

XPS study of lithium disilicate glass crystallisation

P. C. Soares Jnr, P. A. P. Nascente¹ & E. D. Zanotto²

LaMaV–Vitreous Materials Laboratory, Department of Materials Engineering, Federal University of São Carlos, 13565–905 São Carlos, SP, Brazil

Manuscript received 13 July 2001
Revision received 7 December 2001
Accepted 1 February 2002

The failure of the classical nucleation theory to quantitatively describe crystal nucleation rates in glasses may be attributed to several causes. Some authors speculate that a possible reason for this discrepancy is the formation of metastable phases in the early stages of crystallisation prior to the equilibrium phase. This issue has been a subject of controversy for the last 40 years but our recent transmission electron microscopy (TEM) analysis clearly shows the precipitation of a second phase (lithium metasilicate) in addition to the stable phase lithium disilicate in a slightly hyper-stoichiometric lithium disilicate glass (34.5 mol% Li₂O) heat treated at $T_g \sim 450^\circ\text{C}$. Additionally, an x-ray photoelectron spectroscopy (XPS) study reported in the literature indicated that a metastable phase precipitates in the early stages of crystallisation of a lithium disilicate glass heat treated at 450°C . This work aims to confirm the XPS results for lithium disilicate glass samples treated for several time periods in the vicinity of T_g . However, in none of the samples investigated by XPS were found any evidence of metastable phase or even of the second phase previously observed by TEM. Possible causes for the discrepancy between the present and XPS results of the literature are discussed.

Due to the scientific and technological importance of glass crystallisation and glass ceramics, numerous studies were carried out and thousands of papers were published in the last 40 years to get a deeper insight of the crystallisation kinetics and microstructural evolution of these materials.

The failure of the classical nucleation theory (CNT) to quantitatively describe crystal nucleation rates in glasses has been assigned to several reasons, including the extremely small size and diffuse interface of the crystalline nuclei at high undercoolings, a possible temperature or size dependence of the surface energy⁽¹⁾ or

the slow relaxation of elastic stresses that arise on crystal nucleation.^(2,3)

In addition to such possibilities, some authors proposed that the precipitation of metastable phases in the early stages of crystallisation, prior to the appearance of the stable phase, could contribute to CNT's failure. Hence, the issue of metastable phase formation is of considerable importance because it may offer a possible explanation for (at least part of) the observed discrepancies between theoretically predicted and experimentally determined nucleation rates in glasses.⁽⁴⁾

Jacquim *et al.*,⁽⁵⁾ Zanotto & Leite,⁽⁶⁾ Zanotto⁽⁷⁾ and Burgner *et al.*^(8,9) reviewed numerous publications and described their own experiments dealing with microscopy and x-ray diffraction (XRD) studies in search of possible metastable phases on glass compositions near lithium disilicate (LS₂) but the matter has not yet been conclusively solved. For instance, Zanotto & Leite⁽⁶⁾ and Zanotto⁽⁷⁾ studied the crystallisation of a LS₂ glass at 500°C by optical microscopy and found that any metastable phase, if present at all, does not have a significant impact on the overall crystallisation kinetics of the stable phase (LS₂). The XRD results of Burgner *et al.*^(8,9) showed only diffraction patterns of stable LS₂ crystals, contrary to the findings of Iqbal *et al.*⁽¹⁰⁾ who reported the appearance of α -LS₂ and β' -LS₂ phases. These discrepant findings reinforce the history of controversy on the crystallisation of LS₂ glasses.

However, ongoing TEM study⁽¹¹⁾ of the same slightly hyper stoichiometric LS₂ glass used in this research (34.5 mol% Li₂O) heated from 2.5 to 312 h at 454°C , clearly shows the presence of a second phase, lithium metasilicate (LS), in samples treated up to 120 h.

Additionally an isolated x-ray photoelectron spectroscopy (XPS) study, by Adams *et al.*,^(12,13) observed an extra peak in the Li 1s photoelectron line of a LS₂ glass subjected to 0.5–6 h at $T_g \sim 450^\circ\text{C}$. This peak was suggested to be due to the precipitation of a metastable phase (LS) because it disappeared after 6 h. The motivation for the present work was due to these unexpected XPS results (our TEM study demonstrated

¹CCDM – Centro de Caracterização e Desenvolvimento de Materiais

² Author to whom correspondence should be addressed. (e-mail: dedz@power.ufscar.br)

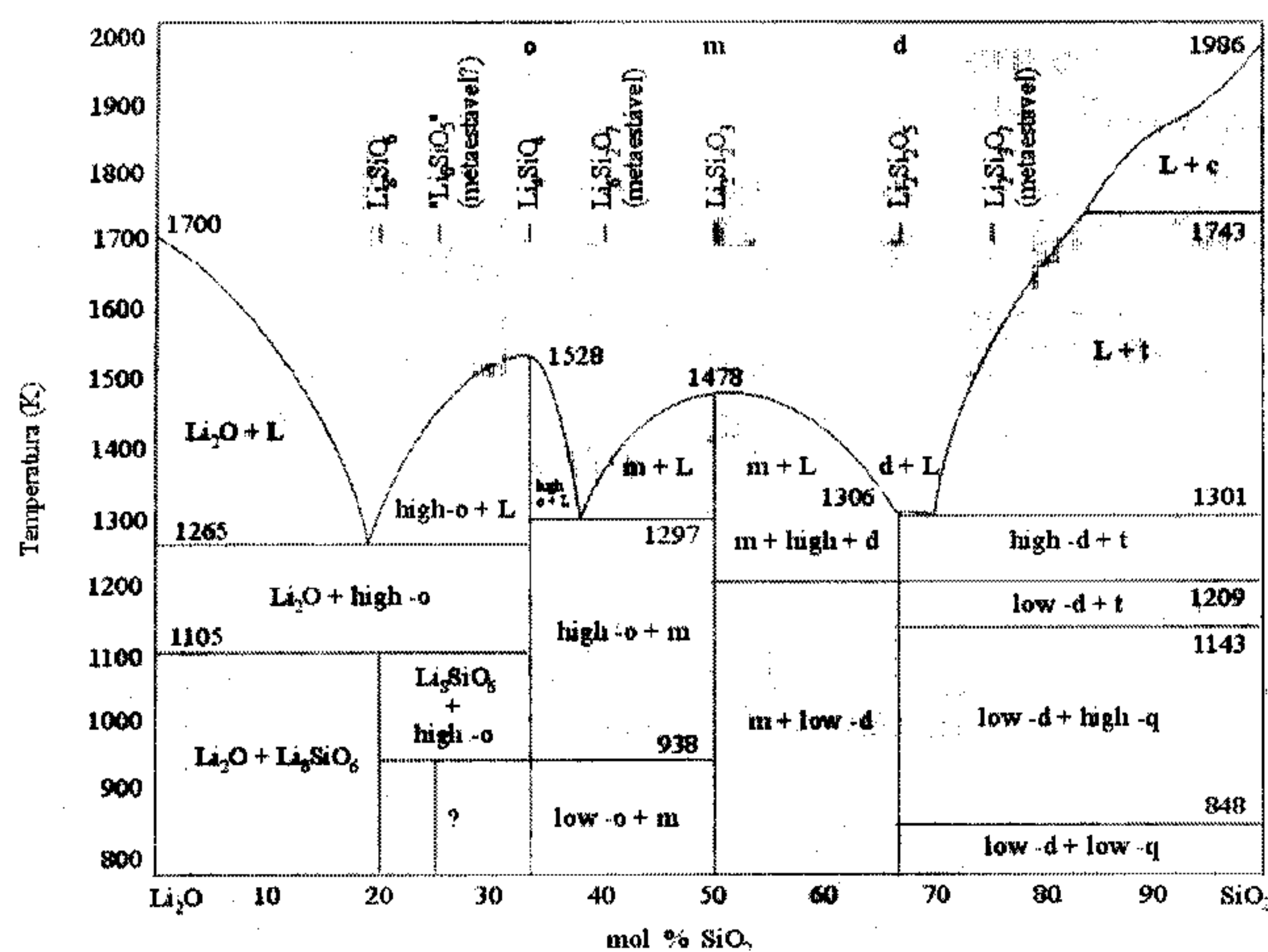


Figure 1. $\text{Li}_2\text{O}-\text{SiO}_2$ phase diagram according to Migge⁽¹⁴⁾

that the total volume fraction of crystals in LS_2 glass treated for 5 h at 454°C is $<1\%$ and due to the fact that this was the only XPS study on the subject but, if confirmed, could give additional evidence of the precipitation of metastable phases.

We present here the results of new XPS measurements in a slightly hyper stoichiometric lithium disilicate glass (34.5 mol% Li_2O) subjected to similar heat treatments as those used by Adams *et al.*^(12,13) According to the phase diagram of the $\text{Li}_2\text{O}-\text{SiO}_2$ system, Figure 1, the nucleation of a second phase, lithium metasilicate, is expected for this composition.⁽¹⁴⁾ Therefore, this study will allow us to test the sensitivity of XPS to detect small amounts of crystal as the extra Li 1s peak attributed to the metastable lithium metasilicate should appear for this hyper stoichiometric glass.

Experimental

Two lithium silicate compositions: $\text{Li}_2\text{O}.2\text{SiO}_2$ (glass 1) and $\text{Li}_2\text{O}.\text{SiO}_2$ (melt 2) were prepared using standard reagent grade Li_2CO_3 (Aldrich Chem. Co., 99+%) and SiO_2 (ground quartz, >99.9%). The batches were melted in a Pt crucible at 1400°C for 2 h in an electric furnace. To ensure homogeneity, the poured melts were ground and remelted at the same temperature for 1 h. The melts were quenched in air by pressing them between steel plates. Subsequent chemical analysis revealed the composition of the prepared glass 1 to be 34.5 ± 0.5 mol% Li_2O . The second melt resulted in totally crystallised samples.

Heat treatments were carried out in a horizontal tube furnace with the temperature controlled within $\pm 1^\circ\text{C}$. Samples of glass 1 were given single stage heat treatments at 450°C for periods of 1, 5 and 24 h. The samples nucleated for 24 h were given a second treatment at 610°C for 30 min to fully crystallise them. The surface crystallised layers of the heat treated samples were removed and the remaining materials were separated in two types of samples: powder and plates.

The XPS analyses were performed using two different instruments. We analysed powder samples of glass 1 and melt 2 (right after being ground) by a XSAM HS spectrometer of Kratos Analytical (at the Federal University of São Carlos, São Carlos, Brazil) using a

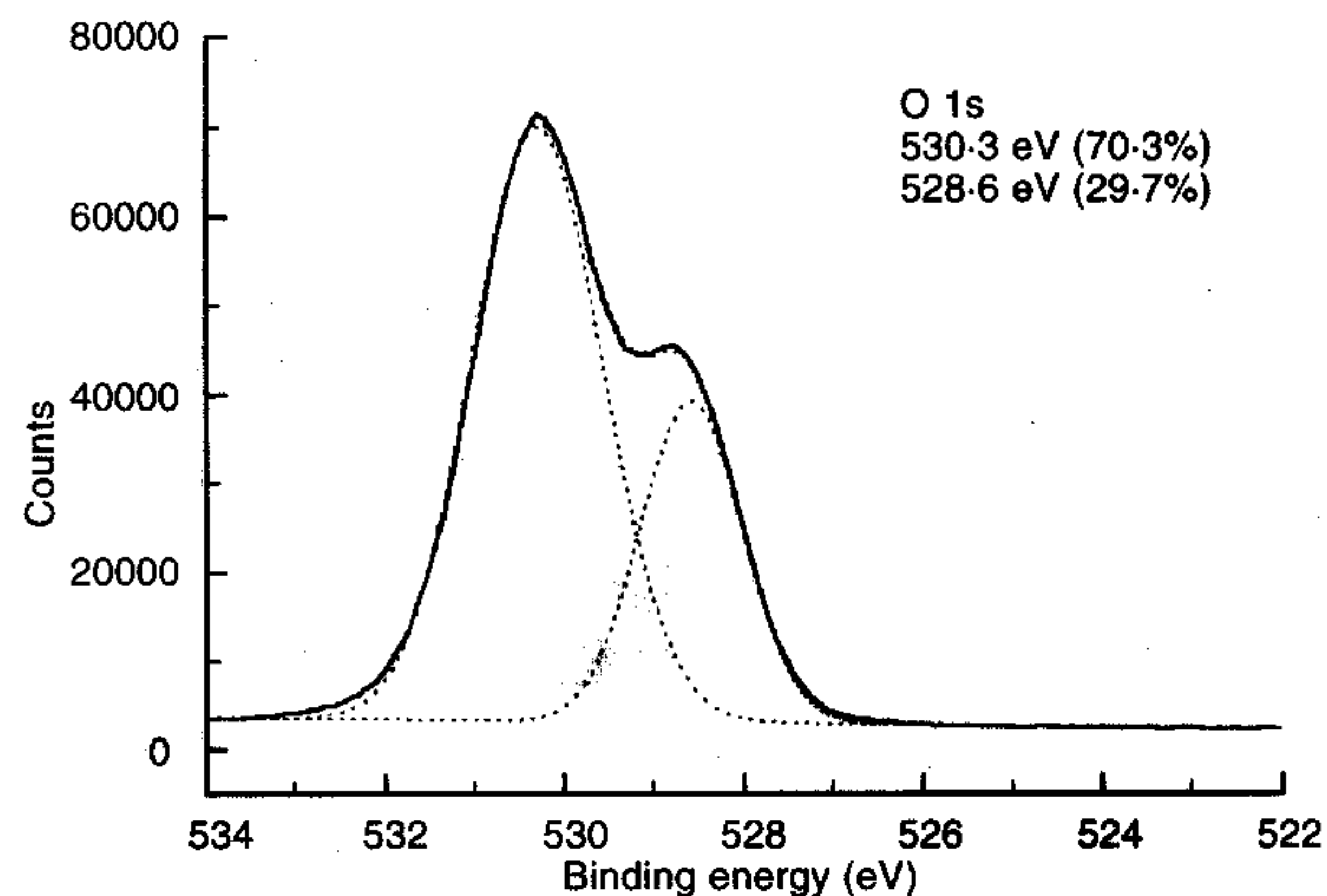


Figure 2. O 1s photoelectron spectrum of $\text{Li}_2\text{O}.2\text{SiO}_2$ heat treated for 5 h at 450°C . Fractured sample

dual Mg/Al anode, employing Mg- $\text{K}\alpha$ radiation with energy of 1253.6 eV. The chamber pressure was in the low 10^{-9} Torr range. The other instrument was a Scienta ESCA300 spectrometer (at Lehigh University, Bethlehem, USA) where the plate samples of glass 1 were fractured *in situ* at pressures in the low 10^{-8} /high 10^{-9} Torr range. The data were obtained from an area of about 3×0.3 mm on the fractured surface using Al- $\text{K}\alpha$ radiation with energy of 1486.6 eV. The insulating surface required the use of a low energy electron flood to compensate the surface charging. Charge referencing was done by using the C 1s line set at a binding energy of 284.8 eV. The carbon on the surface results from interactions of the very active fractured surface with residual hydrocarbons in the vacuum chamber.

The gathered data result from survey scans over the entire binding energy range and high resolution regional scans over the Li 1s, O 1s, Si 2p and C 1s lines. Each spectrum was deconvoluted and fitted with Gaussian peaks and a least squares fit routine.

Results and discussion

Figure 2 presents the O 1s XPS spectrum which is constituted by two components. According to Brückner *et al.*⁽¹⁵⁾ the two O 1s photoelectron peaks observed in alkali silicate glasses can be attributed to the bridging oxygen atoms (Si-O-Si), at a higher binding energy, and

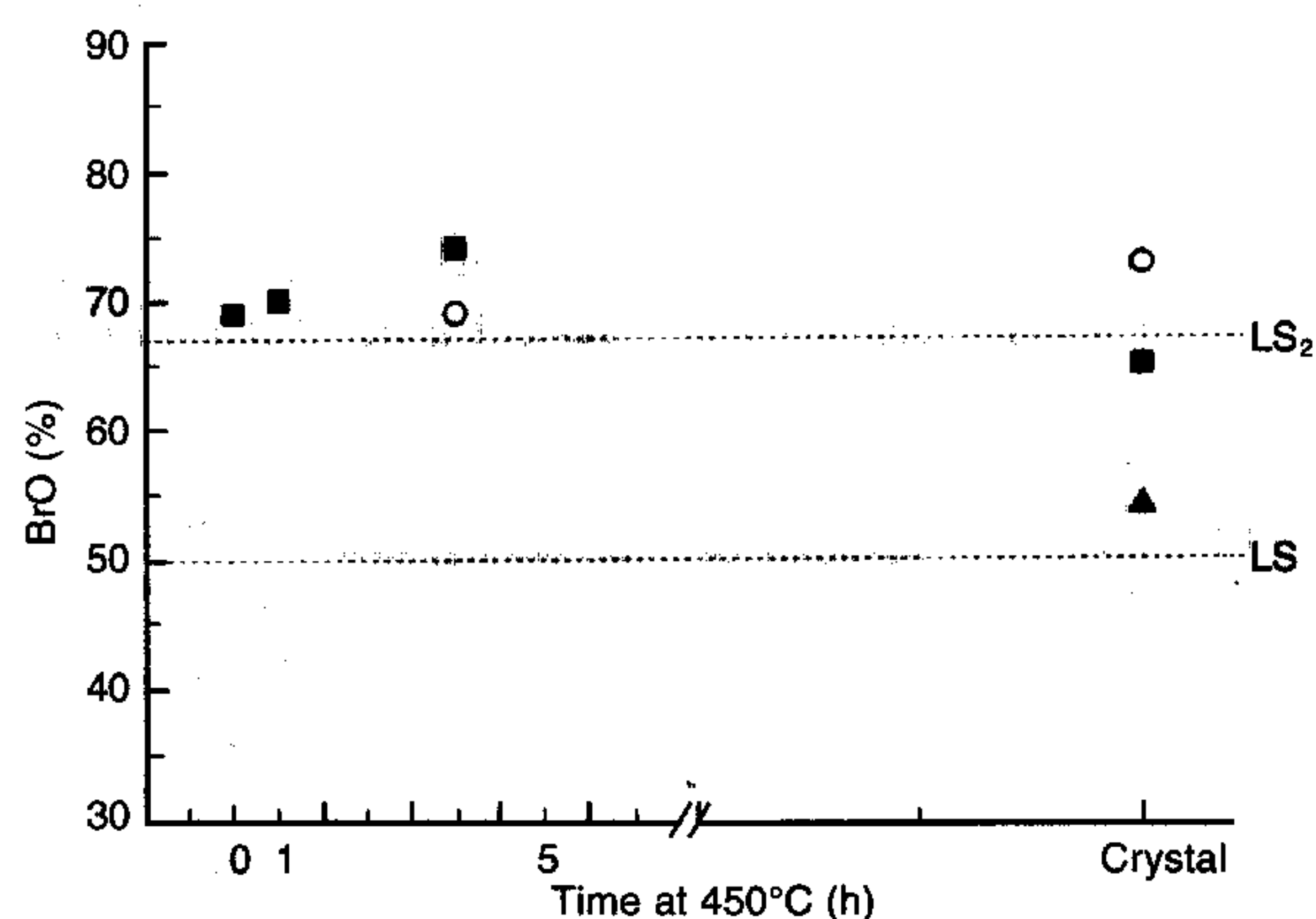


Figure 3. Concentration of bridging oxygens (BrO) as a function of heat treatment. Dotted lines indicate the calculated percentages of BrO in LS_2 and LS

■ LS_2 powder ○ LS_2 fracture ▲ LS powder

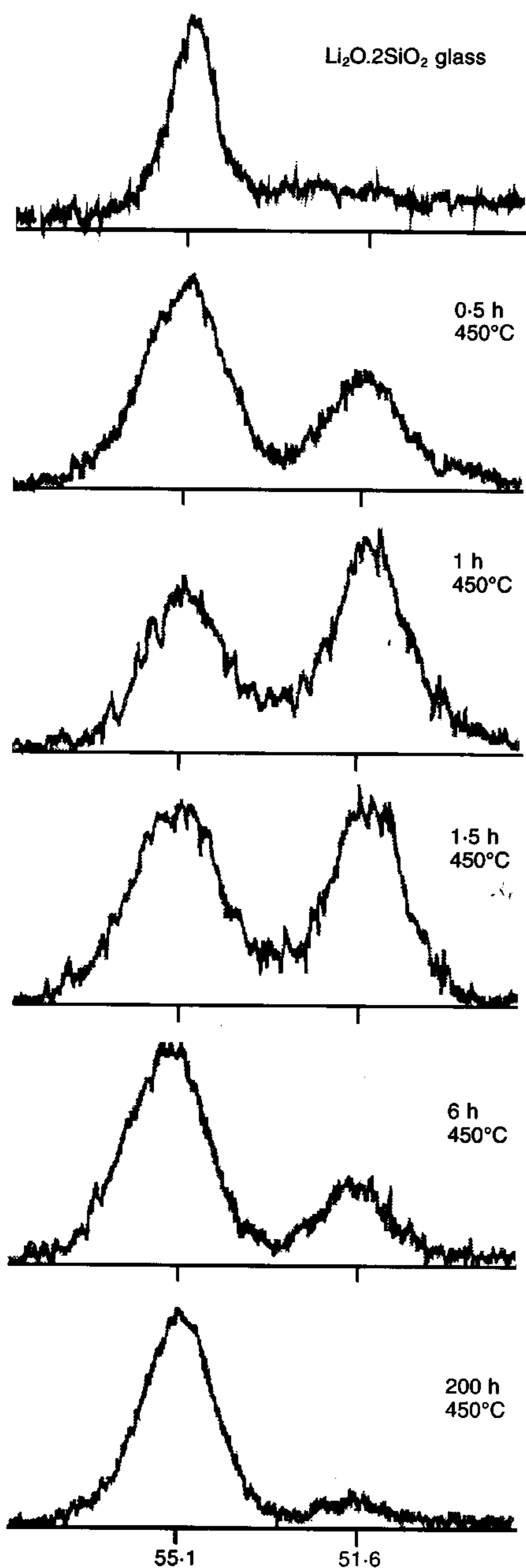


Figure 4. Li 1s photoelectron spectra of lithium disilicate obtained by Adams⁽¹³⁾

to nonbridging oxygen atoms (Si-O-Li), respectively. The O 1s peak has been extensively studied due to its high intensity and sensitivity to the changes of the chemical environment surrounding the oxygen atoms.⁽¹⁶⁾

In Figure 3 the proportion of bridging oxygens determined from the area ratios for both powder and fractured samples is compared to the values predicted for crystalline lithium disilicate and lithium metasilicate.

According to Ref. 17 the Li 1s peak at 55.5 eV corresponds to Li₂O. Adams *et al.*^(12,13) attributed the presence of a metastable phase formed during the nucleation treatment to the component with binding energy of 51.7 eV. Their results showed only one Li 1s peak at 55.1 eV for glass and crystalline lithium disilicate plate samples. However, after a short heat treatment of 30 min their spectra showed an additional

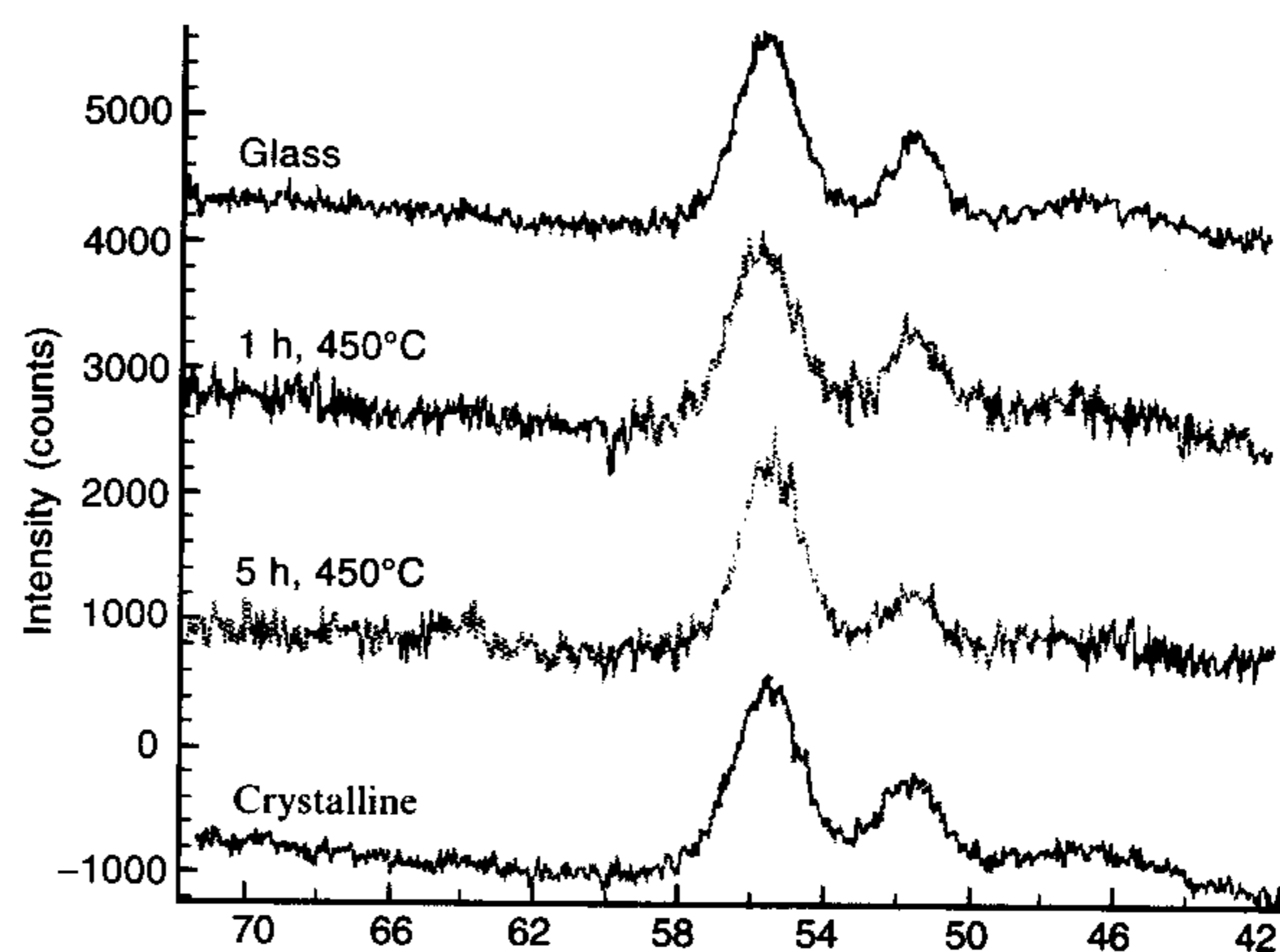


Figure 5. Li 1s photoelectron spectra of lithium disilicate obtained from powder samples using the XSAM-Kratos instrument

peak at 51.7 eV located at ~3.5 eV lower binding energy than the original peak, which increased steadily in relative intensity up to a maximum after 1 h at 450 °C and then decreased.

Thus the Li 1s spectra obtained by Adams⁽¹³⁾ showed changes in the electronic structure during nucleation, Figure 4, which was attributed to the precipitation of a metastable phase. However, our results showed the two peaks in all (glass to fully crystallised) powder samples, Figure 5, suggesting that there is no relation between the second peak and the formation of a metastable phase (that should disappear after some time). The peak positions and relative intensities are given in Table 1.

We observed that the 51.5 eV peak intensity decreased after ion bombarding the plate surface samples. This suggested that there could be a cross contamination of Al-K α as we used a dual Mg/Al x-ray anode of the Kratos instrument, the same kind of anode used by Adams. Cross contamination leads to ghost lines which are small peaks appearing in a spectrum resulting from impurity elements in the x-ray source.^(18,19) The most common ghost lines are due to Al-K α from a Mg-K α source, or vice versa, in a dual anode source.^(18,19) The difference between the two radiation energies is 233 eV, hence a ghost peak of C 1s excited by the Al-K α radiation would appear at ~51.8 eV (284.8–233 eV).

The atomic sensitivity factor for XPS of Li 1s is 12.5 times smaller than that of C 1s.⁽¹⁸⁾ The C 1s ghost lines observed in Figure 5 are less than half the size of the Li 1s peaks, implying that the carbon content in the surface of each sample is less than 25 times smaller

Table 1. XPS O 1s, Si 2p and Li 1s binding energy of powder samples

Nucleation time at 450°C	Binding energy (eV) and peak relative intensity (%)					
	Si 2p (eV)	(%)	Li 1s (eV)	(%)	O 1s (eV)	(%)
Glass	102.7	100	51.6	29	530.7	31
			55.7	71	532.4	69
1 h	102.8	100	51.6	34	530.8	30
			55.8	66	532.5	70
5 h	102.7	100	51.7	24	530.4	26
			55.6	76	532.2	74
Crystalline	102.1	100	51.7	32	531.1	35
			55.6	68	532.8	65

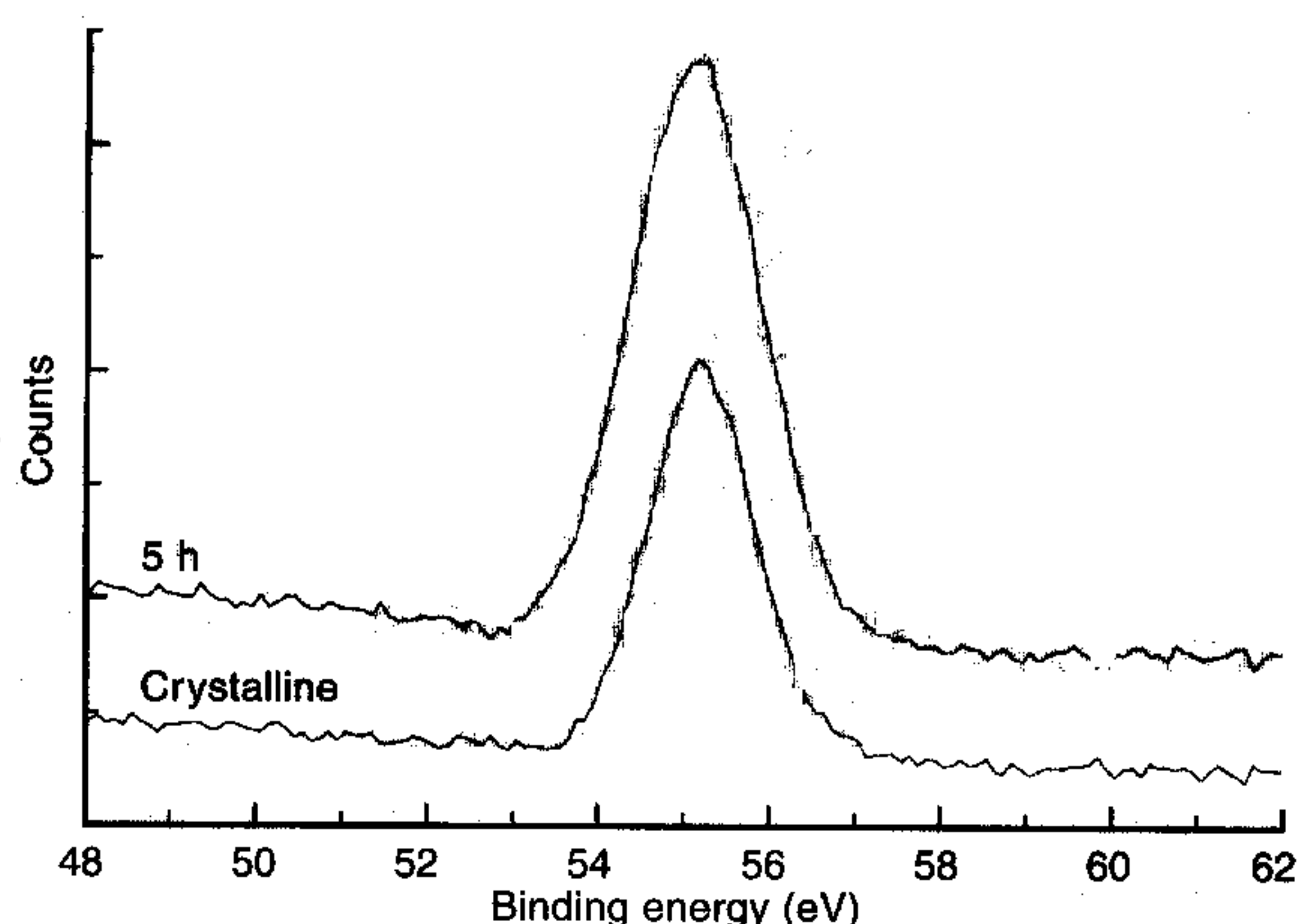
Table 2. XPS O 1s, Si 2p and Li 1s binding energies for fractured samples

Nucleation time at 450 °C	Binding energy (eV) and peak relative intensity (%)					
	Si 2p (eV)	(%)	Li 1s (eV)	(%)	O 1s (eV)	(%)
5 h	102.3	100	55.2	100	530.3	31
Crystalline	102.7	100	55.2	100	532.0	69
					532.3	72.8

than the lithium amount. At ultra-high vacuum regime in the XPS chamber, the dominant residual gases are H₂, H₂O, CO, CO₂ and hydrocarbons, which lead to carbonaceous deposits on the sample surface. We had to perform several scans to obtain a reasonable Li 1s spectrum thus the acquiring time was quite long (about 12 h). As the atomic sensitivity factor for the Li 1s XPS spectrum is much smaller than that of C 1s, a significant carbon peak appeared.

To avoid the cross contamination effect, we analysed fractured samples with a monochromatic Al-K α source using a Scienta-ESCA300 instrument. The results, Table 2, showed just one peak for Li 1s at 55.2 eV, Figure 6, proving that the second peak observed at ~51.5 eV in the spectra obtained by dual Mg/Al x-ray anode, Figure 5, is a ghost peak of C 1s.

The sizes of the ghost C 1s peaks depend on the amount of carbon present on the surface. Adams *et al.*^(12,13) used samples in the form of plates which were sputtered by low energy argon ions inside the ultra-high vacuum chamber. The amount of residual carbon on their samples would depend on the effectiveness of such *in situ* cleaning treatment. Therefore, the differences in the spectra would probably reflect only the

**Figure 6.** Li 1s photoelectron spectra for fractured samples using the SCIENTA ESCA300 instrument

state of surface cleaning not structural changes in the samples. In addition the long acquiring times could cause build-up of carbon layers.

Conclusions

From the XPS results presented herein, we conclude that the second Li 1s peak observed at ~51.7 eV is not due to lithium metasilicate crystals but instead is a C 1s ghost peak caused by the cross contamination of the dual Mg/Al x-ray anode. On the other hand, our recent TEM results on similar samples clearly show that lithium metasilicate crystals appear in the early stages of nucleation and survive up to 120 h at ~ T_g . Therefore XPS is not a suitable technique to detect structural changes in this glass (and probably in any other glass) when the volume fraction of crystals is very low.

Acknowledgements

The authors acknowledge the financial support of the Brazilian agencies PRONEX, FAPESP and CNPq/CYTED. We are grateful for the use of the XPS spectrometer at the Sinclair Laboratory, Lehigh University, Bethlehem, PA, USA. We are also indebted to Mr A. C. Miller and Dr H. Jain for their assistance and helpful discussion.

References

- Weinberg, M. C., Manrich, S. & Zanotto, E. D. *Phys. Chem. Glasses*, 1992, **33** (3), 99–102.
- Moller, J., Schmelzer, J. & Gutzow, I. *J. Non-Cryst. Solids*, 1998, **240** (1–3), 131.
- Schmelzer, J., Gutzow, I. & Moller, J. *Glass Phys. Chem.*, 1998, **24** (3), 244.
- Neilson, G. F. & Weinberg, M. C. *J. Non-Cryst. Solids*, 1979, **34**, 137.
- Jacquin, J. R. & Tomozawa, M. *J. Non-Cryst. Solids*, 1995, **190**, 233.
- Zanotto, E. D. & Leite, M. G. L. *J. Non-Cryst. Solids*, 1996, **202**, 145.
- Zanotto, E. D. *J. Non-Cryst. Solids*, 1997, **219**, 42.
- Burgner, L. L., Weinberg, M. C., Lucas, P., Soares Jnr, P. C., Jnr, Zanotto, E. D. *J. Non-Cryst. Solids*, 1999, **255**, 264.
- Burgner, L. L., Weinberg, M. C., Soares Jnr, P. C., Jnr & Zanotto, E. D. *J. Non-Cryst. Solids*, 2000, **274** (1–3), 188.
- Iqbal, Y., Lee, W. E., Holland, D. & James, P. F. *J. Non-Cryst. Solids*, 1998, **224**, 1.
- Soares Jnr, P. C., Zanotto, E. D. & Jain, H. *J. Non-Cryst. Solids*, 2002, submitted.
- Adams, J. W. & De Jong, B. H. W. S. *MRS 1993 Fall Meeting Symp. Proc.*, 1994, **321**, 239.
- Adams, J. W. *PhD Thesis*. University of Cambridge. 1993.
- Migge, H. *J. Nucl. Mater.*, 1988, **151**, 101.
- Brückner, R., Chun, H. U., Goretzki, H. & Sammet, M. *J. Non-Cryst. Solids*, 1980, **42**, 49.
- Nasu, H., Heo, J. & Mackenzie, J. D. *J. Non-Cryst. Solids*, 1988, **99**, 140.
- Moulder, J. F., Stickle, W. F., Sobol, P. E. & Bombem, K. D. *Handbook of x-ray photoelectron spectroscopy*. 1992. Edited by J. Chastain. Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie.
- Briggs, D. & Seah, M. P. (Editors). *Practical surface analysis*. 1990. John Wiley & Sons, Chichester.
- O'Connor, D. J., Sexton, B. A. & Smart, R. St C. (Editors). *Surface analysis methods in materials science*. 1992. Springer-Verlag, Heidelberg.