

Title	Structure of Slag (VIII) : Optical Properties of Slag
Author(s)	Iwamoto, Nobuya
Citation	Transactions of JWRI. 8(1) P.139-P.149
Issue Date	1979-06
Text Version	publisher
URL	http://hdl.handle.net/11094/8333
DOI	
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Structure of Slag (VIII)†

— Optical Properties of Slag—

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Abstract

Optical property measurement using IR and Raman spectroscopical mean gives powerful insight to solve structure of slag. The applications to know behavior of various components such as network-modifiers, fluorine ion, amphoteric aluminium ion and water vapor in slag were readjusted. Former uncorrect opinion, shift of absorption peak in IR spectra, was revised with Raman scattering study.

Furthermore the application to determine SiO₄ tetrahedra containing non-bridging oxygens seems fruitful.

KEY WORDS: (Slag) (Structure) (Optical Property)

1 Introduction

Molten slag is widely used for metallurgical refining not only in iron- and steel-making but also in welding, but there exists many unsolved problems to choose a suitable slag composition. Furthermore it has been necessary to have profound knowledge concerning the structure of slag which can be applied on an effective desulphurization and phosphorus elimination of molten metal with the development of atomic energy industry to use higher quality of steel.

In previous reports, the author summarized the problems on structure of slag such as basicity¹⁾, role of CaF₂ added²⁾, structural theories³⁾, behavior of amphoteric oxides⁴⁾, solubility of gases⁵⁾, diffusion behavior⁶⁾ and indicators for determining basicity⁷⁾. In this review,

results obtained by optical mean of infrared (IR) and Raman spectroscopy are readjusted and an issue is derived. Further it is discussed what information can be derived from the measurement at higher temperature.

2 IR absorption and Raman scattering studies

As have been described in many books⁸⁾⁻¹⁰⁾, IR spectroscopy was widely utilized to identify crystal structure of minerals and the related inorganic compounds. Especially Simon studied IR absorption of SiO₂ polymorphs, namely α - and β -quartz, α - and β -cristobalite, and tridymite in detail for the basis of silicate study¹¹⁾.

Simon and McMahon thought that the assignment done earlier on which concerns vibration band was unclear and

Table 1 Assignments of Vibrational Spectra of Silica¹⁵⁾

Band (cm ⁻¹)	1100	800	625	475	300
Author					
Landort-Börnstein ¹⁶⁾	F ₂ stretching	A ₁ stretching	F ₂ Bending	E Bending	
J. Etchepare ¹⁷⁾	F ₂ stretching	A ₁ stretching		F ₂ Bending	E Bending
E. R. Lippincott et al ^{18), 22)~24), 12)}	Si-O-Si stretching	Si-Si stretching		Si-O-Si Bending	
R. J. Bell et al ¹⁹⁾⁻²¹⁾	Si-O stretching	Si-O-Si stretching		Si-O-Si Rocking	

† Received on March 31, 1979

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also studied the transition behavior from crystalline to vitreous state^{12), 14)}.

In Table 1¹⁵⁾, assignments of vibrational spectra of silica are summarized from the reports by many investigators.^{16)-21), 12), 22)-24)}

2.1.1 Binary system

Simon and McMahon studied IR reflection of glasses in binary systems, and applied dispersion theory to induce the imaginary part of the complex dielectric constant^{12), 13)}. The results can be summarized as follows:

1) As for ν_3 frequency, small shift toward lower frequency can be observed for glasses in the Li_2O - and $\text{Na}_2\text{O-SiO}_2$ systems and a larger shift in the $\text{K}_2\text{O-SiO}_2$ system. They concluded that the Si-O bond force is decreased by the cationic field of the network modifier.

2) As shown in Figure 1, the potassium ion gave an anomalous effect on exceeding the critical concentration. It was assumed that the occurrence of new band at approximately 950 cm^{-1} appeared to be largely independent of the atomic mass of the network-modifying cation. It will be understood from Figure 2.

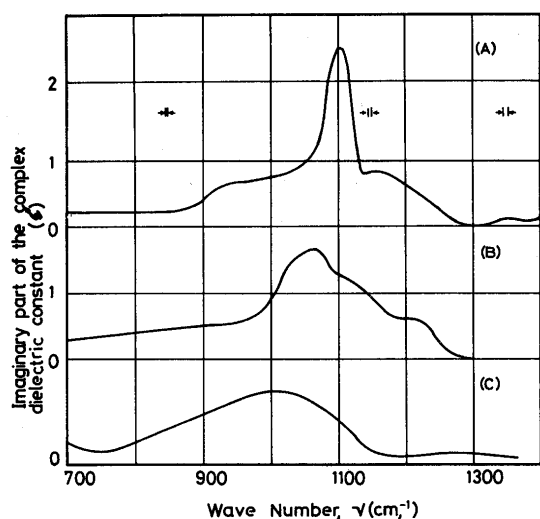


Figure 1. Plots of ϵ'' for the potash-alkali glass (A); vitreous silica, (B); 22 mol% K_2O , (C); 40 mol% K_2O ¹³⁾

Suginohara and Yanagase applied transmission IR on glasses in the binary systems such as PbO- , ZnO- , BaO- , CaO- , and $\text{Na}_2\text{O-SiO}_2$ respectively²²⁾. As an example, the variation of transmittance with the change of CaO concentration of glass in the system CaO-SiO_2 is shown in Figure 3. From the diagram, the following conclusions were derived:

1) ν_3 frequency which appears at approximately 1110 cm^{-1} for fused silica shifts to 1100 cm^{-1} with the

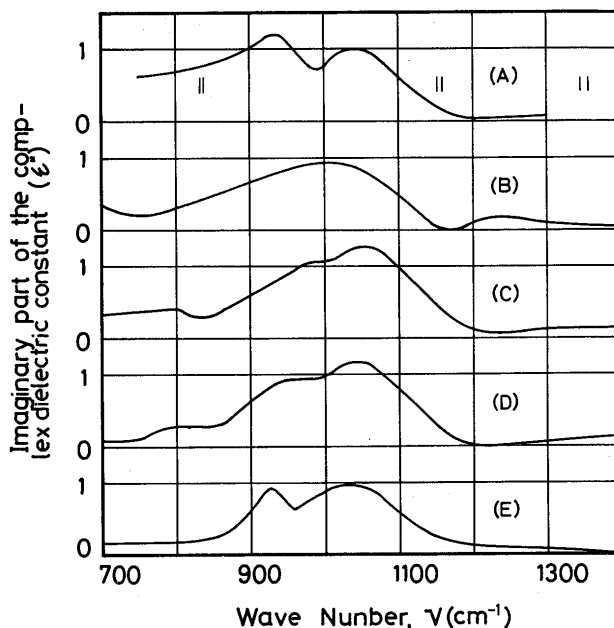


Figure 2. Plots of ϵ'' for the alkali- and alkaline earth-silica series with constant silicon-to-oxygen ratio $\text{Si/O} = 0.37$ (A); 43% Na_2O , (B); 40% K_2O , (C); 42% CaO , (D); 46% SrO and (E); 43% BaO ¹³⁾

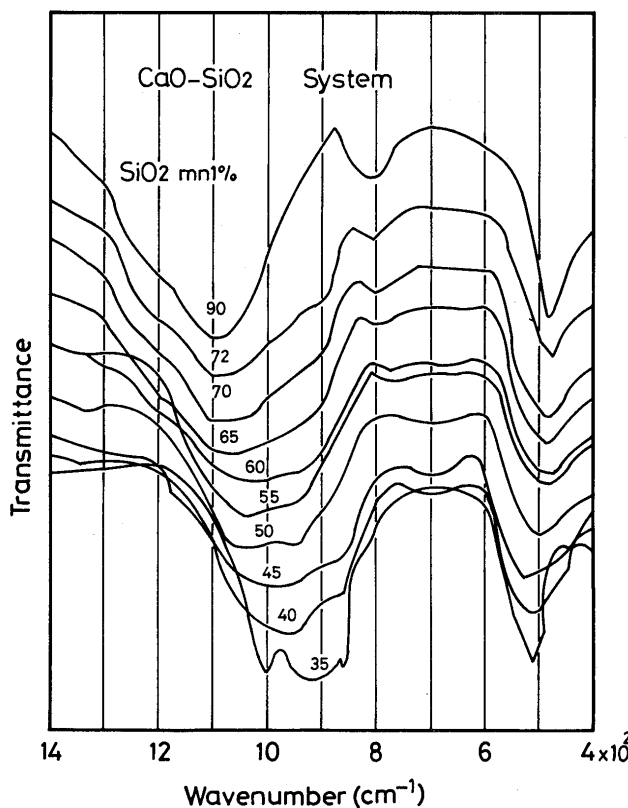


Figure 3. IR transmittance of glasses in the system CaO-SiO_2 ²⁵⁾

addition of 10% CaO and remains without shift until 65% CaO.

2) Absorption band having peak at 930 cm^{-1} begins to appear on 72 mol% SiO_2 glass and the peak position remains without shift.

However the absorption becomes larger with increasing CaO content until 55% SiO_2 composition.

3) There appears another absorption peak and the following shift can be observed as given in Table 2.

In Figure 4, the relation between wave number of frequency and SiO_2 composition can be compared for the glasses in the five systems. The dotted lines shown in the diagram represent six characteristic absorption positions which appear with the addition of network modifier. From the comparison with the absorption band given by other investigators and with the result from representative silicate minerals, they assigned each absorption bands to be induced from various silicate anions. In Table 3, the result is given.

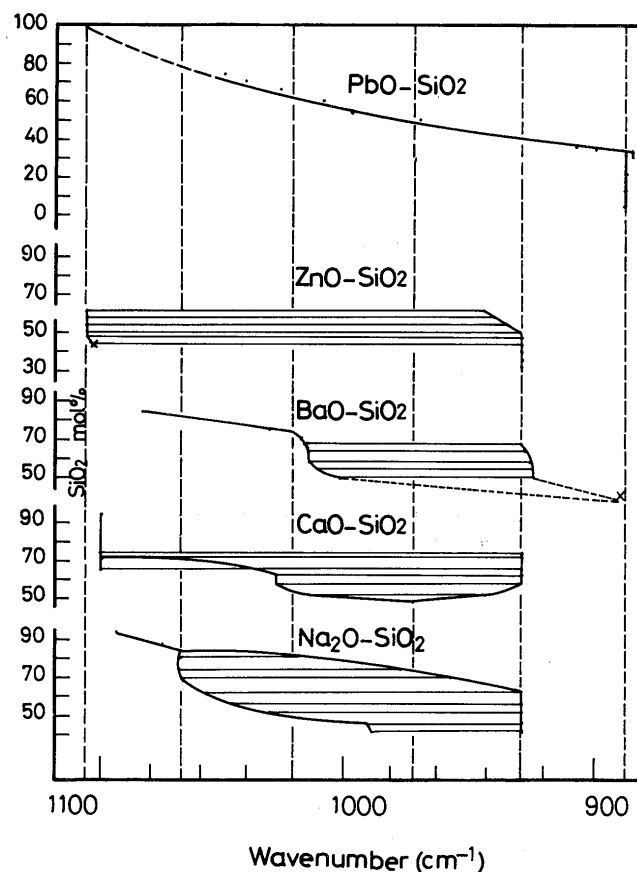


Figure 4. Relation between ν_3 frequency and SiO_2 content in binary system²⁵⁾

Table 2 IR absorption peak found in glasses of the system CaO-SiO_2 ²⁵⁾

SiO_2 (mol%)	peak position (cm^{-1})
70	1065
60 ~ 55	1030
50	1030 ~ 1010, 930 ~ 940 — 950
45 ~ 40	965

Table 3 Assignment of absorption band ν_3 from the result by natural silicates¹⁵⁾

Frequency (cm^{-1})	Silicate anion
890 ~ 900	SiO_4^{4-}
930	$\text{Si}_2\text{O}_7^{6-}$
970	$\text{Si}_n\text{O}_{3n}^{2n-}$ ($n = 3 \sim 8$)
1020	$\text{Si}_{2n}\text{O}_{5n}^{2n-}$
1065	$\text{Si}_{12}\text{O}_{27}^{6-}$ or $\text{Si}_{16}\text{O}_{36}^{8-}$

Brawer and White emphasized that the structural interpretation of IR spectra would be difficult because of powders specimen which could not reveal true intensity and line shape²⁶⁾. They compared scattering peak from glassy and crystalline materials composed from binary system. The results obtained are as follows:

- 1) The peaks of spectra from glass become broader than that in the crystal. In the disilicate and metasilicate glass, peaks at 950 and 850 cm^{-1} become much more intense.
- 2) As shown in Figure 5, the band width for glasses in the systems $\text{Na}_2\text{O-}$, and $\text{K}_2\text{O-SiO}_2$ first decrease and then rise. However glass in the $\text{Li}_2\text{O-SiO}_2$ system exhibited without minimum and they attributed it to phase separation.
- 3) Based on the fact that the 950 cm^{-1} band decreases rapidly with the increase of SiO_2 content, they showed the ratio of intensities, I_{950}/I_{1100} , as a function of the average number of nonbridging oxygen x per silicon. The result is shown in Figure 6.

Likewise Konijnendijk and Stevels compared Raman spectra of glass and crystal specimens composed from binary system.²⁷⁾ The results obtained are as follows:

- 1) It was thought that Raman peaks at 950 and $965 \sim 975\text{ cm}^{-1}$ of metasilicate compounds were originated from SiO_4 tetrahedra with two non-bridging oxygen ions.
- 2) In the range of $0 \sim 33$ mol% alkali oxide, SiO_4 tetra-

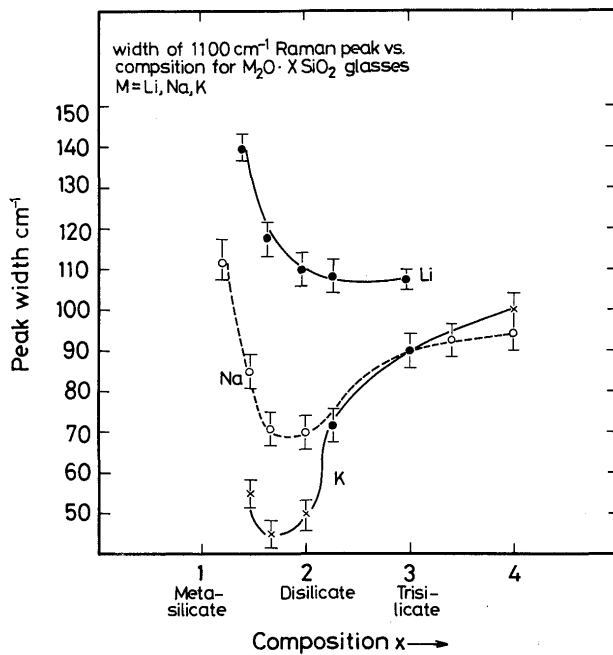


Figure 5. The width of the highest-frequency peak of the glass spectra for composition $M_2O \cdot X SiO_2$ ²⁶⁾

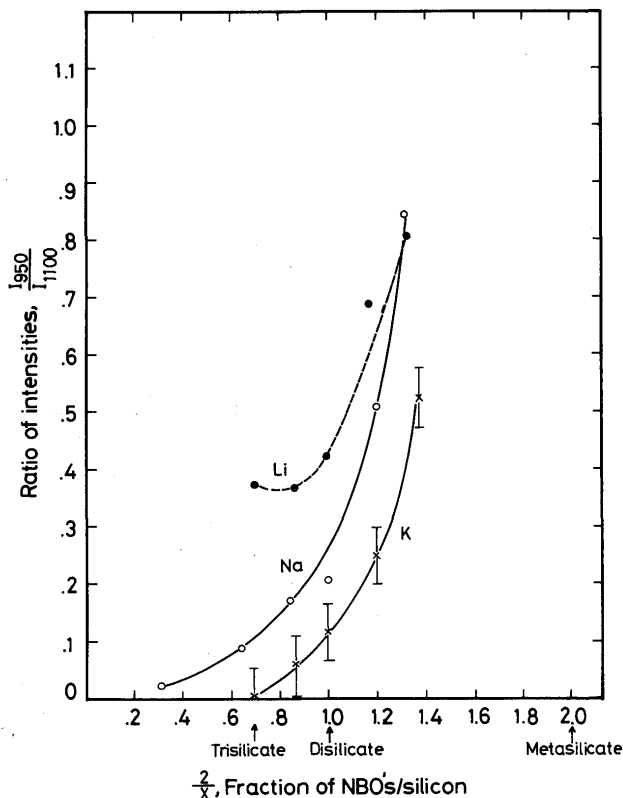


Figure 6. The ratio of the intensities of the 950 cm^{-1} to 1100 cm^{-1} peaks in the glass spectra as a function of $2/x$, the average number of non-bridging oxygens (NBO's) per silicon ²⁶⁾

hedra with two non-bridging oxygen ions are not formed, but only one non-bridging oxygen ions should be considered.

3) As for 33 ~ 50 mol% alkali oxide, replacement of SiO_4 tetrahedra with one non-bridging oxygen ion with those containing two non-bridging oxygen ions occurs.

4) Formation of SiO_4 tetrahedra with three non-bridging oxygen ions could not confirm within such alkali oxide composition.

We have studied ²⁸⁾ Raman spectra from glasses in binary systems and performed peak separation of ν_3 frequency appeared at about 1100 cm^{-1} into five which were identified as those from SiO_2 network, SiO_4 tetrahedra having one, two, three and four non-bridging oxygens with the help of the investigation by Götz et al ²⁸⁾ and the application of IR reflection study with Kramers-Kronig analysis. ^{29), 30)} As an example, the relation between the concentration of each SiO_4 tetrahedra having four kinds of non-bridging oxygen and network modifier oxide content is given in Figure 7.

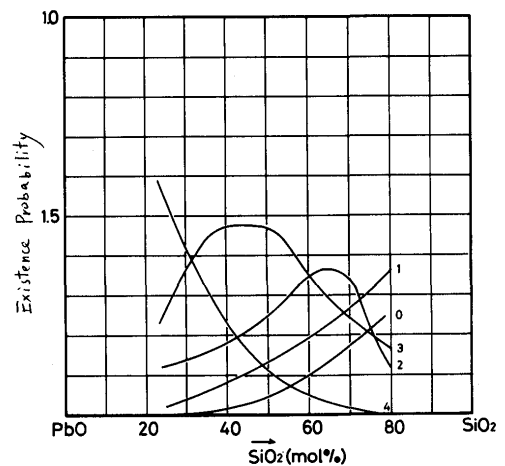


Figure 7. Existence probabilities of various silicates containing or without non-bridging oxygen in the system $PbO-SiO_2$ (0): SiO_2 network, (1), (2), (3) and (4): SiO_4 tetrahedra having one, two, three and four non-bridging oxygen

2.1.2 Multicomponent system

As previously described, ⁴⁾ IR study was applied on multicomponent system having amphoteric oxide such as Al_2O_3 to know the behavior in glass.

With IR absorption spectra of alkali aluminosilicate glass, Kolesova has certified that the absorption band near 760 cm^{-1} commenced to develop two maxima with the increase of Al_2O_3 content ³¹⁾.

From the IR studies about some silicate minerals, Saksena reported that it was impossible to distinguish

four- or six- coordination of aluminium ions from absorption spectra³²⁾.

Tarte classified the main absorption of XO_4 and XO_6 (X: cation)³³⁾.

Day and Rindone studied IR spectra of glasses in the $Na_2O-Al_2O_3-SiO_2$ system and reported that an absorption band, could be assigned to AlO_6 groups, did not appear in glasses having an Al/Na ratio greater than unity.³⁴⁾

Brawer and White studied the change of Raman scattering profile as for the substitutional effect of CaO, MgO, and Al_2O_3 on glasses in the Na_2O-SiO_2 system.²⁶⁾

The results obtained are as follows:

- 1) Substitution of CaO into Na_2O has a relatively small effect on the Si-O network. Only the information as for the amount of disorder was determined.
- 2) Substitution of MgO into Na_2O created more disorder in the glass than does CaO.
- 3) Some of aluminium ions were considered to occupy the sixfold sites because of the rapid growth of the 950 cm^{-1} peak with increasing Al_2O_3 concentration.

Konjenedijk studied the behavior of aluminium ion in the glasses of K_2O-SiO_2 system.³⁵⁾ Based on the consideration of peak intensity of about 1100 cm^{-1} and disappearance of peak about 965 cm^{-1} when Al_2O_3 was added to be the compositional ratio $Al/K \leq 1$, it was concluded that aluminium ions occupied the tetrahedral sites in glass. The Raman scattering result is given in Figure 8.

Further Sugihara and Yanagase studied behavior of aluminium ion in glass with IR absorption.²⁵⁾ As an example, the change of IR band of glasses in the system $Na_2O \cdot 2SiO_2 + Al_2O_3$ is shown in Figure 9. They re-

ported that one absorption peak about 990 cm^{-1} splitted into two ν_3 peaks, about 950 and 1070 cm^{-1} , when Al_2O_3 was added.

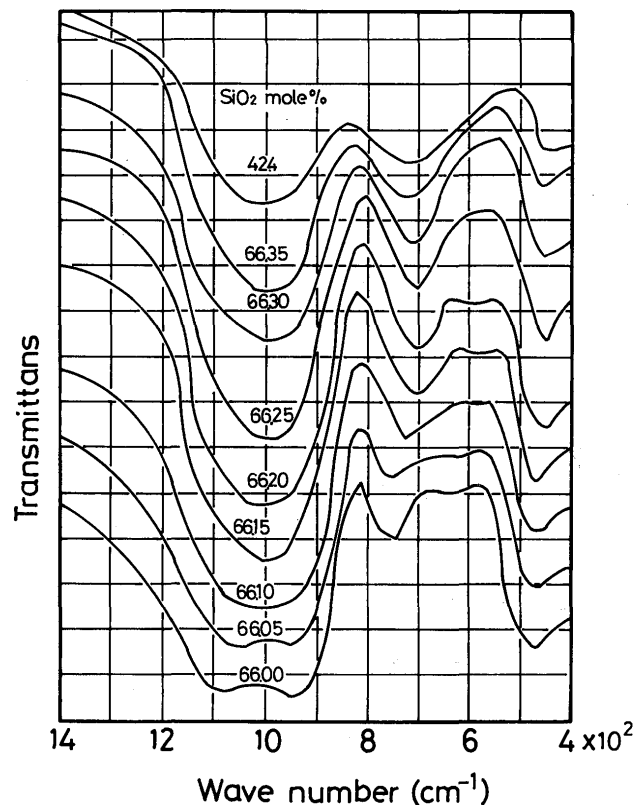


Figure 9. IR transmittance spectra of glasses in the system $Na_2O \cdot 2SiO_2 - Al_2O_3$ ²⁵⁾

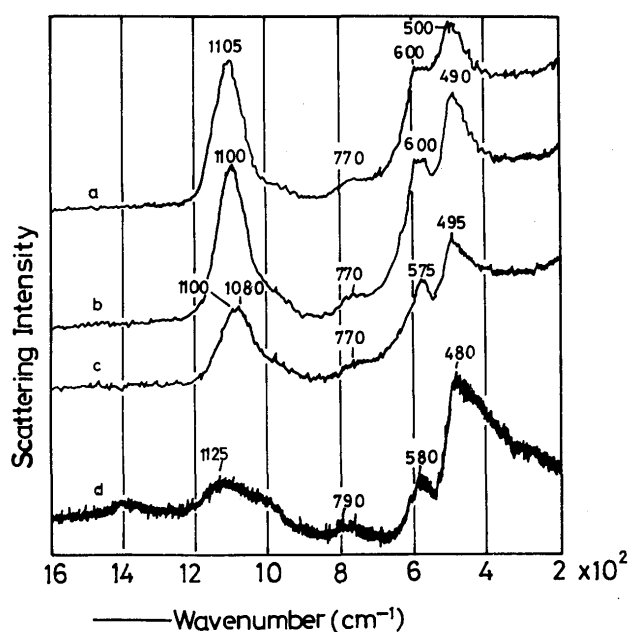


Figure 8. Raman spectra of aluminosilicate glasses $K_2O: Al_2O_3:SiO_2$ ³⁵⁾(A); 0.20:0.10:0.70, (B); 0.20:0.15:0.65, (C); 0.20:0.20:0.60, (D); 0.125:0.125:0.75

We performed profile analysis of Raman spectra of glass in the systems Na_2O -, and $K_2O-SiO_2-Al_2O_3$ with the use of iterative least-square procedure under the condition that every spectrum is consisted from two Gaussian bands.³⁶⁾ As an example, Raman spectra of glasses in the system $Na_2O-SiO_2-Al_2O_3$ are shown in Figure 10. The result of profile analysis about ν_3 frequency is given in Figure 11. Accordingly, it can be considered that the shift or unification of two ν_3 frequencies is nothing but unclear resolving power which was originated from the change of mutual intensities of about 980 and 1100 cm^{-1} frequencies with Al_2O_3 addition.

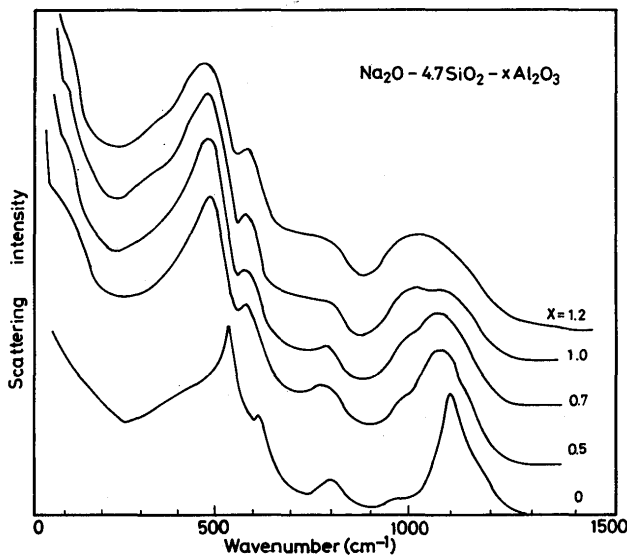


Figure 10. Raman spectra of glasses in the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ system³⁶⁾

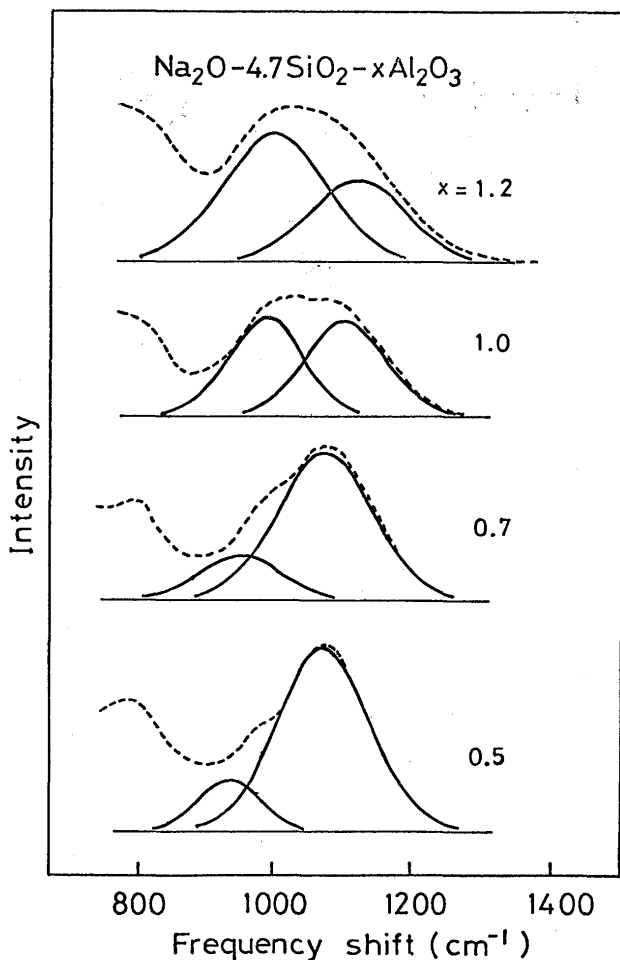


Figure 11. Raman spectra of $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ glasses separated into two Gaussian bands³⁶⁾

2.1.3 Special problems

2.1.3.1 Behavior of fluorine ion in slag

As previously summarized²⁾, it is important matter to know the role of fluorine ion in slag from the standpoint of air pollution and raw material's preservation. However the addition of fluoride to slag has been done to decrease the viscosity of molten slag in steelmaking as well as welding.

With an attempt to know the cause of decreasing viscosity of slag, Kumar, Ward and Williams studied IR transmittance of solid glasses containing fluoride.^{37), 38)} They concluded that the absorption band at 875 cm^{-1} was probably originated from the braking effect of fluorine ion on silicate network.

Ito, Yanagase, Suginozaki and Miyazaki studied IR absorption of glasses in the systems, $\text{PbO}-\text{Na}_2\text{O}-$ and $\text{CaO}-\text{SiO}_2$ containing 10 mol% various fluoride.³⁹⁾ They concluded that the position of ν_3 frequency did not shift with fluoride addition and therefore fluorine ion had not an effect to break silicate network.

At present many investigators are studying to make clear this reaction mechanism with other physical means.⁴⁰⁾

In the field of glassmaking, Cleek and Scuderi applied IR transmittance study to know the behavior of fluoride added in glass.⁴¹⁾ As shown in Figure 12, much higher transmittance was obtained over the wave-length range

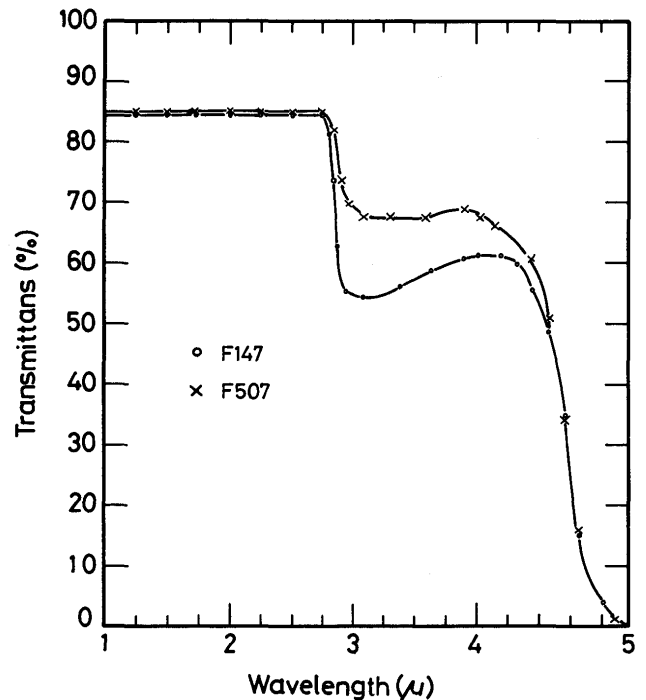


Figure 12. IR transmittance spectra for the glass in the system $\text{BaO}-\text{TiO}_2-\text{SiO}_2$ (F147) and of glass replaced 2 mol%BaO by BaF_2 (F507)⁴¹⁾

As an example, IR transmission of glasses in the system $\text{Na}_2\text{O}-\text{SiO}_2$ is shown in Figure 15. It will be seen that the

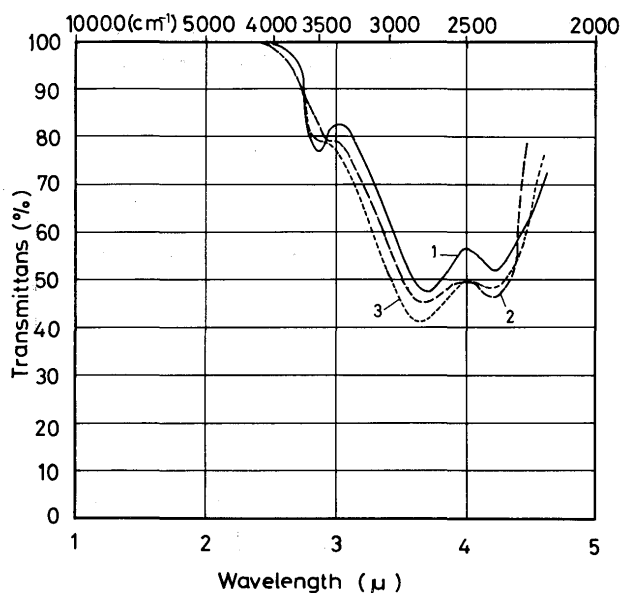


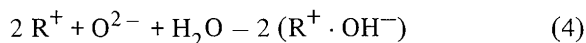
Figure 15. IR transmittance spectra of glasses in the system $\text{Na}_2\text{O}-\text{SiO}_2$ (water concentration, 0.04mol/l)⁵⁰⁾ (1); 15 mol% Na_2O , (2); 20 mol% Na_2O , (3); 25 mol% Na_2O

bands at about 3.7 and 4.25μ become lower, that is to say, the absorption intensities become greater with increasing network-modifier.

Franz and Kelen thought the solution mechanism of water in alkalisilicate as follows:⁶¹⁾

Absorption at 2.8μ Model (A)
 3.6μ (B), (C), (D)
 4.25μ (D)

However, in the case of glasses containing higher content of alkali oxide, the solution behavior of water shown in Figure 16 can not explain the abrupt change of water solubility with the model above-described. They thought the following reaction figure:



Up to now, it is hardly to find new band which can explain OH vibration attributed to alkali-hydroxide formation. Only an easiness of vaporization of alkali-oxide from glass containing 40 mol% alkali-oxide can be suggested to recognize the separation of R^+ and O^{2-} in glass. Depending on equation (4), it can be accepted the increase of water solution.

Furthermore it is interesting that they paid their attention to know the behavior of alkali ion and the bond length between neighboring alkali ions in glass from the difference of bands intensities.

Scholtze studied an effect of Al_2O_3 addition on the

change of absorption bands, below 3 and 3.6μ ⁵⁰⁾. As shown in Figure 17, the peak position does not change

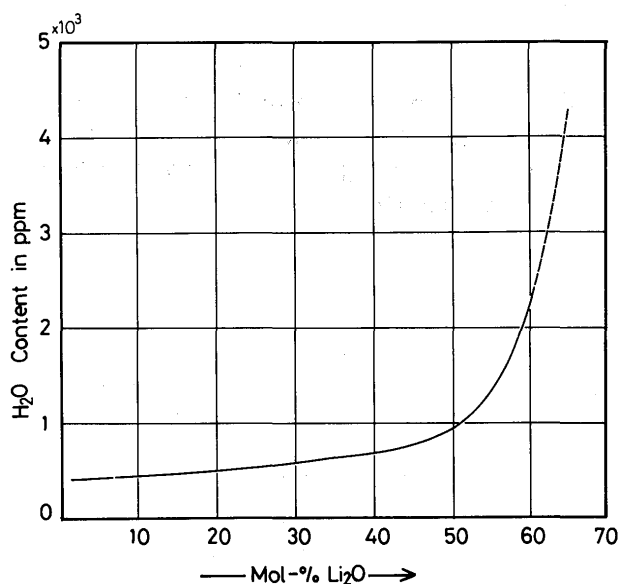


Figure 16. Solubility of water vapor in the molten glasses in the system $\text{Li}_2\text{O}-\text{SiO}_2$ at $\text{P}_{\text{H}_2\text{O}} = 146\text{ mmHg}$ ⁵⁷⁾

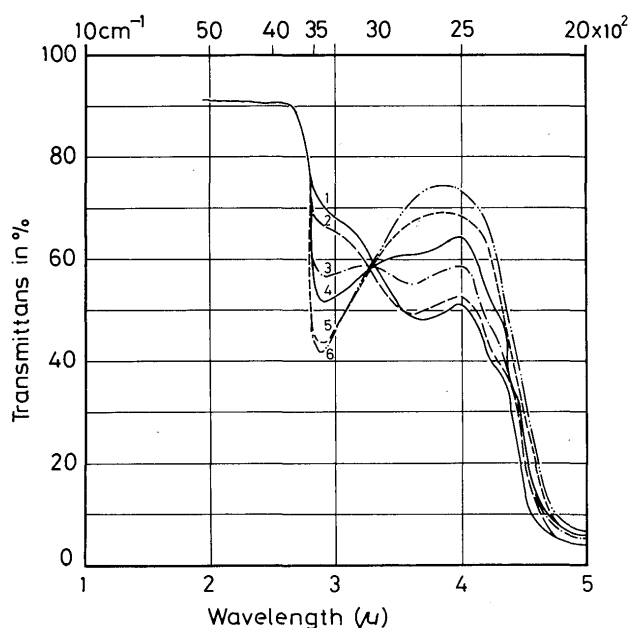


Figure 17. IR transmittance spectra of glasses in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ⁵⁰⁾ $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$, (1); 20:0.80, (2); 20:4:75, (3); 20:10:70, (4); 20:12:68, (5); 20:15:65, (6); 20:20:60

but the absorption below 3μ becomes greater with increasing Al_2O_3 . He concluded that aluminium ion takes tetrahedral site accompanying proton H^+ and makes stable a free OH^- bonding.

2.1.3 Experiment at high temperature

To know the correct temperature of the heated material, measurement of emissivity has been performed for a long time.⁶⁶⁾⁻⁸⁹⁾

Schematic representation of the measurement of a simple way can be given as Figure 18.⁶⁶⁾

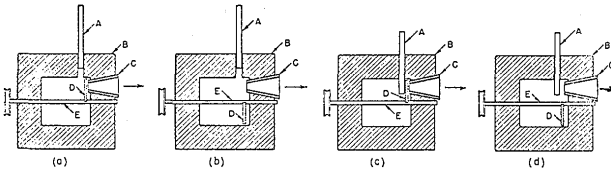


Figure 18. Schematic arrangement of sample within the furnace:⁶⁶⁾

(a); flux intensity is $J(\lambda, t) + J_b(\lambda, t) T'(\lambda, t)$, (b); flux intensity is $J_b(\lambda, t)$, (c); flux intensity is $J(\lambda, t)$ and (d); flux intensity is zero, where
 $J(\lambda, t)$ = spectral emissive power of the glass
 $J_b(\lambda, t)$ = spectral emissive power of a black body and $J(\lambda, t) + J_b(\lambda, t) T'(\lambda, t)$ = sum of emission + transmission

2.1.4.1 Solid materials

Grove and Jellyman have given an apparatus for measuring a transmission spectral of glass at high temperature.⁷⁴⁾ The experiment at temperature up to 1400°C was applied to iron- and nickel-containing glasses. As an example, the result is shown in Figure 19. With the exception of change in intensity at 1.1 μ originated from "ferrous" state the absorptions, 2.8 and 3.7 μ , which were resulted from water decreased with an increase of temperature.

Afterwards, Grove studied an effect of Fe₂O₃ and Cr₂O₃ addition on the absorption bands at 2.8 and 3.7 μ of glasses in the system Na₂O-CaO-SiO₂⁸⁰⁾. For a glass containing iron the decrease in absorption intensities occurred with increasing temperature.

On the other hand an increase in absorption intensities was found for a glass containing chromium. However he did not give an explanation.

Similarly Genzel,⁶⁷⁾ and Neuroth^{68), 70), 73)} studied an effect of temperature of IR absorption in many kind of glasses.

Neuroth summarized his result as follows.⁶⁸⁾

- 1) At temperature up to about 500 – 600°C, absorptions at about 1.1 and 2.8 μ decrease with an increase of temperature.
- 2) In the range of softening temperature (500 – 1000°C), the absorption changes remarkably and depends on composition of glass.
- 3) When glass takes fluid state, the absorption becomes

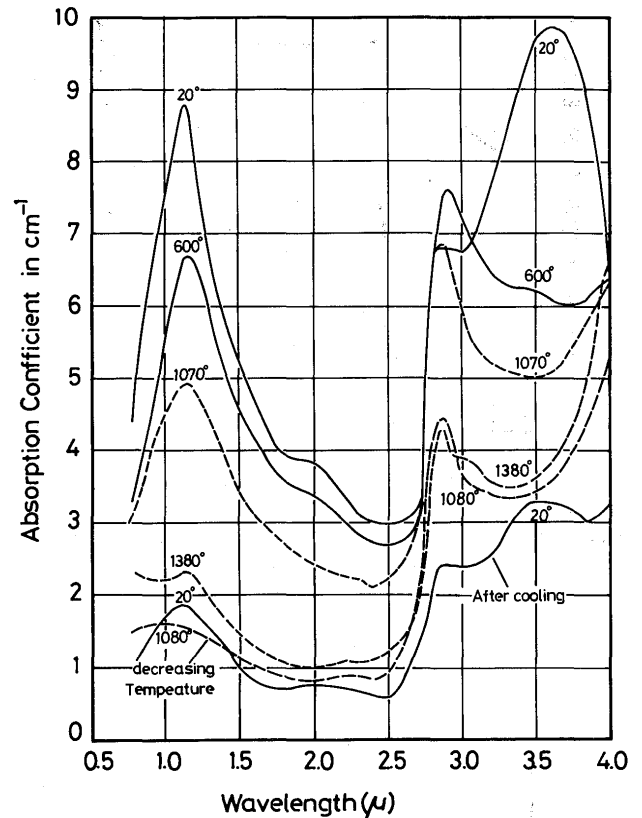


Figure 19. IR absorption spectra of glass containing iron oxide within temperature range 20 ~ 1380°C⁷⁴⁾
 (SiO₂:Na₂O:CaO:Al₂O₃:Fe₂O₃ = 67:17:12:3:0.86 wt%)

greater.

- 4) In general, temperature rise makes absorption band to flatten.

With an increase of temperature the band shifts to longer wavelength.

- 5) With temperature rise, it must consider the structure change in glass.

2.1.4.2 Molten state

Kurbatov et al studied an emissivity from molten slag and compared the result with the one from solid slag.⁹⁰⁾⁻⁹²⁾

For an example, the result is shown in Figure 20. From this diagram, they concluded that any difference about emissivity between solid and molten slag could not determine. They found only a proof that silicate network can be broken with an increase of basicity from the shift in absorption band.

Likewise, Shiraishi and Kusabiraki studied an emission spectral from molten glass.¹⁵⁾ In Figure 21, an emittance and transmittance behaviors from glasses in the system Na₂O-SiO₂ at 1130°C and the crystallized material at

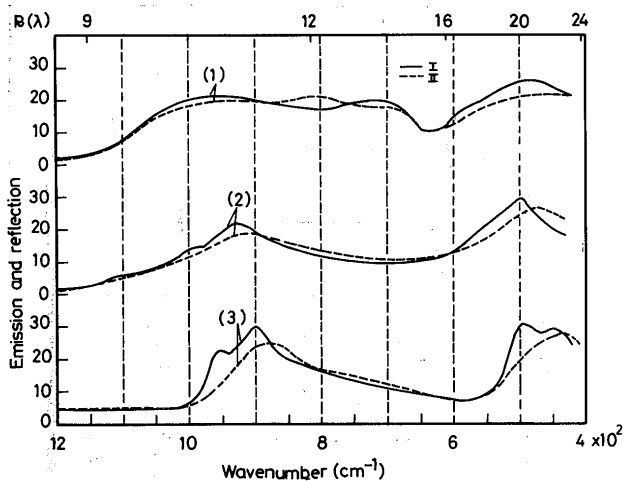


Figure 20. The emission and reflection spectra of liquid and solid open hearth furnace slag of the system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO-Fe}_2\text{O}_3\text{-MnO}^{90}$ (I); 20°C, (II); 1500°C, Oxygen/network cation ratio; (1); 2.3 ~ 2.8, (2); 2.8 ~ 3.5, (3); 3.5 ~ 4

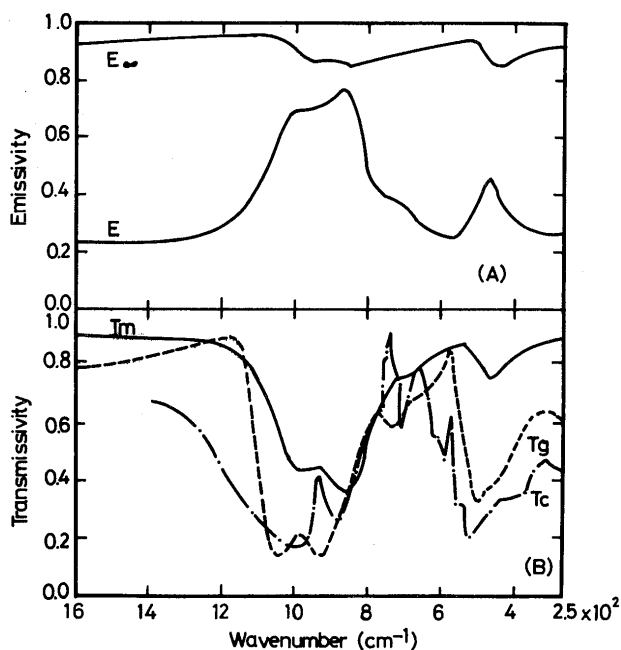


Figure 21. IR emission spectra (A) and transmission spectra of molten $\text{Na}_2\text{O} \cdot \text{SiO}_2$ at 1130°C and the transmission spectra of the glass (T_g) and crystallized material (T_c) at room temperature¹⁵⁾

room temperature were compared.

The splitting of an emitted spectral can be observed and an absorption band at longer wavelength becomes remarkable in molten glass. At that case it can be concluded that an absorption band shifts to longer wavelength and the profile becomes broader.

3. Summary

In this review, the author treated the application of IR and Raman spectroscopy to solve many important problems in glass manufacture and slag for steel-refining. Although IR spectroscopy is convenient for an identification of minerals, it has many difficult problems. For instance, it is difficult matter to determine appropriate conditions of specimen for obtaining accurate information even though reflectance or transmittance was chosen. Furthermore, as Tarte pointed out, IR spectroscopy has more drawbacks such as lack of sensitivity and uncorrect assignment of band. Therefore it was wanted to apply laser Raman spectroscopy.

It stimulated progress to obtain an information as for internal structure of slag.

With the combination of other analytical means, it will be distinct the substitution behavior of network modifier on the chemical reactions such as water solubility and distribution ratio of element between molten slag and metal in future.

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