Mechanisms for Ce$^{3+}$ excitation at energies below the zero-phonon line in YAG crystals and nanocrystals

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Excitation of YAG:Ce$^{3+}$ crystals and nanocrystals was performed at $\lambda_{exc}=473–584$ nm over a wide temperature range. It was observed that the luminescence of both nano- and single-crystal YAG:Ce samples is efficiently excited with photon energies well below the Ce$^{3+}$ absorption band and at least 1650 cm$^{-1}$ below the ZPL of the 4f$^1$(2F$^5$/$^2$)–4f$^0$5d$^1$ transition, located at 489 nm. The studies of Ce$^{3+}$ fluorescence spectra as a function of temperature and excitation wavelength and of their temporal evolution point to the role of phonon-assisted nonradiative energy transfer between different groups of Ce$^{3+}$ centers in the excitation mechanism.

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1. Introduction

$Y_3Al_5O_{12}$:Ce$^{3+}$ (YAG:Ce$^{3+}$) is a well-known luminescent material with a broad electron–phonon emission band which is due to a fast (65 ns) electric dipole allowed 4f$^0$5d$^1$–4f$^1$ radiative transition. In this Ce$^{3+}$ doped dielectric the emission occurs in the visible part of the optical spectrum (the other examples are Sc$_2$O$_3$:Ce$^{3+}$ and Y$_2$O$_2$S:Ce$^{3+}$). YAG:Ce$^{3+}$ has attracted much attention because it is widely used as a scintillator and a solid state laser operating below the ZPL of the 4f$^1$(2F$^5$/$^2$)–4f$^0$5d$^1$ transition, located at 489 nm. This cannot be explained by room-temperature thermal population of the 4f$^1$(2F$^5$/$^2$) ground state vibronic levels or of the 4f$^1$(2F$^7$/$^2$) state (1700 cm$^{-1}$ above 2F$^5$/$^2$). In order to explain this observation we performed studies of cw and time-resolved fluorescence spectra of the bulk and nanocrystalline YAG:Ce$^{3+}$ and of their dependencies on temperature and excitation intensity.

2. Experiment

Experiments were performed with bulk YAG:1%Ce samples and with powder samples of nanocrystalline (30 nm) YAG:Ce with Ce concentrations of 1% and 0.1% (see Ref. [1] for more details). Luminescence was excited with cw diode-pumped solid state (DPSS) lasers operating at 532 nm and at 473 nm, or with a DPSS laser-pumped CW R6G dye laser (Coherent CR-599); typical power of all lasers was of about 40–80 mW. A Q-switched DPSS laser operating at 532 nm with a pulse duration 10 ns, repetition rate 10 kHz and average power 30 mW was used as a pulsed excitation source in time-resolved measurements. The Ce$^{3+}$ luminescence was detected with a double-grating monochromator and a PMT operating in a photon-counting regime or with a grating spectrometer equipped with a CCD camera. In time-resolved measurements the gated photon counting and start/stop photon registration technique were used.
The temperature dependencies of the fluorescence spectra were measured under very weak excitation (1 W/cm²) using the cold finger of a liquid helium refrigerator. The nanocrystalline YAG:Ce³⁺ powder samples were pressed onto the cold finger. The monotonous increase of the observed fluorescence intensity down to 100 K suggests that, at least in this range, the sample temperature does not differ much from that of the cold finger. Some spectra were obtained with the samples immersed in liquid nitrogen.

3. Experimental results

Figs. 1 and 2 show the temperature dependencies of fluorescence spectra of the bulk and nanocrystalline YAG:Ce³⁺ excited at 532 nm. The fluorescence spectra are labeled with the cold finger temperature. Some fluorescence was observed down to the lowest (20 K) temperatures. The comparison of the two figures shows that below-ZPL excitation of Ce³⁺ occurs in both nanocrystalline and bulk samples; thus the effect is not due to spatial confinement at the nanoscale level.

The Arrhenius plots displaying the Ce³⁺ fluorescence intensities (logarithmic scale) in the Stokes (at 560 nm and integral) and anti-Stokes (at 512.5 nm) spectral regions vs. reciprocal temperature for YAG:Ce crystals and nanocrystals are shown in Fig. 3. The temperature dependencies in Fig. 3 significantly deviate from straight lines, suggesting the non-activational character of fluorescence excitation. The activation temperatures that can be roughly estimated from these plots are 1000 K (695 cm⁻¹) for nanocrystals and 2000 K (1390 cm⁻¹) for the bulk for both Stokes and anti-Stokes emission (dashed and solid lines respectively). These temperatures do not match either the energy difference between the excitation energy and ZPL energy (1650 cm⁻¹), or the ²F₃/₂−²F₅/₂ splitting (1700 cm⁻¹). The dotted line in the figure shows the slope corresponding to this splitting (2450 K in temperature scale). The plot of the 512 nm intensity for YAG:Ce single-crystal does come close to the 2450 K activation at higher temperatures, but does not match it below 200 K.

Most of the experiments on below-ZPL excited fluorescence were performed with the bulk samples in order to minimize the effects of heating with the laser beam and to exclude the additional inhomogeneous broadening in nanoparticles.

The dependencies of the YAG:Ce crystal fluorescence intensity on cw 532 nm excitation intensity are shown in (Fig. 4a).
The fluorescence was registered at both anti-Stokes and Stokes wavelengths. The shapes of the spectra did not vary with excitation intensity. These dependencies are significantly sub-linear. The lines in (Fig. 4a) are square root dependencies that serve as guides for the eye.

The dependencies of YAG:Ce crystal fluorescence on excitation intensity were also measured under a pulsed (10 ns, repetition rate 10 kHz) 532 nm laser excitation. The time-integrated fluorescence intensity is shown in (Fig. 4b) vs. the average laser power. In contrast to the cw excitation, these intensity dependencies are almost linear (or even slightly super-linear).

Depending on excitation wavelength and temperature very different Ce$^{3+}$ fluorescence spectral shapes may be observed. The comparison of the spectra of YAG:1%Ce bulk crystal fluorescence excited at 473 nm and 532 nm at 295 K as well as at 532 nm at 77 K is shown in Fig. 5.

The comparison of the spectra of nanocrystalline YAG:Ce fluorescence excited at 473 nm and 532 nm at 295 K as well as at 532 nm at 77 K is shown in Fig. 6.

The comparison of Figs. 5 and 6 suggests that the main difference between the fluorescence of the bulk YAG:Ce and that of nanoparticles is additional inhomogeneous broadening observed in nanoparticles as usual with doped ionic insulators [2]. In general, the effect of below-ZPL excitation of fluorescence is similar in the two kinds of samples.

The fluorescence of Ce$^{3+}$ ions in YAG crystal may be observed under excitation with even lower-energy photons in the 565–590 nm spectral region (CW R6G dye laser; Figs. 7 and 8), though the excitation efficiency significantly drops with the increase of excitation wavelength.

The 77 K spectra shown in Fig. 8 reveal differences that are due to some selectivity in excitation of Ce$^{3+}$ ions within the strongly inhomogeneously broadened ensemble by light with different wavelengths. It may also be seen in the spectra that the emission due to transitions to the upper $2F_{7/2}$ state is weaker than that due to transitions to the lower $2F_{5/2}$ state. A similar difference may be seen in Fig. 5 for the spectra under “regular” excitation above the ZPL. The anti-Stokes parts of the spectra (in contrast to the spectra shown in Figs. 1 and 2) may be well described with the Boltzmann distributions for corresponding temperatures (see Figs. 7 and 8).

The fluorescence spectrum of nanocrystalline YAG:1%Ce excited at 572 nm and $T=77$ K (Fig. 9) very clearly reveals the structure that may be due to the existence of additional distinct groups of Ce$^{3+}$ centers in nanoparticles, e.g. Ce ions close to the...
particles surface. Again, the anti-Stokes parts of the spectrum may be well described with a Boltzmann distribution for $T = 77$ K.

The fluorescence spectra of the bulk YAG:Ce at room temperature exhibit a quite peculiar temporal evolution after the pulsed (10 ns) excitation at 532 nm (Figs. 10 and 11). The kinetics of fluorescence at different wavelengths is shown in Fig. 10a on a logarithmic scale. The nearly exponential decay ($\tau = 63$ ns) is preceded in the Stokes part of the spectrum by a much faster decay, whereas in the anti-Stokes part the decay shows almost no fast component. More clearly the differences in the fluorescence temporal evolution at different wavelengths may be seen in Fig. 10b, in which the fluorescence is divided (normalized) by $e^{-t/\tau}$, which represents the overall decay of Ce$^{3+}$ excited states. Assuming the same direct fluorescence decay rate for all Ce$^{3+}$ centers, dividing by $e^{-t/\tau}$ eliminates the contribution of this decay from the decay curves and leaves only the kinetics due to excitation transfer among different kinds of centers.

The fluorescence spectra obtained in 200 ns time gates with different delays after the laser excitation pulse at 532 nm are shown in Fig. 11 (these time gates are shown in Fig. 10 with horizontal bars). The shape of the fluorescence spectra drastically changes in time, demonstrating quite peculiar shapes at some time intervals. It is interesting that the decay time observed at all wavelengths is almost identical (63–65 ns, Fig. 10a), so just small non-exponentialities of the decay process (Fig. 10b) are responsible for the evolution of the fluorescence spectrum shape. The time-resolved spectra (Fig. 11) are, in general, consistent with the results on the fluorescence kinetics (Fig. 10b). Indeed, the increase of normalized intensity of 512.5 and 540 nm fluorescence during the first 20 ns after the laser pulse (Fig. 10b) corresponds to the relative increase of anti-Stokes fluorescence—compare the $-150$–50 ns and $50–250$ ns spectra in Fig. 11; the following decrease of normalized intensity at 540 nm and less pronounced decrease at 512.5 nm on the 100 ns scale correspond to achieving almost equal anti-Stokes and Stokes intensities at later times (see 350–550 ns spectrum in Fig. 11). The opposite temporal behavior of the normalized intensity of 650 nm fluorescence (Fig. 10b) is in agreement with these comparisons. It should be acknowledged that the possible comparison of the results presented in Figs. 10b and 11 is only qualitative: (i) the normalization of the spectra in Fig. 11 is approximate (made in the course of the experiment in
order to avoid saturation of the photon-counting system), (ii) the 200 ns time window is too large, (iii) the time-resolved kinetics signal becomes noisy at late times and (iv) dividing by $e^{-t/63\text{ ns}}$ assumes identical radiative lifetimes for all Ce$^{3+}$ centers, whereas different groups of centers contribute to the fluorescence.

At $T=200$ K most of the observable temporal evolution of the shape of fluorescence spectra of bulk YAG:Ce is gone. The fluorescence decay at all wavelengths is almost purely exponential with $\tau=65$ ns. The spectra observed at 200 K at different delays after the laser pulse are very similar, except a small difference in the anti-Stokes part of the spectrum, where a small rise of relative intensity may be observed in the very beginning of the decay.

4. Discussion

The experimental results suggest that the observed below-ZPL excitation of Ce$^{3+}$ ions in YAG cannot be explained by an equilibrium thermal population of the $4f(^{2}F_{3/2})$ ground state vibronic levels and of the electronic $4f(^{2}F_{5/2})$ state. The observed temperature dependencies (Fig. 3) do not exhibit the activation behavior and the estimated activation energies in most cases differ from that required to populate these states. The difference between the temperature activation of fluorescence for the bulk YAG:Ce and the nanoparticles indicates that the thermal population is not responsible for below-ZPL excitation, because the energy splittings are not sensitive to spatial confinement (not taking into account the inhomogeneous broadening) and are the same in the bulk and nanocrystalline samples. The difference in the spectra of the nanocrystalline samples with different Ce concentrations (Fig. 2) also does not support a thermal population mechanism, because thermal population of electronic and vibronic levels is expected to be concentration-independent. Also, the 295 K Boltzmann curve for energies measured from the excitation energy (thin solid line in Fig. 1) stretches much less into the anti-Stokes part of the spectrum than the experimental room-temperature spectrum. Thus the mechanism of the below-ZPL excitation of Ce ions involves the addition of energy to the exciting photons either from phonons via some highly nonequilibrium process or from a source other than the thermal reservoir.

The sub-linear dependence of YAG:Ce crystal fluorescence on excitation intensity (Fig. 4a) is not due to saturation of the $4f(^{2}F_{5/2}) \rightarrow 4f^{5}d^{1}$ transition. Indeed, the dependence of fluorescence on excitation does not saturate even for much higher pulsed excitation levels (Fig. 4b; note that the excited state lifetime is 65 ns). This also suggests that some complicated process is responsible for the below-ZPL excitation of Ce ions.

The fluorescence spectra obtained at lower temperatures (Figs. 1 and 5–9) clearly show the existence of a subset of Ce$^{3+}$ ions with significantly decreased energy of the $4f^{5}d^{1}$ state. The spectra, obtained under 532 nm excitation at 100 K and below, and under 565–590 nm excitation up to 295 K, are due to a distinct group of Ce$^{3+}$ centers whose local environment is distorted. These spectra are significantly shifted to lower energies relative to the spectra of regular Ce centers (see spectra excited at 473 nm in Figs. 5 and 6) and may be observed down to the lowest (20 K) temperatures. The distorted centers within the crystal volume may be due to nearby defects such as antisites [3,4], interstitial non-stoichiometric Yttrium or vacancies. The spectra of these distorted centers are very strongly, inhomogeneously broadened. These centers may be excited directly via their
electron-vibrational states by a single photon of 532–590 nm wavelength.

At higher temperatures the fluorescence of the main ensemble of regular Ce\(^{3+}\) ions appears in the spectra excited at 532 nm (Figs. 1 and 2). The shape of the luminescence band of the main Ce\(^{3+}\) ensemble is given by the spectra excited at 473 nm (Figs. 5 and 6). These ions cannot be excited by 532 nm photons directly, so some kind of transfer of energy from the directly-excited distorted centers must occur.

Different mechanisms of energy transfer from directly-excited distorted Ce\(^{3+}\) centers to regular Ce\(^{3+}\) may be suggested.

4.1. Two-photon mechanisms

The mechanism of the below-ZPL excitation of Ce ions may involve the addition of energy to the exciting photons energy from the exciting light itself. In such mechanisms the additional energy, required for below-ZPL excitation comes from photons—more than one photon is involved in excitation. Energy transfer from excited distorted Ce\(^{3+}\) centers to the regular ions of the main ensemble may occur via different processes. Non-radiative energy transfer and/or cooperative processes may be responsible for such transfer.

The energy of a second photon absorbed by a distorted ion excited to 4\(^{f}5\)d\(^{1}\) may excite this ion to a high-lying charge-transfer state with a large radius. Nonradiative energy transfer may then occur to the high-lying excited states of regular Ce\(^{3+}\) centers.

Alternatively, the mechanism of energy transfer from excited distorted Ce\(^{3+}\) centers to the regular ions of the main ensemble may include two-step photoionization. Indeed, for regular Ce\(^{3+}\) ions in YAG efficient two step photoionization occurs [5,6] and charge transfer may play a significant role in Ce\(^{3+}\) fluorescence [7]. It may be expected that the distorted Ce\(^{3+}\) ions can also be photoionized by a two-step process. The released electrons may recombine with Ce\(^{4+}\) ions present in the matrix, resulting in Ce\(^{3+}\) ions in their excited 5d states that will emit 4\(^{f}5\)d\(^{1}\) → 4\(^{f}\) luminescence.

Obviously, most Ce ions, including Ce\(^{3+}\), occupy the main and not the distorted sites, so the process will result in fluorescence of regular ions. The problem with this mechanism is that it would lead to a depletion of the ensemble of distorted Ce\(^{3+}\) ions in the course of excitation. Indeed, if most of the electrons released from distorted Ce\(^{3+}\) ions recombine with Ce\(^{4+}\) ions in regular sites, the process will at some point terminate itself. A continuous process must involve the backwards transfer of electrons from regular Ce\(^{3+}\) ions in their ground state to Ce\(^{3+}\) ions in distorted sites without participation of photons.

The problem for all two-photon mechanisms is the excitation intensity dependence of the process. The two-step excitation of electrons to localized or delocalized states should be, at least in some intensity range, quadratic in intensity, which is not the case—see Fig. 4.

Another issue is that in contrast to the spectra obtained under 532 nm excitation (Figs. 1 and 2), the spectra under 565–590 nm excitation (Figs. 7 and 8) even at \(T = 295\) K show no fluorescence of the main ensemble of regular Ce\(^{3+}\), these spectra are entirely due to distorted Ce\(^{3+}\) centers. This observation is an argument against the mechanisms of below-ZPL excitation of regular Ce\(^{3+}\) centers that involve two-photon processes. Indeed, in the two-photon process, the amount of energy available from the second photon significantly exceeds the energy deficit not only under 532 nm excitation, but under 532–590 nm excitation as well.

4.2. Nonequilibrium phonon-assisted energy transfer

A mechanism involving the receipt of energy from the thermal reservoir may be considered. The observed anti-Stokes fluorescence of distorted Ce\(^{3+}\) centers at \(T = 295\) K (Fig. 7), which is well described by a Boltzmann distribution, stretches up to higher energies more than 1500 cm\(^{-1}\) above the excitation energy. This means that the corresponding vibronic levels of the excited 4\(^{f}5\)d\(^{1}\) state are populated. Similar population of the excited vibronic levels of distorted Ce\(^{3+}\) centers may be expected under the 532 nm excitation at 295 K. Under the 532 nm excitation the phonon-assisted energy transfer from the thermally excited vibronic levels of distorted Ce centers (1500 cm\(^{-1}\) above the excitation energy) to the 4\(^{f}5\)d\(^{1}\) state of regular Ce\(^{3+}\) centers (1650 cm\(^{-1}\) above the excitation energy) would require a 150 cm\(^{-1}\) phonon which is available from the equilibrium phonons reservoir at room temperature. Of course excitation at 532 nm occurs both in the sidebands and in the ZPL of the distorted centers which span a large range of energies, so 1650 cm\(^{-1}\) is just an estimate of the energy deficit. The situation is different for 570 or 580 nm excitation, when the ZPL of distorted centers lies more than 2500 cm\(^{-1}\) below that of the main centers, preventing thermally activated energy transfer to the main centers at 295 K.

The mechanism of below-ZPL excitation of regular Ce ions, which involves the addition of energy to the exciting photon energy from the thermal reservoir, seems to be in contradiction with the estimated anti-Stokes fluorescence activation temperatures (Fig. 3) that do not match the additional energies required. It should be taken into account though, that actually the experimental situation is one of high nonequilibrium, so that a Boltzmann population of states may not be achieved. Indeed, if the phonon-assisted energy transfer (phonon absorption) occurs from the excited vibronic state of 4\(^{f}5\)d\(^{1}\) of the distorted Ce\(^{3+}\) center to the excited 4\(^{f}5\)d\(^{1}\) state of regular Ce\(^{3+}\) center, in order to achieve the thermal equilibrium between the excited states, the reverse process of phonon-assisted energy transfer (phonon emission) should also be included. This backwards energy transfer from excited regular Ce\(^{3+}\) center to a distorted Ce\(^{3+}\) center competes with radiative decay of the 4\(^{f}5\)d\(^{1}\) state of regular center. Thus, if the radiative decay rate \((1/\tau_k = 1.5 \times 10^7 \text{s}^{-1})\) is higher than that of the backwards phonon-assisted energy transfer (or comparable to it), the distribution of the excited states may be in high nonequilibrium and not describable by activation energies. Indeed, in the Arrhenius plots (Fig. 3) the experimental data exhibit some deviations from straight lines.

The above considerations may be supported by a simple rate equation for the population of the excited states of regular Ce\(^{3+}\) centers:

\[
\frac{dN_0^\ast}{dt} = anN_0^\ast(N_0^\ast/\tau_1) - (n+1)N_0^\ast,
\]

where \(N_0^\ast\) and \(N_0^\ast\) are the populations of the excited states of regular and distorted Ce\(^{3+}\) centers respectively, \(n\) is the occupation number of effective phonons, and \(a\) is the phonon-assisted process rate. In stationary conditions under the cw excitation, \(dN_0^\ast/dt = 0\) and

\[
N_0^\ast = \frac{an}{(1/\tau_k) + a(n+1)}N_0^\ast.
\]

If the radiative decay of the excited states of regular Ce\(^{3+}\) centers is faster than the energy transfer back to distorted ions \((1/\tau_k > a(n+1))\) then

\[
N_0^\ast = ant_0N_0^\ast.
\]

This represents a strongly nonequilibrium population of the excited states of regular Ce\(^{3+}\) centers, significantly different from the Boltzmann distribution \(N_0^\ast = (1/T_k)\). The rough assumption in this consideration is the use of a single occupation number of effective phonons \(n\)—actually, there is a distribution of distorted
centers with different energies relative to the main center requiring phonons of different energies, but a strongly nonequilibrium population of the excited states will still occur.

Under longer-wavelength excitation, in the range 565–590 nm, the centers of the strongly inhomogeneously broadened distorted Ce$^{3+}$ ensemble that are excited are at lower energy than the centers excited at 532 nm. The energy of effective phonons required for the nonequilibrium phonon-assisted energy transfer to the regular ions is 1000 cm$^{-1}$ larger than that required under 532 nm excitation, and their occupation numbers $n$ at $T$=295 K are low; thus nonequilibrium energy transfer to regular ions becomes impossible.

The temporal evolution of the spectra (Figs. 10 and 11) also supports the nonequilibrium phonon-assisted energy transfer mechanism. The competition involving phonon-assisted energy transfer between the two kinds of Ce$^{3+}$ centers and the radiative decay of the excited 4f$^5$5d$^1$ states of regular Ce$^{3+}$ centers may be seen in Fig. 11. Indeed, the comparison of the spectra obtained in the −150–50 ns and 50–250 ns time gates (Fig. 11) directly shows the existence of energy transfer from the distorted Ce$^{3+}$ centers to regular Ce$^{3+}$ that occurs at early (0–75 ns, see Fig. 10b) stages of relaxation—the relative intensity in anti-Stokes increases. (The cw spectra of regular and distorted Ce$^{3+}$ from Fig. 5 are shown at the bottom of Fig. 11.) The quite peculiar spectral shapes observed at later times (150–500 ns) also demonstrate the efficient energy transfer; at this stage the transfer within the inhomogeneously broadened ensembles of regular and distorted Ce$^{3+}$ centers results in a larger separation of corresponding spectral maxima. It is important that the most significant contribution to the time-averaged (analogous to cw excited) spectrum comes from the initial stages of decay (at, say, $t < 200$ ns), so the peculiar spectra, obtained at later times, do not significantly influence the time-averaged spectrum. Of course, most energy transfer processes, responsible for excitation of regular ions, should occur at very short times (<10 ns, hardly resolved in Fig. 10b), but the existence of energy transfer from lower to higher energies was directly observed in these spectra on a longer timescale. The different rates of energy transfer between the Ce$^{3+}$ centers due to different distances between them and different energy mismatches result in a complicated picture of the temporal evolution of the spectrum. The dynamics may also include energy transfer among the distorted centers tending to shift the spectra to the red during the decay.

The temperature dependencies of the spectra may be explained, assuming the suggested mechanism. Firstly, the efficiency of excitation of distorted ions (with a lower energy of their 4f$^5$5d$^1$ states) increases with temperature—indeed, at elevated temperatures excitation via the populated ground state vibronic levels becomes possible. Secondly, the noneradiative energy transfer processes are temperature-dependent (1)–(3). Thermally activated energy migration in YAG:Ce$^{3+}$ was considered in Ref. [8] as a mechanism of thermal quenching of Ce$^{3+}$ fluorescence.

The nonequilibrium energy transfer process is expected to be more efficient in the samples with higher Ce concentration. Indeed, in Fig. 2 the relative integral intensity of anti-Stokes emission is stronger in YAG:1%Ce nanopowder than in the 0.1% Ce sample.

The above considerations show that the suggested nonequilibrium phonon-assisted nonequilibrium energy transfer (mechanism (b)) is responsible for below-ZPL excitation of Ce$^{3+}$ ions. Thus the fluorescence of Ce$^{3+}$ ions excited at 532 nm consists of (1) directly excited fluorescence of distorted ions with significantly decreased energy of the 4f$^5$5d$^1$ state and (2) fluorescence of regular ions excited by energy transfer from the distorted ions. Indeed, Figs. 5 and 6 show that the spectrum observed under 532 nm excitation at 295 K may be considered as consisting of fluorescence from regular Ce$^{3+}$ ions (see the spectrum excited at 473 nm) and fluorescence of distorted ions (see the spectrum excited at 532 nm at 77 K). These distinct different groups of Ce$^{3+}$ ions are also revealed in the time-resolved spectra (Fig. 11), where the temporal evolution of the spectra of different groups of Ce$^{3+}$ may be seen.

It should be mentioned that the observed nonequilibrium phonon-assisted nonradiative energy transfer process is potentially interesting from the point of view of laser cooling of solids (see Ref. [9] for a review). Indeed, such an energy transfer process involves annihilation of phonons followed by emission of anti-Stokes luminescence. If the backwards transfer is significantly less efficient than the radiative decay of acceptor ions, the cooling may occur. Obviously, in our experiments with YAG:Ce no cooling occurs as the Stokes emission of both donor and acceptor Ce$^{3+}$ ions results in creation of more phonons than are annihilated in the energy transfer process (compare anti-Stokes and Stokes intensities in Figs. 1 and 2), but the principle of the energy transfer-based cooling process is demonstrated. The advantage of the energy transfer-based cooling compared to a single-ion process, which is commonly used [9], is that cooling may be optimized by proper donor–acceptor pair selection and by adjustment of both donor and acceptor concentrations. Interestingly, recently YAG:Ce was suggested as an object for a new approach to radiative cooling of solids [10], but the considered cooling mechanism is quite different from nonequilibrium phonon-assisted nonradiative energy transfer.

5. Conclusions

Based on the experimental studies, the mechanism of below-ZPL excitation of Ce$^{3+}$ ions in the bulk and nanocrystalline YAG samples is suggested, which includes extraction of the necessary additional energy from the phonon reservoir which occurs in a significantly nonequilibrium nonradiative energy transfer process. The observations reveal a complicated character of Ce$^{3+}$ ions excitation in YAG, which is an important phosphor material. The below-ZPL excitation of Ce$^{3+}$ should be taken into account in experiments on fluorescence line narrowing, hole-burning and single ion detection in YAG:Ce.

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