JOURNAL OF SOLID STATE CHEMISTRY 98, 423–425 (1992)

BRIEF COMMUNICATIONS

Raman Microprobe Investigation of Bubbles Formed in $NaPO_3$ Glass from Nitriding with Ammonia*

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Received September 26, 1991; in revised form November 22, 1991

Raman microprobe analysis was used to investigate the gas content of bubbles formed in $NaPO_3$ glass during nitridation of its melt. The analysis of the spectral data clearly indicated the presence of mainly N_2 and H_2. There was no indication of large concentrations of other gases in the investigated bubbles.

Introduction

Phosphate glasses possess useful optical and thermal expansion properties. However, they lack adequate chemical durability for some applications. Recent study has shown that incorporating nitrogen into the phosphate glass network can improve its chemical durability (*1*). Such nitrogen can be incorporated by the reaction of the phosphate glass melt with ammonia. During the preparation of such phosphorus oxynitride glasses, gas bubbles can be formed in the glass. The presence of such bubble inclusions in glass can alter its aesthetic value or its physical properties. In this investigation, we applied Raman microprobe analysis to investigate the gas contents of bubbles formed in a $NaPO_3$ glass due to its nitridation with ammonia.

* Based on a thesis submitted by S.W.L. for the Ph.D. degree in ceramics.

Experimental

Purified sodium metaphosphate was used as the starting material to form the glass. Phosphate powder (ca. 10 g) was placed directly into a graphite crucible which was stepwise inserted into a specially designed furnace. This furnace was mounted on a metal stand allowing its use as a horizontal or verticle tube furnace or at any angle in between. For these nitridation studies, an angle of ca. 18° was used. The tube was flushed with nitrogen during the insertion and removal of the sample. After the tube was sealed and the furnace was in equilibrium at the set-point temperature, an ammonia stream was introduced for a specified amount of time. The crucible was rotated at 2 rpm during the heat treatment procedure. Annealing of the sample was done by removing the sample at a rate of 1 inch per 2 min from the tube. Treatment temperature reduced to ca. 60°C in 38 min.

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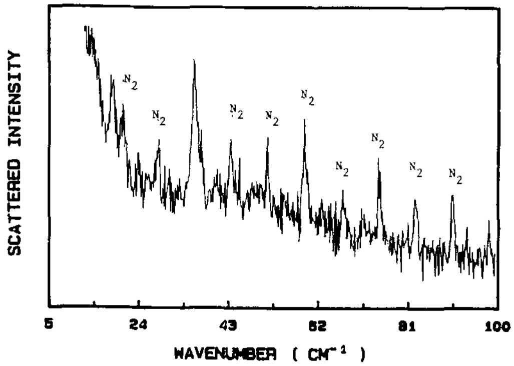

FIG. 1. Rotational Raman spectra of a bubble in $NaPO_3$ glass in the 5–100 cm^{-1} region indicating N_2.

An Instruments SA U1000 double grating spectrometer was used to measure the Raman spectra. All spectra were measured using Raman microprobe optics with a backscattering geometry. The rotational Raman spectra were measured for the gases in the bubbles in either the 5–100 cm^{-1} or the 550–650 cm^{-1} range, depending upon the nature of the investigated gas components. The magnification of the objective lens in the microscope was 100×. The bubble was focused within the working distance of this lens. The laser beam size with this objective was 3–5 μm in diameter. The diameters of the investigated bubbles in this study were at the least an order of magnitude larger than that of the laser beam. The excitation source for the Raman spectra was an Innova 90 argon-ion laser. The green line (514.5 nm) was used for Raman spectral excitation with a power of ca. 1 W.

Results and Discussion

Raman microprobe data readily determine the gas contents of a bubble that was formed in a $NaPO_3$ glass during the nitridation of the melt with ammonia. Figures 1 and 2 illustrate the rotational Raman microprobe spectra that were measured in two different regions for a bubble that was formed during such treatment in an ammonia atmosphere. The illustrated spectral results are for a glass melt that was treated for 50 hr at 700°C. Interpretation of the rotational Raman bands clearly identifies N_2 and H_2 as the major gas components in the investigated bubbles. The observed band locations for the rotational Raman bands are consistent with earlier observed band locations in the literature (*2–4*). There is no indication of NH_3, H_2O, P_4, or PH_3 from the spectral data. Day and co-workers predicted (as would be expected) the formation of water due to reaction between NH_3 and the glass material (*5–7*). Possibly, the water resulting from this reaction has diffused into the glass so that it is not present in the bubble in sufficient quantity to be detected by our Raman microprobe technique. Using a mass spectroscopic technique which destroys the glass sample in order to obtain gas compositional data for a bubble, Heuberger and Pye have studied bubbles that were formed during nitridation of phosphate glass under similar conditions in an ammonia atmosphere (*8*). There was also no indication of water or ammonia in their bubbles. Similar to our Raman microprobe results, their major gas components were nitrogen and hydrogen. Peng and Day observed that negligible nitrogen dissolution occurred in such phosphate

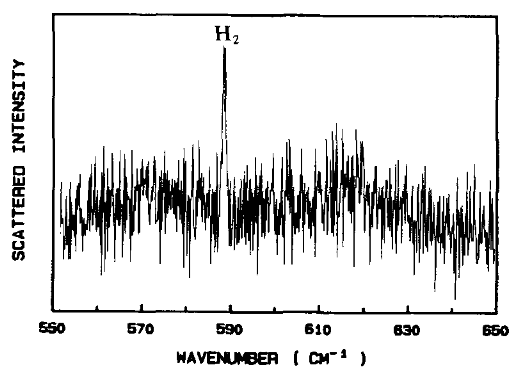

FIG. 2. Rotational Raman spectra of a bubble in $NaPO_3$ glass in the 550–650 cm^{-1} region indicating H_2.

glasses when they were melted at 710°C under a stagnant rather than a flowing ammonia atmosphere (*7*). They suggested that the slow dissolution was due to the decomposition of NH_3 to N_2 and H_2. If the bubbles that were formed in our investigated phosphate glasses in an ammonia atmosphere initially contained NH_3, their final resulting gas compositions might be explained using the same chemical reasoning that was developed for explaining the low nitrogen dissolution for phosphate glasses which were melted under a stagnant ammonia atmosphere. In the former case, NH_3 in the bubbles would be expected to decompose to H_2 and N_2 because of the longer periods of heat treatment.

Finally, rotational Raman microprobe spectra could not be obtained in this study for gases in bubbles in glasses treated in ammonia atmospheres at much higher temperatures with higher ammonia flow rates. In these cases, dark brown coloration occurred in the glasses, thereby screening the expected Raman spectra scattered from bubbles within these glasses.

Acknowledgment

We acknowledge the generous support from the University/Industrial Center for Glass Research in the New York State College of Ceramics at Alfred University to conduct this Raman Microprobe investigation.

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