Neutron Diffraction Study of the Structure of Li₂O-SiO₂ Binary Glasses

M. DOMENICI,* F. POZZA**
SORIN, Centro Ricerche Nucleari, SALUGGIA, Italy

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 Li₂O in SiO₂ have been obtained which were extended up to a value of $S_{\text{max}} = 4\pi \sin \theta / \lambda$ 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 SiO₄ 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 Na₂O 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 Na₂O 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
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, Ni⁶⁺): 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 Li₂O-SiO₂ 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 Li₂O: beyond the 40% molar concentration, considerable spontaneous devitrification takes place. Concentrations of less than 10% in mole of Li₂O require fairly high fusion temperatures.

The samples prepared by us range between 18 and 36.5 mole % Li₂O. For SiO₂ the raw material employed was silice acid calcined at 1400°C with a final SiO₂ content > 99.7%; for Li₂O, lithium carbonate with a final Li₂O 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 ½ 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 Li₂O concentrations; in practice, for all the examined samples, the ratio

\[
\frac{I}{I₀} = e^{-\mu R}
\]

where \( R \) is the radius of the sample holder and \( \mu \) 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.