JOURNAL OF SOLID STATE CHEMISTRY **123,** 183–185 (1996)
ARTICLE NO. 0166

BRIEF COMMUNICATION

Raman Spectral Investigation of Sulfate Inclusions in Sodium Calcium Silicate Glasses

R. P. Hapanowicz and R. A. Condrate, Sr.

Industry/University Center for Glass Research, NYS College of Ceramics at Alfred University, Alfred, New York 14802

Received September 29, 1995; in revised form November 7, 1995; accepted December 19, 1995

Raman microprobe spectra were measured to identify the crystalline nature of solid inclusions found on the surfaces of bubbles in glasses formed during the sulfur oxide treatment of sodium calcium silicate glass melts. Analysis of the spectra clearly indicates that the major component in the solid inclusions was the sodium sulfate (form III) phase. © 1996 Academic Press, Inc.

INTRODUCTION

Sulfate crystals can appear either in the so-called bloom on the surface of sodium clacium silicate glasses during SO_2/O_2 surface treatment to improve their surface strength properties or in crystal inclusions on the surfaces of bubbles in soda lime silicate glasses when one fines such glasses using a sulfate as one of the starting materials (1–4). Although sulfate phases have been identified in such inclusions, their exact crystalline phase nature has not been determined (1, 2). These inclusions can be formed possibly from various crystalline sulfate phases containing sodium or calcium. There are a significant number of crystalline structural possibilities for such sulfates. In this study, the exact crystalline phase nature of such inclusions will be identified by using Raman microprobe spectroscopy. This information will lead to a better understanding of the chemistry that is associated with the fining or surface treatment processes for soda lime silicate glasses in order to minimize the presence of such solid inclusions.

EXPERIMENTAL PROCEDURES

Glass samples of a soda lime silicate ($74SiO_2$–$16Na_2O$–$10CaO$ wt%) composition containing no additions, a 1 wt% addition of sodium sulfate, and a 1 wt% addition of sodium chloride were prepared by melting the raw materials also containing sodium carbonate, calcium carbonate, and silica in platinum crucibles at 1673 K. They were completely fined, removed from the furnace and cast into slabs. The above-mentioned glass samples containing no observable solid inclusions were used to illustrate representative glasses containing sulfate ions in their glass networks. A second set of glass specimens which also possessed a soda lime silicate composition ($70SiO_2$–$20Na_2O$–$10CaO$) were prepared by melting. These glass specimens were used to prepare glass samples containing bubbles with solid inclusions inside them. A pair of bulk silicate glass pieces were cut with areas of 1 cm × 1 cm. A depression was drilled with a diamond point on the surface of one of the glass pieces, forming the source of the bubble. The glass pieces were cleaned of contaminants on their surfaces, using a procedure that was described earlier (5), and were then placed into a tube furnace. The surface of the glass piece with no depression has been placed against the surface of the glass piece with the depression. This sandwiched pair was then kept in the tube furnace under the applied flowing oxygen/sulfur oxide gas mixture for 1 h at 100°C, and then heated to 900°C in order to form the desired bubble with the inclusion. After cooling the bubble/glass specimen, its outer surfaces were polished for the spectral investigation.

A Jobin-Yvon U1000 double monochrometer with an attached Olympus microscope was used to measure the Raman spectra. The green laser line (514.5 nm) of an argon-ion laser was used as the excitation source to measure the vibrational spectra of the crystalline material. The laser power at the entrance of the microscope was on the order of <250 mW for the measurements. A photomultiplier tube was used as the detector. The bubble inclusion was investigated in the backscattering mode through the polished glass surface of the bubble/glass specimen. The instrument was calibrated using a silicon metal standard sample.

RESULTS AND DISCUSSION

Sulfur oxide species can be found in the silicate glass network even though solid inclusions containing sulfur may

0022-4596/96 $18.00

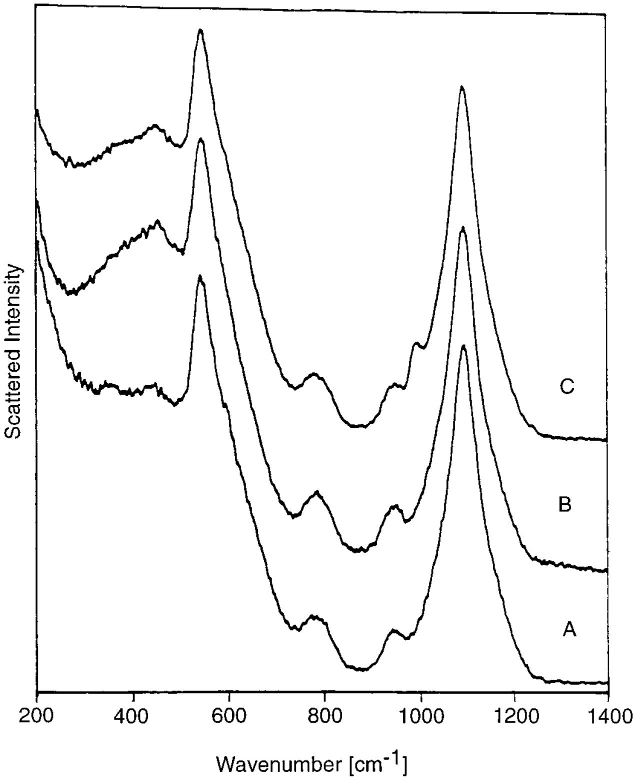

FIG. 1. Raman spectra of soda lime silicate glasses (10-16-74): (A) base glass, (B) base glass with 1 wt% NaCl, and (C) base glass with 1 wt% Na_2SO_4.

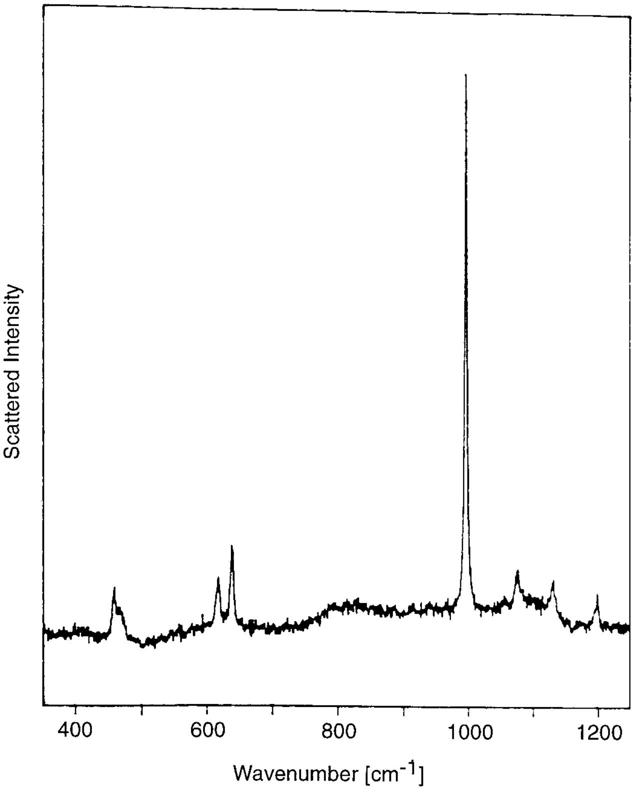

FIG. 2. Raman microprobe spectra of solid phase formed at synthetic bubble interface.

not be found in the glass material. Details in the Raman spectra of soda lime silicate glasses that were prepared with small amounts of sodium sulfate as a raw material can indicate the structural nature of the sulfur oxide species in the glass network. Such sulfate species can be detected in the glass even if no sulfate inclusions are present as long as the glass composition is appropriate. Figure 1 illustrates the bulk Raman spectra obtained for soda lime silicate glasses that were prepared with sodium sulfate or sodium chloride. The Raman spectrum for the sample that was prepared with 1 wt% sodium sulfate clearly indicates the presence of a vibrational band at ca. 990 cm^{-1} which can be associated with the presence of sulfate ions. This Raman band relates to the most intense Raman band noted for the SO_4^{2-} ion in aqueous solution that occurs at 983 cm^{-1}, and is associated with the symmetric S–O stretching mode of the SO_4^{2-} ion (6). Optical microscopic investigation of the glasses prepared with sodium sulfate and analysis of their X-ray diffraction patterns clearly indicate that crystalline inclusions are not present in the glasses, and therefore, the sulfate ions must be present as structural species in the network of these glasses.

More spectral detail can be seen with respect to the vibrational bands of a sulfate inclusion in silicate glass that are observed in the Raman microprobe spectrum when focusing the laser beam on the inclusion. Figure 2 illustrates the Raman microprobe spectrum of an inclusion on a syn-

TABLE 1
Band Locations (cm^{-1}) for Sulfate Phases

Compound	ν_1	ν_2	ν_3	ν_4
Na_2SO_4 (thenardite)	990	448	1099	618
(form V)		463	1129	629
			1149	644
Na_2SO_4 (form III)	992	445	1072	612
		463	1127	633
			1195	
Na_2SO_4 (form I)	989	455	1100	623
Gypsum	1016	417	1111	608
		427	1129	628
		495	1156	669
				675
Anhydrite	1013	414	1106	605
		495	1124	624
			1155	671
Bubble interface	992	445	1072	612
phase		463	1127	633
			1195	

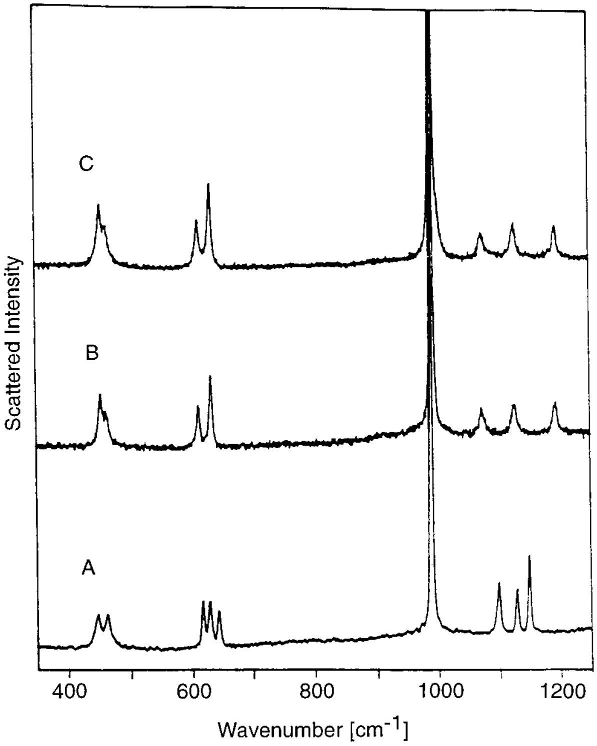

FIG. 3. Raman microprobe spectra of related crystalline sodium sulfate phases: (A) form V, (B) form III, and (C) form III containing 1 wt% calcium sulfate.

thetic bubble interface that was formed in a sulfur dioxide and oxygen furnace atmosphere. The phase nature of the crystalline sulfate inclusion found on the bubble in the soda lime silicate glass can be clearly identified by comparing its Raman spectrum with those of related sodium and calcium sulfate phases that were investigated in earlier studies (7, 8). Table 1 lists the band locations for their major Raman bands and shoulders along with those for the sulfate inclusion. ν_1, ν_3, ν_3, and ν_4 represent the vibrational frequencies associated with the symmetric S–O stretching vibration, the doubly degenerate bending vibration, the triply degenerate S–O stretching vibration, and the triply degenerate bending vibration, respectively, of the SO_4^{2-} ion. Fine-structure differences are noted for the various vibrational modes of the sulfate phases which are due to factor group splitting effects that are generated from symmetry differences in the united cells of the compared crystalline phases. Figure 3 illustrates the Raman spectra of the two most pertinent sulfate phases (forms III and V of sodium sulfate) which show Raman bands in closely similar locations of the spectra to those of the inclusion phase. Conclusively, the comparison of the Raman spectral details indicates that the major sulfate phase on the bubble surface is an orthorhombic phase (from III) of sodium sulfate. The Raman band locations and intensities of the inclusion phase most closely pattern those of the form III phase. Treating form V (thenardite) of sodium sulfate through a heating and cooling cycle in a dry atmosphere converts it to form III. This sulfate phase was also observed in solid inclusions formed on surfaces of bubbles in soda lime silicate glasses that were prepared with sodium sulfate as a starting material.

There might be some question whether impurity doping of form III can be a dominant factor in terms of altering the Raman spectrum of form III. Comparing the Raman spectrum of pure form III with that of form III containing 1 wt% calcium sulfate clearly indicates that impurity doping causes only slight effects upon the Raman spectral features.

REFERENCES

1. N. A. Sharaf, S. M. Brzytwa, R. A. Condrate, Sr., R. P. Hapanowicz, W. C. LaCourse, and P. Shen, *in* "The Physics of Non-Crystalline Solids" (L. D. Pye, W. C. LaCourse, and H. J. Stevens, Eds.), p. 236. Taylor and Francis, London, 1992.
2. S. W. Lee, K. S. Hong, R. A. Condrate, Sr., R. P. Hapanowicz, and R. F. Speyer, *J. Mater. Sci.* **27,** 4961 (1992).
3. H. R. Golob and E. L. Swarts, *J. Am. Ceram. Soc.* **67,** 564 (1984).
4. T. D. Taylor and K. C. Rowan, *J. Am. Ceram. Soc.* **66,** C227 (1983).
5. S. W. Lee, R. A. Condrate, Sr., N. Malani, D. Tammaro, and F. E. Woolley, *Spectrosc. Lett.* **23,** 945 (1990).
6. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" 4th ed. Wiley–Interscience, New York (1986).
7. R. P. Hapanowicz and R. A. Condrate, Sr., *Spectrosc. Lett.* **29,** 133 (1996).
8. R. P. Hapanowicz, Ph.D. Thesis, Alfred University, 1995.