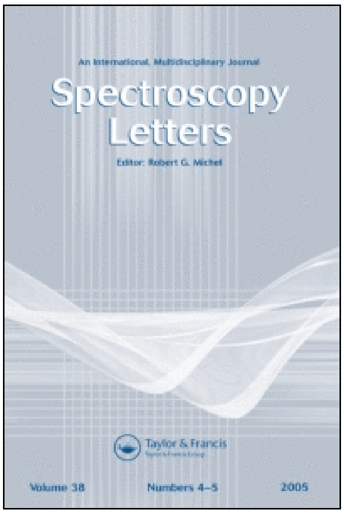

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Considerations Concerning the Application of Raman Microprobe Technique to the Systematic Analysis of Bubbles in Glass

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CONSIDERATIONS CONCERNING THE APPLICATION OF RAMAN MICROPROBE TECHNIQUE TO THE SYSTEMATIC ANALYSIS OF BUBBLES IN GLASS

Key Words: Glass, Silicates, Bubbles, Gases, Raman Spectra

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ABSTRACT

The application of Raman microprobe spectroscopy for the analysis of the gas contents in bubbles in glass was studied in terms of various aspects of the applied experimental procedure. The rotational Raman spectra of bubbles for various gases in the bubbles could be measured with good sensitivity. The Raman microprobe spectra for small bubbles (less than 30 μm diameter) could be measured with good signal-to-noise ratios. The possibility of applying this technique to the quantitative analysis of gas contents in bubbles was examined. The importance of the cleaning procedure for the glass materials during bubble

preparation was also discussed in terms of controlling the gas contents in bubbles that will be used for systematic heat treatment investigations.

I. INTRODUCTION

Inclusions such as bubbles, crystalline seeds, and cords that are formed during the commercial production or treatment of glasses have been significant problems for the glass industry. These defects are not desired in a commercial glass material because of their effect on either the appearence or the optical and mechanical properties of the glass object. In order to eliminate inclusions such as gas bubbles in glasses, one must diagnose the origins of such bubbles, understanding the chemistry that is associated with their formation. This type of study involves a systematic investigation of the heat treatment of glasses containing bubbles, varying parameters such as glass composition, gas content in the bubbles, bubble size, treatment temperature, treatment period, etc. in order to understand such chemistry. Bubble/glass specimens have to be prepared for such studies with reasonably controlled glass compositions, bubble sizes and gas compositions in the bubbles so that data obtained with respect to their heat treatment can be clearly and easily interelated in terms of the chemistry of the bubble dissolution.

During the last fifty years, different types of techniques have been applied to analyze bubble contents in glasses after heat treatment. These analyses have included techniques such as traditional micro-chemistry, mass spectrometry, gas chromatography and Raman spectroscopy. Micro-chemical techniques are very time consuming, and their reliability depends upon the skill of the analyst. Each of these techniques except for the Raman spectral methods involves the isolation of the gas bubbles followed by the controlled fracture of the glass sample under conditions whereby the entire gas contents of bubbles can be recovered and analyzed. In contrast, the application of Raman spectral techniques does not require the fracture and destruction of the glass samples in order to determine the gas contents of bubbles in the glasses. Because of this, it is possible to measure the Raman spectra of the same bubble before and after treatment.

Raman spectroscopy has been applied by several investigators to study gas contents in bubbles in glasses [1-3]. They have mainly used a macro-Raman spectral technique, involving the 90^o scattering geometry. Even though they were able to measure the Raman spectra for bubbles as small as 35 μm in diameter[3], it was very difficult to align and focus the optical system in order to obtain Raman spectra only from a specific bubble in the glass. Recently, the Raman micro-probe technique which involves the back scattering geometry has been developed to obtain Raman spectra from specific inclusions. This latter technique is not normally applied to analyze gas contents in bubbles using the vibrational spectra of the gas components, because it is not possible to collect only this type of Raman spectra from the gases in the bubble without overlapping vibrational Raman spectra from the surrounding glass.

In this current Raman microprobe study, the rotational spectra of the gas components in the bubbles were used to determine the gas contents in the bubbles, because in this region of the Raman spectra, overlap from the vibrational bands of the surrounding glass appeared to be negligible. Various aspects will be discussed concerning the preparation of suitable bubble/glass specimens that are necessary for use in a systematic Raman microprobe study which investigates changes in the gas contents in bubbles in glass from heat treatment. Also, various points concerning the application of this technique to the determination of the relative concentrations of oxygen and carbon dioxide in bubbles will be discussed.

II. EXPERIMENTAL PROCEDURES

A.) Details of the Preparation of the Bubble/Glass Specimens

A pair of bulk silicate glasses which were cut with 1 cm x 1 cm areas were used to prepare the bubble/glass specimens whose bubbles contained the desired gas contents. One or two depressions were drilled with a diamond point on the surface of one of the above- mentioned glass pieces. By controlling the size of the drilled depression, the size of the resulting bubble could be controlled. The two glass pieces were then cleaned in several steps. First, glasses were cleaned in a trichlorotriflouroethane solution for 30 minutes using an ultrasonic cleaner. Then, these glass samples were cleaned ultrasonically in acetone and methanol solution, respectively, for 30 minutes each. After this precleaning procedure, the samples were finally cleaned using the RCA method. This method involved placing the glass samples into a cooled solution containing distilled water, hydrochloric acid and hydrogen peroxide, and heating the resulting mixture at 75°C for 15 minutes. The glass samples were removed from the solution and rinsed with distilled water.

The glass samples were placed in a tube furnace. The surface of the glass piece with no depression were placed against the surface of the glass piece possessing depressions. These sandwich pairs were kept under the desired controlled atmosphere for an hour at 100°C, and then heated upto 900°C in order to form bubbles in the resulting glass specimen.

The above-described cleaning procedure is important in order to prepare bubbles in glasses with reasonably controlled gas contents. Various aspects concerning this cleaning process with respect to bubble formation in glasses will be discussed in a later section.

B.) Details of the Raman Microprobe Technique

An instrument SA U1000 double grating spectrometer was used to measure the Raman spectra. All rotational spectra were measured using Raman microprobe optics with a backscattering geometry in either the 5 - 100 cm^{-1} range or the 300 - 500 cm^{-1} range depending upon the nature of the investigated gases. The resolution for the instrument was set at ca. 1 cm^{-1} by adjusting the slit width. The magnification of objective lens in the microscope component was 100X. The bubble was focused within the working distance of this lens. The laser beam size on the bubble with this objective was ca. 3-5 μm in diameter. The excitation source for the Raman spectra was an Innova 90 Argon-ion laser. The green laser line (514.5 nm) was used for Raman spectral excitation with a power of ca. one watt.

III. RESULTS AND DISCUSSION

A.) Differences Noted between the Micro- and the Macro- Raman Spectral Techniques

Either micro- or macro-Raman spectroscopy can be used for the analysis of bubbles in glasses. Macro-Raman spectroscopy usually uses a 90°-type of scattering geometry. The major advantage of this geometry is that it is possible to collect only the Raman spectra from the bubble without scattering spectra adding from the surrounding glass. Therefore, the vibrational spectra of the included gases can be measured as well as their rotational spectra. However, this latter technique possesses several weaknesses during its application. First, it is relatively difficult to align the laser directly onto the bubble, especially in the case of a very small bubble. Second, the bubble that one desires to analyze should be located at a position so that the path of the laser beam does not cross other bubbles. Such crossings can make the alignment of the laser beam into the desired bubble difficult. Therefore, it is usually necessary to isolate the bubble that is to be analyzed. Third, the investigated bubble/glass sample should possess flat surfaces which are normal to the direction of the incident laser beam and the direction of the investigated Raman scattered beam. If the investigated sample has curved rather than flat surfaces with repect to these beams (such as found for tubes or spheres), these surfaces may cause the scattering of incident laser beam so that the intensity of laser beam on the bubble gas may be decreased. Finally, it is usually necessary with this technique to use a "pin hole" type of slit in order to isolate the Raman scattering spectra from a single small bubble [3].

Many of the problems listed above can be eliminated by using Raman microprobe technique with a back scattering geometry. It is very easy to focus and align the laser beam into the bubble with this geometry. Also, it is easier to obtain the Raman spectra from these bubbles whose diameters are as small as 15 μm. With this back-scattering mode for collection of Raman spectra, each individual bubble facing the laser beam can be analyzed by the focussing the laser beam directly on it without using bubble isolation that is necessary with the macro technique. Futhermore, there is almost no effect from the curved shape of the bubble in the glass sample because with high magnification objectives in the microscope optics, the curved shape of the bubble surface appears to be relatively flat so that scattering from the curved surface is minimized. Despite the alignment advantages with this back scattering technique, there are some weaknesses with repect to its use. One major disadvantage occurs because the Raman spectra associated with vibrational spectra of the gas components in a bubble are usually quite weak. Therefore, it may be nearly impossible in many cases to detect the vibrational spectra of such gases using this back scattering technique with currently available instrumentation. This disadvantage is also enhanced by other factors. Vibrational bands occur for many bubble gas components in the same spectral regions where bands are found for the glass matrix so that these latter bands screen the vibrational bands for the gas component. Also, the glass matrix may scatter the vibrational Raman spectra from gases in bubbles, and thereby decreases the intensities of the vibrational bands observed at the spectrometer's detector.

As mentioned earlier, there have been several studies of bubble compositions in glass using Raman spectroscopy [1-3]. All of them were conducted using 90°-optical geometries. The main reason why the Raman microprobe technique was not applied for bubbles study was that earlier investigaters believed that spectral overlap from the glass matrix was too high for the rotational spectra of bubble gases to be satisfactorily detected by this technique. As mentioned above, the vibrational spectra of gases in bubbles could not be used because of various spectral problems. However, it appears that rotational Raman spectra of gases in bubbles are in a convenient region so that Raman bands of the glass matrix do not overlap them. Since rotational bands of gases are distinct and easily identifiable for gases, and their intensities are relatable to their gas concentrations, the Raman microprobe technique seems to be a useful method for analyzing gas compositions of individual bubbles in glasses.

B.) Spectra of Gases in Bubbles

Figures 1 - 3 illustrate the rotational spectra for bubbles in silicate glasses containing pure oxygen, carbon dioxide and hyrogen bubbles, respectively,

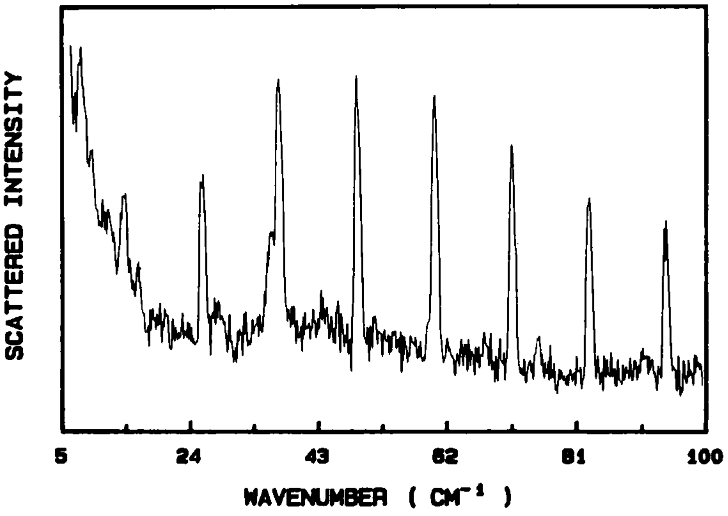

Fig. 1 . Raman microprobe spectrum of a bubble in a silicate glass containing oxygen.

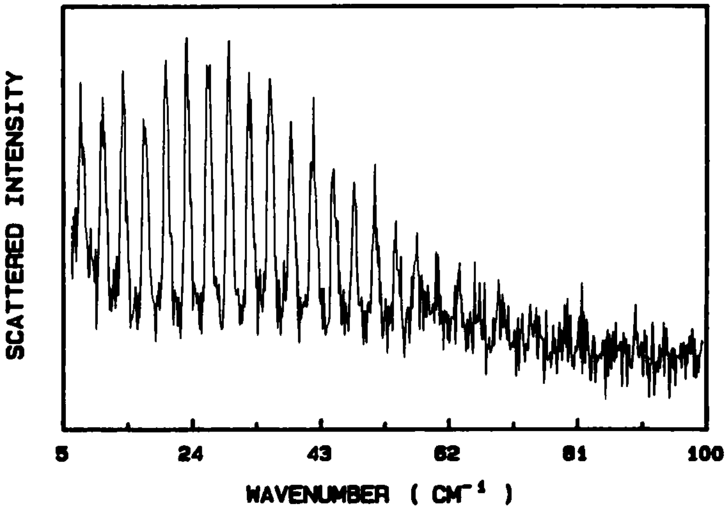

Fig. 2 . Raman microprobe spectrum of a bubble in a silicate glass containing carbon dioxide.

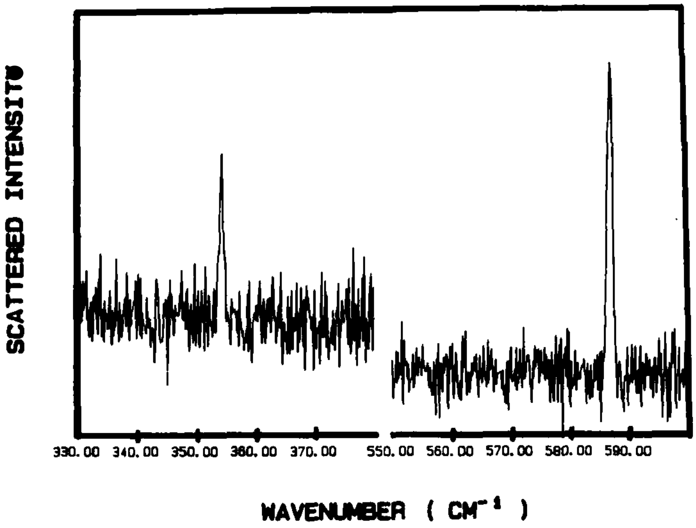

Fig. 3 . Raman microprobe spectrum of a bubble in a silicate glass containing hydrogen.

that were measured by the Raman microprobe technique. All Raman spectra were measured in the 5 - 100 cm^{-1} region except for the bubble containing hydrogen. Because the mass of the hydrogen molecule is smaller than those of the other gas molecules, its rotational bands occur in a higher wavenumber region. One may note that in the case of bubbles containing pure oxygen and carbon dioxide, little spectral overlap occurs from the bands of the surrounding glass matrix. One may note that the investigated rotational Raman bands for hydrogen can also be readily identified in Fig. 3 even though Raman bands occur in their region from the glass matrix. These observations clearly indicate that the Raman microprobe technique can be applied to identify gas components in bubbles in glass, and to determine their relative gas compositions. It is believed that the intensities of the bands generated in the scattering spectra from the surrounding glass matrix are usefully lower than the intensities of the rotational bands of the gases in the bubbles under the conditions of measurement in this study.

C.) Size Limitation for Bubbles

The detection limits that are measured for gases in bubbles by Raman spectroscopy can be defined in several different ways. Often, the detection limits for many applied characterization techniques in bubbles analysis are defined simply on the basis of the size of the analyzed bubbles. However, this definition is not completely appropriate for the Raman microprobe technique. There are other parameter aspects that have to be considered for the detection limit along with the size of the bubble. One important consideration is the diameter size of the applied laser beam. This aspect is important because the measured Raman scattering spectra is mainly generated in the region of the focused laser beam. If the bubble size is much smaller than the laser beam size, it would be impossible to measure only the Raman spectra from the gases in the bubble. The Raman spectra of the glass matrix would superimpose on the rotational Raman spectra of the gases. How intensely the glass matrix background spectra screens the Raman spectra of the gases depends upon the ratio of the laser beam diameter to the bubble diameter. Obviously, background spectra from the glass matrix can be decreased by lowering the laser beam diameter. In this case of measurements involving a 90°-scattering geometry, this background spectra can be minimized by placing a "pin hole" slit on the entrance slit of the spectrometer whose diameter is the same as or smaller than the diameter of the focussed bubble image on the spectrometer. This procedure was used by Janssen et al. [3] who were able to measure a Raman spectrum for an individual bubble whose diameter was 35 μm. However, the use of "pin hole" slits can be very tedious in terms of alignment of the bubble/glass specimen for Raman spectral measurement, and may not be suitable for routine bubble analysis. For routine measurement of Raman spectra of small bubbles, the Raman microprobe technique can be applied, using reduced focussed laser beam diameters (3-5 μm). Using this technique, the Raman spectra can be measured routinely with good background spectra to gas spectra ratios.

Figures 4 - 7 illustrate the rotational Raman spectra for bubbles with different bubble diameters containing either oxygen or carbon dioxide. Raman microprobe spectra for bubbles whose diameters are larger than 24 μm containing either oxygen or carbon dioxide show very good signal-to-noise ratios (see Figs. 4 - 6). When the bubble diameter is smaller than 15 μm, the signal-to-noise ratio seems to decrease (see Fig. 7). However, even though the signal-to-noise ratio is lower for this bubble diameter than for other diameters, the observed rotational spectrum can be clearly identified as the rotational spectrum for carbon dioxide.

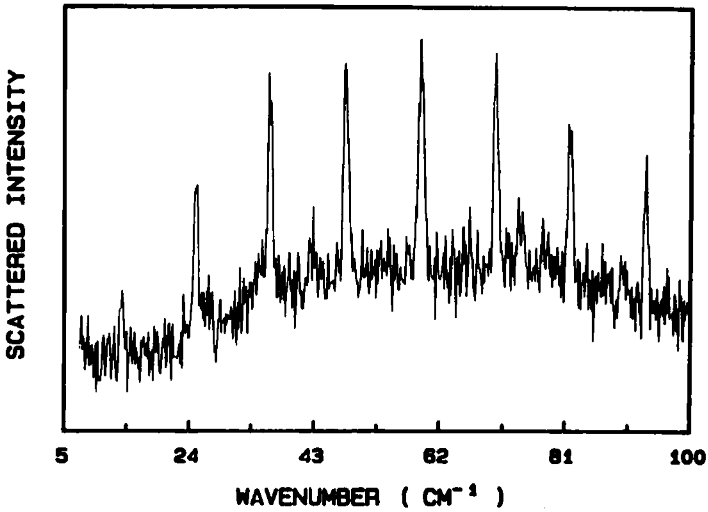

Fig. 4 . Raman microprobe spectrum of a bubble in a silicate glass containing oxygen (140 μm diameter).

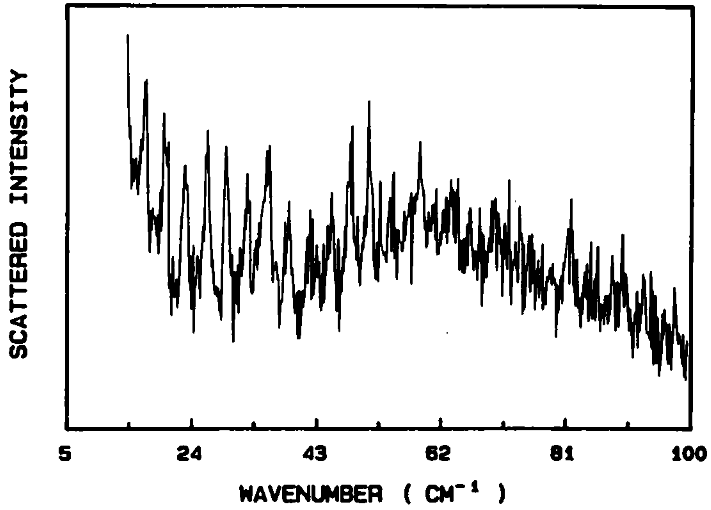

Fig. 5 . Raman microprobe spectrum of a bubble in a silicate glass containing carbon dioxide (30 μm diameter).

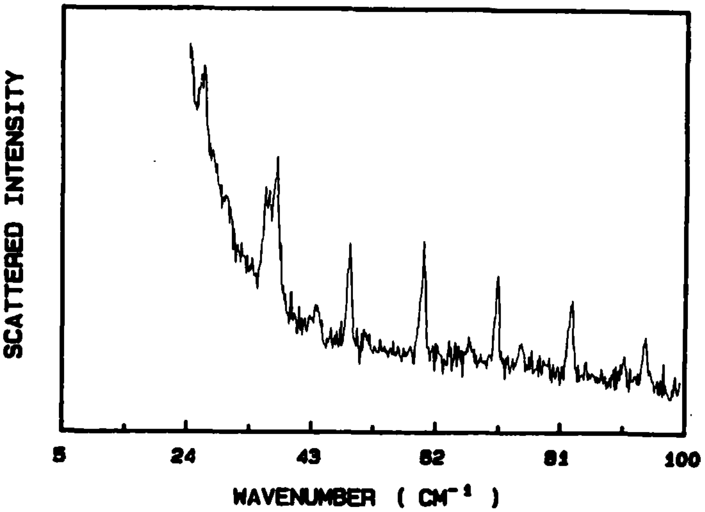

Fig. 6 . Raman microprobe spectrum of a bubble in a silicate glass containing oxygen (24 μm diameter).

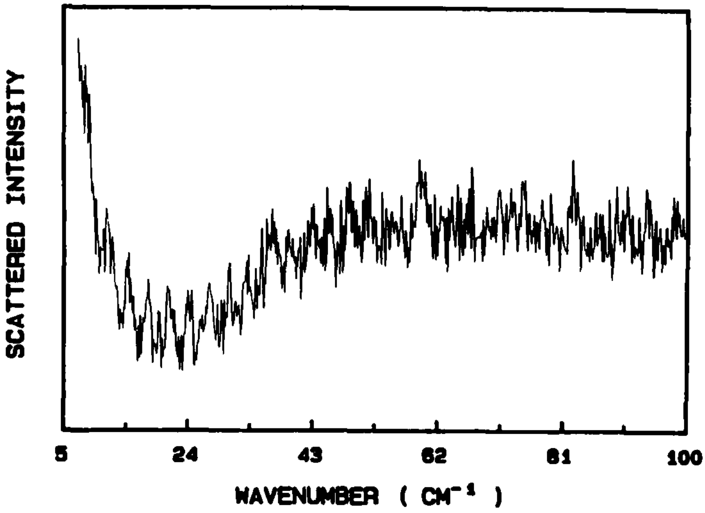

Fig. 7 . Raman microprobe spectrum of a bubble in a silicate glass containing carbon dioxide (15 μm diameter).

Another important consideration in terms of application of this technique to quantitative analysis of bubble gas contents is the difference in level of detectability for the rotational Raman bands of different gases. The absolute intensities for rotational bands depend upon the changes that occur in the polarizability of the gas molecule during the rotational transition. These changes strongly relate to the structure of the gas molecules that are involved. Different gases can have dramatic differences in the relative intensities of their compared bands because of differences in their structural arrangement. For example, theoretically-calculated values for the differential cross sections of pure rotational Raman backscattering of N_2, O_2 and CO_2 excited at the wavelength of 337.1 nm are 1.14×10^{-27}, 1.96×10^{-27} and 8.3×10^{-27} cm^2/sr, respectively[4]. From these cross section values, one can expect that if the bubble is the mixture of gases mentioned above with same volume %, the intensity of carbon dioxide rotational band will be higher than that of other gases. Therefore, the detectablity of carbon dioxide is the highest for the above-mentioned gases, while that of nitrogen is the lowest. Finally, another important consideration in terms of detection limits for the microprobe technique is the intensity of the excitation source. The intensity of the excited Raman bands depends the power of the laser line that is applied . Therefore, gas components which possess weak Raman bands can be analyzed using a laser line with adequate power.

As mentioned earlier, the diameter of the smallest investigated bubble in our study was ca. 15 μm. Its Raman-scattered rotational spectrum clearly identified the bubble gas as carbon dioxide (see Fig. 7). For oxygen, the smallest investigated bubble diameter was 24 μm (see Fig. 6).

D.) Cleaning Aspects concerning Bubble Formation

Even though the cleaning procedure might not be critical for the preparation of bubble/glass specimens containing large bubbles, it is very important for preparation of specimens containing small bubbles. The main reason for this difference is the carbon-containing contamination which is present on the surface of glasses that is either present initially before specimen preparation or introduced by drilling or scratching the surface. The amount of carbon dioxide that will be added to the bubble gas composition critically depends upon the surface area/volume ratio for the bubble. Bubbles possessing smaller bubble diameters will have more contaminant-generated carbon dioxide added to its bubble gas composition. Therefore, the applied method for cleaning such contaminants from the surfaces of the glasses is critical. Fig. 8a shows an optical micrograph for a bubble with a diameter of 300 μm prepared in an oxygen atmosphere without any cleaning treatment. The small bubbles around the large bubble appear to be generated by the contamination on the surface before bubble formation. Fig. 9a illustrates the Raman spectrum of one of those small bubbles indicating mainly the rotational Raman bands of carbon dioxide. There is no indication of oxygen bands in this spectrum. However, after using the earlier-described cleaning procedure, such contamination appears to be eliminated. Fig. 8b shows an optical micrograph for a bubble

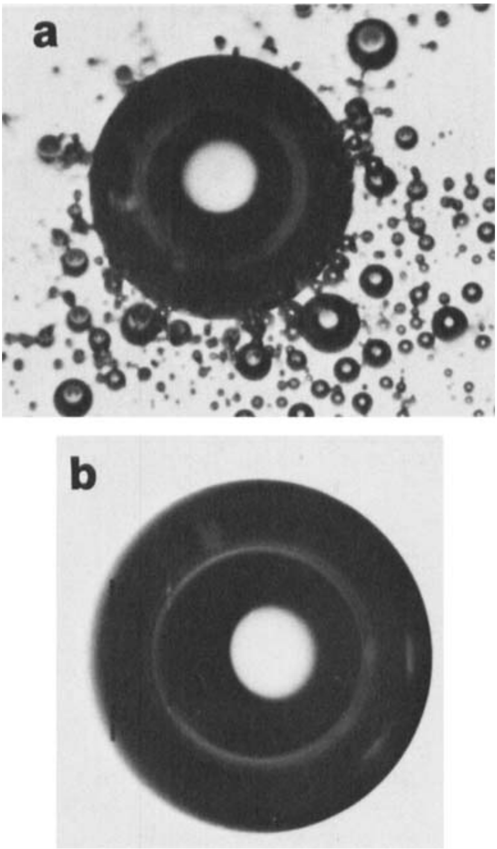

Fig. 8 . Optical micrograph of bubbles prepared a) without cleaning procedure; b) with cleaning procedure.

with a diameter of 400 μm prepared in an oxygen atmosphere after using the cleaning procedure. As may be noted, small bubbles are not noted around the large bubble, and only this bubble is present in the glass/bubble specimen. Its Raman microprobe spectra shows the rotational Raman bands for oxygen, and there is no indication of carbon dioxide in this spectra (see Fig. 9b).

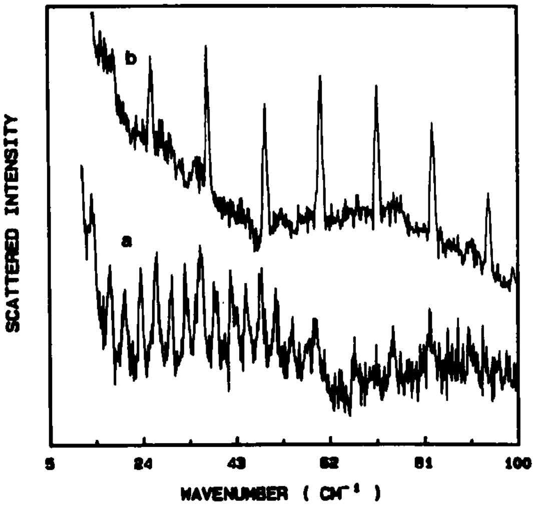

Fig. 9 . Raman spectra of bubbles prepared a) without cleaning procedure; b) with cleaning procedure.

Therefore, the cleaning procedure is important for producing the desired bubbles in bubble/glass specimens possessing bubbles with a resonably controlled atmospheres.

E.) Quantitative Analysis of Gas Compositions in Bubbles

It is difficult to determine the absolute amounts of different gas components in bubbles because the intensities of rotational Raman bands do not depend simply on the size of the bubbles and/or the concentration of the gas components. However, it is possible to characterize the gas content of bubbles in terms of the relative concentrations of the various gas components. For such analyses it is necessary to generate sets of standard Raman spectra for various gas mixtures containing different concentration of gas components that can be intercompared with respect to each other. Because each gas component possesses different Raman scattering coefficients for their comparable Raman bands, it is necessary to analyze the concentrations of the gas components in the Raman-investigated bubbles by mass spectroscopy in order to compare the resulting mass spectral data with the interpretation of Raman spectral data.

Six bubble/glass specimens were prepared under different mixture of oxygen and carbon dioxide atmosphere and these bubbles were analyzed by Raman microprobe technique. After the Raman microprobe measurement, the volume percentages of oxygen and carbon dioxide were determined for the investigated specimen by mass spectrometer. Then, the ratio of volume percent of oxygen to the volume percent of carbon dioxde was plotted against the ratio of intensity of the Raman band for oxygen at ca. 95 cm^{-1} to the intensity of the Raman band for carbon dioxide (at ca. 56 cm^{-1}). As may be noted in Fig. 10, a plot of the mass and Raman spectral data shows a linear relationship. In other words, the relative content of oxygen and carbon dioxide in a bubble can be determined by measuring its Raman microprobe spectra, as long as one compares this spectral data to the measured spectral data for calibrated bubble standards. The possibility of measuring the relative gas compositions by this technique is useful for investigating changes in the gas composition of bubbles before and after heat treatment, because their analyzed specimens can be used again for further treatment. In contrast, the bubbles that are analyzed once by mass spectroscopy can not be used again for further heat

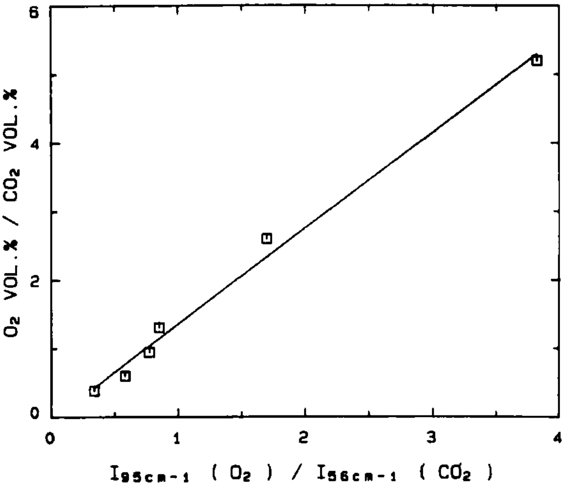

Fig. 10 . The relationship between the Raman intensity ratio (O_2/CO_2) and the ratio of volume percent of oxygen and carbon dioxide for bubbles silicate glasses.

treatment, because this type of analysis involves the destruction of the bubble/glass specimens.

IV. CONCLUSIONS

Raman microprobe analysis is a useful technique for the analyses of gas contents in bubbles in glasses. Spectral overlap from the Raman spectra of the glass matrix during the Raman microprobe measurement of bubbles seems to be minimal so that the rotational Raman spectra of gases in bubbles can be essentially measured alone. The Raman microprobe technique is more useful than Macro-Raman spectroscopy because it is much easier to align the sample during it application for spectral measurement, and its bubble diameter limitation is much lower. With higher magnification of objective in the microscope component and higher laser power, we believe that smaller bubbles (with diameters less than 15 μm) can be analyzed. The applied cleaning procedure seems to be critical for the preparation of standard bubble/glass specimens with bubbles possessing the appropriate diameter and containing the desired gas content for specific research such as studying the changes in the gas contents of bubbles after heat treatment. The relationship between Raman microprobe and mass spectral data for bubbles possessing controlled amounts of carbon dioxide and oxygen indicates that quantitative determinations of the relative gas contents in bubbles can be conducted, providing that appropriate bubble/glass standards are used.

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