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Characterization of gas components and deposits in bubbles in silicate glasses prepared with sodium sulphate

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The gas contents and surface deposits in bubbles that were formed at various temperatures in sodium calcium silicate glasses using sodium sulphate as a starting material were investigated by means of Raman microprobe and scanning microscopic techniques. Either elemental sulphur or sodium sulphate could be readily detected in the deposits, depending on treatment conditions for the glass. Higher amounts of elemental sulphur were found as deposits on bubble surfaces for glasses prepared using both carbon and sodium sulphate. SO_2 or CO_2 could be detected as gas components in various bubbles.

1. Introduction

Sodium sulphate, one of the most common sulphate compounds, has been used as a minor additive in sodium calcium silicate glass batches to improve their melting and fining rates [1, 2]. The aim of the present work is to study the role of sodium sulphate as a fining agent by adding it alone or together with carbon in such silicate glass batches. The nature of gases that were generated in the bubbles of these glasses, and the crystal deposits that appeared on the surfaces of bubbles after various treatments of their melts were investigated, using a Raman microprobe along with a scanning electron microscope with an energy dispersive spectroscopy (EDS) attachment.

Sodium sulphate accelerates the glass melting process [3]. It is quite insoluble in silicate melts, and collects at all interfaces (both undissolved batch particles and bubbles) in the glass melts. Investigators have argued that sodium sulphate increases melt fluidity and wettability at the interface, thereby enhancing the melting rate (a surfactant effect) [1]. At higher temperature ($\simeq 1300\,°C$), sodium sulphate decomposes significantly in the presence of molten glass on the basis of the reactions:

$$Na_2SO_4 \rightarrow Na_2O + SO_3 \qquad (1)$$

and

$$2SO_3 \rightarrow 2SO_2 + O_2 \qquad (2)$$

Some of the Na_2O that is left behind at interfaces diffuses into the melt, thereby altering the interfacial tension. The change of interfacial tension has been argued to cause a stirring action in the melt (an interfacial turbulence effect) [1].

Two significant aspects concerning fining mechanisms are the buoyant rise of bubbles in the glasses to the surface, and the dissolution of gases in the bubbles during heat treatment [4]. At higher temperatures, the SO_2 gas that is liberated during decomposition forms large bubbles which sweep the small bubbles in the melt during their buoyant rise to the surface. The presence of SO_2 in the atmosphere over the melt lowers the surface tension so that rising bubbles tend to burst immediately upon reaching the surface. Applying glass redox (oxidation-reduction) considerations to glass fining, sulphur possibly dissolves as S^{-2} under reducing conditions, replacing non-bridging oxygen, and as SO_3 under oxidation conditions, coordinating with non-bridging oxygen [5]. Thus, both sulphide and sulphate solubilities increase with alkali content of a melt. However, in contrast, the sulphide solubility increases with temperature as the SO_3 solubility decreases [6].

The addition of reducing agents along with sodium sulphate to the batch promotes the decomposition of the sulphate due to the decreased solubility of SO_3, improving fining. In the presence of reducing agents in the batch, more SO_3 is evolved as SO_2. Manring *et al.* [1] reported that sodium sulphate is not completely reduced to sodium sulphide by carbon in the batch by the reaction:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \qquad (3)$$

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at 740–800 °C, and that both Na_2SO_4 and Na_2S should be present. Above 860 °C, the sodium sulphate and sulphide begin to react with silica according to the reaction:

$$Na_2SO_4 + Na_2S + 2SiO_2 \rightarrow 2Na_2SiO_3 + SO_2 + S \quad (4)$$

The extent of this reaction depends on the temperature, the atmosphere, and the sulphate to carbon molar ratio for the glass batch [7].

SO_2-containing bubbles may be generated by either the decomposition of dissolved sulphate or the diffusion of SO_2 into the pre-existing bubbles. Elemental sulphur deposits on the surface of the bubbles by the disproportionation reaction.

$$6SO_2 \rightarrow 4SO_3 + S_2 \quad (5)$$

SO_2 gas can react with sodium oxide at the internal surface of a bubble, and form both sodium sulphate and elemental sulphur deposits on the bubble surface by the reaction

$$6SO_2 + 4Na_2O \rightarrow 4Na_2SO_4 + S_2 \quad (6)$$

thereby depleting the sodium oxide in the glass near the surface of the bubble [8].

2. Experimental procedure

The raw starting materials for forming glass were commercial-grade sand, soda ash, calcite, dolomite, feldspar, saltcake (sodium sulphate), and Carbocite (77 wt % C – 18 wt % ash – 5.0 wt % volatile matter) obtained from Corning Inc. The composition of prepared glass was based on that of a commercial container glass:

$$73.40\ \text{wt}\,\%\ SiO_2 - 13.05\ \text{wt}\,\%\ Na_2O - 8.03\ \text{wt}\,\%\ CaO - 2.97\ \text{wt}\,\%\ MgO - 2.07\ \text{wt}\,\%\ Al_2O_3$$

The particle sizes of these materials were chosen in the range of 120 to 170 mesh by grinding and sieving. Batches with and without additives were mixed for 12 hours by dry ball-milling. Approximately 15 g batches were loaded in Pt-5%Au crucibles (non-wetting) and were melted at 10°C min^{-1}. At temperatures of 1300, 1350 and 1400 °C, samples were held for 3 min and then cooled by immediate exposure to room temperature conditions.

Thermogravimetric analysis (TGA) was conducted using a Cahn/Harrop microbalance with an Innovative Thermal Systems interface. The heating rate for these measurements was 10 °C min^{-1}. Such measurements were made in a stagnant air atmosphere.

The Raman microprobe technique was used to analyse the gas contents in the bubbles along with the deposits on the wall of the bubbles. An Instrument SA U1000 double grating spectrometer with a CA Innova 90 argon ion laser was used for these measurements. The magnification of the objectives in the microscope of the instrument was either 100X or 50X. The rotational spectra of the gases in bubbles were measured in the 5–100 cm^{-1} region, using the green laser line (514.5 nm) with a power of $\simeq$ 1 W. The vibrational spectra of deposits on the surfaces of the bubbles were measured in the 100–1400 cm^{-1} region, using the blue laser line (488 nm) with a power of $\simeq$ 100 mW.

3. Results and discussion

The chemical reactions involving sodium sulphate that occur during the formation of the sodium calcium silicate glass were investigated initially using TGA data in order to help to determine its role as a refining agent. The TGA trace for pure sodium sulphate in Fig. 1a shows that a very small amount of weight loss commenced at $\simeq$ 1200 °C owing to the decomposition reactions [1]:

$$Na_2SO_4 \rightarrow Na_2O + SO_3 \quad (1)$$

and

$$2SO_3 \rightarrow 2SO_2 + O_2 \quad (2)$$

Above 1300 °C, sodium sulphate decomposed rapidly but the weight loss was less than 2 wt % of total sodium sulphate. When 15 wt % sodium sulphate was mixed with glass powder which had been prepared by melting at 1450 °C, the decomposition of sodium sulphate began approximately 100 °C earlier at 1100 °C (See Fig. 1b). Sodium sulphate also decomposed rapidly at 1300 °C, and more than 50% of the sodium sulphate ($\simeq$ 8% of mixture weight) decomposed up to 1400 °C. This result implies that the thermal decomposition rate for sodium sulphate becomes more significant at these temperatures in the presence of glass.

The TGA trace for the glass batch with no additives in Fig. 1c does not show any weight loss above 950 °C at which temperature the raw materials have already released their gases. When 1.0 wt % sodium sulphate was added to the glass batch, a small amount of weight loss was found at $\simeq$ 1200 °C in Fig. 1d, and a slight weight loss continued up to 1400 °C. When the glass batch (15 g) was melted in the furnace at the same heating rate (10 °C min^{-1}), the glass melt was observed to boil over at $\simeq$ 1200 °C, showing a lot of foam. One can postulate that sodium sulphate which was added as a refining agent decomposed significantly at $\simeq$ 1200 °C, releasing gases. The residual sodium sulphate continued to decompose slightly up to 1400 °C. When 1.0 wt % sodium sulphate was added along with 0.06 wt % carbon to the glass batch, a small amount of weight loss was also found at $\simeq$ 1200 °C. However, above that temperature, weight loss was not observed in Fig. 1e. One can postulate that sodium sulphate decomposed completely in this temperature range.

When sodium sulphate was added to the glass batch along with carbon, the number of bubbles in the resulting glass was observed to be less, and their sizes were bigger compared with those of glass prepared with sodium sulphate alone. This result indicates that sodium sulphate added along with carbon is more effective as a fining agent. When sodium sulphate was added along with carbon, the colour of the Pt-5%Au crucible surface where a bubble was attached was violet, indicating probable reaction between the crucible and sulphur which is a very reactive elemental material.

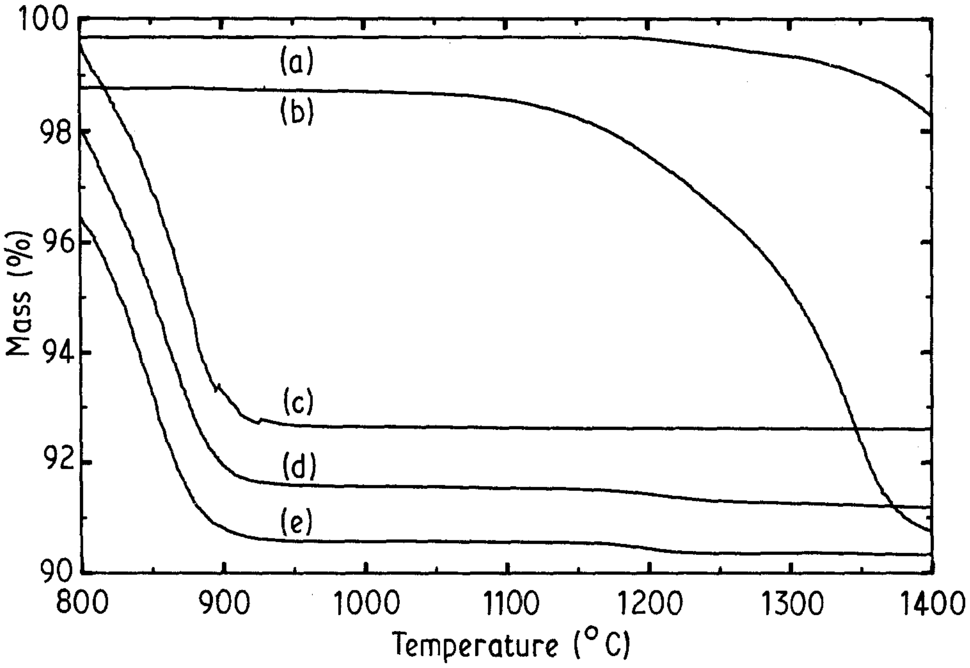
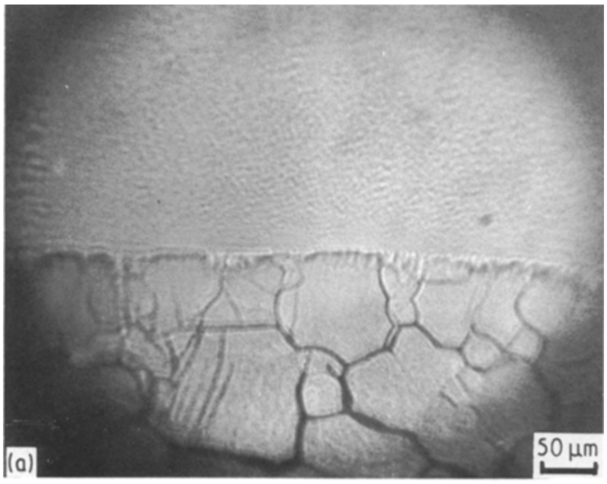
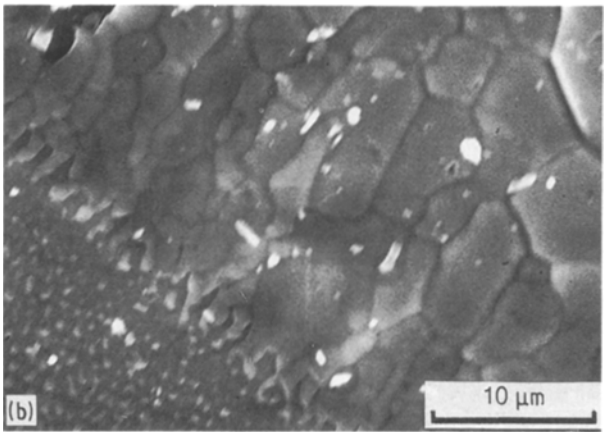


Figure 1 Thermal gravimetric analysis (TGA) traces of various investigated materials scanned at 10 °C/min in a stagnant atmosphere. (a) sodium sulphate, (b) mixture of 15 wt % sodium sulphate and 85 wt % glass powder, (c) glass batch, (d) glass batch with 1 wt % sodium sulphate, (e) glass batch with 1 wt % sodium sulphate and 0.06 wt % carbon.

Glass samples were prepared by melting batches containing 1.0 wt % sodium sulphate at the rate of $10\,^{\circ}\mathrm{C\ min^{-1}}$. At 1250, 1300 and 1400 °C, melts were held for 3 min, and were then air-cooled. Fig. 2 shows the morphology of the deposits on the internal surface of the bubbles in the glasses that were melted at 1400 °C. There are two different morphologies for the deposits. A *postmortem* cracked deposit (polycrystalline shaped) covered the half of the bubble that was found to be near the free surface crucible. The other





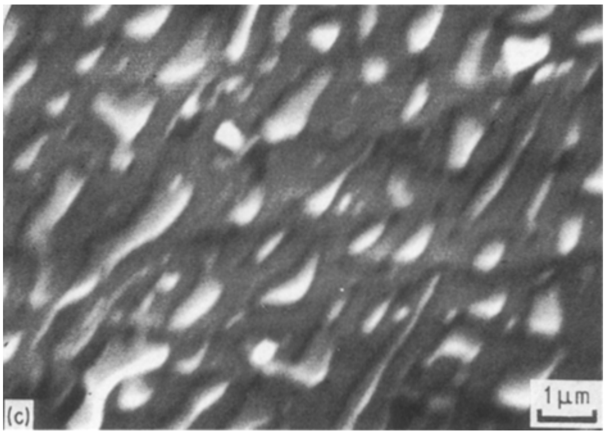


Figure 2 a) Optical photograph of bubble containing deposits, b) SEM micrograph of polycrystalline shaped deposits, c) the SEM micrograph of small dot shaped deposits.

half was opaque (small dot shaped) to the centre of the sample. Fig. 2b shows the cracked deposits (polycrystalline shaped) as well as the boundary of two different morphologies. Fig. 2c shows the elongated small dot shaped species attached to the internal bubble surface. EDS analysis indicated that both types of deposits contained sodium and sulphur. The polycrystalline shaped deposits can be identified as sodium sulphate by the Raman microprobe technique. Fig. 3a illustrates the Raman microprobe spectra for the polycrystalline shaped deposits in Fig. 2b. The vibrational bands at $\simeq 456$, 471, 635, 998, 1093 and 1110 cm^{-1} indicate the presence of sodium sulphate as deposits on the internal half surface of the bubble in glass melted at 1400 °C. However, the small dot shaped species could not be identified as sodium sulphate by the Raman microprobe technique even though EDS analysis indicated that they contained sodium and sulphur. This limitation probably occurs because the particles for this deposit species were too small and thin for identification with the Raman microprobe or else they exist in the amorphous state, thereby producing weak, broad Raman bands.

The Raman microprobe spectrum of the deposit in glass melted at 1400 °C in Fig. 3a shows that there are additional vibrational bands at $\simeq 153$ and 221 cm^{-1} other than those of sodium sulphate. These vibrational bands indicate that the deposits also contained elemental sulphur. The relative intensities of the bands for these two phases also indicates that the amount of elemental sulfur was very small compared to that of sodium sulphate in this deposit. The formation of elemental sulphur at 1400 °C can be explained by the reaction between the SO_2 gas and sodium oxide in the glass matrix that was suggested earlier by Swart *et al.* [8]:

$$3SO_2 + Na_2O \rightarrow 2Na_2SO_4 + S \qquad (7)$$

The gas contents in the bubbles were also analysed by the Raman microprobe technique. This technique had been successfully applied earlier in our study involving the investigation of O_2/CO_2 dissolution rates for bubbles found in silicate glasses [9, 10]. In this current study, it was very difficult to measure the Raman microprobe spectra of gases in bubbles in many of the investigated glass specimens because the deposits on the wall of bubbles blocked the path of laser beam, especially in the case of sodium sulphate crystal deposits. However, when the deposits were small or thin so that the laser beam could pass through the deposits, it was possible to measure the Raman microprobe spectrum of the gases in the bubbles. Fig. 4a illustrates the Raman microprobe rotational spectrum for a bubble potentially containing mainly SO_2 which was measured through a bubble surface of small dot shaped deposits.

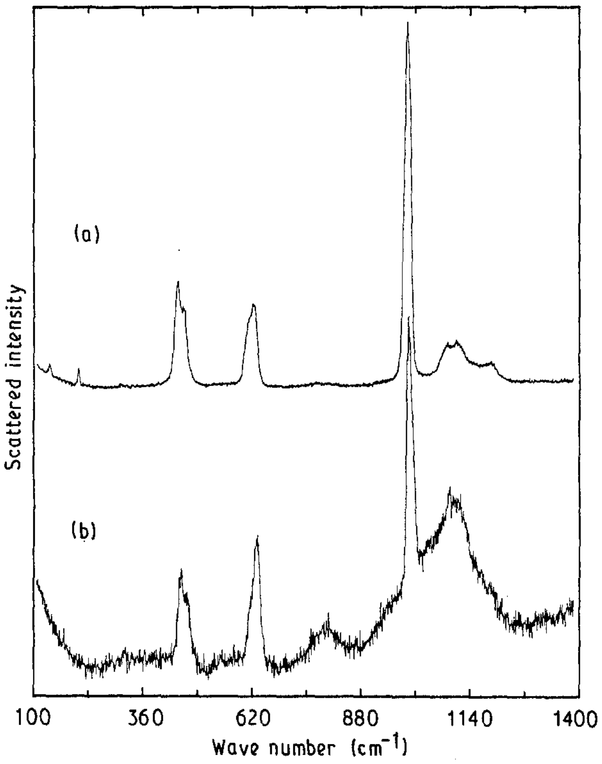


Figure 3 Raman microprobe spectrum of deposits in bubbles found in glasses prepared with the addition of sodium sulphate alone that were melted at a) 1400 °C and b) 1300 °C.

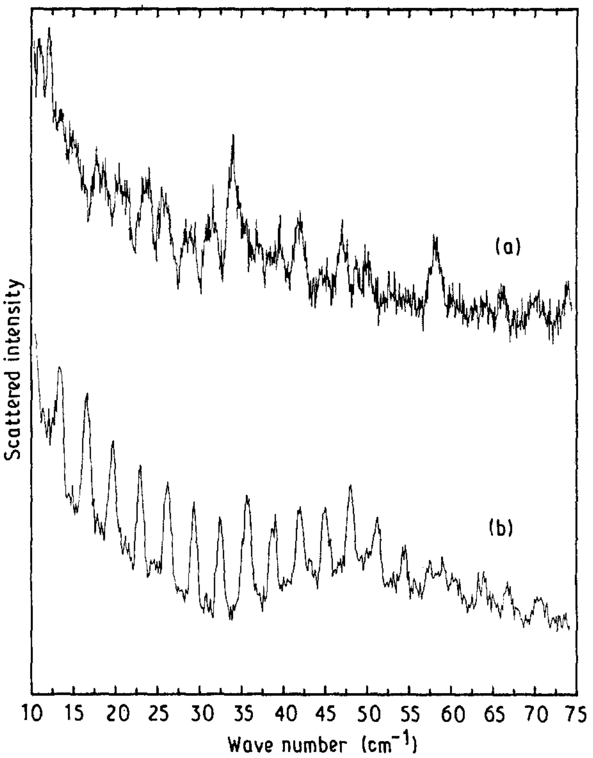


Figure 4 Raman microprobe spectra of gases in bubbles in glasses, a) potentially containing SO_2 gas in bubble and b) containing CO_2 gas in bubble.

Based on the interpretation of the observed SEM and Raman microprobe data, one can consider that the liquid sodium sulphate which collected on the surface of undissolved raw material particles (sand relics) generated bubbles by decomposition of the part that was in contact with the sand relics. The remaining (undecomposed) sodium sulphate coated the bubble. When the temperature decreased below the melting point of sodium sulphate (865 °C), the liquid sodium sulphate began to crystallize, moving from the colder surface of the bubble near the free surface/crucible region, and growing along the surface of the bubble in the direction of the opposite surface (centre of sample). This crystal growth consumed liquid sodium sulphate on the colder half sphere of the bubble, leaving behind the small dot shaped deposits which attached to the bubble surface.

The glass that was melted at 1300 °C showed almost the same morphology for the deposits and the gas contents in the bubbles as those observed for the glass melted at 1400 °C. However, elemental sulphur was not found in the deposits on bubbles in the glasses melted at 1300 °C (see Fig. 3b).

Raman microprobe–investigated bubbles in glass that was melted at 1250 °C did not show the presence of any deposits. There were a number of bubbles in the glass melted at this temperature. Since the number of analysed bubbles was finite, it cannot be conclusive that there were no deposits in all bubbles in glass melted at this temperature. Most of the bubbles contained CO_2 for which the Raman microprobe rotational spectrum is illustrated in Fig. 4b.

Fig. 5 illustrates the optical photograph of scum found on the surface of a sand relic on the free surface of glass melted at 1400 °C. Region A in the centre of scum was identified as sodium sulphate using Raman microprobe analysis. Region B surrounding region A shows a cracked morphology. Analysis of these data suggests that a sodium–rich phase formed on the surface of the sand relic after sodium sulphate decomposed. The thermal extension coefficient of the sodium–rich phase is expected to be higher than that of the sand relic below this phase. During cooling, cracking of the sodium–rich phase occurred owing to a tensile stress that developed by the thermal expansion difference.

To study the effect of carbon that was added along with sodium sulphate on the role of sodium sulphate, 0.06 wt % carbon was added along with 1.0 wt % sodium sulphate into the glass batch. The resulting glass batches were melted at 10 °C min^{-1}. At 1250, 1300 and 1400 °C, melts were held for three minutes and then air-cooled. In this case, scums were not found on the free surface of glasses melted at 1300 and 1400 °C. Raman microprobe analysis suggested that the bubbles in both of the latter-mentioned glasses contained mainly SO_2 (as in Fig. 4). The bubbles generated during melting of glass prepared with additions of both carbon and sodium sulphate did not possess any cracked deposits (polycrystalline shaped) as observed in bubbles in glasses prepared with sodium sulphate alone. Fig. 6a shows the scanning electron micrographs of the deposit on the internal surface of bubbles in a glass at 1400 °C. EDS analysis determined that the large white crystals contained elemental sulphur. The small dot shaped deposits contained both sodium and sulphate. Fig. 7a illustrates the Raman microprobe spectrum for such deposits. The spectrum indicates the presence of both sodium sulphate (small dot shaped) and elemental sulphur (white large crystals) in the deposits. However, the Raman spectrum for the small dot shaped deposits could not be measured separately by this technique. One should note that comparison of the spectra in Figs. 3a and 7a (both glass specimens melted at 1400 °C), indicated that the deposits found in the glass prepared with both carbon and sodium sulphate contained a higher amount of elemental sulphur than that of the glass prepared with sodium sulphate alone. The formation of these deposits can be explained by the reaction that was suggested earlier by Swart *et al.* [8]:

$$3SO_2 + Na_2O \rightarrow 2Na_2SO_4 + S \quad (7)$$

The gas contents in the bubbles were determined by Raman microprobe, suggesting that they contained SO_2.

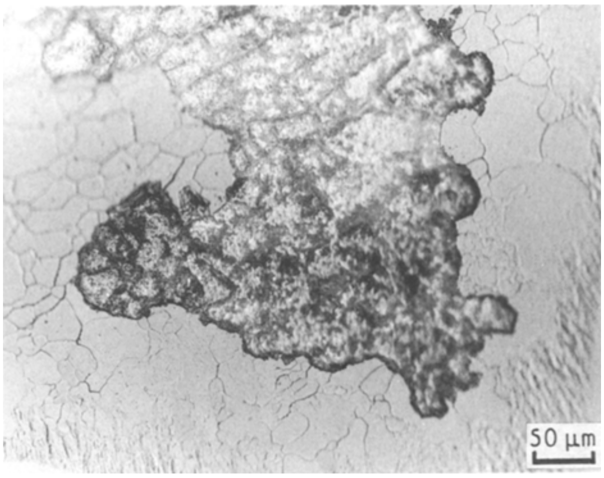


Figure 5 Optical photograph of scum on the free surface of glass prepared with 1.0% sodium sulphate addition that was melted at 1400 °C.

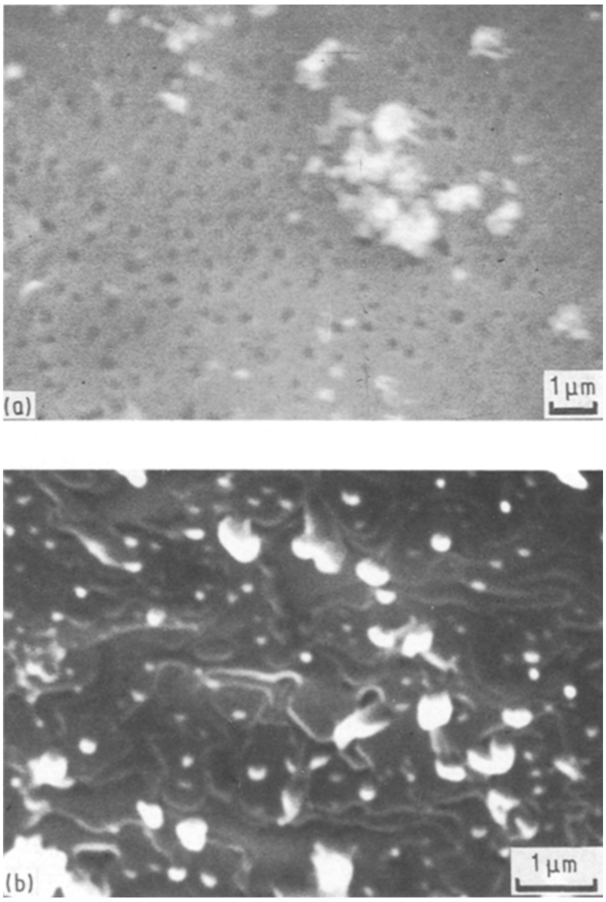


Figure 6 SEM micrographs of deposits in bubbles in glasses prepared with 1.0% sodium sulphate and 0.06% carbon addition that were melted at a) 1400 °C and b) 1300 °C.

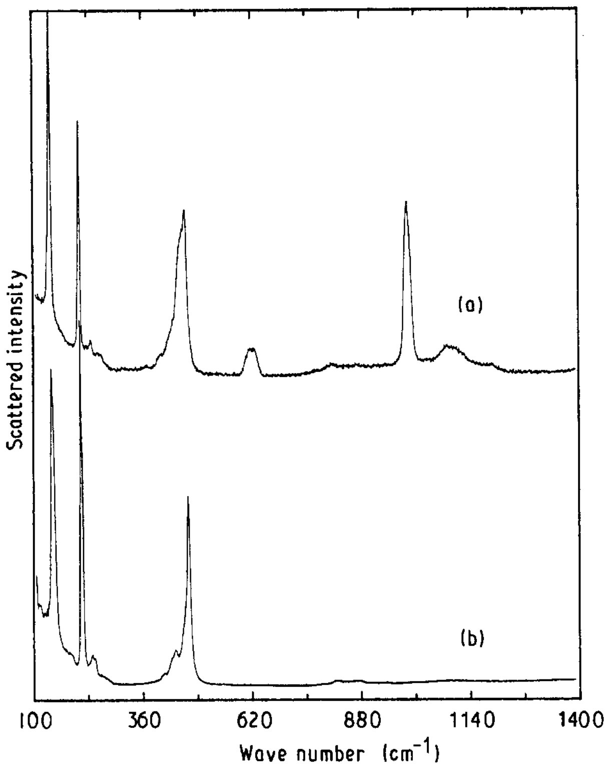


Figure 7 Raman microprobe spectra of deposits in bubbles in glasses prepared with the addition of both sodium sulphate and carbon that were melted at a) 1400 °C and b) 1300 °C.

Fig. 7b illustrates the Raman microprobe spectrum of sulphur in deposits for glasses prepared with carbon and heated up to 1300 °C. There was no indication of the presence of sodium sulphate in these deposits. Fig. 6b indicates essentially elemental sulphur deposits (white particles) on the internal surfaces of the bubbles in this investigated glass. Because these deposits contained mainly elemental sulphur, the reaction suggested by Swart *et al.* which involves the formation of both sodium sulphate and elemental sulphur from SO_2 reaction cannot be used to explain satisfactorily the formation of only elemental sulphur in bubble deposits. Manring *et al.* [1] have suggested that sodium sulphate reacts with carbon and forms sodium sulphide at low temperatures before sodium sulphate decomposition occurs in the presence of glass by the following reaction:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \text{ (740–800 °C)} \qquad (8)$$

The resulting sodium sulphide then reacts with the remaining sodium sulphate and silica to form sodium silicate, SO_2 and S by the following reaction:

$$Na_2SO_4 + Na_2S + 2SiO_2 \rightarrow 2Na_2SiO_3 + SO_2 + S \text{ (above 800 °C)} \qquad (9)$$

This reaction is probably responsible for the formation of elemental sulphur as deposits on the internal surface of the bubbles in the investigated glasses. In addition, the sodium-rich phase formed on the internal surface of the bubble is caused by the reaction described above. The sodium-rich phase is interpreted to cause a wrinkled surface of bubble due to thermal expansion coefficient differences, as is indicated in Fig. 6b. Since this reaction occurs at a low temperature, sodium sulphate in a glass batch with both sodium sulphate and carbon begins to decompose at a lower temperature than that in a glass batch with sodium sulphate alone. As a result, the sodium sulphate can act more effectively as a refining agent by releasing SO_2 gas at low temperature when carbon was added along with sodium sulphate to the glass batch.

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