Optical Measurement of Narrow Band Rare-Earth 4f Levels with Energies Greater than the Band Gap of the Host

T. Schweizer,[1] P. E.-A. Möbert,[3] J. R. Hector,[2] D. W. Hewak,[1] W. S. Brocklesby,[1] D. N. Payne,[1] and G. Huber[3]
[1]*Optoelectronics Research Centre, University of Southampton, Southampton, SO17 1BJ, United Kingdom*
[2]*Department of Physics, University of Southampton, Southampton, SO17 1BJ, United Kingdom*
[3]*Institut für Laser-Physik, Universität Hamburg, Jungiusstraße 9a, 20355 Hamburg, Germany*

(Received 19 June 1997)

Excited-state absorption spectra of erbium and thulium doped gallium lanthanum sulfide glasses reveal transitions whose final 4f states do not appear in the ground state absorption spectra due to resonance with the fundamental absorption of the glass host. The results give direct evidence for the model of isolated rare-earth ions with highly shielded 4f levels showing no noticeable interaction with the host material despite resonance. Only the energy splitting of the 4f levels is relevant for energy transfer processes between rare-earth ions and the host material, whereas the absolute energetic position is unimportant. [S0031-9007(98)05305-8]

PACS numbers: 78.66.Jg, 31.50.+w, 42.70.Hj

Excited-state absorption (ESA) describes the absorption from a populated excited electronic state of a system to higher-energy states. In rare-earth (RE) doped materials, ESA at the emission or pump wavelengths can impede or completely prevent laser action. The final states of an ESA transition from an excited RE level can either be a higher lying RE level of the same configuration or the conduction band of the host material [1–6].

In this Letter, we present ESA measurements on erbium (Er^{3+}) and thulium (Tm^{3+}) doped gallium lanthanum sulfide (GLS) glasses that can be classified as wide-band-gap semiconductors with an energy gap of 2.6 eV, which corresponds to a visible transparency down to about 500 nm. The problem arises whether ESA transitions from RE 4f levels to the conduction band of the glass or to 4f levels that are "higher" than the conduction band will occur.

ESA transitions from RE dopants to the host material have been observed in a variety of divalent and trivalent RE doped materials [1–6]. The reported ESA transitions into the conduction band originate from the $4f^{n-1}5d$ states of the RE ions and have typical cross sections of 10^{-18}–10^{-17} cm^2 [2–4]. These values are much larger than the values for the dipole forbidden $4f$-$4f$ transitions (10^{-21}–10^{-20} cm^2) and even for the dipole allowed $4f^n$-$4f^{n-1}5d$ transitions (10^{-18}–10^{-19} cm^2) [2–4]. ESA transitions have not been measured from highly shielded $4f^n$ levels into the conduction band. Transitions from $4f^n$ levels to the conduction band are expected to be weak compared to those from $4f^{n-1}5d$ levels, due to the much smaller spatial overlap of the $4f^n$ levels with the delocalized Bloch states of the conduction band. In all of the mentioned examples, the ground and excited 4f states of the RE ions lie within the wide band gaps of the insulating host materials ($E_{\mathrm{gap}} \sim 6$ eV for yttrium aluminum garnet and 12.2 eV for CaF_2) [1–6]. The observed localized to delocalized transitions, i.e., the transfer of an electron from the impurity ion to the host material, while not uncommon in semiconductors, are quite rare in insulators.

In this Letter, we look at chalcogenide glasses which can be classified as semiconductors, most of which have hole-type conductivity [7,8]. Interband gap states formed by extrinsic impurities and intrinsic defects cause the typical weak absorption tail below the Urbach edge [7]. In semiconductors, energy transfer between 4f levels of RE ions and the host is a common phenomenon and is the proposed basis for electrically pumped RE lasers [9]. The main processes discussed in the literature are impact excitation (intraband) and Auger recombination (interband) which transfer energy from the semiconducting host material to the RE ions through Coulomb interactions [10,11]. The probability for Auger excitation can be increased by localized electron states in the forbidden gap, such as donors or acceptors, which may be formed by the RE impurity itself [10,12–14]. The inverse processes cause deexcitation of excited RE ions. Only the splitting of the highly localized and shielded 4f levels of the RE ions is of importance for the energy transfer; the absolute energetic position is unimportant. The absolute position of the 4f levels is expected to be much lower than the valence band, in contrast to the RE doped insulators discussed earlier [10,11]. Energy transfer between RE ions and the semiconductor hosts has been observed in Er^{3+} doped silicon, Nd^{3+} and Yb^{3+} doped semiconductors, and also in Nd^{3+} doped β-La_2S_3 crystals which have comparable spectroscopic properties to GLS glass [10,12–16]. A broad-band excitation mechanism including absorption by the glass host and energy transfer to the RE ion has been reported in other Er^{3+} doped chalcogenide glasses [17].

Commonly, lasers are designed so that both pump and signal photons are smaller than half of the band gap, in order to avoid ESA interactions with the host material [1,4]. The problem arises whether ESA transitions from RE 4f levels to the conduction band of the semiconducting

GLS glass or to impurities in the band gap could occur. As soon as the sum of the energy of an excited $4f$ level plus the energy of an incoming photon matches the energy of the band gap or an impurity state, energy transfer to the host material might be expected. Such an ESA process could cause a potential loss mechanism for RE lasers in GLS glasses. In order to check these ideas, we performed ESA measurements on Er^{3+} and Tm^{3+} doped GLS glasses and used $\mathrm{YLiF_4}$ (YLF) crystals with the same dopants as control samples.

The samples under investigation were an Er:GLS glass ($n_{\mathrm{Er}} = 2.73 \times 10^{20}$ ions/cm^{-3}), an Er:YLF crystal ($n_{\mathrm{Er}} = 6.85 \times 10^{20}$ ions/cm^{-3}), a Tm:GLS glass ($n_{\mathrm{Tm}} = 2.63 \times 10^{20}$ ions/cm^{-3}), and a Tm:YLF crystal ($n_{\mathrm{Tm}} = 5.48 \times 10^{20}$ ions/cm^{-3}). The higher RE concentration in the crystals leads to similar absorption coefficients in the crystals and the glasses. This is due to larger cross sections in the glasses due to higher covalency of the glass bonds (see Figs. 1 and 2) [18,19]. The room temperature absorption spectra (Figs. 1 and 2) show the difference in the size of the band gap of the glass and the crystal. Both the Er^{3+} and the Tm^{3+} ions in either material have absorption bands around 12 500 cm^{-1} (800 nm). These absorption bands were used to excite the ions for the ESA experiments.

The experimental setup for the ESA measurements and the evaluation and interpretation of the spectra are described in detail in Ref. [20]. The setup is based on the pump-and-probe technique using an 810 nm laser diode as the pump source and a white light source as the probe beam. The transmission of the pumped samples compared to the unpumped samples increases in spectral regions with ground state absorption (GSA) due to the reduced population of the ground state ("bleaching," positive signal ΔI). The population of excited states can lead to an increase in intensity of the probe beam in spectral regions with stimulated emission (SE) (positive signal ΔI) and to a decrease in intensity in regions with ESA (negative signal ΔI). The ratio of ΔI to I is proportional to the cross sections

$$\Delta I/I \propto \sigma_{\mathrm{GSA}} + \sum_i (n_i/n_e)(\sigma_{\mathrm{SE},i} - \sigma_{\mathrm{ESA},i}).$$

The absorption cross section σ_{GSA} is first used to calibrate the $\Delta I/I$ spectra for absolute cross sections and is then subtracted from the $\Delta I/I$ spectra. The remaining spectra give the SE and ESA cross sections weighted with the population of the levels n_i with respect to the total density of excited ions n_e (Figs. 3 and 4). The determination of the absolute cross sections requires the knowledge of the relative population densities.

The Er^{3+} ions are excited into the short-lived $^4\mathrm{I}_{9/2}$ level (Fig. 1). Nonradiative and radiative decay populates the metastable $^4\mathrm{I}_{11/2}$ and $^4\mathrm{I}_{13/2}$ levels. Lifetime measurements show that the $^4\mathrm{I}_{13/2}$ level will have the largest relative population density n_i/n_e, followed by the $^4\mathrm{I}_{11/2}$ level [19,21]. The assignment of the possible ESA transitions as derived from the Er:YLF absorption spectrum (Fig. 1) is indicated at the top of Fig. 3. A detailed spectroscopic study of Er^{3+} doped GLS glass is given in Ref. [19].

The Tm^{3+} ions are excited into the $^3\mathrm{H}_4$ level. Nonradiative and radiative decay populates the $^3\mathrm{H}_5$ and $^3\mathrm{F}_4$ levels. As for the Er^{3+} ions, lifetime measurements show that the $^3\mathrm{F}_4$ level will have the largest relative population density n_i/n_e, followed by the $^3\mathrm{H}_4$ level [21]. Possible ESA transitions from the short-lived $^3\mathrm{H}_5$ level do not fall

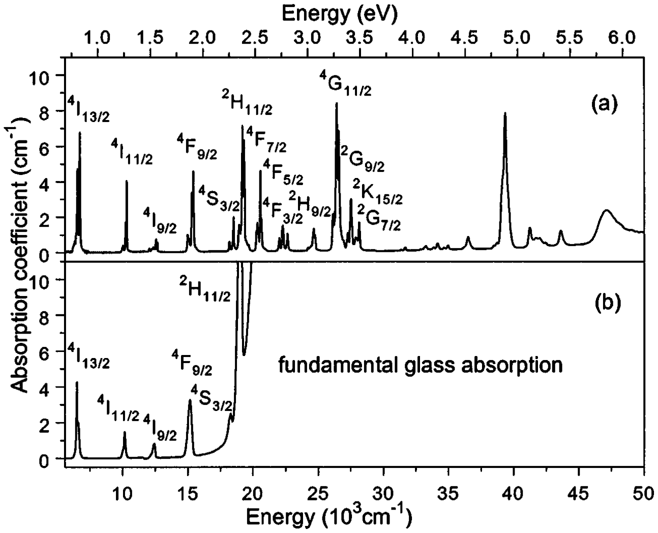

FIG. 1. Unpolarized ground state absorption spectra of (a) Er:YLF and (b) Er:GLS show the small band gap of the glass compared to the crystal. The final energy levels of the ESA transitions between 20 000 and 30 000 cm^{-1} in the Er:YLF spectrum are masked by the fundamental glass absorption in the Er:GLS spectrum.

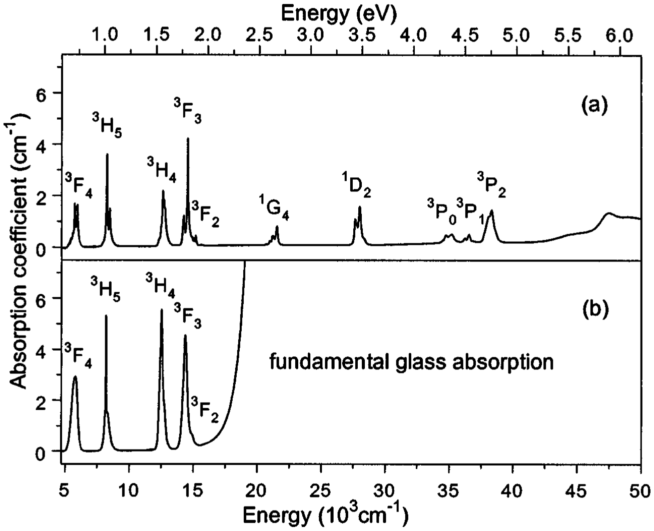

FIG. 2. Unpolarized ground state absorption spectra of (a) Tm:YLF and (b) Tm:GLS show that two of the final energy levels of the ESA transitions lie at energies relative to the ground state of about 22 000 and 28 000 cm^{-1} which are larger than the energy gap of the glass.

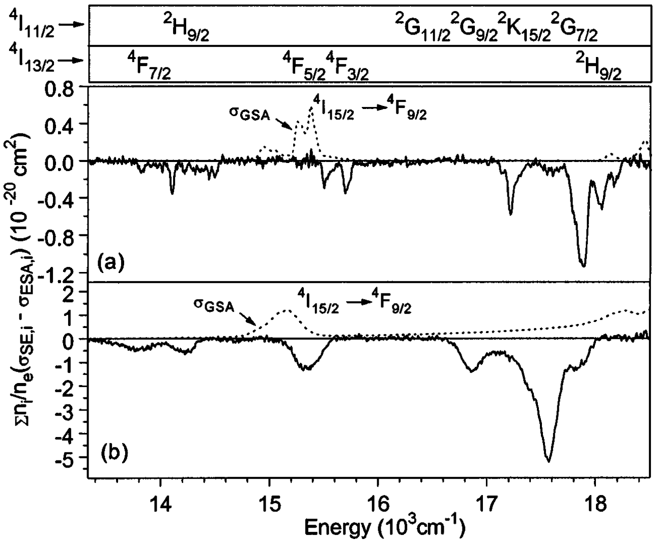

FIG. 3. Unpolarized ESA spectra (solid line) and GSA spectra (dotted line) of Er^{3+} doped YLF (a) and GLS (b) at energies in the region of the glass absorption edge show almost identical features. None of the final ESA levels indicated at the top of the figure can be seen in the GSA spectrum of the glass (Fig. 1).

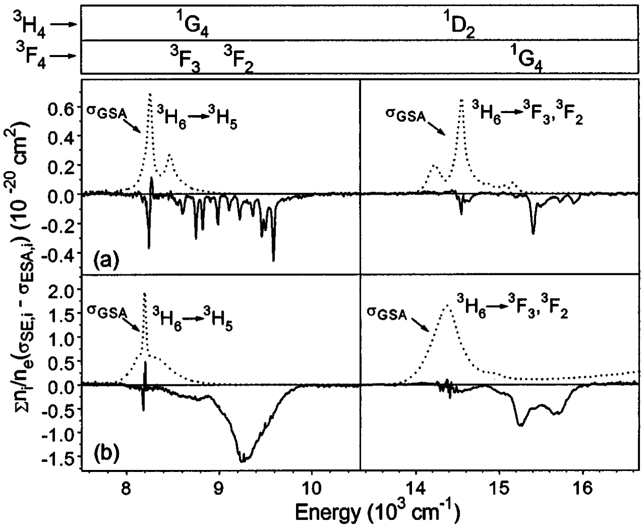

FIG. 4. The unpolarized ESA spectra (solid line) and GSA spectra (dotted line) of Tm^{3+} doped YLF (a) and GLS (b) for two energy regions at either side of the pump energy (~12 500 cm^{-1}) show ESA and GSA peaks at similar wavelengths for the two materials. Two of the final ESA levels indicated at the top of the figure ($^1G_4$ and $^1D_2$) cannot be seen in the GSA spectrum of the glass (Fig. 2).

into the energy regions measured. The assignment of the possible ESA transitions as derived from the Tm:YLF absorption spectrum (Fig. 2) is indicated at the top of Fig. 4. The peaks in the ESA spectra (Fig. 4) at 8200 cm^{-1} are caused by the subtraction of the GSA bleaching spectra. A detailed spectroscopic study of Tm^{3+} doped GLS glass will be published elsewhere.

The ESA spectra of the birefringent YLF crystal and the GLS glass were measured unpolarized and at room temperature. The position and relative strength of the ESA transitions are very similar for each dopant in the two materials. The ESA peaks are slightly broader and smoother and at lower energies in the glass due to the stronger inhomogeneous broadening and the nephelauxetic effect. As for the GSA cross sections, the ESA cross sections in the glass are several times stronger than in the crystal due to the higher covalency and higher refractive index (2.52 compared to 1.45 at around 640 nm). As expected, there was no measurable stimulated emission (positive signal) in the energy regions measured for both dopants in either material. This was due to the short lifetimes and, therefore, low relative populations (n_i/n_e) of the energy levels that could show stimulated emission, at energies covered by the measurement ($^4I_{9/2}$, $^4F_{9/2}$, and $^4S_{3/2}$ for Er^{3+} and $^3H_5$, $^3F_3$, and $^3F_2$ for Tm^{3+}). The GSA spectra show the rising glass absorption towards higher energies which renders ESA measurements at higher energies impossible (Figs. 3 and 4). No emission from the final states of the ESA transitions was observed, due to immediate reabsorption by the fundamental glass absorption and likely quenching of these levels due to efficient cross relaxation between the RE ion and the glass.

The two most striking points about the ESA spectra of both RE ions in the GLS hosts are (i) that all of the possible final states of the ESA transitions shown in Figs. 3 and 4 (except for the $^3F_4 \rightarrow {}^3F_2, {}^3F_3$ transition in Tm^{3+}) lie at energies relative to the ground state which are larger than the energy gap of the glass and, hence, do not appear in the GSA spectra of the glass (Figs. 1 and 2), and (ii) that the oscillator strengths of the ESA peaks, calculated using the integrated absorption strengths, do not show any increases. This rules out any increase of transition strengths by admixture of resonant states. The integrated absorption strength is a much more sensitive measure of transition strength than studies of the linewidth of the transitions, which in glasses are subject to significant inhomogeneous broadening. These results show that the RE ions in GLS can be treated as isolated ions with strongly shielded $4f$ levels that have only a little overlap with the extended Bloch waves of the glass.

No additional absorption features that could be related to either charge transfer or energy transfer from the RE ion to the host material have been detected within the sensitivity of our experiment. Charge transfer transitions, which have been observed in other RE doped systems, provide a measure of the "offset" of the RE levels relative to the band gap of the semiconductor, analogous to band offsets in quantum well systems. From previous studies of semiconductor systems, it is generally assumed that the $4f$ levels lie deep in the valence band [10,11]. This assumption is supported by x-ray and ultraviolet photoelectron spectroscopy of the sesquisulfides γ-RE_2S_3 (RE = Sm, Gd, Dy) and α-Gd_2S_3 which show that the binding energies of the $4f$ ground levels are larger than the binding energies of the sulfur $3p$

levels, which form the upper part of the valence band of the crystals [22,23]. Thus, the absence of charge-transfer transitions within the wavelength range of our experiments is consistent with previous measurements.

Additional absorption features caused by the energy transfer from an excited RE energy level and an incoming photon to the conduction band of the host via a virtual level do not appear in the ESA spectra. This type of transition has been observed between RE ions [24]. Such transitions would probably be broad and would start at energies of 10 000 cm^{-1} and 13 500 cm^{-1} from the $^4I_{11/2}$ and $^4I_{13/2}$ levels in Er^{3+} doped GLS glass and at energies of 7500 cm^{-1} and 12 000 cm^{-1} from the $^3H_4$ and $^3F_4$ levels in Tm^{3+} doped GLS glass.

As in semiconductors, energy transfer between RE ions and the GLS glass host depends only on the energy splitting and not on the absolute energetic position of the $4f$ levels. ESA measurements can, therefore, be used to obtain information about energy levels that cannot be otherwise measured. A similar way of gaining information about energy levels which cannot be measured by GSA has been reported in Co doped ZnSe but, to our knowledge, not yet in RE doped systems [25].

An important implication of the ESA experiments is that pumping RE ions with wavelengths close to the fundamental glass absorption is feasible in chalcogenide glass lasers and is only limited by the fundamental glass absorption and the weak absorption tail and not by ESA into the conduction band of the glass.

Chalcogenide starting materials were supplied by Merck Ltd., Poole, UK, and YLF crystals were grown by B. H. T. Chai at CREOL, Orlando, Florida.

[1] J. F. Owen, P. B. Dorain, and T. Kobayasi, J. Appl. Phys. **52**, 1216 (1981).

[2] J. K. Lawson and S. A. Payne, Phys. Rev. B **47**, 14 003 (1993).

[3] J. K. Lawson and S. A. Payne, J. Opt. Soc. Am. B **8**, 1404 (1991).

[4] Y. M. Cheung and S. K. Gayen, Phys. Rev. B **49**, 14 827 (1994).

[5] D. S. Hamilton *et al.*, Phys. Rev. B **39**, 8807 (1989).

[6] J. J. Ju *et al.*, Mater. Lett. **28**, 149 (1996).

[7] A. B. Seddon, J. Non-Cryst. Solids **184**, 44 (1995).

[8] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1979).

[9] L. Suchow and N. R. Stempel, J. Electrochem. Soc. **111**, 191 (1964).

[10] I. N. Yassievich and L. C. Kimerling, Semicond. Sci. Technol. **8**, 718 (1993).

[11] S. Schmitt-Rink, C. M. Varma, and A. F. J. Levi, Phys. Rev. Lett. **66**, 2782 (1991).

[12] F. Priolo *et al.*, J. Appl. Phys. **78**, 3874 (1995).

[13] J. Yu, T. Zhao, and W. Li, J. Lumin. **33**, 427 (1985).

[14] A. Taguchi and K. Takahei, J. Appl. Phys. **79**, 3261 (1996).

[15] V. F. Masterov and L. F. Zakharenov, Sov. Phys. Semicond. **24**, 383 (1990).

[16] M. Leiss, J. Phys. C **15**, 1071 (1982).

[17] S. Q. Gu *et al.*, J. Appl. Phys. **77**, 3365 (1995).

[18] R. Reisfeld and A. Bornstein, Chem. Phys. Lett. **47**, 194 (1977).

[19] C. C. Ye *et al.*, J. Non-Cryst. Solids **208**, 56 (1996).

[20] J. Koetke and G. Huber, Appl. Phys. B **61**, 151 (1995).

[21] C. Li *et al.*, in *Proceedings of the 15th Symposium on Advanced Solid-State Lasers, New Orleans, LA, 1993,* edited by A. A. Pinto and T. Y. Fan, OSA Technical Digest Series Vol. 15 (Optical Society of America, Washington, DC, 1993).

[22] S. Kaciulis, A. Latisenka, and A. Plesanovas, Surf. Sci. **251–252**, 330 (1991).

[23] M. Leiss, Ph.D. thesis, Universität Hamburg, Germany, 1981.

[24] F. E. Auzel, Proc. IEEE **61**, 758 (1973).

[25] A. Ehlert, J. Dreyhsig, H.-E. Gumlich, and J. W. Allen, J. Lumin. **60–61**, 21 (1994).