Journal of Alloys and Compounds 611 (2014) 111–116

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Photoluminescence study of Er-doped zinc–sodium–antimonite glasses

J. Zavadil [a,*], Z.G. Ivanova [b], P. Kostka [c], M. Hamzaoui [d], M.T. Soltani [d]

[a] Institute of Photonics and Electronics AS CR, Prague, Czech Republic
[b] Institute of Solid State Physics Bulgarian Academy of Sciences, Sofia, Bulgaria
[c] Institute of Rock Structure and Mechanics AS CR, Prague, Czech Republic
[d] Laboratoire de Physique Photonique et Nanomatériaux, Universite de Biskra, Algeria

ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form 13 May 2014
Accepted 14 May 2014
Available online 23 May 2014

Keywords:
Antimonite glasses
Rare-earth ions
Erbium
Photoluminescence
Stark levels

ABSTRACT

Bulk samples of Er-doped zinc–sodium–antimonite glasses have been investigated by transmission and photoluminescence (PL) spectroscopy. Two series of compositions, $(Sb_2O_3)_{90-x}(Na_2O)_{10}(ZnO)_x$ and $(Sb_2O_3)_{80-x}(Na_2O)_{20}(ZnO)_x$, doped with 0.25 mol% Er_2O_3, have been chosen for this study. Transmission spectra exhibit sharp absorption bands centred at 450, 489, 521, 545, 652, 795, 975 and 1530 nm, which correspond to absorption of Er^{3+} ions and they are attributed to the optical transitions from the ground state $^4I_{15/2}$ to the excited states $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$, respectively. The optical gap has been found to vary from 3.09 to 3.15 eV with a tendency to decrease at higher Na_2O and/or ZnO contents. Four extrinsic bands due to OH^-, Si–O, CO_2, and $(CO_3)^{2-}$ carbonate group vibrations have been identified in the infrared region. Emission spectra are overwhelmed by narrow 4f–4f emission bands. Fine structure of emission bands at 980 and 1530 nm, corresponding to radiative transitions from two lowest excited states of Er^{3+} ions to the ground state manifold have been investigated at room temperature and at 4 K. A schematic energy diagram of Stark levels splitting for the three lowest manifolds $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$ has been deduced and the nature of temperature broadening of 4f–4f PL bands has been discussed.

1. Introduction

Heavy metal oxide glasses have been the subject of numerous studies due to their interesting physical, thermal and optical properties. They possess high refractive index, optical transmission reaching from visible to middle infrared region [1–4], low phonon energies, high solubility of rare earth ions (RE^{3+}) and non-linear optical properties [5,6] that make them promising materials for optical devices, such as ultrafast optical switches, power limiters and broad band optical amplifiers [7,8]. Among them, antimonite glasses attract an increasing interest because of their interesting properties including stability against devitrification and lower characteristic temperatures making glass processing easier. Infrared transmission is enhanced while refractive index keeps large values [2,3,8–10].

The glass forming ability of antimony oxide Sb_2O_3 has been predicted by Zachariasen [11] and confirmed in various oxide [12], halide or sulfide [13] systems. This compound participates in the glass network with SbO_3 structural units in form of trigonal pyramids with the oxygen situated at three corners and the lone pair of electrons of antimony at the fourth corner. The presence of this pair could enhance nonlinear optical susceptibility in the antimonite glasses, described by third rank polar tensors [14]. Antimony may also exist in fifth oxidation state, participating in the formation of glass network with SbO_4 structural units.

Alkali antimonite glasses have been the subject of several studies in the binary Sb_2O_3–A_2O or in the ternary Sb_2O_3–A_2O–M_mO_n glass systems, where A = Li, Na, K, or Cs and M = Pb or Al [15–17]. In these studies the emphasis has been put on the glass formation and some basic properties such as their high thermal stability, the extended optical window in the infrared and thermal expansion of glasses in question. There are many reports on erbium doped glasses containing Sb_2O_3 as the second glass former in antimony–borate glasses [18,19], antimony–silicate glasses [20], or antimony–phosphate glasses [21].

In a previous paper, we reported the radiative and spectroscopic properties of Er^{3+} doped $(Sb_2O_3)_{70}(Na_2O)_{20}(ZnO)_{10}$ glasses by using the Judd–Offelt analysis [22]. We investigated the effect of Er^{3+} doping level and examined the potential of these glasses as optical glasses for laser and optical amplifiers. In this work we investigate the influence of host composition, for constant Er_2O_3 doping concentration, on the transmission and photoluminescence (PL) properties. In addition, the Stark level splitting of the three lowest

* Corresponding author. Address: Institute of Photonics and Electronics AS CR, Chaberska 57, 182 51 Praha 8, Czech Republic. Tel.: +420 266 773 436; fax: +420 284 680 222.

E-mail address: zavadil@ufe.cz (J. Zavadil).

http://dx.doi.org/10.1016/j.jallcom.2014.05.102
0925-8388/

manifolds of Er^{3+} ions has been deduced from comparison of PL spectra measured at room temperature and at 4 K.

2. Experimental

Compositions of $(Sb_2O_3)_{90-x}(Na_2O)_{10}(ZnO)_x$, hereinafter referred as 10Na$_2$O series, and of $(Sb_2O_3)_{80-x}(Na_2O)_{20}(ZnO)_x$, below referred as 20Na$_2$O series, where $x = 5$, 10, 15, 20, were selected for this study. All studied glass samples were doped with 0.25 mol% Er_2O_3. Bulk glasses were prepared using the conventional melt–quenching method from starting compounds Sb_2O_3 (Acros, 99%), ZnO (Aldrich, 99%), Na_2CO_3 (Aldrich, 99.95%), and Er_2O_3 (Acros, 99.99%), melting was carried out in open quartz glass tubes under air atmosphere. The glass synthesis is described in more detail in [22]. Starting sodium carbonate was thermally decomposed during glass preparation to Na_2O and gaseous CO_2, which leaves to atmosphere. The amorphous nature of prepared samples was checked by X-ray diffraction (XRD), using a Philips PW3020 diffractometer with Cu Kα radiation. Semiquantitative analysis of prepared samples was performed using Energy-dispersive X-ray spectroscopy (EDS) detector (EDAX Apollo X) coupled with scanning electron microscope (Quanta 450).

Transmission spectra were measured by using Specord 210 Analytic Jena and Nicolet 6700 FTIR spectrometers in the VIS and IR regions, respectively. Photoluminescence spectra were measured at 4 and 300 K by using an optical He closed cycle cryostat. The 1 m focal length monochromator coupled with GaAs photomultiplier and/or a cooled high purity Ge detection system enables sensitive and high resolution measurement in the spectral range of 400–1800 nm by using the lock-in technique and computer controlled data collection. Typical spectral resolution in reported experiments was in the range of 0.04–0.08 nm and 30 measurements were typically collected for each wavelength of the spectrum. The Ar ion laser (514.5 nm line) was used for excitation.

Transmission and photoluminescence spectra were obtained by measuring polished samples whose thickness was 1.19 ± 0.06 mm for 10Na$_2$O series, and 1.18 ± 0.02 mm for samples from the 20Na$_2$O series.

3. Results

Prepared glasses exhibit a broad transparency range with short wavelength absorption edge located at around 420 nm, and the long wavelength one placed at about 6.5 μm. The position of the short wavelength absorption edge depends slightly on the glass composition – with increasing Na and/or Zn concentration it shifts towards longer wavelengths. Typical transmission spectra for the 20Na$_2$O series are presented in Fig. 1. The shifts of the absorption edge due to changes in initial glass composition for both investigated series (10Na$_2$O and 20Na$_2$O) are shown in Fig. 2. A modest shift of the absorption edge to longer wavelength could be seen with increasing Na and/or Zn concentration. In view of the fact that the fundamental absorption edge is at about 420 nm, we could not observe transitions to manifolds higher than $^4F_{5/2}$. Eight absorption

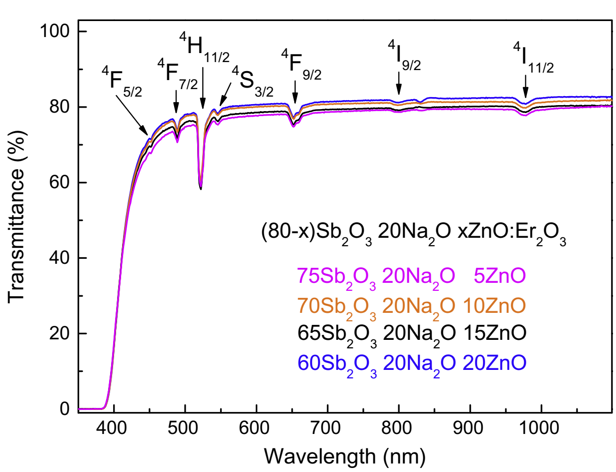

Fig. 1. Transmission spectra of $(Sb_2O_3)_{80-x}(Na_2O)_{20}(ZnO)_x$ glasses doped with 0.25 mol% of Er_2O_3 are shown for $x = 5$, 10, 15 and 20. The assignment of curves to samples is indicated in the inset. Narrow absorption bands due to 4f–4f up-transitions from the ground state of Er^{3+} ions are also indicated.

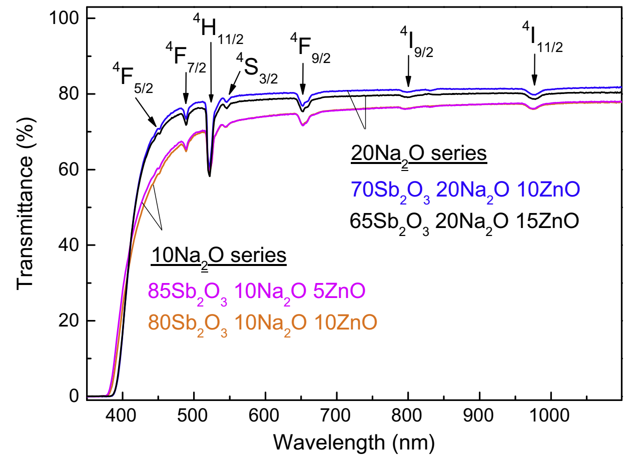

Fig. 2. Transmission spectra of two samples from 10Na$_2$O and from 20Na$_2$O series each, are shown. A small shift of the absorption edge due to changing glass composition could be seen.

bands corresponding to transitions from the ground state $^4I_{15/2}$ to excited manifolds of Er^{3+} ions have been found, within the range of transparency of studied glasses. Seven bands falling into the range of 400–1100 nm could be seen in Figs. 1 and 2. The absorption band corresponding to transition $^4I_{15/2} \rightarrow {}^4I_{13/2}$ at 1530 nm can be seen in Fig. 3, where typical infrared transmission spectra are shown.

Infrared transmission spectra of studied 10Na$_2$O and 20Na$_2$O series are found to be similar. Four noticeable absorption bands, besides Er^{3+} related transition $^4I_{15/2} \rightarrow {}^4I_{13/2}$ at 1530 nm, could be seen in Fig. 3.

Two strong absorption bands at 3 μm (3260 cm^{-1}) and 5.5 μm (1800 cm^{-1}), together with two minor ones at 2.3 μm (4348 cm^{-1}) and 4.2 μm (2380 cm^{-1}) are found. The broad bands at 3 μm and 5.5 μm correspond to OH^- groups and Si–O bonds, respectively [23]. The weak band at about 4.2 μm is due to fluctuations in concentration of atmospheric CO_2 during measurements [23]. A very weak band at 2.3 μm marked by arrow in Fig. 3, is probably due to Si–OH vibrations [24] with possible contribution from $(CO_3)^{2-}$ carbonate groups [25]. Contamination by Si comes from the crucible used for preparation of the glass.

We have also estimated the values of optical gap (E_g) from calculated absorption coefficients. Absorption coefficient was

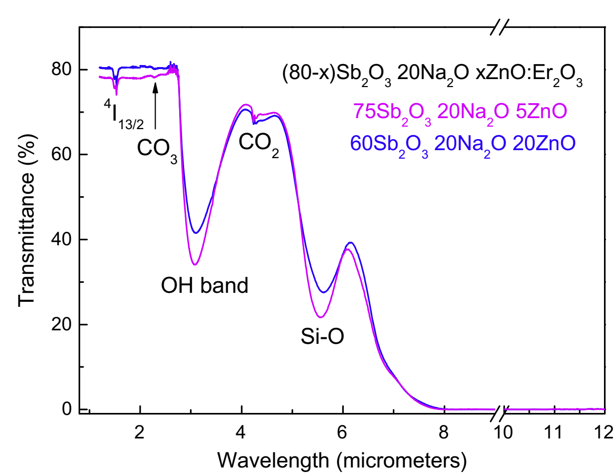

Fig. 3. Typical infrared spectra for two samples from 20Na$_2$O series are shown. Absorption band due to $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition in Er^{3+} ions is shown together with four extrinsic bands. The assignment of impurities to respective absorption bands is indicated.