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Spectrophotometric Studies on High Iron Content Silicate Glasses

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Spectrophotometric investigations were carried out on soda-lime-silica glasses containing iron in high content, corresponding to 4.9 wt. % Fe_2O_3, and melted under the various reducing conditions, as a part of series of studies on the redox behavior of glass. Absorption measurement was made in the range from 340 mμ to 1000 mμ. Ferric ions could not be reduced to ferrous ions completely even by the amount of carbon of four equivalents. The ratio of the strength of light absorption at 1000 mμ as a typical band of Fe^{2+} ions and that at 380 mμ of Fe^{3+} ions was expressed as E_{1000}/E_{380}, which was examined for glass compositions as well as various carbon amount added to glass batches. The ratio decreases as the carbon amount increases and increases with decreasing content of Na_2O or CaO. These changes of spectrophotometric properties of glasses were discussed from the view point of state of the the iron ions. Besides, some results on oxidized glasses were also added.

§ 1. Introduction

The state of irons contained in glass changes with the various conditions, namely, composition of base glass, content of iron, atomospheric condition, melting temperature, heat treatment etc. To the understanding of these behaviors of iron in glass the spectrophotometric information has been playing very important role, for it is sensitively influenced by valence and configuration of iron ions.

According to the previous works sodium silicate glasses containing iron indicate the absorption bands approximately at 380, 425, 440 and 1200 mμ. These absorption spectra in near ultraviolet and near infrared regions are respectively assigned to Fe^{3+} ions and Fe^{2+} ions both subject to an octahedral ligand field of oxigen ions. Many studies on the nature of these absorption bands including some attempts to relate them to the concentrations of ferric and ferrous ions have been carried out from the viewpoint of coloring of glass as well as approaching structure of glass.[1~8]

The purpose of the present investigation is also to study the spectrophotometric properties of soda-lime-silica glasses containing iron in high content corresponding to 4.9 wt. % Fe_2O_3 and melted mainly under the various reducing conditions which were produced by added carbon powder. This was intended as a part of the overall series of studies on the redox reaction and equilibrium in glass.

§ 2. Preparation of glass samples

Three groups of glasses were used in this study. One was the group of the standard composition, that is 74.0 SiO_2, 16.0 Na_2O, 10.0 CaO,[7] by wt. % and the other two were soda rich group and lime rich group. The glass batches were prepared from high purity silica sand, reagent grade sodium carbonate, precipitated calk and ferric oxide as the iron source together with required amount of carbon powder. Ferric oxide used were prepared by decomposing reagent grade ferric oxalate in the oxidizing atomosphere. The amount of carbon added to the batch was varied within the range from one to four times of the following stoichiometric requirement.

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$$2Fe_2O_3+C=4FeO+CO_2, \quad (1)$$

The glasses were melted in sintered alumina crucibles in the electric furnaces heated by silicon carbide heating elements. The batch corresponding to about 25 gram glass was weighed precisely and divided into several parts being about 7 gram each in weight. They were charged one after another every 20 minutes into the crucible in the furnace kept at 1400°C.

After all batch charged the furnace temperature was elevated to 1440°C and kept there for an hour. Then the molten glass was poured on the stainless steel plate which was previously heated up to about 550°C and pressed with another plate of the same temperature so that the glass sheet was obtained. The process mentioned above was followed by keeping the glass at 520°C for 10 minutes, after this, the glass was cooled at the rate of 10°C a minute to 200°C, and then it was allowed to be cooled in the air.

The glasses thus obtained generally showed a dark green colour, but in some cases a dark brown colour. Even when extremely excess carbon, that is, four equivalents, was added to the batch, reduction of the iron ions to the metal was not observed. The samples used for measurement of optical transmission properties were prepared by grinding and polishing the glasses to 0.3~0.5 mm shickness.

§ 3. Results of spectrophotometric measurement and discussion

The optical transmission properties of the sample glasses were measured as a function of wavelength in the region between 340 mμ and 1000 mμ. Of the data obtained the principal ones are indicated in the figures. In Table I the composition of glasses corresponding to the spectrophotometric data cited is shown together with the amount of carbon used as the reductant. The colour of polished glass plates as viewed with white transmitted light is also involved in the table. At first in Fig. 1 are shown the transmittance curves of the iron free glasses, that is, base glass (001), soda rich glass (002), and glass containing Al_2O_3 (003). The glass 003 was prepared to examine the influence of Al_2O_3 came into the glass from crucible.

Table I Glass used

Glass No.	Glass composition wt. %					Added carbon (equivalent)	Added $NaNO_3$* (equivalent)	Colour of glass
	SiO_2	CaO	Na_2O	Al_2O_3	Fe_2O_3			
001	74.0	10.0	16.0					
002	67.8	9.7	15.6	7.0				colourless
003	61.3	11.1	27.8					
310	70.4	9.5	15.2		4.9	0		greenish-brown
311						1		greenish-blue
312						2		
313						3		
314						4		
330	61.6	9.6	24.0		4.9	0		greenish-brown
332						2		greenish-blue
334						4		
342	67.5	9.5	19.9		4.9	2		
352	60.0	19.9	15.2		4.9	2		
213	67.1	9.1	14.5		9.3		3	dark greenish-brown
214							4	dark greenish-blue
412	70.4	9.5	15.2		4.9		2	greenish-brown
414							4	greenish-brown

※ Na_2CO_3 in the batch is partly replaced by $NaNO_3$

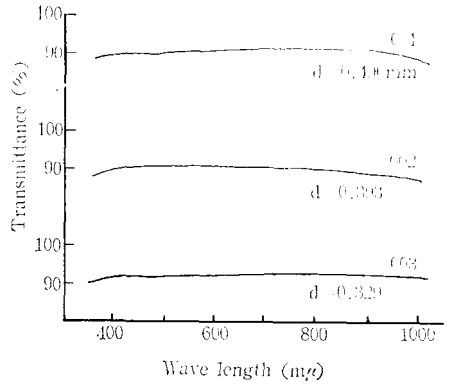

Fig. 1 Transmittance curves of the ironfree glasses, i.e. base glass 001, soda rich glass 002, and Al_2O_3 containing glass 003.

In every case the curves illustrate flat and almost equal percentage transmittance over all range of wavelength from 360 mμ to 1000 mμ. Fig. 2 shows the influence of amount of carbon added to the batch of glass containing 4.9 wt. % ferric oxide on transmittance curve, Fig. 3 shows the similar influence of carbon when Na_2O content was increased. Both of

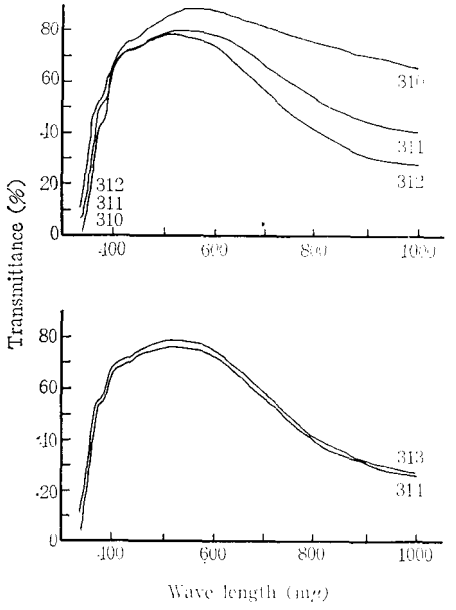

Fig. 2 Influences of amount of carbon added to the batches on transmittance of glasses which contain iron corresponding to 4.9 wt. % Fe_2O_3.

these two groups of glasses whose principal wave length of transmitted light are approximately 500~550 mμ show a deep absorption and which covers from near infrared to visible region and the sharp ones in near ultraviolet region as the glasses containing iron oxide generally do. From the figures it can be said that the principal wavelength of transmitted light shifts to short wavelength side as the amount of carbon increases.

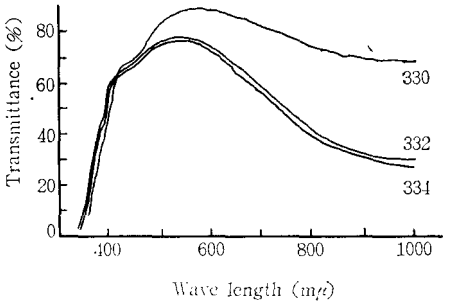

Fig. 3 Influences of amount of carbon added to the batches on transmittance of soda rich glasses which contain iron corresponding to 4.9 wt. % Fe_2O_3.

Moore[2] indicated, as to the soda-lime-silica glass of low iron content, that the strength of absorption bands at 390 mμ and 1000 mμ can be related quantitatively to the concentration of Fe^{3+} and Fe^{2+} ions respectively. Ihara[3] also using soda-lime-silica glasses confirmed that this propotional relation between transmittance at a characteristic wave length and ion concentration may be applied to the extent of iron content 0.5~2.5% Fe_2O_3. For the alkali silicate glass of high alkali content, however, it was shown by Bishay[4] that the relation did not hold. Although the glasses used were soda-lime-silica glasses, in the present case, having the composition near to those used by Ihara, they contained iron oxide as much as two times or more of Ihara's glasses and the proportional relation mentioned above was not confirmed for them. But the authors intend to advance the argument assuming, for the present, that the relation can be also applied, at least as a rough approximation.

Considering from the view point, it can be said that the change of the nature of transmission curves shows the change of the concentration ratio of Fe^{2+} ions to Fe^{3+} in the glasses. A strength of light absorption E generally changes with the changes of the concentration, C, of absorptive substance as well as the thickness, d, of the absorption layer. This relation is given by well known Lambert-Beer's

law which is given using the absorption coefficient k as follows,

$$E = -log \frac{I}{I_0} = log \frac{I_0}{I} = kCd, \qquad (2)$$

where, I_0 and I are the strength of initial incident light and transmitted light, respectively. It is necessary, in general case, to consider the reflection loss at each surface of the glass. The effect of reflection, however, can be approximately calculated from the refractive index of the glass. In the present investigation, curves of transmittance except those for ironfree glasses were corrected by this method. Furthermore, these curves were converted to those of the plate glasses having the thickness of 0.3 mm.

If we select the two absorption bands, 380 mμ as the typical one for the near ultraviolet region and 1000 mμ for the near infrared region, their absorption can be shown by following equations, using the absorption coefficients, k_v and k_r, respectively.

$$E_{380} = 0.03 k_v [Fe^{3+}], \qquad (3)$$

$$E_{1000} = 0.03 k_r [Fe^{2+}], \qquad (4)$$

As it was pointed out in the previous work, k_r has a value of 8~10 times k_v for the glasses used here. Consequently, it can be seen that the change of absorption at 1000 mμ is usually larger than at 380 mμ. From the equations (3) and (4), the proportional relation,

$$\frac{E_{1000}}{E_{380}} = \frac{k_r [Fe^{2+}]}{k_v [Fe^{3+}]} = K \frac{[Fe^{2+}]}{[Fe^{3+}]} \qquad (5)$$

is obtained between the ratio of absorption and that of ion concentration. In Fig. 4 are shown the values of the ratio E_{1000}/E_{380} calculated from the curves in Fig. 2 and Fig. 3. From the figure it may be seen that the ratio E_{1000}/E_{380} increases propotionally to the amount of added carbon increasing to the value of 2 equivalents, beyond which the ratio remains almost constant. This tendency generally looks to be held even when the Na_2O content is changed, but the value of the ratio of absorption decreases with increasing Na_2O content.

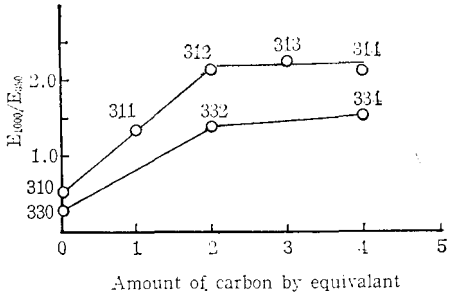

Fig. 4 Plots of the ratio, E_{1000}/E_{380} against amount of added carbon expressed by equivalent.

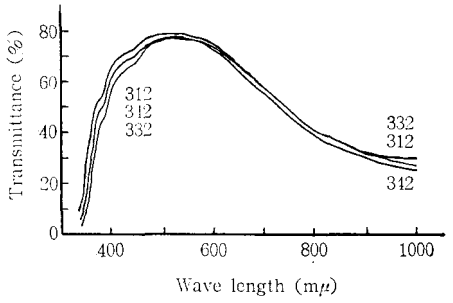

Fig. 5 Transmittance curves of the glasses having different Na_2O content but same carbon addition of 2 equivalents.

Fig. 5 indicates the transmittance curves of the glasses having different Na_2O content but same carbon addition of 2 equivalents. The curves tell the fact that the change of transmittance in the short wavelength region seems to be relatively large, while in the long wavelength region very small. This appears to be a very curious thing when it is recollected that the absorption coefficient k_r of the 1000 mμ light is by far larger[3)8)] than that of 380 mμ light, k_v. In Fig. 6 is shown the ratio of the absorption E_{1000}/E_{380} as a function of Na_2O content. The ratio also decreases linearly with increasing Na_2O content. To explain this experimental results, following inferences can be

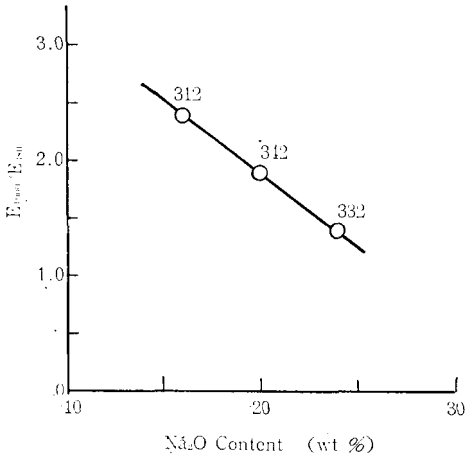

Fig. 6 Plots of the ratio of absorption E_{1000}/E_{380} against Na_2O content.

constructed.

In the first place, it can be said examining Fig. 5 and Fig. 6 that the change of E_{1000}/E_{380} must be attributed not to the change of the amount of ferrous and ferric ions, that is $Fe^{2+} \rightarrow Fe^{3+}$ but to the change of the absorption coefficient Fe^{3+} ion, k_v, originated in the change Na_2O content.

On the other hand, Bishay[4] stated basing on his experimental results that the absorption coefficient of Fe^{2+} ion increases appreciably as the alkali content of the glass increases. If this matter is to be applied for the present case, it is necessary in order to keep E_{1000} constant that the increase of Fe^{3+} ions and decrease of Fe^{2+} ions takes place as $Fe^{2+} \rightarrow Fe^{3+}$. Such change of concentration of ions with alkali content was confirmed by Douglas *et al*[3].

If it is assumed that the former idea of increase of k_v can be acceptable, this change of absorption coefficient may be attributed to the change of the oxigen configuration arround the Fe^{3+} ions. Ferric ions in octahedral co-ordination, $Fe^{3+}(O)_6$, taking the sites which the network midifier ions favor can be expected to change into the state in tetrahedral co-ordination, $Fe^{3+}(O)_4$, as network formers with increasing Na_2O content. The absorption band at 380 mμ is known as the one which arises from $Fe^{3+}(O)_6$ groups. Consequently, the change of strength of this absorption band means the change $Fe^{3+}(O)_6 \rightarrow Fe^{3+}(O)_4$ suggesting the requirement that $Fe^{3+}(O)_4$ group must have the absorption band at 380 mμ, too. In Table II the bands predicted by ligand field

Table II Ligand field predictions for ferric iron[8]

Calculated position (mμ)	Valence state	Co-ordination symmetry
735	Fe^{3+}	Octahedral
570	Fe^{3+}	Octahedral
427	Fe^{3+}	Octahedral
380	Fe^{3+}	Octahedral
500	Fe^{3+}	Tetrahedral
446	Fe^{3+}	Tetrahedral
427	Fe^{3+}	Tetrahedral
380	Fe^{3+}	Tetrahedral

theory are listed.[8] It is shown that both $Fe^{3+}(O)_6$ group and $Fe^{3+}(O)_4$ group have the same absorption band at 380 mμ and the above requirement is satisfied. The other hands, for instance 735, 570 and 427 mμ, in the curves of transmittance in Fig. 5 also seem to be favorable to consider this configurational change.

There is, however, no substantial basis to deny the latter idea, so it is inadequate at present situation to form the conclusion on this problem and further investigation is desired. At all events, Beer's law does not hold for the iron in these glasses.

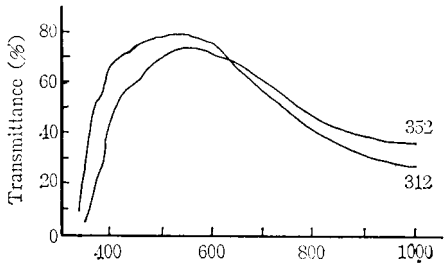

Fig. 7 Transmittance curves of the glasses having different CaO content but same carbon addition of 2 equivalents.

In Fig. 7 which shows the effect of CaO content, it is indicated that the transmittance in the short wave length region decreases and that in the long wave length region increases as CaO content increases. The principal wave length of the transmitted light also shifts to the long wave length side with increasing CaO content. Fig. 8 indicates the change of the ratio E_{1000}/E_{380} when the CaO content increased. From the same stand point as the case of changing Na_2O content, similar deductions can be drawn. For instance, the change $Fe^{2+} \rightarrow Fe^{3+}$ as well as the increase of absorption coefficient of Fe^{3+} is brought about by

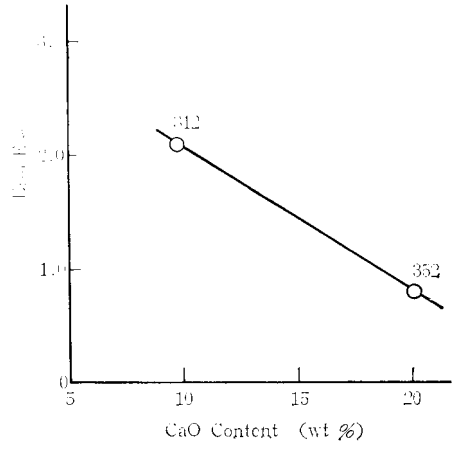

Fig. 8 Plots of the ratio, E_{1000}/E_{380} against CaO content.

the increase of CaO content.

In Fig. 9 are shown, for reference, the transmittance curves of the glasses melted under the various oxidizing conditions. The

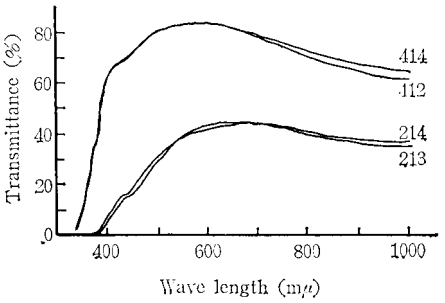

Fig. 9 Transmittance curves of the glasses melted under the various oxidizing conditions.
412, 414 glass and 213, 214 glass contain 4.9 wt. % Fe_2O_3 and 9.3 wt. % Fe_2O_3 respectively.

glasses used were prepared from the corresponding batches added with 2～4 equivalents of $NaNO_3$ as a oxidizer and consisted of 4.9 wt. % Fe_2O_3 and the other part with base glass composition. Melting and sample forming processes were same as those of reduced glasses mentioned already. The glasses of 4 9 wt. % Fe_2O_3 indicated a light greenish brown colour and iron rich ones, namely 9.3 wt. % Fe_2O_3 glasses, a dark similar colour. The iron rich glasses indicate the near ultraviolet cut off at about 380 mμ, and that their principal wave length of transmitted light is approximately 650 mμ. This peak value is 580 mμ in the case of 4.9 wt. % Fe_2O_3 glasses. Strength of absorption at 1000 mμ is not so large for both kinds of glasses and has a tendency of decreasing with increasing amount of oxidizer. The change, however, seems to be very small.

§ 4. Conclusions

1. The principal wave length of transmitted light as to the glasses used is approximately 500～550 mμ and shifts to short wave length side with increasing amount of carbon added to the batch.

2. Ferric ions in the glasses can not be completely reduced even by the amount of carbon of 1～4 times equivalents.

3. The ratio of strength of absorption at 1000 mμ to that at 380 mμ, E_{1000}/E_{380}, increases with incressing carbon amount to 2 equivalents, beyond which the ratio is held at about constant.

4. The ratio E_{1000}/E_{380} decreases with increasing Na_2O or CaO content. For this change the change of absorption coefficient caused from the configuration change of ferric ion, that is $Fe^{3+}(O)_5$, $Fe^{3+}(O)_4$, seems to play the important role.

5. For the iron ions in these glasses Beer's law does not hold.

6. Amount of oxidizer added to the glass batches shows only a little influence.

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