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Structural Study of Vitreous and Crystalline PbO-SiO_2 System by Raman Spectroscopy†

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Abstract

Raman spectra of PbO-SiO_2 glasses have been measured and compared with reflectance spectra in infrared region. The Raman spectrum of $2PbO \cdot SiO_2$ glass, moreover, was compared with that of crystal of the same composition. It was seen that the Raman band in frequency region from 800 to 1100 cm^{-1} consisted of five peaks near 890, 930, 970, 1030 and 1100 cm^{-1} which were attributed to the SiO_4 tetrahedra with four, three, two, one non-bridging oxygen ion and with four bridging oxygens, respectively. The distributions of three kinds of non-bridging, bridging and free oxygens were calculated from the analysis of intensities of these peaks. They were in agreement with those of Flood and Kapoor.

1. Introduction

It is important to elucidate the structure of slag in steel-making and welding to obtain the knowledge of the reactivity between slag and metal. So, various properties of molten and vitreous silicate slag have been measured and studied thermodynamically.

It is convenient to utilize especially the glass of PbO-SiO_2 system to investigate the structure of slag because of the wide compositional spread region of the vitreous state. Moreover, the glasses of PbO-SiO_2 system are important ones from the conventional industrial applications such as crystal glass and optical glass, or from the electronic technology such as low melting glasses and glass-ceramics.

Since Bair1) and Krogh-Moe2) performed X-ray measurement of lead silicate glasses, many workers have been investigating and proposing the structure from their X-ray studies3,4). As other studies there are measurements of viscosity5), electrical conductivity5), molar refractivity6), infrared spectrum7), Raman spectrum8,9), chromatography11~15) and so on. It is noticed that the various complex anions were experimentally found out in silicate glasses by means of chromatography. To correlate the thermodynamical properties such as activity and basicity to the structure of slag, Flood16) and Masson et al.17) deduced the distribution of complex anions in the slag based on the creation and polymerization of the assumed complex anions. On the other hand, Toop et al.18) calculated the distribution of three kinds of oxygens; bridging oxygen (0°), non-bridging oxygen (0^{-}) and free oxygen (0^{2-}) depending on the composition of slag.

In the infrared absorption measurement it is known that glass structure is generally interpreted from the high frequency part of infrared spectra. However, structural interpretation of infrared spectra is difficult because many spectra were measured on powders and do not reveal true intensities and line shapes. We have been showing the efficiency of Raman scattering by investigating the behavior of various elements in glass19,20). In this work the Raman spectra of PbO-SiO_2 glasses were measured and compared with refrectance spectra. The Raman spectrum of $2PbO \cdot SiO_2$ glass, moreover, was compared with that of the crystal of the same composition. After the attribution of the Raman band was explained, it was tested to calculate the distribution of 0^{-}, 0^{2-} and 0° depending on the composition of glass.

2. Experimental Procedure

The glass samples were prepared as follows. After the analytical-grade reagents of PbO and SiO_2 powders were weighed and mixed sufficiently. The batch was held in a platinum crucible for 2 hr at 1000~1300°C according to the melting point. The melt was taken out from the furnace and cooled in air. The compositions are shown in **Table. 1**

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Table 1. Chemical compositions of Pb0-Si02 glasses

glass	composition (mol%)	
	Pb0	Si02
Pb0·2Si02	33.77	66.23
Pb0·1·64Si02	37.85	62.15
Pb0·1·55Si02	39.22	60.78
Pb0·Si02	50.5	49.5
2Pb0·Si02	65.1	34.9

The study of crystalline state in this work was done for only one compositional 2PbO·SiO$_2$. After the 2PbO·SiO$_2$ glass produced as mentioned above was ground to powder in mortar and pestle, it was treated in a platinum crucible by heating under the condition shown in **Table 2.**

Table 2 Heat treatment temperature and during time for preparing crystalline Pb0-Si02

glass	temperature (°C)	time (hr)
2Pb0·Si02	425	24
	500	24
	620	24
	725	24

Measurements of Raman spectra were made with a 350 mW 5145Å Ar ion laser. In the vitreous PbO-SiO$_2$ glasses the laser beam was focused on the polished surface of the specimen and the scattered radiation at an angle of 90° from the incident beam was analyzed by a Spex model 1400 double monochromator with a photomultiplier having cooled S-20 photocathode and recorded using a lock-in detection system. On the other hand, in the crystals of PbO-SiO$_2$ the back scattered method was applied to the mixed and pressed disk of crystalline lead-silicate (about 200 mg) and potassium bromide (about 100 mg) powders. The scattered light from the disk specimen was analyzed by the same instrument as mentioned above.

X-ray diffraction measurements were carried out with GF-3 X-ray diffractometer (Rigaku Denki Co., Ltd.) on the powder specimen of a 2PbO·SiO$_2$ glass and 2PbO·SiO$_2$ crystals treated under the various conditions. The X-ray source was K_α from *Cu* target filtered with *Ni.*

The infrared reflectivity measurements were performed on some glasses with Hitachi 225 type spectrometer in the frequency region from 2000 to 200 cm^{-1}. The results obtained were analysed by Kramers-Kronig method.

3. Results

3.1. Glasses of PbO-SiO$_2$ system

Raman spectra of glasses of PbO-SiO$_2$ system are shown in **Fig. 1.** These spectra are similar as those obtained by Hagiwara et al.$^{8)}$ except the band at 790 cm^{-1} was obviously observed in this work. The feature of the Raman spectra are characterized by small bands at 790 and 1100 cm^{-1}, and large broad band in the frequency range of 800~1100 cm^{-1}. The bands at 790 and 1100 cm^{-1} decrease in intensity with PbO content and reduce in the glasses containing a concentration of PbO higher than 50 mol%. It is considered that these bands are due to Si-O°-Si bond vibration because of the appearance in fused SiO$_2$ glass$^{19)}$. It seems that the intense band at 800~1100 cm^{-1} consists of some peaks because some slight shoulders are observed. Depending on the intensities of these peaks, the broad band may shift apparently to lower frequency with increasing PbO content.

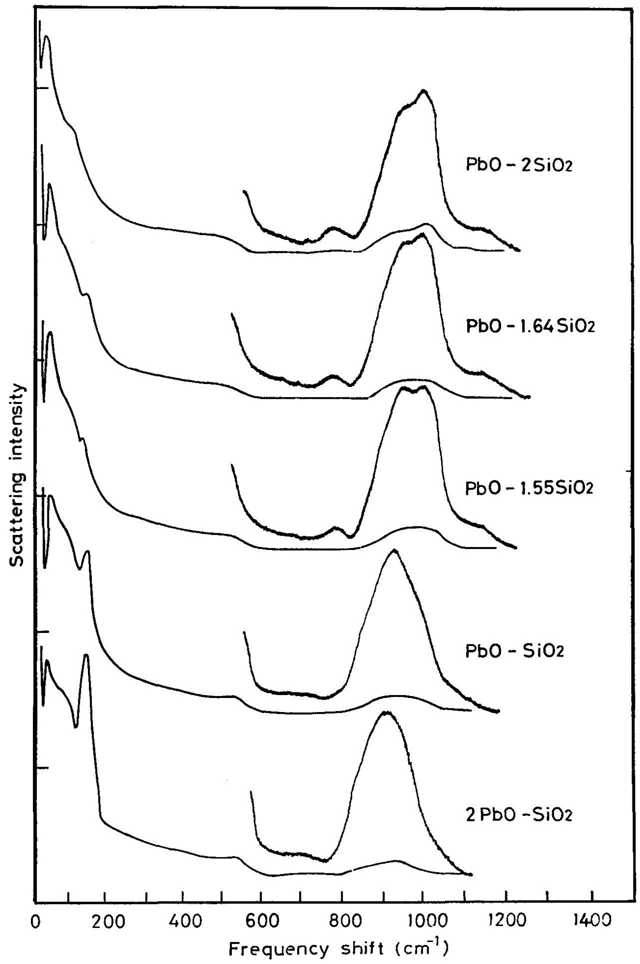
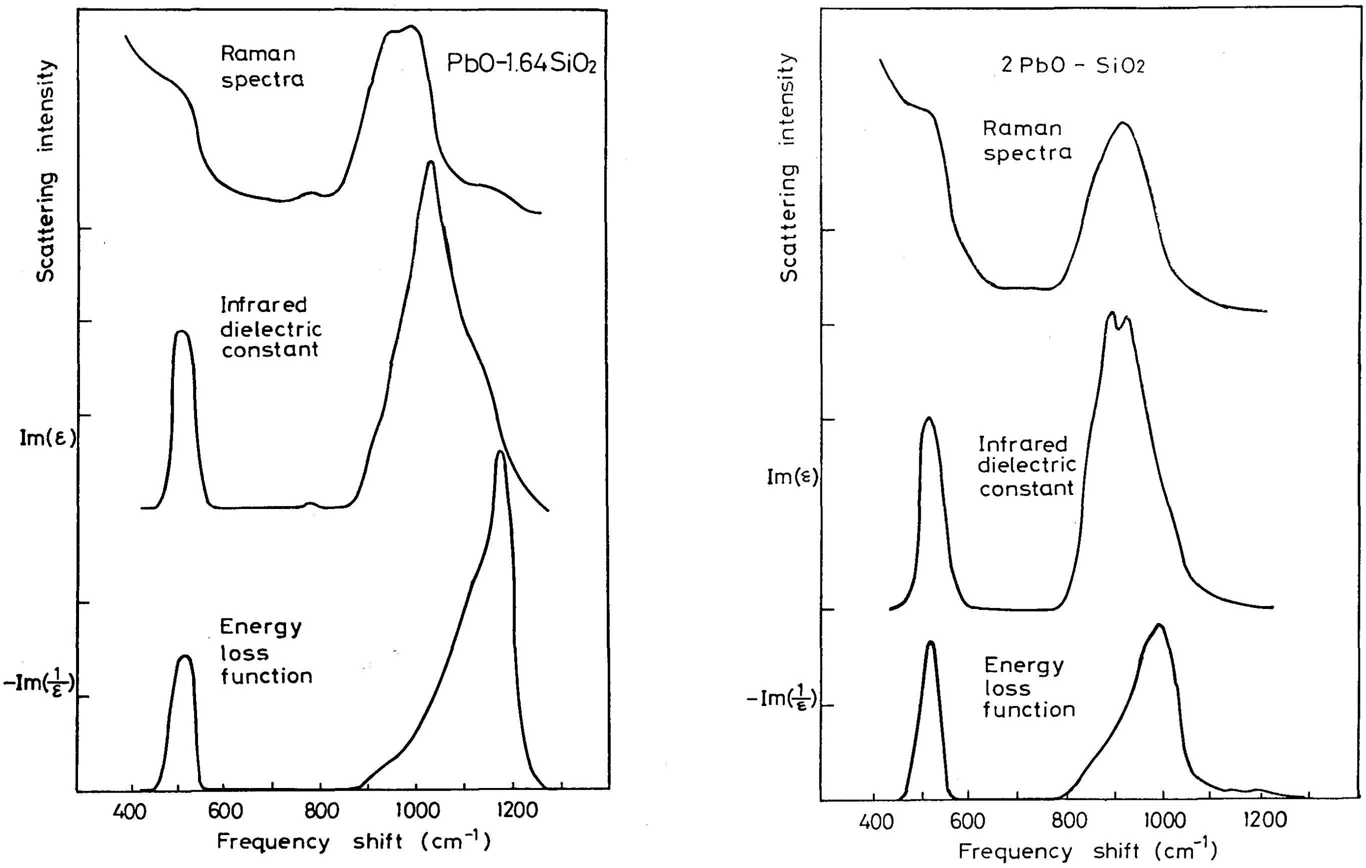


Fig. 1 Raman spectra of glasses of Pb0-Si02.

It is well known that the transverse and longitudinal



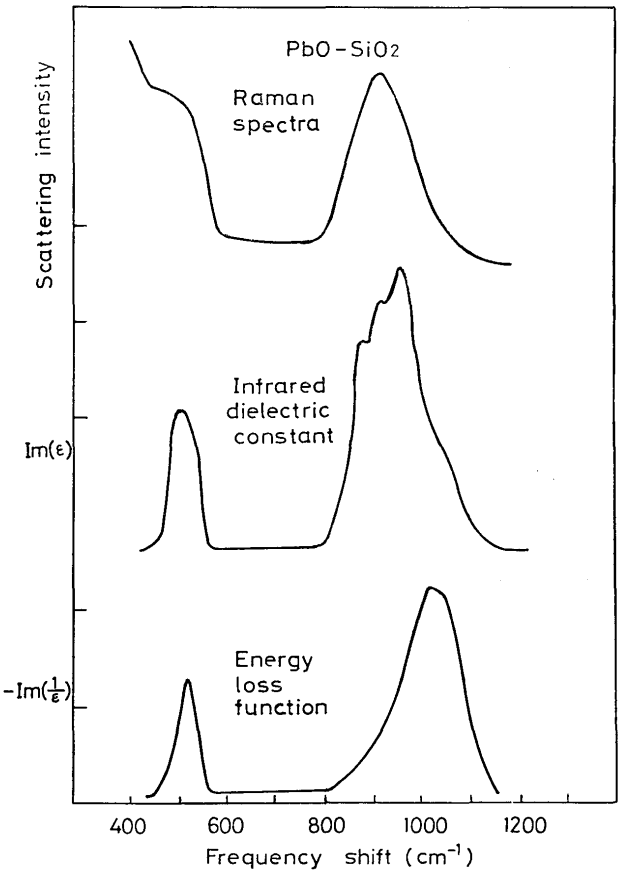


Fig. 2 Comparison of Raman spectrum with infrared dielectric constant (Im(ε)) and energy loss function (–Im(1/ε)) for (a) PbO·1.64SiO2. (b) PbO·SiO2 and (c) 2PbO·SiO2 glasses.

modes in sample are calculated from Kramers-Kronig analysis$^{21,22)}$ of infrared reflectivity of the sample. It is expected that a transverse model (TO) appears as a peak of imaginary part Im(ε) = ε″ of complex dielectric constant ε = ε′ + iε″ while a longitudinal mode (LO) appears as a peak in the energy loss function Im (–1/ε) = $\varepsilon''/(\varepsilon'^2 + \varepsilon''^2)^{23)}$. The calculated values of Im (ε) and Im (–1/ε) of PbO-SiO$_2$ glasses from reflective measurements are shown in **Fig. 2**. It is seen that the peaks near 890, 930, 970, 1030, 1100 and 1170 cm^{-1} appear as TO or LO mode. Comparing the Raman spectra with the transverse (ε′) and longitudinal (Im (–1/ε)) loss functions in Fig. 2, it is deduced that the broad band in the frequency range from 800 to 1100 cm^{-1} in Raman spectra is attributed to those peaks. It seems that the intensity of these peaks at lower frequency increases while those of higher frequency decreases in intensity with increasing of PbO content in glasses.

3.2. Crystals of $2PbO \cdot SiO_2$

$2PbO \cdot SiO_2$ crystal produced from the glass contains various complex anions such as SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, polysilicate and so on, of which the amounts depend on the heating treatment temperature and time[11,12]. Figures 3 and 4 show the Raman spectra and X-ray diffraction result of crystalline polymorphs $2PbO\text{-}SiO_2$ treated under the similar condition as Götz et al.[12]^2, respectively. Our features of X-ray measurements are good agreement with those of Götz except for the line of d=3.13Å observed clearly in the crystal treated in 725°C–24 hr. It is, therefore, considered that our crystalline $2PbO\text{-}SiO_2$ treated at 425, 500, 620 and 725°C correspond to T-Pb_2SiO_4 (which contains mainly $Si_2O_7^{6-}$ complex anion), M_1-Pb_2SiO_4 ($Si_4O_{12}^{8-}$), M_2-Pb_2SiO_4 ($Si_4O_{12}^{8-}$ and $((SiO_3^{2-})_n)$ and H-Pb_2SiO_4 $((SiO_3^{-})_n)$, respectively, according to Götz et al. In the Raman spectra in Fig. 3, characteristic peaks at 930, 950 and 965 cm^{-1} are seen. The peak at 930 cm^{-1} is the most intense in the glass treated at 425°C and reduces rapidly in intensity in glasses treated at higher temperature, while the peak at 956 cm^{-1} shows the opposite behavior. It is, therefore, considered that the intense peaks will reflect the crystallized state, that is, the peak at 930 cm^{-1} is due to $Si_2O_7^{6-}$ and the peak at 965 cm^{-1} due to $Si_4O_{12}^{8-}$ or the larger complex anions.

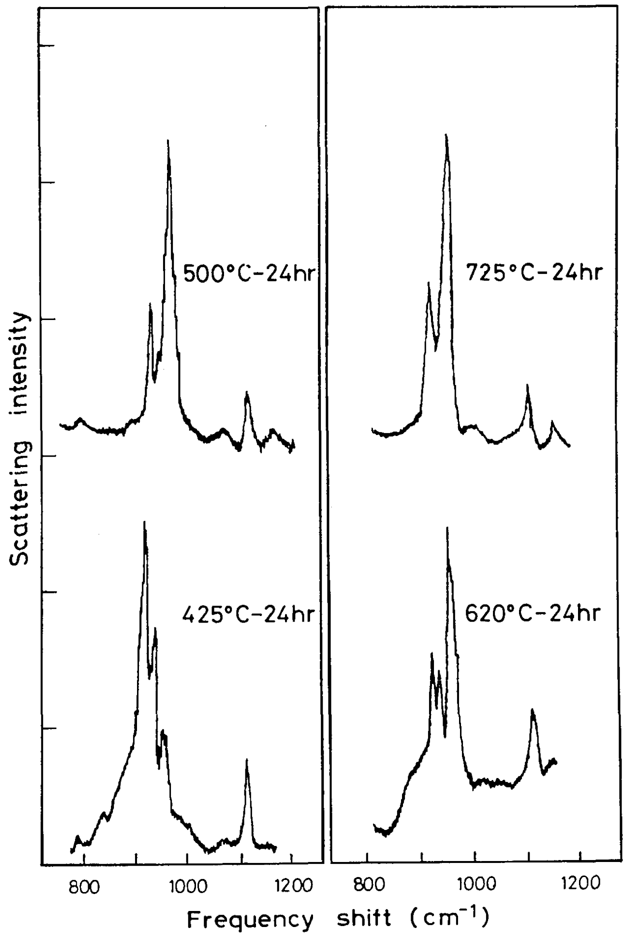


Fig. 3 Raman spectra of crystalline $2PbO \cdot SiO_2$.

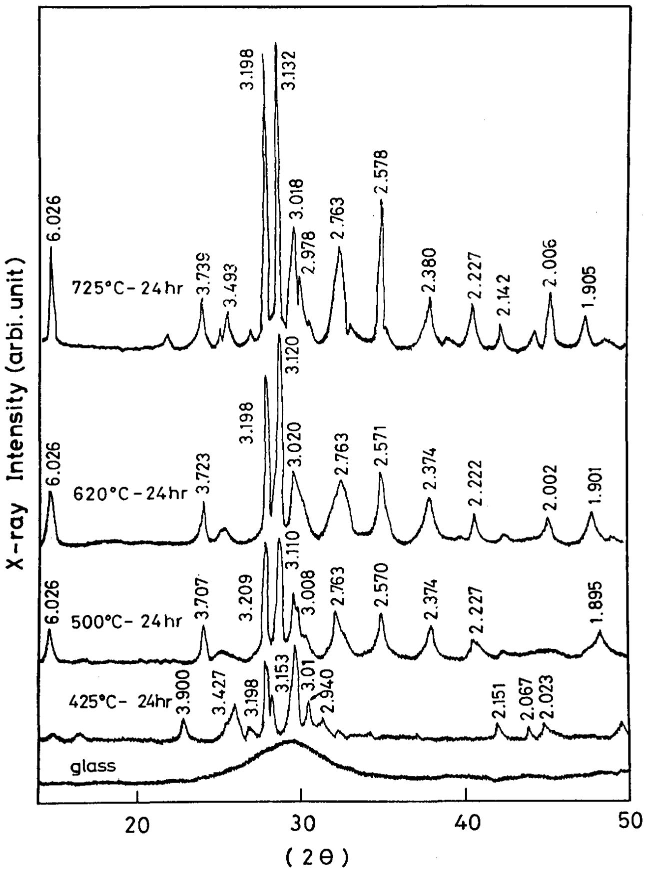


Fig. 4 X-ray diffraction patterns of vitreous and crystalline $2PbO \cdot SiO_2$.

4. Discussions

It is generally known that there is a following close resemblance between Raman spectra of glassy and crystalline silicates at frequency above about 300 cm^{-1}; (1)the dominant peaks of the crystal spectrum appear in the spectrum of glass with similar composition, (2)the weak peaks and shoulders in the glass spectrum are not seen or are very weak in the corresponding crystal spectrum. These facts suggest that the short-range order in silicate glass is similar to the corresponding crystalline silicate. It will be, therefore, possible to deduce of the structure glass from the comparison with crystal.

Yanagase[24] has been showing the correspondence of the complex anions to the absorption frequency in infrared region by comparing his infrared spectra of silicate glasses with those of minerals obtained by Saksena[25]. He indicated that the absorption peaks due to SiO_2°,

$Si_{4n}O_{9n}^{2n-}$, $Si_{2n}O_{5n}^{2n-}$, $Si_nO_{3n}^{2n-}$, $Si_2O_7^{6-}$ and SiO_4^{4-} correspond to 1108, 1068, 1020, 970, 930 and 887 cm^{-1}, respectively. In his infrared absorption spectra of $PbO-SiO_2$ glasses, however, only one broad peak was observed and shifted with PbO content in 800~1100 cm^{-1} 7). In our study as shown in Fig. 1, it is considered that the band in 800~1100 cm^{-1} consists of some peaks which change in intensity according to PbO content in glass. Moreover, the peak positions (890, 930, 970, 1030 and 1100 cm^{-1}) obtained from Kramers-Kronig analysis of reflectance spectrum are well in agreement with those of complex anions proposed by Yanagase24).

Brawer et al.26,27) and Konijnendijk et al.28-30) suggested from their Raman spectra of crystalline and vitreous $M(=Li, Na, K)_2O-SiO_2$ or alkali-alumino-silicate glasses that the peak at about 1000 cm^{-1} was due to the SiO_4 tetrahedra with one nonbridging oxygen ion and 970 cm^{-1} peak was due to the tetrahedra with two non-bridging oxygen ions. The latter result supports that the peak near 965 cm^{-1} in our crystalline polymorphs is attributed to $Si_4O_{12}^{8-}$ or $(SiO_3)_n^{2-}$.

It is deduced from above mentioned discussions that the Raman band in 800~1100 cm^{-1} consists of five peaks near 890, 930, 970, 1030 and 1100 cm^{-1} which are attributed to the SiO_4 tetrahedra with four, three, two, one non-bridging oxygen ions and with all bridging oxygen ions, respectively. Therefore, each Raman spectrum was separated into five peaks by the iterative least square procedure with assumption of Gaussian peak20). Based on the areas under the separated peaks, the ion fractions of 0^-, 0^{2-} and 0° were calculated as shown in **Fig. 5**. The result for $PbO \cdot SiO_2$ glass is not shown because of disconvergence of the iterative calculation. It is seen that these ion fractions agree with those from thermodynamical calculations by Flood 16) and Kapoor et all.32) It is interesting to be able to obtain from Raman spectrum the distribution of 0^-, 0^{2-} and 0° depending on the composition of glass. This method contains some assumptions; each scattering efficiency does not change depending on number of 0^- in a SiO_4 tetrahedra, only main peak corresponding to SiO_4 tetrahedra with various number of 0^- is taken into consideration. However, this procedure seems to be considerably reliable for the glasses containing large amount of basic oxides which do not show 1100 cm^{-1} Raman peak due to Si-0° bond. It will become clear by performing the furthermore Raman studies of various system glasses.

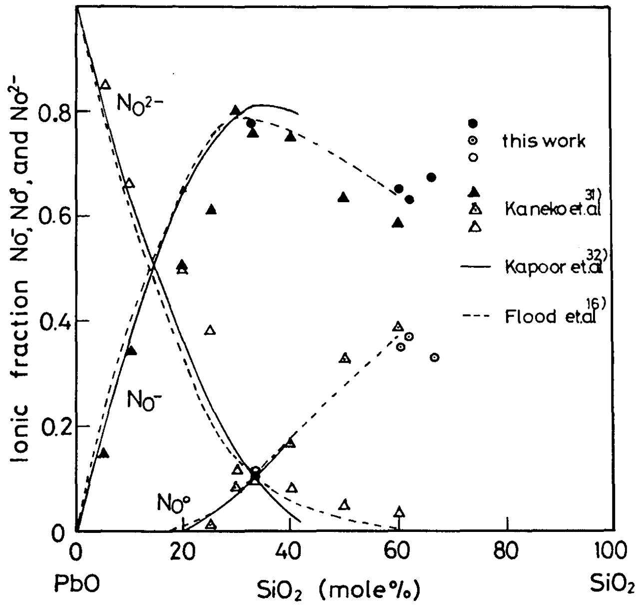


Fig. 5 Distribution of 0^-, 0^{2-} and 0^0 depending on the composition of PbO-SiO2 glasses.

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