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Raman microprobe investigation of oxygen and carbon dioxide dissolution from bubbles in silicate glasses containing antimony oxide

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The effect of addition of antimony oxide and/or sodium nitrate to silicate glass compositions upon the changes in the relative concentrations of oxygen and carbon dioxide in their bubbles from heat treatment was investigated using the Raman microprobe technique. The addition of antimony oxide to these glasses increased the relative rates of oxygen dissolution from their bubbles with respect to glasses containing no refining agents. These increases were closely related to the absolute amounts of Sb^{3+} ions that were present in the glasses. The relative rates were faster for glasses containing antimony oxide than for glasses containing the same molar amounts of arsenic oxide. The higher Sb^{3+}/Sb^{5+} ratios for glasses containing antimony oxide with respect to the As^{3+}/As^{5+} ratios for glasses containing arsenic oxide caused the relative rates of oxygen dissolution to be dramatically greater for the former glasses. In contrast to an earlier investigation with silicate glasses containing arsenic oxide, the addition of sodium nitrate to glasses containing antimony oxide using a similar glass preparation did not significantly change their relative rates of oxygen dissolution.

1. Introduction

The effect of refining agents on bubble gas dissolution in silicate glasses has been studied by many investigators [1–5]. Probably, arsenic oxide has been the most studied refining agent. A recent study by Lee and Condrate [6] has applied the Raman microprobe technique to investigate the relative rates of oxygen and carbon dioxide dissolution from gas bubbles in silicate glasses containing arsenic oxide along with other refining agents. The relative dissolution rates of oxygen from the bubbles into their glasses increased as the concentration of the As^{3+} ions in their glasses was increased. Obviously, higher relative rates for a glass with a given amount of added arsenic oxide were obtained by maximizing the As^{3+}/As^{5+} ratio for it. Antimony oxide has the potential for affecting the dissolution rates of oxygen and carbon dioxide in a similar way. However, very few studies have been conducted using it for bubble refinement in glasses. This study will investigate the changes in the oxygen/carbon dioxide contents for gas bubbles in silicate glasses containing antimony oxide upon their heat treatment. The Raman microprobe technique will be applied to obtain information concerning their oxygen/carbon dioxide concentration ratios upon heat treatment, comparing the relative intensities of the rotational Raman bands for the gas components before and after treatment. Bubbles will be investigated for heat-treated silicate glasses containing either antimony oxide alone or in combination with sodium nitrate.

2. Experimental procedure

2.1. Details of glass preparation

Bulk silicate glasses were prepared from a mixture of the appropriate amounts of sodium carbonate, calcium oxide and silica powder. In some cases, controlled amounts of additives such as antimony oxide and/or sodium nitrate were included. Sodium nitrate replaced appropriate amounts of sodium carbonate in the fired mixture. Batches of 100 g were weighed and mixed by ball milling the mixture for 12 h. These mixed batches were placed in a platinum crucible, and melted at 1450 °C for 3 h. After melting, the glasses were quenched by pouring the melt on a steel plate. The glasses were then annealed and cut into several pieces for glass/bubble specimen preparation. The composition of the glasses without additives was $20Na_2O \cdot 10CaO \cdot 70SiO_2$.

2.2. Preparation of bubble/glass specimens

A pair of bulk silicate glass samples were cut with areas of 1 cm × 1 cm in order to be the original glass pieces which form a bubble/glass specimen whose bubble contained the appropriate gas composition. Nine depressions were drilled with a diamond point on the surface of one of the glass pieces. The size of the final bubbles were ~ 400 μm. The pair of glass pieces were then cleaned of contaminants on their surfaces, using a procedure described earlier [7], and were then placed into the tube furnace. The surface of the glass piece with no depressions was placed against the

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surface of the glass piece with depressions. This sandwiched pair was then kept in the tube furnace under the applied flowing oxygen and carbon dioxide gas mixture for 1 h at 100 °C, and then heated to 900 °C in order to form the desired bubble. This bubble was analysed at room temperature after cooling by the Raman microprobe technique in order to obtain the initial rotational Raman spectra for the gas components in the bubble of the so-called untreated glass/bubble specimen. After spectral measurement, various bubble/glass specimens were heat treated at 1000 °C for various periods of time. After cooling, these treated specimens were then analysed, using the Raman microprobe in order to study the effect of varying heat treatment conditions on the gas compositions in their bubbles.

2.3. Details of the Raman microprobe analysis

An Instrument SA U1000 double grating spectrometer with a CR Innova 90 argon ion laser was used to measure all Raman spectra. All rotational spectra were measured using Raman microprobe optics with a back-scattering geometry in the 10–75 cm^{-1} region. The resolution for the instrument was set at $\sim 1\ cm^{-1}$ by adjusting the slit width. The magnification of objective in the microscope was × 50. The bubble was focused within the working distance of this lens. The green laser line (514.5 nm) was used for the Raman spectral measurements with a power of ~ 1 W for that line.

3. Results and discussion

This investigation will clearly indicate that addition of Sb_2O_3 to a silicate glass composition increases the relative rate of dissolution of oxygen with respect to carbon dioxide from its bubbles during heat treatment. Fig. 1 illustrates the Raman microprobe spectra of bubbles (containing oxygen and carbon dioxide) in glasses containing 0.36 wt % Sb_2O_3 which were heat treated at 1000 °C for different periods of time. As may be noted from the perusal of these spectra, the relative intensity of oxygen bands decreases with respect to those of carbon dioxide as one increases the treatment time. To see this change, one may compare the relative intensity of the Raman rotational band at $\sim 26\ cm^{-1}$ for O_2 with respect to the two Raman rotational bands for CO_2 surrounding it. The rotational bands for oxygen are denoted "o" in Fig. 1. The other rotational bands are due to carbon dioxide. In an earlier study, it has been shown that the addition of arsenic oxide to glass increased the rate of oxygen dissolution into glasses. In the earlier-published Raman microprobe spectra, the intensity of rotational band for oxygen at $\sim 26\ cm^{-1}$ after 2 h heat treatment at 1000 °C decreased to one-half of its relative intensity before treatment in glasses prepared with no refining agent [6]. As shown in Fig. 1, the band Intensity of oxygen at $\sim 26\ cm^{-1}$ disappeared almost completely after 60 min heat treatment at 1000 °C. When comparing these spectral changes with respect to heat-treatment time, it is clear that the addition of antimony oxide to glass enhances the rate of oxygen dissolution into glass.

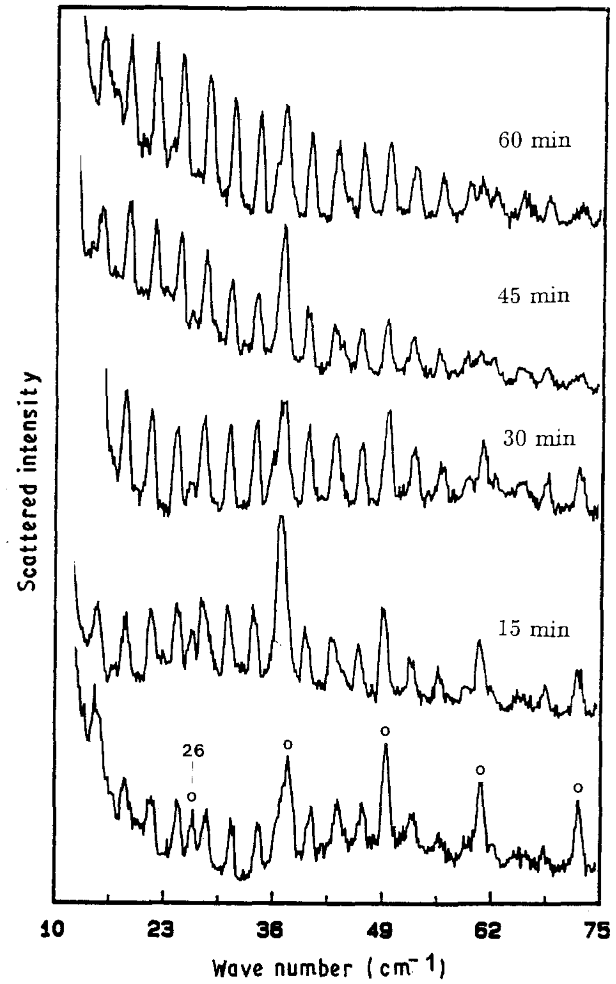

Figure 1 Raman microprobe spectra for O_2/CO_2 bubbles in silicate glasses prepared with 0.36 wt % Sb_2O_3 which were heat treated at 1000 °C for different periods.

When the antimony oxide addition was increased to 1.0 wt %, the relative rate of oxygen dissolution further increased. Fig. 2 illustrates the Raman microprobe spectra of bubbles in glasses containing 1.0 wt % Sb_2O_3 upon heat treatment at 1000 °C for different periods of time. After only 10 min treatment, intensity changes indicated that most of oxygen in bubbles has dissolved into glasses. Therefore, antimony oxide seems to increase drastically the relative rate of oxygen dissolution from the bubble. This effect would be expected on the basis of the earlier study concerning the effect of arsenic oxide on gas compositional changes in bubbles in silicate glasses during heat-treatment [6]. The earlier study showed that the addition of arsenic oxide into silicate glass increased the rate of oxygen dissolution. It also suggested that the mechanism for increased oxygen dissolution in these glasses mainly involved the following overall reaction

$$As_2O_3 + O_2 \rightarrow As_2O_5 \qquad (1)$$

with respect to their glass compositions. The effect of antimony oxide on the composition of bubbles can also be explained by using a similar overall reaction

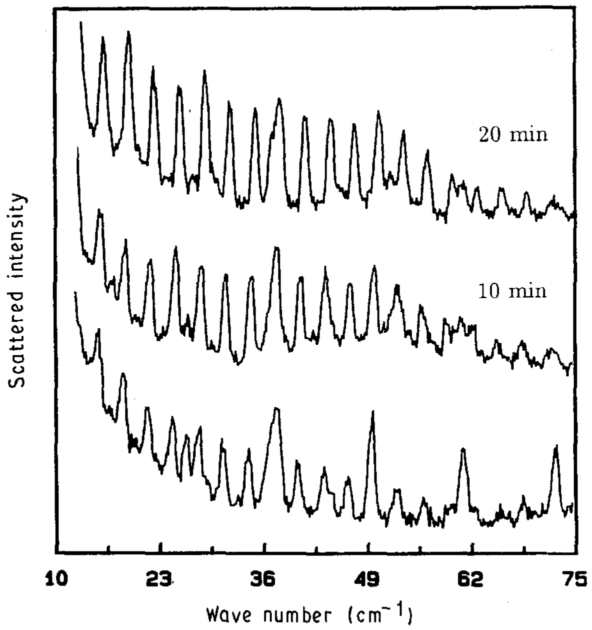

Figure 2 Raman microprobe spectra for O_2/CO_2 bubbles in silicate glasses prepared with 1.0 wt % Sb_2O_3 which were heat treated at 1000 °C for different periods.

with respect to this overall reaction for glass compositions containing arsenic oxide. Because the oxidation behaviour of Sb_2O_3 in glasses should be similar to that of As_2O_3, the increased relative oxygen dissolution involving glasses prepared with antimony oxide can be explained by using following reaction

$$Sb_2O_3 + O_2 \rightarrow Sb_2O_5 \quad (2)$$

Therefore, the role of either arsenic oxide or antimony oxide additives with respect to O_2/CO_2 compositions in bubbles during heat treatment seems to involve the placement of trivalent arsenic or antimony ions in the glass network which can react with the oxygen from the bubbles, and thus convert to pentavalent ions.

However, there are several significant differences between glasses containing either arsenic oxide or antimony that occurred upon their heat treatment with respect to the Raman microprobe spectral and gas compositional changes for their O_2/CO_2 bubbles. First, the relative rate of oxygen dissolution seemed to be much faster for glasses containing antimony oxide than for the glasses containing the similar amount of arsenic oxide. The previous Raman microprobe study [6] has shown that the relative intensity of the oxygen rotational Raman band at $\sim 26\,\mathrm{cm}^{-1}$ for bubbles in silicate glasses that were prepared with 0.25 wt % arsenic oxide decreased as the period of heat treatment increased. However, one should note that the oxygen band did not disappear completely after heat treatment for 1 h. In contrast, the oxygen rotational band at $\sim 26\,\mathrm{cm}^{-1}$ for bubbles in glasses prepared with 0.36 wt % antimony oxide (a similar amount in mol % with respect to 0.25 wt % arsenic oxide) disappeared almost completely (see Fig. 1). Therefore, this comparison seems to indicate that the addition of antimony oxide has a larger effect on the increase of the relative rate of oxygen dissolution than that of arsenic oxide. This difference between glasses containing arsenic oxide and antimony oxide in terms of their relative rates of oxygen dissolution from bubbles into glass is more obvious for glasses containing 1 wt % antimony oxide.

Fig. 2 shows that the relative intensity of the oxygen rotational band at $\sim 26\,\mathrm{cm}^{-1}$ decreased drastically after 10 min heat treatment at 1000 °C for glasses prepared with 1.0 wt % antimony oxide. In contrast, after 10 min heat treatment, the relative intensity of this oxygen band decreased to one-half of its relative intensity before treatment for glasses containing 1.0 wt % arsenic oxide. Therefore, one may note that antimony oxide addition increases the rate of oxygen dissolution to a much higher degree than arsenic oxide addition.

This difference can be clearly explained on the basis of the reaction equations mentioned earlier for the oxygen dissolution process. These reaction equations indicate that the relative rates of oxygen dissolution in these glasses strongly depend upon the amount of trivalent arsenic or antimony ions that are present in the glass. Because the glass containing antimony oxide absorbed more oxygen from the bubble than the glass containing the same molar amount of arsenic oxide, the M^{3+}/M^{5+} ratio should be higher for the glass containing antimony oxide than for the glass containing arsenic oxide. Table I lists the results of chemical analyses for various silicate glasses containing antimony oxide in terms of their wt % contents of trivalent and pentavalent antimony ions. As expected, the Sb^{3+}/Sb^{5+} ratios for glasses containing antimony oxide are higher than the As^{3+}/As^{5+} ratios for glasses prepared with a similar wt % arsenic oxide [6].

Another significant difference between glasses containing arsenic oxide and antimony oxide is the difference in the effect of sodium nitrate addition to these glasses on their gas compositional changes with heat treatment. Fig. 3 illustrates the Raman microprobe spectra for bubbles in glasses prepared with 1.0 wt % $NaNO_3$ and 0.36 wt % Sb_2O_3 after heat treatment at 1000 °C for various periods of time. As may be noted by comparing these spectra with the related spectra in Fig. 1, there seems to be no dramatic differences with respect to gas compositional changes in the bubbles when one heat treats silicate glasses either containing only antimony oxide or containing the same amount of antimony oxide along with sodium nitrate for the same period of time. Most of the oxygen was dissolved after 60 min heat treatment in both cases. Similar comparisons can be made with respect to the Raman microprobe spectra in Figs 2 and 4. Fig. 4 illustrates the Raman microprobe spectra for bubbles in glasses prepared with 1.0 wt % $NaNO_3$ and 1.0 wt % Sb_2O_3 that were heat treated at 1000 °C for

TABLE I Chemical analysis for Sb_2O_3 and Sb_2O_5 in sodium silicate glasses containing various additives

Sample: refining agents used	Results (wt %)		
	Total antimony as Sb_2O_3	Sb^{3+}	Sb^{5+}
Sb_2O_3	0.98	0.96	0.02
Sb_2O_3 + $NaNO_3$	0.98	0.83	0.15

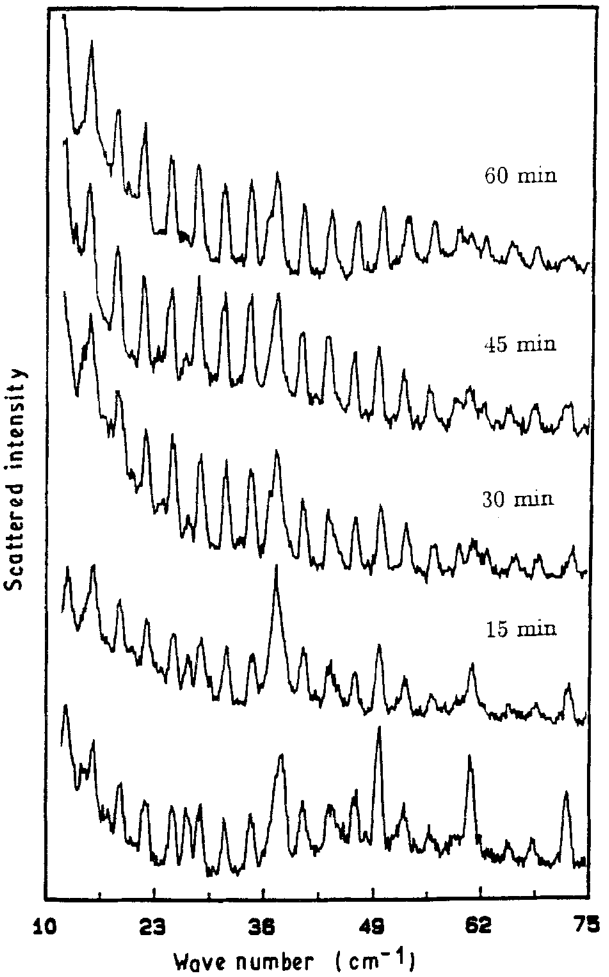

Figure 3 Raman microprobe spectra for O_2/CO_2 bubbles in silicate glasses prepared with 0.36 wt % Sb_2O_3 and 1.0 wt % sodium nitrate which were heat treated at 1000 °C for different periods.

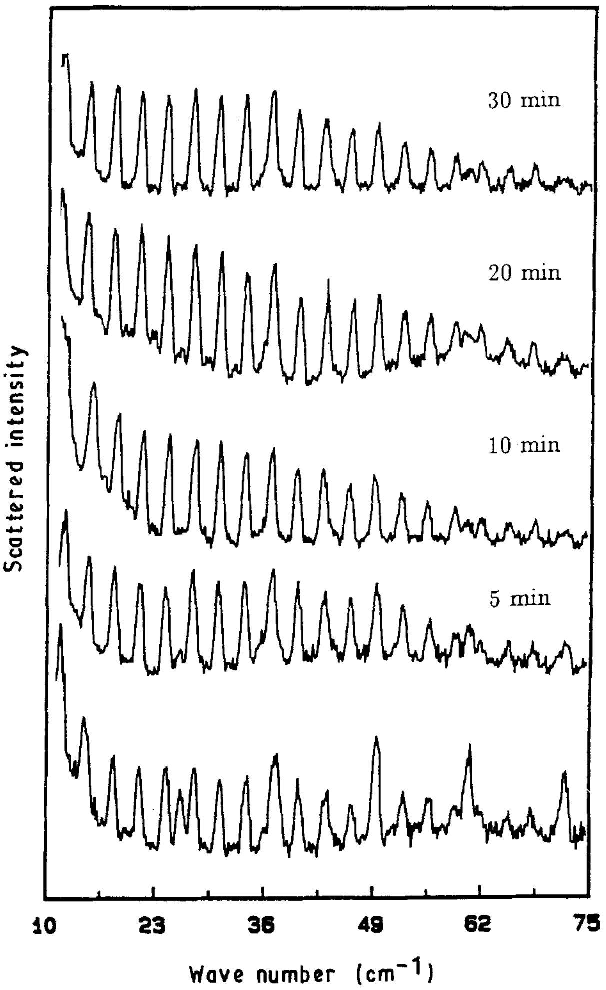

Figure 4 Raman microprobe spectra for O_2/CO_2 bubbles in silicate glasses prepared with 1.0 wt % Sb_2O_3 and 1.0 wt % sodium nitrate that were heat treated at 1000 °C for different periods.

different periods of time. As may be noted from the spectra, oxygen seems to disappear within the noise level of the spectral measurement after 10 min heat treatment, similarly to glasses containing no sodium nitrate. In contrast, stronger differences were noted between compositional changes in bubbles between glasses either containing arsenic oxide alone or containing the same amount of arsenic oxide along with sodium nitrate. These spectral/concentration differences noted during heat treatment of glasses containing arsenic oxide or antimony oxide along with sodium nitrate can also be explained using our model overall reaction equations.

In the case of glasses containing arsenic oxide, addition of sodium nitrate significantly decreased their relative rates of oxygen dissolution because the ratio of the trivalent arsenic ions in the initial glasses was significantly decreased. In the case of glasses containing antimony oxide, oxidation of trivalent antimony ions to pentavalent antimony ions is also expected to occur due to addition of sodium nitrate so that the absolute amount of trivalent antimony ions should decrease. Table I indicates that the absolute amount of trivalent antimony ions has decreased upon addition of sodium nitrate. However, the amount of Sb^{3+} ions converted to Sb^{5+} ions by addition of sodium nitrate is only $\sim$ 14%. In contrast, the addition of sodium nitrate to the glass containing arsenic oxide converted 72% As^{3+} ions to As^{5+} ions. Because the amount of antimony ions in the silicate glasses that were converted upon sodium nitrate addition from the trivalent state to pentavalent state was small in comparison to the amount of antimony ions still in the trivalent state, the differences in the Raman microprobe spectra involving glass samples that were prepared with and without sodium nitrate were not dramatic. However, in the case of the glasses containing arsenic oxide, because the amount of trivalent arsenic ions converted to pentavalent state was high upon sodium nitrate addition in comparison to the amount of arsenic ions still in trivalent states, the effect of sodium nitrate addition to these glass compositions could be distinctively detected in the Raman microprobe spectra.

4. Conclusions

The effect of antimony oxide addition on the change of gas composition in a bubble in silicate glass with heat treatment can be successfully studied using Raman microprobe spectroscopy. Interpretation of the Raman microprobe data clearly indicated that the relative rate of oxygen dissolution from bubbles was much greater for glasses containing antimony oxide than for glasses containing comparable amounts of arsenic oxide. This difference can be explained using a reaction equation suggested earlier, which indicates that the relative rate of oxygen dissolution from the bubble depends on the amount of tirvalent ions (either antimony ions or arsenic ions) that is present in the glass. Therefore, the higher relative rate of oxygen dissolution in glasses containing antimony oxide in comparison to glasses containing the same amount of arsenic oxide is due to the fact that the Sb^{3+}/Sb^{5+} ratio for the former glasses is higher than the As^{3+}/As^{5+} ratio for the latter glasses containing comparable amounts of arsenic oxide. The effect of adding sodium nitrate to a glass batch containing antimony oxide was not as dramatic as on the spectral/concentration data concerning oxygen dissolution from bubbles, as observed earlier with glasses containing arsenic oxide. This difference is due to the small ratio of Sb^{3+} ions which were converted to Sb^{5+} ions during our glass formation procedures by sodium nitrate addition into the silicate glass.

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