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Neutron Diffraction Study of the Structure of Li_2O-SiO_2 Binary Glasses

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The study on vitreous lithium silicates has been carried out within the framework of general research on the structure of simple or multicomponent glasses by means of neutron diffraction, after a study on pure silica and on the soda-silica system.

Besides the general advantages of neutron diffraction in the study of disordered substances, we have exploited the peculiarity of Li, which together with few other atoms, scatters neutrons without the common 180° phase shift or, in other words, has a negative scattering factor.

Consequently, in the atomic radial distribution curve, peaks related to the distances between Li and other different atoms become negative, and so are more easily recognisable.

By means of two different wavelengths, diffraction spectra of a series of vitreous samples in the molar composition range 18 – 36.5% of Li_2O in SiO_2 have been obtained which were extended up to a value of $S_{max} = 4\pi \sin\theta/\lambda$ as large as 14 Å^{-1}.

Interpretation of the results has been attempted on the basis of the so-called "differential method" (Poraj-Koshits) and enabled identification of typical co-ordination distances that revealed a short range chemical order, thus confirming the existence of microheterogeneities recently discovered with other methods (low angle scattering of X-rays and electron microscopy) by some authors.

1. Introduction

Of the vitreous silicates containing alkali oxide, those belonging to the binary systems with sodium and lithium are the most important because they are components of the commonest glasses. Such oxides are indicated as oxides of "modifying" elements in the tridimensional lattice built up by the SiO_4 tetrahedra in vitreous silica where silicon is the "forming" element.

A first study in our laboratory by means of neutron diffraction [1] was made on the structure of pure silica and a well defined radial distribution curve derived which constituted a good basic test for the various theoretical hypotheses on the statistical model of the silica structure [2]. The soda-silica binary system was then studied [3], and by applying the so-called differential method [4], acting on the radial distribution curves of various binary compounds as compared with that of pure silica, the first and principal co-ordination distances between the "modifying" element (Na) and the residual atoms were recognised.

One of the first differences encountered in the study of the lithium-silica binary system, the object of this work, compared to the soda-silica binary system arises from the difficulty of obtaining an equally wide range of compositions in the vitreous state, because of the high tendency to devitrification of the present system.

In the first case we were able to extend our investigation to a composition range up to a maximum molar concentration of about 50% of Na_2O in silica. This permitted us to derive direct conclusions about the type of short range chemical order that progressively takes place in such a system with an increasing Na_2O content. These conclusions were in close agreement with those of a previous study by Poraj-Koshits [4], using X-ray diffraction.

In the present case, no previous studies with

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X-ray diffraction are reported for the vitreous lithium silicates and we were drawn to investigating them with neutron diffraction because of the peculiarity that the Li atom shares with few other atoms (H, Ti, Mn, Ni^{62}): they scatter neutrons without the normal 180° phase shift but exhibit a negative scattering amplitude for neutrons. Consequently, the peaks, which in the atomic radial distribution curve represent the coordination distances of such atoms with atoms having scattering amplitudes of positive sign, will appear as negative or "inverse" peaks and are thus more easily discerned from the others.

In the study of neutron diffraction spectra of fused salts such as LiCl, KCl and CsBr, the exploitation of this peculiarity has already enabled some authors [5] to reveal the greater definition of the peaks in radial distribution of LiCl compared with the corresponding one obtained with X-rays [5, 6].

Previous studies on the structure of the vitreous lithium silicate system concern the techniques of the low angle scattering of X-ray [7] and of electron microscopy [8].

2. Experimental Procedure

2.1. Sample Preparation

The phase diagram of the Li_2O-SiO_2 system has been studied by Kracek [9], and the regions of glass formation and spontaneous or catalysed crystallisation are widely reviewed in [10].

The range of glass formation is between 0 and 40 mole % of Li_2O: beyond the 40% molar concentration, considerable spontaneous devitrification takes place. Concentrations of less than 10% in mole of Li_2O require fairly high fusion temperatures.

The samples prepared by us range between 18 and 36.5 mole % Li_2O. For SiO_2 the raw material employed was silicic acid calcined at 1400°C with a final SiO_2 content $> 99.7\%$; for Li_2O, lithium carbonate with a final Li_2O content $> 99.8\%$.

Owing to the different viscosity that resulted for various compositions, it was considered useful to maintain the same value of viscosity as far as possible by varying the fusion temperatures for each composition.

The preparations steps were as follows, and table I shows the characteristic parameters for the various samples:

(*a*) The raw materials were put in the furnace for $1\frac{1}{4}$ h at 1300° C.

(*b*) Fusion at the cited temperature for 4 h: the melt was periodically agitated.

(*c*) Casting on a steel plate and rapid cooling under a liquid nitrogen spout.

(*d*) Further fusion for different lengths of time, at the same temperature as in (*b*) to render the glass more homogeneous; this treatment was essential and prolonged for high viscosity samples.

(*e*) As in (*c*).

(*f*) Finally, the glasses were milled and sieved, only the portion which was of grains between meshes 100 and 300 μm being retained.

2.2. Neutron Diffraction Measurements

Due to the need for rapid cooling of the melt on a steel plate to prevent devitrification, massive samples of well-defined dimensions, like those obtained in previous work on the soda-silica system [3] were not available, but only uniformly grained powders.

The powders were mounted on the diffractometer in a suitable cylindrical sample-container of 12 mm internal diameter having a vanadium wall 0.2 mm thick. Vanadium was selected because of its high transmission and low coherent scattering cross-section, so that the spectrum of the empty sample-container did not present any appreciable diffraction effect but only a continuous isotropic background, apart from the contribution of the central peak due to the direct beam.

A 12 mm internal diameter was selected as a good compromise to have always the same volume of material uniformly bathed by the radiation and to avoid too large sample absorption values, particularly important for higher Li_2O concentrations; in practice, for all the examined samples, the ratio

$$\frac{I}{I_0} = e^{-2\mu R} \qquad (1)$$

where R is the radius of the sample holder and μ the linear absorption coefficient of the sample under examination, was contained in the range between 50 and 70%, so that it was possible to make corrections by using the tables which give the correction factors as a function of the Bragg angle, like that reported for neutrons [6].

Registration of the spectra was effected in two steps for any single sample. Firstly, neutrons of wavelength $\lambda = 1.049$ Å which constitute the principal wavelength selected by reflection on the planes (1 1 1) of a copper single-crystal set on the direct polychromatic beam were utilised.

TABLE I

Sample no.	Composition	% weight	% molar	Melting temperature	Viscosity	Fusion (b) (b)	Further fusion (d)
30391	Li_2O	9.85	18	1530° C	very high	4 h	3 h
	SiO_2	90.15	82				
30393	Li_2O	14.88	26	1480° C	high	4 h	1 h
	SiO_2	85.12	74				
30394	Li_2O	19.97	33.4	1400-1420° C	low	4 h	1 h
	SiO_2	80.03	66.6				
30395	Li_2O	22.25	36.5	1360-1380° C	very low	4 h	1 h
	SiO_2	77.75	63.5				

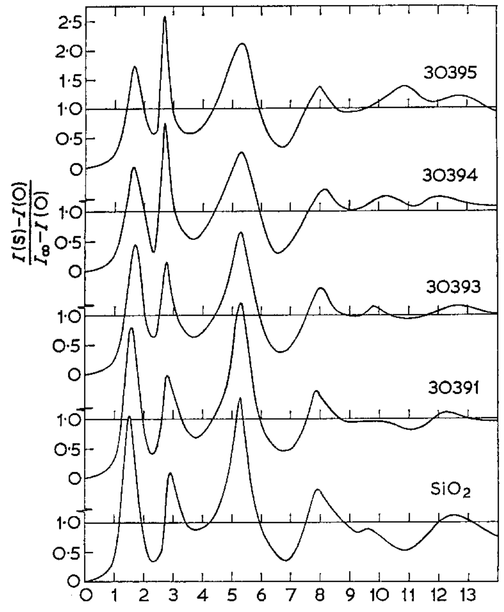

Figure 1 Direct normalised spectra obtained with both the wavelengths used, for the various samples and amorphous silica.

Secondly, neutrons of wavelength $\lambda/2 = 0.525$ Å were utilised, which constitute the second harmonic of the previously defined beam, selected by means of a suitable filter already described [11]. The use of such a short wavelength allowed expansion of the diffraction spectra up to very large values of $S = 4\pi(\sin\theta)/\lambda$ and therefore permitted better resolution for the peaks in the atomic radial distribution function [12].

2.3. Results Obtained and their Elaborations

In fig. 1 are reported the diffraction spectra for the four glasses examined and that of pure silica in comparison, all obtained with both the wavelengths. The intensity values $I(S) - I(0)/I_\infty - I(0)$ are normalised with respect to the asymptotic value $I_\infty - I(0)$, that is after subtraction of the intensity value extrapolated for $S \rightarrow 0$. This last value includes both the incoherent scattering, assumed as practically isotropic, and the multiple scattering [1]. Progressive evolution in the trend of the spectra can be observed, particularly of the second and third peak, starting from the pure silica and ascending to samples richer in lithium: the second peak becomes sharper and higher, and the third one is widened. In addition, with increasing lithium content, a low peak becomes evident for $10 < S < 11$ Å^{-1}.

In the case of non-crystalline substances containing more than one atom, the Fourier transform which enables derivation of the radial distribution functions $Q(r)$ from the intensity spectra $I(S)$ is given by the well-known formula [12, 13]:

$$Q(r) = 4\pi r^2 \bar{g}(r)_{mn} = 4\pi r^2 \bar{g}_0 + \frac{2r}{\pi}\frac{\sum_m b_m{}^2}{b^2(0)}\int_0^\infty S i(S)\sin(rS)\,dS \qquad (2)$$

where

$$S = \frac{4\pi \sin\theta}{\lambda}$$

$$i(S) = \frac{I(S)}{N\sum_m b_m{}^2} - 1 = \frac{I(S)}{I_\infty} - 1$$

$$\bar{g}(r)_{mn} = \frac{\sum_m b_m \sum_n b_n}{b^2(0)}\, g(r)_{mn}$$

$$\bar{g}_0 = \frac{(\sum_m b_m)^2}{b^2(0)}\, g_0 \text{ with } g_0 \text{ density (in atoms/Å}^3\text{)}$$

b_m = nuclear scattering amplitude of the atom m
$\sum_m$ = sum taken over all the m atoms in a molecule
$\sum_n$ = sum on the atoms in the system except for the chosen atom m.

It has been shown, for instance in [13], that the assumption of a finite value as upper limit of integration for the integral at the right of equation 2 gives a series of spurious effects which appear as ripples superimposed on the actual curve with a frequency inversely proportional to S_{max}.

In order to verify that our interpretations were independent of the presence of such spurious effect, we elaborated in two steps the series of spectra reported in fig. 1 assuming two different values of S_{max}. The elaboration consisted in the evaluation of the integral at the right side of equation 2, that is of the function

$$F(r) = Q(r) - 4\pi r^2 \bar{g}_0 = 4\pi r^2[g(r)_{mn} - \bar{g}_0] = \frac{2r}{\pi}\int_0^{S_{max}} Si(S)\sin(rS)\,dS$$

where S_{max} assumed the values 8.7 $Å^{-1}$ in the first step and 14 $Å^{-1}$ in the second.

The function $F(r)$ which represents the atomic radial distribution after subtraction of the continuous contribution due to the average density $\bar{g}_0$, has been calculated for the various spectra by using a computer program [14] set up for the electronic computer ELEA 6001.

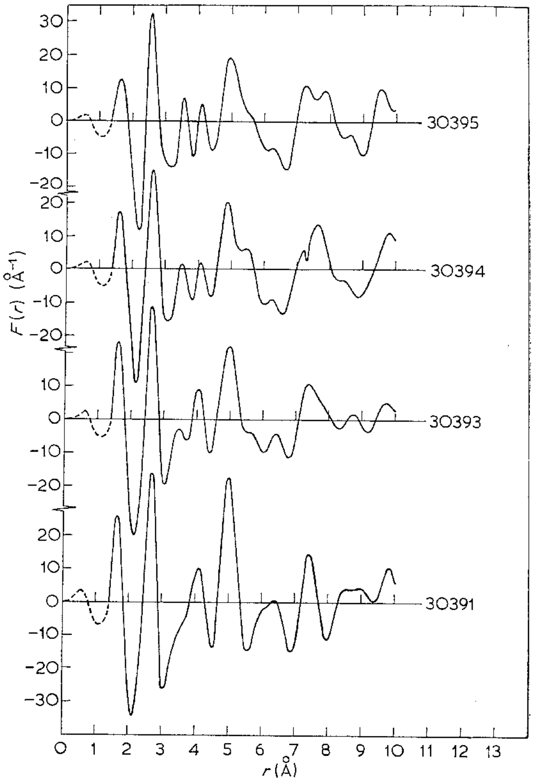

Figure 3 Inverse Fourier transform for the various samples ($S_{max} = 14$ $Å^{-1}$).

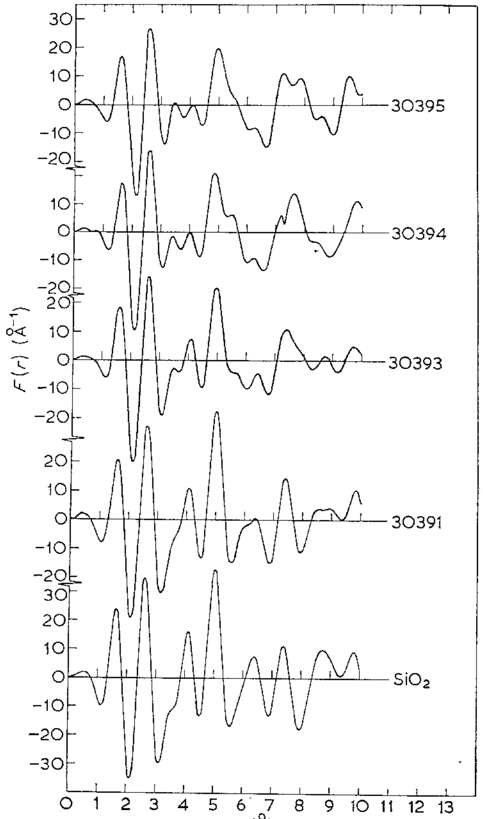

Figure 2 Inverse Fourier transform for the various samples and amorphous silica ($S_{max} = 8.7$ $Å^{-1}$).

The results are reported in fig. 2 for the first step in which a value of $S_{max} = 8.7$ $Å^{-1}$ was selected and in fig. 3 for the second step with $S_{max} = 14$ $Å^{-1}$. At the bottom of fig. 2 the function $F(r)$ for pure silica is also given for comparison purposes.

The extension of the upper integration limit to $S_{max} = 14$ $Å^{-1}$ allows by comparing the curves of fig. 3 and fig. 2 a better definition of the peaks up to $r = 5$ Å and results in the appearance of some spurious oscillations between $r = 0$ and 1.5 Å which are interpolated, as already in [1], by means of the dotted curves.

3. Interpretation and Discussion

The interpretation of the diagrams of figs 2 and 3 has been conducted on the basis of the so called "differential method" earlier applied by Hartleif [15], more recently by Poraj-Koshits [4] and by the authors in the previous study on the soda-silica glasses [3]. The method consists in subtracting from the various radial distribution functions $Q(r)$ or more directly, as in our case, from the Fourier integrals $F(r)$, obtained for the various samples under examination, that of pure silica multiplied for the actual concentration of silica present in the sample.

Among the oscillations which will appear in such difference curves, those stably present for all the samples and which increase with an increase in the modifying element content are to be recognised as co-ordination statistics of the atoms introduced in the system as oxides of the modifying element.

Another condition is that such oscillation must be independent of the termination effect and, in order to verify this, the method has been applied on both the diagrams of figs. 2 and 3, having termination values of $S_{\max} = 8.7$ Å^{-1} and 14 Å^{-1} respectively. The results are reported in figs. 4 and 5, and comparing them it is observed that the principal oscillations are present in both and are better defined in fig. 5, obtained from spectra extended up to larger values of $S_{\max}$.

In analysing the diagrams of figs. 4 and 5 one can take advantage of the fact that the lithium atom has negative scattering amplitude for neutrons and the intensity of the single peaks being proportional to the number of co-ordinated atoms and to the product of the related scattering amplitudes, the distances Li-O can be recognised in the negative peaks present in the diagrams of figs. 4 and 5 which become more pronounced with increasing Li content. The same does not apply for the positive peaks which can be ascribed to Li-Li or O-O co-ordinations. The list of positions of the negative peaks which increase with increasing Li content observed in both the figures is reported in table II. It is observed that the intensities of such inverse peaks in both figs. 4 and 5 seem to be more pronounced in sample 30394 than in sample 30395. The first has a Li$_2$O concentration of 33.4% in moles, that is, it corresponds to the concentration of the disilicate, the second has a concentration (36.5% molar of Li$_2$O) in excess to the disilicate. The possibility of small-scale crystallisation in sample 30395 can not be excluded. It may be significant that the composition of this sample lies outside the region of glass formation quoted by Rawson [15] for melts on a scale of 1 to 2 g (0 to 35.5 mole % Li$_2$O).

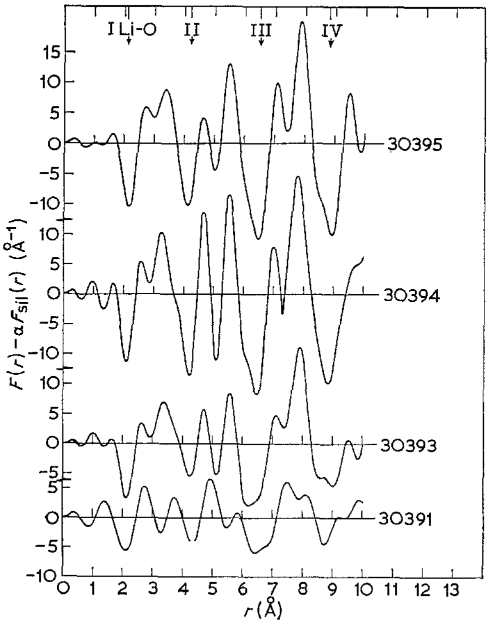

Figure 4 Application of the differential method for the various samples ($S_{\max} = 8.7$ Å^{-1}); α = molar concentration of SiO$_2$.

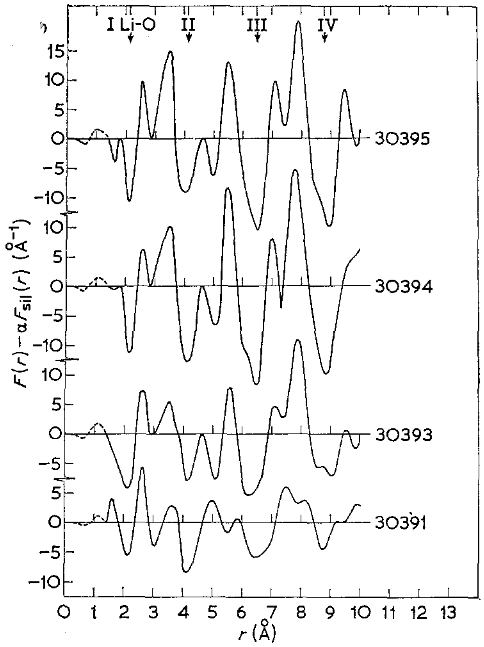

Figure 5 Application of the differential method for the various samples ($S_{\max} = 14$ Å^{-1}); α = molar concentration of SiO$_2$.

The fact that samples having an even higher concentration of Li$_2$O were not available, does not enable us to discuss directly, as was done for the soda-silica system [3], whether the chemical order at short range, taking place among the

TABLE II

	I	II	III	IV
Fig. 4 ($S_{max} = 8.7$ Å^{-1})	$r = 2.1$	$r = 4.2$	$r = 6.5$	$r = 8.8$
Fig. 5 ($S_{max} = 14$ Å^{-1})	$r = 2.15$	$r = 4.15$	$r = 6.5$	$r = 8.8$

atoms of the modifying oxide and the matrix, approximates that of the crystalline meta or disilicate. But the fact, just pointed out, about the intensities of the inverse peaks and the remarks already contained in the literature [8] on the microheterogeneities observed with electron microscopy, whose dimensions become minima when the Li_2O concentration corresponds to the disilicate, make consistent the hypothesis of a set up of a short range chemical order similar to that existing in the crystalline disilicate.

Further confirmation can be obtained by comparing the first distance Li-O observed by us (see table II) with the distances of the first neighbours reported by Liebau [16] for the stable crystalline form of the disilicate. They are

$Li_1 - O_2 = Li_2 - O_3 = 1.85$ Å
$Li_1 - O_4 = Li_2 - O_5 = 2.04$ Å
$Li_1 - O_5 = Li_2 - O_4 = 1.99$ Å
$Li_1 - O_4'' = Li_2 - O_5'' = 1.88$ Å

with a mean value for the first Li-O distances of 1.94 Å.

4. Conclusion

The analysis of the atomic radial distribution curves, by means of the differential method, enabled us to recognise the existence of characteristic co-ordination radii among the atoms introduced as oxide of the modifying element in the silica matrix for the all composition range of the binary glasses examined.

The short range chemical order that takes place is therefore in agreement with the experimental observations of the microheterogeneities existing in such a binary system [7].

Within the limits of the composition range that preparation methods permitted, it can be deduced that such type of chemical order is closely connected with that existing in the crystalline disilicate, in agreement with the observations of W. Vogel with electron microscopy [8], who reported that such microheterogeneities disappear when the concentration of Li_2O attains the value corresponding to the disilicate.

Acknowledgements

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