JOURNAL OF MATERIALS SCIENCE 14 (1979) 2919–2923

Extraction of water from alkali germanosilicate glasses for optical fibres

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A study is reported on the extraction of water from alkali germanosilicate glasses, used for making graded index optical fibres. It is shown that the extraction rate is largely determined by the gas–glass melt interface created during the bubbling of dried O_2 through the melt. Both increased gas stream rates and the use of O_2, containing D_2O, resulted in a significant decrease in water concentration in the glass, thereby reducing the loss of the optical fibres produced from these glasses, e.g. a decrease at 850 nm from 15 to 10 dB km^{-1}, at 1100 nm from 28 to 10 dB km^{-1}.

1. Introduction

In order to make low-loss optical fibres using the double crucible method, compound glasses must be melted with a low concentration of absorbing impurities [1, 2]. The absorption of light in glasses in the relevant spectral range from 800 to 1300 nm is caused, in general, by the presence of transition metal ions and water. In glasses, water is assumed to be present as hydroxyl groups. In fused silica the hydroxyl groups give rise to three absorption bands in the 700 to 1100 nm range (Fig. 1) [3]. The 950 and 725 nm bands are ascribed to the second and third overtone, respectively, of the fundamental O–H stretch vibration frequency, which gives an absorption band at 2.73 μm. A band is also observed at 880 nm, which is ascribed to the combination of the second overtone with the ν_1 fundamental vibration of the SiO_4 tetrahedron [3]. In Fig. 1 a comparison is given of the OH absorption spectra in fused silica, alkali borosilicate and alkali lime germanosilicate glasses, three important glasses for graded index optical fibres [2–5]. In compound glasses the 950 nm band shifts to 970 nm and is considerably broader than that observed in fused silica. The 880 nm band, if present, is not observed as a separate band. The tails of the 960 nm band, found in compound glasses, contribute considerably to the loss of the optical fibre in the 800 to 900 nm and 1000 to 1200 nm ranges, wavelengths at which, at least in the near future, optical fibres will be operative [6]. Consequently it is important to prepare glasses with a low OH concentration. The most effective method by which the OH concentration in compound glasses can be lowered is to bubble dry gas through the melt [7]. When this gas contains D_2O, exchange reactions can be expected between OH groups in the melt and D_2O in the gas phase. The absorption spectrum of OD groups which, in that case, will be introduced into the glass, is shifted to longer wavelengths by a factor of 1.35 relative to the corresponding absorption of OH groups, e.g. the 970 nm band shifts to 1305 nm. This shift makes it possible to introduce

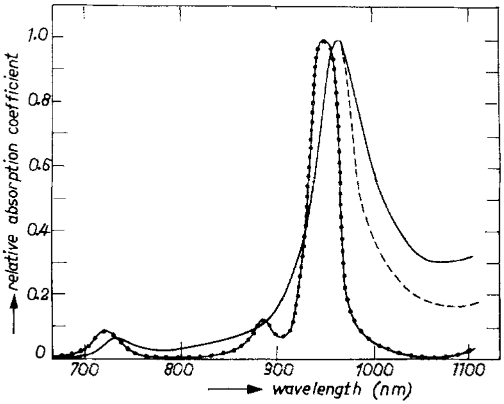

Figure 1 The normalized absorption spectra (maximum = 1) of OH groups in: ——— sodium lime germanosilicate glass; – – – – sodium borosilicate glass [3]; -●-●-●- fused silica [4].

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OD groups without increasing the loss of the optical fibre in the 800 to 1000 nm range. However, a contribution small compared with that of the removed OH groups is expected in the 1000 to 1200 nm range. This paper describes the effect of the use of D_2O on the removal rate and final concentration of water in alkali germanosilicate glasses melted in different conditions during bubbling.

2. Experimental procedures

In order to simplify experimental procedures a relatively low-melting glass of molar composition 0.125 Na_2O 0.125 K_2O 0.28 GeO_2 0.47 SiO_2, containing 0.05% As_2O_3, was chosen as a model for both core and cladding glass of the optical fibre. The glasses were melted in 0.3 kg batches in fused silica (Heralux) crucibles using a resistance furnace. The glasses were prepared from Na_2CO_3, K_2CO_3, $CaCO_3$ and SiO_2 (Merck, FO Optipur) and GeO_2 (Hoboken, Belgium, extra pure). A fused silica (Heralux) experimental set-up as shown in Fig. 2 was designed in order to avoid contamination from furnace lining and atmosphere during bubbling. To stir the melt the bubbler tube was rotated. Dried oxygen containing a residual 0.4 p.p.m. H_2O (dewpoint = − 80° C) was used for bubbling. The O_2 was saturated with D_2O (at 21° C) by bubbling the dried O_2 twice through liquid D_2O. Only 2 to 5 g of D_2O were used for treating each glass batch.

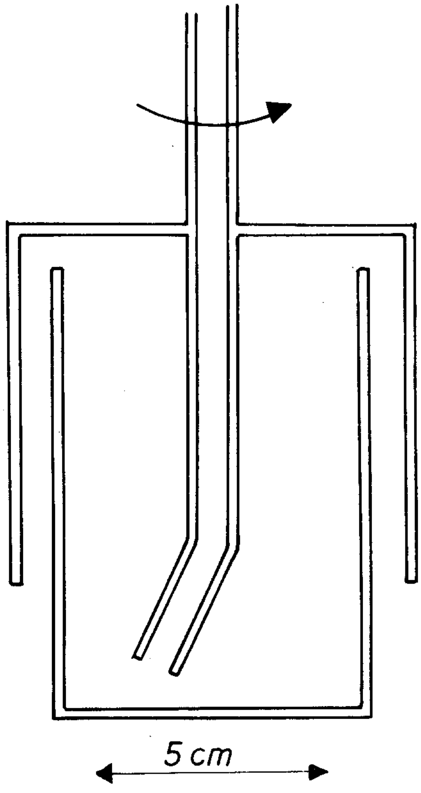

Figure 2 Fused silica melting crucible and bubbler tube.

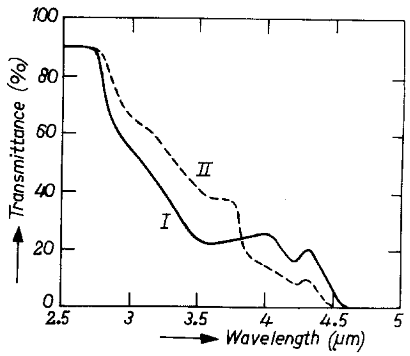

Figure 3 I.r. spectra of glass of composition 0.125 Na_2O 0.125 K_2O 0.28 GeO_2 0.47 SiO_2. I, glass containing OH groups; II, glass containing both OH and OD groups.

The OH and OD concentrations in the glass were measured semi-quantitatively by means of i.r. spectroscopy using a Hitachi spectrophotometer (Type EPI-62). Samples were taken by pouring small quantities of the melt into graphite moulds. The i.r. spectra were obtained from polished samples of 2 to 6 mm thickness. Typical i.r. spectra of glasses containing either OH or both OH and OD groups are shown in Fig. 3. This figure shows absorption bands of OH groups above 2.7 μm [8], the corresponding bands of OD groups are found above 3.6 μm. The OH concentration in a sample was determined from the absorption coefficient at five wavelengths in the 2.8 to 3.5 μm range. The mean α/α_0 ratios, where α_0 is the absorption coefficient at the start of bubbling, were used as a measure of the OH concentration in the sample. α_0 was found to be the same in all experiments. The OD concentration was determined by measuring the additional absorption in the 3.8 to 4.4 μm range; also at five different wavelengths. The OD concentration is again given relative to the OH concentration at the start of bubbling assuming that, at the shifted wavelength, OD groups have the same molar extinction coefficient as OH groups.

3. Results

Fig. 4 shows the decrease of the OH concentration in the melt during the bubbling process using dried O_2 and using dried O_2 containing D_2O. The increase in OD concentration in the melt in the

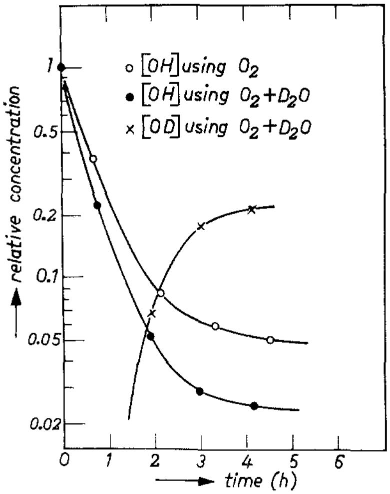

Figure 4 Time dependence of the OH and OD concentration, measured relative to the OH concentration at the start of bubbling (oxygen stream rate $Q = 2.00$ ml sec^{-1}, rotation rate of bubble tube $v_r = 0.05\ \text{sec}^{-1}$, furnace temperature $T = 1300°$ C).

latter case is also shown. Fig. 5 shows the influence of some of the melting conditions on the OH concentration of the melt through which dried O_2, containing D_2O, is bubbled. Curves of the same type were obtained by Beales *et al.* [9] during bubbling of sodium borosilicate glasses. They observed that the OH concentration reached after a certain time depended on the quantity of melt bubbled.

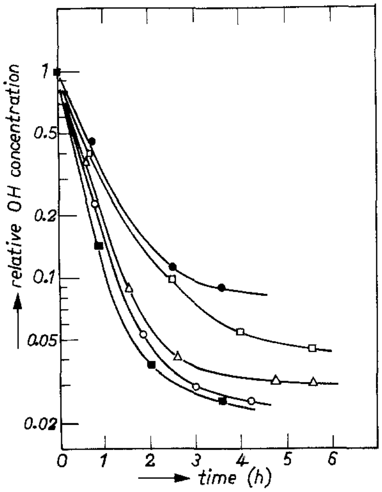

Figure 5 Time dependence of the OH concentration measured relative to the OH concentration as the start of bubbling. ● $v_r = 0.05\ \text{sec}^{-1}$, $Q = 0.66$ ml sec^{-1}, $T = 1300°$ C, SiO_2 crucible; ○ $v_r = 0.05\ \text{sec}^{-1}$, $Q = 2.00$ ml sec^{-1}, $T = 1300°$ C, SiO_2 crucible; □ $v_r = 0.05\ \text{sec}^{-1}$, $Q = 0.66$ ml sec^{-1}, $T = 1300°$ C, Pt crucible; ■ $v_r = 0.05\ \text{sec}^{-1}$, $Q = 2.00$ ml sec^{-1}, $T = 1350°$ C, SiO_2 crucible; △ $v_r = 0.15\ \text{sec}^{-1}$, $Q = 2.00$ ml sec^{-1}, $T = 1300°$ C, SiO_2 crucible.

4. Discussion

The solubility of H_2O in molten glasses has been the subject of numerous investigations, reviewed by Boulos and Kreidl [10]. It is generally observed that the solubility of H_2O vapour in molten glasses is linearly proportional to the square root of the partial pressure of water $(P_{H_2O})^{1/2}$. This relation suggests that every water molecule entering the melt reacts with oxygen to form two hydroxyl ions. The following reactions all account for such a mechanism:

$$2 \equiv\text{ROH} \rightleftharpoons \equiv\text{ROR}\equiv + H_2O(g) \quad (1)$$

$$2\,OH^- + \equiv\text{ROR}\equiv \rightleftharpoons 2 \equiv\text{RO}^- + H_2O(g) \quad (2)$$

$$2\,OH^- \rightleftharpoons O^{2-} + H_2O(g) \quad (3)$$

where R = Si or Ge in the case of alkali germanosilicate melts. Which reaction occurs will depend on the relative concentration and the reactivity of the different reactants. For example Kurkjian and Russell [11] have suggested that in silica-rich alkali silicate melts Reaction 1 occurs and Reaction 2 in glasses with an alkali oxide concentration higher than 25%. For the sake of brevity only Reaction 1 is assumed to take place in alkali germanosilicate melts with 25% alkali oxide. The occurrence of the other reactions, however, does not alter the conclusions.

When D_2O is present in bubble gas it can enter the glass by a mechanism analogous to Reaction 1:

$$D_2O(g) + \equiv\text{ROR}\equiv \rightleftharpoons 2 \equiv\text{ROD} \quad (4)$$

or by an exchange reaction such as:

$$\equiv\text{ROH} + D_2O(g) \rightleftharpoons \equiv\text{ROD} + \text{HDO}(g). \quad (5)$$

When OD groups are introduced into the glass melt either by Reaction 4 or 5 the following reaction, analogous to Reactions 1 and 4, may also occur:

$$\equiv\text{ROH} + \equiv\text{ROD} \rightleftharpoons \equiv\text{ROR}\equiv + \text{HDO}(g) \quad (6)$$

The H_2O and HDO produced by Reactions 1, 5 and 6 are removed by the gas stream. Therefore both Reactions 5 and 6 result in the removal of an additional number of OH groups as compared with the experiment where no D_2O is added, as is observed in Fig. 4.

In order to elucidate the observed influence of gas stream rate and temperature on the OH con-

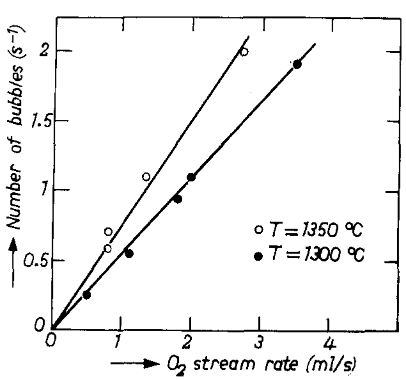

Figure 6 Effect of the gas stream rate (measured at 21° C) on the number of bubbles per second at two temperatures.

centration during bubbling with $O_2 + D_2O$ (Fig. 5), the number of bubbles formed in the melt during bubbling was determined as a function of these parameters. Fig. 6 shows that the number of bubbles is linearly proportional to the gas stream rate and is slightly dependent on temperature. Fig. 5 shows that a three times higher gas stream rate results in an approximately three-fold decrease in OH concentration, while a small temperature dependence is observed. These facts indicate that the quantitiy of OH groups extracted (by O_2 + D_2O) is predominantly determined by the surface of new interfaces, created by the bubbles, at which the reactions occur. The same type of curve is observed when the melt is bubbled with O_2 which indicates that the same mechanism is operative.

Fig. 4 shows that OD groups are not observed in the bulk of the melt during the first hour of bubbling although the OH concentration is lowered considerably by the presence of D_2O in the bubble gas. This indicate that the OD groups which are incorporated into the melt by Reactions 4 and 5 do not diffuse into the bulk of the melt but react at once with OH groups which in the first hour of bubbling are present in a relatively large concentration. The conclusion that OD groups are removed again implies that Reaction 6 is responsible for the lowering of the OH concentration. Only the occurrence of Reaction 6 can explain both the facts that the presence of D_2O lowers the OH concentration considerably while no OD groups are found in the bulk of the melt. When the OH concentration is lowered below a certain concentration the removal rate of OH and OD groups by reaction 6 will become low enough to allow the OD groups to diffuse into the bulk of the melt. Fig. 4 indicates that this happens when the OH concentration falls below the equilibrium OD concentration as determined by P_{D_2O} in the oxygen.

Melting in Pt crucibles lowers the OH concentration as compared to glasses melted in fused silica crucibles. This is due to the fact that the fused silica of the crucible and bubbler tube contains about 500 p.p.m. H_2O (from the intensity of the absorption band at 2.73 μm [12]) while the melt after four hours of bubbling contains only 10 to 50 p.p.m. H_2O (from i.r. spectra using the molar extinction coefficient of H_2O in alkali lime silicate glasses [12]). Therefore diffusion of water from the fused silica of the crucible and tube and dissolution of this material will introduce additional OH groups. Furthermore the increase in OH concentration observed at increased rotation rates of the bubbler tube can be explained as a faster dissolution of both crucible and tube. Unfortunately melting in Pt crucibles produces glasses in which small Pt particles are formed, causing a considerable scattering loss in the optical fibres. However, Fig. 5 shows that the number of OH groups coming from the fused silica is small compared with the numbers that can be extracted from the melt using relatively high gas stream rates and using O_2, containing D_2O, as bubble gas.

5. Application

The method described here to use D_2O to lower the OH concentration in glasses was applied for melting both core and cladding glasses for graded index optical fibres [2]. The composition of these glasses is shown in Table I. Fig. 7 shows the loss spectra of two optical fibres: I was prepared from

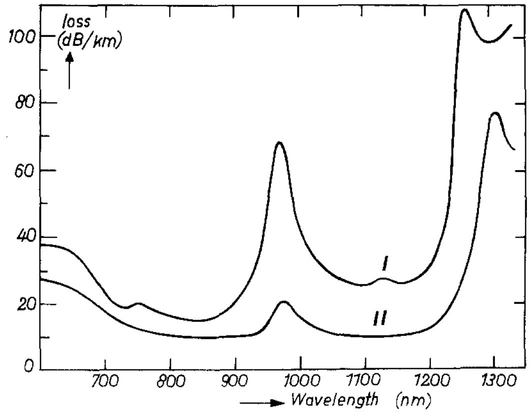

Figure 7 The total loss spectra of alkali lime germanosilicate graded index optical fibres. I, melts bubbled for 1 h with O_2, $Q = 0.40$ ml sec^{-1}; II, melts bubbled for 4 h with O_2, containing D_2O, $Q = 2.50$ ml sec^{-1}.

TABLE I Composition (mol %) of core and cladding glass for alkali lime germanosilicate graded index optical fibres.

	Core	Cladding
SiO_2	45.95	49.45
GeO_2	29.0	27.5
CaO	10.0	8.0
Na_2O	14.0	–
K_2O	1.0	15.0
As_2O_3	0.05	0.05

glasses whose melts were bubbles with dried O_2 at a relatively low gas stream rate, II was prepared from glasses whose melts were bubbles with dried O_2, containing D_2O, at a high gas stream rate. In the latter case the lower OH concentrations results in a considerable decrease in absorption loss. Above 1200 nm the absorption due to the second overtone of the OD vibration frequency at 1305 nm starts to contribute to the loss. The decrease in total loss below 800 nm is largely caused by the lower Cr^{3+} concentration in the core glass of fibre II (5 and 12 p.p.b. by weight, respectively, as determined by neutron activation analysis). This can be concluded from the absorption spectrum and molar extinction coefficient of Cr^{3+} ions in alkali lime germanosilicate glasses [13].

Summarizing, it can be concluded that both the increase of gas stream rates and the use of O_2, containing D_2O, as bubble gas, leads to a decrease in OH concentration in the glass thereby reducing the loss of the optical fibres produced from these glasses.

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Received 6 April and accepted 11 May 1979.