OPTICAL ABSORPTION AND VISIBLE LUMINESCENCE
IN Ga-La-S-O GLASS DOPED WITH Pr^{3+} IONS

A. B. Seddon[a], D. Furniss[a], M. S. Iovu[b*], S. D. Shutov[b], N. N. Syrbu[b], A. M. Andriesh[b], P. Hertogen[c], G. J. Adriaenssens[c]

[a]Novel Photonic Glasses Group, University of Nottingham, Nottingham N67 2RD, UK
[b]Center of Optoelectronics, 1 Academiei St., MD-2028 Chisinau, Republic of Moldova
[c]Laboratorium voor Halfgeleiderfysica, K.U. Leuven, B-3001 Heverlee-Leuven, Belgium

The absorption spectra, photoinduced anisotropy and photoluminescence of Ga-La-S-O glasses with fixed cation ratio Ga/La=0.7/0.3 and two oxygen content 0.65 wt % and 2.95 wt % were studied for two Pr^{3+} doping levels of 0.1 and 1.0 wt %. The presence of oxygen induces a blue shift of the fundamental absorption edge and results in lowering of the low-energy components of the Pr^{3+} absorption bands. The glasses show bright luminescence due to Pr^{3+} ion emission similar to that in other glasses. The effect of oxygen on the luminescence spectra is determined by decreasing of host glass self-absorption of the short-wavelength bands, which becomes visible with the increase of the oxide content.

1. Introduction

Rare-earth doped Ga$_2$S$_3$:La$_2$S$_3$ (GLS) glasses have been recognized as ones of the most promising candidates for optics communication devices [1]. Pr-doped GLS posses many possible radiative electron transitions in Pr^{3+} ions. These transitions are of interest for amplifiers in near-IR spectral region at 1.3 μm and 1.5 μm telecommunication windows. GLS glasses have good rare-earth solubility, good mechanical and chemical durabilities, and high glass transition temperature. It was demonstrated that introduction of extra oxide content into GLS glass increases the glass transformation temperature (T$_g$) and plays a decisive role preventing the glass against devitrification [2]. The increase of oxygen content above the threshold amount of 0.21 wt % of oxide improved the thermal stability and optical characteristics of GLS glass. Preliminary EXAFS results showed that the oxygen bonds to all three elements and adds strong ionic component to all bonds. Incorporation of oxygen results in a decrease of the Urbach edge and in increase of the optical gap, thus improving the optical properties of the glass. It was shown that the presence of oxygen induces blue shift of the fundamental absorption edge and results in lowering of the low-energy components of the Pr^{3+} absorption bands. The effect of oxygen on the luminescence spectra is determined by the shift of the absorption edge in the short-wavelength spectra region with increasing of the oxygen contents, which becomes visible with the increase of the oxide content [3].

It has been assumed, in the theory of lasing transitions of optically active ions embedded in fibers, that the pump light does not affect the refractive index of the host material. However, large metastable photoinduced birefringence (PBi) and photorefraction (Pre) appear in chalcogenide semiconducting glasses after prolonged irradiation with above-gap and even by sub-gap light, thus changing the direction and magnitudes of internal electric fields [4,5]. Recently, an additionally fibre loss of As-Ge,Ga)-S glasses doped with Pr^{3+} in the sub-dB·m^{-1}-range was observed [6]. These losses

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* Corresponding author: iovu@as.md

increased up to shorter wavelengths, and can be explained by photodarkening effects [7]. These changes can affect the cross-section for laser effects in Pr atoms, sinse this is determined by the internal electric fields. Furthermore, the properties of fibers drawn from these glasses can also be changed. The unique combination of light amplification and rejection could be realized in rare-earth doped chalcogenide fibers, if they could process Pre and PBi values similar to undoped chalcogenide glasses [8]. In the present communication, we report the results of study of absorption, photoinduced anisotropy and photoluminescence spectra of Pr^{3+}-doped Ga-La-S glasses with a constant cationic ratio Ga/La=0.7/0.3 and varying oxygen and praseodymium content, the purpose being to investigate the effect of active species in GLS glasses.

2. Experimental

The Ga-La-S (GLS) glasses were prepared by melting from standard sulphides and oxides at 1150 °C inside vitreous carbon crucibles and annealed at 540 °C for 1 hour and cooled to ambient at 1 °C/min. Merck Ltd, UK, supplied the glass precursors (Ga_2S_3, La_2S_3, La_2O_3 and Pr_2O_3). A series of six GLS glasses with a low and higher oxygen contents (0.65 wt%[O] and 2.95 wt.%[O]) and doped with 0.1 and 1.0 wt.% of Pr^{3+} were prepared (70/30GLS$xwt.$%[O]$ywt.$%[Pr] have been examined, where x and y are weight % of O and Pr, respectively). Pale-yellow coloured samples of about 4 mm in thickness were cut and polished under non-aqueous conditions for optical measurements (Table 1). UV-VIS Perkin Elmer and Karl Zeiss, and Perkin Elmer Spectrum 2000 FTIR spectrometers were used to record absorption spectra. An Ar^+-ion laser provided pumping radiation at 0.488 µm for fluorescence measurements. Measurements of photoinduced dichroism and transmission were carried out at discrete time intervals with a probe beam (λ=0.515 µm) as described in Ref. [2].

Table 1. Composition, oxygen and praseodymium contents in the GLS glass samples.

No.	Composition (mol %)	L, mm
1	70/30 GLS·2.95 wt.%[O]	3.80
2	70/30 GLS·2.95 wt.%[O]·0.1 wt.%[Pr]	3.85
3	70/30 GLS·2.95 wt.%[O]·1.0 wt.%[Pr]	3.84
4	70/30 GLS·0.65 wt.%[O]	4.00
5	70/30 GLS·0.65 wt.%[O]·0.1 wt.%[Pr]	4.04
5	70/30 GLS·0.65 wt.%[O]·1.0 wt.%[Pr]	3.95

3. Results and discussion

3.1. Optical absorption

The transmittance region of the GLS glass extends from the fundamental absorption edge region near 0.5 µm up to the lattice vibration threshold at about 8.0 µm (Fig.1). In Pr-free samples this region is transparent, with only weak traces of OH (~2.9 µm) and CO_2 (~4.3 µm). The effect of oxygen is manifested as a strong absorption band near 8.5 µm (at 0.65 wt %[O]), which at higher oxygen concentration 2.95 wt %[O] merges into the phonon absorption edge. This band has been attributed to Ga-O bond vibrations [2]. Introduction of Pr results in strong absorption bands of Pr^{3+}-ion located in the visual and infrared (IR) parts of the transparency region (Fig. 1,2). The position of the absorption bands of Pr^{3+} was similar to previously published data, and the intensity of the bands increased in proportion to the Pr content. The nature of these bands is associated with optical excitation of electrons from the basic $^3H_4$ level to upper Stark manifold states [9].

Presence of oxygen in GLS glass has definite effect on the absorption spectrum of Pr^{3+} – doped samples. Increasing of the oxygen content from 0.65 wt %[O] to 2.95 wt %[O] is followed by abrupt decrease of the low-energy components in the bands near 0.6 µm ($^3H_4$-$^1D_2$), 1. µm ($^3H_4$-$^1G_{4)},$

1.51 μm [$^3H_4$- ($^3F_3$,$^3F_4$)], 2.0 μm [$^3H_4$- ($^3H_6$,$^3F_2$)] and 4.775 μm ($^3H_4$-$^3H_5$). This fact produces the visual effect of an oxygen-induced shift of the absorption band spectrum to higher energies at about 30 to 60 meV. At the same time, the position of narrow band at 4.776 μm remained unchanged with the increase of oxygen concentration indicating the absence of the general spectral shift.
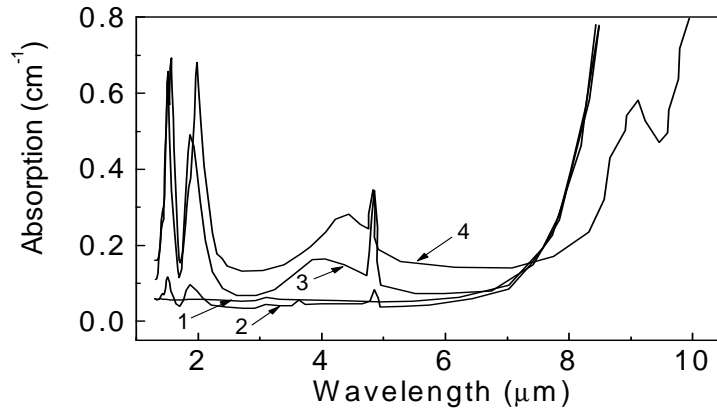

Fig. 1. IR absorption spectra of 70/30GLS 2.95%[O] samples (curves 1 to 3) with Pr content 0% (1), 0.1% (2) and 1.0% (3) and 70/30GLS 0.65%[O]1.0%[Pr] (curve 4).

The band-to-band absorption edge in oxygen containing samples is shifted to higher energy (Fig. 3) indicating the increase of the band-gap with increasing of the oxygen content. The slope of the optical absorption edge decreases suggesting increased tailing of states into the forbidden gap of the GLS glass. In stoichiometric chemically ordered bulk GLS glass both gallium and lanthanum have only sulphur as their nearest neighbours and the valence band edge is supposed to consist of sulphur $2p$ lone-pair states, with the conduction band formed by Ga-S antibonding states [10]. According preliminary EXAFS results [10], the oxygen incorporated into GLS network bonds to all three elements present, adding significant ionic component to all of its bonds and thus increasing the optical gap. The decrease in the slope of the edge, which is usually regarded as a disorder-related parameter, may be associated with the compositional disorder introduced by replacing of sulphur by oxygen in the GLS network.
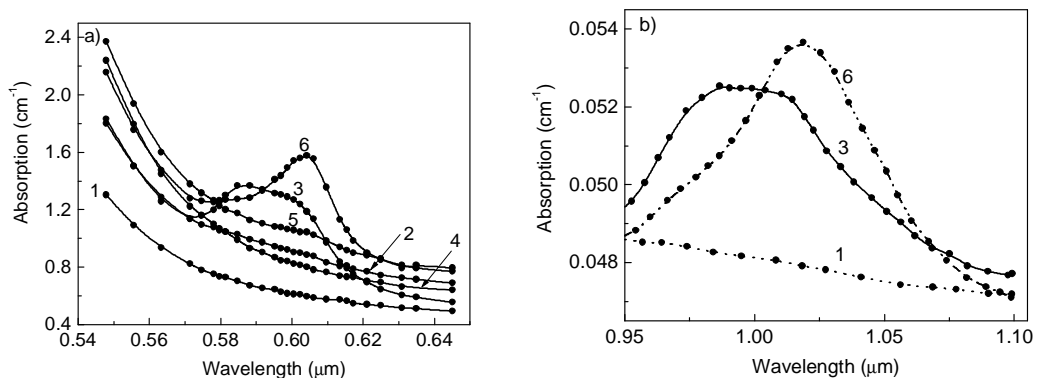

Fig. 2. Absorption spectra of 70/30GLS 2.95[O] samples (curves 1-3) and 70/30GLS 0.65[O] samples (curves 4-6) with Pr content 0 % (curves 1, 4), 0.1 % (curves 2, 5), and 1.0 % (curves 3, 6) in the wavelength regions of 0.6 μm (a) and 1.0 μm (b).

Doping of the Ga-La-S-O glass by Pr affects the position of the optical absorption edge of the glass as well, resulting in a certain edge shift to longer wavelength respective to undoped glass of ~10 meV for 0.65 wt %[O] and ~68 meV for 2.95 wt % [O] for 1 wt.%[Pr] at about 1 cm^{-1} level of absorption [3]. Increasing with the Pr content, this shift may be attributed to superposition of Pr^{3+} absorption bands in the edge region ($^3H_4$-$^3P_0$, $^3P_1$) over the band-to-band tail absorption.
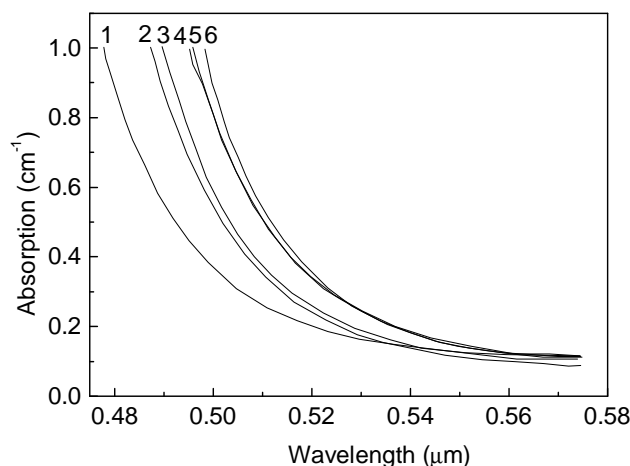

Fig. 3. Edge absorption spectra of 70/30GLS2.95[O] (curves 1-3) and 70/30GLS0.65[O] (curves 4 - 6) glass samples undoped (curves 1, 4), and doped with 0.1 wt.% Pr (curves 2, 5) and 1.0 wt.% Pr (curves 3,6).

3.2. Photoinduced anisotropy

The phenomena of photoinduced optical anisotropy (PA) in chalcogenide glasses doped with rare-earth ions are of great interest for some applications in optoelectronics. Moreover, the effects of PA have been ascribed in terms of photon-assisted rearrangements of some structural units [11]. The interest for the materials under study arises from the changes that take place in the composition, structure and the vitrification temperature of the glass during the doping.

Linear dichroism, $\alpha_\perp$-$\alpha_{/\!/}$,were $\alpha_\perp$ and $\alpha_{/\!/}$ are the absorption coefficients for a probe beam with its polarization perpendicular and parallel to the one of the inducing light, is related to the anisotropy of the relative transmitted intensities $I_\perp$ and $I_{/\!/}$ of probe beams with perpendicular and parallel polarization, and to the film thickness L by the expression

$$A = \frac{2(I_I - I_\perp)}{(I_I + I_\perp)} = (\alpha_\perp - \alpha_{II})L \,. \tag{1}$$

The values for the anisotropy parameter, A, were obtained as a function of time by repeatedly interrupting the inducing illumination, switching the beam – at 5 % intensity – back and forth between parallel and orthogonal polarizations, and measuring the difference signal through lock-in detection. Photoinduced dichroism was measured in all glass samples listed in Table 1. Fig. 4 shows the kinetics of the generation and reorientation of photoinduced dichroism for the sample no. 4. For all samples were obtained similar curves.
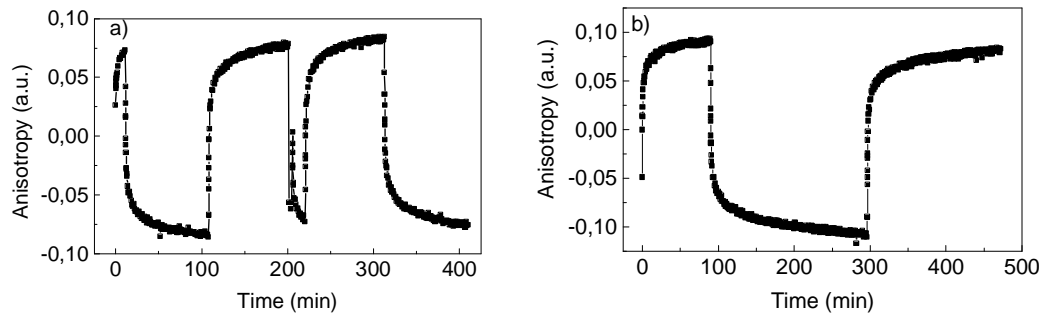
Fig. 4. Re-orientation kinetics of photoinduced dichroism in 70/30GLS0.65 wt.%[O] (a) and
70/30GLS0.65 wt.%[O] doped with 0.1 Wt.% Pr (b) glass.

The linear dichroism *A* may be fitted with the stretched exponential

$$A(t) = A_s \left[1 - \exp(-\frac{t}{\tau})^\gamma \right] , \qquad (2)$$

were *A(t)* is the value of PA at the time *t*, A_s is the saturation value of PA, τ is the relaxation parameter, and γ is the parameter which characterizes the stretched exponential behaviour. Fig. 5 shows the dependence of the parameters of the stretched exponential on the sample composition with low oxygen contents.
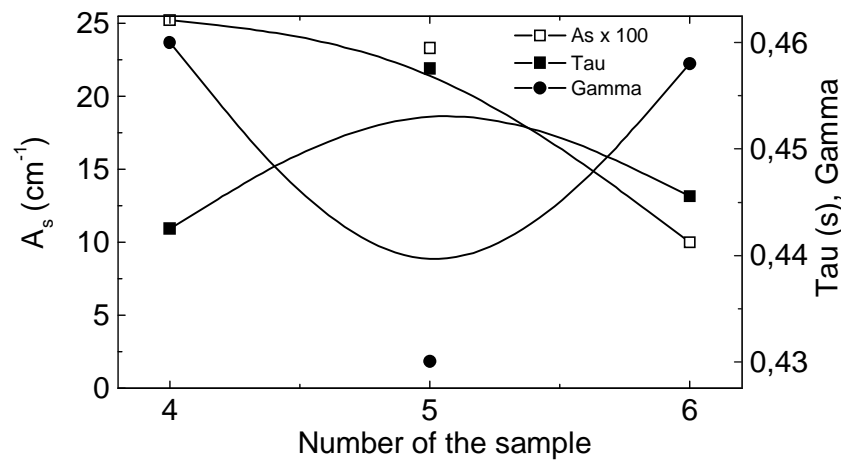

Fig. 5. The dependences of A$_s$, τ, and γ parameters on the sample composition for the
70/30GLS*0.65 wt.%*[O]*y wt.%*[Pr].

As in the case of Ge-Ga-S glasses [8], Pr^{3+} reduces the PA. According to the model proposed in Ref. [8], Pr^{3+} may alter the traps in the host glass, which could capture electrons excited from wrong-bond atoms. In such a way, Pr^{3+} changes the configuration of the charged defects, which are responsible for PA [12].

3.3. Visible luminescence

The luminescence was observed only in Pr-doped samples and could be seen red with the naked eye as in Ref. [13]. The excitation at 0.488 μm populates the $^3P_0$ manifold and provides radiative transitions to lower lying terms. The emission presents broad and unresolved bands characteristic of the inhomogeneously disordered glass matrix. Several wide structured bands characteristic for Pr^{3+} ion emission were clearly seen in the spectra (at 0.5-0.55 μm, 0.57 μm, 0.63-0.66 μm, the latter most intensive, and at 0.7-0.75 μm) (Fig. 6a). The intensity of the bands increased with the Pr^{3+} content without any concentration quenching, indicating the greater solubility of active Pr^{3+} in the investigated glass in comparison with chalcogenide glasses based on As or Ge (less than 500 ppm)[14,15]. The effect of oxygen presence is manifested mainly in the blue shift of the absorption edge.
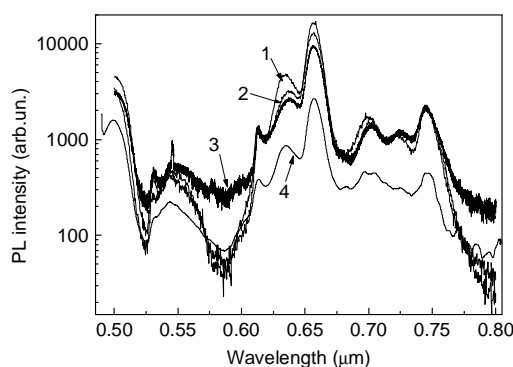

Fig. 6a. Room temperature photoluminescence spectra of 70/30GLS x%[O]y%[Pr] glasses with composition x = 0.65 (1, 4) and x = 2.95 (2, 3), and y = 0.1 (2,4) and y = 1.0 (1,3).
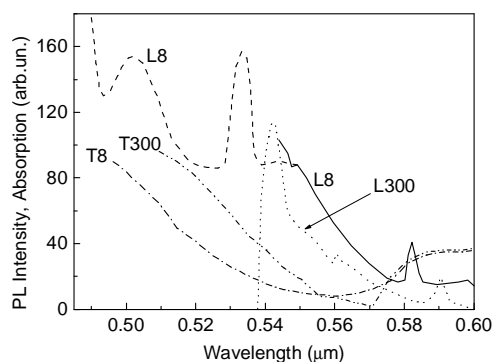
Fig. 6b. Short-wavelength Pr^{+3}-ion emission at the absorption edge of GLS glass: curves L8 and L300 present photoluminescence, and T8 and T300 show absorption at 8K and 300 K, respectively for 70/30 GLS2.95%[O]1.0%[Pr] glass.

Due to this shift, strong photoluminescence bands at about 0.5–0.55 μm ($^3P_1$, $^1I_6$, $^3P_0$ - $^3H_5$) peep out with the contour distorted by background absorption (Fig. 6b).

This effect of enhancement of the short-wavelength emission is revealed as well at decreasing of the temperature from 300 K to 8 K, this time at the expense of temperature lowering of the edge absorption energy. In the remaining part of the spectrum, i.e. in the transparency region, the influence of oxygen content on the position of luminescence bands is insignificant, in contrast to the effect on the absorption bands.

4. Conclusions

In conclusion, the absorption, photoinduced anisotropy and photoluminescence spectra of Ga-La-S-O glasses with fixed cation ratio Ga/La = 0.7/0.3 and two oxygen content 0.65 wt % and 2.95 wt % were studied for two Pr^{3+} doping levels of 0.1 and 1.0 wt %. The presence of oxygen induces a blue shift of the fundamental absorption edge. Increasing of oxygen content results in lowering of the low-energy components of the Pr^{3+} absorption bands. Pr^{3+} ions change the configuration of the charged defects in the host glass, and reduce the PA. The glasses show bright luminescence due to Pr^{3+} ion emission similar to that in other glasses. The effect of oxygen on the luminescence spectra is determined by decreasing of host glass self-absorption of the short-wavelength bands, which became "opened" with growing of the oxide content.

Acknowledgement

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