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Effect of thermal stabilization on the optical absorption of some transition metal ions in glass

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The optical absorption of a $30Na_2O$, $70SiO_2$ glass containing iron, chromium or cerium has been studied after thermal stabilization at various temperatures around the transformation range of the glass. The optical absorptions due to iron(II), iron(III), cerium(III) and cerium(IV) have been found to increase with increasing stabilization temperature; the optical absorptions due to chromium(III) and chromium(VI) do not change significantly with stabilization temperature. The changes in optical absorption due to stabilization at different temperatures have been found to be reversible and reproducible. It has been argued that as the equilibrium volume of a given mass of glass increases with increasing stabilization temperature, and as the ligand field strength surrounding the transition metal ion does not increase due to this enlargement of volume while the optical absorption increases, the high temperature stabilization of a glass probably increases some local randomness of structure (creating extra distortion of the transition metal complex) and does not cause an uniform volume expansion of the glass.

1. Introduction

Many physical and chemical properties of a glass measured at room temperature depend upon the rate at which it has been cooled through the transformation range [1–4]. When exact control of glass properties is required, such as the refractive index of optical glass or the transmission loss of optical fibres, these heat-treatment effects become of considerable practical importance. The absorption loss of optical fibre is mainly due to transition metal ions and hydroxyl group present in the glass [5]. Most transition metals can exist in glass in more than one oxidation state; the oxidation–reduction equilibrium being determined by the nature of the transition metal, the composition of the glass, the oxygen potential and the temperature during melting [6]. During fibre drawing from a melt, the cooling rate is much faster compared to conventional glass fabrication, and thus no significant amount of oxygen can either enter or leave the glass. Different oxidation state of a particular transition metal has different absorption spectrum determined mainly by the number of incomplete d or f electrons of the metal ion, the stereochemistry of the complex formed (coordination number, symmetry etc.) and the ligand field strength [7]. Some transition metal ions of a particular oxidation state again can occur in more than one coordination symmetry in the same glass; the coordination equilibria depend upon the basicity of the glass, the temperature of melting and the rate of cooling of the glass [8–10]. Thus it is apparent that the absorption loss of optical fibre due to transition metal ions present in it may be quite different from conventionally prepared glass (of identical composition) containing the same impurity ions. In this paper some preliminary experiments are described in which the changes of the optical absorption and the concentration of the redox species have been estimated after various heat treatments in, and above the transformation range of a glass containing iron, chromium and cerium individually.

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2. Experimental procedures

A glass of molar composition $30Na_2O$, $70SiO_2$ was used for the present study. This particular composition was chosen since this glass is reasonably durable under laboratory conditions, and is suitable for making good specimens for spectroscopic studies. Besides, many other investigators have studied various properties of the same glass and their findings have often been referred during discussion of the present results [11–14].

The glasses were melted from quartz powder containing less than 5 ppm iron and "Analar" sodium carbonate. Iron, chromium and cerium were added to the batch as ferric oxide/ferrous oxalate, potassium dichromate and cerium dioxide respectively. These chemicals were also of "Analar" grade.

Batch materials to produce 100 g of glass were weighed, thoroughly mixed and melted in Pt/2% Rh crucible in an electrically heated furnace in air at 1400° C. For quantitative optical measurements it is essential to produce a homogeneous seed-free glass free from any cord. This was achieved by stirring the melt mechanically with a platinum tipped stirrer for the initial 4 h of melting followed by fining at 1350° C for another 2 h. After 6 h of melting and fining, the melt was cast carefully on a warm steel mould avoiding overlapping of the melt surface. The block was transferred to an electric muffle furnace at 500° C and the muffle was switched off. No effort was, however, made to pour the whole quantity of the melt out of the crucible in order to avoid the presence of any pour lines and inhomogeneity in the glass block.

Out of this roughly annealed glass block 2.5 cm x 1.0 cm samples were cut for heat treatment at different temperatures around the transformation range of the glass. The thickness of the specimens were chosen so as to give optical densities of about 0.75 to 1.50 at the band maximum. This was because the spectrophotometer used (Cary 14) gave high noise to signal ratio at higher absorptions in the infrared region on the one hand and, on the other hand, if the measured optical density was too small, large errors would arise when the results were corrected for reflection loss and blank glass absorption. A part of every glass specimen was chemically analysed for different oxidation states of the various added transition metals following conventional microchemical methods [14–16]. Great care was taken to grind and polish the specimens to ensure uniformity of thickness and perfect parallelism of the surfaces.

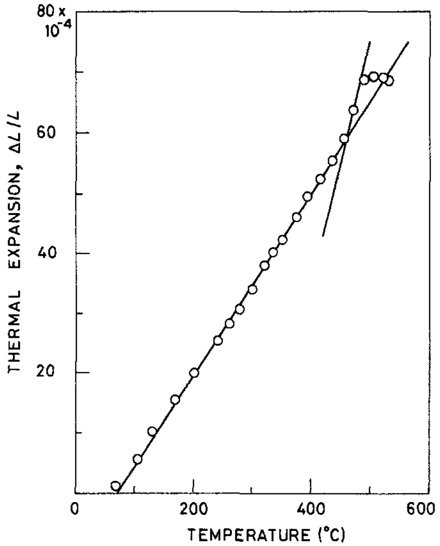

Figure 1 Linear thermal expansion of a $30Na_2O$, $70SiO_2$ glass (heating rate 10° C min^{-1}).

The glass specimens were heat treated towards stabilization at different temperatures around the transformation range in a tubular horizontal type electric furnace controlled with an "Eurotherm" Programmed temperature controller. The isothermal hot zone of the furnace (of about 5 cm length) could be controlled within ± 2° C for over a period of 400 h.

3. Results

3.1. Determination of the transformation range of the glass

The transformation temperature for a glass is usually determined by studying a physical property such as thermal expansion, refractive index, viscosity, etc. The limits of the transformation range in which the effects of the change of configuration can be observed as a function of time depend upon the time scale of the experiment [17, 18]. In the present investigation the transformation temperature of the $30Na_2O$, $70SiO_2$ glass was determined by measurement of thermal expansion and was found to be around 465° C as shown in Fig. 1. Small pieces of this glass were stabilized at temperatures below and above 465° C and their densities were determined by the conventional "Float and Sink" method. A typical set of curves of time taken for this glass to reach equilibrium density at 425° C is

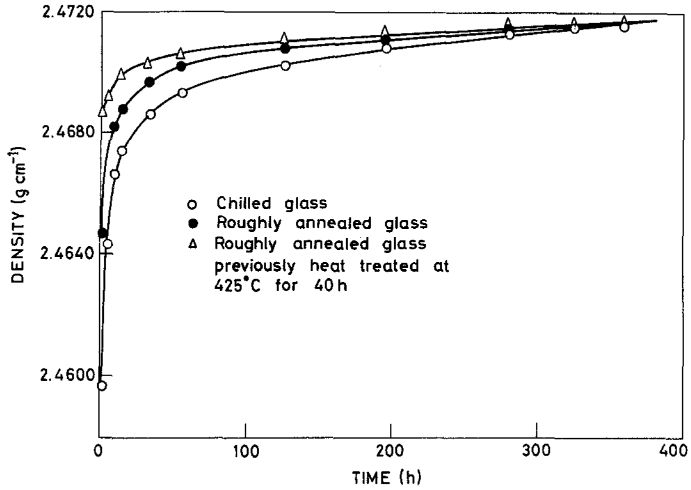

Figure 2 Attainment of equilibrium density of $30Na_2O, 70SiO_2$ glass pieces at 425° C having different thermal histories.

shown in Fig. 2. Similar experiments were made in which the optical density of iron(II) at 1050 nm was monitored in a glass containing 1.0 wt% iron to determine the time taken at 425° C for stabilization. This was found to be well over 350 h as shown in Fig. 3. However, the same glass attained equilibrium density in less than 1 h when heat treated at 505° C as shown in Fig. 4.

3.2. Effect of heat treatment on the optical absorption of iron in glass

The optical absorption of iron(II) and iron(III) in silicate and other types of glass have been extensively studied by various workers [11, 12, 19–23]. Information regarding the coordination number of both iron(II) and iron(III) as well as the change in the extinction coefficients induced by varying the soda content and also by replacing soda with other alkali/alkaline earth oxides in silicate glasses are available from these studies. In the present investigation a $30Na_2O, 70SiO_2$ glass containing 1.0 wt% iron (thickness ~ 0.50 cm) was used for the study of iron(II) absorption; and a glass of the same composition containing 0.02 wt% iron (thickness ~ 0.02 cm) was used for the study of iron(III) absorption in the ultraviolet region. The glass pieces were heat treated to equilibrium optical density at different temperatures ranging from 425 to 505° C and the results are shown in Figs. 5 and 6. The equilibrium optical density of these samples (both due to iron(II) and iron(III) which have been found to be reversible and reproducible) increase with increasing temperature of stabilization.

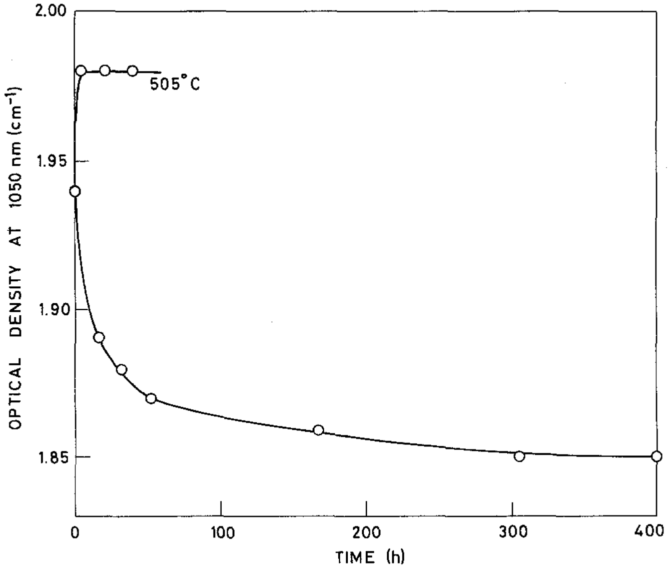

Figure 3 Attainment of equilibrium optical density at 1050 nm of a $30Na_2O, 70SiO_2$ glass containing 1.0 wt% iron.

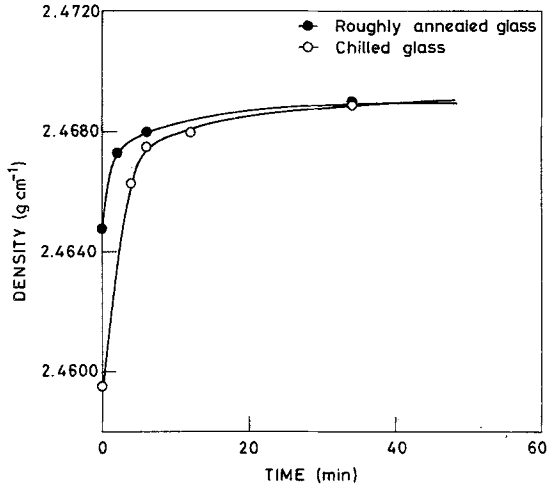

Figure 4 Attainment of equilibrium density of $30Na_2O$, $70SiO_2$ glass peices at 505° C having different thermal histories.

3.3. Effect of stabilization on the optical absorption of cerium in glass

Cerium in glass exists in two stable oxidation states, namely cerium(III) and cerium(IV) [16]; both these ions absorb intensely in the ultraviolet region and the absorption maxima are centred around 315 nm and 240 nm respectively in $30Na_2O, 70SiO_2$ glass [24]. A glass containing 0.25 wt% cerium was prepared and absorption spectrum for samples of 0.02 cm thickness was measured after stabilizing the glass pieces at different temperatures. The results are shown

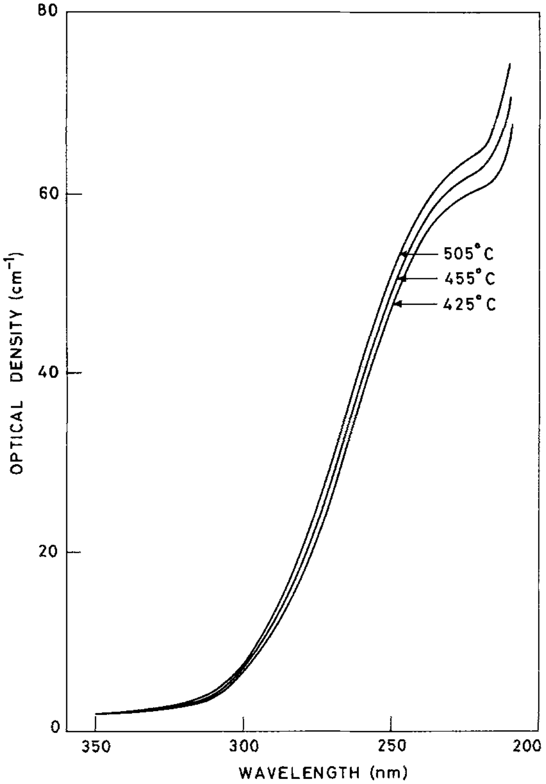

Figure 6 Equilibrium optical density due to iron(III) in $30Na_2O, 70SiO_2$ glass containing 0.02 wt% iron stabilized at different temperatures.

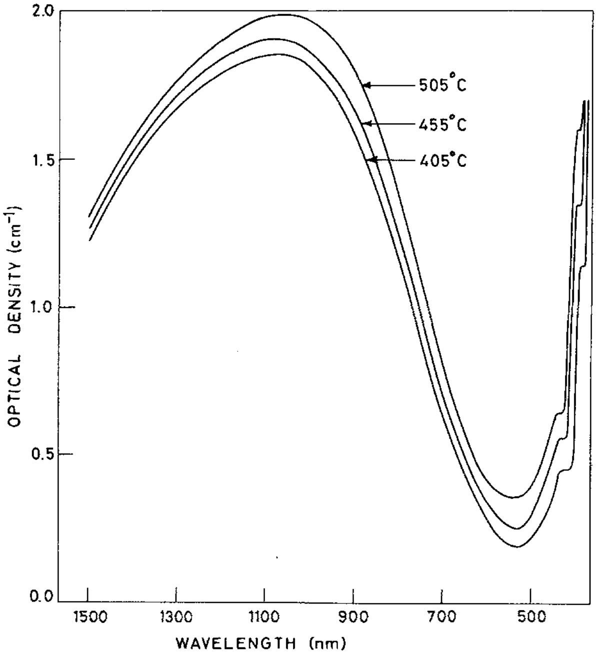

Figure 5 Equilibrium optical density due to iron(II) in $30Na_2O, 70SiO_2$ glass containing 1.0 wt% iron stabilized at different temperatures.

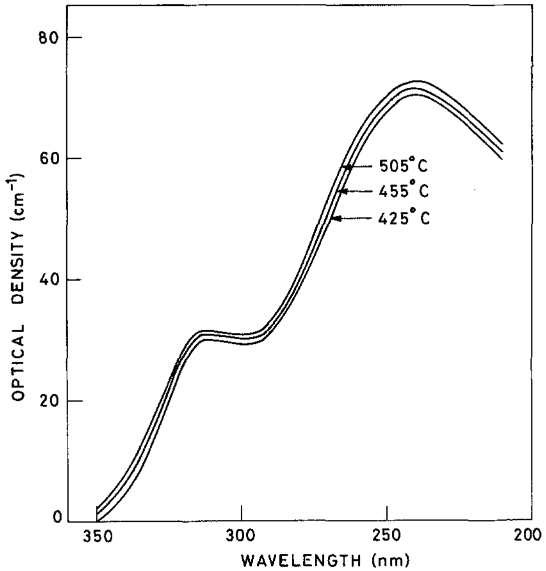

Figure 7 Equilibrium optical density due to cerium(III) and cerium(IV) in $30Na_2O, 70SiO_2$ glass stabilized at different temperatures.

in Fig. 7. As in the case of iron here also the equilibrium optical density due to cerium(III) and cerium(IV) (which have been found to be reversible and reproducible) increase with increasing stabilization temperature of the glass.

3.4. Effect of stabilization on the optical absorption of chromium in glass

Chromium generally exists in two stable oxidation states in glass, chromium(III) and chromium(VI). Chromium(II) is formed only when this glass is melted under severe reducing conditions ($p_{O_2} \sim 10^{-15}$ atm [25]). The charge transfer spectrum of chromium(VI) has two absorption bands centred at 365 nm and 270 nm. The extinction coefficients of chromium(VI) in $30Na_2O, 70SiO_2$ glass has been reported to be 4250 and 3250 l mol^{-1} cm^{-1} at peak positions of 365 and 270 nm respectively [16]. The chromium(III) absorption in the ultraviolet, if there is any, will be completely lost beneath the strong chromium(VI) absorption. The chromium(III) absorption in the visible region has band maxima centred at 685, 655, 637 and 450 nm of which the last one is masked by tailing of charge transfer band from the ultraviolet region. The estimated extinction coefficients of chromium(III) at these band maxima are 18 (685 nm), 21 (655 nm) and 20 (637 nm) l mol^{-1} cm^{-1} [26].

A $30Na_2O, 70SiO_2$ glass containing 0.20 wt% chromium (sample thickness ~ 0.3 cm) was used for studying the optical absorption of chromium(III); and the same glass containing 0.02 wt% chromium (sample thickness ~ 0.02 cm) was used to study the ultraviolet absorption of chromium(VI). The glass specimens were stabilized by heat treatment at different temperatures ranging from 425 to 505° C. Typical results are shown in Figs. 8 and 9. Unlike iron and cerium, the spectrum of a glass containing chromium did not change when stabilized at different temperatures.

4. Discussion

The absorption coefficient of both iron(II) and iron(III) in the same glass increases with increasing stabilization temperature; this clearly demonstrates that these changes of optical density are not due to change of redox condition of the glass; in that case one would have increased at the expense of the other. Microchemical estimation of iron(II) in a particular glass also shows a constant ferrous iron content irrespective of the temperature of stabilization of the glass. Out of all the ions studied in the present investigation,

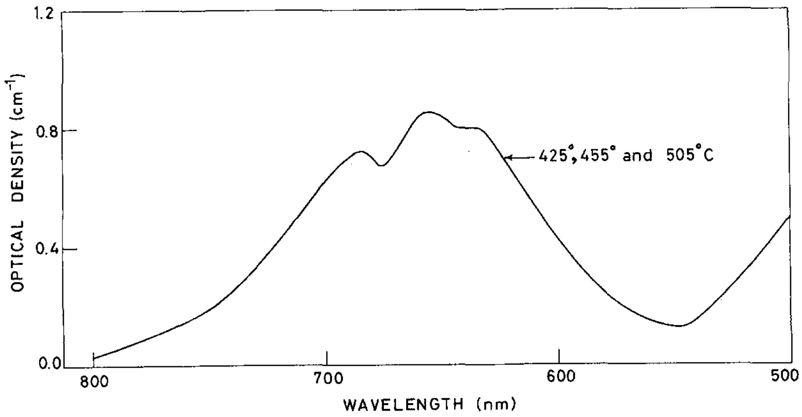

Figure 8 Equilibrium optical density due to chromium(III) in $30Na_2O, 70SiO_2$ glass containing 0.20 wt% chromium stabilized at different temperatures.

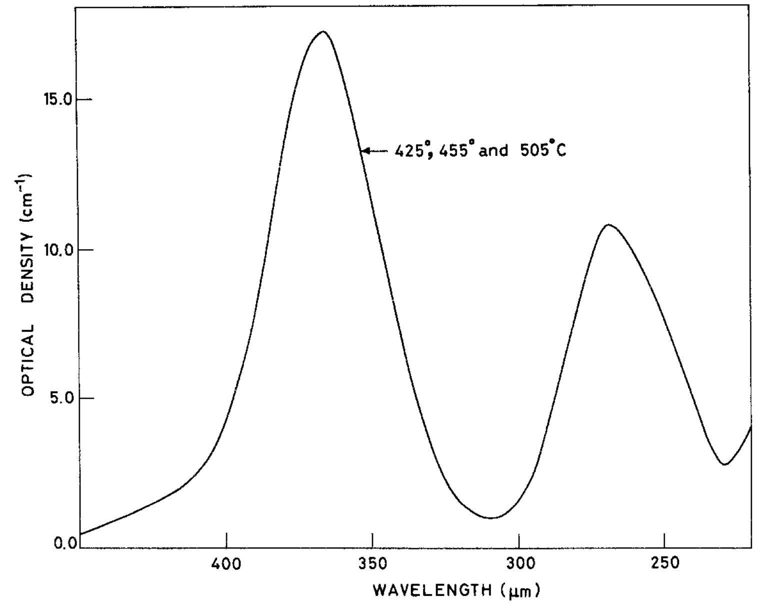

Figure 9 Equilibrium optical density due to chromium(VI) in $30Na_2O, 70SiO_2$ glass containing 0.02 wt% chromium stabilized at different temperatures.

iron(II), iron(III), cerium(III) and cerium(IV) showed changes in optical absorption with stabilization temperature whereas any change of absorption due to chromium(III) and chromium(VI) could not be detected. Stabilization at higher temperatures of a particular glass decreases its equilibrium density. This decrease of density may be due to an uniform swelling of the volume units of the glass or may be due to some extra randomization at some localized areas of the volume. In d–d and f–f transitions, as in the case of iron(II) and cerium(III), the ligand field strength is critically dependent on the metal to ligand distance, r. In fact in simple ionic systems like alkali halides it has been experimentally found that the ligand field strength, Δ, is related to r as follows [27]

$$\Delta = 1/r^n \qquad (1)$$

where $n = 6$ to 10. Although the absorption bands studied in the present investigation are fairly broad and are not necessarily isolated and single absorption bands, no significant shift in position of absorption maximum could be detected due to stabilization at different temperatures. On the other hand the iron(II) (a d^6 system) and cerium(III) (a f^1 system) complexes in glass are subject to a large amount of Jahn–Teller distortion, and the intensity of absorption due to electronic transitions of these ions (which are Laporte forbidden) increases with increasing distortion of the complex; the larger the distortion, the more it deviates from the centro-symmetric group and the greater the probability of the electronic transition probability. Thus from these optical studies it appears that uniform compaction or swelling of a glassy network does not take place as a result of thermal stabilization. Most probably the increase in volume and other physical properties observed as a consequence of stabilization at higher temperature of the glass is due to increased formation of localized disorder in it.

If a transition is electronically forbidden, but is permitted to occur through vibrational–electronic interaction, the corresponding absorption strength strongly depends upon temperature, because the permitting vibration of the ground state may be frozen in at low temperatures. The temperature dependence of the absorption strength of the d–d transitions in several crystalline hydrates have been studied by Holmes and McClure [28]. The temperature dependence of the oscillator strength, f, was found to follow the relationship

$$f = f_0 [1 + \exp(-\theta/T)] \qquad (2)$$

where θ is the frequency of the non-totally symmetric vibration in the temperature units ($\theta/1.44 = \omega\, cm^{-1}$), and f_0 is the value of the oscillator strength at 0 K. However, in the present investigation all the optical measurements were made at room temperature (30° C) and no such vibrational–electronic interaction (which varies with temperature) seemed to occur.

Chromium(III) (a d^3 system), due to its very high octahedral ligand field stabilization energy, invariably occurs as a near perfect octahedral complex in silicate glasses [26]. Probably the local perturbations caused by different stabilization temperatures used in the present investigation could not distort the very stable octahedral complex of chromium(III) and thus no change in optical density occurs.

The presently studied optical absorptions of chromium(VI), cerium(IV) and iron(III) are due to charge transfer transitions. Chromium(VI) in silicate glasses is known to occur as stable CrO_4^{2-} tetrahedral complex [29]; and the small local perturbations caused by stabilizations at different temperatures were not sufficient to produce any significant change in this complex. Consequently the optical absorption of chromium(VI) did not change with stabilization temperature of the glass. Iron(III) (a d^5 system) and probably cerium(IV) (a f^0 system), having no ligand field stabilization energy, are susceptible to changing distortion due to structural perturbation and consequently their absorption intensity changes with changing stabilization temperature of the glass.

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