Optical Spectroscopic Study of Lead Silicate Glasses Doped Heavily with Iron Oxide

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Optical absorption was investigated as for lead silicate glasses containing Fe_3O_4 up to 10 mol%, which have been melted under air or argon atmosphere. The absorption coefficient over the whole optical range increased with increase of iron content. The variations of the spectrum profiles were also observed with Fe^{2+} content; the tail from UV region shifted to low energy side and another absorption band (near 14500 cm^{-1}) beside d-d transitions was observed. These were considered to be caused by the interaction including the charge transfer between Fe^{2+} and Fe^{3+} ions.

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I. Introduction

The optical and electric properties of transition metal ions in oxide glasses have been explored to a great extent. Iron among others is universally present in almost all commercial glasses and causes their coloration. The optical studies of these glasses containing trace amounts of impurities have been worked out using the ligand field theory. On the other hand, oxide glasses with high contents of transition metal ions, like vanadium-containing phosphate glasses, have been reported to conduct electricity. The lead silicate glasses containing iron oxide was studied by Anderson and MacCrone⁽¹⁾.

The electronic transfer (charge transfer) from Fe^{2+} to Fe^{3+} has been observed by optical spectroscopy in some minerals containing ferrous and ferric ions, and the absorption caused by charge transfer was reviewed by Burns⁽²⁾. The absorption due to charge transfer between Ce^{3+} and Ti^{4+} ⁽³⁾, Fe^{2+} and Ti^{4+} ⁽⁴⁾ and Ti^{3+} and Ti^{4+} ⁽⁵⁾ were also observed in oxide glasses. These absorptions cause new stronger coloration compared with the forbidden d-d transition. Weyl⁽⁶⁾ suggested that the interaction between Fe^{2+} and Fe^{3+} exists on the reduced glass, and Montenero *et al.*⁽⁷⁾ suggested the formation of Fe^{2+} - Fe^{3+} cluster in sodium silicate glasses.

The above results suggest that oxide melts containing transition metal oxide over a minimum extent behave beyond ordinary electrolyte melts as well as glasses. In the present work the behavior of optical absorption of apparently opaque lead silicate glasses with a high content of iron oxide was studied. The effect of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio on the absorption were thoroughly investigated. The color-

ation with iron content was attributed to the allowed charge transfer between Fe^{3+} - O^{2-} and Fe^{2+} - Fe^{3+} pairs.

II. Experimental

The starting materials for all the glasses were prepared from SiO_2 and PbO . Magnetite of the reagent grade was added to introduce iron ions. The nominal composition of the glasses were $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + x\text{Fe}_3\text{O}_4$ where x ranged 0 to 0.2. The powder mixture of PbO and SiO_2 was first melted at 1220°C in a platinum crucible. The quenched solvent glasses were ground into powder and melted again with iron oxide. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was controlled exchanging the atmosphere of air or argon. A simple device shown in Fig. 1 was used to prepare the Ar atmosphere and to quench the melt by pulling the system out of the furnace. Active carbon powder was charged on the brick where the crucible is located. This minimized counter current of gaseous oxygen from the outlet. The preparation of definite oxygen pressure was not intended. In some cases the atmosphere of Ar had been maintained for differing periods. Response shown in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio to the atmospheric change was very rapid.

After the sample melts were quenched, they were cut into plates and polished prior to the absorption measurement. The glasses containing high contents of iron oxide had to be cut and polished very thin in order to obtain detailed spectra. The thickness ranged from 0.002 to 0.2 cm. Shimadzu UV-365 was used to measure and record the absorption profile over 4000 to 40000 cm^{-1} at room temperature. The effect of the surface reflection was observed in thin samples and had to be corrected.

As for the chemical analysis of glasses, the total iron content was determined with Perkin Elmer Atomic Absorption Spectrometer 3110 after they were dissolved in HF solution. The Fe^{3+} ion content in the sample was determined by spectrometry with the aid of 1, 10-phenanthroline, as reported by Uchida *et al.*⁽⁸⁾ The sam-

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Fig. 1 The simple device to melt the sample under Ar atmosphere.

ple numbers and the data on the total and ferrous iron contents are listed in Table 1. X-ray diffractometer, RINT 2000 (RIGAKU), was employed to detect any crystalline mineral in the glass samples as shown in Fig. 2.

III. Results

When prepared under air atmosphere the sample with $x > 0.14$ proved to contain hematite, and when prepared under Ar atmosphere the sample with $x > 0.11$ was found to include magnetite (Fig. 2). Those were eliminated from spectroscopic measurement. Since the reflection from the sample surface affected very much the observed absorption spectrum, the correction of absorption spectra has

Fig. 2 X-ray diffraction pattern of $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + x\text{Fe}_3\text{O}_4$ melted under (a) air atmosphere or (b) Ar atmosphere.

to be performed as for thin samples. In order to carry out this correction, the absorption spectra of glasses with various thicknesses were measured and the relation $\alpha = (A_1 - A_2) / (l_2 - l_1)$ was used to obtain the value of ab-

Table 1 The results of chemical analysis of ferric and ferrous ions in the lead silicate glasses.

Sample No.	Batch composition		Results of chemical analysis			
	$x\text{Fe}_3\text{O}_4^*$	$\text{Fe}_{\text{total}}^{**}$ (nominal)	$\text{Fe}_{\text{total}}^{**}$ (analyzed)	$[\text{Fe}^{2+}]^{***}$	$[\text{Fe}^{3+}]^{***}$	$[\text{Fe}^{2+}] / \text{Fe}_{\text{total}}$
A-1	0 (Air)	0	0.00028			
A-2	0.002(Air)	0.006	0.0075	0.001	0.0065	0.14
B-2	0.002(Ar)	0.006	0.0079	0.0035	0.0044	0.45
A-3	0.01 (Air)	0.029	0.026	0.0034	0.023	0.13
B-3	0.01 (Ar)	0.029	0.03	0.0079	0.022	0.27
A-4	0.05 (Air)	0.13	0.13	0.0099	0.12	0.07
C-1	0.05 (Ar5)	0.13	0.13	0.01	0.12	0.08
C-2	0.05 (Ar15)	0.13	0.13	0.017	0.116	0.13
C-3	0.05 (Ar30)	0.13	0.13	0.022	0.112	0.16
B-4	0.05 (Ar)	0.13	0.13	0.037	0.096	0.28
A-5	0.09 (Air)	0.21	0.21	0.014	0.2	0.067
B-5	0.09 (Ar)	0.21	0.22	0.066	0.15	0.3
A-6	0.10 (Air)	0.23	0.23	0.0098	0.22	0.043
C-4	0.10 (Ar5)	0.23	0.24	0.015	0.22	0.065
C-5	0.10 (Ar15)	0.23	0.23	0.024	0.21	0.1
C-6	0.10 (Ar30)	0.23	0.24	0.04	0.2	0.17
B-6	0.10 (Ar)	0.23	0.23	0.072	0.16	0.31
A-7	0.105(Air)	0.23	0.24	0.016	0.22	0.068
A-8	0.11 (Air)	0.25	0.25	0.013	0.23	0.052
A-9	0.12 (Air)	0.26	0.28	0.0094	0.27	0.034

*Numerical value x in $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + x\text{Fe}_3\text{O}_4$. (Air) and (Ar); the atmosphere of melting for 120 min. (Ar5); in Ar for 5 min after air atmosphere of melting for 120 min.

**Numerical value y in $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + y\text{Fe}_{\text{total}}$.

***Numerical value shows v or w in which $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + v[\text{Fe}^{2+}] + w[\text{Fe}^{3+}]$.

sorption coefficient, where A_1 and A_2 mean the absorbance of sample 1 and 2 respectively and l_1 and l_2 mean thickness of sample 1 and 2.

Some of absorption spectra of glasses with various contents of iron oxide prepared under air or Ar atmosphere are shown in Fig. 3. It is to be noted that, in proportion to iron oxide content, the intensity of the absorption at high frequency and of the absorption near 10000 and 5000 cm^{-1} becomes high irrespective of the atmosphere of the preparation. Glass samples containing the same amount of iron oxide show stronger absorption at high frequency of sample when prepared under the atmosphere of Ar rather than air. This is especially true at high iron content.

The spectra of glass samples with $x=0.05$ prepared under various melting condition were compared in Fig. 4. The sample glasses C-1, C-2 and C-3 were prepared as follows. After they were prepared by melting first in the air atmosphere for 90 minutes, they were melted again under Ar atmosphere for 5, 15, 30 min respectively. The absorptions in a higher region over 10000 cm^{-1} and near 5000 cm^{-1} increase with increasing ratio of $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$, although the behavior of the absorption band becomes obscure due to the increasing tail of the ultraviolet absorption.

The spectrum of the glass sample with a low content of iron oxide has been ordinarily analyzed assuming the Gaussian profile for absorption bands of the d-d transition and the exponential approximation for the tail from ultraviolet absorption⁽⁹⁾. We attempted to apply this

Fig. 3 Absorption spectra of $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + x\text{Fe}_3\text{O}_4$ ($x=0 \sim 0.105$) glasses prepared under air or Ar atmosphere condition.

Fig. 4 Absorption spectra for $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + 0.05\text{Fe}_3\text{O}_4$ glasses prepared under various melting condition. (see text.)

Fig. 5 Logarithm absorption coefficient vs. wavenumber for $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + x\text{Fe}_3\text{O}_4$ ($x=0 \sim 0.05$) glasses prepared under air atmosphere.

method to the spectrum analysis, and the following procedure was employed. At first, the profile of the glass sample with Fe_3O_4 ($x=0.002$) was deconvoluted. A logarithm of absorption coefficients was plotted against the absorption energy in a high frequency range (Fig. 5). The tail from ultraviolet absorption was approximated by this linear lines and subtracted from the observed intensity curve. Then, four absorption bands (B, C, D, E) were obtained. The example of sample B-2 is shown in Fig. 6. The obtained band positions and half widths at half maximum are listed in Table. 2.

Other examples of $x=0.05$ are shown in Figs. 7(a) and (b). Figure 7(a) shows how the tail part shifts with the preparation conditions, i.e. $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$. Four absorp-

Fig. 6 Absorption spectrum of B-2 glass with a exponential tail and four Gaussian functions.

tion bands in Fig. 7(b) were obtained by referring to those of the glass (with $x=0.002$) melted under Ar atmosphere. The positions of bands B, C, and D were assumed to remain the same as in sample B-2. The position of band E is listed in Table 3. The intensities of absorption bands B, C, D and E are plotted versus Fe^{2+} ion content in Fig. 8. The intensities of the four absorption bands increase with Fe^{2+} ion content.

IV. Discussion

1. Assignment of bands B, C and D

It is well known that the absorption observed in the near infrared region can be attributed to excitation of the Fe^{2+} ion. The two main absorption bands near 1000 nm (10000 cm^{-1}) and 2000 nm (5000 cm^{-1}) were interpreted by the ligand field theory. Thus, the former band is attributed to the transition from ${}^5\text{T}_{2g}$ to ${}^5\text{E}_g$ of octahedrally

Fig. 7 Absorption spectra for $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + 0.05\text{Fe}_3\text{O}_4$ glasses prepared under various melting condition. (see Fig. 4). (a) Parts of the exponential tail. (b) Parts of spectra whose exponential tails were subtracted.

Table 2 The Gaussian function parameter of absorption bands B, C and D.

Band Band position	D 10050 cm^{-1}		C 7450 cm^{-1}		B 4950 cm^{-1}	
	Intensity cm^{-1}	HFHM* cm^{-1}	Intensity cm^{-1}	HFHM* cm^{-1}	Intensity cm^{-1}	HFHM* cm^{-1}
A-2 0.002(Air)	0.3	2700	0.045	1300	0.11	1150
B-2 0.002(Ar)	1.6	2700	0.30	1300	0.65	1150
A-3 0.01 (Air)	1.2	2600	0.21	1200	0.70	1150
B-3 0.01 (Ar)	6.7	2600	0.77	1200	2	1150
A-4 0.05 (Air)	11	2600	0	1200	2.6	1150
C-1 0.05 (Ar5)	12	2600	0	1200	2.9	1150
C-2 0.05 (Ar15)	20	2600	0.40	1200	5.0	1150
C-3 0.05 (Air90)	27	2600	2.0	1200	7.2	1150
B-4 0.05 (Ar)	50	2600	4.0	1200	16	1150

*Half width at half maximum.

Table 3 The Gaussian parameter of the band E.

Sample No.	$\nu_{\max}$ (cm^{-1})	$\Delta_{1/2}$ (cm^{-1})	Intensity (cm^{-1})	$\Delta_{1/2}^2/2240$ (cm^{-1})
A-2 0.002(Air)	14550	5040	0.16	11600
B-2 0.002(Ar)	14200	4250	0.50	9900
A-3 0.01 (Air)	14700	5400	0.62	13500
B-3 0.01 (Ar)	14200	5160	3.2	13000
A-4 0.05 (Air)	14700	5700	16	14500
C-1 0.05 (Ar5)	14600	5700	17	14500
C-2 0.05 (Ar15)	14600	5600	25	14500
C-3 0.05 (Ar30)	14400	5580	33	14000

Fig. 8 Intensity of absorption coefficient vs. Fe^{2+} ion concentration as for bands B, C, D and E of $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + 0.05\text{Fe}_3\text{O}_4$ glasses.

coordinated Fe^{2+} ^{(4)(7)(10)–(14)}. The latter has been assigned in two ways, i.e., the transition from ${}^5\text{E}_g$ to ${}^5\text{T}_{2g}$ of tetrahedral Fe^{2+} spices⁽⁴⁾⁽⁷⁾⁽¹⁰⁾⁽¹¹⁾ or the transition of the distorted octahedral Fe^{2+} spices^{(12)–(14)}. The absorption splitting caused by the dynamic Jahn-Teller effect and by the octahedral distortion have been observed in aqueous solution and in some crystals containing Fe^{2+} ion. Nolet⁽⁴⁾ concluded that the absorption near 5000 cm^{-1} should be assigned to the d-d transition of Fe^{2+} in tetrahedral coordination from absorption measurements at different temperature and the asymmetry at 10000 cm^{-1} was caused by the dynamic Jahn-Teller effect. The band profile at 10000 cm^{-1} in our result also shows some asymmetry and two Gaussian components were separated out (Fig. 6).

Ades *et al.*⁽¹⁰⁾ carried out convolution of the spectrum of soda lime silica glass containing ferrous and ferric ions by the Gaussian profiles. The positions of absorption band of our result are similar to their result in the near infrared region. However, they did not assign the band near 7500 cm^{-1} which corresponds to the band C in our result and suggested only the possibility of the vibronic transition $\text{Fe}^{2+}\text{--OH}$ group or a spin forbidden d-d transi-

tion of Fe^{2+} . The possibility of splitting by the dynamic Jahn-Teller effect was not mentioned.

In accordance with the result of Nolet⁽⁴⁾, bands B and D were attributed to the d-d transitions of tetrahedral Fe^{2+} and of octahedral Fe^{2+} respectively. The band C was assigned to the absorption induced by the dynamic Jahn-Teller effect.

The intensities of these absorption bands in spectra of glass samples with $x=0.05$ also increased linearly with Fe^{2+} ion concentration. Even in the high concentration region of iron oxides these band seems to be attributable to the transition in levels isolated in the Fe^{2+} ion.

2. Assignment of band E

In accordance with the previous optical study of oxide glasses containing low content of iron oxide, the absorption band near 14000 cm^{-1} was attributed to the transition of ${}^6\text{A}_{1g}$ to ${}^4\text{T}_{1g}$ of octahedrally coordinated Fe^{3+} . However, in the course of band assignment, it was more plausible to assume an additional absorption band, which is called band E. Its intensity increase with Fe^{2+} content and more intense than band D.

As for the origin of band E, we assumed an absorption of the intervalence charge transfer transition from Fe^{2+} to Fe^{3+} which has been observed in some crystals containing Fe^{2+} and Fe^{3+} . This absorption of intervalence charge transfer transition is observed in the region from 10000 to 18000 cm^{-1} ⁽¹⁵⁾ and its intensity depends on the concentration of the less abundant cation of Fe^{2+} or Fe^{3+} . There is found the edge shared or face shared octahedral structure of Fe^{2+} and Fe^{3+} ions in the crystal in which this band is observed.

The position of E band were observed near 14500 cm^{-1} independent of the ratio of $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ and its absorption increased with the Fe^{2+} ion concentration. On the other hand Hush⁽¹⁶⁾ suggested that the correlation between the frequency of absorption energy (wave number) and full width at half maximum ($\Delta_{1/2}$) of the intervalence charge transfer band at 298 K is described as follows:

$$\nu = \frac{\Delta_{1/2}^2}{2240}. \quad (1)$$

As shown in Table 3, this correlation were consistent in the present peak E.

In this way the E absorption band was attributed to an intervalence charge transfer between Fe^{2+} and Fe^{3+} , judged from the absorption energy and intensity, the dependence of intensity on the concentration of Fe^{2+} and the relation between its absorption energy and its width at half maximum height. This kind of band becomes popular when the solute content is increased since the band becomes more intense due to the increasing chance of the ions to approach each other.

3. Behavior of the tail of absorption A

The strong absorption in the ultraviolet region could be attributed to the charge transfer transition from O^{2-} to Fe^{3+} or Fe^{2+} ions or the transition from $6s$ to $6p$ in the lead ion in the lead silicate glass containing iron oxide.

Fig. 9 Variation of wavenumber at $\alpha/[\text{Fe}^{3+}]=100$ as a function of $[\text{Fe}^{2+}]/[\text{Fe}_{\text{tot}}]$ for tail A for $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + 0.05\text{Fe}_3\text{O}_4$ glasses prepared under various melting condition. (see Fig. 4.) α : absorption coefficient.

However, the absorption of tail A appears only when iron oxide is added to the sample and becomes intense in the low frequency region with increasing iron oxide content. It is also found from chemical analysis of such glasses that Fe^{3+} ions are present more often than Fe^{2+} ions, even the glasses were prepared under the Ar atmosphere. The absorption energy of charge transfer from oxygen to Fe^{3+} and Fe^{2+} ions in sodium silicate and borate were reported by Steele and Douglas⁽⁹⁾. They showed that the absorption energy of charge transfer of Fe^{2+} was higher than that of Fe^{3+} . Thus, absorption A were tentatively attributed to the charge transfer from oxygen to Fe^{3+} ions.

The intensity of the tail of A increases with increasing ratio of $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ for the sample glass of high iron oxide content ($x=0.05$) (Fig. 7(a)). In order to find the factor to cause the red shift of the tail A, the absorption coefficient per unit concentration of Fe^{3+} ion was evaluated. Then, the wave number at the intensity of 100 were plotted against the ratio of $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ (Fig. 9). Its wave number decreased with increasing ratio. This result suggests that the increase of the absorption coefficient is caused not by the increasing intensity of absorption A but by the shift to a lower frequency of absorption A. This shift indicates that the local structure of iron ions becomes favorable to the charge transfer as is observed in some minerals in which the edge-shared or face-shared octahedral Fe^{2+} and Fe^{3+} exist. The electronic state of Fe^{3+}

ions in the covalent bond with its neighboring oxygen atoms may change so as to give rise to the shift to a lower energy with increasing concentration of Fe^{2+} . However, the origin of this shift is not yet fully understood in this study.

V. Conclusions

- (1) Silicate glasses of $0.5\text{PbO} \cdot 0.5\text{SiO}_2 + x\text{Fe}_3\text{O}_4$ (x , 0–0.1) were studied as for the optical absorption in order to elucidate their electronic states of Fe^{2+} and Fe^{3+} ions.
- (2) The tail of huge absorption of UV range shifts to the visible range with increasing Fe oxide content.
- (3) A new absorption centered around 14500 cm^{-1} was found beside ordinary spectra due to the d-d forbidden transition.
- (4) These absorption in correlation to Fe^{2+} ion content indicate the Fe^{2+} – Fe^{3+} interaction including the charge transfer through O^{2-} ion and suggest important optical and electronic characters of silicate glasses heavily doped with transition metal oxides.

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