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Interaction of sodium with simple glasses

Part 1 *Vitreous silica*

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The discolouration of vitreous silica by sodium was viewed as a surface phenomenon, hence techniques such as electron spectroscopy for chemical analysis (ESCA) and infra-red reflection spectroscopy (IRRS) along with a variety of other analytical tools were used to investigate the interaction. When vitreous silica was exposed to sodium vapour at about 300° C, the formation of Si–O^- bonds were observed. In addition sodium which had diffused into the glass was found to be in an ionic state. At a higher temperature of exposure to sodium, about 450° C, crystalline sodium metasilicate (and possibly silicon) was formed. Using the experimental results presented here and elsewhere, a model has been developed based on the formation of sodium metasilicate and non-stoichiometric silicon oxide when vitreous silica is exposed to sodium vapour. The discolouration phenomenon is attributed solely to the formation of non-stoichiometric silicon oxide.

1. Introduction and background

In a practical device such as a sodium vapour lamp where the alkali metal is being used at elevated temperatures, the problem of selecting suitable materials for the components of the device arises because of the reactive nature of sodium. In view of the growing application of sodium in new technology, such as the high specific energy sodium/sulphur battery and in thermonuclear reactors; a clearer understanding of the interaction between sodium and an important class of materials, namely, oxide glasses, would seem to be desirable.

The interaction of glasses with sodium vapour has been investigated by a number of authors over several decades [1–9] and a few mechanisms have been speculated to describe the blackening of glasses by sodium at elevated temperatures. From the earliest work [1], the discolouration phenomenon was suggested to be due to the formation of metallic sodium of colloidal size in the glass or the chemical reduction of the glass to its elements. However, more recent authors have favoured either the chemical reduction mechanism [2, 3], or they have attributed the discolouration to the formation of colour absorbing centres [4, 7]. There are also differing views with regard to the kinetics or the rate of discolouring of the glasses by sodium. It has been argued that a simple diffusion type of equation could not be used to describe the phenomenon [2] whilst others have produced reasonable fits to data using simple diffusion equations [4, 6, 8, 9]. One aspect of the blackening phenomenon, where all the authors cited here are in agreement, is that the discolouration only occurs at the surface of the glass where it has been exposed to sodium. The thickness of this discoloured layer is typically of the order of a few microns [2, 4].

Since the nature of the discolouration mechanism is not well understood, the object of the present work is to study the fundamental processes which are involved when a glass comes into contact with sodium vapour at elevated temperatures. In order to fulfil this aim, it was felt that a study of simple glass systems would be more fruitful in gaining a better insight than the more complex multi-component glasses despite their commercial importance. The silicate system was chosen for investigation and the results on vitreous silica are presented in the first part of this paper, whilst the two and three component silicates will be the subject of the second part of this paper to be published later. Since the discolouration of glasses

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is recognized as a surface phenomenon here, a greater emphasis was placed on applying surface sensitive techniques such as electron spectroscopy for chemical analysis (ESCA) and infra-red reflection spectroscopy (IRRS) in the present investigation. Other techniques such as electron spin resonance (ESR), optical absorption spectroscopy, X-ray diffraction (XRD) and differential thermal analysis (DTA) were also used.

2. Experimental procedure

The vitreous silica used in the present work was Spectrosil B purchased from Thermal Syndicate in the form of 1 mm thick polished slides. In cases where flat specimens were required, the silica was used in the as-received condition. In cases where powder specimens were required, the silica was crushed and sieved to < 300 mesh for XRD and between 100 and 150 mesh for DTA. The glass powders were normally stored in an evacuated desiccator until needed.

General purpose reagent grade sodium metal which came in the form of bars in liquid paraffin was used. Before an exposure experiment, a small piece of the metal was washed in dried diethyl ether to remove the paraffin and then transferred to the exposure chamber with the minimum of contact with the atmosphere. However, slight oxidation of the sodium metal was unavoidable.

2.1. Exposure to sodium

The technique relied on the exposure of the specimens to a saturated vapour of liquid sodium. The samples were placed inside a stainless steel chamber and were baked at 500° C for at least 1 h at 10^{-6} Torr. They were then allowed to reach thermal equilibrium at the desired exposure temperature over a period of 12–24 h before a pellet of sodium weighing about 0.5 to 1 g was introduced into the exposure chamber. After exposure to sodium vapour, the chamber was quenched to room temperature to prevent sodium vapour from condensing on to the specimens. The chamber was opened in a dried nitrogen atmosphere and the exposed specimens were kept in either a nitrogen atmosphere or evacuated desiccators to prevent contamination by oxygen or water vapour.

2.2. Surface investigation by ESCA and IRRS

ESCA was used to establish whether any changes in the oxidation states of vitreous silica had taken place after exposure to sodium and this information could be obtained qualitatively by simply measuring the core electron binding energies. However, one of the problems inherent in the study of insulators by electron spectroscopy is the charging of the specimen whilst undergoing excitation; this renders the determination of absolute binding energies inaccurate. To circumvent this problem, a quantity called the "Auger parameter" [10] or the related "modified Auger parameter" [11] which is independent of charging effects was measured instead and the results were compared with current literature values [11–14] to deduce any chemical changes.

The experiment was carried out at room temperature in a V.G. ESCA 3 spectrometer using a 260 W aluminium X-ray source ($h\nu = 1486.6$ eV) and a hemispherical electron analyser. Wide sweeps (0 to 1200 eV) of the kinetic energy spectrum and narrow scans (20 eV wide) of the individual peaks were taken and were computer-averaged over five sweeps to minimize noise. In cases where the specimens showed surface contamination owing to unavoidable contact with the atmosphere, they were cleaned with argon ions.

IRRS was used as an alternative technique to probe the sodium attacked surface. By measuring changes in the vibrational spectrum, structural information concerning the discoloured layer could be obtained qualitatively, if not quantitively. Reflection spectra were taken at room temperature in the wavelength range 2 to 25 μm. The measurements were carried out using a Grubb Parsons Spectromaster double beam spectrometer with a vertical reflectance attachment having a fixed angle of 15°, and the standard used was an aluminized mirror. Specimen contamination was minimized by taking measurements soon (about a few minutes) after exposure to sodium and by flushing the sample compartment of the spectrometer with dried nitrogen during the measurement.

2.3. ESR and optical absorption

Following the suggestion that the discolouration could be attributed to colour absorbing centres [4] and that paramagnetic defects are present in sodium exposed glasses [7], the use of ESR as part of the investigation was a natural choice. Spectra were taken at room temperature using a Decca Xl ESR spectrometer operating at 9.27 GHz and carbon (coke) was used as a g-marker for the free electron resonance. To complement the ESR measurements, optical absorption measurements were made using a Cecil double beam spectrophotometer in the range 200 to 700 nm at room temperature. To avoid contamination of the samples by oxygen or water vapour during measurement, the specimens were placed inside silica sample holders appropriate for the spectrometers and then sealed with air-tight stoppers whilst in a dried nitrogen atmosphere.

2.4. XRD and DTA

XRD was used to trace the products of any reaction between vitreous silica and sodium. Vitreous silica powder was exposed to sodium vapour using the procedure described. After exposure to sodium, the powders were sealed inside Pyrex glass capillaries (about 0.5 to 0.8 mm diameter) to prevent contamination. Diffraction patterns were obtained using a Debye-Scherrer powder camera and radiation from a copper source. The identification of possible crystalline products were carried out by comparing with standard JCPDS powder diffraction data.

Finally, DTA was used to study the heat changes involved when sodium interacts with silica. This was carried out by sealing a powdered specimen and sodium metal inside an evacuated stainless steel capsule. Thermal analyses were performed using a Stanton-Redcroft 67/4 DTA apparatus at about 8° C min^{-1} and 100 to 150 mesh alumina particles in a similar steel capsule as reference.

3. Results

3.1. Surface investigation by ESCA and IRRS

Fig. 1 shows the binding energy specta of vitreous silica after having been exposed to sodium vapour at 280° C for 3 h. Spectrum A was obtained on the "original surface" i.e. no other surface treatments apart from sodium exposure. The sodium *kll* and 1*s* peaks appeared very prominently in contrast to the total absence of any silicon peaks and the presence of a small carbon 1*s* peak suggested signs of contamination. Therefore, to ensure a more representative analysis, the specimens were cleaned with argon ions (about 3 nm steps). The criterion used to determine whether the specimens were freed from contaminants was by monitoring the size of the C(1*s*) signal until it fell to a level comparable to the background. Spectrum B was obtained after about 6.5 nm of the surface was removed. The intensity of the sodium peaks decreased whereas those of oxygens increased, and whilst the C(1*s*) peak disappeared, the expected silicon 2*p* and 2*s* peaks emerged. The small Au (4*f*) peak which appeared in both spectra was due to the gold-plated specimen holder.

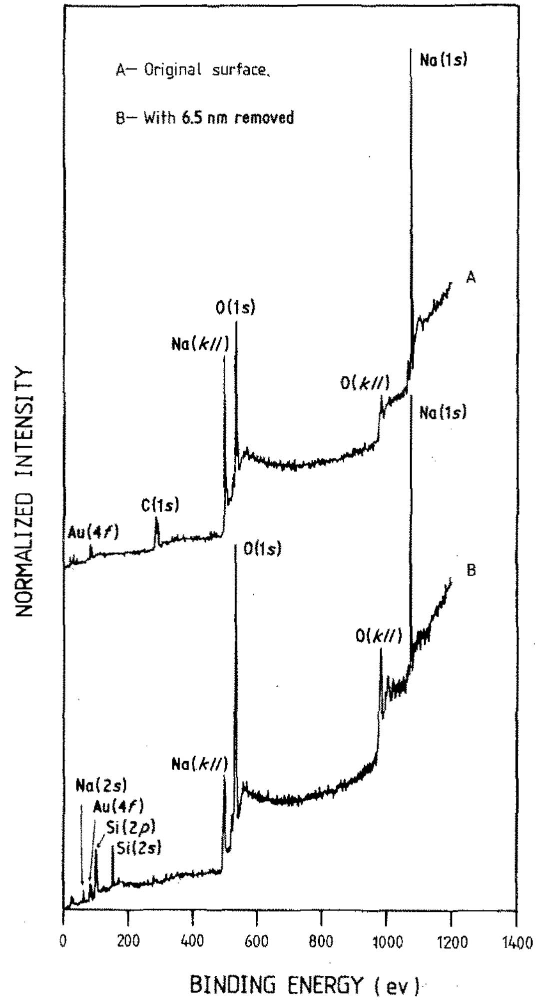

Figure 1 X-ray induced photoelectron specta (in the binding energy scale) of vitreous silica having been exposed to sodium at 280° C for 3 h. Spectrum A was obtained after the specimen was exposed to sodium vapour only, and spectrum B was obtained after about 6.5 nm of the surface of the specimen was removed by argon ion bombardment.

The modified Auger parameter α_i^* for a particular element i is given by:

$$\alpha_i^* = E_{\text{ke}}\,(kll) + E_{\text{be}}\,(\text{core}) \qquad (1)$$

where E_{ke} (kll) is the kinetic energy of the strongest Auger line and E_{be} is the binding energy of a

TABLE I Modified Auger parameter of samples of vitreous silica having been exposed to sodium. Error in $\alpha^* = \pm 0.2$ eV.

Modified Auger parameter (eV)	Sodium treatment			
	280° C 3 h	300° C 6 h	350° C 3 h	400° C 3 h
α^*_{Na}	2061.4	2061.4	2061.3	2061.3
α^*_{Si}	1711.8	1711.8	1711.7	1711.8

particular core level. α^*_i of sodium and silicon for specimens exposed under different conditions are presented in Table I. In the case of sodium, α^*_{Na} was calculated using the Auger (kl_2l_3) and the Na(1*s*) lines; and for silicon, α^*_{Si} was calculated using the Auger (kl_2l_3) and the Si (2*p*) lines. By comparing with the modified Auger parameters of various known sodium and silicon compounds given in Table II, two salient features can be deduced. Firstly, sodium is present in vitreous silica in the ionic state since α^*_{Na} for all the exposed specimens (up to 400° C) is close to that of sodium metasilicate and albite, and definitely very different from metallic sodium. This result then totally discounts the possibility that discolouration in vitreous silica may be due to sodium metal present in a colloidal form. The fact that sodium is present as an ion implies ionization has taken place and it is possible that the freed electron may take part in colour centre formation. The second important feature to emerge is that the chemical environment of the silicon atom for all the specimens exposed up to 400° C resembles that of a silicate much more than elemental silicon. This result then discounts the possibility that the discolouration may be due to the scattering of light by minute particles of silicon.

One further feature observed in this investigation was that the shape of the O(1*s*) peak was found to change with increasing temperature of exposure to sodium, and the results are shown in Fig. 2a. The O(1*s*) peak broadened and became less symmetric on the low binding energy side with increasing temperature of exposure. The shape of the O(1*s*) peak suggests that it could be composed of two separate line-shapes. To test this hypothesis, two Gaussian lines were assumed and adjusted to make a best fit to the measured data. The results of the curve fitting are presented in Table III and an example of one of the better fits to data is shown in Fig. 2b. The assumed Gaussian line-shapes, which were labelled peak 1 and peak 2 corresponding to the low and high binding energy peaks, respectively, can be seen to fit the measured data very well; and although the other fitting results showed larger root mean square (rms) deviations, the fits were not considered unreasonable. Of course an intrinsic problem with this kind of curve fitting is that the initial assumption that the line-shapes are Gaussian may be incorrect and that the final fit to data may not be unique. Therefore, any conclusions drawn at this stage must be viewed with caution.

With regard to the significance of these two peaks, Bruckner *et al.* [15] and Jen and Kalinowski [16] have also observed the presence of two O(1*s*) lines in sodium silicate glasses with the intensity of the lower binding energy peak increasing with increasing soda content. The lower binding energy O(1*s*) line was assigned to oxygens in the non-bridging position (i.e. Si–O$^-$), whilst the higher binding energy O(1*s*) was attributed to oxygens in the bridging positions (i.e. Si–O–Si). The separation in energy between these two peaks was found to be about 2.0 eV, in agreement with the results found in the present work (see Table III). This leads to the belief that two kinds of oxygens are being formed as a result of sodium exposure, or to be more specific, Si–O–Si bonds

TABLE II Modified Auger parameter of various sodium and silicon compounds.

Element	Compound	Modified Auger parameter (eV)	Reference
Na	Na	2066.3	[12]
	Na_2O	2062.5	[12]
	NaCl	2061.8	[11]
	Na_2SiO_3	2061.3	[14]
	$NaAlSi_3O_8$	2061.1	[14]
Si	Si	1716.0	[13]
	SiO_2	1712.0	[11]
	Na_2SiO_3	1711.6	[14]
	$ZnSiO_3$	1711.8	[13]
	Zeolite (Na)	1711.8	[11]

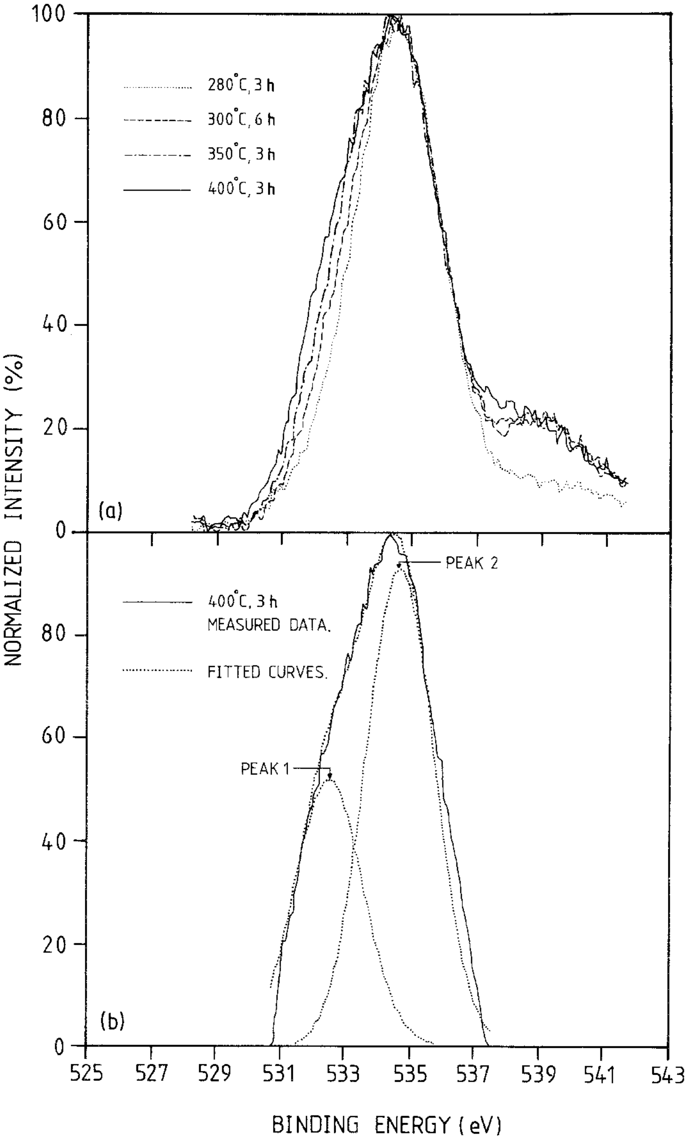

Figure 2 (a) Oxygen (1*s*) spectra for various samples of vitreous silica having been exposed to sodium. (b) The fitting of two Gaussian curves to the O (1*s*) peak measured for the sample which had been exposed to sodium at 400° C for 3 h.

were broken to form Si–O$^-$ bonds in the presence of sodium, and the number of bonds broken increased with increasing temperature of exposure to sodium.

Infra-red reflection spectra of sodium exposed vitreous silica are shown in Fig. 3. Spectrum A is the untreated specimen, the prominent peaks at about 8.9 μm and at 21.0 μm are generally agreed to be due to the asymmetric stretching of the Si–O bond and the "rocking" or bending of the Si–O bond, respectively [17–19]. After the specimens had been exposed to sodium, a new shoulder emerged at about 10.9 μm (spectra B and C) which increased in magnitude with increasing temperature of exposure whilst the Si–O stretching and bending modes decreased

TABLE III Results of the fitting of two Gaussian curves labelled peak 1 and peak 2 to the measured O(1*s*) line-shape.

Sodium treatment given to specimen	Separation in energy between peak 1 and peak 2 (eV)	Relative height of peak 1 with respect to peak 2 (%)	Root mean square deviation of fit to measured data (%)
280° C, 3 h	2.4	27.9	8.15
300° C, 6 h	2.2	36.5	9.28
350° C, 3 h	2.1	45.2	13.49
400° C, 3 h	2.2	55.8	5.01

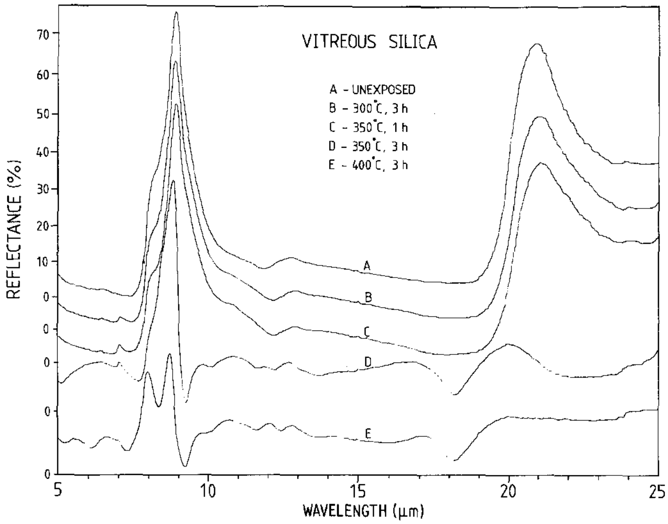

Figure 3 Reflection spectra of vitreous silica after having been exposed to sodium at various temperatures for different times.

in intensity. The shoulder at about 10.9 μm is associated with the Si–O$^-$ stretching mode [20, 21].

This particular finding adds strong support to the previous ESCA result where it was thought that bridging and non-bridging oxygens might have been found. As the temperature of exposure to sodium was raised to 350° C and beyond, drastic changes occurred and the spectra (D and E) became difficult to interpret. However, interference fringes which can be seen clearly between 5 and 7 μm suggest the formation of a thin film which has a very different character to the substrate. The thickness of this film can be estimated using an equation of the form [22]:

$$d = \frac{m\lambda}{2n \cos \phi} \qquad (2)$$

where d is the thickness of the film, m the order of the fringe, λ the wavelength at minimum, n the refractive index and $\cos \phi$ the angle of refraction. By choosing $n = 1.5$ and $\cos \phi = 1$, the thickness of the films were estimated to be about 5 and 14 μm for spectra D and E, respectively. This is roughly the same order of magnitude estimated by other investigators [2, 4].

3.2. ESR and optical absorption

All the specimens which had been exposed to sodium showed a symmetric electron spin resonance at $g = 2.002 \pm 0.001$ corresponding to the free electron value (see Fig. 4). In all cases the resonance lines were extremely weak. This is rather surprising since the detection limit of the technique is well within the parts per million range. However, there is a strong correlation between the size of the peaks and the temperature of exposure which suggests that the observed effect is real. Another feature of the spectra is the width of the reasonance lines, of the order of 30 to 40 gauss at 9.27 GHz (measured from the peak-to-peak

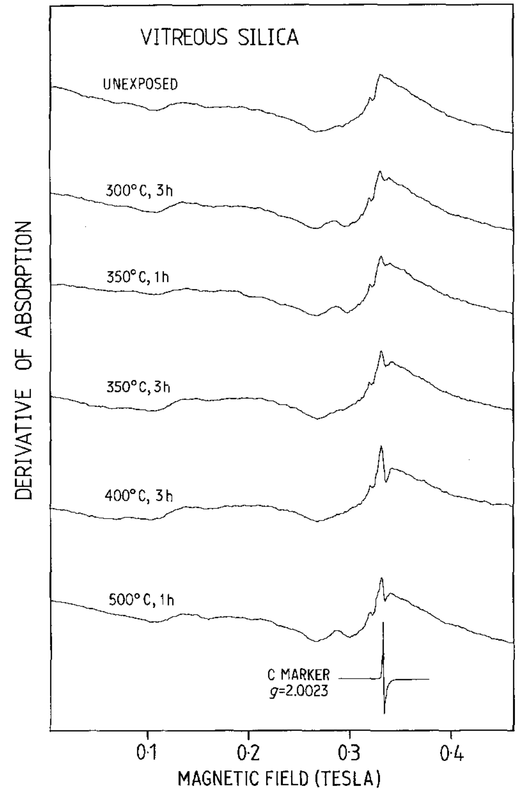

Figure 4 Room temperature ESR spectra of vitreous silica after having been exposed to sodium at various temperatures for different times.

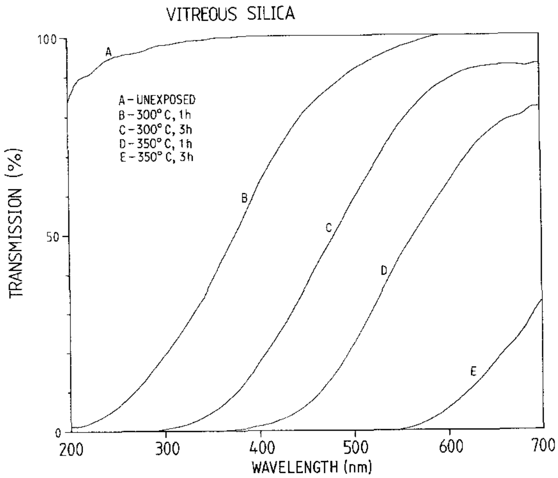

Figure 5 Transmission spectra of vitreous silica having been exposed to sodium at various temperatures for different times. The thicknesses of the samples were 1.00 ± 0.05 mm.

separation in the derivative spectrum) depending on the exposure temperature. This is much wider (by a factor of 2 to 10) than resonance due to defect centres in glasses which have been irradiated with ionizing radiation [19]. The fact that measurements were taken at room temperature might have contributed to the broadening.

Fig. 5 shows the optical transmission of the sodium exposed vitreous silica. The spectra are fairly typical of what is normally observed in other sodium exposed glasses [2, 7] in that they showed a broad featureless absorption band extending over the entire visible region. Attempts to correlate the absorption quantitatively to the temperature and time of sodium exposure have so far been unsuccessful.

The implication of these ESR and optical absorption results will be the subject of discussion later on.

3.3. XRD and DTA

The diffraction patterns of vitreous silica and α-quartz are shown in Fig. 6. α-quartz was included in the investigation since its structure is thermodynamically stable at the temperatures of interest and where equilibrium thermodynamics can be applied with confidence. As can be seen from Fig. 6, both materials behaved in a similar manner in that they were relatively undisturbed by sodium up to about 400° C but both were found to react with sodium to form a crystalline compound identified to be sodium metasilicate Na_2SiO_3 (JCPDS card number 16-818) beyond this temperature.

Taking the case of α-quartz, the above finding suggests the reaction

$$4\,Na + 3\,SiO_2 \xrightarrow{\sim 700\,K} 2(Na_2SiO_3) + Si$$

$$\Delta G = -322.2\,kJ$$

$$\Delta H = 400.4\,kJ \qquad (3)$$

has occurred. The change in free energy ΔG [23] is negative, therefore, the reaction is favoured; also the heat of reaction ΔH is large and exothermic.

The reaction indicated by Equation 3 should be accompanied by the formation of silicon. Whether the silicon, if it was formed, is in the crystalline or amorphous state is not known, but no silicon lines were found in the diffraction patterns. A factor to bear in mind is that although the conditions of exposure to sodium were standarized as far as possible, it has not been feasible either to control or to monitor the oxygen level in the exposure environment. A parallel reaction that can occur is:

$$4\,Na + O_2 \xrightarrow{\sim 700\,K} 2\,Na_2O$$

$$\Delta G = -644.3\,kJ \qquad (4)$$

and then

$$2\,Na_2O + 2\,SiO_2 \xrightarrow{\sim 700\,K} 2\,Na_2SiO_3$$

$$\Delta G = -461.1\,kJ \qquad (5)$$

Although the source of oxygen necessary for these reaction paths is not obvious, oxygen is presumably present in the vacuum at about 10^{-6} Torr as well as in the sodium metal as an oxide. Therefore, the amount of silicon formed, whether in the crystalline or amorphous state, will be less than that indicated by Equation 3. In another experiment, a small amount of sodium was sealed inside an evacuated silica ampoule and it was then heated in a bunsen flame (about 700 to 800° C) for a few minutes. Analysis of the reaction products by XRD had revealed the presence of elemental silicon. Ihnat [26] has also reported the formation of silicon, sodium metasilicate and soda when Pyrex glass is exposed to sodium at about 900° C.

Fig. 7 shows the DTA traces for α-quartz and vitreous silica. For α-quartz, a slow exothermic drift can be seen to begin from about 405° C until 527° C where a sharp exothermic peak occurred.

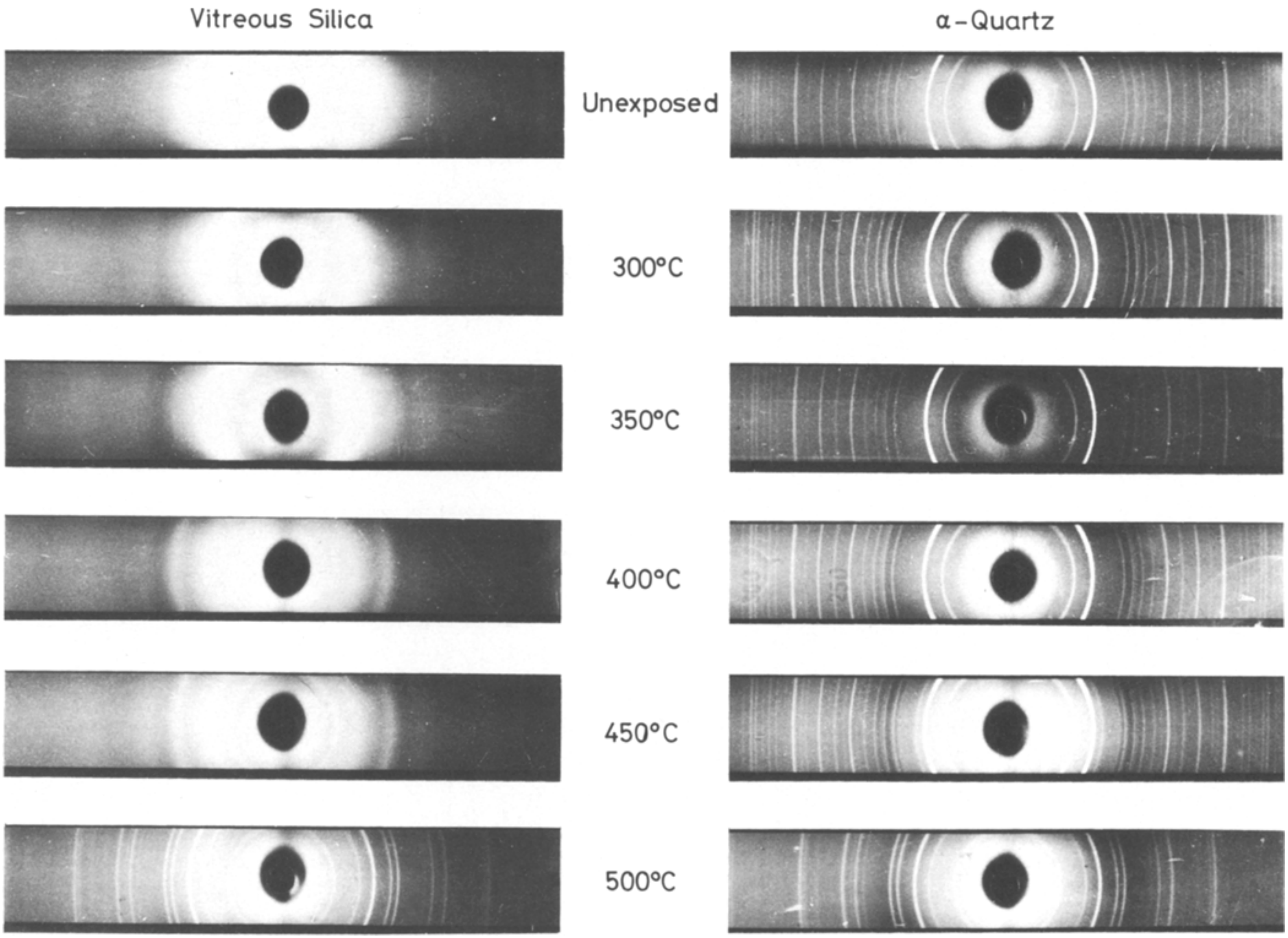

Figure 6 X-ray powder diffraction patterns of vitreous silica and α-quartz having been exposed to sodium vapour at different temperatures for 3 h.

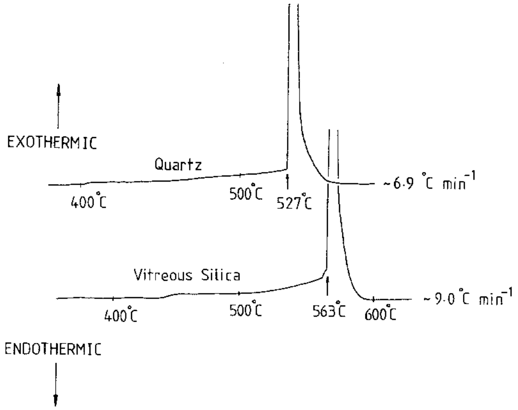

Figure 7 DTA traces of the silicas reacting with excess sodium. All specimens had the same particle size (100 to 150 μm), same weight (100 ± 0.2 mg) and all the traces were recorded on the same scale.

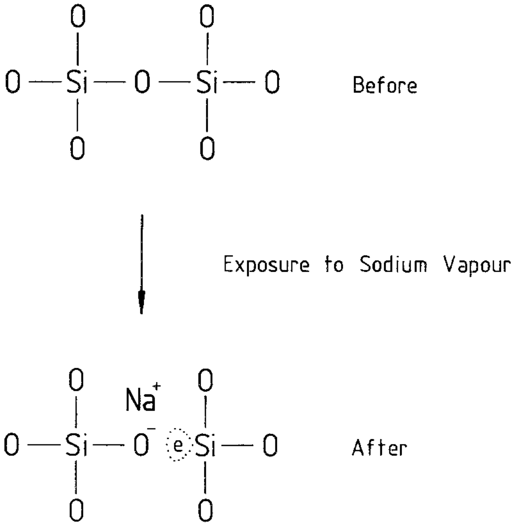

Figure 8 Model of discolouration of a silicate by sodium proposed by Stryjak and McMillan [7].

In the case of vitreous silica, a more pronounced exothermic drift can be seen to initiate at about 440° C until 563° C where an equally sharp exothermic peak occurred. It is worth noting that the thermal analysis for vitreous silica was carried out at a higher rate of heating (about 9.0° C min^{-1}) compared with that for α-quartz (about 6.9° C min^{-1}). In DTA, the rate of reaction is dependent on the heating rate [24], and the effect of a faster heating rate is to promote the reaction to occur at a higher temperature. Therefore, the differences in temperature between the exothermic peaks of vitreous silica and α-quartz is in fact less than that indicated. At temperatures below the occurrence of the exothermic peak (say 400 to 500° C), it is very likely that the materials had already been discoloured by sodium. The exothermic drift in both cases can be interpreted as being related to the situation when the materials were beginning to be attacked by sodium, corresponding to the discolouration phenomenon. The larger drift observed in vitreous silica indicates that the material is more prone to be discoloured by sodium than α-quartz, in accordance with the results of Elyard and Rawson [3]. The exothermic peaks observed presumably correspond to the formation of the compound Na_2SiO_3. There is as yet no apparent reason to explain the sharpness with which the exothermic peaks occurred.

To summarize the results above, both materials were found to be reduced by sodium to form Na_2SiO_3 (and possibly silicon) in a similar manner. The difference in thermodynamic properties between vitreous silica and α-quartz is therefore not significant enought to affect their overall reaction with sodium.

4. Discussion

This section collates the experimental evidence presented here and elsewhere [1–9] with the aim of building a consistent picture of the interaction between vitreous silica and sodium. To begin, the model proposed by Stryjak and McMillan [7] is an integral part of the present discussion; it is therefore worthwhile highlighting its salient features. When a silicate glass is exposed to sodium, the authors suggested that sodium diffuses or penetrates into the glass network causing the breakage of Si–O bonds, thus giving rise to the formation of non-bridging oxygens and oxygen ion vacancies (see Fig. 8). The electrons from the sodium atoms would tend to localize around the oxygen vacancies, thus forming defect centres similar to the *E'* centres [25], while the remaining sodium ions reside near the non-bridging oxygens to maintain charge neutrality.

From the present study most of the experimental evidence pertinent to this model was found to be fairly consistent. Starting from the ESCA results, sodium which has diffused through the surface of the glass was found to be in the ionic state and the electrons released could give rise to the possibility of colour centre formation. From the deconvoluted oxygen (1*s*) spectra, non-bridging oxygens were thought to have formed and their number increased with increasing temperature of exposure to sodium. The IRRS results have also suggested the formation of non-bridging oxygens as a consequence of sodium exposure. Finally, from the ESR investigation, a resonance line at $g = 2.002$ of the free electron type was found, and the intensity of this resonance line, although extremely weak, increased with increasing exposure temperature.

It would be imprudent though to regard the model as being irrefutable since there are observations which have as yet to be explained. The discolouration phenomenon caused by exposure to sodium has been attributed to defect centres similar to E' centres produced by either neutrons or γ-rays. To be more specific, two types of E' centres have been established from irradiation studies [19], the E'_1 centre where an electron is trapped at an oxygen vacancy, and the E'_2 centre where an electron is trapped at an oxygen vacancy in the near vicinity of a proton or alkali ion. Both of these centres which are applicable to the model have been found to show distinct absorption bands at 212 nm and 235 nm for the E'_1 and E'_2 centres, respectively.

It will be seen that for the silica exposed to sodium at 300° C (Fig. 5) strong absorption occurs in the wavelength region of about 200 to 230 nm and this would be consistent with the presence of centres similar to E' centres produced by irradiation. However, at higher exposure temperatures, greater than 300° C, the broadness of the absorption band cannot be explained by the E' defects alone, and some other mechanism or a different approach must be invoked to describe the almost total absorption in the visible region.

It was Burns [4] who noted that the optical absorption of sodium attacked silica showed a remarkable resemblance to silicon monoxide. To explore this possibility, the work on silicon oxides by Philipp [27] is most relevant. His data showed that quartz and vitreous SiO_2 have essentially identical spectral dependences (from 1 to 26 eV). The absorption edge for both materials is located at about 8.5 eV, thus there are virtually no optical processes below this energy level and all the electronic transitions which occur above 8.5 eV can only be ascribed to the character of the Si–O bonds. In the case of crystalline silicon, the reflectance curve showed several sharp features in the energy range 3 to 8 eV. In amorphous silicon though, these features are broadened out resulting in a smooth curve over the range 2 to 8 eV with the absorption edge located at about 1.5 eV. Thus absorption by crystalline and amorphous silicon in the visible region is attributed solely to the Si–Si bonding characteristics. Philipp [27] went on to investigate other amorphous silicon oxides with the general chemical formula SiO_x where $0 < x < 2$. These materials exhibited absorption which varied smoothly and continuously between the composition extremes of Si and SiO_2, i.e. the absorption edge shifted from about 1.5 to 8 eV as x increased from 0 to 2. Analysis of his data led to the conclusion that SiO_x is composed of $Si\text{–}Si_yO_{4-y}$ tetrahedra where $y = 0$, 1, 2, 3 or 4, and the absorption of SiO_x below about 8 eV is entirely due to the presence of Si–Si bonds in these $Si\text{–}Si_yO_{4-y}$ ($y \neq 0$) tetrahedra.

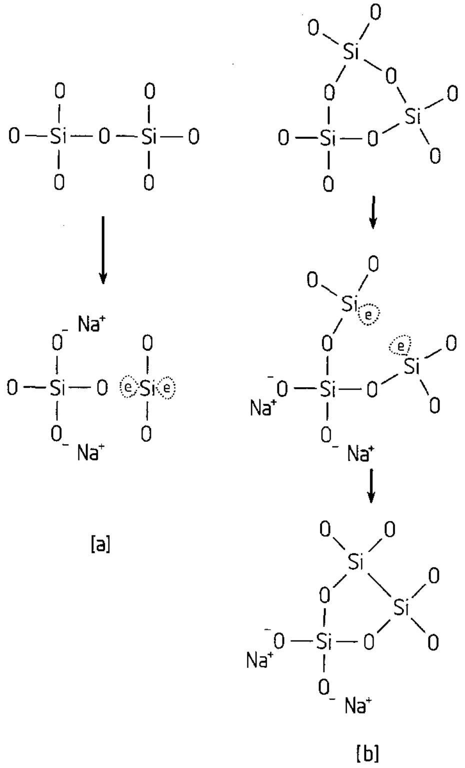

Figure 9 Alternative models of discolouration of silica by sodium. (a) Localization of two E' type defects on a SiO_4 tetrahedron. (b) Formation of a Si–Si bond from two oxygen vacancies.

In relation to the present work, the absorption curves of SiO_x [27] do indeed show a great similarity to sodium attacked silica. To pursue this strong resemblance in optical properties, if the model proposed by Stryjak and McMillan is modified, it is quite conceivable that the situations depicted schematically in Fig. 9 can occur. In Fig.

9a, two Si–O bonds in a SiO_4 tetrahedron are broken to form two E' centres in close vicinity to one another and this would presumably give rise to a very different absorption spectrum. This situation, though, of essentially removing two oxygens from a SiO_4 unit is not favoured from an energetic viewpoint. In Fig. 9b, two SiO_4 units each having one oxygen vacancy have combined together to form a Si–Si bond. Thus the result of exposure to sodium is the formation of a mixture (on an atomic scale) of sodium silicate and non-stoichiometric silicon oxide of composition SiO_x where $x < 2$. Here the sodium silicate is not expected to make any contribution to the absorption in the visible region. However, SiO_x for $0 < x < 2$ according to Philipp [27] will absorb continuously in the energy range 1.5 to 8 eV (or 155 to 827 nm) owing to the presence of Si–Si bonds. With regard to consistency with other experimental results available, one would still expect to find sodium in the ionic state and the formation of $Si–O^-$ bonds. Incidentally, this model also predicts that exposure to other alkali vapours such as lithium would result in the same kind of discolouration [7]. Since data on the silicon Auger parameters of SiO_x with well-defined values of x are not readily available at the moment, comparison with the present results has to be deferred. It is worth noting that with the current model, the elimination of two oxygen vacancies to form a Si–Si bond means that the number of paramagnetic defects remaining will be small. Hence the rather low intensity electron spin resonance measured is to be expected. Finally, the thermal bleaching of sodium blackened silica (or silicates) can be more readily understood using this model. Previous authors [1, 2, 4, 7] have found that bleaching occurs when blackened specimens are heated to about 350 to 600° C. However, the discolouration can still persist after heat treating at 350° C for 500 h [2] and complete bleaching will only occur after a heat treatment of 1000° C for 8 h [4]. Yet, if the discolouration was indeed due to E' defects alone, one would expect bleaching to take place with more modest heat treatments. For example, in γ-ray irradiated silicas, exposure to ultra-violet radiation at temperatures in the range 77 to 298 K for a few hours or heating to about 500° C for 30 min will result in complete bleaching [25], and in r.f. sputtered silica films where E' centres are also found, total bleaching of these defects will occur after heating for 30 min at about 300 to 600° C [28]. According to the model proposed here for sodium discolouration, the optical behaviour in the visible region is dominated by the presence of SiO_x. The thermal treatment of SiO_x depending on the experimental conditions, and in particular the partial pressure of oxygen, will cause the oxidation of Si–Si bonds thus resulting in a drop in absorption in the visible region. This oxidation of Si–Si bonds is expected to occur at high temperatures, about 700° C [28], and the kinetics of the reaction would presumably be governed by the diffusion of oxygen. Alternatively, heat treatment could result in a redistribution of $Si–Si_yO_{4-y}$ tetrahedra such that the proportion of $Si–Si_3O$ or $Si–Si_2O_2$ units becomes small, consequently reducing the contribution to absorption in the low energy spectral region. This redistribution of the proportions of $Si–Si_yO_{4-y}$ tetrahedra has been observed in SiO_x films [27] and can take place by heating in a vacuum at about 300° C.

To present an overall picture using the model developed here, the interaction between sodium and vitreous silica can be expressed as a general equation of the form:

$$\chi\,\mathrm{Na} + \mathrm{SiO_2} \rightarrow \frac{\chi}{2}\,\mathrm{Na_2SiO_3} + \mathrm{Si}_{1-\chi/2}\,\mathrm{O}_{2-3\chi/2} \tag{6}$$

where χ is interpreted as either the number of moles of sodium which have diffused through the surface of the glass or the local concentration of sodium in the silica. At low exposure temperatures (about 300° C), χ is expected to be small (say $\chi < 1$). Then according to Equation 6, the formation of sodium silicate and silicon oxide will result. At prolonged or higher exposure temperatures (about 450° C), χ will increase such that when $\chi = 4/3$, the situation is then equivalent to Equation 3, i.e. the formation of sodium silicate and silicon.

5. Conclusion

To summarize, a model has been developed which involves the formation of a Si–Si bond from two oxygen ion vacancies (Fig. 9b) to explain the nature of the discolouration of vitreous silica by sodium (or other alkali metals). This model is consistent with the experimental evidence available in that it can account for the presence of sodium in an ionic state, the formation of $Si–O^-$ bonds, the broad absorption band in the visible region and the thermal bleaching behaviour of discoloured silica (and silicates). The kinetics of the reaction between sodium and silica, however, is beyond the scope of the present model.

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