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# State Analysis on Chromium Ion in a Few Silicate Glasses†

**Nobuya IWAMOTO* and Yukio MAKINO****

**Abstract**

*Optical absorption spectra of soda-silicate glasses were measured. ESR was also used to characterize the electronic environment of chromium ions in soda - and lime-silicate glasses. In the glasses produced in very strong reducing conditions, the formation of $Cr^{2+}$ was suggested by the broad absorption in the range of 10000 $cm^{-1}$ to 25000 $cm^{-1}$ and no absorption in ESR spectra. From ESR results, it was suggested that three different states of $Cr^{3+}$ ions, that is, strong electrically coupled $Cr^{3+}$ ion pair, weak electrically coupled $Cr^{3+}$ ion pair and isolated $Cr^{3+}$ ion in an elongated teragonal site or a site with other low symmetry can exist in these glasses. From ESR results, the existence of $Cr^{5+}$ ion was also suggested in soda-silicate glasses. Further, it was indicated that critical partial oxygen pressure for the formation of $Cr^{2+}$ ion is in the vicinity of $P_{O2}=10^{-8}$ atm.*

**KEY WORDS:** (State Analysis) (Chromium Ion) (Silicate)

## Introduction

State of chromium ion in oxide glasses has considerably been investigated with various methods such as optical absorption and chemical analysis.[1),2)] In these studies, $Cr^{6+}$ – $Cr^{3+}$ redox reaction was widely investigated whether it can be use to expless the basicity of glass.[3),4)] However, the investigation on $Cr^{2+}$ ion in oxide glass is seldom except the investigation in $Li_2O$-CaO-$SiO_2$ glass using optical absorption by Paul.[5)] Some investigators indicated an existence of $Cr^{2+}$ in spinels using optical absorption method.[6),7),8)] In practical aspect, the investigation on chromium ion in oxide glasses also is an important subject. For example, it is important to redistribute metallic chromium from slag as much as possible in refining alloy containing chromium such as stainless steel. In such cases, it is necessary to stabilize low valency chromium ion, that is, $Cr^{2+}$ ion in slag. However, the investigations on chromium ion in metallurgical slags, in most cases, have been performed by only thermodynamical approaches[9),10)].

ESR studies on transition metal ions in glass have been widely performed since Sands observed ESR spectra due to several transition metal ions[11)]. For example, ESR spectrum of $Fe^{3+}$ ion in glass were considerably measured and theoretical explanations have been performed by many investigators[12),13)]. However, ESR study on chromium ion, especially $Cr^{2+}$ ion, in oxides has not so widely been performed and state of chromium in oxide glasses was scarcely investigated with ESR spectroscopy[14),15)].

In this study, state of chromium ion in soda- and lime-silicate glasses was investigated with ESR spectroscopy. Optical absorption spectra of soda-silicate glasses were also measured. Both optical and ESR absorption spectra of the glasses produced in several reducing conditions were mainly measured because we have much interest to the formation of divalent chromium ion in glass. Further, the dependency of these spectra upon glass composition was also investigated.

## Experimental Procedures

Specimen glasses were prepared from reagent grade $CaCO_3$, $Na_2CO_3$, $SiO_2$ and $(NH_4)_2CrO_4$. Chromium additions were performed in the form of $Cr_2O_3$ which was produced by heating $(NH_4)_2CrO_4$ in air at 1300°C. These materials were accurately weighed and mixed in an agate mortar and pestle. Specimen glasses were produced by melting in a platinum or molybdenum crucible at the temperature of 100°C or 200°C higher than their melting points. These glasses were held for 2 hr under various oxygen pressures produced by mixing CO and $CO_2$ gases or $H_2$ and $CO_2$ gases.

Optical absorption measurement was performed with a spectrometer of Hitachi 323 type. Experimental conditions were as follows;

wave length range: 340 nm – 2600 nm,

specimen shape: circular disk.

Molar extinction coefficients of chromium ion in glasses were calculated from following equation;

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$$E = \log(I^{\circ}/I)/ct$$

where E : molar extinction,
C : gram ion of coloring ion per liter of glass,
$I^{\circ}$: intensity of the incident light,
t : thichness of the glass specimen (cm).

ESR spectra were measured using a spectrometer of Varian E-109 type. Experimental conditions were as follows;
method: X-band, field range: 0 – 7000 gauss,
modulation frequency and field: 100 KHz and 10 gauss,
specimen shape: powder.

## Experimental Results and Discussion

### (1) Optical absorption measurement

Optical absorption spectra of chromium ion in lime silicate glasses were measured in our previous study[16]. In this study, therefore, optical absorption spectra of chromium in soda silicate glasses were measured. These results are shown in Figs. 1, 2 and 3. In Fig. 1, the dependency

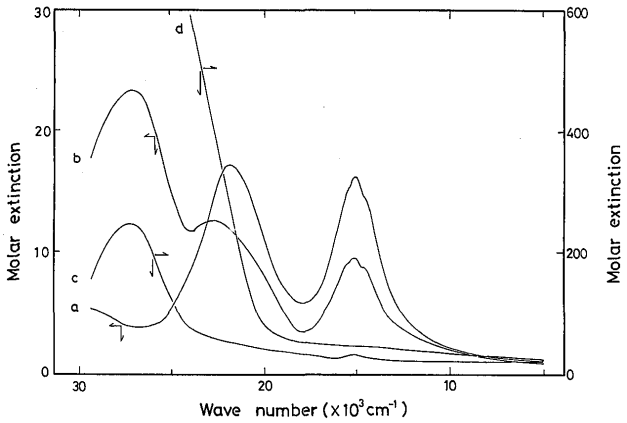


**Fig. 1** Optical absorption spectra of chromium ion in soda-silicate glasses produced in air.
(a) $Na_2O/SiO_2$=10/90, 0.5mol% $Cr_2O_3$
(b) $Na_2O/SiO_2$=20/80, 0.5mol% $Cr_2O_3$
(c) $Na_2O/SiO_2$=30/70, 0.02mol% $Cr_2O_3$
(d) $Na_2O/SiO_2$=40/60, 0.02mol% $Cr_2O_3$

of absorption spectra of glasses produced in air upon the composition are shown. From this figure, it was shown that $Cr^{3+} - Cr^{6+}$ redox equilibrium deviates to $Cr^{6+}$ side as $Na_2O$ content increases. Fig, 2 shows the dependency of absorption spectra upon partial oxygen pressure ($P_{O_2}$) in the glasses with $Na_2O/SiO_2$=20/80. The absorption peak due to $Cr^{6+}$ ion was inclined to disappear with decreasing soda content and $P_{O_2}$ and then two absorption peaks due to $Cr^{3+}$ in an octahedral site developed. In the glasses produced in CO gas, a broad peak appeared in the range of 10000 $cm^{-1}$ to 25000 $cm^{-1}$ as shown in Fig. 3. The result by Paul is also shown in Fig. 3. Comparing our result with one by Paul, the difference of molar extinction

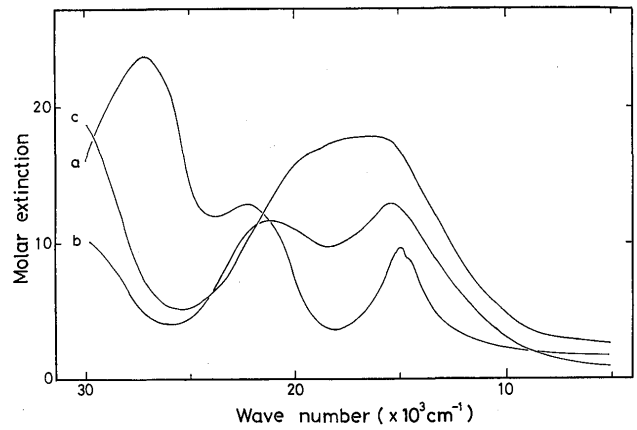


**Fig. 2** Optical absorption spectra of chromium ion in soda-silicate glasses with $Na_2O/SiO_2$=20/80 and 0.5mol% $Cr_2O_3$ produced under various partial oxygen pressures.
(a) in air,
(b) $CO/CO_2$=1/1,
(c) all CO

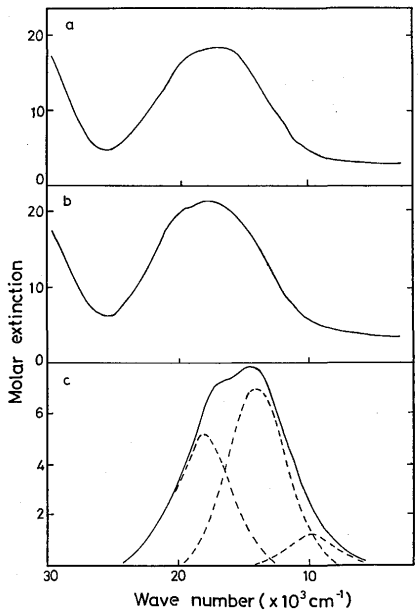


**Fig. 3** Optical absorption spectra of chromium ion in soda-silicate glasses containing 0.5mol% $Cr_2O_3$ produced in CO gas.
(a) $Na_2O/SiO_2$=20/80,
(b) $Na_2O/SiO_2$=10/90,
(c) $15Li_2O$-10CaO-$75SiO_2$ (quoted from the result by Paul[5])

coefficient of chromium ion was remarkable whereas the difference between their peak positions was not so noticeable. Paul measured the absorption spectra of chromium ion in $Li_2O$-CaO-$SiO_2$ glasses whereas soda silicate glasses were used in this study. Further, the difference in partial oxygen pressure must be also considered. Thus, the differences in peak position and molar extinction coefficient seem to be attributed to the differences of glass composi-

tion and experimental condition.

Paul interpreted that the broad absorption in the glasses containing chromium is attributed to divalent chromium ion in an elongated tetragonal field. Further, he considered that the broad band was produced by overlapping of three absorptions due to $B_{1g} \rightarrow A_{1g}$, $B_{1g} \rightarrow B_{2g}$ and $B_{1g} \rightarrow E_g$ transitions as shown in Fig. 4. Fackler

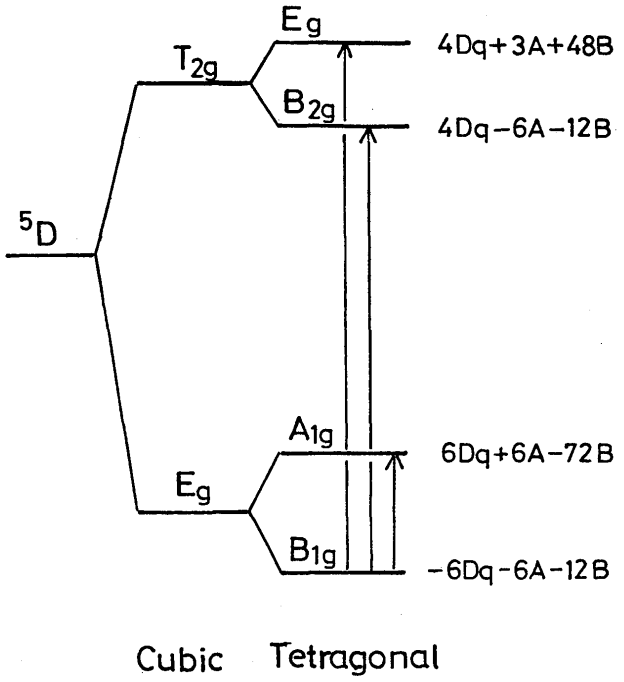


**Fig. 4** Energy levels of $3d^4$ configuration in octahedral and tetragonal crystal fields calculated by the point charge model. ($A=-2e^2\delta r^4/63a^6$, $B=2e^2\delta r^2/7a^4$, where r; distance of a 3d electron from the origin, a; interionic distance, e; electron charge, $\delta$; a small distortion of the octahedron)

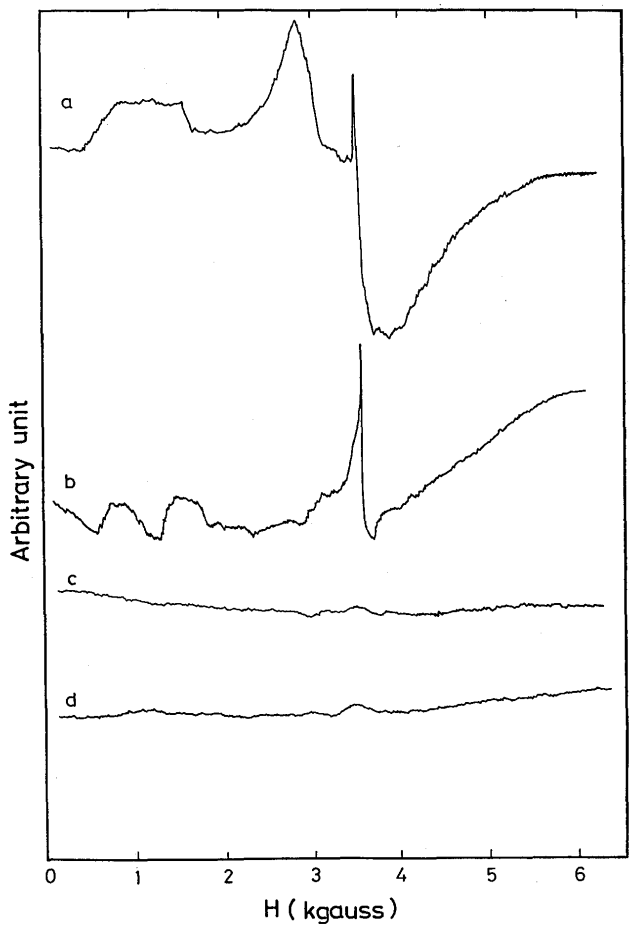


**Fig. 5** Electron spin resonance spectra of chromium ion in soda-silicate glasses
(a) $Na_2O/SiO_2$=10/90, 0.5 mol% $Cr_2O_3$, in air
(b) $Na_2O/SiO_2$=30/70, 0.02 mol% $Cr_2O_3$, in air
(c) $Na_2O/SiO_2$=10/90, 0.5 mol% $Cr_2O_3$, in CO gas
(d) $Na_2O/SiO_2$=30/70, 0.02 mol% $Cr_2O_3$, in CO gas

and Holah investigated the optical absorption of $Cr(H_2O)_6^{2+}$ and suggested that the broad band due to $Cr^{2+}$ ion can be resolved into four absorptions[17]. In this study, it is difficult to determine whether divalent chromium ion is in an elongated tetragonal field or more lower symmetric field because the broad band was not resolved into each band. However, it is reasonable to consider that the broad absorption band in this study is attributed to divalent chromium ions. Further, it can be considered that the formation of $Cr^{2+}$ ion in soda silicate glass begins in the vicinity of $P_{O2}=10^{-8}$ atm.

### (2) Elecron spin resonance measurement

In order to obtain some detailed information on the surroundings of chromium ion, ESR spectra of several soda- and lime-silicate glasses were measured. These results are shown in Figs. 5, 6 and 7. As shown in Fig. 5, three absorptions were detected in the soda-silicate glass with $Na_2O/SiO_2$=10/90 produced in air. O'Reilly and MacIver considered that sharp absorption at g=2.0 is attributed to single electrons trapped on $Cr^{6+}$, that is, $Cr^{5+}$ ions because a considerable amount of $Cr^{6+}$ is formed upon oxidation at 500°C[18]. Thus, it would be reasonable to interpret that the sharp absorption in the glass is attributed to isolated $Cr^{5+}$ ions. However, the absorption band near 27000 $cm^{-1}$ was assigned to $Cr^{6+}$, that is, chromate ion groups in optical absorption measurement. Therefore, it must be reconsidered whether chromate ion corresponds to $Cr^{6+}$ ion trapping a single electron or not.

Landry et al. indicated in a phosphate glass that the broad absorption at g=2.0 is assigned to an exchange coupled $Cr^{3+}$ ion pair[14]. Carman and Kroenke measured ESR spectra of polycrystalline $\alpha$-$Cr_2O_3$-$Al_2O_3$ solid solutions and showed that three elctrically different type of $Cr^{3+}$ ions exist at low chrome concentrations[19]. These are

isolated $Cr^{3+}$ ions (g=3.3), $Cr^{3+}$ ions coupled by weak electronic exchange interactions (g=2.3) and $Cr^{3+}$ ions coupled by strong electronic exchange interactions (g=2.0). Thus, it can be considered that $Cr^{3+}$ ions coupled by strong electronic exchange interactions produce the broad absorption at g=2.0 in the soda-silicate glass.

Subsequently, it seems to be reasonable to assign the broad absorption near g=5.0 to an isolated $Cr^{3+}$ ion. Landry et al. observed a broad absorption at g=5.25 in a phosphate glass[14]. O'Reilly and MacIver also observed a similar broad absorption at g=4.7 in $\alpha$-$Cr_2O_3$-$Al_2O_3$ solid solutions[18] whereas Carman and Kroenke observed an sharp absorption at g=3.3 in the same compound the following interpretation on the absorption was performed by Landry et al.. Trivalent chromium ion is in an orthorhombic field and two doublets with $M_s=\pm\frac{1}{2}$ and $M_s=\pm\frac{3}{2}$ are mixed each other. Thus, the absorption near g=5.0 can be observed because transition probability with $\Delta M_s=3$ does not become zero. On the other hand, Carman and Kroenke explained that, in the dilute $\alpha$-$Cr_2O_3$-$Al_2O_3$ solid solutions, the isolated $Cr^{3+}$ ions are subjected to a strong axial crystal field in a highly ordered lattice and consequently the resonance is narrow, symmetrical and well-deffined. Taking the broadness and intensity into consideration, the absorption near g=5.0 in the soda silicate glasses seems to be attributed to isolated $Cr^{3+}$ ions in an orthorhombic or other low symmetrical field. In the soda-silicate glass with $Na_2O/SiO_2$=30/70, the intensity of the sharp absorption at g=2.0 increased whereas the intensity of the broad absorption at g=2.0 decreased. This seems to be due to the difference in glass composition. The absorption in the lowest field in the glass was not interpreted. Any absorption in ESR spectra of the glasses produced in CO gas was not observed. This suggests the formation of $Cr^{2+}$ ion in these glasses because ESR absorption attributed to $Cr^{2+}$ ions can not be observed at room temperature on account of short spin-lattice relaxation time.

ESR absorption spectra of chromium ion in several lime silicate glasses are shown in Figs. 6 and 7. A new absorption was observed at g=2.2 in the glasses produced in strong reducing conditions. It would be reasonable to assign the absorption to $Cr^{3+}$ ions coupled by weak electronic exchange interaction as indicated by Carman and Kroenke[19]. According to their result, the absorption at g=2.2 was not appeared in a low chromium concentration. The appearance of the absorption in lime silicate glasses may be due to the content of chromium. The observation of very small absorptions in the glass with $CaO/SiO_2$=1 produced in the mixed gas with $H_2/CO_2$=15 also supported the formation of $Cr^{2+}$ ions in the glass. However, in

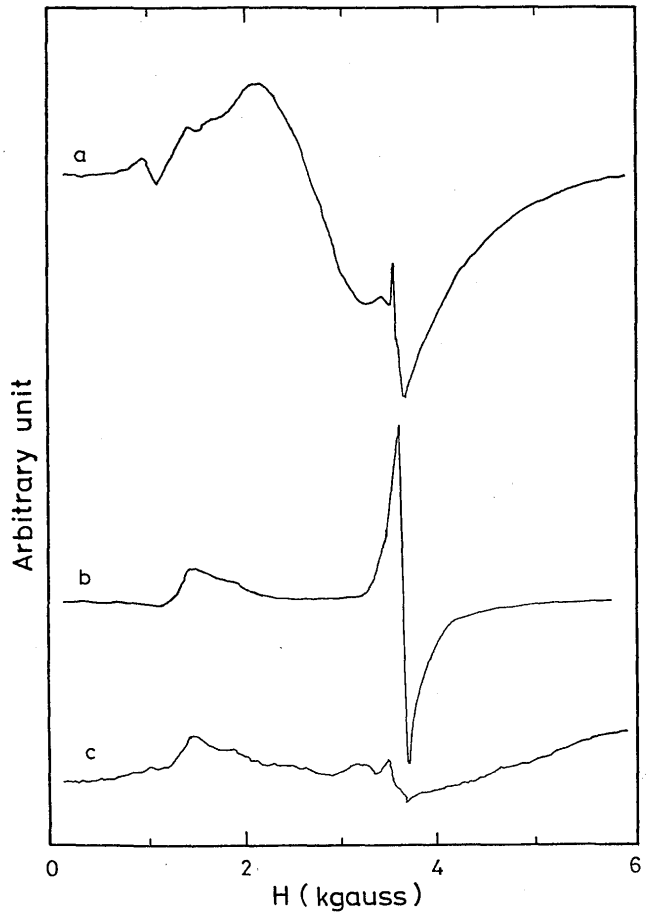


**Fig. 6** Electron spin resonance spectra of chromium ion in lime-silicate glasses with $CaO/SiO_2$=1/1 and 0.4 mol% $Cr_2O_3$
(a) air, (b) $H_2/CO_2$=1, (c) $H_2/CO_2$=15

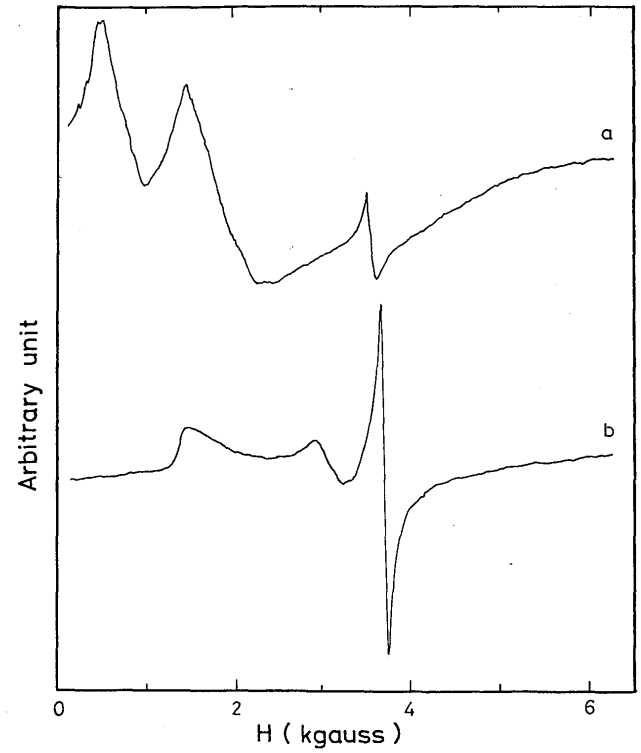


**Fig. 7** Electron spin resonance spectra of chromium ion in lime-silicate glasses with $CaO/SiO_2$=35/65 and 0.4 mol% $Cr_2O_3$
(a) air, (b) $H_2/CO_2$=15

order to certify the existence of $Cr^{2+}$ ion in oxide glasses, further detailed investigations are necessitated.


## Summary

State of chromium ion in soda- and lime-silicate glasses was investigated with optical absorption method. A broad absorption band was observed in the range of 10000 $cm^{-1}$ to 25000 $cm^{-1}$ in the glasses produced in the very strong reducing conditions. It was suggested that the absorption is attributed to divalent chromium ions in an elongated tetragonal or more lower symmetrical field. In the glasses produced in more oxidizing conditions than $P_{O2}=10^{-7}$ atm, two absorptions due to octahedrally coordinated $Cr^{3+}$ ions were observed near 22000 $cm^{-1}$ and 15000 $cm^{-1}$. Chromate ions were stable in most glasses produced in air but they were unstable in the glass with $Na_2O/SiO_2$=10/90. ESR measurement was also performed to obtain detailed information on the surroundings of chromium ions in soda- and lime-silicate glasses. Three absorption peaks were observed at g=2.0 (sharp), g=2.0 (broad) and g=5.0 in ESR spectra of these glasses produced at the higher $P_{O2}$ than $10^{-7}$ atm whereas any absorption was not observed in the glasses produced in CO gas. These three absorption peaks were assigned to isolated $Cr^{5+}$ ions, strong electrically coupled $Cr^{3+}$ ion pairs and isolated $Cr^{3+}$ ions in an orthorhombic or other low symmetrical field, respectively. A absorption which seems to be attributed to weak electrically coupled $Cr^{3+}$ ion pairs was also observed at g=2.2 in a few lime-silicate glasses. Further, it was indicated that the critical partial oxygen pressure for the formation of $Cr^{2+}$ ions in soda- and lime-silicate glasses is in the vicinity of $10^{-8}$ atm. Detailed dependencies of ESR spectra in these glasses upon composition and partial oxygen pressure are now being investigated.


### References


1) C.R. Bamford: Phys. Chem. Glasses, **3** (1962), p.189.
2) T. Bates and R.W. Douglas: J. Soc. Glass Tech., **43** (1959) P.289.
3) P. Nath and R.W. Douglas: Phys. Chem. Glasses, **6** (1965), p.197.
4) P. Nath and R.W. Douglas: ibid., p.203.
5) A. Paul: ibid., **15** (1974), p.91.
6) C. Greskovich and V.S. Stabican: J. Phys. Chem. Solids. **27** (1966), p.1379.
7) G.C. Ulmer and W.B. White: J. Amer. Ceram. Soc., **49** (1966), p.50.
8) J.S. Reed: ibid., **54** (1971), p.202.
9) M.G. Frohberg and K. Richter: Arch. Eisenhüttenwes., **39** (1968), p.799.
10) W.J. Rankin and A.K. Biswas: ibid., **50** (1979), p.7.
11) R.H. Sands: Phys. Rev., **99** (1955), p.1222.
12) T. Castner, Jr., G.S. Newell, W.C. Holton and C.P. Slichter: Phys., **32** (1960), p.668.
13) J.S. Griffiith: Mol. Phys., 8 (1964), p.214.
14) R.J. Landry, J.T. Fournier and C.G. Young: J. Chem. Phys., **46** (1967), p.1285.
15) D. Loveridge and S. Parke: Phys. Chem. Glasses, **12** (1971), p.19.
16) N. Iwamoto, Y. Makino and K. Ogino: Trans. JWRI, **1** (1972), p.17.
17) J.P. Fackler, Jr. and D.G. Holah: Inorg. Chem., **4** (1965), p.954.
18) D.E. O'Reilly and D.S. MacIver: J. Phys. Chem., **66** (1962), p.279.
19) C.J. Carman and W.J. Kroenke: J. Phys. Chem., **2** (1968), p.2562.