Journal of Non-Crystalline Solids 460 (2017) 161–168

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Effect of the addition of Al_2O_3, TiO_2 and ZnO on the thermal, structural and luminescence properties of Er^{3+}-doped phosphate glasses

Pablo Lopez-Iscoa [a], Laeticia Petit [b,c], Jonathan Massera [c], Davide Janner [a], Nadia G. Boetti [d], Diego Pugliese [a], Sonia Fiorilli [a], Chiara Novara [a], Fabrizio Giorgis [a], Daniel Milanese [a,e,*]

[a] Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia (DISAT) and INSTM UdR Torino Politecnico, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[b] Optoelectronics Research Centre, Tampere University of Technology, Korkeakoulunkatu 3, 33720 Tampere, Finland
[c] Department of Electronics and Communications Engineering, Tampere University of Technology, Korkeakoulunkatu 3, 33720 Tampere, Finland
[d] Istituto Superiore Mario Boella, Via P. C. Boggio 61, 10134 Torino, Italy
[e] IFN - CNR, CSMFO Lab., Via alla Cascata 56/C, 38123 Povo, TN, Italy

ARTICLE INFO

Article history:
Received 20 November 2016
Received in revised form 13 January 2017
Accepted 19 January 2017
Available online xxxx

Keywords:
Phosphate glass
Raman spectroscopy
Infrared spectroscopy
Er luminescence property

ABSTRACT

Er-doped phosphate glasses were fabricated by melt-quenching technique. The changes in their thermal, structural and luminescence properties with the addition of Al_2O_3, TiO_2 or ZnO were studied. Physical and thermal properties were investigated through density measurement and differential thermal analysis. Structural characterization was performed using the Raman and Infrared spectroscopy. In order to study the influence of the composition on the luminescence properties of the glasses, the refractive index, the luminescence spectra and the lifetime values were measured.

The results show that with the addition of Al_2O_3 and TiO_2 the phosphate network becomes more connected increasing the glass transition temperature, whereas the addition of ZnO does not show significant changes in the optical, thermal and structural properties but it leads to a larger emission cross-section at 1540 nm as compared to the other glasses. As the site of the Er^{3+} is not strongly affected by the change in the glass composition, we think that the emission properties of the glasses depend on the glass structure connectivity, which has an impact on the Er^{3+} ions solubility.

1. Introduction

Since the initial discovery of the Bioglass®, with a composition known as 45S5 corresponding to 45.0 wt% SiO_2, 24.5 wt% CaO, 24.5 wt% Na_2O and 6.0 wt% P_2O_5 [1], the interest in bioglasses for tissue regeneration has increased [2–5]. Besides silicate glasses, phosphate glasses with a P_2O_5 content equal to 50 mol% have shown to be bioactive, degradable and suitable for fiber drawing [6–12]. These bioactive glasses form a hydroxyapatite layer, which is capable of bonding to the connective tissue when placed into body fluids [13]. They have been studied in many biomedical applications, especially for use in bone repair and reconstruction [14] as well as for peripheral nerve regeneration, because they allow neuronal cells growth along the fiber's axis [9,15]. The glass system employed in this study is based on the composition 50 P_2O_5–40 SrO–10 Na_2O (in mol%), whose bioactivity was previously assessed by J. Massera et al. [10]. However, the influence of the addition of erbium and metal oxides on the thermal, structural and luminescence properties of this glass system has never been reported before.

Phosphate glasses are of interest for the engineering of photonic devices, thanks to the following properties: easy processing, good thermal stability and excellent optical characteristics, such as high transparency in the UV-Visible-Near Infrared (UV-Vis-NIR) region [16–20]. Besides, phosphate glasses allow high rare earth (RE) ions solubility. Thus, quenching phenomenon does only occur at very high concentrations of RE ions [20,21]. Due to these properties, phosphate glasses have recently become appealing for optical communications [22] and laser sources as well as optical amplifiers [20,21,23–25]. However, to the best of our knowledge, up to now only few studies focusing on glass compositions that combine both biocompatibility and suitable optical properties have been reported [8,26,27].

The dopant environment around the RE ions plays a significant role in the RE-doped glasses. Specifically, parameters such as the covalency, mass and charge of the ligand atoms affect the luminescence properties as well as the solubility of RE ions in glassy hosts [28]. By adding different metal oxides such as Al_2O_3, TiO_2 and ZnO, phosphate based glasses are able to modify their structural network, thus changing the glass

* Corresponding author at: Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia (DISAT) and INSTM UdR Torino Politecnico, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.
E-mail address: daniel.milanese@polito.it (D. Milanese).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.01.030
0022-3093/

chemical durability, biocompatibility and other properties [29–33]. In this study, the dopants were selected on the basis of their high covalency and their ability to change the structure of the phosphate glass matrix. In particular, Al_2O_3 and TiO_2 are known to create cross-linking bonds such as Al—O—P [29,34] and Ti—O—P [35], respectively, while ZnO is considered as a modifier and is responsible for the depolymerization of the glass network [36].

In this paper, we report on the effect of the addition of Al_2O_3, TiO_2 and ZnO on the thermal, structural and luminescence properties of erbium-doped phosphate glasses.

2. Experimental

2.1. Glass preparation

Glasses with the compositions in mol% (0.5 P_2O_5–0.4 SrO–0.1 $Na_2O)_{100-x}$–$(TiO_2/Al_2O_3/ZnO)_x$, with x = 0 and x = 1.5 mol%, were prepared. A fixed amount of Er_2O_3, 0.25 mol%, was added to the 100 mol% composition for all the glasses manufactured. The glasses with 1.5 mol% Al_2O_3, TiO_2 and ZnO were labeled as AlG, TiG and ZnG, respectively, while the glass with x = 0 was labeled as RefG. The glasses were prepared by the conventional melt-quenching technique using $NaPO_3$ (Alfa Aesar), $SrCO_3$ (Sigma-Aldrich, ≥99.9%), Er_2O_3 (MV Laboratories Inc., 99.999%), Al_2O_3 (Sigma-Aldrich, ≥99.5% α-phase), TiO_2 (Sigma-Aldrich, 99.99% rutile) and ZnO (Sigma-Aldrich, ≥99%). $Sr(PO_3)_2$ precursor was independently prepared using $SrCO_3$ and $(NH_4)_2HPO_4$ as raw materials and with a heating up to 850 °C. The chemicals were ground and mixed to prepare a 40 g batch, then placed in a quartz crucible and heated up to 1100 °C for 30 min with a heating rate of 10 °C/min. The melt was poured into a preheated brass mold and annealed at 400 °C for 5 h to decrease the residual stress. Finally, the glasses were cooled down to room temperature. All the glasses were cut and optically polished or ground, depending on the characterization technique.

2.2. Physical and thermal properties

The density of the glasses was measured using Archimedes' method with an accuracy of ±0.02 g/cm^3, using distilled water as immersion liquid.

The glass transition temperature (T_g) and crystallization temperature (T_p) were measured by differential thermal analysis (DTA) using a Netzsch JUPITER F1 instrument. The measurement was carried out in a Pt crucible at a heating rate of 10 °C/min. T_g was determined as the inflection point of the endotherm obtained by taking the first derivative of the DTA curve, while T_p was taken as the maximum peak of the exotherm. All measurements were performed with an error of ±3 °C.

2.3. Structural properties

The structural properties of the glasses were assessed using Fourier Transform Infrared (FTIR) spectroscopy, both in Transmission mode and Attenuated Total Reflection mode (FTIR-ATR), and Raman spectroscopy. FTIR-ATR spectra were acquired on glass powders with a Bruker Tensor 27 spectrometer equipped with a liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector, operating at 2 cm^{-1} resolution, equipped with an ATR cell. The spectra were recorded in the range from 600 to 1400 cm^{-1} and were normalized to the band with maximum intensity (~880 cm^{-1}).

Raman spectra were acquired with a Renishaw inVia Reflex micro-Raman spectrophotometer (Renishaw plc, Wotton-under-Edge, UK) equipped with a cooled CCD camera using a 785 nm excitation line. The spectra were recorded in the range 600–1400 cm^{-1} and were normalized at the maximum point (~1170 cm^{-1}).

Semi-quantitative analysis was carried out by using a Scanning Electron Microscope (FESEM, Zeiss Merlin 4248) equipped with an Oxford Instruments X-ACT detector and Energy Dispersive Spectroscopy Systems (EDS/EDX) in order to determine the final composition of the glasses. The composition of all the glasses was found to be in agreement with the nominal one, within the accuracy of the measurement (±1.5 mol%). Despite the use of quartz crucibles, no Si was found in the EDS analysis of the investigated glasses.

2.4. Optical and luminescence properties

The refractive index (n) of the glasses was measured at 5 different wavelengths (633, 825, 1061, 1312 and 1533 nm) by prism-coupling technique (Metricon, model 2010). Ten scans were performed for each wavelength. Estimated error of the measurement was ±0.001. The experimental data were fitted using Sellmeier's equation:

$$n^2(\lambda) = 1 + \frac{B_1 \cdot \lambda^2}{\lambda^2 - C_1} + \frac{B_2 \cdot \lambda^2}{\lambda^2 - C_2} + \frac{B_3 \cdot \lambda^2}{\lambda^2 - C_3} \quad (1)$$

where λ is the wavelength and $B_{1,2,3}$ and $C_{1,2,3}$ are the experimentally determined Sellmeier's coefficients.

The absorption spectra in the range 2500–4000 cm^{-1} were recorded by means of a FTIR spectrometer (Alpha, Bruker Optics, Ettlingen, Germany) working in transmission mode and equipped with a DTGS detector. The measurements were performed at room temperature and corrected for Fresnel losses and glass thickness.

The UV-Vis absorption spectra were measured at room temperature from 190 to 1600 nm using an UV-Vis-NIR Agilent Cary 5000 spectrophotometer (Agilent, Santa Clara, CA, USA). The absorption cross-section (σ_{Abs}) was calculated from the experimentally measured absorption coefficient and from Er^{3+} ions concentration in the glass, using the following formula:

$$\sigma_{Abs}(\lambda) = \frac{2.303}{NL} \log\left(\frac{I_0}{I}\right) \quad (2)$$

where $\log(I_0/I)$ is the absorbance, L is the thickness of the sample (in cm) and N is the rare-earth ion concentration (ions/cm^3). The Er^{3+} ions concentration was calculated from the measured glasses density.

The emission spectra in the 1400–1700 nm range were measured with a Jobin Yvon iHR320 spectrometer equipped with a Hamamatsu P4631-02 detector and a filter (Thorlabs FEL 1500). Emission spectra were obtained at room temperature using an excitation monochromatic source at 976 nm, emitted by a single-mode fiber pigtailed laser diode (CM962UF76P-10R, Oclaro). The glass samples used for the absorption and emission measurements were optically polished disks of 1 mm of thickness.

The emission cross-section (σ_e) spectra were calculated from the absorption cross-section spectra using the McCumber's equation [37]:

$$\sigma_e = \sigma_{Abs} \cdot exp\frac{(\varepsilon - E)}{kT} \quad (3)$$

where σ_{Abs} is defined by Eq. (2), ε is the photon energy at which the two spectra cross at temperature T, E is the energy in eV and k is the Boltzmann's constant.

The fluorescence lifetime of Er^{3+}:$^4I_{13/2}$ energy level was obtained by exciting the samples with a fiber pigtailed laser diode operating at the wavelength of 976 nm, recording the signal using a digital oscilloscope (Tektronix TDS350) and fitting the decay traces by single exponential. Estimated error of the measurement was ±0.20 ms. The detector used for this measurement was a Thorlabs PDA10CS-EC.

3. Results

The physical and thermal properties of the investigated glasses are reported in Table 1. The addition of Al_2O_3 (AlG), TiO_2 (TiG) or ZnO (ZnG) has no impact on the density. However, the addition of Al_2O_3