Journal of Molecular Structure 1160 (2018) 428–433

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

The influence of Ag content and annealing time on structural and optical properties of SGS antimony-germanate glass doped with Er^{3+} ions

J. Zmojda [a,*], M. Kochanowicz [a], P. Miluski [a], A. Baranowska [b], A. Basa [c], R. Jadach [d], M. Sitarz [d], D. Dorosz [d]

[a] Faculty of Electrical Engineering, Bialystok University of Technology, Wiejska Street 45D, 15-351 Bialystok, Poland
[b] Faculty of Mechanical Engineering, Bialystok University of Technology, Wiejska Street 45B, 15-351 Bialystok, Poland
[c] Institute of Chemistry, University of Bialystok, ul. Ciołkowskiego 1K, 15-245 Bialystok, Poland
[d] Faculty of Materials Science and Ceramics, AGH University of Science and Technology, 30 Mickiewicza Av., 30-059 Krakow, Poland

ARTICLE INFO

Article history:
Received 29 December 2017
Received in revised form
7 February 2018
Accepted 8 February 2018
Available online 9 February 2018

Keywords:
Local field effect
Ag nanoparticles
Erbium ions
Antimony-germanate glass
Luminescence properties
Raman spectra

ABSTRACT

A series of erbium doped SGS antimony-germanate glass embedding silver (Ag^0) nanoparticles have been synthesized by a one-step melt-quench thermochemical reduction technique. The effect of NPs concentration and annealing time on the structural and photoluminescent (PL) properties were investigated. The Raman spectra as a function of temperature measured *in-situ* allow to determine the structural changes in vicinity of Ag^+ ions and confirmed thermochemical reduction of Ag^+ ions by Sb^{3+} ions. The surface plasmon resonance absorption band was evidenced near 450 nm. The impact of local field effect generated by Ag^0 nanoparticles (NPs) and energy transfer from surface of silver NPs to trivalent erbium ions on near-infrared and up-conversion luminescence was described in terms of enhancement and quench phenomena.

1. Introduction

In the fields of nanotechnology and nanophotonics, the new glasses with noble metal nanoparticles are very attractive material with unique optical properties and huge potential of applications such as solar cells, frequency up-converters, biosensors, optical waveguides and amplifiers [1–8]. The reason is that the collective oscillation of the noble metal free electrons resonantly excited by visible light causes a tremendous enhancement of the electromagnetic near-field in the vicinity of nanoparticles. If this phenomenon, called surface plasmon resonance (SPR), exists in inorganic glasses doped with rare-earth (RE) ions, the luminescence signal may be amplified or quenched. In fact there are many important key factors, such as particles size and geometry, refractive index of glass, concentration of metal ions and excitation wavelength, which influence the interaction mechanisms of dopants with light and the energy transfer between RE ions and nanometals [9]. Another important factor is the proper selection of the inorganic host for metal nanoparticles embedding. Up to now, the SPR phenomenon has been investigated in many different hosts such as tellurite [10], phosphate [11], silicate [12,13] and antimony [14] glasses. Especially, antimony oxide based glasses have attracted a considerable interest for their combination of chemical durability, low phonon energies (~600 cm^{-1}) and high transparency in a wide range. However, the low field strength (0.73) of Sb^{3+} makes it a poor glass former and it is unable to exist, particularly in the bulk monolithic form which is very much essential for practical applications. In our earlier investigations, we proposed the solution of this problem and synthesized a glass with a combination of different phonon energy of glass-forming elements [15,16]. Another important fact is that Sb_2O_3 is a mild reducing agent of noble metal ions. This mild reduction property enables in-situ reduction of Ag^+ ($AgNO_3$) to Ag^0 in a single-step during the melting process, thereby providing a simple, low cost method for the preparation of bulk photonic materials.

Among rare-earth ions, the erbium is considered as the most

* Corresponding author.
E-mail address: j.zmojda@pb.edu.pl (J. Zmojda).

https://doi.org/10.1016/j.molstruc.2018.02.030

important element due to its energy level structure which allows to generate strong luminescence in vis-NIR spectral range [17]. Due to fine overlapping of energy state from visible spectra (green and red emission of erbium ions) with SPR absorbance band of silver and gold nanoparticles the local field effect in the vicinity of Er^{3+} ions was observed in lead germanate glass [18] and antimony glass containing silver [14] and gold [19] NPs. These and other studies shows that the mechanism of luminescence enhancement or quenching is complex and there are plenty of rooms for further investigations.

In our experiment we focused on the effect of Ag concentration, as well as the heat-treatment (hT) duration, on near-infrared (NIR) and up-conversion (UC) luminescent properties of Er^{3+} doped SGS antimony-germante glasses. All glasses were synthetized by standard melt-quenching method and nanoparticles creation was taken by thermochemical reduction during heat-treatment process. Structural properties have been analysed by XRD and Raman spectra. *In situ* Raman measurements as a function of temperature were conducted to confirm Sb_2O_3 role as a reduction agent of silver ions. The local field effect responsible for luminescence enhancement of erbium ions in NIR (1533 nm) and visible (546 nm) spectral range as well as energy transfer mechanisms between metal NPs and RE ions have been also described.

2. Experimental

The molar glass composition of SGS glass: $25Sb_2O_3 - 25GeO_2 - 39.2SiO_2 - 5Al_2O_3 - 5Na_2O - 0.8Er_2O_3 - xAgNO_3$ where: x = 0; 0.1; 0.2 and 0.4 were prepared by a conventional melt quenching technique. The optimal erbium oxide concentration was determined at the level 0.8 mol % [20]. All reagents are characterised by 99.99% of chemical purity. A homogenized set (10 g) was placed in a platinum crucible and melted in an electric furnace in temperature range 1350–1550 °C for 60 min in oxide atmosphere. In order to obtain dimension repeatability, the glass melt was poured into a brass mold and then subjected to annealing process in conditions nearly to transition temperature of each sample for 12 h. A uniform and transparent glass without visible effect of crystallization was obtained. Characteristic temperatures of fabricated glasses were analysed by DSC measurement performed with 10 °C/min using the SETARAM Labsys thermal analyser. In order to optimize growth of silver nanoparticles in glass matrix all samples were heated at the temperature of 450 °C from 1 h to 2 h. The XRD patterns of fabricated glasses were measured in the range from 10° to 80° using an X'Pert Pro diffractometer. The Cu X-ray tube with Kα radiation was used. Raman studies "*in situ*" as a function of temperature were carried out using Horriba Yvon Jobin LabRAM HR micro-Raman spectrometer equipped with a CCD detector. Excitation wavelength of 532 nm was used and beam intensity was about 10 mW. Acquisition time was set to 30 s. The TEM images were collected by Tecnai G2 20 X-TWIN 200 kV TEM (FEI) operating at 200 kV, equipped with a source: LaB6. The sample was deposited on TEM carbon coated 300 mesh copper grid. Measurement of the spectral absorbance was performed using the Acton Spectra Pro 2300i monochromator with Si detector in the range of 0.35–1.1 μm. The up-conversion luminescence spectra of the glasses in a range of 500–700 nm were measured using the Stelarnet GreenWave monochromator and laser diode (λ_{exc} = 976 nm). The NIR luminescence was performed using the Acton Spectra Pro 2300i monochromator with InGaAs detector in the range of 1.4–1.7 μm.

3. Results and discussion

DSC curve of the SGS glass doped with Er_2O_3 and $AgNO_3$ recorded in the range of 200 – 1100 °C and at a heating rate of 10 °C/min is shown in Fig. 1. The glass transition temperature T_g = 430 °C and two crystallization onset T_{x1} = 600 °C and T_{x2} = 885 °C have been determined. Difference between T_{x1} and T_g ($\Delta T = T_{x1} - T_g$) is known parameter determining thermal stability of the glass [21,22]. To achieve a large working range during operation such as fiber drawing, it is desirable to have ($\Delta T = T_{x1} - T_g$) value as large as possible [23]. In our case the thermal stability parameter ΔT is 170 °C and is higher than in HMO (ΔT = 125 °C) [24], tellurite (ΔT = 126 °C) [10] or phosphate (ΔT = 107 °C) [11] glasses. Based on the glass transition temperature, the annealing temperature to diffuse and grow the silver NPs was selected to be 450 °C (red point on Fig. 1).

Fig. 2 shows the absorbance spectra of antimony-germanate-silicate glasses doped only with 0.8mol%Er_2O_3 (black line) and co-doped with 0.8mol%Er_2O_3/0.1mol%$AgNO_3$ before (red line) and after (green line) heat-treatment process. In analysed spectral range 350 nm–1000 nm several absorption bands were localized at the wavelengths of 365 nm, 380 nm, 408 nm, 452 nm, 488 nm, 522 nm, 544 nm, 651 nm 800 nm 978 nm, corresponding to transitions from the ground state energy level of Er^{3+}: $^4I_{15/2}$ to higher localized energy levels $^2G_{9/2}$, $^2G_{11/2}$, $^2H_{9/2}$, $^4F_{3/2}$+$^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$, respectively. Absorption band at the wavelength of 978 nm (GSA $^4I_{15/2} \rightarrow {}^4I_{11/2}$) has been used for optical excitation process with high power semiconductor diode laser (λ_{exc} = 980 nm). The sample labelled as 08Er01Ag_hT (after heat-treatment) displays the well-defined broad plasmon absorption band which confirms the formation of silver nanoparticles (NPs) inside glassy matrix. It is known, that the surface plasmon resonance peak (SPR) is depend on the refractive index (RI) of glass [25]. In silica-based glasses with RI around 1.5 the maximum of SPR band of Ag NPs is at 410 nm [26]. The increase in RI of host shift the plasmon peak to the longer wavelength, even 545 nm for KBS glasses (n = 1.947) [14]. In our SGS glass the refractive index is around 1.707 hence the maximum of plasmon peak has been localized near 450 nm. This SPR band is perfectly matched with the integrated absorption band of erbium $^4F_{3/2}$ and $^4F_{5/2}$ multiplets, thus allowing coupling at absorption [27].

The X-ray diffraction (XRD) patterns of the fabricated erbium-doped SGS antimony-germanate glasses without Ag ions and co-doped with Ag ions and annealed for 2 h are presented in Fig. 3. In all samples, the presence of broad and continuous halo effect in the range of 20–35° confirms the amorphous nature of fabricated glasses.

In order to confirm the presence of silver NPs, transmission

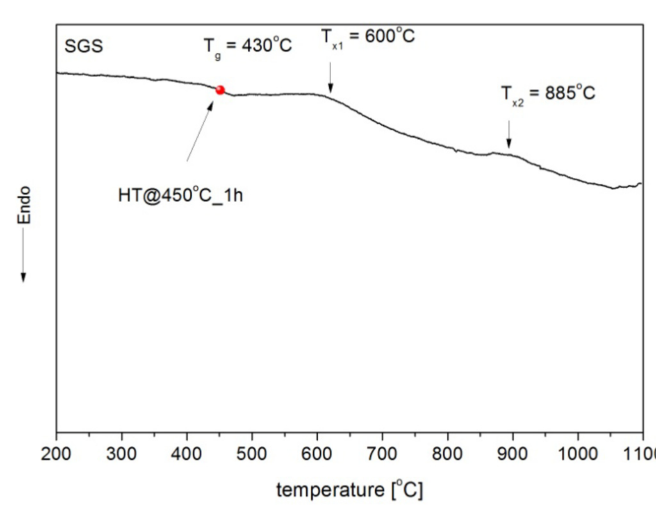

Fig. 1. DSC curve of SGS glass.