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State of sulphur and Iron-Sulphur Interaction in Soda Silicate Glasses †

Nobuya IWAMOTO*, Yukio MAKINO** and Taisuke NISHIMURA***

Abstract

State of sulphur and interaction between sulphur and iron ions in soda silicate glasses were investigated by optical absorption, electron spin resonance (ESR) and S $K\alpha$ emission spectroscopies. An absorption was observed near 24000 cm^{-1} in the optical absorption spectra of the glasses produced in the moderately ($P_{O_2} = 10^{-5.1}\text{ atm.}$) and strongly ($P_{O_2} = 10^{-6.7}\text{ atm.}$) reducing atmospheres. From ESR measurement, the increase of the absorption near $g=6.0$, which suggests the formation of $Fe^{3+}-S^{2-}$ bond, was observed in the glasses with sulphur and iron which were produced in the strongly reducing atmosphere. Chemical shift study in S $K\alpha$ emission X-ray spectra supported that sulphur in soda silicate glass was in the form of S^{6+} in oxidizing condition (in air) and in the mixed state of S^0 and S^{6+} in the strongly reducing condition. From these results, it was suggested that polysulphide ion such as S_2^- ion was formed in soda silicate glass as intermediate stage. Further, it was indicated that iron ion group coordinated with sulphur such as $Fe^{3+}O_5S$, $Fe^{3+}O_4S_2$ or $Fe^{3+}O_3S$ was formed in soda silicate glasses produced in the strongly reducing condition.

KEY WORDS: (State Analysis) (Sulphur) (Iron-Sulphur Interaction) (Slag)

1. Introduction

Although it is important to utilize a large amount of slag from the standpoint of saving materials, yellow water originated from sulphur in slag is one of the most troublesome problem in the utilization of blast furnace slag. In the previous paper¹⁾, we investigated the state of sulphur in a synthetic blast furnace slag using optical absorption, ESR and S $K\alpha$ emission X-ray spectroscopies. Further, the existence of the interaction between ferric and divalent sulphur ions was suggested. However, it is necessary to investigate state of sulphur in a simple oxide slag in order to make its state in slag more clear.

In glass technology, it is well-known that some glasses containing sulphur take various colors such as blue, yellow and green²⁾. Further, some investigators reported that there exists the interaction between ferric and divalent sulphur ions in soda and potash silicate glasses by optical absorption method^{3),4)}. In this study, soda silicate glass was selected as parent slag in order to compare with these previous results and to obtain fundamental information on sulphur in a simple oxide slag. The wide glassy region in soda silicate and the inclusion of small amount of alkaline oxides in practical blast furnace slag become also important reasons in selecting soda silicate glass as parent slag. In iron- and steel-making, it is noteworthy to obtain fundamental information on the interaction between iron and sulphur ions in a simple oxide slag because state of sulphur in slag is closely related to yellow water and

desulphurization of molten iron. Therefore, in this study, state of sulphur and iron-sulphur interaction in soda silicate glass were investigated by optical absorption, ESR and S $K\alpha$ emission X-ray spectroscopies.

2. Experimental Procedures

Reagent grade SiO_2 , Na_2CO_3 , Na_2SO_4 and Fe_2O_3 were used for preparing specimen glasses. These reagents were accurately weighed at the desired ratio and mixed in an agate mortar and pestle. As immersion liquid, acetone was used in the mixing. After drying enough, these mixtures with desired compositions were melted at 1600°C for 1 hr in an electric furnace. The mixtures with $Na_2O/SiO_2 = 1/9$ were melted at 1700°C . For each melting, platinum crucible was used and partial oxygen pressure of each atmosphere was controlled by using CO/CO₂ mixed gas. All specimens were taken out in the top of the furnace and cooled in air or CO/CO₂ mixed gas. In this study, partial sulphur pressure was not controlled because state of sulphur and iron-sulphur interested. The specimen glasses for optical absorption interested. The specimen glasses for optical absorption measurement were polished with emery paper (from No.80 to No.1500) and buffed using aluminas which particle sizes were $5\ \mu$ to $0.5\ \mu$. The specimens for ESR measurement were prepared by pulverizing each glass in an agate mortar and sealing in an evacuated silica tube. The

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conditions of optical absorption, ESR and chemical shift study of S $K\alpha$ emission X-ray were as follows;

Optical Absorption

Specimen Shape: Circular Disk,
Wave Number: $400\text{ cm}^{-1} - 4000\text{ cm}^{-1}$,

ESR

Specimen Shape: powder, Method: X-band,
Field Range: $0 - 7000$ gauss,
Modulation Field and Frequency: 20 gauss and 100 kHz,

Chemical Shift Study of S $K\alpha$ Emission X-ray

Target: Rh, Crystal: Ge (111),
Current and Voltage: $50\text{ kV} \times 40\text{ mA}$,
Standard Material: Elemental Sulphur,
Method: Fixed Time Method (80 sec).

Sulphur content of each slag was analyzed using Sulphur/Carbon determinator(LECO Co. Ltd.).

3. Experimental Results

1) Optical absorption measurement

First of all, absorption spectra of soda silicate glasses with sulphur were measured. The result is shown in

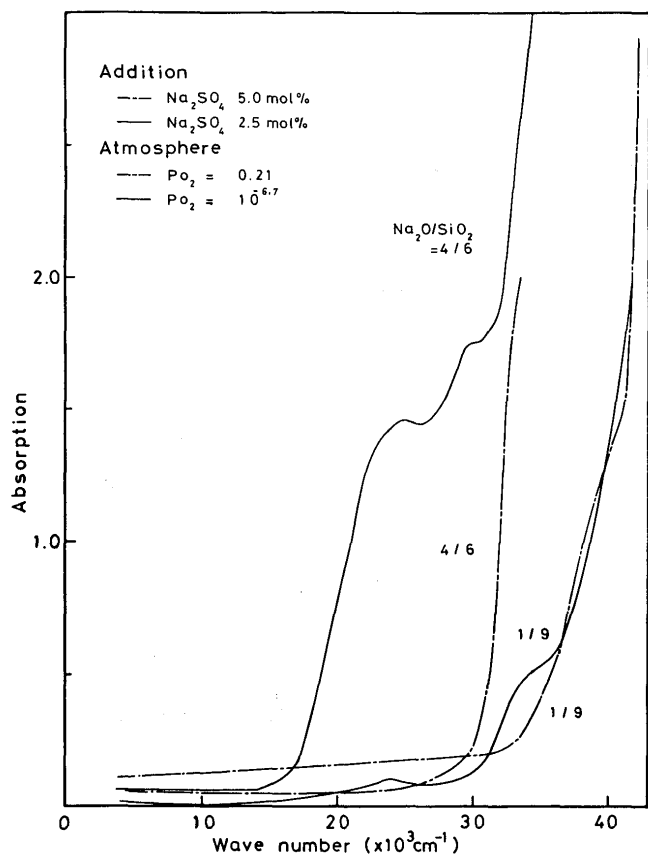


Fig. 1 Optical absorption spectra of soda silicate glasses containing sulphur (see Table 2)

Fig. 1. Any absorption was not observed in the spectra of the glasses produced in air except the absorption due to charge transfer. On the other hand, a shoulder was observed near 24000 cm^{-1} in the glasses produced in the atmosphere with $P_{\text{O}_2} = 10^{-6.7}$ atm.. The intensity of the absorption depended on $\text{Na}_2\text{O}/\text{SiO}_2$ ratio. Another shoulder was observed near 30000 cm^{-1} to 34000 cm^{-1} .

Subsequently, absorption spectra of soda silicate with iron and sulphur were measured. In these glasses, the dependences of absorption spectra upon $\text{Na}_2\text{O}/\text{SiO}_2$ ratio and partial oxygen pressure were examined. These results are shown in Figs. 2, 3 and 4. In the glasses produced in air, as shown in Fig. 2, an absorption was observed near 10000 cm^{-1} . In the glasses produced in the atmospheres with $P_{\text{O}_2} = 10^{-5.1}$ atm. and $P_{\text{O}_2} = 10^{-6.7}$ atm., another strong absorption was observed near 24000 cm^{-1} irrespective of $\text{Na}_2\text{O}/\text{SiO}_2$ ratio. The result in the glasses produced in the atmosphere with $P_{\text{O}_2} = 10^{-5.1}$ atm. were not shown because it was similar to the result in the glasses produced in the atmosphere with $P_{\text{O}_2} = 10^{-6.7}$ atm. except the difference of intensity. The dependence of the spectra $20\text{Na}_2\text{O}\cdot 80\text{SiO}_2$ glasses with iron and sulphur upon partial oxygen pressure are shown in Fig. 4. The absorption near 24000 cm^{-1} seems to appear when partial oxygen pressure becomes lower than about 10^{-3} atm. or so.

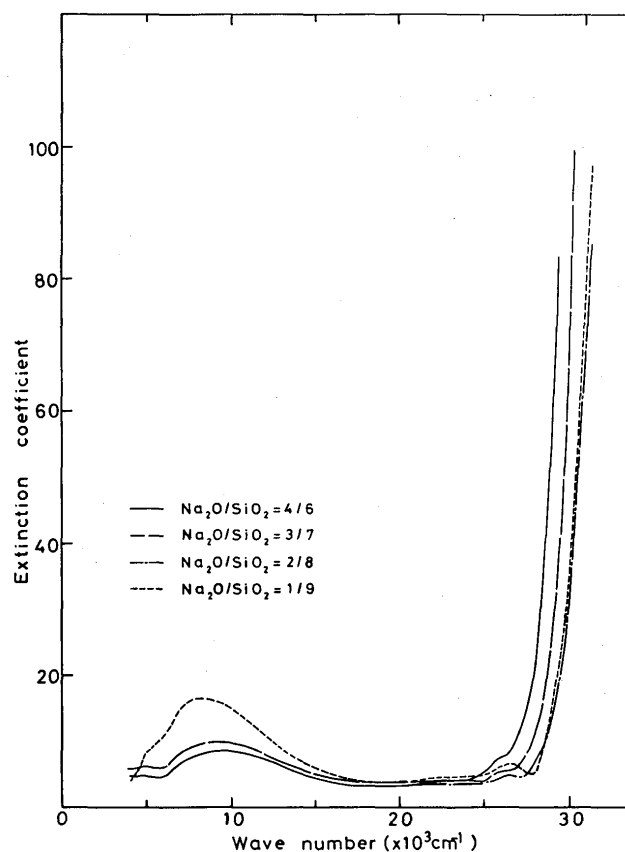


Fig. 2 Optical absorption spectra of soda silicate glasses containing sulphur and iron produced in air (see Table 2)

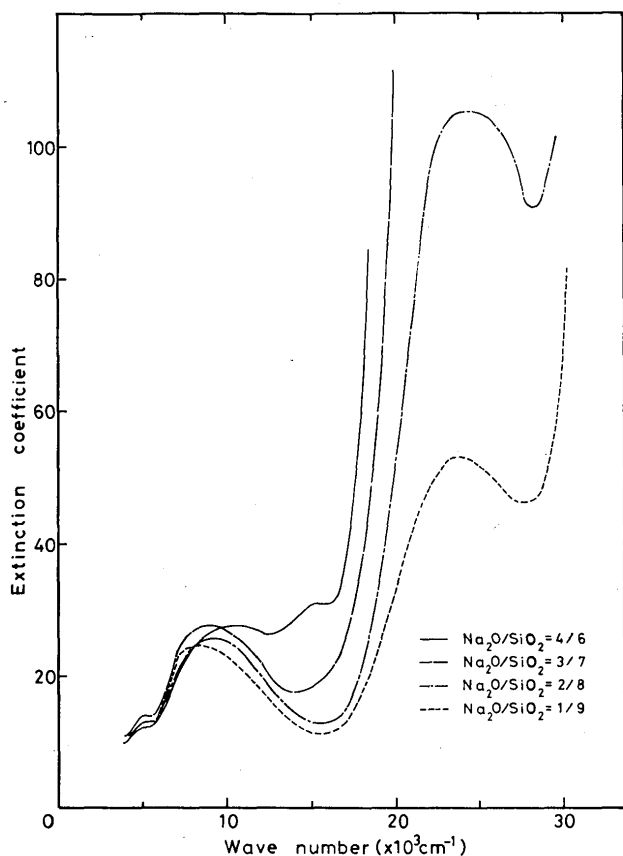


Fig. 3 Optical absorption spectra of soda silicate glasses containing sulphur and iron produced in the CO/CO₂ mixed gas with P_{O₂} = 10^{-6.7} atm..

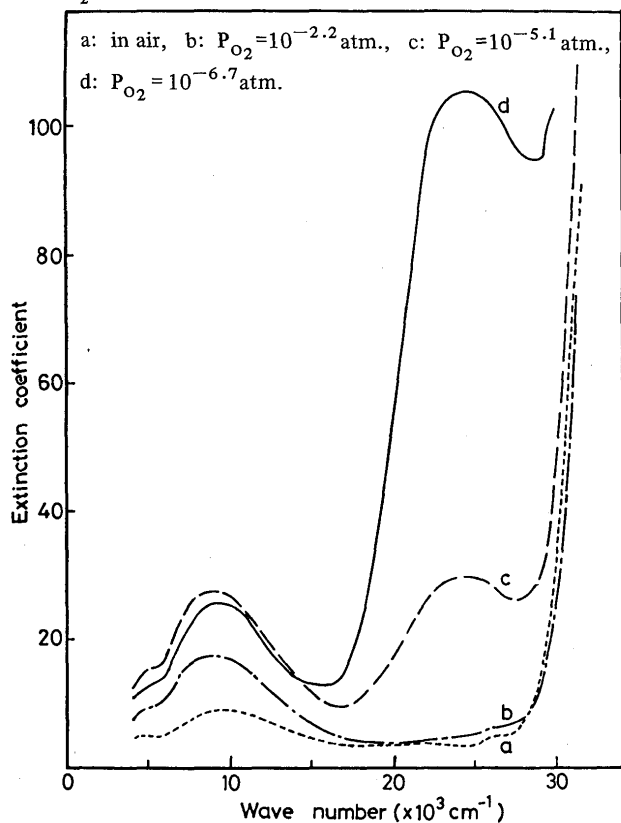


Fig. 4 Dependence of optical absorption spectra upon partial oxygen pressure in the 20Na₂O·80SiO₂ glasses with sulphur and iron.

2) ESR measurement

ESR spectra of soda silicate glasses containing iron which were produced in air are shown in Fig. 5. A sharp and strong absorption was observed near g= 4.3 and two weak and broad absorptions were observed near g= 2.0 and g= 6.0, respectively. These absorptions showed a almost same patterns irrespective of Na₂O/SiO₂ ratio. However, the intensity ratio of the absorption near g= 2.0 to that near g= 4.3, though qualitatively, increased with increasing SiO₂ content.

Subsequently, ESR spectra of soda silicate glasses with iron and sulphur were measured at room temperature. The result are shown in Figs. 6, 7 and 8. In this experiment, partial oxygen pressure and Na₂O/SiO₂ ratio were also selected as parameters. The spectra of soda silicate

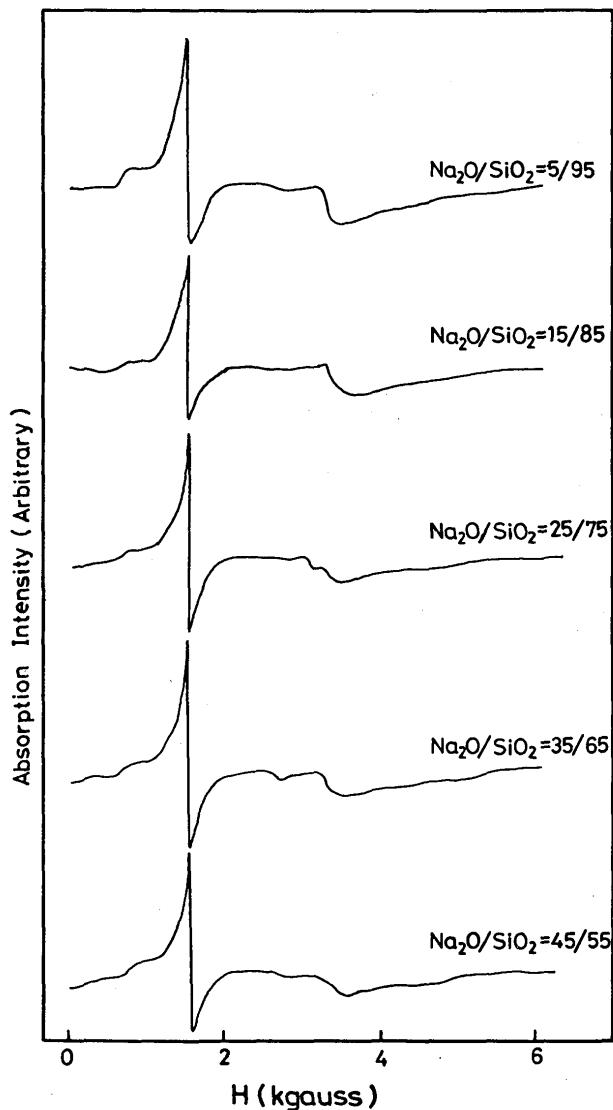


Fig. 5 ESR spectra of soda silicate glasses with iron and no sulphur produced in air.

glasses produced in the atmosphere with $P_{O_2} = 10^{-5.1}$ atm. were, as shown in Fig. 7, similar to those in the glasses produced in the oxidizing condition. As shown in Fig. 6, no change was observed in the spectra of soda silicate glasses produced in air. In the spectra of soda silicate glasses produced in the atmosphere with $P_{O_2} = 10^{-6.7}$ atm., the intensity of the absorption near $g=6.0$ increased except the glass with $Na_2O/SiO_2 = 10/90$. In the glass with $Na_2O/SiO_2=10/90$, the pattern of the spectrum changed entirely and the absorption near

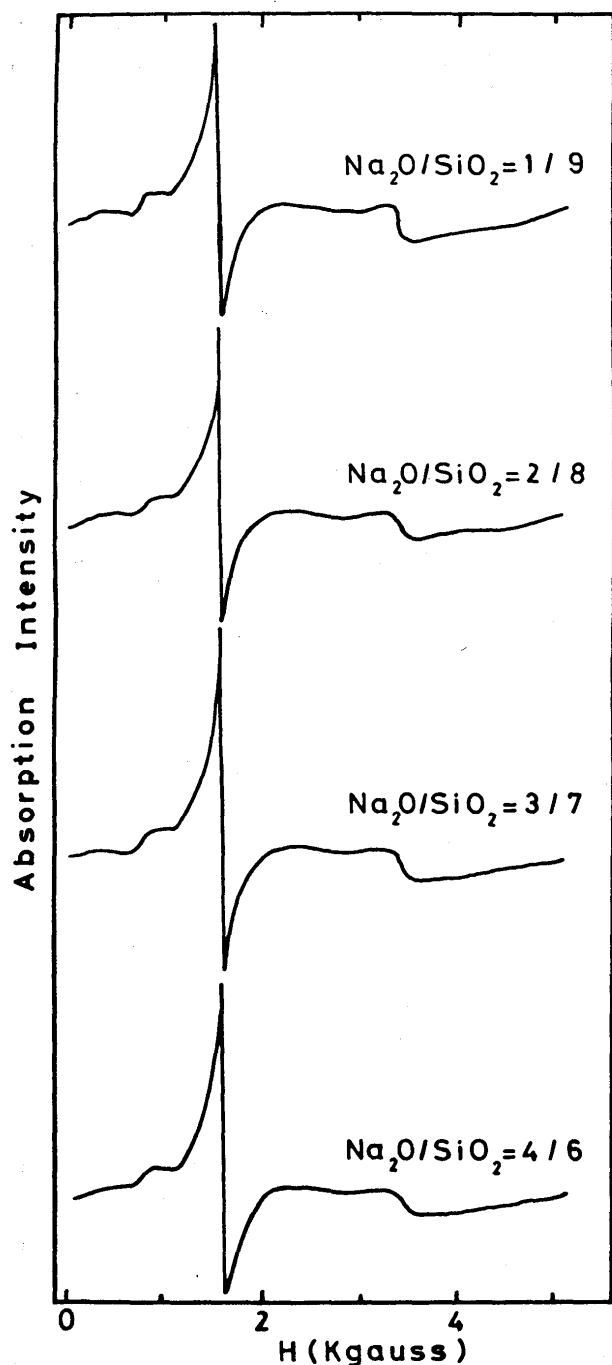


Fig. 6 ESR spectra of soda silicate glasses with iron and sulphur produced in air.

$g=6.0$ disappeared. Besides, the absorption near $g=2.0$ became complicated and its intensity increased. Furthermore, the intensity of the absorption near $g=4.3$ decreased. In the glasses with Na_2O/SiO_2 ratio of 20/80 to 30/70, very weak absorptions were observed near $g=2.3$. In order to examine whether these absorptions were noise or not, ESR absorption spectra were measured at $77^\circ K$ in several glasses. The result, though not illustrated, seems to support the existence of these weak absorptions.

3) Chemical shift measurement in S $K\alpha$ emission X-ray spectrum

S $K\alpha$ emission X-ray spectra of the several glasses with iron and sulphur are shown in Fig. 9. The peak positions of these glasses measured at half value width are also shown in Table 1. Chemical shift in S $K\alpha$ emission X-ray spectrum was largely dependent upon partial oxygen

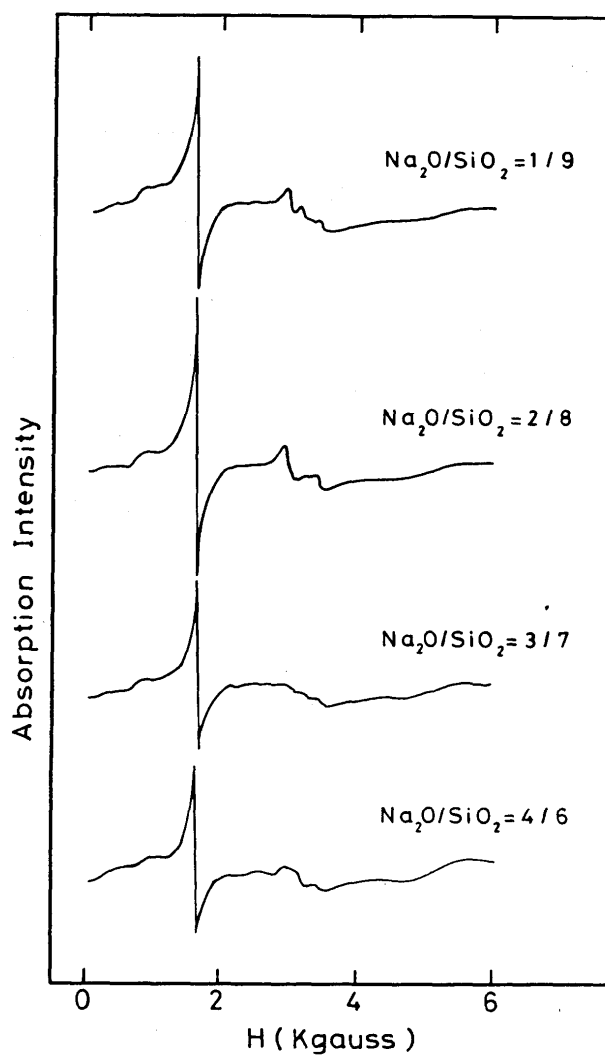


Fig. 7 ESR spectra of soda silicate glasses with iron and sulphur produced in the CO/CO_2 mixed gas with $P_{O_2} = 10^{-5.1}$ atm..

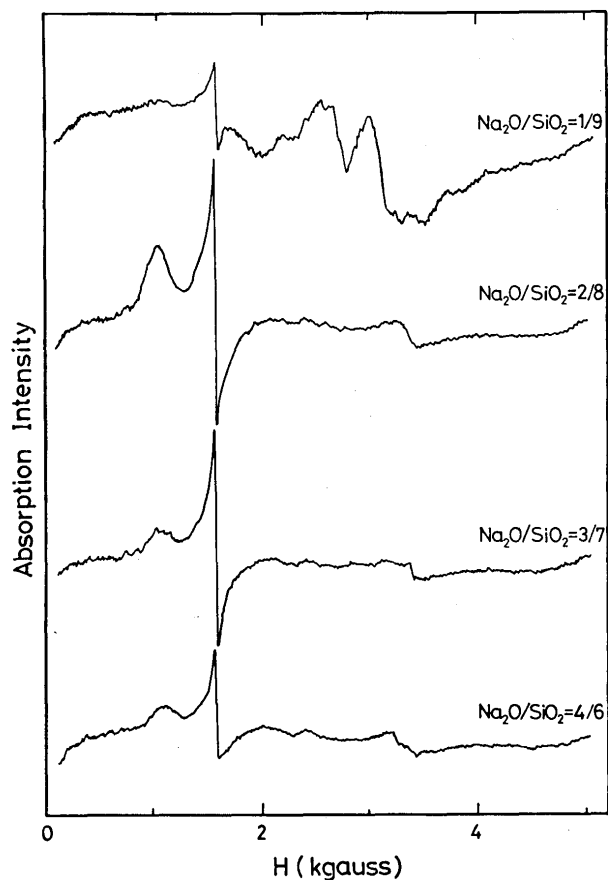


Fig. 8 ESR spectra of soda silicate glasses with iron and sulphur produced in the CO/CO₂ mixed gas with P_{O₂} = 10^{-6.7} atm..

pressure but scarcely upon glass composition. The chemical shift values in the glasses produced in air were almost similar to that in CaSO₄ whereas the values of chemical shift in the glasses produced in the CO/CO₂

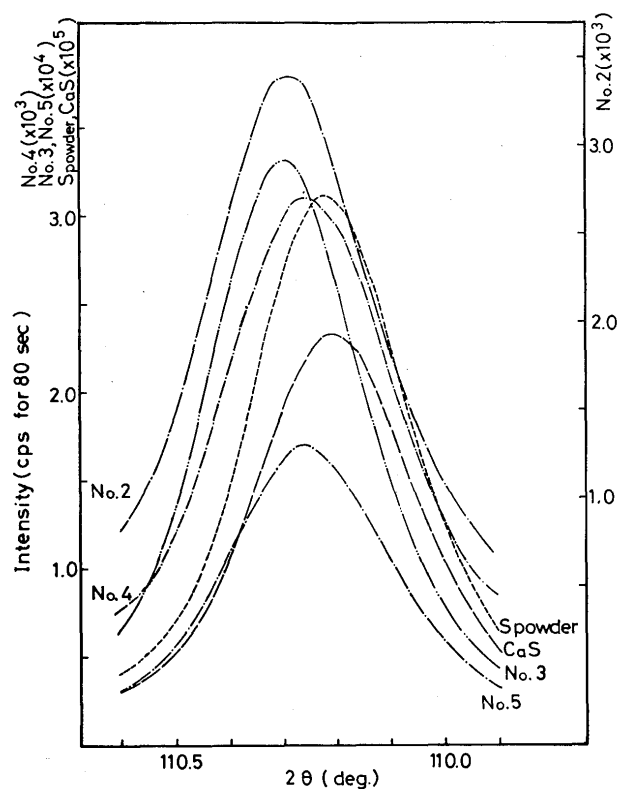


Fig. 9 S K α emission X-ray spectra of soda silicate glasses with iron and sulphur (Specimen compositions are shown in Table 1.)

mixed gas with P_{O₂} = 10^{-6.7} atm. lay between those in elemental sulphur and CaSO₄.

4) Analysis of sulphur content

The analytical value of sulphur content in soda silicate glasses were shown in Table 2. The substantial content of sulphur decreased with increasing silica content in glass.

Table 1 Chemical shift values of S K α emission X-ray in soda silicate glasses with iron and sulphur.

Specimen	Peak position of S K α ($^{\circ}2\theta$)	$\Delta^{\circ}2\theta$	Remark
CaSO ₄	110.703	-0.085	
Elemental sulphur	110.788	0.000	
CaS	110.799	0.011	
No. 1	110.698	-0.090	Na ₂ O/SiO ₂ = 1/9, Na ₂ SO ₄ = 5.0 mol% Fe ₂ O ₃ = 0.2 mol%, P _{O₂} = 0.21 atm
No. 2	110.708	-0.080	Na ₂ O/SiO ₂ = 4/6, Na ₂ SO ₄ = 5.0 mol% Fe ₂ O ₃ = 0.2 mol%, P _{O₂} = 0.21 atm
No. 3	110.751	-0.037	Na ₂ O/SiO ₂ = 1/9, Na ₂ SO ₄ = 2.0 mol% Fe ₂ O ₃ = 0.2 mol%, P _{O₂} = 10 ^{-6.7} atm
No. 4	110.749	-0.039	Na ₂ O/SiO ₂ = 4/6, Na ₂ SO ₄ = 2.0 mol% Fe ₂ O ₃ = 0.2 mol%, P _{O₂} = 10 ^{-6.7} atm

Table 2 Substantial contents of sulphur in soda silicate glasses.

Partial oxygen pressure	Initial additive content			Sulphur content
	Na ₂ O/SiO ₂	Na ₂ SO ₄	Fe ₂ O ₃	
0.21 (atm)	10/90	5.0 mol%	0.0 mol%	0.02 wt%
	40/60	5.0	0.0	0.34
	10/90	5.0	0.2	0.02
	20/80	5.0	0.2	0.16
	30/70	5.0	0.2	0.14
10 ^{-5.1}	40/60	5.0	0.2	0.34
	10/90	2.0	0.2	0.02
	20/80	2.0	0.2	0.06
	30/70	2.0	0.2	0.14
10 ^{-6.7}	40/60	2.0	0.2	0.04
	10/90	2.5	0.0	0.04
	40/60	2.5	0.0	0.18
	10/90	2.0	0.2	0.02
	20/80	2.0	0.2	0.10
	30/70	2.0	0.2	0.07
	40/60	2.0	0.2	0.20

4. Discussion

As shown in Figs. 1 to 4, from the fact that the absorption was observed near 24000 cm⁻¹ as shoulder or a peak in soda silicate glasses with or without iron, it can be considered that the absorption is originated from a sulphur compound or ion group containing sulphur and iron. Paul et al. have investigated the state of sulphur in soda borate glass using optical absorption method⁵). According to their result, two absorptions were observed at 17000 cm⁻¹ and 24000 cm⁻¹ and they explained that the former absorption could be attributed to S₂⁻ ion. However, the assignment of the latter absorption remained unclear. Bamford observed three absorptions at 0.41 μ (24400 cm⁻¹), 0.36 μ (27800 cm⁻¹) and 0.29 μ (34500 cm⁻¹) in several soda glasses containing sulphur and iron⁴). He considered that these absorptions might be originated from sulphide and/or polysulphide ions.

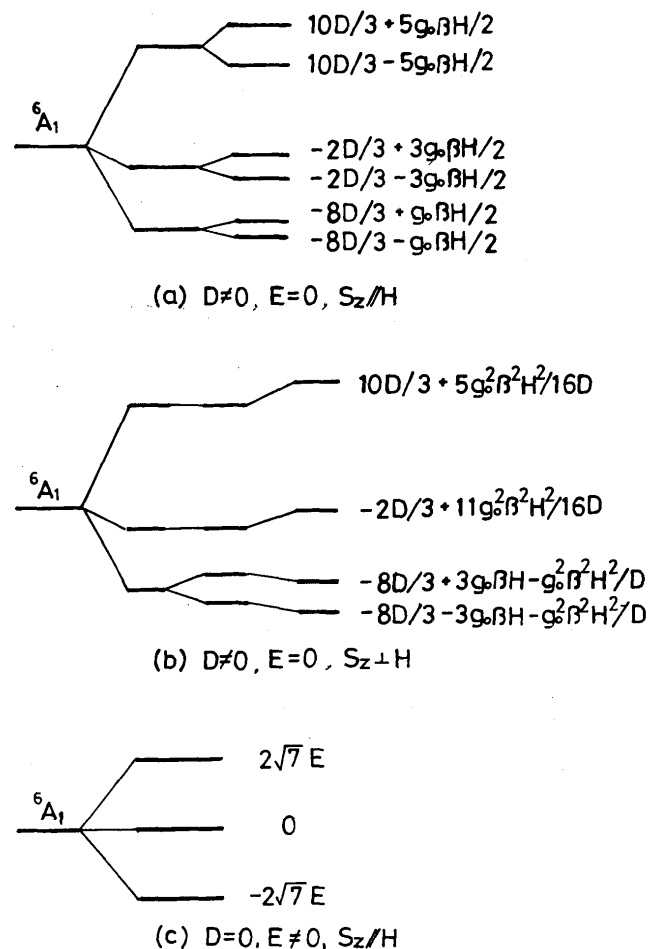
Taking these previous results into account, it is reasonable to consider that the absorption near 24000 cm⁻¹ could be attributed to polysulphide ions consisting of no more than several sulphurs. Further, most probable polysulphide ion may be S₂⁻ ion as indicated in borate glasses⁵) because polysulphide ions consisting of more than several sulphurs would be unstable at high temperature. If one considers the molecular orbital of S₂⁻ ion^{5),6)}, it seems reasonable to assign the absorption near 24000 cm⁻¹ to the transition 3pπ → 3pπ*.

ESR absorption due to Fe³⁺ ion in glass was firstly reported by Sands⁷⁾ and three absorptions due to Fe³⁺

ion in Na₂O-CaO-SiO₂ glass were theoretically explained by Castner et al.⁸⁾. According to their result, three absorptions were observed at g=2.0(broad), g=4.27(sharp) and g=6.0(broad). They considered that the absorptions at g=4.27 and g=6.0 were originated from Fe³⁺ ions occupying tetrahedral sites with orthorhombic and axial symmetrical fields, respectively. It was also explained that the absorption at g=2.0 could be attributed to Fe³⁺ ion in a tetrahedral site with axial symmetrical or weak field. Further, no contribution of Fe³⁺ ion in an octahedral site to ESR absorption was indicated in their explanation. The last explanation seems unreasonable because both Fe³⁺ ions in an octahedral and tetrahedral sites can be in a same symmetry. Fig. 10 shows the energy diagrams calculated from the following effective spin hamiltonian;

$$H = g_0 \beta H S_z + D S_z^2 + E (S_x^2 - S_y^2)$$

where g₀, β, H, S_z, D, E, S_x, S_y and S_z are the g value for free electron, Bohr magneton, magnetic field, spin

Fig. 10 Energy diagrams of ⁶A₁ term in Fe³⁺ ion.

component along z' which is the axis of the static field H , axial and orthorhombic crystal fields and components of spin along three mutually perpendicular crystalline axes x , y and z , respectively. Loveridge and Perke discussed ESR absorption of Fe^{3+} ion in glass from the standpoint of group theory⁹⁾ and modified the result reported by Castner et al.. They indicated that ESR spectroscopy can not distinguish between Fe^{3+} ions in a tetrahedral and an octahedral sites if they have a same symmetry. Therefore, both Fe^{3+} ions in a tetrahedral and an octahedral sites could give an absorption at the same position. Thus, it is questionable whether the coordination of Fe^{3+} ion can be distinguished by ESR spectroscopy. However, information about symmetry around Fe^{3+} ion can be identified using ESR.

As shown in Fig. 6, it was concluded that Fe^{3+} ion did not interact with sulphur in the glasses produced in air and the state of sulphur in these glasses was almost similar to that in the glasses with iron and no sulphur (as shown in Fig. 5). That is, most of Fe^{3+} ions were found to occupy orthorhombic symmetrical sites and a small number of Fe^{3+} ions were in axial symmetrical sites. Further, the increase of the intensity of the absorption near $g=6.0$ shows the increase of Fe^{3+} ion groups with C_{4v} , C_{3v} and D_{4h} symmetry. In other words, this explanation suggests the occurrence of $Fe^{3+}-S^{2-}$ interaction. According to Loveridge and Parke, the formation of ion groups such as $Fe^{3+}O_5S$, $Fe^{3+}O_4S_2$ and $Fe^{3+}O_3S$ can be acceptable. It is natural to consider that one or two sulphur coordinates with ferric ion because substantial content of sulphur is very small (see Table 2) and polysulphide ions will be easily formed in soda silicate glasses. Furthermore, the intensity of the absorption near $g=6.0$ did not raise in the glasses produced in the atmosphere with $P_{O_2} = 10^{-5.1}$ atm., so that ferric ion groups with divalent sulphur seem to be formed in the vicinity of $P_{O_2} = 10^{-6.0}$ atm. although the very weak absorption near $g=2.3$ were observed at 77°K, detailed investigation

on the absorption are required on account of the weakness.

From chemical shift study of S $K\alpha$ emission X-ray, sulphur in the glasses produced in air was identified as being in the form of S^{6+} ion. Further, the mixed state of S^0 and S^{6+} ion was suggested in the glasses produced in the CO/CO₂ mixed gas with $P_{O_2} = 10^{-6.7}$ atm.. However, considering ESR results in these glasses, a small amount of S^{2-} ions must be considered. The existence of S^{6+} ion is likely to be due to no control of partial sulphur pressure. In the previous paper¹⁾, it was suggested that sulphur in a blast furnace slag, which were produced in the CO/CO₂ mixed gas with about $P_{O_2} = 10^{-8.0}$ atm. identified as being in the form of S^{2-} ion. Therefore, the existence of S^{6+} ion does not relate to adding sulphur in the form of sulphate. Conclusively, it would be due to the fact that sulphur of higher valence state becomes more stable in soda silicate glasses compared with that in a synthetic blast furnace slag.

5. Summary

State of sulphur and iron-sulphur interaction in soda silicate glass were investigated by optical absorption, ESR and S $K\alpha$ emission X-ray spectroscopies. An absorption was observed near 24000 cm^{-1} in the glasses produced in the reducing atmospheres with $P_{O_2} = 10^{-5.1}$ atm. and $P_{O_2} = 10^{-6.7}$ atm. except the absorption near 10000 cm^{-1} due to ferrous ion. The absorption near 24000 cm^{-1} was assigned to a polysulphide ion consisting of no more than several sulphurs. S_2^- ion was considered as the most probable polysulphide ion. From ESR results, iron-sulphur interaction was suggested from the increase of the absorption near $g=6.0$ in the glasses produced in the strongly reducing atmosphere with $P_{O_2} = 10^{-6.7}$ atm.. Chemical shift study in S $K\alpha$ emission spectra indicated that sulphur in soda silicate glass was in the form of S^{6+} ion in the oxidizing atmosphere (in air) and in the mixed state of S^0 and S^{6+} ion in the strongly

Table 3 Summary of optical absorption, ESR and S $K\alpha$ emission X-ray measurements.

Method	Noticed peak	Detectable state	Partial oxygen pressure		
			0.21	$10^{-5.1}$	$10^{-6.7}$
ESR	peak near $g=6.0$	$Fe^{3+}-S^{2-}$ interaction	unchanged	unchanged	increase
Optical absorption	peak near 24000 cm^{-1}	$Fe^{3+}-S^{2-}$ interaction or polysulphide ion	undetected	detected	detected
Emission S $K\alpha$ x ray	chemical shift	valency state	S^{6+}	—	S^0 small S^{2-} and S^{6+}

reducing atmosphere. The results described above are summarized in Table 3. These results suggest that a polysulphide ion consisting of no more than several sulphurs can be formed in soda silicate glass as intermediate stage. Further, it was concluded that ferric ion interacts with divalent sulphur ion in the form of ion group such as $\text{Fe}^{3+}\text{O}_5\text{S}$, $\text{Fe}^{3+}\text{O}_4\text{S}_2$ or $\text{Fe}^{3+}\text{O}_3\text{S}$ in soda silicate glasses produced in a reducing atmosphere under the oxygen pressure of about 10^{-6} atm..

Acknowledgement

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