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Understanding the influence of nanoenvironment on luminescence of rare-earth ions

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Abstract. This paper presents an overview of the recent results on upconversion and photoluminescence of rare-earth ions in nanoenvironments. The role of the rare-earth ion concentration, crystal size and crystal phase on the up- and downconversion emission of rare-earth ions in oxide nanocrystals and their underlying mechanisms are discussed. It is also found that the luminescence lifetime of the excited state rare-earth ions is sensitive to the particle crystalline phase and size. The analysis suggests that the modifications of radiative and nonradiative relaxation mechanisms are due to local symmetry structure of the host lattice and crystal size respectively.

Keywords. Nanocrystals; rare-earth; upconversion; luminescence; lifetime.

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1. Introduction

An enormous interest in rare-earth doped nanostructured materials for photonic applications has emerged in recent years [1–9]. Recently, a great deal of research on IR-to-visible frequency upconversion has been focused to find their fascinating applications, such as upconversion lasing, display and two-photon imaging in confocal microscopy [1–9]. As these potential applications are still very much in the design-phase, further fundamental research in the field of upconversion spectroscopy remains a challenge. The process of photon upconversion is a way to convert long-wavelength excitation radiation into shorter wavelength output radiation. Upconversion is one of the most studied nonlinear optical processes after second harmonic generation and two-photon absorption. The upconversion is based on the existence of at least two real, metastable emitting states, which is the basic difference from second harmonic generation and two-photon absorption. As a result, upconversion has the potential to be a very efficient process. The predominant mechanisms of upconversion processes are excited state absorption and energy transfer upconversion. In both of these cases, a simple cw diode laser can be used for the upconversion process, in contrast to expensive mode locked lasers used in two-photon upconversion in organic fluorophore. Efficient upconverting rare-earth doped nanocrystals can be good replacement of organic dyes in two-photon confocal microscope imaging. The efficiency of these materials is dependent on the dynamics of rare-earth ions and their interactions with the host matrix. This interaction can be a function of the host phase, the dopant concentration, energy migration between the active ions, the statistical distribution of active ions and site symmetry of the active ions in the host matrix [10–21]. In the case of rare-earth ions, the electronic f–f transitions involve electrons that are localized in atomic orbitals of the ions. Therefore, no size-dependent quantization effect (due to confinement of delocalized electrons) is found in these transitions. However, a nanostructure controls either by judiciously choosing the nanoenvironment of the species to be excited or a nanoconfined structure can be utilized to manipulate the excitation dynamics. A very broad range of unprecedented optical properties can be observed by changing the host lattice and dopant concentration. The main goal of this work is to study the luminescence efficiency of a rare-earth doped nanoparticle by changing the dopant concentration, crystal structure and crystal phase [10–21]. Generally, the luminescence lifetime can be written as

$$\tau = \frac{1}{W_{\mathrm{RAD}} + W_{\mathrm{NR}} + W_{\mathrm{ET}}}, \tag{1}$$

where W_{RAD} is the radiative (photon) emission rate and W_{NR} is the nonradiative (multi-phonon) emission rate. The term W_{ET} is the energy transfer rate between neighboring RE ions and for a dipole–dipole interaction it scales with the inverse of the sixth power of the interatomic distance between the donor and the acceptor. The contribution due to W_{ET} is considered for high concentration of ions. The term W_{RAD} depends basically on the lattice morphology and symmetry while the term W_{NR} depends basically on the host phonon spectrum (cut-off phonon energy). It is well-known that the modification of phonon spectrum, i.e. nonradiative relaxation mechanism (W_{NR}) occurs in the different size of nanoparticles. However, local symmetry change, i.e. the modification of radiative relaxation mechanism (W_{RAD}) occurs in different crystal phases of the sample.

Here, we present an overview of our recent results on upconversion and photoluminescence of rare-earth doped nanocrystals by changing the dopant concentration, crystal size and crystal structure.

2. Experimental details

Here, we use sol–emulsion–gel process to prepare rare-earth ions doped oxide nanoparticles [3,4,10]. Zirconia propoxide (Fluka) and erbium acetate were used as the starting materials. First, three milliliters of glacial acetic acid was slowly added to 10 ml of zirconia propoxide and stirred for 30 min. Then 20 ml of n-propanol was added to the solution, which was further stirred for 15 min at room temperature. Four milliliters of 50% aqueous acetic acid was slowly added to the above solution under stirring which resulted in a clear transparent solution. Then, a stoichiometric amount of erbium acetate was added to this sol. The emulsified sol droplets were obtained through water-in-oil (w/o) type emulsions with cyclohexane and sorbitan monooleate (Span 80, fluka) as the organic liquid (oil phase) and nonionic surfactant respectively. The principle of the process involves the dispersion of an aqueous sol containing the desired constituents under agitation into a water-immiscible organic liquid for low dielectric constant. The crystalline phases of calcined powders were identified by X-ray diffraction (XRD). The average crystal sizes of 1.0 mol% Er-doped ZrO_2 nanocrystals are about 23 and 27.7 nm for 800 and 1000°C heat-treated samples respectively. We pressed the particles to form a smooth, opaque flat disk for optical study. For upconversion measurements, the samples were irradiated with a diode laser tuned to 980 nm. A CCD-coupled spectrometer recorded the fluorescence spectra. The absolute fluorescence intensity was measured with a Minolta LS-110 Luminance meter.

3. Results and discussion

3.1 *Effect of concentration*

A typical energy level diagram for the upconverted emission of Er^{3+} ions under infra-red excitation is shown in figure 1. The upconverted fluorescence spectra of the $Er^{3+}:ZrO_2$ nanocrystals in different concentrations of Er^{3+} are shown in figure 2. A significant drop in the overall intensity and a change in the spectral nature of these bands are observed with an increasing concentration of Er^{3+} ions [3]. The relative increase in intensity of red emission with respect to the intensity of green emission was observed with an increasing concentration of erbium. The mechanism of the upconverted emission of Er^{3+} has been well-established in refs [1–5]. The diode-laser wavelength (980 nm) matches the absorption transition between the ground state, $^4I_{15/2}$, and the excited level $^4I_{11/2}$. After first-level excitation, the same laser pumps the excited atom from the $^4I_{11/2}$ to the $^4F_{7/2}$ level. Subsequent nonradiative relaxation populates the $^4S_{3/2}/^2H_{11/2}$ and the $^4F_{9/2}$ levels.

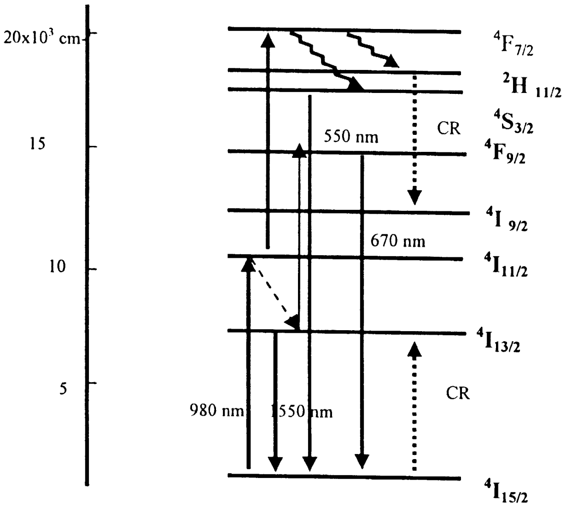

Figure 1. The energy level diagram of Er^{3+} ion under infra-red excitation.

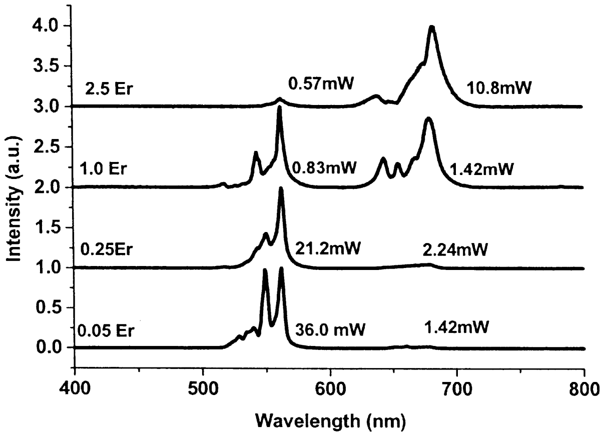

Figure 2. Upconverted emission spectra of different concentrations of Er^{3+} in ZrO_2 nanoparticles heated at 1000°C.

Bright green (550 nm) and red (670 nm) emission were observed due to the transitions $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively. Usually, the erbium ions are randomly distributed in the host lattice at low concentration, but at higher concentration, some of the Er^{3+} ions have a closer nearest neighbour than others and concentration quenching can occur. At low dopant concentration, the $^4S_{3/2}/{}^2H_{11/2}$ levels decay mostly radiatively to $^4I_{15/2}$. Therefore, the green emission has a higher intensity and this emission will be mainly contributed by the excited-state absorption process. At a higher concentration, the luminescent lifetime of $^4S_{3/2}/{}^2H_{11/2}$ levels are shortened as a result of the cross-relaxation processes between $^2H_{11/2} \rightarrow {}^4I_{9/2}$ and $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transitions as shown in figure 1. At high dopant concentration, the energy transfer upconverting process will become dominant at this time. As a result, the green emission disappears and the red one is observed upon excitation at 980 nm. The enhanced interactions between the ions induce increased relaxation of $^4I_{11/2} - {}^4I_{13/2}$ at higher dopant concentration (figure 1). Because of the long lifetime of $^4I_{13/2}$ level, the electrons populated in this level will reabsorb the excited light of 980 nm to arrive at $^4F_{9/2}$ level, and then go back to the ground state to emit the red light (670 nm). We also measure the lifetime of level $^4I_{13/2}$ of Er^{3+} ions in ZrO_2 nanocrystals to investigate the role of dopant concentration on the luminescence efficiency [11,16]. The luminescence lifetime ($^4I_{13/2}$ level of Er^{3+} ions) decreases from 3.36 to 2.16 ms by increasing the doping levels from 1.0 to 2.5 mol% Er_2O_3 in ZrO_2 nanocrystals sintered at 1000°C, due to cross-relaxation nonradiative process.

3.2 *Effect of crystal phase*

The upconversion luminance values are 255.7, 478.2 and 11960 Cd/m^2 for 800, 900 and 1000°C heated 0.05 mol% Er^{3+}-doped ZrO_2 nanocrystals, respectively [5]. It is seen from XRD study that the tetragonal phase is dominant at 800 and 900°C, whereas monoclinic phase is dominant at 1000°C sintered samples. The drastic increase in intensity of the luminescence band with changing phases indicates the lowering of the site symmetry (due to monoclinic phase) in which the ion is situated [15]. It is well-known that the f–f transitions arising from forced electric dipole which are parity forbidden, become partially allowed when the ion is situated at low symmetry site. Such situation allows intermixing of the f states with higher electronic configuration and as a result the optical transition probability increases, i.e. the radiative emission rate increases. It clearly reveals that the upconversion process in these particles depends upon crystal phase. The variations of the fluorescence intensity of the green and red emission vs. pump intensity have been examined and results confirm that the upconversion in all these materials is due to two-photon excited state absorption process. We also measure the lifetime of level $^4I_{13/2}$ of Er^{3+} ions in ZrO_2 nanocrystals to investigate the role of crystal structure on the luminescence intensity. At a concentration of 1.0 mol% Er_2O_3, the decay is single exponential and the luminescence lifetimes are 1.94 ms and 3.36 ms for 800 and 1000°C for tetragonal and monoclinic crystal phases, respectively [11]. Considering the phonon frequencies of tetragonal and monoclinic phases, the number of phonons is 15.02 and 24.21 for tetragonal and monoclinic phases, respectively. Nonradiative relaxation rate decreases with increasing number of phonons and as a result the radiative lifetime increases. Again, in the case of 0.5 mol% Ce-doped Y_2SiO_5 nanocrystals, a significant increase in the overall lifetime from 8.78 ns to 35.21 ns is observed for X_1-Y_2SiO_5 phase and X_2-Y_2SiO_5 phase, respectively [10]. Results reveal that the crystal structure plays an important role in rare-earth doped nanocrystals.

3.3 *Effect of crystal size*

Generally, the fluorescence intensity ratio (FIR) method involves measurements of the fluorescence intensities from two closely spaced electronic energy levels which are thermally coupled and which are assumed to be in a thermodynamical quasi-equilibrium state [18]. Figure 3 shows the upconversion fluorescence from Er^{3+}-doped $BaTiO_3$ nanocrystals in different temperatures. The experimental data are fitted with a linear curve $\log_e[\mathrm{FIR}] = -(\alpha/T)+\beta$. The slope of the linear curve (the parameter α) is related to the sensitivity of the sensor defined as the rate in which the FIR changes with temperature [18]. Note that α does not change, within the experimental error, with Er^{3+} concentration for the samples with the same size but it changes when the nanoparticle size is reduced while keeping Er^{3+} concentration fixed. To understand this behavior we discussed the physical origin of α [18]. In conclusion, we have demonstrated that Er^{3+}-doped $BaTiO_3$ nanocrystals are suitable for use as FIR-based temperature nanosensors. The sensitivity of the nanothermometer is influenced by the nonradiative relaxation channels which depend on the size of the nanocrystal. The lifetime of level $^4F_{9/2}$ of Er^{3+} ions in ZrO_2 nanocrystals is used to investigate the effects of crystal size on the luminescence intensity. The lifetime values are 2.19, 2.66 and 2.97 μs for 23, 31 and 44 nm crystal size of 0.05 mol% Er_2O_3-doped ZrO_2 nanocrystals [16]. In the case of 0.5 mol% Ce-doped Y_2SiO_5 nanocrystals, the overall lifetimes are 8.78 and 3.45 ns for 30 and

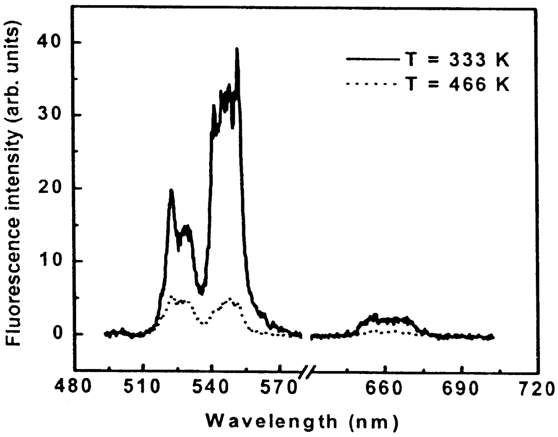

Figure 3. Upconversion fluorescence from Er^{3+} ions doped (2% mol) in 60 nm-diameter $BaTiO_3$ nanocrystals under diode laser irradiation. Sample temperatures are 333 K (solid line) and 466 K (dotted line).

50 nm crystal size with the same crystal structure (X_1-Y_2SiO_5 phase), respectively [10]. Thus we conclude that the changes observed in the lifetime of excited state of rare-earth ions must be mainly due to modifications of radiative and nonradiative relaxation processes due to crystal structure and crystal size respectively.

4. Conclusions

In summary, the luminescence properties of rare-earth ions in nanocrystals are found to be dependent on the crystalline structure, crystal size and dopant concentration. The analysis suggests that modification of relaxation mechanism is due to the crystal structure of the host and concentration of ions. An asymmetric crystal host and judicious choice of dopant concentration are also responsible for efficient emission of rare-earth ions doped oxide nanocrystals.

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