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Excited state absorption in glasses activated with rare earth ions: Experiment and modeling

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ABSTRACT

We present semiempirical approach based on the Judd–Ofelt theory and apply it for modeling the spectral properties of fluoride glasses activated with the rare earth (RE) ions. This method provide a powerful tool for simulating both ground state absorption (GSA) and excited state absorption (ESA) spectra of RE ions, e.g. Nd^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} in the ZBLAN glass matrix. The results of theoretical calculations correspond to the experimentally measured data. We also demonstrate that the spectra obtained using the presented approach are applicable in the analysis of up-conversion excitation schemes in these optoelectronically relevant materials.

1. Introduction

The up-conversion process observed for the rare earth ions is one of the most efficient mechanisms that convert low-energy photons into high-energy ones [1]. At the same time, variety of observed 4f ↔ 4f transitions provide an excellent spectral selectivity required for numerous applications of RE-activated materials, regardless whether in crystals, ceramics or glasses. Recently, the concepts of using up-conversion of the RE ions was extended to nano-materials, although traditionally it has been widely studied for bulk or fiber-like geometry for applications in high-power laser systems and telecommunication amplifiers as well as luminescence phosphors, secure printing or advanced bioimaging probes [2–4]. For instance up-converting light amplifiers (lasers) can be efficiently and cheaply pumped using high power infrared laser diodes, whereas up-converting phosphors and bioimaging probes feature no luminescence background in their emission range due to large anti-Stokes shift that results in high signal-to-noise ratio. Moreover, it is highly improbable to induce up-converted emission from other molecules in bioimaging applications. These unique properties of the up-converting RE-doped materials are virtually impossible to mimic in other luminescing systems. It is therefore important to understand in detail the spectral properties of RE ions in order to design imaging probes and more advanced systems for optoelectronics.

Over the years many up-conversion mechanisms have been recognized and described in the literature, including energy transfer up-conversion (ETU), where nonradiative energy transfer plays a dominant role, excited state absorption up-conversion (ESAU), often called sequential absorption of two photons, and finally photon avalanche up-conversion (PAU), being a specific combination of the ETU and ESAU [5,6]. Among them excited state absorption up-conversion in the RE-activated materials is one of the best known. In contrast to the ETU and PAU, the ESAU takes place within a single RE ion, therefore it is insensitive to a dopant concentration and has no threshold behavior like the PAU.

In spite of extensive research, there are quite limited number of ESA spectra published in the literature, moreover frequently they feature ESA from only one level, characterized with the longest lifetime and thus the highest population under CW excitation. Starting from the first experiments performed by Kushida [7], there were only few experimental groups with the capability to perform the ESA measurements [8–12]. Therefore an alternative method of predicting the ESA spectra remains still a challenge.

In this work we present a simple method to calculate the ESA spectra of various RE ions in glass matrices using Judd–Ofelt approach. The energy and intensity parameters used in the calculations were taken from the GSA analysis and used to determine both the energies and intensities of the ESA transitions. The calculated spectra are compared with the results of experiment carried out for a series of RE ions in ZBLAN glass. Surprisingly good agreement between the two sets confirms the validity of our approach and demonstrate its potential for predicting the up-conversion processes in these application-relevant optical materials.

2. Description of the ESA

In principle the ESA is quite straightforward. In the first step significant population of ions is promoted to the metastable level (E_1) due to efficient absorption of the photons of energies $\tilde{\nu}_1$ (Fig. 1). Afterwards photons of energies $\tilde{\nu}_2$ activate ESA transitions and

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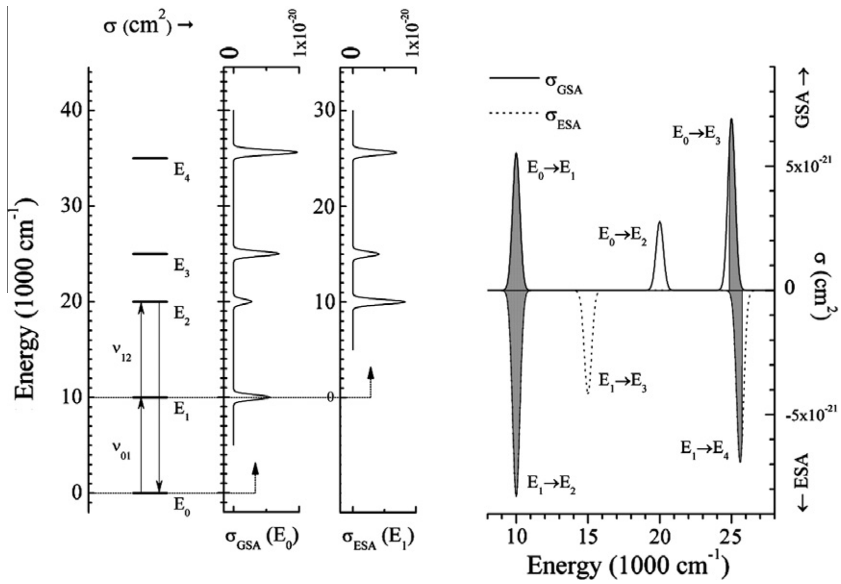

Fig. 1. Exemplary energy diagram and spectral relations between GSA and ESA transitions.

populate excited level E_2. Finally, if the emission $E_2 \rightarrow E_0$ occurs, energies of the emitted photons would be much higher than those of absorbed ones. This effect is called up-conversion or anti-Stokes emission.

The efficiency of the ESA-type up-conversion depends upon many parameters. First of all, the longer the lifetime of the intermediate state the higher the probability of excited state absorption (i.e. higher conversion efficiency). In addition, the spectral overlap between the ground state and excited state absorption plays an important role in determining the efficiency of the process. Importantly, owing to the broad variety of the observed 4f ↔ 4f transitions, ESAU provides a way to selectively realize many spectrally distinguishable one-color ($\tilde{\nu}_1 = \tilde{\nu}_2$) or two-color ($\tilde{\nu}_1 \neq \tilde{\nu}_2$) excitation schemes. Of course the energies of the exciting photons should be precisely adjusted to the particular excitation scheme. For instance, in the case of two-color excitation, the first laser should be tuned resonant with the GSA transition, while the second laser should be resonant with the ESA transition. On the other hand, one-color excitation scheme is much more difficult to realize as there are only few cases of energy matching between the GSA and the ESA transitions for a given laser frequency. As presented in Fig. 1, the energies of the GSA and ESA transitions may be resonant ($E_0 \rightarrow E_1$ and $E_1 \rightarrow E_2$), slightly off-resonant ($E_0 \rightarrow E_3$ and $E_1 \rightarrow E_4$) or completely off-resonant ($E_0 \rightarrow E_2$ and $E_1 \rightarrow E_3$). Therefore, the spectral overlap between the GSA and ESA transitions should be investigated in detail in order to optimize excitation conditions and thus improve the efficiency of the ESAU.

3. Model

Semiempirical methods aimed at calculating the spectral properties of the rare earth ions have been developed over many years and successfully applied for describing the ground state absorption in these systems. Energy levels, radiative and nonradiative transition rates as well as energy transfer parameters can be obtained and have been helpful for analyzing and interpreting experimental results [13]. Here we present the formalism that enable us to model spectra of the ESA transitions.

3.1. Energy levels

The ground state configuration of the rare earth (III) ions is $[Xe]4f^n$, where n denotes number of the optically active 4f electrons and change from 1 up to 13 in the cerium–ytterbium series. The electronic energy levels of the free ion can be expressed by a semiempirical Hamiltonian

$$H_{free} = E_{AVG} + \sum_{k=2,4,6} F^k f_k + \zeta A_{s-o} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{k=2,3,4,6,7,8} T^k t_k + \sum_{k=0,2,4} M^k m_k + \sum_{k=2,4,6} P^k p_k \quad (1)$$

with the empirical parameters describing: electron repulsion (F^k), the spin-orbit interaction (ζ) and the two-body configuration interaction (α, β, γ). The remaining parameters represent the three-body configuration interactions (T^k) and other magnetic interactions like spin-other-spin, and orbit-other-orbit (P^k, M^k) [14]. The energy levels as well as intermediate coupling coefficients, required for further calculations, can be obtained by diagonalizing such Hamiltonian matrix.

3.2. Transition intensities

Optical spectroscopy of the $4f^n$ levels is dominated by the forced electric-dipole and magnetic-dipole transitions. According to the Judd–Ofelt theory, oscillator strength of the electric-dipole transition can be expressed as following

$$f_{ed} = \frac{8\pi^2 m_e c \tilde{\nu}}{3h(2J+1)} \chi_{ed} \sum_{k=2,4,6} \Omega_k \mid \langle \gamma' S' L' J' \| \boldsymbol{U}^{(k)} \| \gamma S L J \rangle \mid^2 \quad (2)$$

where m_e is the mass of the electron, c is the velocity of light, $\tilde{\nu}$ is the mean energy for the transition (in cm^{-1}), χ_{ed} is the local field correction, approximated by $(\eta^2+2)^2/9\eta$ for absorption and $\eta(\eta^2+2)^2/9\eta$ for emission where η is the refractive index, h is the Planck's constant and J is the total angular momentum of the initial state in the transition [15–17]. Radiative transition rates are determined by at most three empirical intensity parameters: Ω_2, Ω_4, Ω_6, and the squared reduced matrix elements of the unit tensor operator $U^{(k)}$ with ranks 2, 4 and 6. The selection rules for the forced electric-dipole transitions in the LS coupling are as follows: $\Delta S = 0$, $|\Delta L| \leqslant 6$ and $|\Delta J| \leqslant 6$. Because of the spin-orbit interaction the selection rule for ΔS is usually relaxed [18].

Magnetic-dipole transitions can also contribute to the observed bands. The magnetic-dipole oscillator strength is given by the equation