Supplementary information for

Near-Infrared Wavelength-dependent Nonlinear Transmittance Tailoring in Glass Ceramics Containing Er\textsuperscript{3+}:LaF\textsubscript{3} Nanocrystals

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1. Theoretical analysis and simulations

1.1 Upon 808 nm excitation

We present simplified three levels model of Er\(^{3+}\) as shown in Figure 1a. The incoming laser is first absorbed by sample, with decrease of \(N_1\), increase of \(N_3\), and non-radiative relaxation from the third level to the second level. When \(N_2\) accumulate above the critical concentration, the produced ions pair cooperatively transition to the third level, prompting the enhancement of \(N_1\) and \(N_3\). However, when the laser pumping is at strong level, \(N_1\) is still reduced. Hence, we only consider the effect of \(N_2\), and overlook the stimulation emission and absorption between the second and third level, but the spontaneous emission probability from the third to the second and first level should be taken into account. The rate equations describing the evolution of absorption and emission upon 808 nm excitation are:

\[
\frac{\partial N_3}{\partial t} = C_{up}N_2^2 + \omega_{13}N_1 - (\omega_{31} + A_{31} + A_{32})N_3
\]

\(N = N_1 + N_2 + N_3\)

Where \(N_1\), \(N_2\), and \(N_3\) denote the population densities of electrons for each level (cm\(^{-3}\)). \(C_{up}\) represents cooperative up-conversion coefficient related to Er\(^{3+}\) ions concentration; \(\omega_{ij}\) \((i, j = 1, 3)\) accounts for the probability of electronic transition; \(A_{ij}\) \((i = 3, j = 1, 2)\) stands for spontaneous emission probability. The values of emission cross-section \(\sigma_{em}\) \((1.5 \times 10^{-25} \text{ m}^2)\) is assumed, and thus the transition probability \(\omega_{13}\) can be expressed as:

\[
\omega_{13} = \frac{\sigma_{em} P(z)}{\hbar \nu_{808} A_{eff}}
\]

The parameters used in computer calculations are \(r = 0.25 \text{ mm}\), \(A_{eff} = \pi r^2 = 1.96 \times 10^{-7} \text{ m}^2\), \(A_{32} = 10000\), and \(A_{31} = 100\). From Eq. (3) we find that \(\omega_{13}\) is adjustable with the input power changing, which is the major factor for the reverse saturable absorption. Herein, the power transmission equation is introduced to describe the nonlinear transmittance at 808 nm:

\[
\frac{\partial P(z)}{\partial z} = (\sigma_{em}N_3 - \sigma_{ab}N_1 - 0.1)P(z)
\]

Where \(z\) is the power propagation direction, \(\sigma_{em} = 4.0 \times 10^{-25} \text{ m}^2\), \(\sigma_{ab} = 1.0 \times 10^{-25} \text{ m}^2\). The excited state absorption (ESA) steps have considerable contribution, leading to larger ESA cross-section than ground state absorption (GSA). Through solving numerically the equations presented above and simulation analysis, as depicted in Figure 1d, the nonlinear transmittance at 808 nm presents optical limitation feature.

1.2 Upon 980 nm excitation

In this analysis, as sketched in Figure 1b, we also considered three levels model of
Er$^{3+}$. The rate equations and power transmission equation are utilized to analysis and simulate the transmittance at 980 nm:

$$\frac{dN_1}{dt} = -\omega_{12}N_1 + \omega_{31}N_3$$

(5)

$$\frac{dN_2}{dt} = \omega_{12}N_1 - \omega_{23}N_2$$

(6)

$$\frac{dN_3}{dt} = \omega_{23}N_2 - \omega_{31}N_3$$

(7)

$$N = N_1 + N_2 + N_3$$

(8)

$$\frac{dP(z)}{dz} = (-\sigma_{12}N_1 - \sigma_{23}N_2 - \alpha)P(z)$$

(9)

The system is solved for the stationary state populations, and the expressions are as follows:

$$0 = -\omega_{12}N_1 + \omega_{31}N_3$$

(10)

$$0 = \omega_{12}N_1 - \omega_{23}N_2$$

(11)

$$0 = \omega_{23}N_2 - \omega_{31}N_3$$

(12)

Where,

$$\omega_{ij} = \frac{\sigma_{ij}P(z)}{\hbar \nu_{980} A_{eff}}, \:(i, j = 1, 2, 3)$$

(13)

From Eqs. (5) – (13), we get

$$\frac{dP(z)}{dz} = (-\frac{2N}{\sigma_{12} + \frac{1}{\sigma_{23}} + \frac{1}{\sigma_{31}}} - \alpha)P(z)$$

(14)

Integration of Eq. (14) yields the familiar exponential law:

$$P(z) = P(0) exp\left[\left(-\frac{2N}{\sigma_{12} + \frac{1}{\sigma_{23}} + \frac{1}{\sigma_{31}}} - \alpha\right)z\right]$$

(15)
Figure 1e shows the simulation of the transmittance at 980 nm vs incoming power, with the parameters: sample thickness $z = 1$ mm, $A_{\text{eff}} = \pi r^2 = 1.96 \times 10^{-7}$ m$^2$. The GSA and ESA absorption cross-section and spontaneous emission cross-section are $\sigma_{12} = \sigma_{23} = \sigma_{31} = 10^{-24}$ m$^2$,\textsuperscript{1, 4, 5}$ spontaneous emission probability $A_{31} = 1000$.\textsuperscript{1, 4, 5}$ The equilibrium constants for the transmittance at 980 nm can be obtained, which is easily achieved for Er$^{3+}$ concentration in the range from 1% to 5% (in molar).

1.3 Upon 1550 nm excitation
A numerical analysis is undertaken for the simplified four level model we proposed, as shown in Figure 1c, and the rate equations and power transmission equation pumping at 1550 nm are written as follows:

$$\frac{dN_1}{dt} = -\omega_{12}N_1 + \omega_{41}N_4 + A_{21}N_2$$

(16)

$$\frac{dN_2}{dt} = \omega_{12}N_1 - \omega_{23}N_2 - A_{21}N_2$$

(17)

$$\frac{dN_3}{dt} = \omega_{23}N_2 - \omega_{34}N_3$$

(18)

$$\frac{dN_4}{dt} = \omega_{34}N_3 - \omega_{41}N_4$$

(19)

$$N = N_1 + N_2 + N_3 + N_4$$

(20)

$$\frac{dP(z)}{dz} = (\sigma_{12}N_1 - \sigma_{23}N_2 - \sigma_{34}N_3 + \sigma_{21}N_2 + h\nu_{1550}A\nu_{1550}\sigma_{21}N_2 - \alpha)P(z)$$

(21)

To verify and make a theoretical interpretation of the saturation absorption behavior at 1550 nm, we utilized the following steady-state equations:

$$0 = -\omega_{12}N_1 + \omega_{41}N_4 + A_{21}N_2$$

(22)

$$0 = \omega_{12}N_1 - \omega_{23}N_2 - A_{21}N_2$$

(23)

$$0 = \omega_{23}N_2 - \omega_{34}N_3$$

(24)

$$0 = \omega_{34}N_3 - \omega_{41}N_4$$

(25)

Approximately,
\[ \omega_{ij} \approx \frac{\sigma_{ij} P(0)}{h \nu_{1550} A_{\text{eff}}}, (i, j = 1, 2, 3, 4) \]  

(26)

Owing to no more than one order of magnitude increase in power, so it will not trigger strikingly improvement of quantity in the process of estimation. Herein, we use the power at \( z = 0 \) instead of that at \( z \) position, and Eq. (21) can be simplified:

\[
\frac{dP(z)}{P(z)} = \left( \frac{-\sigma_{12} N_1 + (\sigma_{21} - 2\sigma_{23}) \frac{\omega_{12}}{\omega_{23} + A_{21}} N}{1 + \frac{\sigma_{23}}{\sigma_{34}} \frac{\omega_{12}}{\omega_{23} + A_{21}} + 1} \right) + h \nu_{1550} \Delta \nu_{1550} \sigma_{21} N_2 - \alpha)dz
\]

(27)

Eq. (27) can be numerically solved with the boundary conditions:

\[
P(z) = P(0) \exp\left( \left( \frac{-\sigma_{12} N_1 + (\sigma_{21} - 2\sigma_{23}) \frac{\omega_{12}}{\omega_{23} + A_{21}} N}{1 + \frac{\sigma_{23}}{\sigma_{34}} \frac{\omega_{12}}{\omega_{23} + A_{21}} + 1} \right) + h \nu_{1550} \Delta \nu_{1550} \sigma_{21} N_2 - \alpha)z \right)
\]

(28)

The parameters used in the calculation are: sample thickness \( z = 1 \) mm; \( A_{\text{eff}} = \pi r^2 = 1.96 \times 10^{-7} \) m\(^2\); GSA absorption cross-section and stimulation emission cross-section \( \sigma_{12} = \sigma_{21} = 3 \times 10^{-25} \) m\(^2\); \( \Delta \nu_{1550} = e9 \times P_0^2 \times 10^{17.1} \); stimulation emission probability \( A_{31} = 1900 \). The ESA cross-section is smaller than the GSA cross-section, and the stimulation emission step occupy the main position. As displayed in Figure 1f, the nonlinear transmittance at 1550 nm increases with the incident laser intensity of 1550 nm increased.
Figure S1: (a)-(f) Two-dimensional mapping distribution images of La, Er, F, Ge, O, and Al elements of 3% Er$^{3+}$-doped GCs, respectively.
**Figure S2:** The 3% Er\(^{3+}\)-doped GCs sample heat-treated at 680 °C for 4 h. (a) UC emission spectra upon CW LDs of 808, 980, and 1550 nm, respectively. (b) UC fluorescence ratio of red/green corresponding to (a).
References