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Mössbauer and X-ray photoelectron spectroscopic studies of heat-treated calcium borate glasses containing iron

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^{57}Fe Mössbauer and X-ray photoelectron spectroscopic studies have been carried out on a number of iron-containing calcium borate glasses which show large changes in d.c. conductivity upon annealing. The Mössbauer spectra of the unannealed glass samples are compatible with the presence of predominantly ferric iron in a six-co-ordinate oxygen environment. Upon annealing a partial ordering of the glassy phase is found as indicated by a reduction in the linewidth of the Mössbauer resonances. Longer annealing times lead to the precipitation of α-Fe_2O_3 clearly identified by the gradual appearance of a six-line magnetically split pattern in the Mössbauer spectra. These changes are qualitatively correlated with changes in d.c. conductivity of the samples. The binding energies and full width at half maxima of representative core levels of each element present show a remarkable consistency for all samples. Moreover the 2p spectra of iron incorporated in the glassy phase are essentially similar to that of the precipitated Fe_2O_3.

1. Introduction

During the course of a systematic study of the electrical and thermoelectric properties of a variety of glasses based on boric oxide [1], it emerged that, within a certain range of composition of a vitreous mixture of B_2O_3 + CaO + Fe_2O_3, exceptionally large changes in d.c. conductivity were observed as a function of the time of annealing. The extent of these changes is represented diagrammatically in Fig. 1, from which it may be seen that, when the iron content (as Fe_2O_3) is around 17 mol %, the resistance first increases, by some three decades during the initial 3 h anneal at 750° C, and then decreases progressively to a steady value of about 3×10^3 Ω cm^{-1} after 20 h.

It is not a simple matter to elucidate, by conventional techniques, the nature of the processes taking place at the atomic level during the course of these quite major changes in electrical conductivity that occur upon annealing; and so we have utilized for analytical purposes hitherto less widely used procedures – ^{57}Fe Mössbauer spectroscopy (MS) on the one hand and X-ray induced photo-electron spectroscopy (XPS) on the other. It will be demonstrated that whereas the former technique offers useful insights into the microstructural characteristics of the heat-treated glass, the latter is rather less illuminating, for reasons which we shall duly adumbrate.

2. Experimental

Samples of glass were prepared by mixing proportions of B_2O_3 (53 mol %) of CaO (30 mol %) and of Fe_2O_3 (17 mol %) (all chemicals of Analar purity) and firing, in air at 1200° C for 3 h before cooling to room temperature at a rate of less than 1° C min^{-1}. The samples were then heat-treated for different periods of time at a temperature of 750° C in air. After completing the electrical measurements the samples were ground to a fine powder prior to spectroscopic analyses.

The d.c. electrical measurements were carried out in an evacuated cell using a G.R. Megohm bridge type 1644A. X-ray diffraction patterns were obtained using a General Electric XRD-6

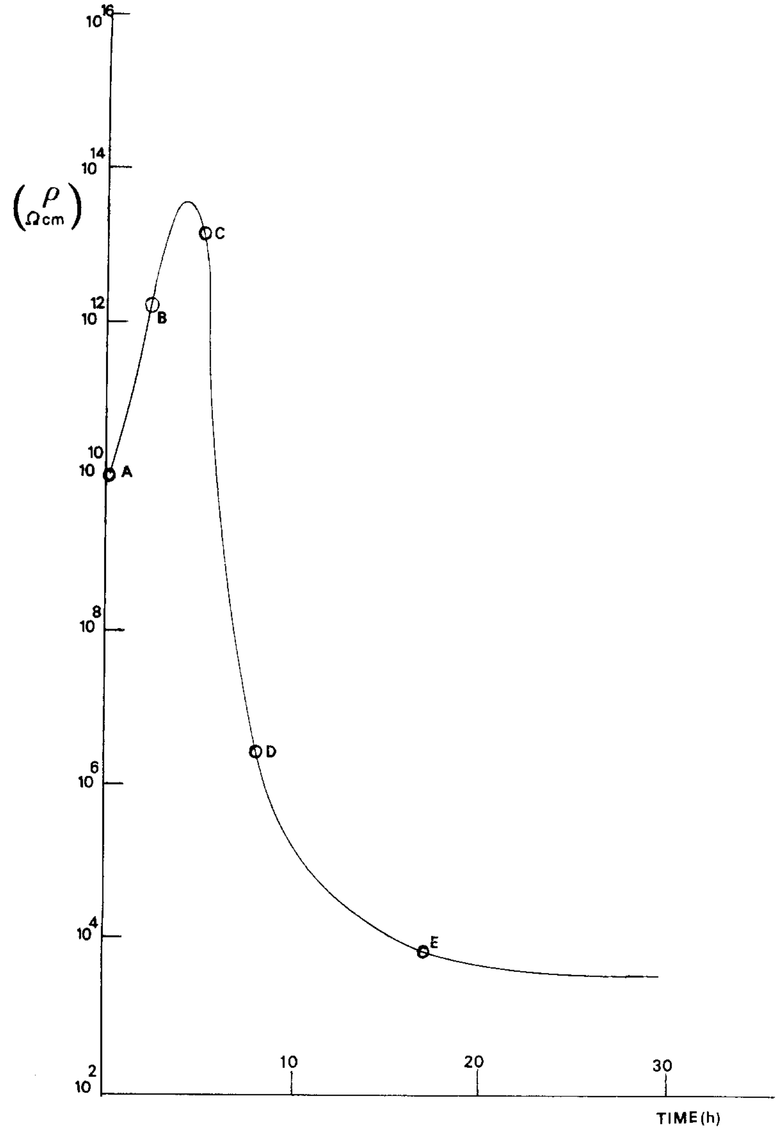

Figure 1 Typical curve illustrating variation of change of resistivity of glass with time of annealing when iron content (as Fe_2O_3) is 17 mol%.

diffractometer with a cobalt target and an iron filter. ^{57}Fe Mössbauer spectra were recorded using a Harwell spectrometer, of the constant acceleration type, and 10 Mc ^{57}CoPd source. The spectrometer was calibrated using iron foil or a standard sodium nitro-prusside absorber. All glassy absorbers were powdered and their spectra recorded at room temperature. X-ray photoelectron spectra were recorded, in vacuum of about 10^{-8} Torr at temperatures of about 310K in an AEI ES 200 spectrometer having of an Al anode (stimulating primary radiation 1486.8 eV). The instrument resolution, as gauged from the FWHM of the Cls line of single crystal of graphite was 1.00 eV. "Absolute" binding energies were estimated relative to the small Cls peaks (arising from adventitious pump-oil impurity – see later) which were taken to be 285.0 eV.

3. Results and discussion

We shall first consider the Mössbauer data which

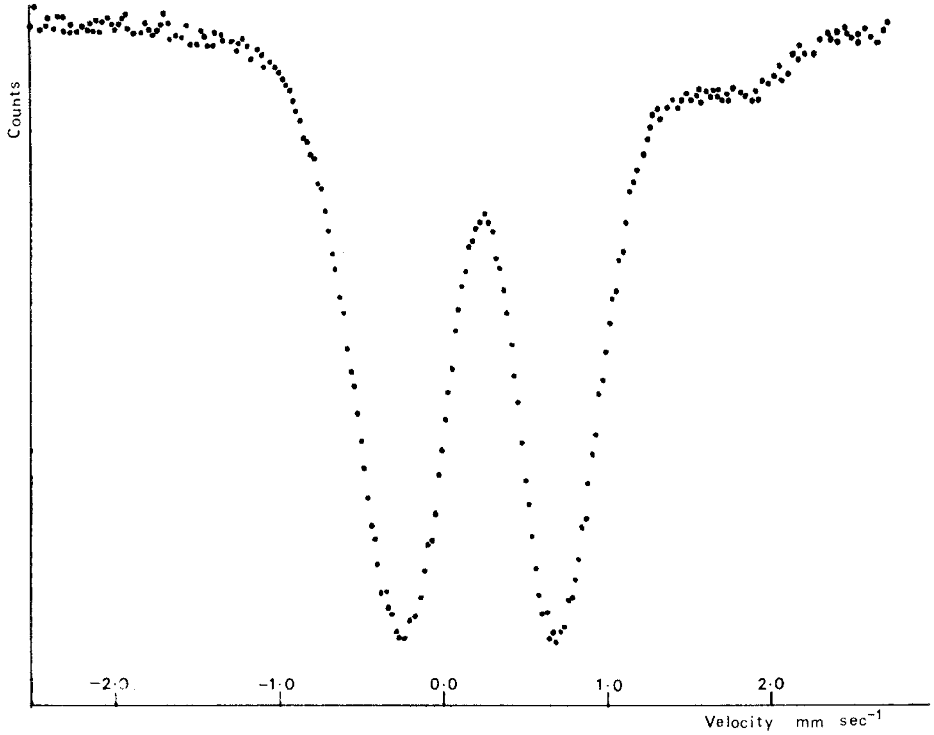

Figure 2 ^{57}Fe Mössbauer spectrum of glass sample A. Note broad lines and small ferrous resonance at high energy.

TABLE I Mössbauer parameters for constitutional iron in glass samples (mm sec^{-1}) (error ± 0.01 mm sec^{-1} in each case)

Sample	δ (rel. S.N.P. standard)	Δ	FWHM
A	0.68	1.01	0.69
B	0.65	0.74	0.54
C	0.65	0.69	0.42
D	0.65	0.69	0.42

are summarized in Table I, the designations A, B, C, D and E referring to samples of a fixed initial concentration of total iron but annealed for different lengths of time as signified in Fig. 1.

Glass A (unheat-treated) yielded a broad resolved quadrupole doublet with a weak, broad shoulder at high energies (Fig. 2). The isomer shift (δ) of the doublet (0.68 mm sec^{-1}) is characteristic of high-spin ferric iron in a six-co-ordinate environment of oxygens [2]. The shoulder at high energies is attributable to one half of a ferrous doublet, the low energy peak being obscured by the ferric iron absorption. Assuming the recoil free fraction of the ferrous and ferric sites are identical, the ratio of ferric to ferrous iron in the sample is approximately 5.4:1. The quadrupole splitting (Δ) of 1.01 mm sec^{-1} is high for ferric iron and indicates that a very distorted octahedral arrangement of oxygens surrounds the iron [3]. The extreme broadness of the resonance lines (see Table I) is the expected result for a glass, in which the disordered structure leads to a range of electric field gradients acting at iron sites thereby producing similar overlapping spectra.

The spectrum of glass B (Fig. 3) consists of a quadrupole doublet arising from the ferric iron, the ferrous line at high energy having been reduced in intensity in comparison with that for sample A. The isomer shift of the ferric doublet has decreased somewhat from that of sample A but it is again consistent with high-spin ferric iron in six-co-ordination. The decrease in the quadrupole splitting demonstrates a lessening of the distortion of the environment of the iron atoms: and the concomitant diminution of the line-width is indicative of the reduction in the total number of different iron sites and the

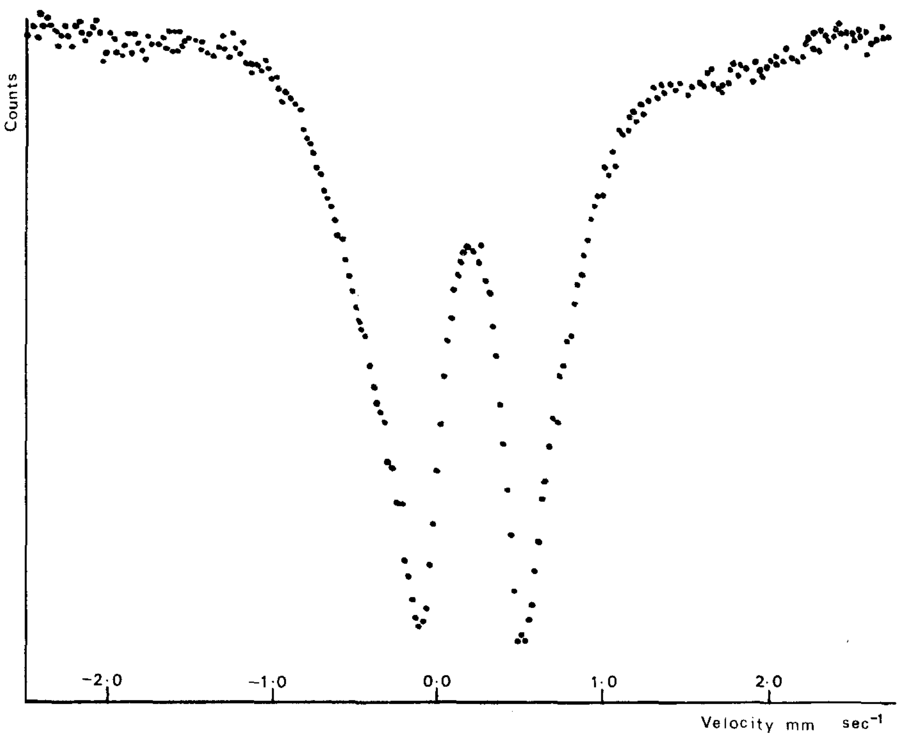

Figure 3 ^{57}Fe Mössbauer spectrum of glass sample B. Note reduction in line width and quadrupole splitting compared to sample A.

possible onset of partial crystallization of the glass. The quadrupole splitting in ferric iron is attributable entirely to the deviation of charged lattice ions from spherical symmetry. Since the contribution to the electric field gradient of an ion decreases as the inverse third power of its distance from the chosen origin, [4] we may expect the quadrupole splitting to be particularly susceptible to short-range ordering in glasses.

In sample C (Fig. 4), a central doublet is again present, there being the same isomer shift as with sample B. The trends in the reduction of line width and quadrupole splitting are maintained but this spectrum now shows a weak six-line magnetically split pattern having H_{int} = 515 kG (± 2 kG), a fact which signifies the commencement of the precipitation of α Fe_2O_3 from the glass [5].

This six-line pattern increases in intensity, and there is a corresponding fall in the intensity of the ferric doublet in samples D and E. Indeed the spectrum of sample E reveals that almost all the iron is now present in the form of α-Fe_2O_3.

It is clear, therefore, that the highly disordered structure present initially in the glass gives way on annealing to a well-ordered crystalline phase Rather similar behaviour has been reported previously [6] in the study of sodium borate glasses, containing iron, which were also analysed by Mössbauer spectroscopy. Heat-treatment first of all led to partial crystallization and prolonged treatment resulted in precipitation of Fe_2O_3. X-ray diffraction studies further confirm our results. For the sample A, the X-ray diffraction pattern (Fig. 6) showed no evidence for a well-ordered crystalline phase. Sample B, however, revealed the appearance of a crystalline phase resulting from heat-treatment for 2½ h at 750°C. Analyses of the X-ray data showed that the crystalline phase was α-Fe_2O_3, the lines of which increase in number and intensity on prolonged heat-treatment.

Before we proceed to discuss the XPS data, which are summarized in Table II, it is pertinent to state what results could, under ideal conditions, have emerged from such a study. On the basis of previous discussions we might have expected both the absolute magnitude of the core-electron binding energies and the line-widths of core-level peaks (see typical spectra

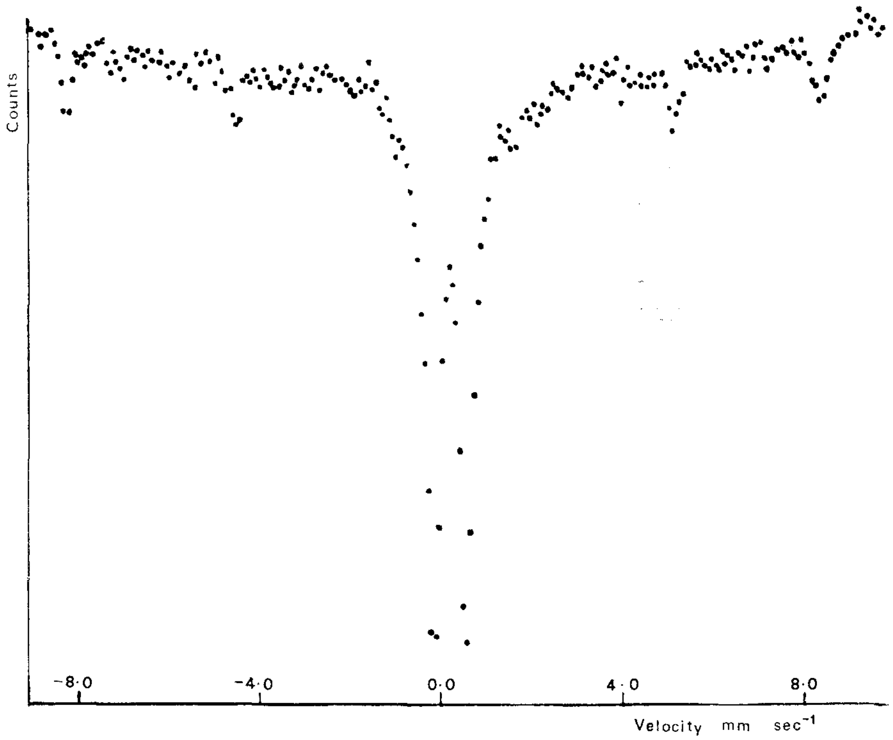

Figure 4 ^{57}Fe Mössbauer spectrum of glass sample C. Note appearance of six-line magnetically split pattern, due to the precipitation of Fe_2O_3 within the glass.

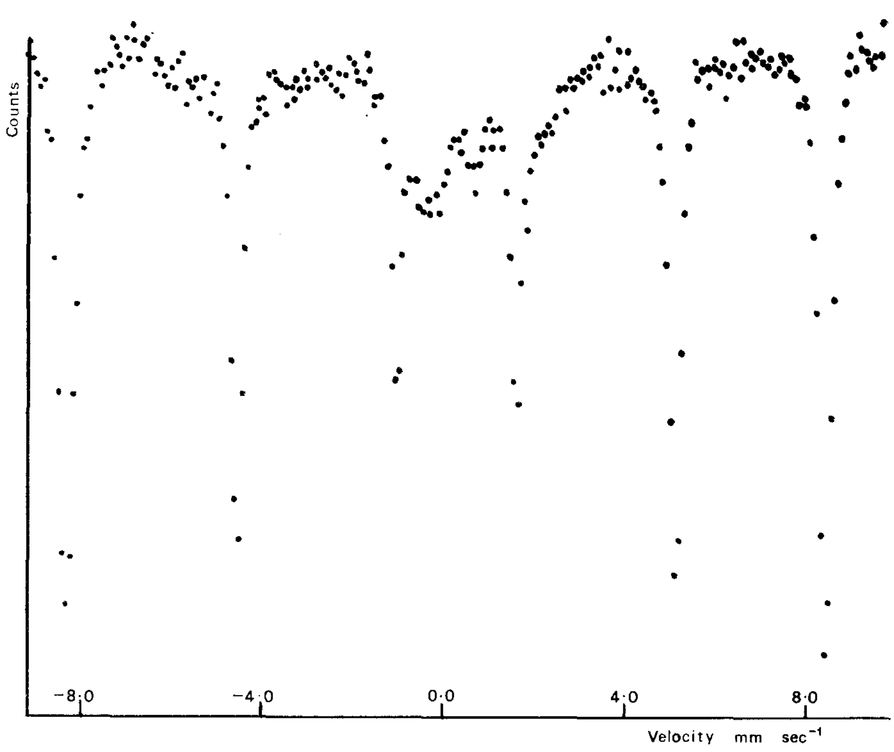

Figure 5 ^{57}Fe Mössbauer spectrum of glass sample E, demonstrating that the bulk of iron present is as Fe_2O_3

TABLE II Absolute binding energies (relative to Cls taken as 285.0 eV) of core levels in glass samples. All energies in eV ± 0.3 eV. Numbers in brackets FWHM (± 0.2 eV)*

Sample	Fe ± 0.6 eV		Ca		B 1s	O 1s
	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$		
A	723.8 (8.0)	710.4 (6.0)	351.0 (2.2)	347.3 (2.2)	192.3 (2.0)	531.3 (2.7)
B	723.2 (7.0)	710.0 (6.0)	351.2 (1.9)	347.6 (2.3)	192.4 (2.2)	531.7 (2.6)
C	724.5 (8.0)	710.0 (5.5)	351.2 (2.2)	347.6 (2.2)	192.5 (2.1)	331.5 (3.0)
D	723.7 (8.0)	710.0 (5.0)	351.0 (2.0)	347.4 (2.0)	192.3 (2.2)	331.3 (2.7)
E	724.5 (6.0)	710.3 (6.5)	351.0 (2.3)	347.5 (2.2)	192.6 (2.2)	531.7 (2.9)

*Line widths reported for Fe $2p_{1/2}$ and $2p_{3/2}$ may be in error by 1 eV due to difficulty in locating the rising background of secondary electrons.

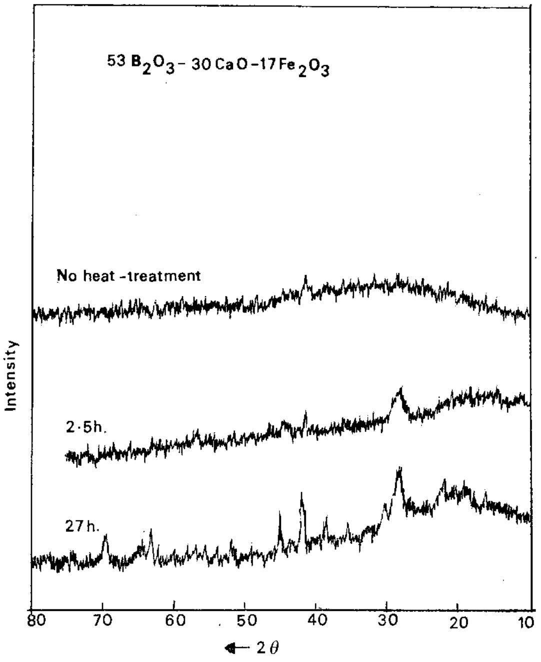

Figure 6 X-ray diffraction patterns for the samples studied after various lengths of heat-treatment at 750°C.

shown in Fig. 7) to be modified as the disordered material changed into a more crystalline, ordered state. Moreover the combined Mössbauer isomer shifts and XPS binding energy shifts could, in principle, (see [7]) have yielded some detailed information about forward and back donation of electrons between the surrounding ligands and the central iron cation. All such possibilities were nullified when it transpired that there is remarkable constancy in the values of the binding energies and line widths (Table II) of the various elements. It is particularly noteworthy that the onset of partial crystallization and eventual precipitation of Fe_2O_3, convincingly demonstrated by the Mössbauer spectra, are not reflected in the changes of the Fe 2p binding energies or line widths (Fig. 8), but it must be emphasized that line widths for Fe 2p, being so large because of exchange interaction and shake-up [8, 9] are not trustworthy guides of crystalline order.

One possible explanation, which is difficult to confirm by independent means (except possibly refined high-energy reflection electron diffraction data), is that the surface regions of all the glass samples are essentially identical. XPS, since it relies on the escape of elastically scattered electrons generated within a solid, usually probes no more than about 5 to 8 atomic diameters below the external surface [10]. Such an interpretation, though not impossible, is unlikely to be the valid one in the present instance. A more realistic one can be formulated in terms of the simple electrostatic model first proposed by Siegbahn [11] and co-workers to interpet chemical shifts in core electron binding energies. The argument proceeds as follows. A chemical shift of a core level is due to the change in electrostatic potential at the nucleus produced by (a) an effective sphere of charge describing the valence region of the atom, and (b) the summed potential arising from all charges, external to the atom, in the lattice. These terms are of opposite sign. Line broadening would, therefore, be expected in a glassy material as the second term would vary from site to site of a given type of ion.

As the lattice potential term is an inverse function of r (in contrast to the operative term in Mössbauer quadrupole splitting which is a

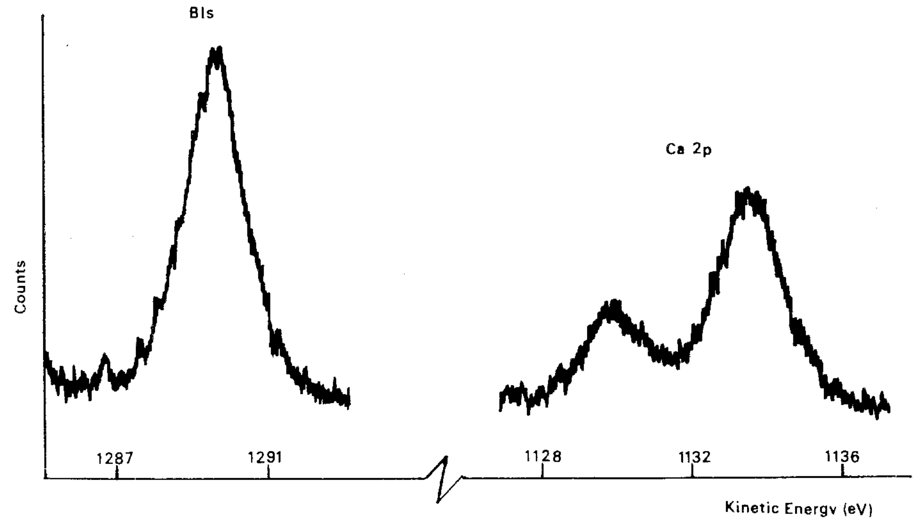

Figure 7 Typical ESCA spectra of glass samples studied showing that the line widths are not unduly broadened. The kinetic energy scale is uncorrected for charging effects.

function of $1/r^3$) longer range order would be needed to produce constancy of this term at the sites of the atoms in question. Furthermore the insensitivity of XPS in distinguishing crystallographically distinct ions (see for example LaF_3 [12]) we cannot rule out the possibility that ions in different co-ordination spheres, more or less distorted, can adjust either their partial charge or the radius of the effective sphere of charge leading to an equalisation of slightly different lattice potentials at these sites, with the consequential effect of preserving narrow spectral peaks [13].

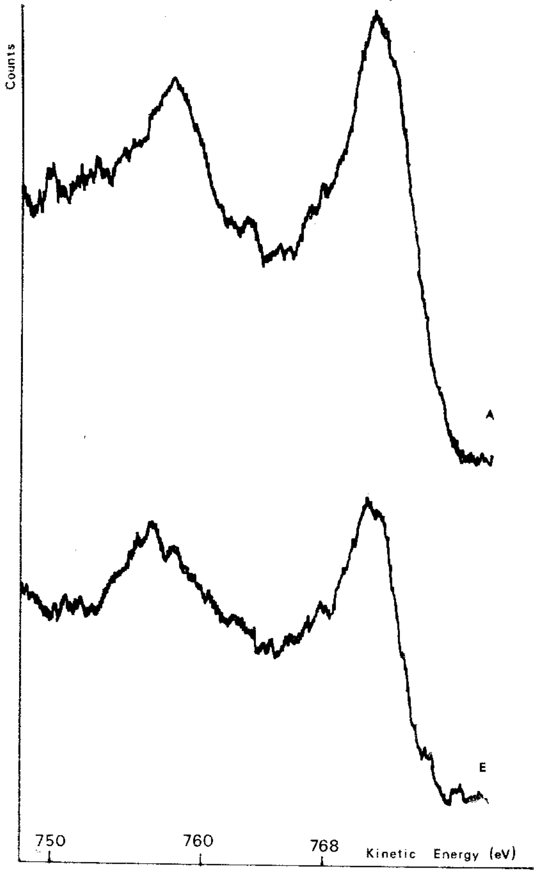

Figure 8 ESCA spectra of the Fe $2p_{1/2}$ to $2p_{3/2}$ region of samples A and E. Both spectra are similar even though in sample A the ferric iron is incorporated in a glassy matrix and in sample E as Fe_2O_3. The kinetic energy scale is uncorrected for charging effects.

It is evident that Mössbauer spectroscopy is of considerably greater investigative value than XPS for the structural study of iron-containing glasses. Though the details are not clear, it is evident that the rise in resistivity (Fig. 1) coincides with the onset of crystallization, as detected by Mössbauer spectroscopy and X-ray diffraction, and moreover, the sharp drop beyond the maximum is a consequence of the precipitation of α-Fe_2O_3.

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