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Invited Paper

Effect of concentration ratio of iron/manganese on coloration in borate glass

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Abstract. In this research, effect of concentration ratio of iron/manganese on coloration in borate glasses have been investigated. The glass samples were prepared by the normal melt-quench technique at 1,200 ^{o}c for 3 hours in normal atmosphere. The ratio of iron/manganese study was separated into two sections, the concentration of MnO_2 was varied from 0.0 to 0.5 mol% with a fixed Fe_2O_3 concentration at 0.3 mol% and the Fe_2O_3 concentration was varied from 0.0 to 0.5 mol% when MnO_2 concentration was constant at 0.3 mol%. The results show that the optical absorption spectra of glass samples reveal three peaks of Fe^{3+}, Fe^{2+} and Mn^{3+}. The intensity of Fe^{2+} is deceased and Fe^{3+} is increased with increasing of MnO_2 content. While the absorption peak of Mn^{3+} was decreased with increasing of Fe_2O_3 concentration. Moreover, the density, the refractive index and the molar volume of glass samples were investigated.

1. Introduction

Recently, glasses containing transition metal (TM) ions give rise to optical absorption spectra, due to electron transitions between normally degenerate energy levels of d-electron that is the source of the glass coloration. Each 3d-transition metal can exist in more than one oxidation or coordination states and normally gives rise to specific absorption spectra [1-3]. Among various transition metal oxides, iron and manganese oxide is very interesting optical properties with redox reaction. Fe_2O_3 in glasses exists as equilibrium between the yellow ferric ion (Fe^{3+}), and the blue ferrous ion (Fe^{2+}) [4]. While the form of MnO_2 mainly exist in two common oxidation states of Mn^{2+} and Mn^{3+} [5]. In the presence of both manganese and iron ions, multivalent ions can bring together interaction take place between them. Resulted valence balance for each element is different from that state that these elements existed by themselves [6]. To the understanding of these redox reaction of iron and manganese in glass, Effect of concentration ratio of iron/manganese on coloration in borate glasses have been investigated.

2. Experimental

2.1 Sample preparation

The glass samples were prepared by conventional melt-quenching technique with using high purity chemical powder of B_2O_3, Al_2O_3, CaO, Na_2O, MnO_2 and Fe_2O_3. This research was separated into two sections for the effect of concentration ratio of iron/manganese on coloration in borate glass. First, the concentration of MnO_2 was varied from 0.0 to 0.5 mol% with a fixed Fe_2O_3 concentration at 0.3 mol%. Second, the Fe_2O_3 concentration was varied from 0.0 to 0.5 mol% when MnO_2

concentration was constant at 0.3 mol%. The concentration ratio of Fe/Mn chemical were added in glass composition as illustrated in Table 1. All chemical composition were mixed in whole of composite and filled in a high purity alumina crucible. Each batch weighs about 20 g was placed in an electrical furnace and then melted at 1200^{o}C for 3 hours to ensure complete melting of all components. After complete melting, the melts were quickly poured onto a preheated stainless steel mould The quenched glasses were annealed at 500^{o}C for 3 hour for reduce thermal stress, and cooled down to room temperature. Finally, all glass samples were cut and then finely polished to a dimension of 0.3cm x 0.5cm x 1.0cm for further investigation

Table 1. Chemical compositions of the glass samples

	Sample	Ratios of Fe/Mn	Glass composition (mol%)					
			B_2O_3	Al_2O_3	CaO	Na_2O	Fe_2O_3	MnO_2
Varied MnO_2 Concentration	BMn00	0.3/0.0	39.7	20	20	20	0.3	-
	BMn01	0.3/0.1	39.6	20	20	20	0.3	0.1
	BMn02	0.3/0.2	39.5	20	20	20	0.3	0.2
	BMn03	0.3/0.3	39.4	20	20	20	0.3	0.3
	BMn04	0.3/0.4	39.3	20	20	20	0.3	0.4
	BMn05	0.3/0.5	39.2	20	20	20	0.3	0.5
Varied Fe_2O_3 Concentration	BFe00	0.0/0.3	39.7	20	20	20	-	0.3
	BFe01	0.1/0.3	39.6	20	20	20	0.1	0.3
	BFe02	0.2/0.3	39.5	20	20	20	0.2	0.3
	BFe03	0.3/0.3	39.4	20	20	20	0.3	0.3
	BFe04	0.4/0.3	39.3	20	20	20	0.4	0.3
	BFe05	0.5/0.3	39.2	20	20	20	0.5	0.3

2.2 Measurements

The refractive index (RI) was measured by DR-M2 refractometer. The sodium vapor lamp as the light source (539 nm) was used for measurement and the mono-bromonaphthalene was used as an adhesive coating. The density (ρ) was measured by Archimedes' principle using a sensitive microbalance (AND, HR-200).

$$\rho = \left[\frac{w_a}{w_a - w_b}\right]\rho_l \quad (1)$$

where w_a and w_b represent the weight of the glass in air and water respectively, and ρ_l is the density of the water (~0.9982 g/cm^3).

The molar volume (V_m) of glass samples were calculated using the formula [7]:

$$V_m = \frac{M_t}{\rho} \quad (2)$$

Where M_T is the total molecular weight of the multicomponent glasses system given by

$$M_t = x_{B_2O_3}Z_{B_2O_3} + x_{Al_2O_3}Z_{Al_2O_3} + x_{CaO}Z_{CaO} + x_{Na_2O}Z_{Na_2O} + x_{Fe_2O_3}Z_{Fe_2O_3} + x_{MnO_2}Z_{MnO_2} \quad (3)$$

Where $x_{B_2O_3}$, $x_{Al_2O_3}$, x_{CaO}, x_{Na_2O}, $x_{Fe_2O_3}$and $x_{MnO_2}$are the mole fractions of the constituent oxides, And $Z_{B_2O_3}$, $Z_{Al_2O_3}$, Z_{CaO}, Z_{Na_2O}, $Z_{Fe_2O_3}$and $Z_{MnO_2}$are the molecular weights of the constituent oxides. The density and molar volume of glass samples are presented in Table 2.

The optical absorption spectra of glass samples were measured in wavelength range 300-1,050 nm by the uv-visible spectrophotometer (Cary-50). All measurements were carried at room temperature

3. Result and discussion

3.1 Glass sample

The glass samples (BMn00-BMn05) were prepared in composition (39.7-x)B_2O_3 : 20Al_2O_3 : 20CaO : 20Na_2O : 0.3Fe_2O_3 : xMnO_2, where x= 0.00, 0.01, 0.02, 0.03, 0.04, and 0.05 mol%, respectively. All glass samples show the yellow color and the intensity of color increase with increasing of MnO_2 content. While the glass samples (BFe00-BFe05) were prepared in composition (39.7-x)B_2O_3 : 20Al_2O_3 : 20CaO : 20Na_2O : 0.3MnO_2 : xFe_2O_3, where x= 0.00, 0.01, 0.02, 0.03, 0.04, and 0.05 mol%, respectively. The glass without Fe_2O_3 concentration shows red-brown color whereas the color was changed to the yellow color when the Fe_2O_3 is doped in the glass matrix as illustrated in Fig 1.

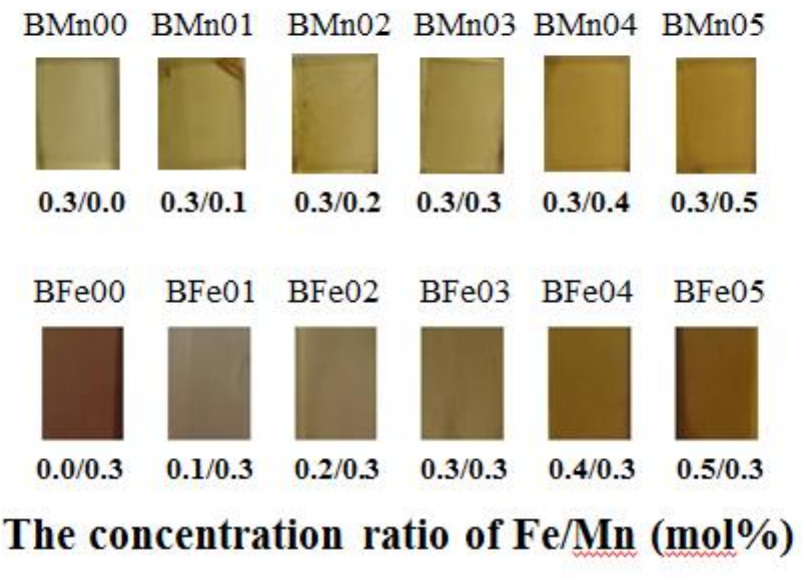

Fig. 1. The glass samples with different concentration ratio of Fe/Mn.

3.2 Density, molar volume and refractive index

The density, the refractive index and the molar volume of glass samples are shown in Table 2. The measured density values of BMn00-BMn05 and BFe00-BFe05 are in the range of 2.4706-2.4824 g/cm^3 and 2.4692-2.4983 g/cm^3. The refractive index values are in the range of 1.5468-1.5544 and 1.5454-1.5585 while the molar volume values are in the range of 29.0674- 29.1922 cm^3/mol and 28.9614-29.1568, respectively. It has been observed that Fe_2O_3 affect more than MnO_2 in these parameters. Actually, when high density component are added in glass composition, the density and the refractive index are increased [8]. Although the atomic weight of iron (55.85) close to manganese (54.94), Fe_2O_3 was added in glass structure by 2 atom of iron while manganese was added by just 1 atom. For that reason, the atomic weight of iron in glass matrix more than manganese.

Table 2. The density, refractive index and molar volume values of glass samples

	Sample	Ratios of Fe/Mn	Parameters		
			ρ , (g/cm^3)	V_m, (cm^3/mol)	RI
Varied MnO_2 Concentration	BMn00	0.3/0.0	2.4706	29.1922	1.5468
	BMn01	0.3/0.1	2.4699	29.2075	1.5500
	BMn02	0.3/0.2	2.4824	29.0674	1.5544
	BMn03	0.3/0.3	2.4790	29.1142	1.5469
	BMn04	0.3/0.4	2.4740	29.1801	1.5477
	BMn05	0.3/0.5	2.4782	29.1376	1.5479
Varied Fe_2O_3 Concentration	BFe00	0.0/0.3	2.4786	29.0099	1.5454
	BFe01	0.1/0.3	2.4692	29.1568	1.5455
	BFe02	0.2/0.3	2.4816	29.0474	1.5466
	BFe03	0.3/0.3	2.4857	29.0357	1.5474
	BFe04	0.4/0.3	2.4891	29.0323	1.5585
	BFe05	0.5/0.3	2.4983	28.9614	1.5585

3.4 Optical absorption spectra

The optical absorption spectra of glass samples were analyzed by the uv-visible spectrophotometer at room temperature in the range of 300-1,050 nm, as shown in Fig. 2 (a) and (b). The absorption peak of BMn00-BMn05 reveal 2 board peaks around 445 nm and 950 nm are attributed to the transitions of Fe^{3+} ($^6A_{1g} \rightarrow {}^4T_2g$) and Fe^{2+} ($^5E \rightarrow {}^5T_2$), respectively [9-10]. The intensity of Fe^{2+} is deceased and Fe^{3+} is increased with increasing of MnO_2 content. The result can be explained by the equilibrium between iron and manganese ions, as represented by $Fe^{3+} + Mn^{2+} \leftrightarrow Fe^{2+} + Mn^{3+}$. Manganese in glass structure mainly exists in Mn^{3+} ions and act as oxidizing agent in redox reaction. When the Mn^{3+} was added in the glass structure, Fe^{2+} was oxidized to Fe^{3+}. This reason confirm by the absorption peak of BFe00-BF05. The absorption peak of Mn^{3+} was decreased with increasing of Fe_2O_3 concentration. Actually, the absorption peak of Mn^{3+} ions locate at 465 nm and show the red-brown color in borate glass [5-6]. The decreasing in the absorption peak of Mn^{3+} cause by the addition of Fe_2O_3 which can convert Mn^{3+} to Mn^{2+}.

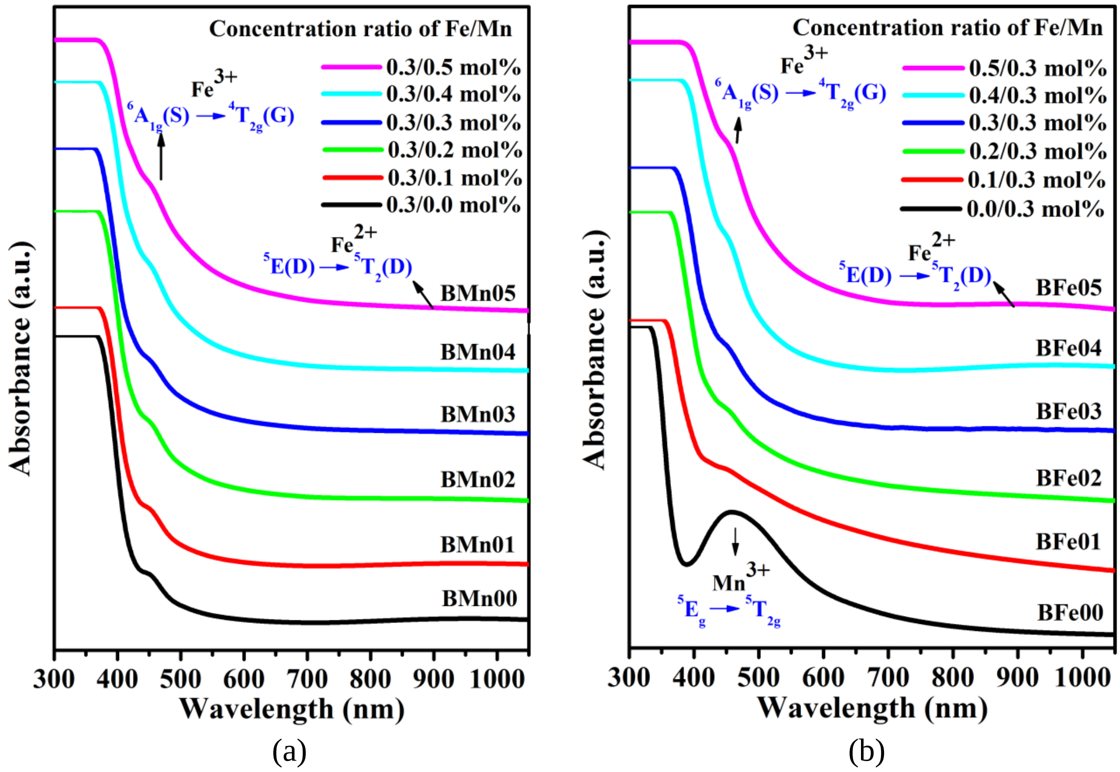

Fig. 2 (a) The absorption spectra of glass samples BMn00-BMn05
(b) The absorption spectra of glass samples BFe00-BFe05

4. Conclusion

In this work, the effect of concentration ratio of iron/manganese on coloration in borate glasses have been investigated. The glass samples were prepare by melted quenching technique. The physical and optical properties were characterized. The results show that the addition of Fe_2O_3 affect more than MnO_2 on the density, the refractive index and the molar volume values. The optical absorption spectra of glass samples reveal three peaks of Fe^{3+}, Fe^{2+} and Mn^{3+}. The intensity of Fe^{2+} is deceased and Fe^{3+} is increased with increasing of MnO_2 content. Whereas the absorption peak of Mn^{3+} was decreased with increasing of Fe_2O_3 concentration. The result can be explained by the equilibrium between iron and manganese ions, as represented by $Fe^{3+} + Mn^{2+} \leftrightarrow Fe^{2+} + Mn^{3+}$.

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