Theoretical Simulation on a Nonlinear Photonics Process of Er(1%)Yb(8%):FOV Oxyfluoride Nanophase Vitroceramics

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\textbf{Abstract.} We numerically simulate a photonics phenomenon of what we call intensity inversion between red and green fluorescence in oxyfluoride nanophase vitroceramics Er(1%)Yb(8%):FOV through the integration of whole fluorescence’s theories. We found that it is essential to introduce a coefficient presenting the difference between the Stokes energy transfer and anti-Stokes energy transfer processes in nano-material when calculating the energy transfer rate. Under this consideration, and with the total crystallized volume ratio set to be 17.6\%, the simulation results of the population probabilities values of all energy levels of Er\textsuperscript{3+} ion are coincident with the experimental result perfectly.

\textbf{AMS subject classifications:} 78A60, 37M05, 37N20, 65L07, 65Z05

\textbf{Key words:} Energy transfer, theoretical simulation, Stokes and anti-Stokes processes, rare earth ions, oxyfluoride nanophase vitroceramics.

\section{Introduction}

Energy transfer is one of the most important processes in the fluorescence of rare earth ion doped material [1]. Many phenomena that attract much interest, especially for hot
frontier nano-material, are directly related to energy transfer processes. So the determination of energy transfer rate is critical to reveal various fluorescence processes. Generally there are two methods to obtain the energy transfer rate. One is the experimental method to determine the rate using a set of materials doped with rare earth ions with different concentrations [2]. The other is the theoretical method to be discussed in the present paper. The study by Kushida in 1973 [3] has laid the foundation for this theoretical method, which led us to obtain the energy transfer rate through Judd-Oflet intensity parameters. After introducing the phonon theory by Dexter and Miyakawa [4], this method became even more practical as it allows us to solve the questions of phonon-assisted energy transfer involving energy mismatch. In fact, there are two cases of energy mismatch [5]. When the energy transferred by the donor is larger than the energy accepted by the acceptor, it is a Stokes process. On the contrary, if the transferred energy is less than the accepted energy, it is an anti-Stokes process. Usually we pay much attention on the magnitude of the energy mismatch and ignore the difference between the Stokes and anti-Stokes processes. However, in the numerical simulation on the intensity inversion phenomenon in Er(1%)Yb(8%):FOV nanophase oxyfluoride vitroceramics, we found that it is essential to consider the effects of this difference, particularly for the nano-materials where energy transfer plays a key role in the whole processes, because in the nano-scale the energy transfer rate increases greatly with the reduction in the distance between ions.

## 2 Experiment

The composition of Er(1%)Yb(8%):FOV is 8%YbF$_3$, 1%ErF$_3$, 30%PbF$_2$, 16%ZnF$_2$, and 45%SiO$_2$. The pure raw materials were put in a platinum crucible for heating at about 900°C for 100 minutes and then cooled fast at an iron plate to form oxyfluoride glass. The transparent oxyfluoride vitroceramics were obtained by annealing at the glass transition temperature for 7 hours.

The absorption spectrum was measured by using UV-365 spectrophotometer, which is shown as Fig. 1. And the fluorescence spectra were measured by using JY-ISA Fluorolog-Tau-3 fluorescence spectrophotometer. In the Stokes excitation spectra, two relatively strong excitation peaks at 378.5nm and 522.3nm, corresponding to $^4G_{11/2}$ and $^2H_{11/2}$ of Er$^{3+}$ ion respectively, were observed. Then the Stokes emission spectra of the sample under the 0.3mw excitation at these two wavelengths were studied, as shown in Fig. 2. It can be seen that the fluorescence of $^4S_{3/2} \rightarrow ^4I_{15/2}$ is stronger than that of $^4F_{9/2} \rightarrow ^4I_{15/2}$ when the Er(1%)Yb(8%):FOV is excited by 522.3nm light, but the proportional relationship between the green and red fluorescence intensities is reversed when the sample is excited by 378.5nm light. This is the fluorescence intensity inversion phenomenon [6]. We can define the common intensity ratio $\alpha$ which equals to the ratio of the green fluorescence intensity $I(^4S_{3/2})$ to the red one $I(^4F_{9/2})$ when $^2H_{11/2}$ is excited, while the unusual intensity inversion ratio $\gamma$ is equal to the ratio of $I(^4F_{9/2})$ to $I(^4S_{3/2})$ when $^4G_{11/2}$ is excited directly. Thus the range of intensity inversion is $\Sigma = \alpha \times \gamma$. The experimental value