Materials Research Bulletin 70 (2015) 47–54

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Erbium-doped borosilicate glasses containing various amounts of P_2O_5 and Al_2O_3: Influence of the silica content on the structure and thermal, physical, optical and luminescence properties

Kevin Bourhis [a], Jonathan Massera [b,c], Laeticia Petit [d,e,*], Joona Koponen [e], Alexandre Fargues [f], Thierry Cardinal [f], Leena Hupa [d], Mikko Hupa [d], Marc Dussauze [g], Vincent Rodriguez [g], Monica Ferraris [a]

[a] Politecnico di Torino, DISAT, Istituto di Ingegneria e Fisica dei Materiali, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy
[b] Department of Electronics and Communications Engineering, Tampere University of Technology, Korkeakoulunkatu 3, FI-33720 Tampere, Finland
[c] BioMediTech, Tampere, Finland
[d] Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Turku, Finland
[e] nLIGHT Corporation, Sorronrinne 9, FI-08500 Lohja, Finland
[f] CNRS, Université de Bordeaux, ISM, 351 Cours de la Libération, F-33405 Talence, France
[g] CNRS, Université de Bordeaux, ICMCB, 87 Avenue du Dr Schweitzer, F-33608 Pessac, France

ARTICLE INFO

Article history:
Received 1 November 2013
Received in revised form 16 March 2015
Accepted 9 April 2015
Available online 11 April 2015

Keywords:
A. Glasses
B. Luminescence and optical properties
C. Infrared spectroscopy
C. Photoelectron spectroscopy
D. Luminescence

ABSTRACT

The influence of the silica content on several properties of Er-doped borosilicate glasses in the presence of various amounts of P_2O_5 and Al_2O_3 has been investigated. The introduction of P_2O_5 and/or Al_2O_3 are responsible for structural modifications in the glass network through a charge-compensation mechanism related to the formation of negatively-charged PO_4 and AlO_4 groups or through the formation of $AlPO_4$-like structural units. In this paper, we show that an increase in the SiO_2 content leads to a silicate-rich environment around the Er^{3+} site, resulting in an increased dependence of the Er^{3+} ions optical and luminescence properties on the P_2O_5 and/or Al_2O_3 concentration. The highest emission intensity at 1.5 μm was achieved for the glass with an equal proportion of P and Al in the glass system with 60 mol% of SiO_2.

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1. Introduction

Rare-earth (RE) ions (e.g. Nd^{3+}, Er^{3+}, Yb^{3+}, Tm^{3+}) have been widely used as the active ions in glasses for several decades in optoelectronic devices [1,2]. Continuous efforts are done all over the world to produce new erbium-doped silica-based fibers for solid-state lasers and amplifiers with improved performances [1,3]. It is well known that the optical properties of erbium ions in glasses (e.g. spectral shapes and cross-sections of the absorption, emission spectra or excited state lifetimes) strongly depend on the glass host material [4,5]. Thus, effort has been focused on modifying the silica glass composition in order to improve the Er^{3+} ions luminescence properties. Most of the work reported on Er^{3+}-doped fiber lasers and amplifiers has used high silica-content glasses co-doped with various combinations of Ge, P, and Al [2,3,5]. The technological limitations in the production of Er-doped silicate fibers arise from the high tendency of erbium to form aggregates (like Er–Er pairs) in most solid hosts when doping the silica glass with a high Er_2O_3 concentration. Er–Er energy transfers most often result in the non-radiative de-excitation of the ions pair which constitutes an energy loss mechanism leading to a luminescence quenching. To prevent such clustering, alumina or phosphorus pentoxide can be introduced into the fiber core [6]. It has been shown that the addition of 8–10 Al or 15 P per RE (mainly for Yb^{3+} and Nd^{3+}) ion in silica glasses can prevent RE clustering [7–10] due to strong modifications in the structure of the silica network [11]; for example the introduction of aluminum cations in $Na_2O—SiO_2$ glasses leads to the formation of negatively-charged $[AlO_4]$ groups [12]. The glass structure undergoes a charge compensation mechanism resulting in the transformation of the silicate units with non-bridging oxygen atoms (noted Si-NBO) into units with bridging oxygen atoms (noted Si-BO). The Na^+ ions located close to the Si-NBO atoms are transferred to the $[AlO_4]$ tetrahedra [12,13].

Co-doping silica glass simultaneously with Al_2O_3 and P_2O_5 presents an interesting cooperative behavior. Likhachev et al.

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* Corresponding author.
E-mail address: laeticia.petit@nlight.net (L. Petit).

http://dx.doi.org/10.1016/j.materresbull.2015.04.017
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showed that the rare-earth dissolution in the ternary Al_2O_3—P_2O_5—SiO_2 host systems was higher than in the binary P_2O_5—SiO_2 or Al_2O_3—SiO_2 glasses [14]. Although doping with Al_2O_3 or P_2O_5 increases the refractive index (RI) of silica glasses, co-doping the silica glass with Al_2O_3 and P_2O_5 leads to the formation of a glass with a lower RI than silica, probably due to the formation of [$AlPO_4$] units in the glass network [6,15]. [$AlPO_4$] units are created at the expense of [PO_4] and [AlO_4] units, resulting in the formation of Al—O—P bridging bonds with similar bond strength than those in Si—O—Si bonds [15]. This offers the possibility of doping the glass with higher concentrations of P_2O_5 and Al_2O_3 to improve the RE dissolution, thus limiting the RE clustering in the fiber while maintaining a low refractive index. Silica-based glasses exhibit some constraints: glasses with a low SiO_2 content tend to undergo devitrification, whereas the viscosity of glass melts with a high SiO_2 content is high and requires high processing temperatures. However, the difficulties in melting glasses with high silica contents can be overcome by extending the glass forming domain by adding B_2O_3 which helps in decreasing the melt viscosity [16].

The properties of borosilicate glasses of compositions (in mol%) zSiO$_2$–$(100-z) \times [(43.6Na_2O–56.1B_2O_3–0.25Er_2O_3)]$ and zSiO$_2$–$(100-z) \times [41Na_2O–52.7B_2O_3–0.235Er_2O_3–(6-x)P_2O_5–xAl_2O_3]$, where x ranges from 0 to 6 have been discussed as a function of x for $z = 50$ in our previous paper [17]. The changes in some physical and optical properties with x were attributed to changes in the structure of the glasses. The main parameters affecting the luminescence at 1.5 μm have been related to the structural modifications of the glass network induced by the introduction of P_2O_5 and/or Al_2O_3 in agreement with Ref. [18].

The aim of this paper is to investigate the effect of the SiO_2 content on the physical, thermal, optical and luminescence properties of the borosilicate glasses with elevated SiO_2 content ($z = 60$). The effect of the silicate groups (acting as ligands) at the expense of the borate ones in the coordination sphere of the RE ions is expected to impact the optical and luminescence properties in a different way in the glasses with a larger SiO_2 content than in the ones with a lower SiO_2 content.

2. Experimental

2.1. Glass preparation

The glass composition studied was zSiO$_2$–$(100-z) \times [(43.6Na_2O–56.1B_2O_3–0.25Er_2O_3)]$ (in mol%) and zSiO$_2$––$(100-z) \times [41Na_2O–52.7B_2O_3–0.235Er_2O_3–(6-x)P_2O_5–xAl_2O_3]$, where $z = 50$ and 60 and x ranges from 0 to 6 (in mol%). For the P/Al co-doped glasses, a fraction of the B_2O_3, Na_2O and Er_2O_3 content is substituted by P_2O_5 and/or Al_2O_3. $NaH_2PO_4{\cdot}H_2O$ (Merck, 99%), H_3BO_3 (Aldrich, 99.99%), Na_2CO_3 (Sigma–Aldrich, >99.5%), Al_2O_3 (Sigma–Aldrich, >99%), SiO_2 (Sigma–Aldrich, 99%) and Er_2O_3 (MV Laboratory, 99.999%) were used as raw materials in powder form. Before melting, the batches were treated at 400 °C for 15 h and then melted in ambient atmosphere in alumina crucibles for 30 min between 1450 and 1475 °C, depending on the glass composition. After quenching on a pre-heated brass mold, the glasses were annealed for 3 h at 40 °C below their respective glass transition temperature (T_g) to remove the internal stress. Finally the samples were cut, ground and polished. The glass compositions were checked by electron-probe micro-analysis and were found to be in accordance with the theoretical ones, within the accuracy of measurement (~0.1 wt%). The Er^{3+} concentration is the same in all glasses except for the glass matrices for which it is slightly higher than in the substituted glasses.

2.2. Optical properties

A fully automated Metricon, model 2010 prism-coupled refractometer was used to measure the refractive index (RI) at 1312 nm. The accuracy of the measurement is estimated to be ±0.003. Each measurement was repeated 5 times and at least 3 measurements were performed on different areas of the glass. When the standard deviation (SD) of the measurements was superior to 0.003, the SD was used as uncertainty.

The absorption spectra were measured on 2 mm-thick samples with a double-beam spectrophotometer (CARY 5000 UV–vis–NIR) over the 250–2500 nm spectral region. The absorption spectra over the 2500–4000 cm^{-1} range were performed on a FTIR Bruker Alpha-T spectrometer with a spectral resolution of 2 cm^{-1}. The measurements were performed at room temperature and were corrected for the Fresnel losses. The absorption cross-sections, $\sigma_{abs}(\lambda)$, were calculated from the absorption spectra using Eq. (1).

$$\sigma_{abs}(\lambda) = 2.303 \times \frac{\log(I_0 I)}{NL} = \frac{\alpha(\lambda)}{L} \quad (1)$$

where $\log(I_0/I)$ is the absorbance, N the rare earth ion concentration calculated from the composition and the density of the glass, L the thickness of the sample and $\alpha(\lambda)$ the absorption coefficient.

2.3. Thermal and physical properties

The glass transition (T_g) and glass crystallization (T_x) temperatures were measured by differential thermal analysis (Mettler Toledo TGA/SDTA851) at a heating rate of 15 °C min^{-1}. The T_g was taken at the inflection point of the endotherm, as obtained by taking the first derivative of the DSC curve. The T_g was determined with an accuracy of 2 °C. The T_x was measured at the maximum point of the exotherm point. The T_x was determined with an accuracy of 5 °C, and was hardly or not distinguishable in some cases.

2.4. Luminescence properties

The emission spectra in the 1400–1700 nm range were measured at room temperature using an AOC (Applied Optronics Corp.) laser diode excitation source emitting at 980 nm, an Edinburgh Instruments monochromator (M300) and a liquid nitrogen cooled germanium detector (ADC 403L). The emission spectra of the samples were collected on powder between quartz plates to allow for quantitative comparisons between the glasses of the different series.

2.5. Structural properties

The X-ray photoelectron spectra were obtained using a PHI 5000 VersaProbe (PHI Electronics) spectrometer. Monochromatic Al Kα radiation (1486.6 eV) was operated under a residual pressure of 5×10^{-9} mbar. The spectrometer was calibrated using the photoemission lines of Au (Au $^4f_{7/2} = 83.9$ eV, with reference to the Fermi level). Survey spectra were recorded from 0 to 1400 eV with a pass energy of 187.5 eV using 1 eV steps and four scans. High resolution spectra of the O 1s, C 1s and Si2p bands were recorded with a pass energy of 23.50 eV. Scan accumulation enabled to reach a satisfactory signal/noise ratio. Binding energies have been corrected using adventitious hydrocarbon carbon (C 1s peak at 284.8 eV) as a reference.

The reflectance infrared (IR) spectra were recorded with a spectral resolution of 2 cm^{-1} on a Nicolet 6700 FTIR spectrometer equipped with a DTGS detector and a germanium-coated KBr beam splitter or hybrid FIR beam splitter, using an external reflection

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