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Interaction of sodium with simple glasses

Part 2 Na_2O-SiO_2 and Na_2O-Al_2O_3-SiO_2

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The interactions of binary and ternary silicates with sodium were found to be similar to that of vitreous silica in that the number of $Si-O^-$ bonds was observed to increase at the expense of the Si–O bonds as the temperature of exposure to sodium is raised. From the model developed for vitreous silica [1], it was argued that $Si-O^-$ bonds are more stable than Si–O bonds in the presence of sodium. Using this concept, the discoloration behaviour of these binary and ternary silicates could be explained. The more general problem of selecting materials compatible with sodium is also dealt with by collecting a set of criteria based on equilibrium thermodynamics, and the shortcomings of these criteria are discussed.

1. Introduction

In the first part of this paper [1], the reaction between vitreous silica and sodium was found to be purely a surface effect and a model was presented to explain the discoloration phenomenon that occurs as a result of the reaction. The model involves the formation of sodium metasilicate and SiO_x where $x < 2$, and the darkening was attributed to absorption in the visible region by the nonstoichiometric silicon oxide. The second part of this paper deals with two- and three-component silicates, namely Na_2O–SiO_2 and Na_2O–Al_2O_3–SiO_2. It has been found that the addition of modifying oxides to silica improves markedly the resistance to sodium attack by showing a much smaller tendency to become discoloured [2]. The aims of this work then are to see (a) whether the model used for vitreous silica could be extended to these more complex silicates and (b) whether some general trends could be established for selecting materials which are resistant to sodium.

2. Experimental procedure

The compositions of the glasses studied are given in Table I. The glasses were prepared in 200 g batches using Analar grade reagents. The constituents were ball-milled for 3 h prior to melting in a platinum–2% rhodium crucible in an electric furnace and the technique of crushing and remelting was used to ensure homogeneity. After annealing, the glasses were cut to an appropriate size (20 x 5 x 2 mm) and polished on both sides to an optical finish using paraffin as a lubricant. The specimens were washed in methanol in an ultrasonic bath and were stored in an evacuated desiccator until required.

The method of exposing the glasses to sodium vapour and the experimental details of the techniques used to this investigation which include infrared reflectance spectroscopy and X-ray powder diffraction have already been described [1]. In order to compare the resistance to sodium as other oxides are added to silica, it was convenient to measure the optical absorption of the glasses before and after exposure to sodium. From the Beer–Lambert relationship at a particular wavelength, λ,

$$I_g = I_0 \exp[-\alpha_g l]$$

where I_0 is the incident intensity and I_g, α_g and l are the transmitted intensity, the absorption coefficient and the thickness of the glass, respectively.

After the exposure to sodium, the transmitted intensity I_{gd} is given by

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TABLE I Compositions of glasses studied

	Composition (mol %)		
	Na_2O	Al_2O_3	SiO_2
NaS(1)	20		80
NaS(2)	30		70
NaSAl(1)	30	5	65
NaSAl(2)	30	10	60

$$I_{gd} = I_0 \exp\left[-\alpha_g(1-l_d)-\alpha_d l_d\right] \quad (1)$$

where α_d and l_d are the absorption coefficient and thickness of the discoloured layer, respectively. Both of these quantities are unknown; however previous work [1] has estimated l_d to be in the order of 10 μm and therefore much less than l, which is typically 1 to 2 mm thick. Hence Equation 1 can be rewritten as

$$I_{gd} \simeq I_0 \exp\left[-\alpha_g l-\alpha_d l_d\right]$$
$$\simeq I_g \exp\left[-\alpha_d l_d\right]$$

or

$$\alpha_d l_d \simeq \ln \frac{I_g}{I_{gd}} \quad (2)$$

I_g and I_{gd} can be measured, and $\alpha_d l_d$ the absorbance due to the discoloured layer alone at a particular wavelength can be calculated.

3. Results

The absorption spectra shown in Fig. 1 are typical of all the glasses studied after they had been exposed to sodium. Using the above treatment, the absorbance of the discoloured glasses after having been exposed to sodium at different temperatures for 3 h was calculated at 500 nm. Fig. 2 shows the absorbance as a function of exposure temperature along with the results for vitreous silica and α-quartz for comparison. As can be seen, vitreous silica was severely discoloured beyond 300° C, while α-quartz was one of the most resistant silicates investigated. For the binary-silicate glasses, the addition of 20 mol% soda to silica [NaS(1)] made very little difference to the resistance to the discoloration as compared with vitreous silica. A possible explanation is that sodium silicate glasses containing up to 20 mol% soda, according to Rawson [3], can undergo metastable immiscibility giving a silica-rich phase which is readily dis-

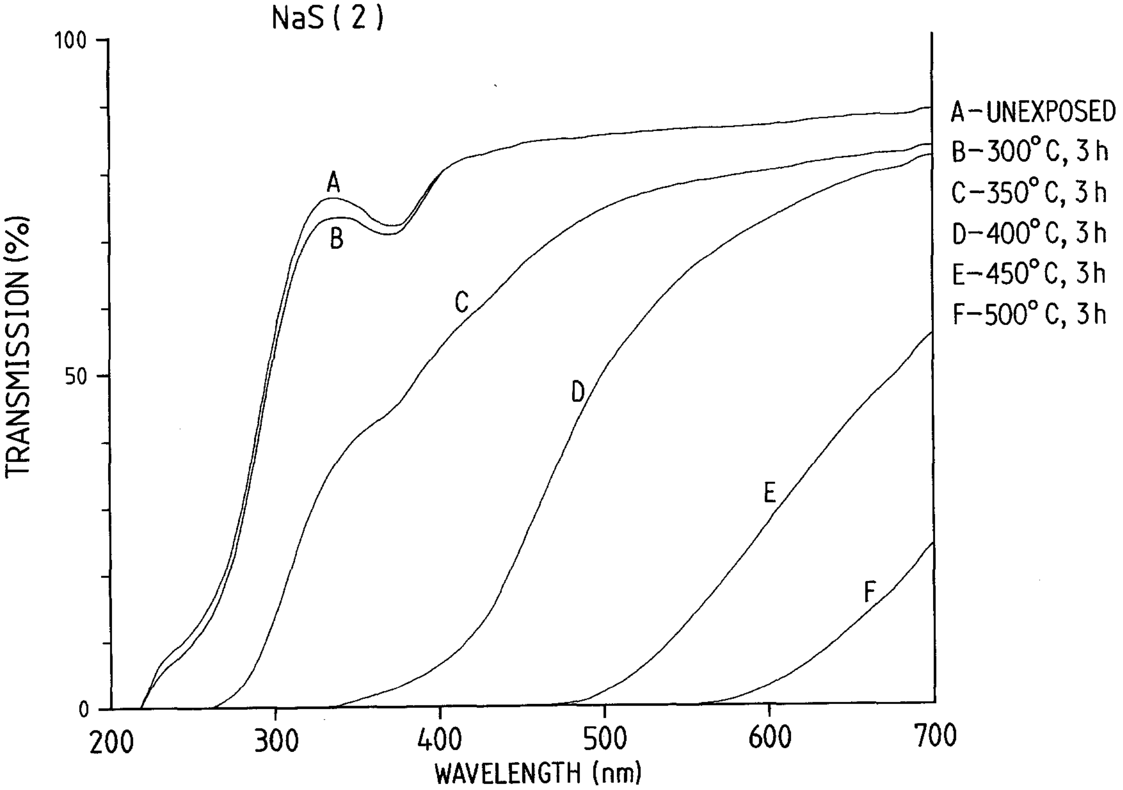

Figure 1 Transmission spectra of glass NaS(2) after having been exposed to sodium at various temperatures for 3 h. The thicknesses of the samples were 1.5 ± 0.1 mm.

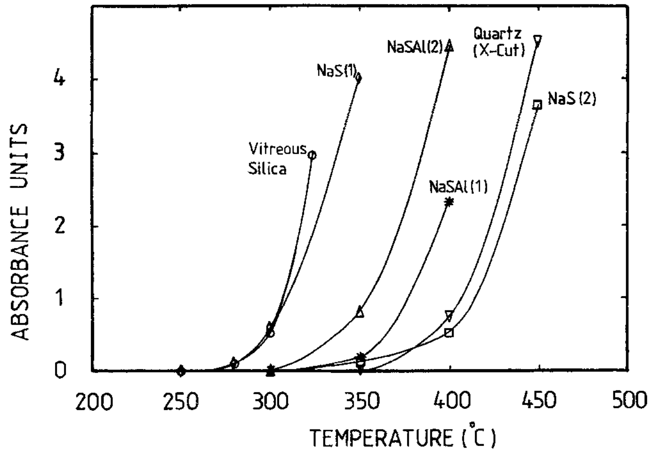

Figure 2 Absorbance of the discoloration at 500 nm against temperature of exposure to sodium for 3 h.

coloured by sodium. For a further 10 mol% increase in soda content through [NaS(2)], the resistance to sodium was vastly improved.

The substitution of 5 mol% of alumina for silica in NaS(2) to give [NaSAl(1)] had a detrimental effect on the resistance and this trend continued for NaSAl(2) where a further 5 mol% alumina was substituted for silica. This result is intuitively inconsistent with the fact that alumina is known to be much more resistant than silica [3, 4]; however it is in agreement with the findings of Elyard and Rawson [2], who had observed the same result in simple borate and phosphate glasses. This particular trend of decreasing sodium resistance with initial additions of alumina will be discussed later with respect to the structure of these glasses.

Table II shows the crystalline product identified by X-ray powder diffraction after the glasses had been exposed at various temperatures for 3 h. In all cases, only crystalline sodium metasilicate was found. Also from Table II, one can deduce that the addition of soda to silica suppresses the crystallization of Na_2SiO_3 from ~ 425° C to ~ 450° C, and the addition of alumina inhibits this crystallization process even further. Comparing with Fig. 2, there is no correlation between the crystallization of these glasses and the resistance to being discoloured by sodium.

Owing to the lack of thermochemical data, it has not been possible to examine the free-energy changes associated with the crystallization of Na_2SiO_3 for any of the glasses except NaS(2), which is close to the disilicate composition. Taking the data for sodium disilicate liquid [5] and the result found for NaS(2), the reaction can be written as

$$4Na + 3Na_2Si_2O_5 \xrightarrow{\sim 750\,K} 5Na_2SiO_3 + Si;$$

$$\Delta G = -340.4\,kJ,\ \Delta H = -513.7\,kJ.$$

Both ΔG and ΔH are negative, hence the above reaction is favoured.

The infrared reflection spectra of the glasses after exposure to sodium at various temperatures for 3 h are shown in Figs. 3 and 4. For NaS(1) and NaS(2), the spectra for the unexposed glasses are typical of those reported in the literature [6, 7]. The Si–O and the Si–O⁻ stretching modes are assigned to the bands occurring at ~ 9.1 μm and at ~ 10.5 μm, respectively, and the broad band at ~ 20 μm is attributed to the Si–O–Si bending vibration. In NaS(1) and NaS(2), the intensities of the Si–O⁻ stretching mode can be seen to increase

TABLE II Reaction products (identified using X-ray powder diffraction) of glasses and quartz after having been exposed to sodium for 3 h

	Temperature of exposure to sodium (° C)						
	300	450	400	450	500	550	600
Vitreous silica			←	—	Na_2SiO_3	—	→
α-quartz			←	—	Na_2SiO_3	—	→
NaS(1)				←	Na_2SiO_3	—	→
NaS(2)				←	Na_2SiO_3	—	→
NaSAl(1)				←	Na_2SiO_3	—	→
NaSAl(2)					←	Na_2SiO_3	→

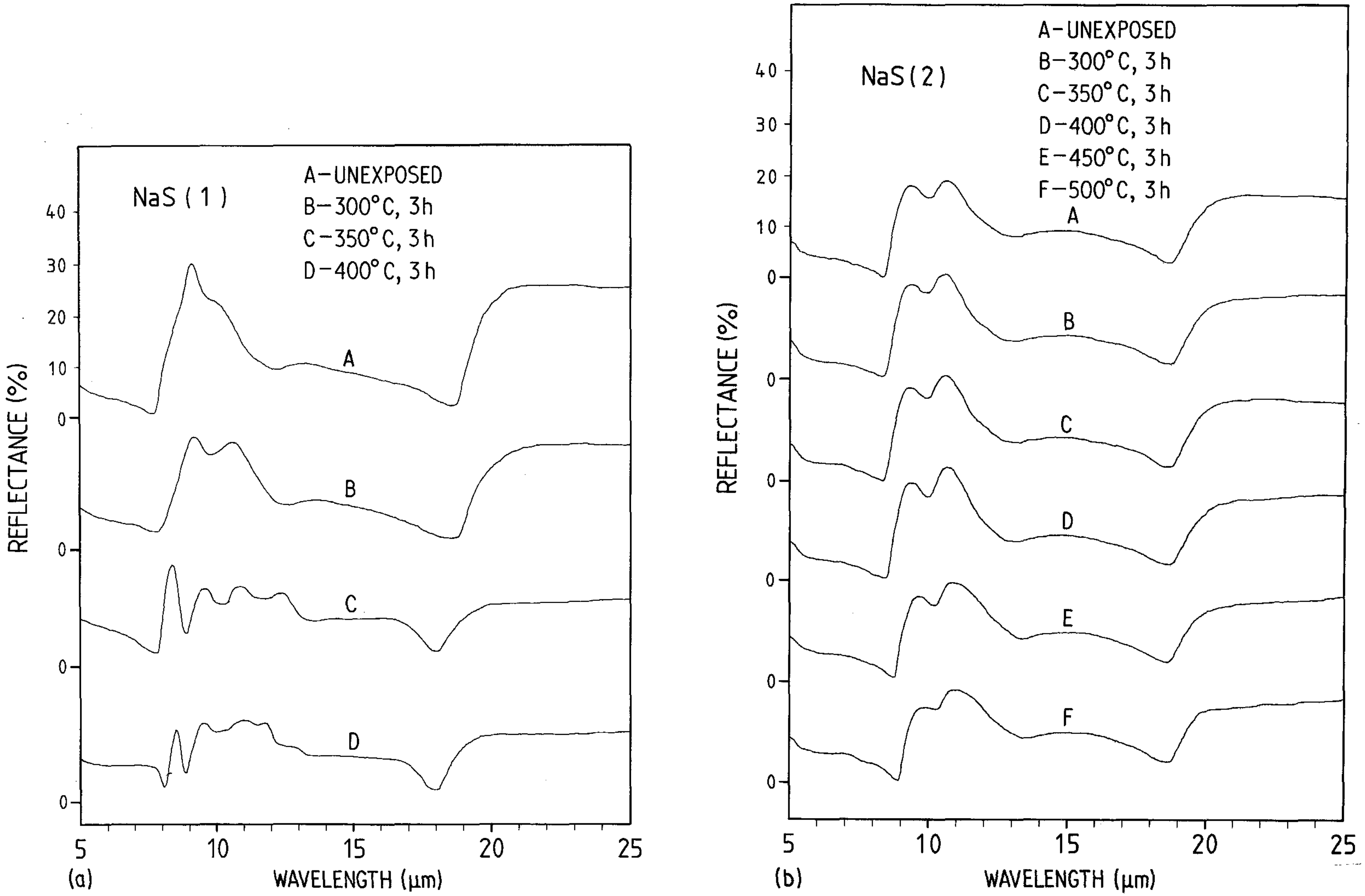

Figure 3 Reflection spectra of NaS(1) and NaS(2) after having been exposed to sodium at various temperatures for 3 h.

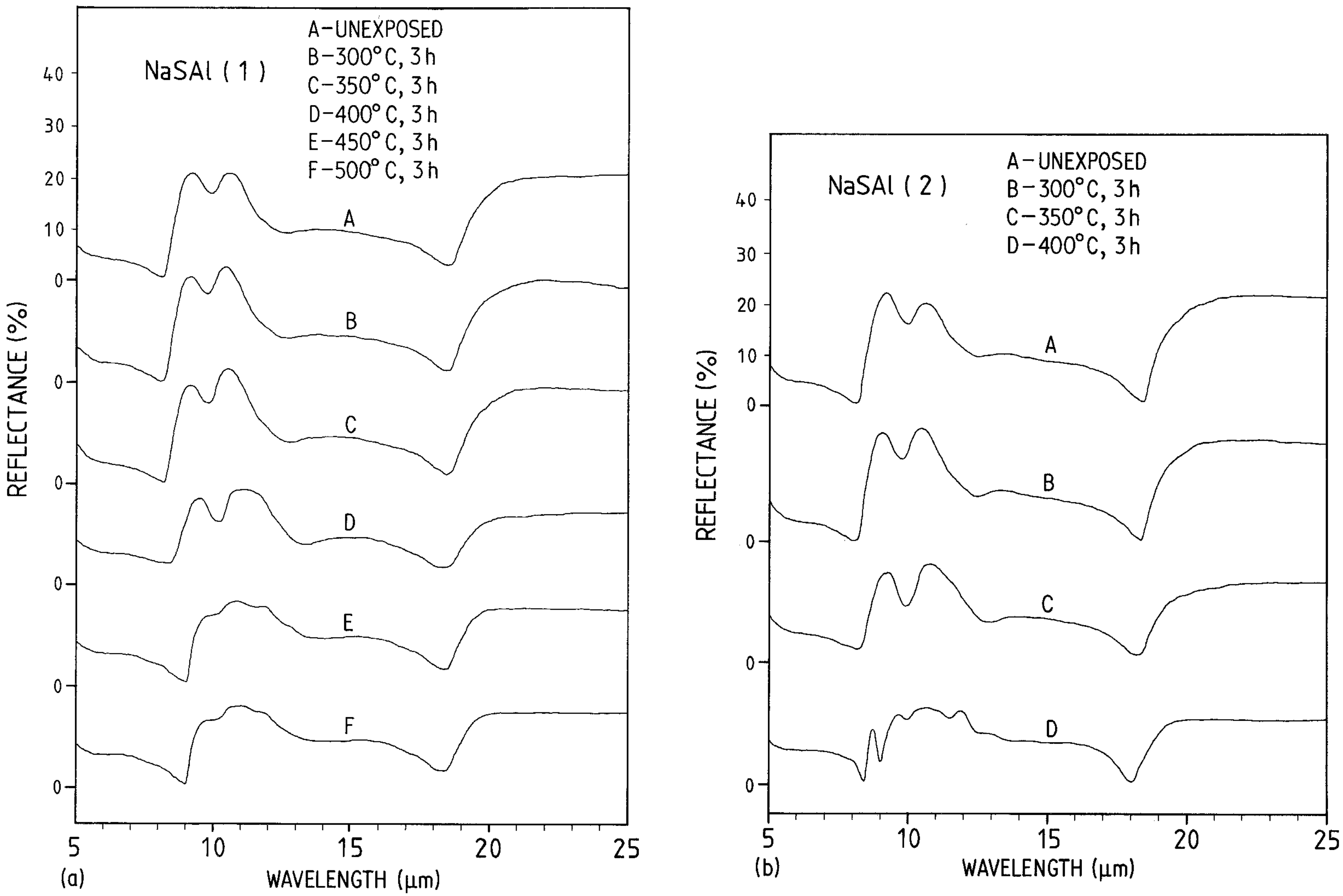

Figure 4 Reflection spectra of NaSAl(1) and NaSAl(2) after having been exposed to sodium at various temperatures for 3 h.

as the intensities of the Si–O vibration decrease after exposure to sodium. This indicates that Si–O bonds are being broken to form nonbridging oxygens. In fact this trend can also be found in Fig. 4 for NaSAl(1) and NaSAl(2). On closer inspection, the positions of the Si–O and Si–O$^-$ peaks for all the glasses can be seen to shift to longer wavelengths as the exposure temperature increases. This signifies a decrease in the force constants between the silicon and the oxygen atoms. A similar shift of this kind is also observed in sodium silicates as the soda content increases [8, 9], and it is due to the formation of ionic bonds between sodium ions and nonbridging oxygens in the Si–O$^-$ linkages [10].

At higher exposure temperatures, the less sodium-resistant glasses such as NaS(1) and NaSAl(2) showed drastic changes in their reflection spectra and these can no longer be interpreted easily except as indicating a severe departure from their original structure.

4. Discussion

4.1. Sodium silicates

Since the aim of this paper is to see whether the model developed for vitreous silica could be extended to more complex silicates, it is worth while recapitulating the relevant features of the model. The reaction between sodium and silica was described by an equation of the form

$$x\mathrm{Na} + \mathrm{SiO_2} \rightarrow \frac{x}{2}\mathrm{Na_2SiO_3} + \mathrm{Si}_{1-x/2}\mathrm{O}_{2-3x/2} \quad (3)$$

where the products of the reaction are sodium metasilicate and nonstoichiometric silicon oxide. The former compound explained the presence of sodium in an ionic state after reaction with the glass and the appearance of nonbridging oxygens, while the latter compound is responsible for the observed discoloration in the reacted material.

In the reaction between sodium and sodium silicate glasses, the infrared reflection spectra in Fig. 3 have indicated increases in the concentration of Si–O$^-$ bonds at the expense of Si–O bonds as the reaction proceeds to higher temperatures. At a sufficiently high temperature, the crystallization of sodium metasilicate occurred in much the same way as in vitreous silica. Referring to Fig. 1, the broad absorption in the visible region is also similar to that which occurred in vitreous silica [1]. This evidence led to the conclusion that sodium silicate glasses react with sodium in the same way as does silica and the reaction can be represented by an equation of the form

$$x\mathrm{Na} + \mathrm{Na_2O}\cdot y\mathrm{SiO_2} \rightarrow \left(1 + \frac{x}{2}\right)\mathrm{Na_2SiO_3} + \mathrm{Si}_{y-(1+x/2)}\mathrm{O}_{2y-(2+3x/2)} \quad (4)$$

where $y > 1$.

The question is why sodium silicates are less prone to discoloration by sodium than is vitreous silica, particularly when $y < 2$. Looking at the self-diffusion of sodium ions in vitreous silica at, say, 350° C, the diffusion coefficient is $\sim 4 \times 10^{-10}\ \mathrm{cm^2\ sec^{-1}}$ [11]. This is close to an order of magnitude lower than values for NaS(1) and NaS(2) where the coefficients are $\sim 1.2 \times 10^{-9}\ \mathrm{cm^2\ sec^{-1}}$ and $\sim 4.5 \times 10^{-9}\ \mathrm{cm^2\ sec^{-1}}$, respectively [11]. From the point of view of kinetics, one would anticipate sodium to react faster with sodium silicates than with silica. However, the results of Fig. 2 contradict this line of argument.

If one examines the change in free energy in Equation 3 on a gram-atom of oxygen basis, for $x = \frac{4}{3}$, Equation 3 becomes

$$\tfrac{2}{3}\mathrm{Na} + \tfrac{1}{2}\mathrm{SiO_2} \xrightarrow{700\ \mathrm{K}} \tfrac{1}{3}\mathrm{Na_2SiO_3} + \tfrac{1}{6}\mathrm{Si}$$

$$\Delta G = -55.7\ \mathrm{kJ}. \quad (5)$$

From Equation 4 for a sodium disilicate, the change in free energy for $x = \frac{4}{3}$ on a gram-atom of oxygen basis is

$$\tfrac{4}{15}\mathrm{Na} + \tfrac{1}{5}\mathrm{Na_2O}\cdot 2\mathrm{SiO_2} \xrightarrow{700\ \mathrm{K}} \tfrac{1}{3}\mathrm{Na_2SiO_3} + \tfrac{1}{15}\mathrm{Si}$$

$$\Delta G = -23.4\ \mathrm{kJ}. \quad (6)$$

As can be seen, the "driving force" for the reaction with sodium disilicate is ~ 2.4 times lower than that for silica. Also, the amount of silicon formed which is responsible for the discoloration is 2.5 times less than that of silica. These are suggested to be the primary reasons for the higher discoloration resistance in sodium silicates.

Another way of looking at the sodium resistance is to recall from the model developed for vitreous silica that Si–O bonds were broken in their reaction with sodium to form Si–Si bonds and Si–O$^-$ bonds, and it is the Si–Si bonds which are responsible for the observed discoloration. The experimental evidence [1] showed that the discoloration became more severe as the exposure temperature increased, thus implying more Si–Si bonds were formed. Also from previous ESCA and infrared studies, the number of Si–O$^-$ bonds were found to increase as the number of Si–O bonds decreased.

The facts that the discoloration became more drastic, and that the number of Si–O$^-$ bonds increased at the expense of the Si–O bonds as the exposure temperature increased, suggest that the Si–Si and Si–O$^-$ bonds are more stable than Si–O bonds in the presence of sodium. Hence a sodium silicate possessing fewer Si–O bonds should be less susceptible to attack by sodium. Conversely, a silicate having a larger number of Si–O$^-$ bonds should be more stable. One might even expect a metasilicate which possesses on average two bridging and two nonbridging oxygens per silicon atom to react with sodium further to form an orthosilicate which has four nonbridging oxygens per silicon atom. According to the thermochemical data of Barin *et al.* [12], the reaction (per gram-atom of oxygen)

$$\tfrac{1}{3}\mathrm{Na} + \tfrac{1}{3}\mathrm{Na_2SiO_3} \xrightarrow{700\,\mathrm{K}} \tfrac{1}{4}\mathrm{Na_4SiO_4} + \tfrac{1}{12}\mathrm{Si};$$

$$\Delta G = -1.88\,\mathrm{kJ} \qquad (7)$$

gives a negative change in free energy. However the driving force for the reaction is so small that in practice it might take a long time to reach equilibrium.

4.2. Sodium aluminosilicates

The situation alters when alumina is added to sodium silicates. It has long been suspected [13, 14], and more recently confirmed by ESCA studies [15, 16], that the majority of alumina enters the glass network as AlO_4 units for glasses where the ratio $Al/Na < 1$. Therefore for a given level of soda, the substitution of a small amount of alumina for silica would effectively reduce the amount of oxygens available to form nonbridging oxygens. Thus glasses such as NaSAl(1) and NaSAl(2), assuming the AlO_4 units do not take part in the reaction with sodium, are expected to show less resistance to sodium than does NaS(2). To rationalize this argument further, if R is the ratio of Si–O$^-$/Si–O bonds, then the resistance to sodium should increase as R increases. For vitreous silica, $R = 0$ and it should be the least resistant. For the glasses NaS(1) and NaS(2), $R = 0.143$ and 0.273, respectively; therefore NaS(2) should be more resistant than NaS(1). For the glass NaSAl(1) and NaSA(2), assuming all the alumina enters the glass as AlO_4 units, then $R = 0.238$ and 0.200, respectively. Hence NaSA(1) should be more resistant than NaSAl(2), furthermore the resistance of these two aluminosilicates should fall in between those of NaS(1) and NaS(2). This line of reasoning is in accord with the results shown in Fig. 2. Therefore, using the concept that Si–O$^-$ bonds are more stable than Si–O bonds, which is derived from the basic model for vitreous silica, the experimental results presented here could be explained.

4.3. Criteria for selecting compatible materials

From the point of view of basic understanding, the present investigation into the interaction of sodium with simple silicates provided an adequate insight into the reaction mechanisms. However, in addressing technological questions, such as whether a particular glass will be attacked by sodium, or what the criteria are for selecting suitable materials for the containment of sodium, such a detailed approach might not be appropriate and a more convenient method of choosing compatible materials is desired.

The paper by Singh [4] has attempted to do this by considering the change in free energy for the reduction reaction

$$\mathrm{M}_m\mathrm{O}_x + 2x\mathrm{Na} \rightarrow x\mathrm{Na_2O} + m\mathrm{M} \qquad (8)$$

where $\mathrm{M}_m\mathrm{O}_x$ is the oxide under consideration. The method readily identifies oxides which could be reduced by sodium by showing a negative ΔG. In the case of glasses though, this approach runs into difficulty because equilibrium thermodynamics cannot be applied legitimately to glasses where the state parameters describing the material are measured when the system is not in equilibrium, and they will therefore vary, depending on the time scale of the measurement. However, if the deviation in free energy between the glassy state and its corresponding crystalline state is small compared with the free-energy change in its reaction with sodium, then equilibrium thermodynamics is expected to be applicable.

The free-energy difference between the glass and its corresponding crystalline state can be estimated [17]. For most glasses, the deviation at T_g, the glass transformation temperature, is $\sim \frac{2}{9} H_m$, where H_m is the heat of crystallization, and for most temperatures below T_g the deviation is $\sim \frac{1}{4} H_m$. Taking silica as an example, $H_m \sim 4.5$ kJ; the difference in free energy between vitreous silica and quartz is therefore quite small. It is not surprising, then, to find that they reacted with sodium to form metasilicate at around the same temperature [1].

Bearing in mind the restriction in equilibrium thermodynamics when applied to glasses, an argument based on simple reduction reactions alone is not a sufficient criterion for selecting suitable materials. As pointed out by Anderson [5], who used the translucent sintered alumina Lucalox as an example, it is necessary to consider all the possible chemical pathways since reactions to form mixed oxides may sometimes be more favourable than the reduction reaction. The present study has also demonstrated this and these mixed-oxide reactions can be written as

$$(x+y)\mathrm{MO} + 2x\mathrm{Na} \rightarrow x\mathrm{Na_2O}\cdot y\mathrm{MO} + x\mathrm{M} \quad (9)$$

$$(x/3+y)\mathrm{M_2O} + 2x\mathrm{Na} \rightarrow x\mathrm{Na_2O}\cdot y\mathrm{M_2O_3} + \frac{2x}{3}\mathrm{M} \quad (10)$$

$$(x/2+y)\mathrm{MO_2} + 2x\mathrm{Na} \rightarrow x\mathrm{Na_2O}\cdot y\mathrm{MO_2} + \frac{x}{2}\mathrm{M} \quad (11)$$

for the divalent, trivalent and tetravalent metal oxides, respectively. The main difficulty here is that often only limited thermochemical data are available and the problem is exacerbated further when dealing with multicomponent glasses or ceramics. Therefore in cases where thermochemical information is incomplete, one has to resort to making inferences. As an example, if one examines the JCPDS index, which is a fairly comprehensive compilation of powder-diffraction data of known compounds, one finds for the alkaline earth oxides that, apart from BeO (which forms $3\mathrm{Na_2O}\cdot 2\mathrm{BeO}$), the combination of $\mathrm{Na_2O}$ with MgO, CaO, SrO or BaO to form $x\mathrm{Na_2O}\cdot y\mathrm{Mo}$ has not been reported. It is probably safe, then, to assume that these oxides do not form mixed oxides with $\mathrm{Na_2O}$ and that they are resistant to sodium. In fact apart from SrO, these oxides are already being used in most commercial sodium-resistant glasses [18, 19]. As a further example, take $\mathrm{ZrO_2}$ for instance. This oxide cannot be reduced by sodium according to Equation 5, but the formation of $\mathrm{Na_2O}\cdot \mathrm{ZrO_2}$ has been reported in the JCPDS index, therefore $\mathrm{ZrO_2}$ is not expected to be resistant to sodium and this conclusion has been confirmed in practice by Henderson and Marsden [21].

Of course this kind of selection procedure for suitable materials is fairly crude and limited to a large extent by the amount of information available. Therefore oxides which are suggested to be resistant can only be truly verified by experiments. On the other hand, materials which are suggested to be nonresistant cannot be excluded automatically since a high activation energy for the reaction may exist and a long time is required for the reaction to reach completion. A notable example is Lucalox, currently used in high-pressure sodium lamps, where the life expectancy is ~ 5000 to 10 000 h. The magnitude of the activation energy is intimately related to the structure of the material and this has been demonstrated in case of vitreous silica and quartz where the latter material, being denser, has a high resistance to discoloration. This area of relating the structure of materials to the activation energy of the reaction has not been investigated in depth in the present study, but it is anticipated to be an interesting area for further research.

5. Conclusion

From the model developed for vitreous silica, it has been shown that Si–O bonds are less stable than $\mathrm{Si{-}O^-}$ bonds in the presence of sodium. Using this concept, the interaction of sodium with sodium silicates and sodium aluminosilicates can be adequately explained.

An attempt was also made to collate a set of criteria based on equilibrium thermodynamics for selecting materials which are compatible with sodium, and the shortcomings of these selection procedures were discussed.

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