Spectroscopy of titanium-doped gallium lanthanum sulfide glass

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Received April 24, 2008; revised June 19, 2008; accepted July 3, 2008;
posted July 14, 2008 (Doc. ID 95403); published August 15, 2008

Titanium-doped gallium lanthanum sulfide (Ti:GLS) and gallium lanthanum oxysulfide (Ti:GLSO) glasses have an absorption band at ~500–600 nm that cannot be fully resolved because of its proximity to the band edge of the glass. At concentrations >0.5% a shoulder at 980 nm is observed in Ti:GLS but not in Ti:GLSO. The emission spectra of Ti:GLS and Ti:GLSO both peak at 900 nm with lifetimes of 67 and 97 μ s, respectively. We propose that the absorption at ~600 nm is due to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition of octahedral Ti^{3+} and the 980 nm shoulder is due to Ti^{3+} – Ti^{4+} pairs. © 2008 Optical Society of America

OCIS codes: 300.2530, 140.3380.

1. INTRODUCTION

Solid-state lasers that use transition metals as the active ion have a long history and can in fact be traced back to the first demonstration of laser action—the chromium-doped ruby laser [1]. Apart from being of considerable academic interest, the demonstration of laser action from one of these elements in a glass host would have important implications for other optical devices. An example of this would be a broadband gain medium that could be incorporated into existing fiber and planar optical devices.

To date there has been no demonstration of a d -block transition metal laser that uses glass as a host. The high maximum phonon energy and resulting rapid nonradiative decay mechanisms of oxide-based glasses such as silica make conventional glasses unlikely candidates for the host material. On the other hand chalcogenide glasses have low maximum phonon energies due to the relatively large atomic mass of the constituent atoms. In particular gallium lanthanum sulfide glass (GLS) has a maximum phonon energy of 425 cm^{-1} [2]. This low maximum phonon energy may allow emission from transition metal dopants that are weakly or not at all observed in silica for example.

Titanium-doped Al_2O_3 (Ti:sapphire) has been used as a gain medium in room temperature tunable lasers since laser action was first reported by Moulton in 1982 [3]. The Ti:sapphire laser is the most widely used near-infrared (IR) tunable laser source and is tunable from 650 to 1100 nm. It is also used to generate ultrashort laser pulses with durations as low as 8 fs [4]. Due to the success of the Ti:sapphire crystal as a tunable laser source little attention has been paid to titanium-doped glass as an active medium. We also note that reports in the literature of photoluminescence from titanium-doped glasses are extremely scarce. A titanium-doped glass laser in a fiber geometry could potentially have several advantages over a Ti:sapphire laser, in that it could be more compact and have a higher alignment stability and robustness. In this work we present spectroscopic data for titanium-doped GLS (Ti:GLS) that contains around 0.5% (molar) oxygen for stability against crystallization, and of titanium-doped gallium lanthanum oxysulfide (Ti:GLSO), which contains around 15% (molar) oxygen.

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2. EXPERIMENTAL

A. Glass Melting

Samples of Ti:GLS were prepared by mixing 65% gallium sulfide, 30%–X% lanthanum sulfide, 5% lanthanum oxide, and the appropriate proportion (X%) of titanium sulfide (percent molar). Samples of Ti:GLSO were prepared by mixing 75%–X% gallium sulfide, 25% lanthanum oxide, and the appropriate proportion (X%) of titanium sulfide (percent molar). Batching was carried out in a dry-nitrogen purged glove box. Melt components were batched into vitreous carbon crucibles, weighed using a balance with a resolution of 0.001 g. Batches were then transferred to a furnace using a custom-built sealed atmosphere transfer pod. Gallium and lanthanum sulfides were synthesized in-house from gallium metal (9N purity) and lanthanum fluoride (5N purity) precursors in a flowing H_2S gas system. Before sulfurization lanthanum fluoride was purified and dehydrated in a dry-argon purged furnace at 1250°C for 36 h to reduce OH^- and transition metal impurities. The lanthanum oxide and titanium sulfide were purchased commercially and used without further purification. The glass was melted at 1150°C for around 24 h, in a silica tube furnace, with an initial ramp rate of 20°C min^{-1} and under a constant argon atmosphere (flow of 200 $ml\ min^{-1}$). This method was chosen in favor of the sealed ampoule method because volatile impurities such as OH^- are carried downstream away from

the melt and because of safety concerns about the ampoules exploding. The melt was rapidly quenched (at around 500°C/min) to form a glass by pushing the crucible holder into a silica water jacket. The quenching process is designed to prevent crystallization of the glass by rapidly increasing the viscosity of the glass through a rapid temperature drop, hence arresting the nucleation and growth of crystals. The glass was then annealed at 400°C for 12 h. The final glass is homogeneous and crack free.

B. Spectroscopic Measurements

Absorption spectra were taken on a Varian Cary 500 spectrophotometer that operates over a range of 175–3300 nm with a resolution of ± 0.1 nm in the UV-VIS (visible) region (200 to 800 nm) and ± 0.4 nm in the IR region (801 to 3300 nm). The absorption coefficient spectra [$\alpha(\lambda)$] were calculated from

$$\alpha(\lambda) = \frac{\log_{10}(P_0/P)}{b}, \quad (1)$$

where P_0 is the incident radiant power, P is the transmitted radiant power, and b is the sample thickness.

Photoluminescence (PL) spectra were obtained with a 633 nm HeNe laser excitation source. The laser beam was chopped with a Scitec optical chopper and a reference signal was sent to a Stanford research system's SR830 DSP lock-in amplifier in the form of a square wave. The laser beam struck the sample at a shallow angle, such that the reflected and most of the scattered laser light does not hit CaF₂ lenses, which were used to collimate and focus the fluorescence into a Bentham TMc300 monochromator. The exit beam from the monochromator was detected by a Newport 818-IG InGaAs detector. A long-pass filter with an appropriate cut-off wavelength was used to cut out the laser light but allow PL into the monochromator. The system was corrected for the wavelength-dependent response of the gratings, detectors, and other system components by calculating a correction spectra [$C(\lambda)$] with $C(\lambda) = I_{\text{cal}}(\lambda)/I_{\text{meas}}(\lambda)$, where $I_{\text{meas}}(\lambda)$ is the luminescence spectrum of a Bentham IL6 quartz halogen white light source measured by the detection system and $I_{\text{cal}}(\lambda)$ is the luminescence spectrum of the calibrated white light source supplied by the manufacturer.

To obtain photoluminescence excitation (PLE) spectra, white light from a Philips 250 W tungsten halogen bulb was focused by a 40 mm diameter silica lens into an Acton Spectrapro 300i monochromator that dispersed the light to give a variable energy exciting light source. The exciting light was focused onto the edge of the sample by a 20 mm diameter silica lens, then the fluorescence, collected at 90° to the excitation, was collimated and focused by two CaF₂ lenses onto a Newport 818IG InGaAs detector. A silicon filter was placed in front of the InGaAs detector to give an effective detection range of 1000–1700 nm. A 715 nm long-pass color glass filter was placed in front of the monochromator when scanning wavelengths longer than 750 nm to cut out second-order light; from absorption measurements the response of the filter was taken to be flat.

The PLE system was corrected for the varying intensity of exciting light, due to the varying grating response and spectral output of the white light source, by obtaining the white light response [$R_{\text{wl}}(\lambda)$] for each grating with Newport 818-SL and 818-IG detectors. The correction curves for each grating were then calculated using the calibration report supplied with the detectors. The calibration reports gave the responsivity of the detectors in steps of 10 nm. The spectral responsivity data was entered onto a computer and smoothed with a running average algorithm, with a sampling proportion of 0.05, to give detector responsivity spectra [$R_{\text{det}}(\lambda)$] in steps of 1 nm. The correction spectra [$C(\lambda)$] for each grating were then calculated with: $C(\lambda) = R_{\text{wl}}(\lambda)/R_{\text{det}}(\lambda)$.

To collect lifetime measurements the 633 nm excitation source was modulated by a Gooch and Housego M080-1F-GH2 acousto-optic modulator (AOM). The modulation signal was generated by a Thurlby Thandar TG230 2 MHz sweep-function generator, which then activated a Gooch and Housego A103 radio frequency generator. The fluorescence was detected with a New Focus 2053 InGaAs detector that was set to a gain that corresponded to a 3 dB bandwidth of 3 MHz. The data was captured by a Picoscope ADC-212 virtual oscilloscope with a 12 bit intensity resolution and a maximum temporal resolution of 700 ns, the signal was averaged for around 2 min to improve signal-to-noise ratio (SNR) in the measurement. Lifetime measurements were taken several times at different alignments in order to give an estimate of random experimental error.

3. RESULTS AND DISCUSSION

A. Absorption Measurements

Figure 1 shows the absorption spectra of GLS doped with varying concentrations of titanium. At concentrations up to 0.2% absorption from titanium is only visible as a red-shift in the band edge of GLS indicating absorption from titanium at ~500–600 nm. At concentrations of 0.5% and greater a shoulder at ~1000 nm is observed; there is also a weak and broad absorption centered at around 1800 nm. Figure 2 shows the absorption spectra of GLSO doped with varying concentrations of titanium. Similar to

Fig. 1. (Color online) Absorption spectra of 0.1% to 1% molar titanium-doped GLS and undoped GLS in 3 mm thick slabs.

Fig. 2. (Color online) Absorption spectra of 0.05% to 1% molar titanium-doped GLSO and undoped GLSO in 3 mm thick slabs.

Ti:GLS, there is also a redshift in the band edge with increasing titanium concentration in the higher oxide containing glass; however, there is no evidence of a shoulder at ~ 1000 nm or a broad weak absorption at ~ 1800 nm as in Ti:GLS. The 1% Ti:GLSO sample had partially crystallized, which meant that its baseline absorption was higher than expected because of increased scattering.

To confirm the observation of a shoulder at ~ 1000 nm or a broad weak absorption at ~ 1800 nm as in Ti:GLS but not in Ti:GLSO, derivatives of the absorption spectra of 0.5% Ti:GLS and 0.5% Ti:GLSO were taken. The mathematical differentiation of spectroscopic data is often used as a resolution enhancement technique to facilitate the detection and location of poorly resolved spectral components including peaks that appear only as shoulders as well as the isolation of small peaks from an interfering large background absorption [5]. All spectral features that are attributed to optical transitions in transition metals are assumed to be composed of a sum of Gaussian peaks. The standard Gaussian curve function for an absorption band peaking at x_0 with absorbance A is

$$A = A_0 e^{\{-4 \ln 2 [(x - x_0)/w]^2\}}, \quad (2)$$

where A_0 is the maximum band height at x_0 and w is the full width at half-maximum (FWHM). The second derivative of Eq. (2) is

$$\frac{d^2A}{dx^2} = \left(\frac{16 \ln 2 (x - x_0)^2 A_0}{w^4} - \frac{8 \ln 2 A_0}{w^2} \right) e^{\{-4 \ln 2 [(x - x_0)/w]^2\}}. \quad (3)$$

Higher-order derivatives discriminate strongly in favor of narrower bands [6]. However, the SNR is degraded with increasing differentiation order [5,7]. Setting $x = x_0$ for Eq. (3) gives the peak amplitude in Eq. (4), this shows that second derivatives are inversely proportional to the square of the FWHM,

$$\frac{d^2A}{dx^2} = - \frac{8 \ln 2 A_0}{w^2}. \quad (4)$$

Therefore absorption peaks in second derivative absorption spectra correspond to where $d^2a/d\lambda^2 < 0$, where a is

the absorption coefficient. The second derivative absorption spectra in Fig. 3 clearly show that there is an absorption peak at 980 nm in Ti:GLS but not in Ti:GLSO. Absorption peaks at 615 and 585 nm are also identified for Ti:GLS and Ti:GLSO, respectively. The second derivative absorption peak at 980 nm was much stronger in 1% Ti:GLS than in 0.5% Ti:GLS but could not be identified at concentrations of 0.2% or lower.

The Ti^{3+} ion has a single d electron and it is therefore expected to exhibit a single absorption band in ideal symmetry. In crystals of Al_2O_3 , Ti^{3+} ions have octahedral coordination with trigonal symmetry [8] and their absorption is characterized by a broad double humped absorption band extending from 400 to 600 nm. The main peak occurs at 490 nm with the shoulder at 550 nm; these are attributed to transitions from the ${}^2T_{2g}$ ground state to the Jahn–Teller split ${}^2E_g(E_{3/2})$ and ${}^2E_g(E_{1/2})$ excited states [9]. A weak residual IR absorption has been identified in Ti:sapphire from around 650 to 1600 nm, peaking at 800 nm [9] and has been shown to be due to Ti^{3+} – Ti^{4+} pairs [10]. We therefore propose that the absorption at ~ 600 nm in Ti:GLS and Ti:GLSO is due to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition of octahedral Ti^{3+} and the absorption at 980 nm in Ti:GLS is due to Ti^{3+} – Ti^{4+} pairs. The residual IR absorption coefficient of $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ has been shown to be proportional to the square of its blue–green absorption coefficient [9,10]. Because absorption due to Ti^{3+} – Ti^{4+} pairs is detrimental to the performance of the Ti:sapphire laser, much effort has been made to minimize it. In Ti:sapphire the valence of Ti ions has been controlled by melting temperature and oxygen partial pressure [9,11]. In silica the concentration of Ti^{3+} relative to Ti^{4+} ($[\text{Ti}^{3+}]/[\text{Ti}^{4+}]$) increased with melting temperature and decreasing oxygen partial pressure and was maximized by melting in deoxidized argon, i.e., a reducing atmosphere [12]. This is the same atmosphere that GLS is melted in so the oxygen partial pressure parameter is already maximized for the reduction of the Ti^{4+} concentration. In silicate, borate, and phosphate glasses the redox reaction of $\text{TM}^{m+} \leftrightarrow \text{TM}^{(m+1)+}$ is related to the glass basicity (B) [12,13], TM is a transition metal ion, and glass basicity is calculated in terms of the Coulombic force between the cation and oxygen ion of each glass component as in Eq. (5) [12],

Fig. 3. (Color online) Second derivative of the absorption coefficient of 0.5% Ti:GLS and 0.5% Ti:GLSO.

$$B_i = \frac{(r_i + 1.4)^2}{Z_i \times 2}, \quad (5)$$

where Z_i and r_i are the valency and radius of the cation; the values of 2 and 1.4 are the valency and radius of the oxygen ion, respectively; and B_i is the basicity of glass component i . The higher La_2O_3 content of GLSO compared to GLS is thought to cause the formation of oxide negative cavities [14] whereby the oxygen coordination of gallium is increased from 0 to 1, therefore GLSO should have a higher basicity than GLS. In silicate glass $[\text{Ti}^{3+}]/[\text{Ti}^{4+}]$ is inversely proportional to B , in borate glass $[\text{Ti}^{3+}]/[\text{Ti}^{4+}]$ is proportional to B , and in phosphate glass there is no dependence of $[\text{Ti}^{3+}]/[\text{Ti}^{4+}]$ on B [12]. The relationship between $[\text{Ti}^{3+}]/[\text{Ti}^{4+}]$ and B in the GLS system is not known, however, it is assumed that $[\text{Ti}^{3+}]/[\text{Ti}^{4+}]$ is proportional to B since there is no absorption due to $\text{Ti}^{3+}-\text{Ti}^{4+}$ pairs in the more basic GLSO glass. This assertion is, however, dependent on assignment of the 980 nm absorption in GLS to $\text{Ti}^{3+}-\text{Ti}^{4+}$ pairs being correct.

The absorption of titanium has been characterized in a variety of glasses [12,15–22]. In all of the glasses a broad double-humped absorption band extending from 400 to 750 nm was observed and attributed to Ti^{3+} in tetragonally distorted octahedra, except in silicate glass where a single absorption peak at 560 nm was observed and attributed to a continuous range of Jahn–Teller splittings. As no similar absorption shoulder could be resolved in GLS and GLSO this is therefore attributed to the same effect as in silica glass. In some of the glasses an IR absorption at ~ 800 nm was attributed to $\text{Ti}^{3+}-\text{Ti}^{4+}$ pairs.

B. Emission Spectra Measurements

In $\text{Ti}:\text{Al}_2\text{O}_3$, the emission peaks at ~ 750 nm when excited at 514 nm [3]. Of the titanium-doped glasses investigated previously [12,15–22], emission from $d-d$ transitions in Ti^{3+} was only reported in sodium phosphate aluminate glass [16]; in the other glasses emission was either not investigated or not detectable. In Ti^{3+} : sodium phosphate aluminate glass, emission centered at 860 nm with a FWHM of 2020 cm^{-1} was detected from excitation with a 633 nm HeNe laser. This is close to the emission of Ti:GLS and Ti:GLSO in Fig. 4, where the emission peaked at 900 nm when excited at the same wavelength. This further backs up the hypothesis that titanium is in a 3+ oxidation state in GLS and GLSO. The broadness of the PL spectrum indicates that the titanium ion is in a low crystal field site, i.e., the energy of the lowest excited state is strongly dependent on crystal field strength. No emission in the range 1200–1800 nm was detected from Ti:GLS when exciting with a 500 mW 1064 nm laser source.

The observation that emission from Ti:GLS peaks at 900 nm, which is at a higher energy than the weak absorptions at 980 and 1700 nm, implies that these absorptions cannot be due to the same coordination and oxidation state and of titanium that produces the emission. This supports the hypothesis that these weak absorptions are due to $\text{Ti}^{3+}-\text{Ti}^{4+}$ pairs.

Figure 5 shows the excitation spectra of 0.1% titanium-doped GLS and GLSO, both of which show a single excitation peak at 580 nm that is in good agreement with the derivative absorption measurements. The excitation sig-

Fig. 4. (Color online) Photoluminescence spectra of 0.1% titanium-doped GLS and GLSO excited with a 5 mW 633 nm laser source.

nal was relatively weak and the apparent increase in excitation in Ti:GLS at 800 nm is caused by a correction for the system response. Due to the weak signal and the proximity of the GLS band edge, Fig. 5 may not give an accurate representation of the absorption bandwidth. No further excitation signal was detected up to 1000 nm.

C. Emission Lifetime Measurements

The emission decay profiles of a range of titanium doping concentrations were investigated. The decay was found to be non-single-exponential and was analyzed using both the stretched and double exponential decay models. This data is used to infer the optimum concentration and composition of an active optical device based on Ti:GLS.

Many relaxation processes in complex condensed systems such as glasses have long been known to follow the stretched exponential function given in Eq.(6) [23],

$$I(t) = y_0 + I_0 \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right), \quad (6)$$

where I_0 is the initial fluorescence intensity, y_0 is the offset, τ is the characteristic fluorescence lifetime, and β is

Fig. 5. (Color online) PLE spectra of 0.1% Ti:GLS and 0.1% Ti:GLSO. Emission was detected at 1000–1700 nm and the excitation source was dispersed with a 1200 lines/mm grating.

the stretch factor. The closer β is to 0 the more the function deviates from a single exponential. The stretched exponential function has been shown to describe many relaxation processes in amorphous and crystalline materials such as nuclear relaxation [23], magnetic susceptibility relaxation [23], fluorescence decay [24–29], and photoinduced dichroism [30]. Though stretched exponential behavior has been observed in many relaxation processes, particularly in disordered materials such as glasses, there has been considerable debate as to the physical interpretation of the characteristic lifetime τ and stretch factor β . Stretched exponential relaxation is commonly interpreted as a sum of pure exponential decays with a probability distribution P of τ_i lifetime values for a given value of β [31]. Recently, the probability distributions $P(\tau/\tau_i)$ of the stretched exponential function for different β values have been calculated [31–33]. Analysis of these distributions leads to the following physical interpretations: (i) that τ is that τ_i , which is equally likely to be less than τ as it is to be greater; (ii) that β is a measure of the intrinsic long lifetime cutoff of $P(\tau/\tau_i, \beta)$ [31]. Some emission decays were found to be well-described by the double exponential function given in Eq. (7),

$$I(t) = y_0 + I_1 \exp\left(-\frac{t}{\tau_1}\right) + I_2 \exp\left(-\frac{t}{\tau_2}\right), \quad (7)$$

where τ_1 and τ_2 are the two characteristic lifetimes; I_1 and I_2 are their respective coefficients. The presence of two lifetime components indicates the presence of two distinct emission centers. Regression analysis was implemented using the Marquardt–Levenberg algorithm [34]. The goodness of the fit was measured using the coefficient of determination (R^2). The coefficient of determination indicates how much of the total variation in the dependent variable can be accounted for by the regressor function. If $R^2=1$ then this indicates that the fitted model explains all variability in the observed dependent variable, while $R^2=0$ indicates no linear relationship between the dependent variable and regressors.

The linearity of the detector used to collect the decay data was around 0.5%. The decay curves of erbium-doped GLS [35], taken with a similar detector over a similar dynamic range, showed no deviation from single exponential behavior as would be expected from a rare earth ion. This indicates that the nonexponential decay observed in titanium-doped GLS is a physical phenomenon and is not related to a deviation from linearity in the detector.

Figure 6 shows the fluorescence decay of 0.05% titanium-doped GLS fitted with a stretched exponential. The best fit to the experimental data was with a lifetime of $67 \mu\text{s}$ and a stretch factor (β) of 0.5. Visual inspection indicates an excellent fit to the experimental data. Figure 7 shows the fluorescence decay of 1% Ti:GLS, fitted with the stretched and double exponential. The stretched exponential is no longer a good fit ($R^2=0.9355$) and the double exponential fit is better ($R^2=0.9824$). The lifetimes of the double exponential were 15 and $160 \mu\text{s}$. The fact that the characteristic slow lifetime of $67 \mu\text{s}$ is no longer observed at high concentrations when using the double exponential fit is believed to be because the stretch factor is 0.5 and a single exponential is not a good approximation.

Fig. 6. (Color online) Fluorescence decay of 0.05% titanium-doped GLS excited with a 10 mW 658 nm laser source and stretched exponential fit. The lifetime was $67 \mu\text{s}$ and the stretch factor was 0.5.

To illustrate this problem assume that the characteristic stretched exponential decay with a lifetime of $67 \mu\text{s}$ and a stretch factor of 0.5 is present in the fluorescence decay in Fig. 7. Fitting to this decay can only occur once the fast lifetime component has decayed, which, from the inspection of Fig. 7, occurs around $t > 50 \mu\text{s}$. For $t > 50 \mu\text{s}$ only much slower lifetime components are present, therefore fitting this part of the decay with a single exponential will give a much longer lifetime than the stretched exponential. To overcome this problem a stretched exponential, starting at time zero, was fitted to the fluorescence decay but the stretched exponential was only fitted to the fluorescence decay at $t > 50 \mu\text{s}$; in other words the fit was not dependent on $t=0$ to $50 \mu\text{s}$. This fit

Fig. 7. (Color online) Fluorescence decay of 1% titanium-doped GLS excited with a 10 mW 658 nm laser source fitted with a double exponential, a stretched exponential, and a stretched exponential starting at $t=0$ but where the fit is only dependent on $t > 50 \mu\text{s}$. The inset shows the fluorescence decay minus the stretched exponential fit where the fit is only dependent on $t > 50 \mu\text{s}$, and a single exponential fit.

had the characteristic slow lifetime of $\sim 67 \mu\text{s}$ and a similar stretch factor of 0.6. The inset of Fig. 7 shows the fluorescence decay minus the stretched exponential fit, where the fit is only dependent on $t > 50 \mu\text{s}$, fitted with a single exponential with a lifetime of $10 \mu\text{s}$. This is relatively close to the fast component of the double exponential fit; however, there are too few data points in this region of the decay to accurately characterize this part of the decay. Figure 8 shows the emission decay of 0.05% titanium-doped GLSO fitted with a stretched exponential with a lifetime of $97 \mu\text{s}$ and a stretch factor (β) of 0.5. Visual inspection indicates an excellent fit to the experimental data. Figure 9 shows the emission decay of 1% titanium-doped GLSO fitted with a stretched exponential with a lifetime of $60 \mu\text{s}$ and a stretch factor (β) of 0.5. Unlike Ti:GLS the emission decay at this concentration is still well-described by a stretched exponential. Figure 10 shows the R^2 of stretched exponential fits as a function of titanium concentration in GLS and GLSO. At concentrations greater than $\sim 0.1\%$ Ti:GLS the fall in R^2 indicates that the fluorescence decay starts to deviate from stretched exponential behavior. In Ti:GLSO there is relatively little change in R^2 as titanium concentration increases.

We propose that the stretched exponential behavior results from a superposition of a continuous distribution of lifetimes caused by variations in the local environment of the titanium ions. The finding that there is a deviation from stretched exponential behavior in concentrations above 0.1% in Ti:GLS but not in Ti:GLSO and that lifetimes are longer in GLSO indicates that this effect is related to the oxygen content of the glass. GLS contains $\sim 0.5\%$ (molar) oxygen whereas GLSO contains $\sim 15\%$ (molar) oxygen. We therefore propose that two sites for titanium exist in GLS glass: a high-efficiency oxide site and a low-efficiency sulfide site. In GLS the titanium ion preferentially fills the high-efficiency oxide sites until, at a concentration of $\sim 0.1\%$, they become saturated and the low-efficiency sulfide sites start to be filled; this explains the deviation from stretched exponential behavior at concentrations $> 0.1\%$ and the appearance of characteristic fast and slow lifetime components. Although it seems

Fig. 8. (Color online) Fluorescence decay of 0.05% titanium-doped GLSO excited with a 10 mW 658 nm laser source and stretched exponential fit. The lifetime was $97 \mu\text{s}$ and the stretch factor was 0.5.

Fig. 9. (Color online) Fluorescence decay of 1% titanium-doped GLSO excited with a 10 mW 658 nm laser source and stretched exponential fit. The lifetime was $60 \mu\text{s}$ and the stretch factor was 0.5.

counterintuitive that the oxide site is more efficient than the sulfide site when considering their expected phonon energies, one should also consider that transition metals are strongly affected by their local environment. It may therefore be possible that the two sites have a different symmetry in their first coordination sphere, which could affect the efficiency irrespective of local phonon energy. The peak position and shape of the absorption bands of Ti:GLS do not change significantly as concentration increases from 0.05% to 1%; however, one would expect a noticeable redshift in absorption going from an oxide coordinated transition metal to a sulfide coordinated transition metal. So the oxide site probably does not have oxygen directly bonded to the titanium ion. Figure 11 shows how the lifetime fitting parameter of titanium-doped GLS and GLSO varies as a function of doping concentration. The figure shows that the lifetime is longer in Ti:GLSO than Ti:GLS, which indicates that GLSO is the most favorable host for an active optical device. The lifetime is still increasing slightly at the lowest concentration, 0.05% molar titanium, investigated. This indicates that concentration quenching is still occurring at 0.05%, therefore the

Fig. 10. (Color online) Coefficient of determination of stretched exponential fit as a function of titanium concentration in GLS and GLSO.

Fig. 11. (Color online) Lifetimes of titanium-doped GLS and GLSO as a function of doping concentration. The emission decays were fitted with the stretched exponential model.

optimum concentration for an active optical device based on Ti:GLSO may be lower than 0.05%. In Ti:Al₂O₃, laser action has been demonstrated at titanium concentrations of ~0.03% to 0.15% molar [3]. Figure 11 also shows that lifetimes decrease more rapidly as concentration increases in Ti:GLS than in Ti:GLSO. This can be explained by the oxide-sulfide site model discussed above. The higher oxygen content of GLSO means that in Ti:GLSO the high-efficiency oxide sites remain available at higher concentrations, whereas in Ti:GLS the lower oxygen content means that as titanium concentration increases, the proportion of titanium ions in low-efficiency sulfide sites increases. Therefore the lifetime will decrease more rapidly as concentration increases. All the lifetimes in Fig. 11 were determined using the stretched exponential model. As shown in Fig. 10 there is a deviation from the stretched exponential model in Ti:GLS at concentrations > ~0.2%, the lifetime at these concentrations is therefore an approximation. Because of the difficulties in comparing the lifetime of emission where the decay follows different models this is believed to be a valid approximation. We also found that the lifetimes calculated using the stretched exponential in Fig. 11 were within 1% of the first *e*-folding time.

Out of all the references concerning titanium-doped glass collected for this study [12,15–22] there were no reports of emission lifetime. The large difference in Ti³⁺ lifetime between the oxide and sulfide sites in GLSO indicates that the lifetime of the Ti³⁺ ion is highly sensitive to its host environment, which may explain why the lifetime of Ti:GLSO is much longer than that of Ti:sapphire.

4. CONCLUSIONS

Absorption measurements of Ti:GLS identified an absorption band at ~500–600 nm that could not be fully resolved because of its proximity to the band edge of GLS. At concentrations of 0.5% and greater a shoulder at ~1000 nm is observed in Ti:GLS but not in Ti:GLSO. There is also a weak and broad absorption centered at around 1800 nm. The second derivative absorption spectra identified an absorption peak at 980 nm in Ti:GLS but

not in Ti:GLSO; absorption peaks at 615 and 585 nm are also identified for Ti:GLS and Ti:GLSO, respectively. The excitation spectra of 0.1% titanium-doped GLS and GLSO both show a single excitation peak at 580 nm. The emission spectra of Ti:GLS and Ti:GLSO both peaked at 900 nm. It is proposed that the absorption at ~600 nm in Ti:GLS and Ti:GLSO is due to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition of octahedral Ti³⁺ and the absorption at 980 nm in Ti:GLS is due to Ti³⁺–Ti⁴⁺ pairs. The lifetime fitting parameter of 0.05% Ti:GLSO is 97 μs. The optimum doping concentration for an active device based on Ti:GLSO may be lower than the lowest concentration of 0.05% molar investigated in this study. Therefore the investigation of lower doping concentrations of Ti:GLSO is suggested as further work. The fabrication of a Ti:GLSO fiber at the optimum doping concentration for applications as a tunable laser source is also suggested as further work; however, excited state absorption into the band edge of GLSO may be a significant problem.

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