Quadrature frequency resolved spectroscopy (QFRS) of radiative transitions of Er$^{3+}$ and Nd$^{3+}$ ions in chalcogenide glasses (ChGs)

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Abstract. Wideband quadrature frequency resolved spectroscopy (QFRS) of photoluminescence (PL) lifetime distributions from 2 ns to 160 s is shown to be very effective in elucidating the characteristic features of radiative transitions of Er$^{3+}$ ions in GeGaSe and GeGaS chalcogenides glasses (ChGs). Undoped GeGaSe ChGs show triple-peak lifetime distributions of which two short-lifetimes are associated with singlet-triplet excitons and longest-lifetime, $\sim$20 s, with radiative tunnelling (RT) of distant-pairs (DPs). Er-doped GeGaSe and GeGaS ChGs exhibit a double-peak lifetime distribution, consisting of a peak at $\sim$3.3 and $\sim$5.3 ms, respectively, a characteristic of the Er$^{3+}$ luminescence centre and another peak at $\sim$20 s, similar to that of undoped GeGaSe ChGs. It is shown that the QFRS can separate and analyse two mixed radiative transitions of Nd$^{3+}$ ions, $^{4}F_{3/2} \rightarrow ^{4}I_{15/2}$ and $^{4}F_{5/2,2H_{9/2}} \rightarrow ^{4}I_{15/2}$ in GaLaS ChGs. From the QFRS results we can experimentally extract the branching ratio $\beta$ and lifetime $\tau \approx 77 \mu$s for 4 lasing transitions $^{4}F_{3/2} \rightarrow ^{4}I_J$ ($J = 9/2, 11/2, 13/2, 15/2$) of Nd$^{3+}$ ions in GaLaS ChGs, in particular, the weakest transition $^{4}F_{3/2} \rightarrow ^{4}I_{15/2}$.

1. Introduction
Radiative transitions of rare earth (RE) ions such as Er$^{3+}$ and Nd$^{3+}$ embedded in a solid state matrix are of great interest for possible opto-electronic applications. The $f/f$ transitions of RE ions are forbidden in the dipole approximation and become partly allowed owing to an admixture of other orbitals when they are incorporated in a solid matrix. This admixture crucially depends on the immediate vicinity of RE ions and its symmetry. A disordered material such as glass offers a distinct advantage because it lowers the symmetry of the RE environment and its short-range potential fluctuations facilitate the mixing of the wave-functions. Moreover, compared with crystalline matrices, glasses offer a variety of attractive properties. For example, they are optically isotropic, they allow size- and shape-scalability as well as a wide range of variations in their compositions. Glasses usually demonstrate high transparency, allowing operation at high optical power densities, and are less expensive and easier to fabricate than crystals. In particular, chalcogenide glasses (ChGs) possess lower phonon frequencies
and higher refractive indices in comparison with traditionally used oxide and fluoride glasses. Most significantly, they allow effective doping with a large amount of RE ions, and corresponding oscillator strengths are largely enhanced especially in sulphide ChGs because of the high covalence of RE-sulphur bonds [1].

GeGaSe ChGs, in particular, have been shown to be excellent Er-host materials since they allow homogeneous Er-doping in large amounts (e.g., up to 2 at.% Er) with the subsequent formation of Er$^{3+}$ ions [1]. The photoluminescence (PL) of f-f transitions ($^4I_{13/2} \rightarrow ^4I_{15/2}$) in Er$^{3+}$ centres in Er-doped GeGaSe ChGs with a near-stoichiometric composition and a high concentration of Ga features a single dominant peak in the PL spectrum at $\sim 1.5$ $\mu$m with a typical PL lifetime $\tau_{p} \approx 3$ ms, which is almost independent of temperature $T$, and whose exact value only slightly depends on the composition of the host GeGaSe ChGs. The wavelength $\sim 1.5$ $\mu$m of $^4I_{13/2} \rightarrow ^4I_{15/2}$ radiative transitions of Er$^{3+}$ ion matches the telecommunication window of the minimum optical loss of silica-based optical fibres. The relatively long lifetime of a few milliseconds and the ability to dissolve high concentrations of Er$^{3+}$ also make the Er-doped GeGaSe and GeGaS ChGs potential candidate materials for applications in optical amplifiers and lasers [2]. However, the PL mechanisms in these materials are still far from being understood and require further investigation for practical use as well as scientific interest [3–5].

Similarly, glasses doped with Nd are also popular materials widely used in solid-state lasers and optical amplifiers; here ChGs also are very successful as a host matrix for the same reason as Er-doped ChGs. One of the first ChGs lasers was demonstrated in 1996 by Schweizer in a Nd$^{3+}$ doped gallium lanthanum sulphide glass (GaLaS) and this was quickly followed by a GaLaS fibre laser. These lasers operated on the $^4F_{3/2} \rightarrow ^4I_{11/2}$ radiative transition of Nd$^{3+}$ at wavelengths around 1080 nm in both pulsed and CW modes [6, 7]. In a previous paper we investigated the $^4I_{9/2} \leftrightarrow ^4F_{3/2}$ optical transitions of Nd$^{3+}$-GaLaS ChGs using absorption and emission spectra at various temperatures. We determined the positions of Stark levels of $^4I_{9/2}$ and $^4F_{3/2}$ manifolds and the emission cross-section [8]. The radiative lifetime of the metastable $^4F_{3/2}$ manifold was determined independently from PL decay and quadrature frequency resolved spectroscopy (QFRS), both of which methods gave practically identical results. The observed lifetime was almost independent of temperature and agreed fairly well with that estimated from the Judd-Ofelt (JO) analysis. However, little is known about the $^4F_{3/2} \rightarrow ^4I_{15/2}$ radiative transition giving rise to a PL band centred around 1840 nm. The branching ratio calculated using the JO analysis, $\beta_{15/2}$ corresponding to $^4F_{3/2} \rightarrow ^4I_{15/2}$ transition, is about $2 \times 10^{-3}$, which is too small to be experimentally verified, though laser-oscillations were observed at the 1840 nm transition in Nd-doped Yttrium Aluminium Garnet (YAG) [9–11]. For practical applications of Nd$^{3+}$-doped GaLaS (for example in high-power glass lasers and optical amplifiers) the exact branching ratios $\beta_J (J = 9/2, 11/2, 13/2 and 15/2)$ of all four abovementioned radiative transitions, or lasing channels should be known in order to suppress parasitic oscillations and undesirable spontaneous emission.

In addition to PL and PL excitation (PLE) spectroscopy, PL lifetime measurement is very important. Conventional measurement of PL lifetime obtained from PL decay is called time resolved spectroscopy (TRS). On measuring TRS of the PL decay consisting of multi-lifetime components, one must decrease the photocarrier generation rate $G$ sufficiently to avoid the occurrence of non-linearity, and to ensure a geminate recombination condition, where a short-lived component appears in the decay immediately after the cessation of PL excitation. However, sometimes a long-lived component decreases to an undetectable level at a time corresponding to its own lifetime in the PL decay [12]. By contrast, QFRS yields detailed information on widespread lifetime distributions in amorphous semiconductors compared with the TRS and can discriminate a small lifetime component against the main lifetime component with sufficient sensitivity by virtue of the dual lock-in detection techniques used in this measurements system [12]. Nevertheless, QFRS has not been widely applied to the radiative transitions of RE ions as far as the authors know. One of the disadvantages of QFRS is that the minimum lifetime that can be resolved is limited to microseconds owing to the upper limit frequency of the conventional lock-in amplifiers. We have developed a dual-phase double lock-in (DPDL) QFRS system to measure nanoseconds lifetimes by using an RF lock-in amplifier and...
extended the longer lifetime limit to 160 s by using a digital lock-in amplifier in internal mode with synchronous filtering; therefore our wideband QFRS technique covers PL lifetimes of almost 11 decades from 2 ns to 160 s.

In the present paper, we first review previously published results to elucidate the PL mechanisms of undoped and Er-doped GeGaSe ChGs with the abovementioned wideband QFRS [13, 14], adding the QFRS of Er-doped GeGaS of sulphide based ChGs. We also present the results of the detailed analysis on the $^4I_{15/2} \rightarrow ^4I_{15/2}$ radiative transition of Nd$^{3+}$ in GaLaS ChGs with the QFRS improved in accuracy and the doubly-modulated PL spectroscopy at room temperature [15].

2. Experimental procedure

Er-doped GeGaSe ChGs of the actual composition Ge$_{28}$Ga$_6$Se$_{64.7}$S$_{0.8}$Er$_{0.5}$, which has been doped with Er$_2$S$_3$, and undoped ChGs of the actual composition Ge$_{27}$Ga$_9$Se$_{64}$ were prepared at University of Saskatchewan. The density of Er$^{3+}$ centres is estimated as $\sim 5 \times 10^{19}$ cm$^{-3}$ for the 0.5 % Er-doped samples. The sample thickness was $\sim$1.2 mm for the undoped and $\sim$2.4 mm for the Er-doped samples. Er-doped GeGaS ChGs of the actual composition Ge$_{28}$Ga$_6$S$_{65.5}$Er$_{0.5}$ with an estimated Er$^{3+}$ density $\sim 2 \times 10^{20}$ cm$^{-3}$ and a thickness of 1.23 mm were similarly synthesized at the same laboratory.

The samples were excited by various lasers but mostly at $E_x = 2.33$ eV (532 nm), and PL was detected by a Hamamatsu 5509-72 infrared photomultiplier (PMT) at the photon energy $\sim$0.73 eV ($\sim$1.7 µm) or greater with a long-pass filter to cut off the excitation laser light. Occasionally the PL was dispersed by a 10 cm-f/3.0 monochromator with a resolution of $\sim$40 nm, which was installed between the sample and PMT. The PL lifetime distributions were measured by the aforementioned wideband QFRS system [12]. The newly detected slow component was analysed using the QFRS of the PL excited by bandgap light of 2.33 eV in superposition with sub-bandgap light of $\sim$0.37 eV (3.39 µm) from an infrared (IR) laser.

Nd-doped GaLaS ChGs with the molar composition (65Ga$_2$S$_3$):(31.5La$_2$S$_3$):(3La$_2$O$_3$):(0.5Nd$_2$S$_3$) was prepared at the University of Southampton with an estimated concentration of Nd$^{3+}$ $\sim 8.9 \times 10^{19}$ cm$^{-3}$ [15, 16]. A sample with a thickness $\sim$3.3 mm was excited at room temperature by a laser operating at 2.33 eV with power density $\sim 230$ mW cm$^{-2}$. The PL was detected by an electronically cooled InGaAs PIN photodiode (Hamamatsu G5852-21) having the long-wavelength limit of 2050 nm and a cut-off frequency 40 MHz. The PL was dispersed by a 10 cm-f/3.0 monochromator with a resolution $\sim$14 nm. For the measurements of the 900 nm PL band, the InGaAs PIN diode was replaced by a Si photodiode to improve the responsivity of the detector. Both the spectral throughputs of the monochromator and the spectral sensitivity of the detector were calibrated with an incandescent lamp. We used the double lock-in technique to observe the weak PL in the range from 1400 to 2040 nm by doubly-modulating the laser light with an acousto-optic modulator and an optical chopper. Although the PL lifetime of an RE ion has been measured by TRS so far, we applied here the QFRS method because of its better sensitivity and time resolution [12, 15].

Each PL band of Nd$^{3+}$ belonging to $^4F_{3/2} \rightarrow ^4I_J$ ($J = 9/2, 11/2, 13/2$ and 15/2) was selected by a combination of short- and long-pass optical filters for the QFRS. The accuracy of the QFRS was improved as follows. By using the “ratio function” mode of the two lock-in amplifiers, the QFRS signal was normalised to excitation intensity to suppress the influence of the fluctuations of laser power. Compared to previous papers, we reduced the logarithmic lifetime interval of QFRS from 0.15 to $\sim 0.002$, which gave us an actual interval of $\sim 0.4$ µs in the vicinity of the peak of QFRS spectrum around $\sim 80$ µs. In order to recover a true lifetime distribution precisely, QFRS spectrum was deconvoluted with improved accuracy by using the statistics package software of Mathematica.

If two PL bands overlap in spectra but differ in lifetime $\tau$, they can be discriminated by modulating the PL emission. When a PL is modulated at an angular frequency $\omega$, the amplitude of PL with a lifetime $\tau$ is known to decrease as $[1+(\omega\tau)^2]^{-1/2}$ with increasing $\omega$ [12]. Therefore, a fast recombination process may be effectively separated from a slow process by measuring the frequency-dependent PL amplitude.
3. Results and discussion

3.1 Undoped and Er-doped GeGaSe ChGs

Figure 1 shows the QFRS spectra of undoped (host) and Er-doped GeGaSe glasses at 3.7 K and 294 K (room temperature) at the PL excitation energy $E_x = 2.33$ eV and generation rate $G \approx 2 \times 10^{19}$ cm$^{-3}$s$^{-1}$, which corresponds to a power density $\sim 20$ mWcm$^{-2}$. The maxima of the data are normalised to unity.

There are striking differences between the PL of the undoped and Er-doped samples: (1) the QFRS spectrum of the host glass reveals three lifetime peaks centred at $\tau_S \approx 20$ ns, $\tau_T \approx 80 \mu$s and $\tau_H \approx 20$ s, at 3.7 K, whereas that of the Er-doped sample comprises of two peaks: a peak due to intrinsic Er$^{3+}$ radiative transition at $\tau_{Er} \approx 3.3$ ms and slow component at $\tau_H \approx 20$ s similar to that observed in the host: (2) a temperature rise from 3.7 K to 294 K decreases the magnitude of the intrinsic PL of the host by a factor of $\sim 4 \times 10^4$ accompanied by significant changes in the lifetime distribution. The PL of the Er-doped sample decreases only by $\sim 10$ over the same temperature rise without notable changes in the lifetime distribution, including the slow $\tau_H$ component; the deconvolution improved in accuracy by using the non-linear least square fit of Mathematica which gives a FWHM $\sim 1.9$ ms for the lifetime distribution of the $\tau_{Er}$ components at 3.7 and 294 K in stead of $\sim 0.3$ ms in the previous paper [13] (figure 1).

The lifetime peak of the $\tau_S$ component of the undoped sample falls short of the QFRS limit of 2 ns at 294 K, while the $\tau_T$ component in the middle of the lifetime distribution at 3.7 K exhibits a pronounced decrease accompanied by a shift of the lifetime peak from $\sim 80$ $\mu$s to 0.6 $\mu$s with temperature rise from 3.7 K to 294 K [14]. An activation energy of 78 meV estimated from the temperature dependence of ratio of the $\tau_S$ component to the $\tau_T$ component, coincides with the PL peak energy difference $\sim 80$ meV of the PL spectra of both the components obtained from PL emission-
energy-evolved QFRS spectra [14]. Hence the $\tau_S$ and $\tau_T$ components are associated with singlet and triplet excitons, respectively, with a spin-exchange energy of $\sim 80$ meV, as previously reported for a-Si:H and a-Ge:H [17] and ChGs such as As$_2$S$_3$ glass and a-Se [18].

Figure 2 shows the quantum efficiencies (QEs) $\eta_S$ and $\eta_T$ of the corresponding $\tau_S$ and $\tau_T$ components as functions of temperature $T$ in addition to the lifetimes $\tau_S$ and $\tau_T$. Generally the QE is reduced by non-competing non-radiative recombination (NRR) and/or competing NRR in amorphous semiconductors. The non-competing NRR is introduced by defects and impurities, which rapidly capture photoexcited carriers normally within $10^{-12}$ s during the thermalisation of photocarriers from extended or higher tail states after the PL excitation. The non-competing NRR reduces $\eta_S$ and $\eta_T$ without shortening the measured PL lifetimes $\tau_S$ and $\tau_T$, whereas the competing NRR with a lifetime $\tau_{nr}$ reduces $\tau_S$ and $\tau_T$ since the composite or actual lifetime $\tau_m$ in competitive recombination is expressed as $\tau_m^{-1} = \tau_S^{-1} + \tau_{nr}^{-1}$ with a radiative recombination time $\tau_r$ for each exciton, being usually independent of $T$ [14]. With increasing $T$ the QEs $\eta_S$ and $\eta_T$ decrease more strongly than the lifetimes $\tau_S$ and $\tau_T$ (figure 2). This difference indicates the contribution of the non-competing NRR to the decrease in both $\eta_S$ and $\eta_T$. Thus, the non-competing NRR contributes substantially to the thermal quenching of the excitons in undoped GeGaSe ChGs; namely as $T$ rises from 3.7 to 294 K, $\eta_S$ decreases by about two orders of magnitude greater than $\tau_S$ and $\tau_T$ (figure 2). This is the characteristic temperature $T_0 \approx 53$ K estimated from the dotted lines in figure 2, and thus the characteristic temperature $T_0 \approx 53$ K for the competing NRR of both the $\tau_S$- and $\tau_T$-components, despite the difference of more than 3 orders of magnitude in $\tau_S$ and $\tau_T$. This is
attributed to the difference in exciton capture cross sections, from which a characteristic energy of localised states $\epsilon_0 \approx 20$ meV is obtained [14].

The observations are distinctly different for the Er-doped GeGaSe sample. It is shown in figure 2 that the QE $\eta_{Er}$ of the $\tau_{Er}$-component, i.e., the $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission decreases only by an order of magnitude for a $T$ increase from 3.7 to 294 K at $E_x = 2.33$ eV, while the lifetime $\tau_{Er} \approx 3.3$ ms remains the same as shown in figure 1. This suggests the absence of a competing NRR with a lifetime $\tau_{nr}$ that would modify $\tau_{Er}$ through $\tau_{m}^{-1} = \tau_{r}^{-1} + \tau_{nr}^{-1}$. The $\tau_{Er}$-component is thus quenched by the non-competing NRR. In the Er-doped sample, the slow component with $\tau_T \approx 20$ s is still observable at $T = 294$ K and $E_x = 2.33$ eV without appreciable changes in the lifetime distribution obtained from the QFRS spectrum at 3.7 K, except for the magnitude (figure 1); the competing NRR is completely absent even in the slow $\tau_T$-emission process as well as the $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission of the $\tau_{Er}$-component. This implies that the Er$^{3+}$ luminescent centre in GeGaSe ChGs is extremely isolated from the competing NRR and possesses no back-transfer process [19].

Figure 3(a) depicts the excitonic recombination on the basis of Mott-Davis-Street (MDS) model [20]. When the exciting light creates an electron-hole (e-h) pair, the hole is captured by a nearby negatively-charged D$^-$ recombination centre, thereby changing the charge state to D$^0$. This causes a lattice relaxation around the centre and shifts the D$^0$ state deeper into the mid-gap. The excited electron in the conduction band is then bound to the hole captured by the D$^0$ centre, which forms a singlet (S) or triplet (T) bound-exciton. Alternatively, either singlet or triplet exciton bound to D$^0$ can be formed.

![Figure 3](image_url)

**Figure 3.** Possible excitation processes of the Er$^{3+}$ centre. Photoexcitation produces an electron and hole (e-h) pair, each of which is thermalised very fast into the respective tail states. One-type of charge carrier, e.g., hole is immediately captured by a charged defect D$^-$, which undergoes a consequent lattice relaxation and shift in energy to D$^0$. The process D$^- + h \rightarrow D^0$ also takes place when an electron of D$^-$ is photoexcited. (a) Photoexcited electron forms a bound singlet (S) or triplet (T) exciton with the hole captured at D$^0$ as a precursor, and (b) the photoexcited electron is trapped in tail-states, forming an e-h pair with the localised hole at D$^0$, which has an appreciable separation $R$ and subsequently recombines via tunnelling with a slow recombination rate. The complementary process involving the capture of an electron in D$^-$ is also possible. (c) Excitation and recombination at Er$^{3+}$ centre.
by exciting an electron of the D− to the conduction band. The complementary process involving a capture of an electron in D+ is also possible. In the undoped sample, the excitons can then recombine and emit luminescence having different lifetimes τS and τT with appreciable Stokes shifts. In the Er-doped sample, on the other hand, the exciton recombines non-radiatively as a precursor, transferring its energy to a nearby Er3+ ion, and excites it from the ground state to the excited state, followed by an Er3+ luminescence emission as in figure 3(c).

The wideband QFRS technique revealed a third very-long-lived component almost universally in the PL of a-Si:H, a-Ge:H and ChGs, and associated it with the radiative tunnelling (RT) recombination of distant-pairs (DPs) by examining its dependences on the generation rate G, Eξ and the magnetic field. However, this is not the case for the slow τH component of the host, because it has little dependence on G and Eξ to support DP recombination. Nevertheless the recombination rate 1/τH is independent of PL emission energy ħω whereas 1/τS and 1/τT are proportional to (ħω)3 indicating excitonic recombination for the τS and τT components [14]. The independence of the recombination rate 1/τH from ħω suggests recombination of an uncorrelated e-h pair such as DPs [21]. Thus RT within the uncorrelated e-h pair cannot be discarded for the slow τH component. Impurities and defects in the structure open non-radiative channels to e-h pair recombination. The non-radiative tunnelling (NRT) channel, which is an exponential function of the distance between a tail-trapped carrier and a defect-state, competes with the RT channel in recombination events and thus the lifetime τH is a composite of the RT and the NRT recombination. Since the recombination rate is low for the long RT lifetime of the e-h pair appreciably separated by distance R (figure 3(b)), τH is mostly determined by the impurity and defect densities. Such a situation was frequently encountered for glassy As2S3 [22] and defect-rich films of a-Si:H and a-SiN:H [23]. Generally, relatively large quantities of impurities and defects may be present in ChGs and thus they will play a rate-limiting role in the slow τH-recombination.

In order to confirm the above concept, we superposed an infrared (IR) light of 0.37 eV (3.39 μm) and ~10 mWcm−2 in the wideband QFRS excited at Eξ = 2.33 eV and G ≈1015 cm−3s−1 (~1 μWcm−2). Both the samples exhibit a close similarity; IR biasing induces a decrease of the τH component and a shortening of its lifetime peak τH. The results are interpreted in terms of IR-induced release of the trapped carriers from localisation at the tail-states; the IR biasing activates a localised photocarrier, i.e., electron, which makes a hop-up to a higher tail-state or extended-state and then diffuses as shown by a red dashed arrow in figure 3(b). Thus, it may recombine either with a hole captured by a closer D0 centre or with a hole at a closer non-radiative centre such as an impurity or defect, thereby shortening the lifetime τH and decreasing the amplitude of the τH component in both the undoped and doped samples [13, 14, 23].

Figure 4 shows the PL spectra of the Er doped sample obtained by fixing QFRS frequencies correspondingly to τS ~3 ms and τH ~16 s, together with the PL spectrum of the host obtained by DC measurements at 3.7 K. Surprisingly, even the slow τH component of the Er-doped sample exhibits sharp Er3+ emission lines at ~0.8 eV (4I13/2→4I15/2) and ~1.27 eV (4I11/2→4I15/2). However, the background spectrum of the τH component has close resemblance to the PL spectrum of the host, whereas the τS component shows the pronounced Er3+ -emission lines with a quite different background compared with the τH component. This suggests a difference in the energy transfer mechanisms in the two components [13].

Deconvoluting the QFRS spectrum of the undoped sample at 3.7 K in figure 1, we estimated τS, τT and τH components to be ~22, ~70, ~8 %, respectively. We postulate that the PL process occurs in cascade in the Er-doped sample as the precursor transfers its energy to the Er3+ centre, and hence the PL lifetime is determined by the longer-lived process. Thus, the faster excitonic precursors contribute mainly to the τS component (figure 3(a)) and the precursor composed of a tail-trapped photocarrier and an oppositely-charged carrier captured to a D0 centre contributes to the slow τH component.
Figure 4. PL spectra of QFRS signals of Er-doped sample obtained at fixed frequencies corresponding to $\tau_{\text{Er}}$ ($\Delta$) and $\tau_{\text{H}}$ ($\bullet$). Peaks of the spectra for $\tau_{\text{Er}}$ and $\tau_{\text{H}}$ at 0.8 eV ($\sim$1.5 µm) are normalised to unity. PL spectrum of host obtained by DC measurement ($\bullet$) is also shown. Vertical scale is logarithmic with arbitrary unit.

(figure3(b)). Deconvolution of the QFRS for the Er-doped sample at 3.7 K (figure 1) suggests that 51% of the whole excitonic component of the host is converted to the $\tau_{\text{Er}}$ component and 54% of the slow $\tau_{\text{H}}$ component of the host, to that of the Er-doped sample at low temperature [13].

The energy transfer mechanism of the main Er$^{3+}$ emission, i.e., the $\tau_{\text{Er}}$ component is of particular interest for photonic applications. Förster energy transfer is discarded, because this process, in principle, transfers energy between singlet excitons via dipole-dipole interactions whereas the triplet exciton component occupies $\sim$70 % of all recombination events in the host. The Dexter energy transfer can take place between triplet excitons but its critical transfer distance is usually 0.3–1 nm. Since average distance between Er$^{3+}$ centres is estimated to be roughly $\sim$3 nm for the 0.5 % Er-doped sample where density of Er$^{3+}$ centre amounts to $\sim$5×10$^{19}$ cm$^{-3}$, probably being much larger than that of defects (D-states), this process is also not relevant. Thus, we assert defect-related Auger excitation (DRAE) of the Er$^{3+}$ centre to be the most probable energy transfer mechanism at least at low temperatures [5, 13, 24]. The energy transfer mechanism of the slow $\tau_{\text{H}}$ component is different from that of the $\tau_{\text{Er}}$ component, because the precursor consists of a tail-state trapped carrier and oppositely-charged carrier captured by a D$^0$ centre; and experimentally the background spectrum of PL differs from those of the $\tau_{\text{Er}}$ component. However, considering no involvement of excitons in the slow process, we propose the slow component to be controlled by DRAE as well [13].

3.2 Er-doped GeGaS ChGs

Figure 5 shows quite similar QFRS spectra of Er-doped GeGaS, which were excited by the light of energy $E_\chi = 2.33$ eV at generation rate $G \approx 1 \times 10^{16}$ and $1 \times 10^{18}$ cm$^{-3}$s$^{-1}$ at 3.7K and $G \approx 1 \times 10^{15}$ cm$^{-3}$s$^{-1}$ at
Figure 5. QFRS spectra of 0.5at. % Er-doped GeGaS ChGs. (∗) G=10^{16} and (∆) G=10^{18} cm^{-3}s^{-1} at 3.7 K (●) G=10^{15} cm^{-3}s^{-1} at 294 K. The deconvoluted spectrum of the data (∆) has a peak at ~5.3 ms and a FWHM ~ 1.6 ms.

294 K (room temperature). All the maxima of the data are normalised to unity. In the Er-doped GeGaS sample the slow \( \tau_{H} \) component is observable even at room temperature and its peak lifetime hardly depends on \( G \) and \( T \) similar to the behaviour of the Er-doped GeGaSe sample except \( \tau_{Er} \approx 5.3 \) ms differing from 3.3 ms, which is probably due to the difference in the host material (GeGaS). Incidentally, the QFRS on Er-doped GeGaS ChGs gave \( \tau_{Er} \approx 4 \) ms and no useful information about the slow \( \tau_{H} \) component, while the TRS gave \( \tau_{Er} \approx 5.2 \) ms in Ref.[2].

3.3 Nd-doped GaLaS

Figure 6 compares the PL spectra of Nd-doped GaLaS ChGs in the 1400–2040 nm spectral range measured at two sets of double-modulation frequencies of PL excitation light: low frequency set of 800 Hz and 15Hz (LF or closed symbols) and high frequency set of 15 kHz and 150 Hz (HF or open symbols); the double lock-in technique was introduced by doubly-modulating the excitation light to

Figure 6. Normalised PL spectra of Nd^{3+}:GaLaS at room temperature from 1400 to 2040 nm. The spectra shown by solid symbols (●) are measured using a relatively low lock-in modulation frequency of 800 Hz (LF). The spectra shown by open circles (∗) are measured using higher frequency of 15 kHz (HF). \( 2\pi \times \text{HF} \) is higher and \( 2\pi \times \text{LF} \) is lower than the inverse of 77 μs which is characteristic of the \( ^{4}F_{3/2}\rightarrow ^{4}I_{7/2}, (J=9/2 \sim 15/2) \) transitions.
investigate this very weak spectral range in detail. The substantial reduction of peak at 1840 nm and the difference in the spectral shape detected for HF modulation indicates the dominance of a long-lifetime component, which is supported by figure 7(a) of the QFRS spectrum measured for 1840 nm PL band ranging from 1700 to 2040 nm. The deconvoluted QFRS spectrum reveals the presence of two components: dominant peak at 77 µs, which can be attributed to \(^{4}F_{3/2} \rightarrow ^{4}I_{15/2}\) transition, and a small peak at 3.8 µs, whose nature is discussed later. The relative contribution of both components to the 1840 nm band may be estimated by integrating the underlying areas. This procedure attributes ~83% to the \(^{4}F_{3/2} \rightarrow ^{4}I_{15/2}\) transition with lifetime 77 µs and the remaining ~17% to the short-lifetime component.

The PL band between 1500 and 1650 nm with the peak at ~1560 nm in figure 6 (larger arrow) is less sensitive to the variation of modulation frequency from LF to HF in contrast to 1840 nm band, suggesting a higher content of the short lifetime component and thus deserves special discussion. Its overall intensity measured at LF is about 140% of PL band centred at 1840 nm. The deconvolved QFRS spectrum shows the presence of two Gaussian-like components centred at 3.5 and 82 µs and the dominant “fast” component controls about 76% of the overall spectrum (figure 7(b)). The huge difference between the dominant lifetime of 1560 nm band (3.5 µs) and the lifetime of \(^{4}F_{3/2} \rightarrow ^{4}I_{15/2}\) transition (~77 µs) suggests a different origin for this band. From the point of view of spectral position, this band may be assigned to radiative transitions originating from the doublet \((^{4}F_{5/2}, ^{2}H_{9/2})\) to the \(^{4}I_{15/2}\) manifold as illustrated by the dashed arrow in figure 8. These transitions would produce two unresolved lines peaking around ~1630 and ~1580 nm, which fall within the experimentally observed 1560 nm band.

However, the observed short lifetime of 3.5 µs requires further discussion for the transition probabilities of electric-dipole transitions \(^{4}F_{5/2}, ^{2}H_{9/2} \rightarrow ^{4}I_{J}\) in Nd\(^{3+}\):GaLaS ChGs, but unfortunately there is no direct information except that of fluoride glasses [25, 26], in which the total probability of the \(^{4}F_{5/2} \rightarrow ^{4}I_{J}\) transitions is only ~1.4 times larger than that of \(^{4}F_{3/2} \rightarrow ^{4}I_{J}\) transitions. Meanwhile the probability of \(^{2}H_{9/2} \rightarrow ^{4}I_{J}\) transitions is smaller by an order of magnitude. Therefore, the short lifetime of ~3.5 µs cannot be explained by the radiative transitions of \(^{4}F_{5/2}, ^{2}H_{9/2} \rightarrow ^{4}I_{J}\) only. When the energy difference \(\Delta E\) between two levels is relatively small, there is high probability of efficient multiphonon
relaxation from the upper energy level to the lower one by emitting phonons [27]. This may occur between the doublet ($^4\text{F}_{5/2},^2\text{H}_{9/2}$) and the $^4\text{F}_{3/2}$ manifold where the energy gap $\Delta E \approx 850$–1050 cm$^{-1}$ is close to typical phonon energies. Therefore, the radiative transitions compete with non-radiative multiphonon relaxation of $^4\text{F}_{5/2},^2\text{H}_{9/2}\rightarrow^4\text{F}_{3/2}$ as shown by an open arrow in the energy scheme for Nd$^{3+}$ in figure 8. We estimated the multiphonon relaxation time to be about 9.0 $\mu$s at room temperature for $\Delta E = 950$ cm$^{-1}$ which is comparable with the dominant lifetime $\sim 3.5$ $\mu$s of the 1560 nm band in figure 7 (b) [15]. Thus the PL spectrum and lifetime suggest that the 1560 nm band is caused by radiative $^4\text{F}_{5/2},^2\text{H}_{9/2}\rightarrow^4\text{I}_{15/2}$ transitions competing with multiphonon relaxation. It is also worth noting that the 1560 nm band may be effectively smeared due to several factors such as the strong overlapping of Stark components in both transitions and the competing multiphonon relaxation. Therefore the PL of the 1840 nm band may be intermingled with the short-lived PL of the 1560 nm band.

Table 1 presents the branching ratios $\beta_J (J = 9/2, 11/2, 13/2$ and $15/2)$ corresponding to the four

| Transition | Judd-Ofelt analysis | Experiment |
|------------|---------------------|------------|
| $^4\text{I}_{9/2}$ | 890 | 0.539 | 160 | 900 | 0.551 | 78.4 |
| $^4\text{I}_{11/2}$ | 1066 | 0.393 | 219 | 1095 | 0.387 | 77.3 |
| $^4\text{I}_{13/2}$ | 1390 | 0.067 | 1288 | 1370 | 0.060 | 78.4 |
| $^4\text{I}_{15/2}$ | 1893 | 0.002 | 47998 | 1840 | 0.002 | 76.6 |

Table 1. Central wavelength $\lambda$ (nm), branching ratio $\beta_J$ and lifetime $\tau$ ($\mu$s) obtained from Judd-Ofelt analysis and experiments. Four lifetimes obtained by JO analysis give the composite lifetime $\sim 86 \mu$s.
radiative transitions $^4F_{3/2} \rightarrow ^4I_J$ in Nd$^{3+}$:GaLaS calculated by integrating the spectra of corresponding bands [15]. Prior to the integration, the spectra are properly calibrated. As for the band at 1840 nm, only 83% of overall integral are taken into account, which corresponds to the $^4F_{3/2} \rightarrow ^4I_{15/2}$ transition only. It is noteworthy that these values are in a good agreement with previous estimations based on JO analysis. It should also be noted that according to QFRS, all four $^4F_{3/2} \rightarrow ^4I_J$ transitions are competing with each other and therefore exhibit approximately the same lifetime of ~77 µs, with actual QFRS data scattered from 76.6 to 78.4 µs. The above lifetime is slightly different from that reported earlier in Ref. [8] (~90 µs) and might be due to the higher accuracy of the present data. In addition, the JO lifetimes in Table 1 give a composite lifetime ~86 µs.

4. Conclusion
The wideband QFRS discriminated three (triple-peak) PL components of undoped GeGaSe ChGs and two PL components of Er-doped GeGaSe ChGs at 3.7 K. Two components of undoped GeGaSe ChGs with lifetimes 20 ns and 80 µs originate from singlet and triplet excitons, respectively and are influenced by competing NRR with an identical characteristic temperature $T_0 \approx 53$ K as well as non-competing NRR; the latter more strongly. The Er-doped sample has the Er$^{3+}$ f-f emission of narrow lifetime distribution around the mean lifetime $\tau_{\text{Er}} \approx 3.3$ ms, being almost temperature independent. Both the undoped and Er-doped samples have slow emission of a lifetime of 20 s, but the latter does not show appreciable change in both lifetimes of 3.3 ms and 20 s even by elevating the temperature from 3.7 K to room temperature, suggesting little influence of competing NRR on Er luminescence centres. Similar QFRS results were obtained from Er-doped GeGaS ChGs except $\tau_{\text{Er}} \approx 5.3$ ms.

The undoped GeGaSe sample has broad and featureless PL spectra for all the three components but the Er-doped sample has Er$^{3+}$ f-f emission spectra not only for the main Er$^{3+}$ emission of lifetime 3.3 ms, but also for the slow emission of lifetime 20 s. The precursor for the main Er$^{3+}$ emission is the exciton formation and that for the slow emission is a separately localised e-h pair, i.e., the tail-trapped one and the other captured by a D$^0$ centre.

In Nd-doped GaLaS ChGs, two overlapping PL bands in the wavelength range from 1400 to 2040 nm were separated by modulating the PL emission at two different frequencies at room temperature. One PL band possesses a peak wavelength of 1840 nm and a major lifetime 77 µs in common with the four lasing channels of Nd$^{3+}$. This band is attributed to the lowest energy $^4F_{3/2} \rightarrow ^4I_{15/2}$ transition of the four radiative channels of Nd$^{3+}$. The other PL band with a peak wavelength of 1560 nm and a major lifetime 3.5 µs is attributed to the doublet $^2H_{9/2},^4F_{5/2} \rightarrow ^4I_{15/2}$ radiative transitions. Its short-lived lifetime is interpreted by estimating the competing multiphonon relaxation. By suitably interpreting the two mixed radiative transitions $^4F_{3/2} \rightarrow ^4I_{15/2}$ and $^2H_{9/2},^4F_{5/2} \rightarrow ^4I_{15/2}$, we obtained the branching ratios of the four channels in Nd-doped GaLaS ChGs, agreeing with those from the Judd-Ofelt analysis.

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