

Zeeman splitting and confinement effects in Er³⁺-doped nano-glass-ceramics in magnetic fields up to 50 T

D. Saurel,^{1(a)} V. K. Tikhomirov,^{1(b)} V. V. Moshchalkov,¹ C. Görrler-Walrand,² and K. Driesen²

¹*INPAC-Institute for Nanoscale Physics and Chemistry, Katholieke Universiteit Leuven, Belgium*

²*Chemistry Department, Katholieke Universiteit Leuven, Belgium*

(Received 13 December 2007; accepted 4 April 2008; published online 28 April 2008)

A zero-phonon component of the 1.5 μm emission band of Er³⁺ in the nano-glass-ceramics 32(SiO₂)9(AIO_{1.5})31.5(CdF₂)18.5(PbF₂)5.5(ZnF₂):3.5(ErF₃) mol %, shifts to higher energy and splits into Zeeman doublet in external magnetic field. These effects make it possible to flatten the amplification band of the Er³⁺-doped amplifier. The blue photoluminescence shift can be ascribed to quantum confinement effect on the 1.5 μm emission band of Er³⁺ in nano-glass-ceramics, where most of the Er³⁺ dopants are located in the PbF₂ nanocrystals of about 8 nm in diameter. © 2008 American Institute of Physics. [DOI: 10.1063/1.2916823]

The 1.5 μm emission band of the Er³⁺ dopant corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition is a key element of the Er³⁺-doped optical amplifier and other waveguide and bulk optically integrated devices, which operate near the wavelength of 1.5 μm of the telecommunications window, while the large spectral width and flatness of this band are of primary importance, e.g. Ref. 1–3. A highly flat and broad 1.5 μm emission band has been reported in Er³⁺-doped nano-glass-ceramics (NGC) 32(SiO₂)9(AIO_{1.5}) \times 31.5(CdF₂)18.5(PbF₂)5.5(ZnF₂):3.5(ErF₃) mol %.^{2,3} In this NGC, up to 90% of Er³⁺ ions are incorporated into PbF₂-based nanocrystals resulting in a substantial flattening of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission band of Er³⁺.^{2,3}

We are aware only of a few papers about the effect of an external magnetic field on this band, e.g., in Er³⁺-doped crystalline Si, where this effect was used to study symmetry of the Er³⁺ sites.^{4,5} Meanwhile, a Zeeman splitting of the Stark components of the 1.5 μm emission band may provide new options to control the flatness and width of the amplification band of the Er³⁺-doped amplifier. Magnetic confinement of electron orbitals of Er³⁺ can also induce the shift of the Stark levels and thereby change the shape of the 1.5 μm photoluminescence (PL) band of Er³⁺, as shown in this work. Therefore, we have studied the effects of an external magnetic field on the shape and position of the 1.5 μm PL band in Er³⁺-doped NGC at different temperatures and applying external pulsed magnetic field up to 50 T.

The preparation of Er³⁺-doped NGC by means of heat treatment or laser irradiation has been described in Refs. 2 and 6. The nanocrystalline phase consists of spherical PbF₂-based stoichiometric nanocrystals Er₁₀Pb₂₅F₆₅ of about 8 ± 1 nm in diameter, as found from energy dispersive spectroscopy in a transmission electron microscope.^{2,7} The samples have the thickness of 0.3 mm and surface area 3×3 mm². The magnetic field was applied perpendicular to the sample surface area, the Zeeman effect was observed parallel to the applied field. The PL spectra have been measured by using an infrared charge coupled device camera which provides the options to measure the spectrum in a

constant (up to 11 T) and pulsed (up to 50 T) fields.

Figure 1 shows the room temperature (a) and 13 K (b) PL spectra of Er³⁺-doped NGC (thick line) and its precursor glass (thin line). Five Stark components are clearly seen in low temperature PL spectrum in Fig. 1(b), while other Stark components are very weak. The spin-orbit ground state $^4I_{15/2}$ thus splits into five main Stark levels, indicating the presence of a high symmetry “pseudo cubic” site of the Er³⁺ dopants in NGC because the total Stark split of the $^4I_{15/2}$ in the low symmetry crystalline field should have resulted in eight Stark levels for this state. The irreducible representations for pseudo cubic symmetry are $\Gamma_6 + \Gamma_7 + 3\Gamma_8$.⁸ Analysis of the PL Stark components in this emission, and also in its reciprocal absorption spectrum, reveals a Stark-split energy level diagram for the $^4I_{13/2}$ and $^4I_{15/2}$ states in NGC, as shown in inset

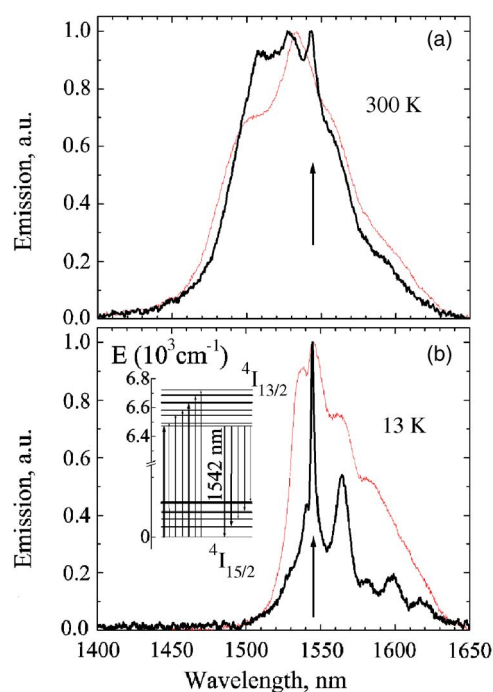


FIG. 1. (Color online) Room temperature (a) and 13 K (b) emission spectra of Er³⁺-doped NGC (thick line, black online) and precursor glass (thin line, red online). Inset in (b) is a Stark-split energy level diagram for the ground $^4I_{15/2}$ and excited $^4I_{13/2}$ states of Er³⁺ in NGC.

^{a)}Electronic mail: damien.saurel@fys.kuleuven.be.

^{b)}Electronic mail: victor.tikhomirov@chem.kuleuven.be.

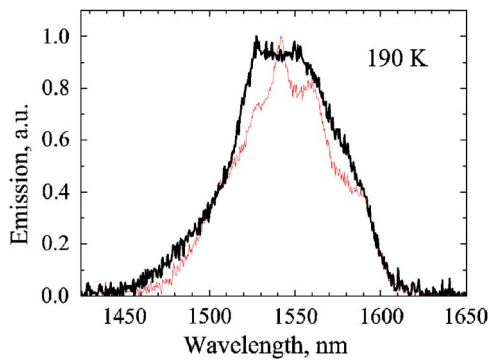


FIG. 2. (Color online) Normalized emission spectra of Er^{3+} -doped NGC in zero field (thin line, red online) and 50 T pulsed magnetic field (thick line, black online) at 190 K.

of Fig. 1(b).³ The lowest Stark levels for both the $^4I_{13/2}$ and $^4I_{15/2}$ states are simple Kramers doublets⁸ permitting only the simplest doublet splitting of these Stark levels in external magnetic field. The arrows at about 1542 nm in Figs. 1(a) and 1(b) indicate the 0-0 transition between lowest Stark levels of the $^4I_{13/2}$ and $^4I_{15/2}$ states in NGC [postsiged in inset in Fig. 1(b)]. Since this transition does not involve emission or absorption of phonon, it may be called “pure electronic” or zero-phonon transition. All other transitions at shorter wavelengths in NGC in Figs. 1(a) and 1(b) are due to emission from the thermally populated Stark levels of the $^4I_{13/2}$ state,³ since their intensities greatly decreased in low temperature spectra at 13 K [Fig. 1(a), zero field, thick line] and even more at 5 K [Fig. 3(a), zero field, thin line]. Figure 1(a) shows that the normalized emission from the thermally populated Stark levels in NGC is stronger than in the precursor glass; the reason for that is discussed further on.

Figure 2 shows an effect of a strong magnetic field on emission spectrum of NGC at 190 K; the highest temperature currently available in our setup in strong magnetic field configuration. A flattening and broadening of emission band of the Er^{3+} in magnetic field are clearly seen in Fig. 2, which potentially can be important for applications in optical amplifiers.¹⁻³ The origin of these effects can be understood from the PL changes in magnetic field at low temperatures, as illustrated in Fig. 3.

Figure 3 presents the photoluminescence data taken, at 5 K, in constant 11 T magnetic field and in zero field. It is seen in Fig. 3(a) (thick line), the 0-0 zero-phonon line in NGC shows the Zeeman splitting of about 8 cm^{-1} ; the value agrees with the Zeeman splitting in Er^{3+} -doped Si.⁵ In addition, these two Zeeman components of the 0-0 line in NGC show a blueshift of 3 and 0.5 nm, respectively, in magnetic field of 11 T [Fig. 3(a), thick line]. This blueshift can be related, as discussed further, to the magnetic confinement.

It is difficult to interpret the effect of magnetic field on other Stark lines in NGC because they are substantially weaker and broader than the 0-0 line at 5 K and overlap with each other.

Contrary to NGC, the zero-phonon line in precursor glass consists of two well resolved components at 1535 and 1545 nm, already in zero magnetic field [Fig. 3(b)]. A spectral deconvolution of this complex zero-phonon line has shown that, e.g., in an external magnetic field of 11 T [Fig. 3(b)], the 1535 nm component shows a minor blueshift of 0.5 nm while the 1545 nm component is invariant with the magnetic field.

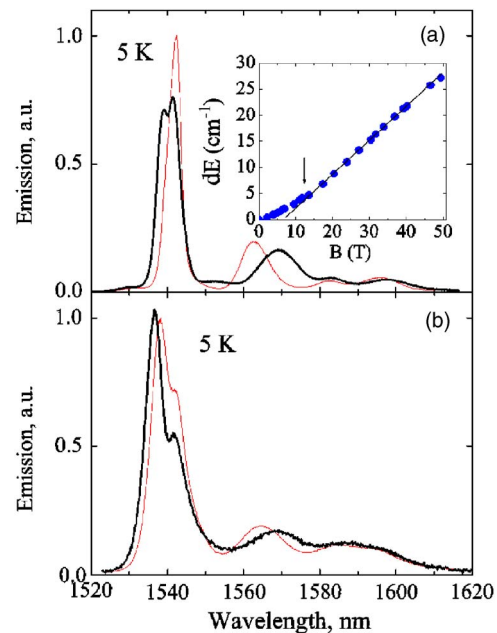


FIG. 3. (Color online) Low temperature emission spectra of NGC (a) and precursor glass (b) in zero field (thin lines, red online) and 11 T (thick lines, black online) constant magnetic field. Inset in (a) is a magnetic field dependence of the blueshift dE of the barycenter of zero-phonon line 0-0 (1542 nm at $B=0$). The arrow in inset indicates a crossover from parabolic to linear dependence.

We start the discussion of the data by recalling that the $1.5 \mu\text{m}$ transition $^4I_{13/2} \rightarrow ^4I_{15/2}$ of the Er^{3+} is a parity forbidden and screened f - f transition, which acquires its intensity due to admixture of wave functions of higher lying states of opposite parity, such as g , d , and s states.¹

The optical gap in nanocrystals, which are PbF_2 -based,^{2,3,7} nears to $E_g = 5.9 \text{ eV}$ (Ref. 9) and it is in all probability smaller than in the surrounding SiO_2 - Al_2O_3 - CdF_2 based glass network¹⁰ because it is smaller than for each of the SiO_2 [$E_g = 8.9 \text{ eV}$ (Ref. 11)], Al_2O_3 [$E_g = 6.24 \text{ eV}$ (Ref. 12)] and CdF_2 [$E_g = 7.6 \text{ eV}$ (Ref. 13)] components of the glass network. Therefore, the upperlying g , s or d states of Er^{3+} may experience quantum confinement as they are located above $50\,000 \text{ cm}^{-1}$, i.e., above 6 eV [so called charge transfer bands of lanthanides (Ref. 14)], and may fall in the quantum well of PbF_2 crystal separated by a barrier from the surrounding glass network. Due to an essential admixture of g , s , and d states to f states of Er^{3+} , some degree of the quantum confinement can be transferred onto f states of Er^{3+} .

The quantum confinement of f electrons in NGC is confirmed by magnetic field dependence of the blueshift of the 0-0 zero-phonon line of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition, see inset in Fig. 3(a). This dependence is parabolic at lower fields and changes to linear at higher magnetic fields with a crossover at about 10.6 T. The linear dependence at high fields is typical for magnetic confinement (compression) of electron wave functions in a variety of materials, while a crossover from the linear to parabolic dependence at lower fields is typical for semiconductor quantum dots, where the crossover corresponds to the compression of the electron wave functions to the size of the magnetic length comparable to the diameter of the quantum dot.^{15,16} At the fields lower than the crossover, a spatial confinement of electrons overcomes the magnetic confinement. The characteristic size a_B of the confined elec-

tronic wave function can be obtained from the crossover magnetic field B_C [marked by arrow in insert of Fig. 3(a)] using the equation^{15,16}

$$B_C = \frac{2\hbar}{a_B^2 e}. \quad (1)$$

We found a_B to be equal to 11 nm, which is comparable to the diameter of the nanocrystals hosting the Er^{3+} dopants. This proves the presence of the spatial confinement of electronic wave functions of Er^{3+} dopants in NGC.

Phonon quantum confinement in Er^{3+} -doped nanocrystals in NGC may also be possible because the optical phonon spectrum in these nanocrystals (phonons are mostly at 150 and 240 cm^{-1}) substantially differs from phonon spectrum in the surrounding $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CdF}_2$ based glass network (phonons are mostly at 900 cm^{-1}).¹⁰ This may result in quantum confinement of phonons¹⁷ and strengthening of the electron-phonon interaction with the 150 and 240 cm^{-1} phonons in Er^{3+} -doped nanocrystals, thus accounting for a stronger emission from higher Stark levels of Er^{3+} dopant in NGC compared to precursor glass, Fig. 1(a). Actually, the higher Stark levels in the emitting level $^4I_{13/2}$ are at energies of 50–200 cm^{-1} above the lowest Stark level in NGC [inset in Fig. 1(b)] providing good resonance especially with 150 cm^{-1} phonon vibrations.

Disappearance of the Zeeman splitting is evidenced in the precursor glass [Fig. 3(b)]. Despite the site multiplicity, one of the Er^{3+} sites in precursor glass may be reminiscent of the Er^{3+} site in NGC, because it nucleates the growth of nanocrystalline phase in NGC.² This minor Er^{3+} site in precursor glass can contribute to a minor blueshift of the 1535 nm component of the 0-0 line of precursor glass in magnetic field [Fig. 3(b)].

The blueshift and Zeeman splitting of Stark levels of the ground state $^4I_{15/2}$ observed at low temperature [Fig. 3(a)], results in broadening and flattening of the 1.5 μm emission band of the Er^{3+} in magnetic field at higher temperatures (Fig. 2). Certainly, the blueshift and Zeeman splitting of Stark levels can be also expected for the excited state $^4I_{13/2}$; this adds to broadening and flattening of the 1.5 μm emission band of Er^{3+} in magnetic field at high temperatures. This has a potential for tuning flattening and broadening of the amplification band of the Er^{3+} amplifier by applying an external magnetic field.

In conclusion, we report on a Zeeman effect and blue PL shift which have been detected in the 1.5 μm emission band ($^4I_{13/2} \rightarrow ^4I_{15/2}$ transition) of the Er^{3+} -doped NGCs. The magnetic field dependence of this blueshift changes from para-

bolic to linear with a crossover at about 10 T indicating a quantum confinement of wave functions of f electrons mixed with wave functions of upper states of Er^{3+} . The size of confined wave function has been calculated from the crossover in the field dependence and it equals to the diameter of nanoparticles hosting Er^{3+} . A phonon confinement may also be possible affecting the electron-phonon interaction and population of Stark levels in these nanocrystals resulting in flattening emission spectrum of Er^{3+} -doped NGC compared to its precursor glass.

The support from the Flemish Science Fund (FWO), the K.U. Leuven Concerted Action Scheme (GOA), the IAP network of the Belgian Government, the FP6-SANDiE, the FP6-EuroMagNET (RII3-506239), and the KULeuven Center of Excellence INPAC are greatly acknowledged. V.K.T. acknowledges Senior Fellowship of KU Leuven.

¹P. C. Becker, N. A. Olsson, and J. R. Simpson, *Erbium-doped Fibre Amplifiers: Fundamentals and Technology* (Academic, San Diego, 1999).

²V. K. Tikhomirov, D. Furniss, I. M. Reaney, M. Beggiora, M. Ferrari, and R. Rolli, *Appl. Phys. Lett.* **81**, 1937 (2002).

³V. Rodriguez, V. K. Tikhomirov, J. Mendez-Ramos, and A. B. Seddon, *Europhys. Lett.* **69**, 128 (2005).

⁴N. Q. Vinh, H. Przybylinska, Z. F. Krasilnik, B. A. Andreev, and T. Gregorkiewicz, *Physica B* **308-310**, 340 (2000).

⁵N. Q. Vinh, H. Przybylinska, Z. F. Krasilnik, and T. Gregorkiewicz, *Physica E (Amsterdam)* **16**, 544 (2003).

⁶V. K. Tikhomirov, J. Koch, D. Wand, and B. Chichkov, *Phys. Status Solidi A* **202**, R73 (2005).

⁷M. Mortier and G. Patriarce, *Opt. Mater. (Amsterdam, Neth.)* **28**, 1401 (2006).

⁸C. A. J. Ammerlaan, *Physica B* **308-310**, 387 (2000); G. Dantele, M. Mortier, and D. Vivien, *Phys. Chem. Chem. Phys.* **9**, 5591 (2007).

⁹H. Jiang, R. Orlando, M. A. Blanco, and R. Pandey, *J. Phys.: Condens. Matter* **16**, 3081 (2004); I. Kosacki and J. M. Langer, *Phys. Rev. B* **33**, 5972 (1986).

¹⁰V. K. Tikhomirov, M. Ferrari, M. Montagna, L. F. Santos, and R. M. Almeida, *Europhys. Lett.* **64**, 529 (2003).

¹¹R. B. Laughlin, *Phys. Rev. B* **22**, 3021 (1980).

¹²S. Mo and W. Y. Ching, *Phys. Rev. B* **57**, 15219 (1998).

¹³A. S. Shcheulin, D. E. Onopko, and A. I. Ryskin, *Phys. Solid State* **39**, 1906 (1997).

¹⁴P. Dorenbos, *J. Phys.: Condens. Matter* **15**, 8417 (2003).

¹⁵P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer, Berlin, 2005), Chap. 9.

¹⁶P. D. Wang, J. L. Merz, S. Fafard, R. Leon, D. Leonard, G. Medeiros-Ribeiro, M. Oestreich, P. M. Petroff, K. Uchida, N. Miura, H. Akiyama, and H. Sakaki, *Phys. Rev. B* **53**, 16458 (1996); K. L. Janssens, F. M. Peeters, and V. A. Schweigert, *Phys. Rev. B* **63**, 205311 (2001).

¹⁷R. Provoost, M. Hayne, M. K. Zundel, K. Eberl, and V. V. Moshchalkov, *Physica B* **256-258**, 203 (1998); Y. Sidor, B. Partoens, F. M. Peeters, N. Schildermans, M. Hayne, V. V. Moshchalkov, A. Rastelly, and O. G. Schmidt, *Phys. Rev. B* **73**, 155334 (2006).