Behavior of Hydroxyl Groups in Quartz Glass during Heat Treatment in the Range 750–950°C

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Received February 20, 2018

Abstract—The concentration of hydroxyl groups in different types of quartz glass tubes, the OH concentration profile across the tube wall, and the kinetics of OH removal during heat treatment in the temperature range 750–950°C have been studied by Fourier transform IR spectroscopy. For TK-I tubes, produced by vacuum electromelting of quartz, followed by annealing in a hydrogen atmosphere, we have calculated the diffusion coefficient of OH groups in this temperature range and the activation energy for diffusion: 215 ± 10 kJ/mol. We have found heat treatment conditions that ensure a considerable decrease in the concentration of OH groups in quartz tubes that are used in the fabrication of reactors for the preparation of extrapure chalcogenide glasses.

Keywords: quartz glass, OH groups, diffusion, IR spectroscopy

DOI: 10.1134/S0020168518090169

INTRODUCTION

Quartz glass is the main material of reactors for the high-temperature synthesis of a large number of extrapure glassy and crystalline substances. Such substances include chalcogenide glasses. Their high optical transmission in the mid-IR spectral region is sensitive to hydrogen and oxygen impurities [1]. Previous work on the preparation of chalcogenide glasses revealed a contaminating effect of the apparatus material, which leads to an increase in the concentration of hydrogen and silicon impurities [2, 3]. Hydrogen passes from quartz glass to the chalcogenide melt during homogenizing melting (750–950°C). This gives rise to impurity bands in absorption spectra of chalcogenide glasses near 4.01, 3.65, 3.11, and 2.0 μm, due to SH groups; near 4.57, 4.12, 3.53, and 2.32 μm, due to SeH groups; and at 4.95 μm, due to Ge–H groups [3]. The presence of hydrogen-containing impurities in chalcogenide glasses markedly degrades their optical properties. Because of this, the ability to determine the hydrogen concentration in quartz glass and the rate of hydrogen release during heat treatment is a topical issue.

Hydrogen is present in glass predominantly as Si–OH groups (OH groups), SiH groups, molecular hydrogen, and water [4–7]. The content of OH groups in commercially available quartz tubes ranges from <0.1 to 1300 ppm by weight. The concentration of hydrogen in the form of OH groups is typically determined using IR spectroscopy: from the intensity of the absorption band around 3675 cm\textsuperscript{-1}. There is conclusive experimental evidence that the diffusion coefficient of hydrogen and the activation energy for hydrogen diffusion in quartz glass depend significantly on the chemical form of the hydrogen and the procedure used to prepare the material. Plotnichenko et al. [7] and Lee et al. [8] reported equations for the temperature-dependent diffusion coefficients of OH groups and molecular hydrogen in quartz glass:

\begin{align*}
D_{\text{OH}} (\text{cm}^2/\text{s}) & = 1 \times 10^{-6} \exp \left( \frac{-76.57 \text{ kJ/mol}}{RT} \right), \quad (1) \\
D_{\text{H}_2} (\text{cm}^2/\text{s}) & = 5.65 \times 10^{-4} \exp \left( \frac{-43.35 \text{ kJ/mol}}{RT} \right), \quad (2)
\end{align*}

where $R$ (J/(mol K)) is the gas constant and $T$ (K) is the absolute temperature. At 950°C, $D_{\text{OH}} = 5.4 \times 10^{-10}$ cm\textsuperscript{2}/s and $D_{\text{H}_2} = 1.4 \times 10^{-5}$ cm\textsuperscript{2}/s. The exact mechanism of hydrogen diffusion in quartz glass is still open to question. As shown by Yongheng and Zhenan [9], glass prepared by melting quartz powder in a hydrogen atmosphere contains a considerable amount of OH groups. Heating such glass in the temperature range 700–900°C leads to molecular hydrogen release. This was accounted for in terms of the following chemical
reaction, which was investigated in detail by van der Steen [4]:
\[ \equiv \text{Si} - \text{OH}^+ \equiv \text{Si} - \text{H} \leftrightarrow \equiv \text{Si} - \text{O} - \text{Si} \equiv + \text{H}_2. \] (I*)

According to this model, the mechanism of hydrogen release from quartz glass involves the O–H and Si–H bond breaking step, the formation of molecular hydrogen, and its subsequent diffusion. According to another mechanism, hydrogen diffuses in the bulk of quartz glass through proton hopping from one oxygen atom to another in the direction of decreasing hydroxyl concentration [7].

The objectives of this work were to study hydroxyl release kinetics during high-temperature annealing of quartz glass tubes and find heat treatment conditions capable of effectively reducing the concentration of hydrogen impurities in such tubes.

EXPERIMENTAL

We studied three types of commercially available quartz tubes, produced by different methods. TKG tubes are produced by melting quartz granules in an oxygen–hydrogen flame. TKEI-2 tubes are made by vacuum electromelting of quartz grit. High-temperature annealing of such tubes in a hydrogen atmosphere yields TK-I tubes. These types of tubes are used as materials of reactors for the preparation of extrapure substances and reagents [10]. The tubes were studied in the temperature range 750–950°C, corresponding to preparation conditions of extrapure chalcogenide glasses in different systems [1].

OH removal kinetics. To study OH removal kinetics, we used TK-I quartz glass tubes 28 mm in length, 3.5 mm in inner radius, and 5.1 mm in outer radius (wall thickness of 1.6 mm). The tubes were placed in an open horizontal furnace, heated to 750–950°C, and withdrawn at regular intervals for characterization by IR spectroscopy. In a number of experiments, samples were placed in quartz ampules, which were connected to a vacuum system, and the tubes were annealed under a dynamic vacuum of 0.3 Pa. The absorption spectra of the tubes were measured on a Tensor 27 Fourier transform IR spectrometer in the range 500–5000 cm–1 at a spectral resolution of 4 cm–1. In our measurements, the incident beam was normal to the horizontal axis of the tube. The concentration of OH groups was evaluated from the intensity of the OH absorption band of quartz glass [6], which impedes hydrogen concentration determination. In connection with this, in our kinetic studies we used the absorption

micrometer stage, and their absorption spectra were measured with a 20-μm step. In addition, we determined the initial content of OH groups and OH concentration profile in TKG and TKEI-2 quartz tubes.

EXPERIMENTAL RESULTS

Figure 1 shows absorption spectra of the quartz glass tubes before and after annealing in an open furnace at 950°C for 2 h. The highest initial content of OH groups (220 ± 10 ppm by weight) is observed in the TKG tubes, produced by melting quartz grit in a gas flame (Fig. 1a, spectrum 1). Annealing these tubes at 950°C causes a noticeable decrease in hydroxyl concentration (Fig. 1b, spectrum 1). Since OH groups were removed from these tubes at a very slow rate, we did not study their diffusion kinetics in this work. The TKEI-2 tubes have a low initial concentration of OH groups: at the level of the detection limit of the analytical technique used (≈0.5 ppm by weight). Annealing these tubes in air at 950°C for 2 h raises the concentration of hydroxyl groups to ≈2 ppm by weight, which is due to chemical interaction between the quartz glass and atmospheric water vapor. Contamination of quartz glass with OH groups during high-temperature annealing of quartz tubes in air was previously reported by van der Steen [4] and Plotnichenko et al. [7]. Because of the low initial concentration of OH groups, neither OH removal kinetics nor the OH concentration distribution across the wall was studied in the case of the TKEI-2 tubes. The concentration of OH groups in the TK-I tubes was 100 ± 5 ppm by weight. Annealing these tubes at 950°C for 2 h leads to a considerable decrease in the concentration of OH groups: to a level of ≈3 ppm by weight (Figs. 1a, 1b, spectra 2).

Figure 2 shows the OH concentration profiles across the wall of the TKG and TK-I quartz glass tubes. A distinctive feature of the OH concentration distribution in the TKG tubes (Fig. 2a, curve 4) is that the OH concentration increases markedly as the outer surface of the tube is approached. The OH profiles of the TK-I tubes annealed in air and vacuum differ in OH distribution near the wall. In the samples annealed in air, the concentration of OH groups rises as the tube surfaces are approached (Fig. 2b, curve 5). In the vacuum-annealed samples, the concentration of OH groups decreases in going from the center of the wall to its periphery (Fig. 2b, curve 6).

Figure 3 shows absorption spectra of the TK-I tubes in the ranges 2150–2400 and 3450–3800 cm–1 after heat treatment at 950°C. The integrated intensities of both bands decrease with increasing annealing time. The absorption band at 2255 cm–1 is a combination of an impurity band of SiH groups and an intrinsic absorption band of quartz glass [6], which impedes hydrogen concentration determination. In connection with this, in our kinetic studies we used the absorption
band of OH groups around 3675 cm⁻¹. Figure 4 shows the fraction of residual OH groups as a function of annealing time for the TK-I tubes annealed at various temperatures.

**DISCUSSION**

**Concentration of OH groups in the quartz tubes.** The present results on the initial concentration, distribution, and behavior of OH groups during annealing of different types of tubes can be interpreted in terms of the chemical form of hydrogen in the tubes, which is determined by the tube fabrication process. The high initial OH concentration in the TKG tubes is due to chemical interaction between the quartz glass and water vapor in the oxygen–hydrogen flame [4]:

\[
(≡Si−O−Si≡)_\text{glass} + H_2O_{\text{gas}} = 2(≡Si−OH)_\text{glass} \cdot (2*)
\]

The high process temperature (2100–2200°C) favors rapid penetration of OH groups into the bulk of the glass.
the quartz tube. Because of the small diffusion coefficient of hydroxy groups in the range 750–950 °C [Eq. (1)], their removal from the tubes is a slow process.

The high initial concentration of OH groups in the TK-I tubes is due to the fact that these tubes were annealed in a hydrogen atmosphere during the fabrication process in order to remove bubbles. High-temperature interaction between molecular hydrogen and quartz glass leads to the formation of Si–OH and SiH groups [inverse reaction of (1*)], which are detected by IR spectroscopy. Annealing these tubes at temperatures in the range 750–950 °C displaces equilibrium of reaction (1*) toward the formation of molecular hydrogen, whose diffusion coefficient considerably exceeds that of OH groups [Eq. (2)]. This is favorable for rather effective removal of hydroxyl groups from the TK-I tubes during annealing. The low initial concentration of OH groups in the TKEI-2 tubes is due to the fact that they were prepared by melting quartz grit in an electric vacuum furnace free of hydrogen.

**OH removal kinetics.** The diffusion coefficient of OH groups in the TK-I quartz tubes was calculated using experimental data and a mathematical model under the assumption that the diffusion rate is the same in all axial sections of the tube. The diffusion of OH groups can be described by a two-dimensional equation in cylindrical coordinates:

$$\frac{\partial c}{\partial \tau} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial y^2} \right),$$

where $c$ is the concentration of OH groups, $\tau$ (s) is time, $D$ (cm$^2$/s) is the diffusion coefficient, $r$ (cm) is a coordinate across the tube, and $y$ (cm) is a coordinate along the tube axis.

Equation (3) is subject to the following initial and boundary conditions:

$$\tau = 0: \ c = 1;$$

$$r = R_i: \ c = c_i, \quad r = R_2: \ c = c_i,$$

$$y = 0: \ c = c_i, \quad y = H: \ c = c_i,$$

where $c_i$ is the concentration of OH groups in the furnace atmosphere, $R_i$ is the inner tube radius, $R_2$ is the
outer tube radius, and \( H \) is the tube length. To find \( c_f \), we should solve the additional differential equation (6), subject to the initial condition (7), which is derived from the material balance constraint in the volume of the furnace, \( V \):

\[
\frac{dc_f}{d\tau} = \frac{2\pi R_1 H}{V} \left( \frac{dc}{dr} \bigg|_{r=R_1} + \frac{R_2}{R_1} \frac{dc}{dr} \bigg|_{r=R_2} \right) \\
+ \frac{\pi(R_2^2 - R_1^2)}{V} D \left( \frac{dc}{dy} \bigg|_{y=0} + \frac{dc}{dy} \bigg|_{y=H} \right).
\]

(6)

\( \tau = 0: c = c_g \),

(7)

where \( c_g \) is the initial concentration of OH groups in the furnace. The time-dependent average integrated concentration of OH groups over the tube thickness, \( C_{av}(\tau) \), is known from physical experiments. The corresponding calculated characteristic \( C_{av}(\tau) \) is given by

\[
C_{av} = \frac{2}{(R_2^2 - R_1^2)H} \int_0^H \int_0^r r C(r, \tau) dr dy.
\]

(8)

The diffusion coefficient was evaluated by minimizing the root mean square deviation of the theoretical concentration \( C_{av}(\tau) \) from the experimentally determined value \( C_{exp}(\tau) \).

Figure 5 presents \( \ln D \) vs. \( 1/T \) data obtained by solving the system of equations (3)–(8). Using a linear fit to these data, we calculated the activation energy for the diffusion of OH groups, which was found to be \( 215 \pm 10 \text{ kJ/mol} \):

\[
D \left( \text{cm}^2/\text{s} \right) = (2100 \pm 300) \exp \left( \frac{-215 \pm 10 \text{ kJ/mol}}{RT} \right).
\]

Figure 5. Logarithm of the diffusion coefficient of OH groups in the TK-1 tubes as a function of inverse temperature.

(9)

This value is comparable to the activation energy for reaction (1*) (266 kJ/mol), which, according to van der Steen [4], determines the mechanism underlying the removal of OH groups from quartz glass at temperatures above 500°C.

OH concentration profiles. Figure 6 shows OH concentration profiles across the TK-1 quartz tube wall at different temperatures at time \( \tau = 60 \text{ min} \). The profiles were calculated using Eqs. (3)–(8). The experimentally determined OH concentration profiles differ from those calculated theoretically (Fig. 2, curves 1–3). Annealing the TK-1 tubes at 800°C for 4 h leads to a uniform decrease in the concentration of OH groups throughout the wall thickness. The observed shape of the experimentally determined profiles is due to the fact that, at temperatures of up to 950°C, the rate-limiting step in the removal of OH groups from quartz glass is not OH diffusion but the chemical reaction (1*) [4, 8]. In this case, the concentration of OH groups can decrease at roughly the same rate throughout the tube wall thickness. Another possible cause of the observed OH distribution is various surface effects, which reduce the rate of OH removal from the tube surface in comparison with its interior [11]. At high annealing temperatures and considerable degrees of dehydroxylation, a considerable contribution to the OH concentration profile across the tube wall can be made by atmospheric moisture. The interaction of quartz glass with water vapor by reaction (2*) leads to an increase in the concentration of OH groups in the surface layer of the tube (Fig. 2b, curve 5). Deeper penetration of hydroxyl groups is hardly possible because they have a small diffusion coefficient.
One possible cause of the asymmetric shape of the OH concentration profile in the TKG tubes is that, during the tube fabrication process, OH groups arrive predominantly from the side of the oxygen–hydrogen flame.

Among the quartz tubes studied here, the TKEI-2 and TK-I tubes can be recommended as materials of reactors for the preparation of extrapure substances. To effectively remove OH groups from the TK-I tubes to a level under 0.5 ppm by weight, the tubes should be annealed at a temperature of 950°C for at least 4 h under dynamic vacuum or in a dry inert gas flow. In the case of TKEI-2 tubes with a low initial concentration of OH groups, a critical role can be played by the presence of a large number of inhomogeneities in the form of bubbles and striae of uncontrolled size and density.

CONCLUSIONS

The initial concentration of OH groups in quartz tubes, the OH concentration profile across the tube wall, and the effectiveness of OH removal during high-temperature annealing are determined by the tube fabrication method and, accordingly, by the predominant forms of the hydrogen impurities present in the tubes.

The diffusion coefficient of OH groups in TK-I tubes in the temperature range 750–950°C has been calculated to be $1.8 \times 10^{-8}$ to $1.2 \times 10^{-6}$ cm$^2$/s. The activation energy for their diffusion is $215 \pm 10$ kJ/mol. Annealing at a temperature of 950°C for 4 h under dynamic vacuum reduces the concentration of OH groups in such tubes by two orders of magnitude. Heat-treated TK-I tubes can be used as materials of reactors for the preparation of chalcogenide glasses with low hydrogen concentration.

ACKNOWLEDGMENTS

This work was supported by the Russian Federation Ministry of Education and Science, state research target no. 0095-2017-0010.

REFERENCES


Translated by O. Tsarev