Non-Cryst. Solids* **293–295** 693
Müller-Simon H 1996 *Glastech. Ber.* **69** 387
Paul A 1990 *Chemistry of glasses* (London: Chapman and Hall) 2nd ed., pp 236–238
Paul A and Douglas R W 1995 *Phys. Chem. Glasses* **6** 212
Pyare R and Nath P 1982 *J. Am. Ceram. Soc.* **65** 549
Schreiber H D 1986 *J. Non-Cryst. Solids* **84** 129
Schreiber H D, Kochanowski B K, Schreiber C W, Morgan A B, Coolbaugh M T and Dunlap T G 1994 *J. Non-Cryst. Solids* **177** 340
Singh S P and Kumar A 1995 *J. Mater. Sci.* **30** 2999
Singh S P, Tarafder Aman and Tarafder Anal 2004 *Bull. Mater. Sci.* **27** 281
Zhang P, Dunlap C, Florian P, Grandinetti P J, Farnan I and Stebbins J F 1996 *J. Non-Cryst. Solids* **204** 294