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Surface-luminescence from thermally reduced bismuth-doped sodium aluminosilicate glasses

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ABSTRACT

We report on the effect of hydrogen annealing on the optical properties of bismuth-doped sodium aluminosilicate glasses. The redox state of bismuth in the as-melted glasses is governed by the composition, viz., NIR luminescence is observed only in the glasses with low optical basicity. Upon thermal reduction, visible emission from Bi^{3+} and, eventually, minor amounts of Bi^{2+} is significantly lowered, depending on heat-treatment time and temperature, and glass composition. Hydrogen treatment was also found to result in a decrease of the NIR emission intensity and, at the same time, formation of metallic bismuth particles in the surface region. Surface-tinting as well as the decrease of visible luminescence follow Arrhenian kinetics, suggesting that hydrogen permeation is the rate-governing process. Upon re-annealing in air, the effects of thermal reduction on the optical properties are reversible only to a limited extent.

1. Introduction

The optical properties of bismuth-doped oxide glasses have been arousing significant and renewed interest over the last few years. This has been motivated by various potential applications such as simple coloring [1], third order optical non-linearity (e.g. [2]), and surface conductivity (e.g. [3]) on the one side, and luminescence in the visible (VIS) and near-infrared (NIR) spectral range on the other side [4,5]. In particular, broadband NIR luminescence has been studied extensively for application in novel laser sources and optical amplifiers [5–8]. However, due to the large variety of redox states in which bismuth may be present in oxide glass matrices, the respective origin of luminescence and other optical properties remains debated [4]. It has therefore become important to be able to manipulate the redox state of bismuth in oxide glasses.

In silicate glasses, Bi^{3+} and metallic bismuth are traditionally regarded as the most prevalent species [9]. For instance, voltammetric studies on a soda lime silicate melt at 1250 °C have confirmed the presence of these two species (Bi^0 and Bi^{3+}), but also indicated the presence of a third species (presumably Bi^{5+}) [10]. The presence of bismuth in additional oxidation states (e.g., Bi^+, Bi^{2+} and Bi^{5+}) has also been suggested by, e.g., X-ray photoelectron spectroscopy [2,11], indicating that the redox chemistry of bismuth in glasses and glass-forming liquids is more complex than first assumed. Currently, this has prevented knowledge-based tools for exploiting ultrabroad NIR photoluminescence of bismuth-doped glasses, and even the nature of the NIR emitting center remains highly debated [5].

Luminescence from Bi^{3+} and Bi^{2+} occurs in the blue and red spectral ranges, respectively [11–13]. The origin of NIR luminescence has been ascribed to Bi^+ and subvalent species [4], and Bi ion clusters such as Bi_2^-, Bi_2^{2-} [14,15], or Bi_5^{3+} [16,17]. In addition, the highly oxidized valence state of bismuth, i.e., Bi^{5+} [15,18] has also been suggested as a source for NIR photoluminescence.

Several different approaches have been attempted to obtain and optimize NIR luminescence from bismuth-doped glasses by manipulating the oxidation state of bismuth. These approaches include controlling the optical basicity of the glass [19–21], controlling the melting atmosphere and temperature [22,23], adding oxidation [24] or reduction agents [23] to the batch, tempering the glass [23], crystallizing the glass [25], and irradiating the glass with femtosecond lasers, γ-rays, or high-energy electron rays [26–28]. Based on these previous efforts it can be stated that the occurrence of NIR-active Bi species is highly sensitive to numerous parameters [29] and that its optimization requires delicate tuning of all parameters which affect the oxidation state of bismuth [23].

Heat-treatment of a glass in a reducing atmosphere offers several levers for such tuning (i.e., gas type, partial pressure, temperature, and duration) [30]. It has been shown that the luminescence properties of rare earth-doped silicate [31], aluminosilicate [32], alkali borosilicate [33], and alkali aluminosilicate [33] glasses can be tuned through

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reduction of the optically active polyvalent ions. However, heat-treatment of a bismuth-doped glass fiber in H_2 atmosphere with subsequent flame brushing negatively affected the NIR luminescence [29]. On the other hand, thermal reduction of bismuth-doped crystalline phosphors has been applied to increase NIR activity [34]. Heat-treatment of bismuth-doped glasses in a reducing atmosphere is thus a potential approach for manipulating the bismuth oxidation state and consequently the NIR luminescence. It should be noted, though, that the thermal reduction may influence the optical properties differently in different matrix materials and process conditions, especially when metallic particles are created [4,35,36]. In addition to affecting the redox state of the material's surface, such heat-treatments of glasses containing polyvalent ions can also induce ionic diffusion in the glass surface layer [37].

In this work, we investigate the luminescence properties of Bi_2O_3-doped sodium aluminosilicate glasses which have been heat-treated under reducing conditions. We also study the effect of the $[SiO_2]/[Al_2O_3]$ ratio in the base glass on the optical properties and discuss our findings in terms of the reduction and luminescence mechanisms.

2. Experimental

2.1. Sample preparation

As a model system and host for bismuth dopants, sodium aluminosilicate glasses of the type $(80-2x)SiO_2{\cdot}(20+x)Na_2O{\cdot}xAl_2O_3$ (mol%) were chosen. The optical basicity and the glass transition temperature (T_g) were varied by varying x, but the number of non-bridging oxygen per tetrahedron (NBO/T) was kept constant. Four glasses with $x=0$, 5, 10 and 15 (denoted Al0 … Al15) were produced and doped with 0.5 mol% Bi_2O_5. The optical basicity was evaluated using the model of Duffy and Ingram [38]. For the present case, it increases from 0.55 to 0.64 from Al0 to Al15. Glasses were prepared by melting batches of SiO_2, Al_2O_3, Na_2CO_3, and Bi_2O_3 powders in alumina crucibles at temperatures given below with subsequent quenching by casting on a preheated brass plate (or a steel plate). Al0 was melted at 1550 °C for 50 min, whereas Al5, Al10, and Al15 were held in a temperature range between 1450 and 1550 °C for 60–90 min in order to refine and homogenize the melts. After casting, samples were annealed slightly below their respective glass transition temperature (T_g) for 1 h, and naturally cooled by turning off the furnace (Table 1). Samples of ~0.8–1.0 cm in diameter and 2.00 ± 0.05 mm thickness were obtained by cutting from each slab of glass with a diamond saw. They were then ground with SiC grinding papers under ethanol and finally polished using a cloth with diamond paste.

2.2. Thermal reduction

Heat treatment of the glasses was conducted in H_2/N_2 atmosphere using a custom designed tube furnace (SF17, Entech, Ängelholm, Sweden). Samples were placed in the furnace at room temperature. The furnace was subsequently evacuated and flushed with the treatment gas three times before commencing experiments. Heating and cooling cycles were performed at 10 K/min. An Fe_2O_3/Fe_3O_4 oxygen buffer was placed in the tube to fix the oxygen partial pressure [37]. Treatment temperatures T_r were chosen with respect to T_g of each sample (Table 1). Reduction experiments were conducted in two different gas mixtures, 1/99 H_2/N_2 and 10/90 H_2/N_2, for two different durations (2 and 4 h). An additional series of experiments was conducted on Al5 in 10/90 H_2/N_2 for 0, 1, and 8 h (0 h refers to a dynamic heat-treatment without isothermal hold at the maximum temperature). Furthermore, Al15 was heat-treated in 10/99 H_2/N_2 at the treatment temperatures of Al0 and Al5, corresponding to $0.94T_g$ (487 °C) and $0.97T_g$ (512 °C) of Al15. Re-annealing of thermally reduced Al10 treated for 2 h in 10/90 H_2/N_2 was conducted in air at T_g for 1 and 44 h, respectively, in order to investigate the reversibility of the thermal reduction process.

Table 1
Glass transformation temperature (T_g), optical basicity (Λ) [38], annealing temperature after melting [T_a], and treatment temperature during thermal reduction (T_r).

	Al0	Al5	Al10	Al15
Λ	0.55	0.58	0.61	0.61
T_g (°C)	483	495	507	528
T_r (°C)	487	498	512	534
T_a (°C)	450	450	450	520

2.3. Characterization

Calorimetric T_g of the as-prepared glasses was determined by differential scanning calorimetry (DSC, Jupiter STA, Netzsch, Selb, Germany) by applying a two scan procedure as described elsewhere [39]. Optical absorption spectra were recorded on two UV/Vis/NIR spectrometers (Lambda 950, PerkinElmer, Waltham MA, USA, & Cary Bio 50, Varian Inc., Palo Alto CA, USA). Photoluminescence spectroscopy in the Vis spectral range was measured on samples treated in 10/90 H_2/N_2 atmosphere on a Vis fluorescence spectrometer (Cary Eclipse, Varian Inc., Palo Alto CA, USA). For measurement of photoluminescence in the infrared spectral region, a spectrofluorometer equipped with an IR photomultiplier tube (PMT, H10330A, Hamamatsu, Shizuoka, Japan on Fluorolog-3, Horiba Jobin Yvon, Unterhaching, Germany) was employed on selected samples. Finally, X-ray diffraction patterns were collected on selected samples at a step size of 0.002°/s (Siemens Kristalloflex D500, Bragg-Brentano, 30 kV/30 mA, Cu Kα).

3. Results and discussion

3.1. As-prepared glasses

Optical absorption spectra of the as-prepared glasses are shown in Fig. 1. Except for Al0, all glasses appear fully transparent and colorless to the naked eye (inset of Fig. 1). The as-melted Al0 glass exhibits a brown tint. Absorption spectra of Al5, Al10, and Al15 follow a similar trend with a UV cut-off around 330 nm, whereas Al0 exhibits an additional broad absorption band over the spectral range of 330 to ~750 nm. No sharp bands can be distinguished in all curves, although for Al0, a shoulder peak is observed around 390 nm.

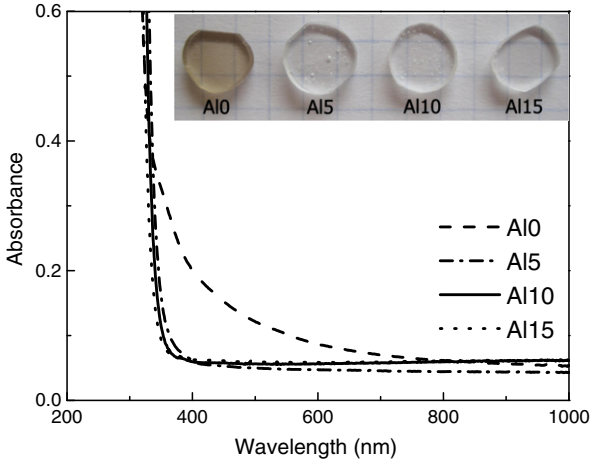

Fig. 1. Optical absorbance as a function of wavelength for the as-prepared glasses. Inset: photograph of the samples with four different Al_2O_3 contents.