**The intense anti-Stokes emission of erbium ions in gallium lanthanum sulphide-oxide glass GaLaS(O) in visible spectral range**

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Rare-earth doped chalcogenide glasses demonstrating effective up-conversion are found to be attractive for many practical applications including up-conversion fiberoptical lasers [1], up-converters for solar cell to convert Sun’s IR radiation into visible [2] and many others. These glasses also may be used as doped glasses where, due to their exceptionally low phonon energy, the up-conversion effects may investigated at its fullest.

In present paper we investigate the intense visible green and red up-conversion in gallium lanthanum sulphide-oxide glass GaLaS(O) doped with trivalent erbium ions Er3+ (Figure 1). These glasses may demonstrate high efficiency up-conversion as well as high quantum yield of “regular” photoluminescence (PL) presumably due to insignificant non-radiative losses which are typical for these glasses. The addition of oxygen into well studied glass matrix GaLaS [3] shifts the optical absorption edge towards higher energies improving further up-conversion conditions by suppressing losses due to energy transfer from excited Er3+ ions to glass matrix [4].

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| Figure 1. Visual impression of GaLaS(O):Er3+glass under 808 nm excitation. | Figure 2. Comparison of PL spectrum (left scale) with optical transmittance (solid line, right scale). The insert shows tentative identification of PL bands. The values above bands allow us to compare their relative peak intensities. |

The Er3+ doped gallium lanthanum sulphide-oxide glass was prepared by melt quenching of raw materials mixed in the following proportions: 72.5%Ga2S3, 27La2O3 and doped with 0.5%Er2S3.All percent are molar. Melting took place in a vitreous carbon crucible for 24 hours in dry flowing argon followed by annealing at 500 °C, ramping up and down at 1°C per minute.The PL was excited by laser diode operating at wavelength of 808 nm coinciding with 4I15/2-4I9/2 absorption band of Er3+.

Figure 2 gives an overview of the experimental results. Under 808 nm excitation several PL bands with Stokes and anti-Stokes shifts have been observed. Two bands centered at 980 nm and 1535 nm have demonstrated “normal” Stokes shift and are easily assigned to 4I11/2-4I15/2 and 4I13/2-4I15/2 transitions, respectively. The bands with anti-Stokes shift have been “red” one centered at around 664 nm due to, presumably, 4F9/2-4I15/2 transition and the “green” one consisting of two lines centered at 525 and 550 nm which may be related to 2H11/2-4I15/2 and 4S3/2-4I15/2 transitions, respectively. We measured the intensity of up-conversion bands in function of pumping intensity (*P*) (see Figure 3). At low *P* the dependence seems to be linear and tends to saturate at high *P*≈1000 W/cm2 as shown in Figure 3.

We offer the theoretical description of experimental results using the radiative and non-radiative transitions within nine excited and one ground manifolds of Er3+ ion (Figure 4). The pumping is considered to be to the manifold 4I9/2 corresponding to 808 nm excitation used in experiments. Figure 4 shows the existence of three possible up-conversion transitions (based on effect of ESA) via excited states 4I13/2, 4I11/2 and 4I9/2. The corresponding system of rate equations along with additional equation of conservation of total number of electrons may be presented in a matrix form as *Ĝ***n**=**b** where the vectors **n** and **b** are defined as n=(*n*9, *n*8,…*n*0)*T* and b=(0,0,…,0,1)*T*. Matrix *Ĝ* has dimension 10×10, that allows to solve the system of equations by using the Cramer’s rule. This approach potentially allows to calculate the coefficients included in expressions for optical transition intensities. However, in multilevel ionic systems dozens or even hundreds of addends must be taken into account, with every addend being a product of several parameters such as generation and relaxation rates. This type of calculations is quite sensitive to uncertainties of above mentioned parameters and may lead to considerable discrepancies. Instead, general equations for level populations may be may be approximated by ratios of polynomials (4th or 3rd orders), which may be simplified further by taking into account the small numbers of addends at zeroth and first degrees of generation rate. As a result, the general equation for radiative transition intensity *J* may be reduced to

 , (1)

where *I* is the pumping intensity and *A*, B, *C, D, E* and *F* are numerical coefficients. Moreover, for optical transitions involving lower three levels the coefficient *A* is simply 0, while for higher levels with a high accuracy *C* is equal to 0. Figure 3 demonstrates the quality of this approximation for two up-conversion bands in GaLaS(O):Er glass. The appropriate adjustable parameters are summarized in Table below.

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|  | A | B | C | D | E | F |
| “Red” band (1) | 106 | 4×108 | 0 | 1 | 150 | 2×106 |
| “Green” band (2) | 4100 | 3.7×106 | 0 | 1 | 451 | 1.64×106 |

In summary, we offer a phenomenological method of describing experimental data by simple equations with adjustable parameters that are established by interpolation using well-defined experimental points. The paper discusses the applicability and usefulness of this approach in the analysis of experimental data.

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| Figure 3.The influence of PL excitation intensity on integral intensities of “green” and “red” PL bands (see Figure 2 and insert for clarification). Solid lines are theoretical fit (eqn.(1)) with coefficients as explained in the text. | Figure 4. Schematic diagram of Er3+ion manifolds and interlevel transitions used in theoretical model. |

[1] Scheps R Upconversion laser processes.1996 Prog. Quantum Electron. 20 271

[2] Kharel P L, Zamborini F P and Alphenaar B W 2018 J.Electroch.Soc. 165 H52

[3] Ye C C, Hewak D W, Hempstead M, Samson B N and Payne D N 1996 J. Non. Cryst. Solids 208 56

[4] Tverjanovich A Grigoriev Y G Degtyarev S V Kurochkin A VA V Man'shina A AIvanova T Y Povolotskiy ATveryanovich Y S 2003 J. Non. Cryst. Solids 326&327 311