Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Non-Crystalline Solids 351 (2005) 3870–3878
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Physical properties of silicate glasses doped with SnO_2

Ervino C. Ziemath *, Bruno Z. Saggioro, João S. Fossa

Departamento de Física, Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista – UNESP, P.O. Box 178, 13500-970 Rio Claro – SP, Brazil

Received 15 March 2005
Available online 18 November 2005

Abstract

The presence of tin in the network of silicate glasses produces changes in several of their physico-chemical properties. Glasses with the composition (mol%) $22Na_2O \cdot 8CaO \cdot 70SiO_2$ containing up to 5 wt% of SnO_2 were analyzed under several experimental techniques. Dilatometric measurements showed an increase of the glass transition temperature with increasing tin content, while the average thermal expansion coefficient is reduced. Vickers microhardness, density, and refractive index also increase with the tin content. Diffuse reflectance spectra in the infrared (DRIFT) showed that the presence of tin, even at low concentrations, is responsible for some structural changes since there is an increase of the bridging oxygen concentration. The doped glasses present a brown color and optical absorption spectra measurements are interpreted as being due to precipitation of tin in the form of colloidal particles during cooling of the melted glass. In the $Na^+ \leftrightarrow K^+$ ion exchange process the presence of tin in the glass network hinders the diffusion of these ions. The diffusion coefficients of those ions were calculated by the Boltzmann–Matano technique, after concentration profiles obtained by EDS measurements. All results obtained present evidences that Sn^{4+} cation acts as a glass network former.

PACS: 61.43.Fs; 82.65.F; 65.70.+y; 78.20.C

1. Introduction

After performing ion exchange in a float glass in melted KNO_3 at 565 °C during 8 h, it was visually observed that one of the sample faces had undergone a more pronounced change than that opposite one. EDS measurements reveal that the most damaged surface was that without tin, known as the top face [1]. This leads us to questioning about the influence of tin in low concentrations on the ionic diffusion and also on other physical properties of such glasses. Therefore, with the aim to analyze these influences, soda–lime–silica glasses with composition near that of float glass, and doped with up to 5 wt% of SnO_2, were synthesized. Samples of these glasses were analyzed by dilatometry, densimetry, Vickers hardness, refractive index, optical absorption, and diffuse reflectance in the infrared (DRIFT). Self-diffusion coefficients for K^+ and Na^+ were calculated from concentration profiles obtained by EDS measured.

In the literature, one can find several studies performed on stannosilicate glasses, in which the oxidation state of tin is almost +2 [2,3], and on the tin side of float glasses, where the main objectives were the understanding of the diffusion process of tin and of the oxi-reduction mechanism undergone by tin in the bottom face during the float process [4,5]. No studies had been found in the literature about soda–lime glasses intentionally doped with low concentrations of SnO_2, which leads us to perform the present study.

2. Experimental procedures

Glasses with composition $22Na_2O \cdot 8CaO \cdot 70SiO_2$ (mol%) with up to about 5 wt% of SnO_2 where prepared. The raw materials were reagent grade sodium and

* Corresponding author. Tel./fax: +55 19 3526 2238.
E-mail address: ziemath@rc.unesp.br (E.C. Ziemath).

0022-3093/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2005.10.016

calcium carbonates (Mallinckrodt), grounded quartz (Mineração Jundu), and SnO_2 (99.9%, Cesbra). For each 100 g glass, an integer weight percentage (wt%) of SnO_2 was added. The corrected concentration of this oxide in the glass is lower than that of the nominal one, as shown in Table 1. In the present work, the corrected values will be mentioned. The glasses were obtained by fusion in an electric furnace at 1450 °C. The melting procedures were performed in a platinum crucible. During the fusion, the melt was stirred with a platinum rod for homogenization. Bubbles were removed from the melt keeping it at rest during about 30–45 min. The melt was poured on steel plates previously heated at 600 °C. As soon as the melt had reached a rigid condition, the glass was transferred to a pre-heated furnace at 600 °C and turned off allowing the glass to cool at the same rate as that of this furnace, in order to release the thermal stresses. The glasses containing SnO_2 presented a brown coloration, whose intensity decreases with increasing concentration of this oxide.

Samples were cut with a diamond saw, lapped with SiC on a plane brass tool and, depending on the experimental technique to be employed, they were polished with CeO_2 on a plane pitch tool.

Samples with about 50 mm length and a cross-section of the order of (5×5) mm^2 were prepared for the determination of the transformation temperature, T_g, as well as the thermal expansion coefficient, both through dilatometric measurements. The measurements were performed using a BP Engenharia equipment (mod. RB-3000-20). Samples were heated at a rate of 10 °C min^{-1}.

Vickers hardness was calculated after measurements of the impression diagonal lengths, d, as function of the applied load, P. The indentations were performed with a MHP 160 device coupled to a Jenavert (Carl Zeiss/Jena) optical microscope. The angular coefficient, m, of the straight lines obtained from d^2 versus P plots were substituted in the expression $H_v = 1854.4\ m^{-1}$ to calculate the hardness in kg mm^{-2}. To obtain the results in GPa the result is multiplied by 9.81×10^{-3}.

The density was determined by Archimedes method. Glass samples were hung into water by a very low diameter polyamide yarn. The water temperature was measured with a chemical thermometer having a resolution of 0.5 °C. An electronic balance (Sartorius, BL 210 S) was employed for mass measurements.

Since the glasses with different SnO_2 concentrations presented variations in their color, optical absorption measurements were performed using a Varian UV–VIS spectrometer (Cary 50).

Table 1
The nominal and corrected values of SnO_2 concentration, c_{Sn}, in the glasses

c_{Sn}^{nom} (wt%)	0	1	2	3	4	5
c_{Sn}^{corr} (wt%)	0	0.99	1.96	2.91	3.85	4.76

Infrared spectra were obtained from polished sample surfaces using a diffuse reflectance device (Spectra Tech) coupled to a Shimadzu infrared spectrometer (mod. FTIR-8300).

Refractive index was determined using an Abbe refractometer (Carl Zeiss/Jena). The optical coupling of the samples placed on a glass prism of the device was made with α-bromonaphtalene. The calibration of the refractometer was made with a BK7 glass, and a sodium vapor lamp ($\lambda_D = 589.5$ nm) has been used.

Polished samples of undoped and doped with 0.99 wt% SnO_2 were submitted to ion exchange in KNO_3 at 500 °C for 2 and 12 h. The concentration profiles of the elements Na and K were obtained with an energy dispersive spectrometer, EDS (EDAX-Oxford), coupled to a scanning electron microscope (Zeiss, DSM 940A). The samples were coated with a thin and uniform gold film. From these profiles the diffusion coefficients were calculated using the Boltzmann–Matano technique [6,7].

3. Results

The concentration of SnO_2 in the glasses was analyzed with EDS. The software of the X-ray equipment performed the ZAF corrections [8]. Fig. 1 shows a plot of the measured SnO_2 concentration as function of the corrected one. The experimental values were fitted by the linear equation $c_{Sn}^{meas} = 0.041 + 1.048 c_{Sn}^{corr}$. For comparison, the EDS measured concentration of SnO_2 at the bottom face of a 3.0 mm thick float glass is 2.04 wt%. The SnO_2 concentrations, obtained by EDS, present a systematic shift to higher values relative to the corrected ones. This can be explained on the basis of the distinct features of tin in the standard SnO_2 and that in the doped glasses: the X-ray L-line of tin has a lower absorption in the glass, and the mean atomic number, Z, of the glass is also lower. Thus, the

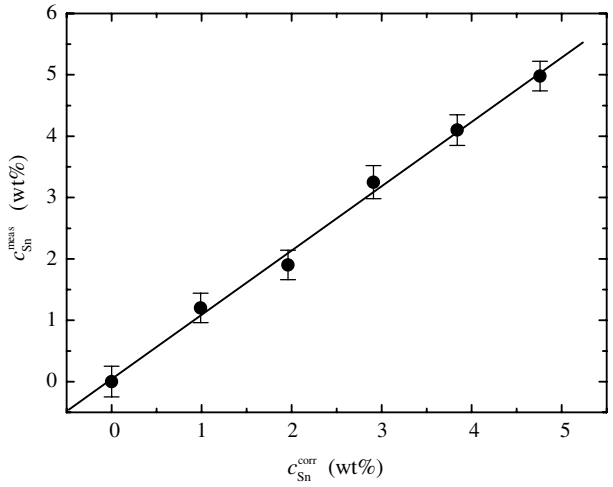

Fig. 1. Concentration of SnO_2 measured by EDS, c_{Sn}^{meas}, as a function of its corrected value, c_{Sn}^{corr} in the glasses. The angular coefficient of the fitted straight line is 1.05.