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Effect of heat treatment on the infrared absorption spectra of Sr–Na borosilicate glass

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Internal modes of vibrations are studied here at different temperatures (27–800 °C) and in the frequency range 200–4000 cm^{-1} through heat treatment. The baseline method was used. The strong bands of SiO_4 tetrahedra in this glass show an increase in absorbance at high temperature (600–800 °C). The deformation of SiO_4 tetrahedra is investigated. This is found to depend on the ionic radius of the divalent metal oxide introduced, and the coordination number of the cation. Also from a study of the temperature dependence of the relative integrated intensity of the modes 600–800 and 850–1450 cm^{-1}, the relaxation time and rotational energy barrier of the glasses selected indicate that the glassy phases are transformed to crystalline phases at $\sim$500 °C.

Introduction

The room-temperature transmission spectra in the middle infrared (i.r.) [1] and far i.r. of vitreous SiO_2 [2–4] and various crystalline polymorphs have been studied [1–4]. Alkali cation vibrational bands at 485 and 230 cm^{-1} were observed in the systems Li_2O–SiO_2 and Na_2SiO_2, respectively [5]. In the Na_2O–SiO_2 systems two bands appearing in the region 8–11 μm are attributed to non-uniform microstructures existing in the glass [6]. The Raman scattering in a series of Na_2O–SiO_2 glasses (0–33 mol % Na_2O) are characterized by the appearance of two bands at $\sim$ 500 and 1100 cm^{-1}, the intensities of which appear to grow with increasing Na_2O content in the glass [7]. Vitreous bands at 1000 cm^{-1}, the intensities and 625 cm^{-1} can be related to the crystal modes at 1015, 860 and 668 cm^{-1}, respectively, and correspond to the vibration of Si–O bonds and deformation of the O–Si–O bond angle. The crystallization may take place in different ways, depending on the temperature of crystallization. It was suggested that the structure of these soda glasses consists of regions of high silica content, which yield the short-wavelength i.r. band, and regions of high sodium content which yield the long-wavelength band. In other words micro-phase separation takes place in the glassy state.

The soda–silica glasses have by far received the most attention in infrared studies of binary silicate glasses. A variety of techniques such as transmission and reflectance (bulk and thin film) have been used at high temperatures as well as high pressure. The compositional dependence of band maximum frequencies has been investigated by a number of authors [8–10]. In SiO_2 deposited by chemical vapour deposition (CVD) the absorption bands occur at lower frequencies and have larger half-band widths, implying that the atomic arrangement is more irregular than that in a thermally grown silicon dioxide film. A weak absorption in the 3 μm region can be seen, indicating the presence of residual hydrogen in the form of OH or absorbed H_2O. A positive frequency shift accompanied by an increase in absorbance at the band maximum was shown at high temperature, and the 3 μm absorption decreases in intensity [11]. The integrated intensity as calculated from the area under each of the intrinsic bands remains invariant, showing no change in the total number of oscillators. When heat-treated to 800 °C and above the resultant spectra are identical to those of a thermal oxide grown at the same temperature. This implies that the shifts to higher frequency and narrowing of the half-band width are merely a manifestation of structural changes in the silica network brought about by thermal annealing. Angular reorientation of the Si–O–Si centres [12, 13] or further condensation of hydrogen-terminated Si–O chains [14], are possibilities for these structural changes. No further change in the SiO_2 spectrum is noted upon heat treatment beyond 800 °C in the range 900–1200 °C. The infrared absorption of as-deposited and heat-treated anodic SiO_2 shows similar behaviour to that of CVD SiO_2 [15].

The aim of the present paper is to study the network structure of soda–borosilicate glass when introducing 2.5% SrO. The effect of heat treatment on strontium–sodium borosilicate glass is investigated. Also the relative integrated intensity, relaxation time and rotational energy barrier are calculated for certain vibrational modes.

2. Experimental procedure

Samples for infrared measurement were prepared with 79% SiO_2 + 12.5% Na_2O + 6% B_2O_3 + 2.5% Sr. Glass in which strontium oxide was introduced in partial replacement of soda was investigated. All the glass compositions are given in weight percentages, and the replacements were made on a cation-for-

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cation basis. The glasses were melted at 1410 °C. Melting was continued until the glass was well refined and homogeneous. The melts were cast into slabs of rectangular shape of about 1 cm^2 and 4 cm in length, and were given proper annealing. Glasses were ground and seived and mixed with spectral-grade KBr in discs for i.r. measurements in the frequency range 200–4000 cm^{-1} with a Beckman double-beam i.r.-spectrophotometer model IR 4250 after heat treatment for 2 h up to 800 °C.

3. Results

Vibrational spectra of strontium–sodium borosilicate glass at room temperature (27 °C) and at different temperatures are shown in Figs 1 to 3. The internal vibration modes of strong bands at 460, 780 and 1075 cm^{-1} are due to Si–O–Si bending vibration, Si–O–Si stretching vibration and Si–O stretching vibration, respectively. The absorbed water bands at 1620 and 3450 cm^{-1} are due to H–O–H bending and O–H stretching, respectively, and decrease with temperature (800 °C). New absorption peaks at 360, 380, 1450 and 1570 cm^{-1} become more pronounced at high temperature. The bands at 925 cm^{-1} of B–O–Si linkage at high temperature are shown in Fig. 2.

The strong bands of SiO_4 tetrahedra shows a slight shift to high frequencies. Also the absorbance of these bands decreases first and then increases at high

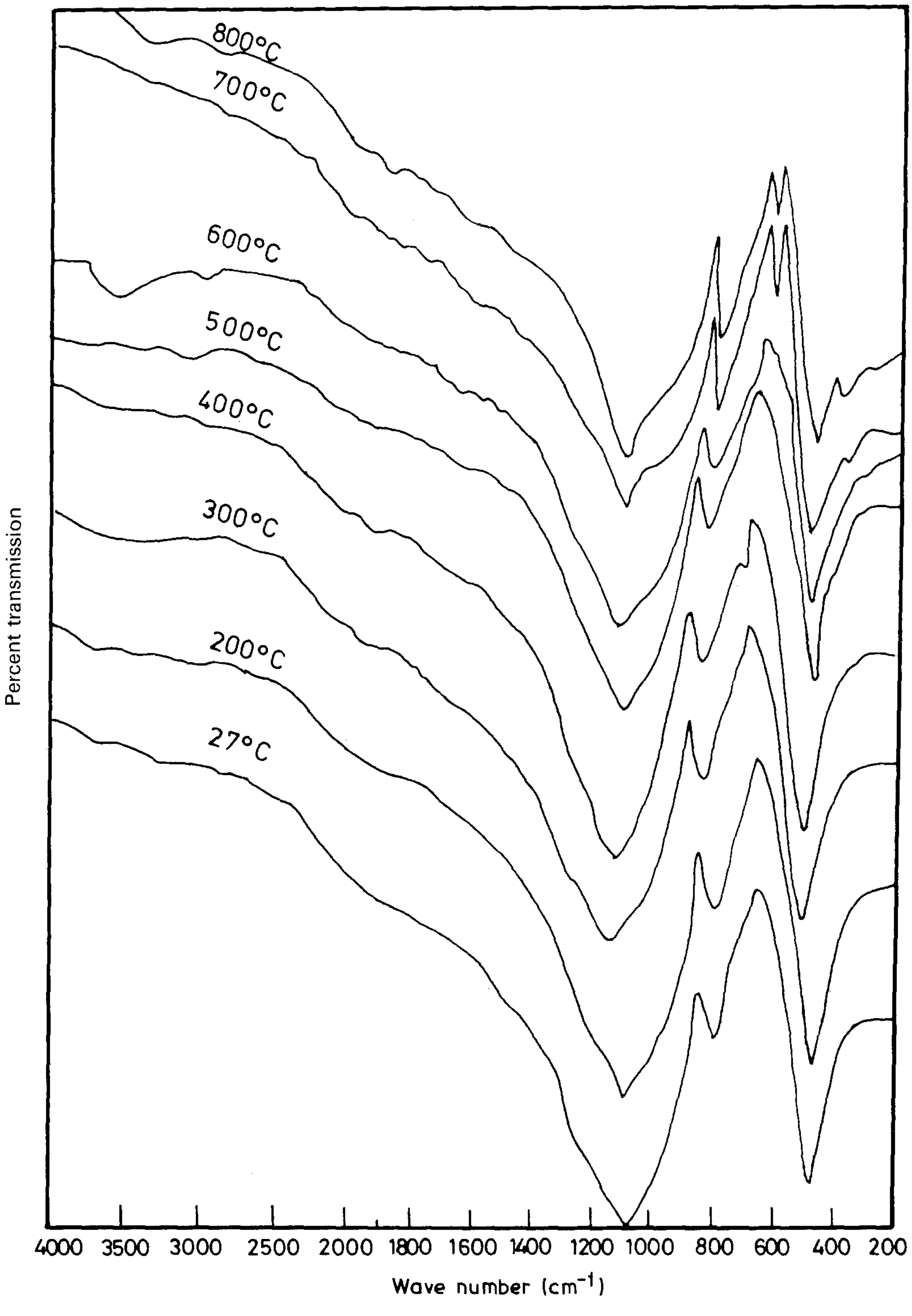

Figure 1 The effect of temperature on the infrared absorption spectra of Sr–Na_2O–borosilicate glass in the temperature range 27–800 °C.

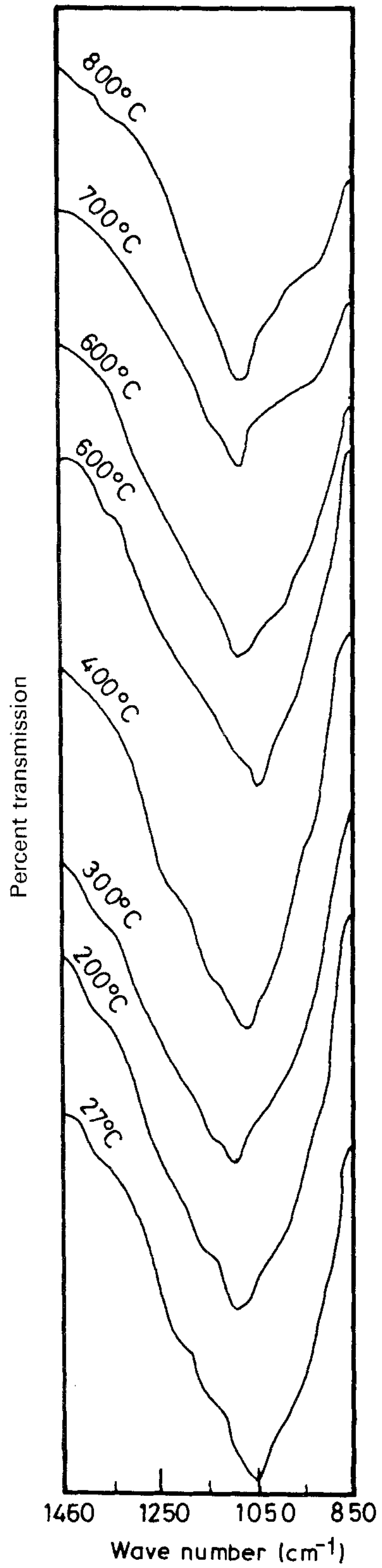

Figure 2 Temperature dependence of the band 850–1450 cm^{-1} of the borosilicate group.

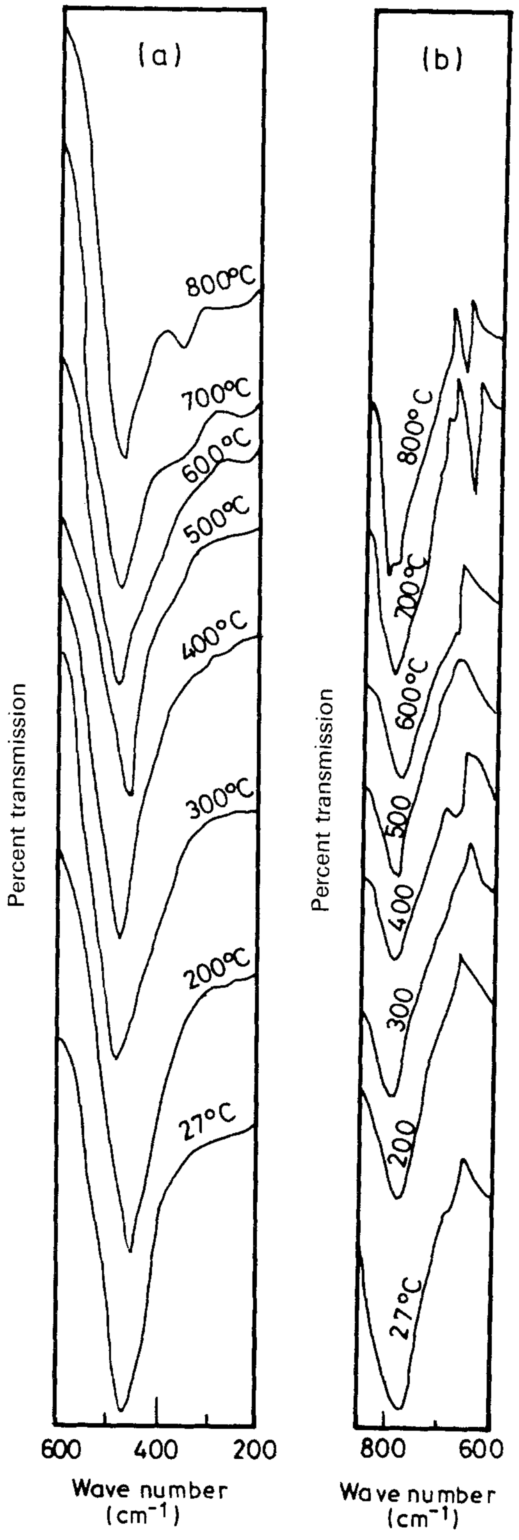

Figure 3 Temperature dependence of the bands of the borosilicate groups: (a) 200–600 cm^{-1}, (b) 600–800 cm^{-1}.

temperature (800 °C). Splitting of bands at 650, 660 and 775 cm^{-1} is shown in Fig. 3. The temperature dependences of relative integrated intensity in the regions 600–800 and 850–1450 cm^{-1} are shown in Fig. 4. The temperature dependences of the relaxation time and potential energy barrier of internal modes are shown in Figs 5 and 6, respectively. These figures show a phase transition from glass to crystal phases at 500 °C.

The energy barrier separating two different phases of the borosilicate glass can be determined by using the relaxation time equation [16] $\tau = \tau_0 \exp (U/kT)$ where U is the rotational energy barrier, k the Boltzmann constant and T the absolute temperature in the region 200–600 cm^{-1}.

4. Discussion

All monovalent Li_2O–Na_2O–K_2O borosilicate glasses have similar spectra at room temperature (27 °C). When the temperature rises the splitting of infrared

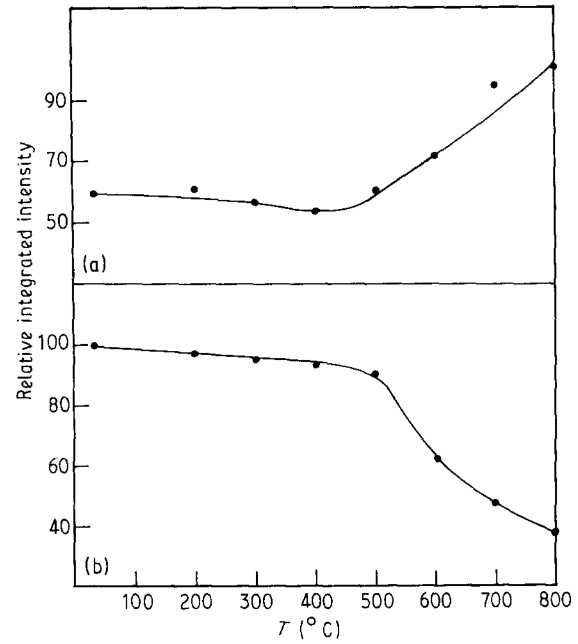

Figure 4 Temperature dependence of the relative integrated intensity of the modes: (a) 600–800 cm^{-1}, (b) 850–1450 cm^{-1}.

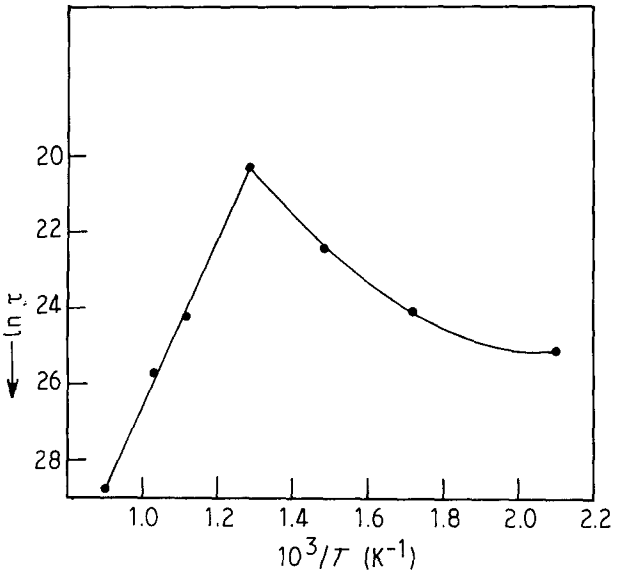

Figure 5 Temperature dependence of the relaxation time (τ) in the region 200–600 cm^{-1}.

bands at 650, 750 and 1080 cm^{-1} appears more pronounced in Li_2O–Na_2O borosilicate glasses than in K_2O–Na_2O glasses. In all crystalline silicates, the silicon ions are coordinated by four oxygen ions. The simplest silicate glass is vitreous silica: all silicon ions are coordinated by four oxygen ions and the structure is uniform at short range. The introduction of alkali or alkaline earth oxide in silica leads to a breaking up of the silicon–oxygen network. This is evinced by the much lower viscosity and higher thermal expansion coefficient of these glasses compared to vitreous silica. Silicon remain coordinated by four oxygen ions although part of these oxygens will be of the non-bridging type; thus the random network is preserved. The effects of temperature between 27 and 800 °C for 2 h on divalent metal oxide i.r. absorption spectra and the deformation of SiO_4 in strontium–sodium borosilicate glass are investigated (Figs 1 and 2).

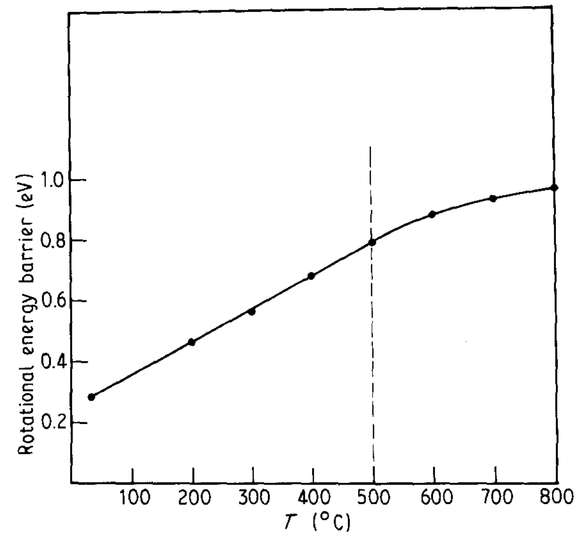

Figure 6 Temperature dependence of the rotational energy barrier in the region 200–600 cm^{-1}.

The irregularity in the frequency shift of these i.r. bands to higher or lower frequencies (200–400 °C) is due to phase separation. A slight shift occurs in the strongest bands of SiO_4 tetrahedra at 450–460, 775–780 and 1060–1075 cm^{-1} for Si–O–Si bending vibration, Si–O–Si stretching vibration and Si–O stretching vibration, respectively.

This shift to higher frequencies indicates an increase in the force constant between the components of the network structure. The increase in absorbance in the temperature range 600–800 °C indicates strengthening of the SiO_4 bands. New absorption bands are pronounced, also very weak peaks of other groups such as BO_3–BO_4 have been sharpened with increase of temperature. This behaviour is a consequence of γ-irradiation and soaking [17]. The relative integrated intensity against temperature was calculated and is drawn in Fig. 4 for different modes of vibration (780 and 1075 cm^{-1}). These figures shows a constant curve (straight line) and then decrease or increase at high temperature (500–800 °C). Also lnτ against temperature show a change of phase at 500 °C.

Charles and Wagstaff [18] observed, after annealing bulk samples of binary borosilicate glass at about 510 °C for many days, evidence of phase separation in the concentration range 60–80 mol % B_2O_3.

Angular reorientation of the Si–O–Si centres [19, 20] and/or further condensation of hydrogen-terminated Si–O chains are possibilities for these structural changes; no changes in the SiO_2 spectrum are noted beyond 800 °C in the range 900–1200 °C.

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