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Advances in theoretical understanding of photon upconversion in rare – earth activated nanophopshors

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Abstract

Photon upconversion in rare earth activated phosphors involves multiple mechanisms of electronic transitions. Stepwise optical excitation, energy transfer, and various nonlinear and collective light-matter interaction processes act together to convert low-energy photons into short-wavelength light emission. Upconversion luminescence from nanomaterials exhibits additional size and surface dependences. A fundamental understanding of the overall performance of an upconversion system requires basic theories on the spectroscopic properties of solids containing rare earth ions. This review article surveys the recent progresses in theoretical interpretations of the spectroscopic characteristics and luminescence dynamics of photon upconversion in rare earth activated phosphors. The primary aspects of upconversion processes, including energy level splitting, transition probability, line broadening, non-radiative relaxation and energy transfer are covered with an emphasis on interpreting experimental observations. Theoretical models and methods for analyzing nano-phenomena in upconversion are introduced with detailed discussions on recently reported experimental results.

1. Introduction

After more than four decades of studies on photon upconversion,[1, 2] research was recently extended to rare-earth doped nanophosphors with potential for applications in biotechnologies and other areas to convert infrared (IR) emission to visible light.[3-6] Photon upconversion involves multiple electronic transitions of rare earth ions influenced by ion-lattice interactions, whereas in nanophosphors, the dynamics of upconversion luminescence become more complicate because of variations in both chemical and electronic structures. Although, the basic theories required for interpreting various upconversion processes have already been established in general along with quantum optics and spectroscopy of rare earths in bulk solids, [7-9] a consistent and predictive understanding of upconversion performance in nanophosphors remains as a theoretical challenge.

Achieved by optical excitation of rare earth ions in inorganic compounds, multiphoton upconversion involves several steps of electronic transitions driven by linear or nonlinear light-matter interactions, single-ion or ion-pair collective actions, and resonant or phonon-assisted energy transfer processes. It is the interplay between the rare earth centers and the host compounds that defines the overall performance of the IR-to-visible upconversion emission of interest. Most of our knowledge in the spectroscopic properties and luminescence dynamics of rare earths in solids applies in order to accomplish a comprehensive understanding on the behaviors of a specific upconversion system. Since the work by Judd, Wybourne and others in the 1960's,[10-14] theories for the electronic properties of rare earth ions in solids have been well-established. The free-ion energy levels and crystal-field splittings of rare earth ions in $4f^N$ and other excited configurations can be calculated using a standard theoretical framework developed by Crosswithe, Carnall and others.[15-17] At the same time, experimental and theoretical studies on optical properties have accomplished fundamental understanding of the intensities of electronic transitions, non-radiative relaxation and energy transfer processes that determine photon upconversion performance. Comprehensive reviews have been given on these topics. [18-21]

Along with progress in experimental observations, understanding of upconversion processes has been developed at various theoretical levels. Review articles by Auzel and others have provided a comprehensive coverage of most aspects of upconversion mechanisms in rare earth-doped solids.[2, 7] Generally, upconversion mechanisms are divided into four categories including excited state absorption, sequential energy transfer, cooperative transitions, and photon avalanche. Besides, nonlinear optical processes such as second harmonic generation and direct two photon absorption from ground state also create photon upconversion. Each of the mechanisms has a specific theoretical base depending on the nature of electronic interactions. Difficulties in systematic analysis of upconversion performance arise primarily from the involvement of multiple mechanisms in one system, which cannot be exclusively verified and quantitatively evaluated. Because energy transfer and excited state absorption have much higher upconversion efficiencies than other mechanisms,[2] in most cases, particularly in sensitizer-activator co-doped systems, they contribute dominantly to the observed upconversion luminescence. Therefore, understanding stepwise electronic excitation and energy transfer processes, including phonon-broadening of electronic transitions and phonon-assisted energy transfer and non-radiative relaxation is essential for designing and improving upconversion materials.

Nanoscale manipulation of rare earth doped upconversion nanocrystals leads to important modification of their optical properties in excited-state dynamics, emission profiles and upconversion efficiency. In a recent review article, Wang and Liu discussed various material properties important for upconversion in nanophosphors.[6] For example, a reduction in particle size provides the ability to modify the lifetime of intermediate states of the doped rare earth ions.[22, 23] The control of spatial confinement of dopant ions in a nanoscopic region can lead to marked enhancement of a particular wavelength emission as well as generation of new types of photoemission. In nanophopshors, upconversion efficiency can be enhanced and the color of upconversion luminescence can be tuned.[3, 24] In comparison with bulk properties, multi-color upconversion emissions can be obtained from engineered nanoparticles activated by doping Yb-Er or Yb-Tm pairs with substantially strong blue emission and diminished green emission. Upconversion in nanophosphors involves the same mechanisms as those in bulk materials. However, because of size confinement in nanophosphors, ion-ion and ion-lattice interactions are modified in various degrees. In a book chapter, Liu and Chen summarized the spectroscopic properties of rare earth ions in nanomaterials.[25] Experimental observations and theoretical understanding of size-dependent phenomena were discussed. The present review focuses on recent studies of the fundamental aspects of electronic interactions of rare earth ions in nanocrystals and their consequences in photon upconversion. In Section 2, modification of energy levels and transition probabilities are discussed with respect to upconversion properties. Key issues including configuration interactions and vibronic coupling are addressed to gain a fundamental understanding of upconversion processes in nanocrystals. In Section 3, the theoretical background of excited state relaxation and energy transfer are reviewed. Discussions are focused on phonon-assisted energy transfer and non-radiative relaxation. Experimental results are reviewed to provide insights into the effects of surface defects and lattice distortion in crystals of nanometer scale, reduced phonon density of states (PDOS) that changes fundamentally the spectroscopic properties and luminescence dynamics of nanophosphors. Section 4 is devoted to size confinement on ion-phonon interaction and energy transfer that influence upconversion in nanomaterials.

2. Tuning energy levels and transition probabilities for multiphoton upconversion

2.1 Crystal-field splitting of electronic energy levels

Except second harmonic generation and cooperative luminescence, photon upconversion is manifested by optical centers with a series of metastable excited states that enable multiple steps of excitation into an upper excited state from which short wavelength photons are emitted.[7] In rare earth activated phosphors, the free-ion energy levels of the $4f^N$ states defined by Russell-Saunders notation of $^{2S+1}L_J$ multiplets with S, L and J being the total spin, orbital and angular momenta of the N 4f electrons, respectively, are utilized for achieving energy upconversion.[26] Photon upconversion has been realized with most of the trivalent rare earth ions (Ln^{3+}) including Er^{3+}, Tm^{3+}, Ho^{3+}, Tb^{3+}, Pr^{3+}, Nd^{3+} and Eu^{3+} in various host materials.[1, 2] The energy levels of trivalent rare earth ions in $4f^N$(N=1 to 13) configurations are shown in Fig. 1. They are calculated using an effective operator Hamiltonian with values of parameters obtained by Carnall et al. for Ln^{3+}:LaF_3.[17] Unlike the 5d states, the energy levels of 4f states are less dependent on host materials. In order to achieve multi-photon upconversion pumped by a narrow band laser in the IR region, an energy level scheme with equally spaced intermediate states are required. One of the trivalent rare earth ions, Er^{3+} in $4f^{11}$ configuration has a unique energy level structure to facilitate IR-to-visible multi-photon upconversions and multi-color emission. Up to 5-photon upconversion can be achieved with a single photon energy around 1.5 μm and 4-

photon upconversion can be achieved with a 0.98-μm pump source.[7] Multi-color upconversion has also been achieved with other trivalent ions such as Tm^{3+} and Ho^{3+}.

The free-ion energy levels split under the influence of crystal-field interaction. It is well known that the 4f electrons have very localized states. Quantum confinement effects on the electronic energy level structure are not expected for the localized electronic states of the rare earth ions doped in insulating nanocrystals. In the framework of crystal-field theory,[14, 26] ion-lattice interactions and the free-ion interactions are treated equally in an effective operator Hamiltonian, in which the crystal-field part is defined as

$$\mathscr{H}_{CF} = \sum_{k,q,i} B_q^k C_q^{(k)}(i)\,, \qquad (1)$$

where the summation involving i is over all the equivalent electrons of the open shell of the ion of interest, B_q^k are crystal-field parameters and $C_q^{(k)}$ are components of the tensor operators that act on the free-ion wave functions defined in terms of spherical harmonics. For f-electrons, k runs from 0 to 6 and q from 0 to $\pm\, k$ to meet the selection rules for angular momentum coupling.[27] The crystal-field parameters B_q^k count for the lattice contribution that depends on ion-ligand distance and site symmetry.

Because the off-diagonal matrix elements between different J-multiplets may not be zero, crystal-field interaction induces J-mixing. Besides, spin-orbital coupling mixes the Russell – Saunders multiplets of the same J. Therefore, a crystal-field energy level cannot be accurately characterized by a single $^{2S+1}L_J$ multiplet. In the intermediate coupling scheme, the eigenfunctions of the free-ion and crystal-field Hamiltonian are of the following form.

$$|\mu\rangle = \sum_{JM} a_{JM}\, |JM\rangle\,, \qquad (2)$$

where, in principle, the summation is over all JM terms of a given $4f^N$ configuration. Because of higher density of states, the upper excited states have more significant L and J mixing than the low-lying states. For instance, the ground state of Er^{3+} in crystals is a relatively pure $^4I_{15/2}$ multiplet, but the excited states are mixed in various degrees. Taking

Er^{3+} in fluoride crystals as an example, the eigenfunctions of the three excited states (e_1=15430 cm^{-1}, e_2=18650 cm^{-1}, e_3=24600 cm^{-1}) that emit, respectively red, green and blue luminescence can be calculated with the parameterized free-ion and crystal-field Hamiltonian.[17, 26] When the components of the M_J crystal-field levels are added for each multiplet, they have the following values.

$$|e_1\rangle = 0.769|{}^4F_{9/2}\rangle + 0.506|{}^4I_{9/2}\rangle + 0.299|{}^2G_{9/2}\rangle + \ldots$$

$$|e_2\rangle = 0.828|{}^4S_{3/2}\rangle + 0.425|{}^2P_{3/2}\rangle + 0.263|{}^4D_{3/2}\rangle + 0.216|{}^4F_{3/2}\rangle + \ldots$$

$$|e_3\rangle = 0.579|{}^2G_{9/2}\rangle + 0.487|{}^4F_{9/2}\rangle + 0.479|{}^2H_{9/2}\rangle + 0.353|{}^4I_{9/2}\rangle + 0.21|{}^4G_{9/2}\rangle \ldots \tag{3}$$

As conventionally labeled, the leading components are ${}^4F_{9/2}$, ${}^4S_{3/2}$ and ${}^2G_{9/2}$, respectively for e_1, e_2 and e_3. For most states in the $4f^N$ configuration, J-mixing is less than 10% and not listed in Eq. (3).

In order to reduce energy mismatches in the multi-step upconversion transitions, tuning the crystal-field splitting by selecting appropriate host materials is essential in developing upconversion phosphors. Depending on site symmetry and crystal-field strength of host materials, energy levels of the $4f^N$ states can shift up to 10%. Based on the superposition model of crystal field theory developed by Newman and co-workers, [28, 29] the dependence of the crystal field parameters on distance and orientation of the coordinated ligands can be expressed as a linear superposition of ion-ligand pair-wise electrostatic interactions.

$$B_q^k = \sum_l B_k\left(R_l\right) g_{k,q}\left(\theta_l, \phi_l\right), \tag{4}$$

where the summation is over ligands l, and B_k and $g_{k,q}$ count for the distance and angle dependence respectively. The distance dependence is defined by

$$B_k(R_l) = B_k(R_0)\left[\frac{R_0}{R_l}\right]^{\tau_k}, \qquad (5)$$

where R_0 is the distance between the f-ion and a reference ligand located on the z-axis of the crystalline lattice, and τ_k are power law exponents reflecting the distance dependence of the ion-ligand interaction. Theoretically, the power exponents have digital values as τ_2=3, τ_4=5, τ_6=7. It should be noted that the parameters τ_k are not generally in agreement with the electrostatic power law components. $B_k(R_0)$ and τ_k are often taken as phenomenological parameters and empirically determined. It is obvious that the values of the crystal field parameter for the k=4, 6 components of short range interaction diminish rapidly as the ion-ligand distance increases. On the other hand, the value for the k=2 parameter $B_2(R)$ decreases much slower with R.

In nanocrystals, the excitation energy of a dopant ion can be tuned by changing the nanoscopic environment electronically and structurally. Beside the lattice structure and site symmetry, particle size also influences. The energy level shifts may not be significant with respect to the overall electronic energy level structure of the $4f^N$ configuration. However, such a shift can enhance upconversion efficiency by reducing energy mismatches, and have a profound effect on the excited state dynamics and luminescence properties. For example, in the case of Pr^{3+}, the strength of crystal field interaction determines whether the intensely absorbing $4f^2$-$4f5d$ transition is above or below the S_0 level of the $4f^2$ configuration. Similarly, the charge transfer states of Eu^{3+} can also be tuned across the $4f^6$ states $^5D_{0,1,2}$ to dramatically change the luminescence dynamics.[30, 31] Because the 5*d* and charge-transfer states are more sensitive to the local environment than that of the 4f states, they induce important consequences that determine the excited state dynamics, especially the efficiency of upconversion luminescence [32, 33].

2.2 Symmetry dependence and the influence of configuration interaction

Among the rare earth fluorides, $NaYF_4$ has a high refractive index and low phonon energy required for performing light conversion. It is well known that, activated by either

Yb^{3+}-Er^{3+} or Yb^{3+}-Tm^{3+} ion pairs, the hexagonal β-$NaYF_4$ is one of the most efficient host among the rare earth doped upconversion materials.[34, 35] In comparison, in cubic structure, the α-phase of $NaYF_4$ also performs upconversion. However, with the same Yb^{3+}-Er^{3+} or Yb^{3+}-Tm^{3+} doping, the α-phase of bulk $NaYF_4$ is known to be about an order of magnitude less efficient than the corresponding hexagonal β-phase.[35] The crystalline structure, specifically, the symmetry of crystal field imposes a significant difference in upconversion efficiency. In the fluoride series, $Na(Y_{1.5}Na_{0.5})F_6$ has the identical formula units as $NaYF_4$ and exists in both cubic and hexagonal symmetries.[36] Wang et al. co-doped Yb^{3+} and Er^{3+} in nanocrystals of $Na(Y_{1.5}Na_{0.5})F_6$ of 50 nm size and observed that the green upconversion luminescence was greatly enhanced and dominant when the cubic nanoparticles were transformed into hexagonal nanoparticles. [37]

The rare earth ions in hexagonal $NaYF_4$ lattice occupy a site of C_{3h} symmetry, whereas in cubic phase, the metal ion site is O_h which may reduce to a tetragonal or lower symmetry if doping-induced site distortion is considered. Obviously, the difference in crystal field symmetry leads to different energy level splitting of the $^{2S+1}L_J$ multiplets, thus influence upconversion transitions with different energy mismatches. Much more significant influence of the crystal field symmetry is on the transition probabilities. According to Judd-Ofelt theory, the parity forbidden intra $4f^N$-$4f^N$ electronic transitions are enabled by crystal-field induced coupling with the un-occupied electronic configurations of the rare earth ion in higher energies or with a ligand-to-metal charge transfer configuration.[38] In general, removal of inversion symmetry is required to enable the intra $4f^N$ transitions. Because the closest excited configuration is $4f^{N-1}5d$, a lattice structure that allows the $4f^N$-$4f^{N-1}5d$ coupling enhances the transitions. The estimated energy levels of $4f^{N-1}5d$ configurations are shown in Fig. 1 along with that of the $4f^N$ states. In comparison with that of the $4f^N$ states, the $4f^{N-1}5d$ energy levels strongly depend on host materials. In Fig. 1, the lowest levels of the $4f^{N-1}5d$ states are for the trivalent rare earth ions in $NaYF_4$. They are calculated using the value for Ce^{3+}:$NaYF_4$ and a systematic relation derived by Dorenbos. [39] For Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+}, electric dipole transitions to the low $4f^{N-1}5d$ states are spin-forbidden. [40, 41]

The $4f^N$-$4f^{N-1}5d$ coupling can only be induced by the odd components of the crystal field $B^k_q C^{(k)}$ with k =1,3,5. The odd crystal field components exist in crystals of three-fold rotational axes and when an inversion center is absent. Accordingly, in these crystals, metal ions occupy a site of hexagonal, trigonal or lower symmetries.[26] At low site symmetries, not only the degeneracy of the free-ion states are removed, the transition probability also increases due to an overall increase in crystal field strength. This explains why the upconversion luminescence is much stronger in the hexagonal $NaYF_4$ than in the cubic $NaYF_4$. For evaluation of crystal-field induced intensity enhancement in crystals of C_{3h} symmetry, Wang et al. [42] derived a theoretical method for calculating the $f^N - f^{N-1}d$ configuration coupling. Using the standard irreducible tensor operator technique,[43, 44] the matrix elements of $4f^N$-$4f^{N-1}5d$ crystal field coupling can be expressed in a general form as [42]

$$\left\langle f^N LSJM \middle| \sum_{k,q} B_q^k C_q^k \middle| f^{N-1} dL'S'J'M' \right\rangle$$
$$= \sum B_q^k (-1)^{J-M+L+S+J'+k} (J,k,J',-M,q,M')\delta_{S,S'}[J,J']^{1/2}\{L,S,k,J',J,L'\}\cdot$$
$$\sum_{\alpha_2 L_{N-1} S_{N-1}} (f^N \alpha_2 LS\{|f^{N-1}\alpha_2 L_{N-1} S_{N-1})\delta_{\alpha_2 L_{N-1},\alpha_2' L_{N-1}'}(-1)^{L_{N-1}+L+k+1}[L,L',3,2]^{1/2}$$
$$\{L_{N-1},3,L',k,L,2\}(3,k,2,0,0,0) \tag{6}$$

where { ..} and (…) are 6-j and 3-j symbols respectively, $(f^N \alpha_2 LS\{|f^{N-1}\alpha_2 L_{N-1} S_{N-1})$ are the coefficients of fractional parentage which can be obtained from Nielson and Koster's table,[45] and α_2 is an additional label to identify the states with the same L and S values, and $[L, L', 3, 2]^{1/2}$ stands for $\sqrt{(2L+1)(2L'+1)\times 7\times 5}$. All matrix elements are vanished for even k, because $(3,k,2,0,0,0) \neq 0$ only when k =1, 3, or 5. In the matrix elements for $4f^N$-$4f^N$ crystal-field coupling, it changes to $(3,k,3,0,0,0)$, so only those with k =2,4,6 are nonzero. After diagonalization of the free-ion and crystal-field Hamiltonian with the free-ion wave functions of both $4f^N$ and $4f^{N-1}5d$ configurations, the eigenfunctions in the intermediate coupling scheme for the i^{th} crystal field state of a 4f ion can be expressed explicitly in two parts

$$|i\rangle = \sum_{JM} a_{JM} \left|4f^N JM\right\rangle + \sum_{JM} b_{JM} \left|4f^{N-1}5dJM\right\rangle, \tag{7}$$

where $|4f^N JM>$ and $|4f^{N-1}5dJM>$ are the $|LSJM>$ bases of the $4f^N$ and $4f^{N-1}5d$ configurations respectively, a_{JM} and b_{JM} are corresponding coefficients. Except in the $4f^N$ and $4f^{N-1}5d$ overlapped regions (see Fig. 1), configuration mixing does not induce significant energy level shifts. But it dramatically enhances the transition probabilities. With the mixed eigenfunctions, electric dipole transitions are no longer forbidden. In the systems of strong odd crystal field components or transitions in high energy region not far from the $4f^{N-1}5d$ states, Judd-Ofelt theory may not be sufficient. No quantitative analysis of transition probability has been reported for upconversion luminescence. Wang et al. demonstrated that in $LaCl_3$ with C_{3h} symmetry crystal-field induces strong mixing the $5f^3$ and $5f^2 6d$ states of U^{3+}, and Judd-Ofelt theory failed to predict transitions intensities.[42] In this case, transition intensities can be calculated directly with the 4f-5d mixed wave functions. Other systems in which Judd-Ofelt theory failed in predicting transition intensities include Er^{3+} in $YAlO_3$ at C_s site symmetry.[46] Because the coefficient b_{JM} depends on the energy gap between the $4f^N$ and $4f^{N-1}5d$, it has a larger value for the upper $4f^N$ states closer to the $4f^{N-1}5d$ states. Therefore, upconversion transitions in the higher energy region are expected to have higher probabilities than that between the low-lying states. To be discussed in the following section, because of increased 4f-5d mixing, vibronic coupling increases in the upper $4f^N$ states as well.

To develop high efficient up-converting green-blue phosphors that utilize the unique energy level schemes of rare earth ions, symmetry breaking in hosting materials is an effective method, particularly for nanophosphors.[25] First of all, doping of rare earth ions into a crystalline lattice induce lattice distortion, thus may breakdown more or less the intrinsic site symmetry. Chen and co-workers [47] have shown that by doping Eu^{3+} into α-$NaYF_4$ and β-$NaYF_4$ crystals, the original crystallographic site symmetries of O_h in the α-phase and C_{3h} in the β-phase are locally distorted into Cs, even though, the crystalline structure of the doped crystals is not altered significantly. As a result, the Eu^{3+} energy level splittings are no longer consistent with O_h and C_{3h}, respectively, in the α-phase and β-phase of $NaYF_4$ crystals.

From the materials synthesis and application point of view, use of the cubic phase of $NaYF_4$ obviates the need to undertake a high temperature transformation to the naturally more efficient hexagonal phase. Enhancement of IR-to-visible upconversion in α-NaYF4 nanocrystals via structure modification is of particular importance. Sudheendra et al recently reported the enhanced upconversion emission from α-$NaYF_4$:Yb:Er/Tm nanophosphors induced by a core-shell structure modification. A layer of gold atoms were coated on the spherical α-$NaYF_4$ nanoparticles doped with Yb/Er or Yb/Tm. It was confirmed that the enhancement was achieved by modulations in the local crystal field created by the plasmonic gold atoms.[48] The plasmonic electric fields modify the crystal field around the sensitizer and activator ions, thus change their energy levels and transition probabilities to facilitate upconversion transitions through energy transfer and excited state absorption. Reported by Q. Luu et al,[49] when modulation of the local radiation field is invoked, the plasmonic effect may also enhance the radiative process of a phosphor. Similarly, several groups have reported that nanoparticles of α-$NaYF_4$ codoped with Yb-Er or Yb-Tm can produce efficient upconversion luminescence.[50, 51] Several mechanisms, including surface modification and doping-induced site distortion, would reduce the actual site symmetry from O_h down to C_s. A recent study reported by Park et al. demonstrated that coating the nanocrystals (~ 28 nm) of $NaYF_4$:Yb-Er by a layer of $NaGdF_4$ to form core-shell structures can improve upconversion efficiency of the nanocrystals in both cubic and hexagonal structures.[52] But the hexagonal-phase core/shell nanocrystals still exhibited much stronger upconversion luminescence among various coated and un-coated structures. It is understood because the coated shell improves the upconversion in the surface layer by reducing defects and modifying local structure. The site symmetry of ions in the core is not affected.

Lowing site symmetry can be achieved also by replacing a portion of ions in the host with others in the same oxidation state but slightly different ionic size. Not only the local site symmetry, but also phase transition may be induced with a higher concentration of host-ion substitution. Liu and co-workers investigated a $NaYF_4$:Er-Yb system in which host ion substitution influences the nanocrystal growth process to give simultaneous control over the crystallographic phase, size and optical emission properties of the resulting nanocrystals.[53] It was demonstrated that $NaYF_4$ nanocrystals can be rationally tuned in size (down to ten nanometres), phase (cubic or hexagonal) and upconversion emission color (green to blue) and intensity by replacing Y^{3+} with Gd^{3+}. As shown in Fig.

2 with data from Ref-51, the maxima integrated intensity of Er^{3+} upconversion was achieved with $NaYF_4$:Gd/Yb/Er (15/18/2 mol%) in which the crystalline structure is significantly disordered. The Gd-Y substitution in the cubic phase of $NaYF_4$ clearly enhance upconversion efficiency by more than two times. However, in the nanocrystals maintained in hexagonal structure, the upconversion luminescence intensity drops with increase of the Gd doping. Severe lattice distortion, defect development and the electronic influence of Gd^{3+} ions together are likely responsible for the decrease in upconversion efficiency.

There are a number of other interesting observations of structure dependence of upconversion in nanophosphors. For instance, Patra et al. observed that the upconversion luminescence intensity depends on the crystal structure and particle size of ZrO_2 nanocrystals.[54] A significant enhancement of luminance of Er^{3+} in monoclinic phase was observed in comparison with the tetragonal phase. In consistent with above analysis in symmetry dependence, they ascribed this enhancement to the lower symmetry of the Er^{3+} site in the monoclinic phase in which the optical transition probabilities increase. Comparison of the upconversion spectra of Er:Lu_2O_3 and Er:Y_2O_3 nanocrystals showed that the upconversion intensity of Er:Lu_2O_3 nanocrystals was approximately 100 times greater than that of Er:Y_2O_3 although Er^{3+} ions in both hosts have very similar energy level structure.[55] In addition, very different from Er:Y_2O_3, noticeable blue upconversion occurs in Er:Lu_2O_3 nanocrystals. Vetrone et al. attributed the enhanced upconversion in Er:Lu_2O_3 to a mechanism that induces mixing of the 4f and 5d orbitals of the Er^{3+} ions via lattice valence-band levels. Based on our symmetry analysis, mixing of 4f and 5d is allowed in the monoclinic structure of Lu_2O_3 but absent in the cubic or tetragonal Y_2O_3 lattice.

Because the $4f^{N-1}5d$ energy levels are close or overlap with that of the $4f^N$, coupling between $4f^N$ and $4f^{N-1}5d$ is the strongest in configuration interactions if the odd crystal-field components are not vanished. In phosphors activated by trivalent rare earth ions, other excited configurations such as $4f^{N-1}6s$ and $4f^{N-1}6p$ may also perturb the $4f^N$ energy levels. Because of large energy gaps, their influence is less significant and already taken into account in the Judd-Ofelt theory by $\Omega_{2,4,6}$ parameters.[11, 15, 17] Beside the on-site configuration hybridization between the lanthanide $4f^N$ and other unoccupied configurations, interaction of the $4f^N$ states with charge transfer configurations involving ligand electron orbitals is also an important mechanism to modify the energy levels and transition intensities of the activators in upconversion materials.[21] Because charge-transfer transitions of rare earths in complexes involve ligand electrons that participate in chemical bonding, the energy levels of charge-transfer states are more sensitive to environments and particle size than that of the 4f and 5d states. The intensity and energy of charge-transfer transitions vary in nanocrystals as a function of particle size. This subject was discussed by Tanner and others. [56]

Faucher and Tanner studied the interaction of Er^{3+} with a charge transfer configuration in the elpasolite compound Cs_2NaErC_6 by theoretical modeling of the electronic energy levels of Er^{3+}.[57] The configuration interaction they studied was one in which the $4f^{11}$ configuration is perturbed by a $4f^{12}3p5$ configuration where a chloride 3p electron is promoted into the 4f orbital. The perturbing configuration was actually a charge transfer configuration with respect to the ground configuration $4f^{11}3p^6$. This is similar to the processes described by Thorne *et al.*[58] and discussed previously by Newman *et al.* [59]as spin-polarized covalence. In addition to B^4_0(4f4f) B^6_0(4f4f) for splitting the energy levels of the $4f^{11}$ states, one crystal field parameter B^4_0(4f5p) was introduced to evaluate the contribution of the $4f^{11}$ and $4f^{12}3p^5$ coupling. In comparison with experimental results, inclusion of the configuration coupling can reduce the fitting deviation from 21.4 cm^{-1} to 10.5 cm^{-1}. Similar effects were considered for Cs_2NaPrC_6 and Cs_2NaTmC_6.[60] In oxide compounds, charge transfer involving the oxygen 2p orbitals would have a stronger influence on the 4f energy levels and transition probabilities. Charge transfer transitions in fluoride crystals have higher energies, thus less influence on $4f^N$-$4f^N$ transitions.

2.3 Line broadening and vibronic side bands

One of the direct consequences of ion–phonon interactions is to broaden the line width of electronic transitions. For weak ion-phonon interactions, temperature-dependent phonon coupling impose homogeneous line broadening, with respect to the inhomogeneous broadening induced by structure defects and strains that shift non-uniformly the static electronic energy levels.[20] Along with line broadening, the lattice dynamics involving electron-phonon interactions leads to temperature-dependent line shift. The contributions to homogeneous line broadening and shift primarily come from direct one-phonon and multiphonon processes including Raman phonon scattering. Theoretically, the temperature-dependent line width Γ and line shifts δE associated with the two levels involved in an electronic transition can be respectively expressed by the McCumber-Sturge equations: [61]

$$\Gamma(cm^{-1}) = \Gamma_0 + \bar{\alpha}\left(\frac{T}{T_D}\right)^7 \int_0^{T_D/T} \frac{x^6 e^x}{(e^x-1)^2}dx \tag{8}$$

and

$$\delta E(cm^{-1}) = \alpha\left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} \frac{x^3}{e^x-1}dx \tag{9}$$

where the residual width Γ_0 is temperature independent and arisen from inhomogeneous line broadening; $\bar{\alpha}$ and α are coupling coefficients for the electron-phonon interactions; and $T_D = h\nu_D/k$ is the effective Debye temperature of the phonon distribution with ν_D being the Debye cut-off frequency of the crystal lattice. $\bar{\alpha}$, α and T_D are treated as adjustable parameters to get the best fit to the experimental data. Eqs (8) and (9) are derived based on the Debye approximation on continuous phonon density of states (PDOS). We will discuss later this approximation is not valid for nanocrystals with radius less than 20 nm in which PDOS becomes discrete and low frequencies are cut off. [62, 63]

The temperature dependent line broadening and shift expressed in Eqs. (8) and (9) are often applied to spectra of rare earth ions in crystals where ion-phonon interactions are weak and vibronic side bands are much weaker than the zero-phonon lines. They are not sufficient for 3d spectra and the 4f-5d transitions in rare earth phosphors such as YAG:Ce^{3+} in which vibronic bands are strong and dominant.[64] They are not sufficient also for some 4f-ion activated upconversion phosphors where vibronic side bands appear along with the zero-phonon lines. The problem arises in part from the selective vibronic coupling in electronic transitions. The local modes, particularly those involved with vibrations of the 4f ions may have much stronger coupling strength than for the lattice phonon modes, thus well-defined side bands appear in the absorption and emission spectra of trivalent rare earth ions in crystals with a line width comparable to that of the zero-phonon lines. [65]

Because of weak electron-phonon interactions, intra $4f^N$ electronic transitions usually do not exhibit strong vibronic side bands. However, due to the increase of configuration interaction and coupling to charge transfer states, electronic transitions involving the upper $4f^N$ states may have stronger vibronic side bands. Vibronic transitions have profound influence on upconversion. In two ways they can improve upconversion efficiency. First, vibronic transitions increase absorption cross section, and secondly, they expand band width which is needed to compensate the energy mismatches. A drawback is that vibronic coupling boosts non-radiative relaxation, therefore, the excited state lifetimes become shorter. The characteristics of vibronic transitions of ions in crystals are understood based on the Franck-Condon principle and Huang-Rhys model of vibronic interactions, which assume that the vibration frequencies and electric dipole moment for electronic transition are invariant.[66, 67] Proven effective for predicting the intensities of vibronic bands with multi-phonon progressing, the Huang-Rhys model applies to a single vibration mode with a constant frequency independent on electronic states. For an electronic transition between two states separated by an energy gap E_0 and coupled to a vibrational mode with frequency ν, the intensity function for the *0-n* phonon line is of the flowing form [68]

$$f_n(E) = \exp(-S)\frac{S^n}{n!}\frac{1}{\sqrt{2\pi n\sigma^2}}\exp\left[-\frac{[E-(E_0+nh\nu)]^2}{2n\sigma^2}\right]. \qquad (11)$$

Eq. (11) defines the intensity and line shape of vibronic transitions that progress harmonically in multi-phonon energy of $nh\nu$ with n = 0, 1, 2 .... The line width of the harmonic progressing bands is proportional to the square root of n^{th} harmonics ($\sqrt{n}\sigma$). Eq. (11) becomes a delta function for the line shape of the zero-phonon (n=0) transition, therefore, a line width for the zero-phone line needs to be added when comparing with experimental results. The line width of the zero-phonon transition accounts for the electronic dispersion and inhomogeneous broadening induced by lattice defects.[69] In Eq.

(11) S is known as Huang-Rhys parameter, that defines the vibronic coupling strength and measures the lattice displacement induced by the electronic transition.[67]

In reality, one has to deal with vibronic coupling that involves multiple electronic energy levels and multiple vibrational modes. Under the restrictions of linear coupling between different vibrational modes and superposition of multiple electronic transitions, the overall absorption intensity as a function of electronic energy (E_k) and vibrational frequency (ν_j) can be expressed as [64]

$$I(E)=\sum_k I_0(k)\sum_{n_j}\left(\prod_j \frac{e^{-S_j}S_j^{n_j}}{n_j!}\right)\left(\frac{E_k+\sum_j n_j h\nu_j}{E_k}\right)\frac{1}{\sqrt{2\pi\left(\sigma_k^2+\sum_j n_j\sigma_j^2\right)}}\exp\left(\frac{-\left(E+E_k+\sum_j n_j h\nu_j\right)^2}{2\left(\sigma_k^2+\sum_j n_j\sigma_j^2\right)}\right) \qquad (12)$$

where the summation over k and j takes account of, respectively, the electronic energy levels and vibrational modes. For example, applying Eq. (12) to a single electronic transition coupled to two vibration mode with frequencies 150 cm^{-1} and 210 cm^{-1}, and assuming s=0.8 and σ=10 cm^{-1} for both modes, we see in Fig. 3 the frequency mixing and multi-phonon progressions in absorption. A low-temperature approximation, $h\nu > kT$, is assumed for deriving Eq. (11). At high temperatures, or $kT > h\nu$, which is true for rare earth ions in most inorganic crystals at room temperature, the vibronic structure may disappear because of line broadening and overlapping. The profile of multi-phonon transitions as a function of temperature T and frequency ν can be approximately expressed by replacing

$$\exp(-S)\frac{S^n}{n!}$$

with

$$\left(\frac{h\nu}{4\pi SkT}\right)^{1/2}\exp\left[-\frac{h\nu(n-S)^2}{4SkT}\right]$$

in Eqs. (11) and (12). Effectively, $h\nu(n\text{-}S)^2/4S$ is the activation energy in the potential surface of ion-lattice vibronic interaction. [66]

For Er^{3+} and Ho^{3+} in fluoride crystals, Auzel demonstrated that multiphonon Stokes and anti-Stokes sidebands stretch above 1000 cm^{-1}.[70] A small value of the Huang-Rhys parameter *S* =0.04 was determined. In other systems, much stronger phonon sidebands were observed. Zhou et al. observed in the absorption and emission spectra of Cs_2NaErF_6, each transition between crystal field levels comprises extensive, well-resolved vibronic side bands. The vibronic side bands are as strong as the zero-phonon lines.[65] As shown in Fig. 4, in the $^4I_{15/2}$-$^2H_{11/2}$ absorption spectrum between 19200 cm^{-1} and 19900 cm^{-1}, there are more than 30 vibronic side bands spread over 400 cm^{-1} and having intensities comparable or stronger than the zero-phonon lines. Comparing the experimental spectra with the model calculation shown in Fig. 3, harmonic multi-phonon progressions are anticipated in the spectra of Cs_2NaErF_6. It is evident that in the spectra shown in Fig. 4, the relative intensities of vibronic transitions increase with energy. Whereas the ground state absorption into the low-lying excited state of $^4I_{13}$ near 6500 cm^{-1} barely exhibits vinronic side bands, strong vibronic side bands dominate the $^4I_{15/2}$-$^2H_{11/2}$ absorption spectrum in the 20000 cm^{-1} region. This trend indicates that the upper excited states are more strongly coupled to lattice vibrations, which is a consequence of increased configurational interaction as we discussed in the previous section. Therefore, multiphoton upconversion of Er^{3+} in fluoride crystals takes a significant contribution from vibronic transitions. In nanocrystals, the vibration frequencies in the surface layer may differ from that in the core. Moreover, the coupling strength characterized by *S* is expected to change as well. In combination, vibronic coupling to electronic transitions in nanocrystals would lead to more complicated upconcversion dynamics.

2.4 **The correlation between nanocrystal size and upconversion luminescence color and decay time**

The upconversion emission color of rare earth doped nanocrystals can be modified by changing the size of the nanocrystals.[6, 24, 51] Because the shifts of the energy levels involved in giving rise to the emission bands are insignificant with respect to the transition energies, it is by no means that the size-reduction induced color changes are due to spectral shifts. In most cases, the change of color means that the relative intensities of the red, green and blue upconversion emission bands of Er^{3+} changes as a function of host particle size in combination with changes in doping concentration, pumping power and temperature. The dependence of upconversion luminescence on concentration, pumping power and temperature is understood based on the excited state dynamics in terms of non-radiative relaxation and phonon-assisted energy transfer.[7, 8] However, experimentally observed size-dependence of upconversion luminescence colors might involve multiple mechanisms that often cannot be exclusively verified. Accordingly, size-dependence in different materials or same materials synthesized under different conditions may have different effects on upconversion color and intensities. A detailed study of the mechanisms of size-color correlations was conducted by Capobianco and co-workers.[71] It was observed that the red emission of Er^{3+} can be enhanced in 20-nm Y_2O_3:Yb-Er nanoparticles relative to their corresponding bulk materials. For nanophosphors, high-energy vibration modes in the surface layer was attributed to increase the multi-phonon relaxation in the metastable state of $^2H_{11/2}$ from which the green emission is originated. Based on experimental evidence that nanocrystalline lattices can adsorb impurities such as CO_3^{2-} and OH^- on their surface which have vibrational energies of 1500 and 3350 cm^{-1}, respectively, It was assumed that the ground state absorption of 978 nm photons from Yb^{3+} would bring the ion to the $^2F_{5/2}$ state, which in turn would donate its energy to an Er^{3+} ion in close proximity, thereby exciting it to the $^4I_{11/2}$ level. Rapid nonradiative decay from this state would populate the $^4I_{13/2}$ level since the energy gap between $^4I_{11/2}$ and $^4I_{13/2}$ (3600 cm^{-1}) could be more easily bridged by the high-energy phonons from the impurities in nanocrystals than in the bulk samples. Subsequent phonon-assisted energy transfer from another Yb^{3+} ion in the excited state would directly populate the $^4F_{9/2}$ level and result in red enhancement. Following another phonon-assisted energy transfer from an Yb^{3+} ion, the Er^{3+} ion could be further excited into the $^2H_{9/2}$ state. At high Yb^{3+} concentration the $^4F_{9/2} \leftarrow {}^4I_{13/2}$ upconversion mechanism could be very efficient and bypasses the $^4S_{3/2}$ state. As a result, the green-emission band in Y_2O_3:Er^{3+}(1%),Yb^{3+}(10%) nanocrystals becomes very weak compared to the red emission. This mechanism is supported by the power dependence of the upconversion emission from $^4S_{3/2}$ in Y_2O_3:Er^{3+}(1%),Yb^{3+}(10%) nanocrystals which indicates that the $^4S_{3/2}$ state is populated via a three-photon process instead of a two-photon process as observed in systems of low Yb^{3+} concentration. Song and co-workers[72] also examined Y_2O_3:Yb/Er nanoparticles with different sizes (13 – 55 nm) and observed that the relative emission intensities of both the blue and red bands to the green band increase in nanoparticles of Y_2O_3. To be discussed in more detail in Sections 3.3 and 4.2, energy transfer mechanisms, especially cross-relaxation in the intermediate states of Er^{3+} and laser excitation-induced thermal dynamics may dominate the observed effects. It is suggested that two cross-relaxation channels, $^2I_{11/2} + {}^2H_{11/2} \rightarrow {}^4I_{13/2} + {}^4F_{3/2}$ and $^4F_{7/2} + {}^2H_{11/2} \rightarrow {}^2H_{9/2}({}^2G_{9/2}) + {}^4F_{9/2}$ would weaken the green emission from $^2H_{11/2}$ and $^4S_{3/2}$ to the $^4I_{15/2}$ ground state, while the red emission from $^4F_{9/2}$ and blue emission from $^2H_{9/2}$ would increase accordingly. Both energy transfer mechanisms and local thermalization depend on the particle size.[25, 73]

A different size dependence was reported for the upconversion spectra of 50-nm $La_2(MoO_4)_3$:Yb,Er nanocrystals,[74] where a strikingly enhanced green upconverted emission was observed in nanocrystals in comparison with the bulk counterpart. This change in relative intensities was also ascribed to surface effects in nanocrystals, but in an opposite way. The green emission was attributed mainly to the surface Er^{3+} ions while the red emission mainly arises from the internal Er^{3+} ions. The weaker interaction between the surface Er^{3+} ions and their surroundings in nanocrystals results in a longer lifetime of $^4I_{11/2}$ thus in more efficient upconversion.

3. Excited state dynamics and upconversion efficiency

We have mentioned above that the spectroscopic properties of rare earth doped nanophosphors depend on local crystalline structure and vibration modes. A variety of nanophenomena, particularly, lifetime of the excited states of rare earth ions in nanostructures may exhibit strong size-dependence.[75] Energy transfer and phonon relaxation in rare earth activated phosphors are also sensitive to particle size and surrounding environment.[3, 25, 73]

3.1. **Radiative relaxation**

According to Judd-Ofelt theory, the rate of relaxation, *A,* from an initial state *J* to final state *J'* through radiative processes is determined by: [38, 76]

$$A\left(J,J'\right)=\frac{64\pi^2\Delta^3}{3h\left(2J+1\right)}\left(\chi\bar{F}^2+n^3\bar{M}^2\right) \qquad (13)$$

where $\bar{F}^2$ and $\bar{M}^2$ are the matrix elements of the electric dipole and magnetic dipole moments, respectively,[10] $\Delta(\mathrm{cm}^{-1})$ is the energy gap between states *J* and *J'*, $\chi = n(n^2+2)^2/9$ is the Lorentz correction for local field with *n* being the index of refraction of the host material.

The size of nanocrsyatls can significantly modify the radiative lifetime. Differing from bulk properties, spontaneous emission of photons in nanocrystals is influenced by two size-dependent mechanisms: modification of the index of refraction[77, 78] and coherent interferences.[78] The dependence of radiative lifetime on the index of refraction, *n*, arises from the change in the density of states for photons in the medium of reduced light velocity and the modification of the polarizability of the surrounding medium. Since the nanoparticles occupy only a small fraction of the total volume, in order to compare the experimental results with Eq. 13, it is necessary to introduce an effective index of refraction for the nanoparticle-medium system, n_{eff}, to take account of the influence of the media with refractive index n_{med}.

$$n_{eff}\left(x\right)=xn_{NP}+\left(1-x\right)n_{med} \qquad (14)$$

where *x* is the ‘‘filling factor’’ showing how much fraction of space is occupied by the nanoparticles. The use of n_{eff} is valid when the average size of the particles is much smaller than the wavelength of the photons. The radiative lifetime can be tuned by varying the particle size and the refractive index of the medium.

Interference between the radiation field and the lattice electrostatic field along the radius of emitting ions in a spherical nanoparticle results in field oscillation, a coherent effect that leads to resonance in spontaneous decay. One may expect that the presence of nanometer scale material could lead to the scattering of the vacuum field and therefore modification of the spontaneous emission rate. Several theoretical reports have predicted this phenomenon for an atom in the near field of nanoscopic spheroids, sharp tips, and substrates with lateral nanostructures.[79-81] The variation of spontaneous decay rate along the radius of nanoparticles can be measured using a near-field optical spectrometer to detect the luminescence lifetime of emitters embedded in isolated single dielectric nanospheres.[78] By varying the diameter of the spheres from 100 nm to 2 μm and by modifying their dielectric surrounding, Schniepp et al.[78] demonstrated a systematic change in the spontaneous emission rate. The experimental results show inhibition of the spontaneous emission up to three times and are in excellent agreement with the results of analytical calculations. The spontaneous emission rate of ions placed in a dielectric sphere can be substantially reduced across the border from the superwavelength regime of field oscillation to the nanoscopic realm of Raleigh scattering. Strong oscillations may occur near the surfaces of the sphere.[79, 82] Modification of spontaneous emission rate inside a nanoparticle and its surface realm would influence energy transfer between sensitizer and activator, therefore influence upconversion efficiency.

3.2 Non-radiative relaxation

As a result of ion-phonon interaction, the population of an excited electronic state decays via nonradiative transition to states of lower energies. The energy difference between two electronic states is converted into phonon energy. This process of population relaxation is characterized by a relaxation rate that depends on the energy gap between the two electronic states, the frequencies of vibration modes, and temperature.[83, 84] At room temperature, the excited state lifetimes of most emitting states of rare earth ions in solids are dominated by the nonradiative relaxation except in a few cases such as the $^5D_0$ state of Eu^{3+} and $^6P_{7/2}$ state of Gd^{3+} for which the energy gap below these states is much larger than the highest phonon frequency of the lattice vibrations. It is also realized that in the materials that provide efficient upconversion, radiative relaxation in the emitting states becomes dominate.

With the assumption that the phonons involved are of equal energy, a commonly used expression for the temperature-dependent multiphonon relaxation rate is [84]

$$W(T) = W(0)\left[\frac{\exp(h\nu_m / kT)}{\exp(h\nu_m / kT) - 1}\right]^{\frac{\Delta E}{h\nu_m}}, \qquad (15)$$

Where $h\nu_m$ is the maximum phonon energy of the lattice vibrations that couples to the electronic transition of the rare earth ion, ΔE is the energy gap between the populated state and the next low-lying state, and $W(0)$ is the spontaneous transition rate at T=0 when the phonon modes are all initially in their ground state. At low temperatures where $h\nu_m >> kT$, the nonradiative relaxation rate is dominated by $W(0)$, which can be expressed as a simple exponential function depending on the energy gap, ΔE:

$$W(0) = C\exp(-\alpha\Delta E / h\nu_m), \qquad (16)$$

where C and α are empirical parameters which are characteristic of the particular crystal. Known as the energy-gap law, this exponential dependence has been used to describe the energy-gap dependence of multiphonon transitions rates for the 4*f* states.[84, 85]

3.3 Energy transfer in upconversion

Energy transfer plays an essential role in photon upconversion in both sensitizer-activator and single-ion systems. As a result of ion-ion interactions, electronic excitation of ions migrates in insulating host materials through resonant energy transfer and phonon-assisted energy transfer processes.[83, 86, 87] The latter is more important because of energy mismatch between the donor and acceptor. The excitation energy differs not only between ions in different electronic states, but also for ions in the same state because of defect-induced inhomogeneous broadening. In nanocrystals or glassy matrices, inhomogeneous line broadening may reach a scale comparable crystal field splitting. Phonon assistance is required to make up the energy mismatches for specific upconversion transitions. On the other hand, phonon-assisted energy transfer enhances non-radiative relaxation and may quench upconversion luminescence.

In phonon assisted upconversion excitation, energy mismatches in electronic energy levels are made up by vibration energies of local and lattice modes. The variations in electronic energy levels due to inhomogeneous broadening are generally more significant in nanostructures than that in bulk crystals. As we will discuss in the following section, the density of phonon states becomes discrete and low frequency phonon modes are absent below a cutoff energy. Because of the restrictions on vibration modes in nanocrystals, one expects that both luminescence lifetime and the efficiency of energy transfer will be modified when compared with bulk crystals.[73]

Based on the classical Dexter-Forster model of inter-ionic interaction induced energy transfer, the excitation population of a sensitizer P_s, and an activator, P_a, can be expressed as:[83, 88-90]

$$\frac{dP_s}{dt} = -\kappa_s P_s - \sum_a W_{sa} P_s$$

$$\frac{dP_a}{dt} = -\kappa_a P_a + \sum_s W_{sa} P_s \tag{17}$$

The first term in each equation is due to spontaneous radiative relaxation and nonradiative phonon relaxation. The second term is due to energy transfer induced by ion-ion interactions with a rate of W_{sa} which includes resonant and phonon-assisted contributions

$$W_{sa} = W_{sa}^{R} + W_{sa}^{PA}. \tag{18}$$

In resonant cases, the Dexter-Forster model defines the energy transfer rate as

$$W_{sa}^{\mathrm{R}} = \alpha \left(\frac{R_0}{R_{sa}} \right)^s \tag{19}$$

where the exponent s = 6, 8, 10, for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions respectively. R_{sa} is the distance between sensitizer and activator, and R_0 is the critical transfer distance for which energy transfer and spontaneous deactivation of the sensitizer have equal probability. For phonon-assisted energy transfer [91]

$$W_{sa}^{PA}=\beta\nu\rho(\nu)\left(\frac{R_0}{R_{sa}}\right)^{s-2}\begin{Bmatrix}n(\nu)+1\\ n(\nu)\end{Bmatrix}\qquad(20)$$

where $n(\nu)+1$ and $n(\nu)$ are for phonon emission and absorption respectively, and ρ is the PDOS, and ν is the phonon frequency. The occupation number of the phonon states is given by

$$n(\nu)=\left[e^{h\nu/kT}-1\right]^{-1}.\qquad(21)$$

If the energy transfer from sensitizers to activators is irreversible, the sensitizers' population decay in the excited state can be expressed as

$$N_s(t)=N_0\exp(-\kappa_0 t)\left\langle\exp\left(-\sum_a W_{sa}t\right)\right\rangle_s\qquad(22)$$

where $\langle\cdot\cdot\rangle_s$ denotes an ensemble average over the lattice. It is clear from Eq. (20) that a modification of the PDOS in nanocrystals influences the efficiency of energy transfer. Because the energy transfer rate depends also on the distance between the donor and aceptor, the transfer in very small nanocrystals is restricted. This restriction may be understood based on the fact that the hopping length and the transfer probability are restricted for a donor to find a matching acceptor in the neighborhood of the nanoparticle.

Because of energy transfer, luminescence decay becomes non-exponential. An analytical solution of Eq. (22) is generally not available for ions doped into nanocrystals. A Monte Carlo method of simulation may be used in modeling spectral migration of optical centers in inhomogeneously broadened systems.[73] Phonon-assisted energy transfer processes may strongly influence the dynamics of luminescence centers in nanocrystals. Assuming energy transfer occurs only from sensitizers to activators without back transfer, and considering the number of activators situated at random in a sphere around a sensitizer such that the activator concentration is constant when the volume of the sphere and the number of activator ions considered goes to infinity, known as Inokuti-Hirayama model,[92] Eq. (22) can be averaged by an integration to obtain the following relation for the decay of the population in the excited state the sensitizers:[90]

$$N_s(t) = N(0)\exp\left[-\kappa_0 t - \frac{4\pi c_a R_0^3 W_0^{3/s}\Gamma(1-3/s)}{3s} t\right]$$

(23)

where κ_0 is the decay constant of the sensitizer in the absence of activators; c_a is the activator concentration, R_0 is the nearest sensitizer-activator distance, W_0 is the energy transfer rate between the nearest sensitizer and activator. Eq. (23) can also be applied to doped phosphors in which sensitizer and activator are the same rare earth ions.

3.4 Surface defects

Phonon-assisted energy transfer and non-radiative relaxation are important in either upconversion or downconversion. Conventionally, analysis of the dynamics of stepwise excitation and relaxation in the excited takes an empirical approach by using rate equations similar to Eq. (17) for specific electronic states and transitions.[2, 8] Because of multi-step direct and energy-transfer excitations, the population (or excitation probability) in the upper emitting state becomes a nonlinear differential function of multiple variables involving the dynamics of the intermediate states. Except numerical calculations, an analytical solution without approximations is practically not available.[93] A large number of experimental observations can only be qualitatively interpreted. It is widely observed that luminescence decays and upconversion efficiency are size dependent. Complexity adds to the upconversion luminescence in nanophopshors. Understanding established for bulk materials does not apply to nanophosphors. In nanophosphors, two additional mechanisms become important. One is the modification the PDOS which will be discussed in the following section. Another is the disordering in the surface layer in which electronic and structural properties differ from that in the core. A simple approach to interpret size effects is to separate the transition and relaxation rates of all upconversion steps into surface and core contributions.

In order to improve upconversion performance, experimental efforts have been devoted to reduce surface quenching. Taking the $NaYF_4$:Yb-Er series as an example, surface modification has been made in numerous studies by coating nanoparticles to form a core-shell structure.[48, 94] Progresses have been made also in understanding how the nanocrystal size affects the intensities of upconversion luminescence. Zhao et al investigated upconversion luminescence of Yb-Er-doped $NaYF_4$ nanocrystals in a broad range of sizes from 6 nm to 45 nm in both cubic and hexagonal phases.[22] As shown in Fig 5, they observed an increasing red-to-green luminescence intensity ratio and reduced luminescence lifetimes with decreasing size. By analyzing the upconversion process with a set of rate equations, they obtained asymptotic analytic solutions to explain lower decay rates of red compared to green upconversion luminescence. Furthermore, they quantified the effect of the surface on luminescence lifetime in a model where nanocrystal emitters are divided between the near-surface and inside regions of each nanocrystal. The excitation probability into an excited state can be separated into surface term $W_{i,s}$ and core term $W_{i,c}$. The observed luminescence decay in a core-shell nanocrystal with radius R and shell thickness d ($<R$) is given by a weighted average of $W_{i,s}$ and $W_{i,c}$. The weights can be determined by the respective fractions of the near surface/core volume. Hence the observed rate becomes a function of the nanocrystal's radius R and shell size d, as follows:[22]

$$W_i(R,d) = W_{i,s}\left[1-\frac{(R-d)^3}{R^3}\right] + W_{i,c}\frac{(R-d)^3}{R^3} \qquad (24)$$

where $W_{i,s}$ and $W_{i,c}$ can be evaluated from the observed value of $W_i(R, d)$ and the structure parameters R and d. Also shown in Fig 5, the decay times of the red and green luminescence decreases along with size decrease. The measured decay times of the red and green upconversion agree with Eq. (24). It was shown that the defect density dominates decay rates for small (below 15 nm) nanocrystals. The results indicate that a defect-reduction strategy is a key step in producing small upconversion nanocrystals with increased brightness for a variety of bioimaging and biosensing applications.

4 Size dependence and confinement on electron-phonon coupling

Although no quantum confinement should influence the electronic energy level structure of rare earths in nanoparticles because of the localized 4f electronic states, the optical spectrum and luminescence dynamics of a doped ion in nanoparticles can be significantly modified through electron-phonon interaction. Confinement on electron-phonon interactions is primarily due to the effect that the PDOS in a nanocrystal is discrete and the low-energy acoustic phonon modes are cut off. As a consequence of the PDOS modification, upconversion in nanoparticles, particularly, phonon-assisted energy transfer and the nonradiative relaxation of ions from the electronically excited states may differ from that in bulk materials. Given that phonon-assisted energy transfer and populating of the intermediate states via multi-phonon relaxation are important in photon upconversion and downconversion, confined electron-phonon interactions can enhance or diminish upconversion efficiency.

4.1 Modification of phonon density of states

For small dielectric nanocrystals, Debye approximation is no longer valid and discrete PDOS must be considered. The vibrational modes of a finite sphere were analyzed previously by Lamb [95] and Tamura [96]. Boundary conditions and nanoscale radius yield discrete spheroidal modes and torsional modes determined by the following eigenvalue equations:

$$\begin{aligned}&2\{\eta^2+(l-1)(l+2)[\eta\frac{j_{l+1}(\eta)}{j_l(\eta)}-(l+1)]\}\xi\frac{j_{l+1}(\xi)}{j_l(\xi)}-\frac{1}{2}\eta^4+\\&[\eta^2-2l(l-1)(l+2)]\eta\frac{j_{l+1}(\eta)}{j_l(\eta)}+(l-1)(2l+1)\eta^2=0\end{aligned}, \qquad (24)$$

$$\frac{d}{d\eta}\frac{j_l(\eta)}{\eta}=0, \qquad (25)$$

where for the reduced frequencies of the spheroidal modes and torsional modes, $\xi=\omega R/v_l$ and $\eta=\omega R/v_t$, with $\omega=2\pi\nu$ being the phonon angular frequency and R the radius of nanoparticles; j_l is the l^{th} order spherical Bessel function; v_l and v_t are the sound velocities of longitudinal and transverse modes respectively. The phonon modes are significantly reduced with size reduction to nanometer scale. Fig. 6 (a) shows the calculated PDOS of Y_2O_2S nanocrystals with a radius 20 nm[73]. There is a cutoff frequency (ν_{min}) in the low frequency side of the phonon spectrum below which all phonon modes are intrinsically eliminated. As a result, the luminescence dynamics, especially the phonon-assisted energy transfer processes in nanocrystals is expected to be different from that in their bulk counterparts.

As a result of confinement on PDOS, the nonradiative relaxation of ions from the electronically excited states is expected to behave differently from that in bulk materials. Liu et al. observed anomalous thermalization phenomena in Er^{3+}-doped Y_2O_2S nanocrystals of approximately 20-nm diameter at low temperatures.[97] Anomalous thermalization was observed in upconversion excitation spectrum in which "hot" bands appear at liquid helium temperature. Fig. 6(b) shows the low-temperature excitation spectra of Er^{3+} in bulk crystals and nanocrystals, which were obtained by using a 5-ns pulse laser and monitoring the Er^{3+} luminescence from the $^4S_{3/2}$ state at 18248 cm^{-1}. Hot bands originating from the upper Stark levels of $^4I_{15/2}$ with an energy gap up to 224 cm^{-1} are observed in the excitation spectrum at 2.6 K,. The unusual thermalization phenomena take place not only in the $^4I_{15/2}\rightarrow{}^4F_{7/2}$ excitation spectrum but also in the emission spectrum from $^4S_{3/2}$ at low temperature.

To gain a theoretical understanding of the anomalous thermalization in $Er^{3+}:Y_2O_2S$ nanocrystals, temperature- and power-dependences of the luminescence intensity in excitation spectra were studied. Integrated intensities of excitation spectra between 20288 and 20334 cm^{-1} (a hot band) as a function of temperature (from 2.2 to 66 K) are shown in Fig. 6(c). In the nanocrystals, the hot bands saturate at liquid helium temperature decreases rapidly to zero as temperature increases from 6 to 8 K, and then increases with temperature as predicted by Boltzmann thermalization behavior. Such a phenomenon is absent in the bulk crystals.

A possible thermalization mechanism was proposed in a simple model based on the rate-equation approach was established to interpret the above phenomena.[63] The equilibrium population in the upper levels of the $^4I_{15/2}$ ground state results from the competition between the laser-induced thermalization through nonradiative relaxation in the excited states (populating) and two-phonon Raman process (depopulating). The calculated result, shown by the solid line in Fig. 6(c) is in agreement with the observations. The anomalous thermalization due to absence of low-frequency phonon modes in nanocrystals should be a general effect in rare earth doped phosphors. Observation of this effect depends on the energy level structure of the luminescent centers along with the crystal size and sample temperature. According to the temperature-dependent multiphonon relaxation rate and the relationship between the cutoff frequency and crystal size, anomalous hot bands from the excited states with higher energies will occur in crystals with a smaller size. The anomalous thermalization that observed by Tissue and co-workers [98, 99] in Eu_2O_3 nanocrystals is similar to that observed in Er^{3+}:Y_2O_2S. In the Eu_2O_3 nanocrystals, intensive hot bands observed in the excitation spectrum at 12 K are due to excitation of Eu^{3+} from three crystal field levels of the $^7F_1$ excited state. Because these excited states are at 300 cm^{-1} higher above the ground state $^7F_0$, diminishing multi-phonon relaxation requires that the crystals have much smaller crystal size so that phonon modes up to 150 cm^{-1} are eliminated or reduced. In Tissue's observation, the hot bands from the $^7F_1$ state are very strong in the 4-6 nm nanocrystals, but become almost not observable in the 12-nm nanocrystals. These results are consistent with the interpretation for the Er^{3+}:Y_2O_2S system.

4.2 Confined energy transfer in nanophosphors

Inter-atomic energy transfer leads to energy upconversion as well as non-radiative relaxation. It is important especially in the co-doped systems in which sensitizer-activator energy transfer is the primary channel of upconversion excitation. On the other hand, energy transfer between the activators would reduce upconversion efficiency. In bulk solids, excitation migrates a long distance either between sensitizer and activator or among sensitizers (activators). Trapping and concentration quenching are the primary mechanisms that prevent efficient excitation of the activators to perform upconversion. Trapping is due to the presence of defect sits or impurities that absorb the excitation energy from the excited ions and followed by non-radiative relaxation or emission of a photon in a lower energy. Concentration quenching includes cross-relaxation and energy transfer between two excited ions, known as exciton annihilation, which is in fact an energy upconversion process. However, this type of process may end with no contribution to the desired upconversion luminescence, because in many cases no upper state that matches the energy summation except cross-relaxation to populate a lower energy states.

Cross-relaxation is a strong relaxation mechanism in Er^{3+}- and Tm^{3+}-doped upconversion phosphors.[7, 100] A common strategy to optimize upconversion luminescence is to control the doping concentration of rare earth ions.[51, 101] However, the phenomenon of concentration quenching of the excited state at high doping levels imposes a significant constraint to the design of upconversion nanomaterials. Thus, the rare earth ions have to be kept at relatively low concentrations to minimize luminescence quenching. In Er-Yb co-doped crystalline upconvcersion phosphors, the optimal concentration is typically 2% for Er^{3+} and 20% for Yb^{3+}.[71, 102, 103]

In nanocrystals, energy transfer for upconversion may significantly differ from that in bulk crystals. The Inokuti and Hirayama model established for bulk materials, especially Eq. (23) does not apply to size-confined nanocrystals in which energy transfer is confined inside the nanocrsyal. Relative to bulk crystals, there are two factors that influence energy transfer in nanocrystals: reduce of both PDOS and the number of acceptors. This means that the probability of sensitizer-to-activator transfer decreases. In the stepwise excitation that requires phonons for energy matches, the upconversion efficiency will drop as well in the nanophosphors. Using the Dexter-Forster model energy transfer rate and the discrete PDOS, Chen et al.[73] performed Monte Carlo simulation of energy transfer and luminescence decay of Er^{3+} in both bulk and nanocrystals of Y_2O_2S. The Monte Carlo simulation was conducted for the decay of the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition in Er^{3+}:Y_2O_2S nanocrystals, and compared with the experimental results obtained by monitoring the fluorescence to an upper level of the $^4I_{15/2}$ ground state at 18044 cm^{-1}. By taking into account contributions from both resonant and phonon-assisted energy transfer processes, the simulated results agree with the experimental results showing that fluorescence decay from the lower level of the $^4S_{3/2}$ state in the 20-nm Er^{3+}:Y_2O_2S nanocrystals increases with the Er^{3+} doping concentrations. In Fig. 7, the calculated Er^{3+} luminescence decays at various doping concentrations are compared with experimental results. The rate (efficiency) of phonon-assisted energy transfer drops as the nanoparticle size reduces. Resulted from the Monte Carlo simulations, the efficiency decreases rapidly from 30 nm to 2 nm as shown in Fig. 8. The energy transfer rate for 10-nm nanocrystals is about 86% of that for the bulk counterparts. The rate of resonant energy transfer also reduces in nanoparticles with radius less than 20 nm. Combination of resonant and phonon-assisted energy transfer rates explains the experimental observation that the upconversion efficiency of the 10-20 nm nanophosphors is typically about 20% of the bulk samples. This effect is understood based on the size confinement on resonant and phonon-assisted energy transfer.

Recently reported by Wang et al., in Er-Yb codoped nanocrystals size-confined energy transfer can significantly enhance upconversion efficiency when energy transfer between Yb^{3+} ions is confined.[3] This confinement cuts off excitation quenching via long distance migration, the concentration of sensitizers in the nanocrystal can be increased to boost upconvertion efficiency. Based on this concept, Wang et al. has demonstrated a novel class of upconversion nanocrystals adopting an orthorhombic crystallographic system in which the rare earth ions are distributed in arrays of tetrad clusters. An unique arrangement of rare earth clusters enables preservation of excitation energy within the sublattice domain and effectively minimizes the migration of excitation energy to defects. Upconversion luminescence increases in $KYb_{2-x}Lu_xF_7$:2%Er^{3+} with increase of the Yb concentration up to formation of a stoichiometric compound of KYb_2F_7:2%Er^{3+}. This allows creation of an unusual four-photon promoted violet upconversion emission from Er^{3+} with intensity more than eight times higher than those previously reported. Fig. 9 shows the experimental results and the mechanisms of confined energy transfer in $KYb_{2-x}Lu_xF_7$:2%Er^{3+} nanocrystals.

Using the Dexter-Forster energy transfer model and assuming dipole interaction between Yb^{3+} ions, Wang et al.[3] performed Mont Carlo simulations of excitation migration of Yb^{3+} in the clustered KYb_2F_7 structure in comparison with a simple cubic structure. Because of the distance between Yb^{3+} in a cluster is smaller than that between clusters, the excitation holds well in the cluster in which an Yb^{3+} was initially excited, while the excitation spreads rapidly in the cubic structure. This work suggests a new paradigm for tuning upconversion through confined excitation energy transfer in subunit-cells of crystalline phosphors.

By using rate equations of multi-steps energy transfer, Quintanilla et al. [104] analyzed Yb^{3+}-Yb^{3+} and Yb^{3+}-Tm^{3+} energy transfer in nanoparticles of YF_3 co-doped with Yb^{3+} and Tm^{3+}. It is shown that the spectroscopic parameters involved, such as emission and absorption rates, remain unaltered when the material size is reduced in certain scales. The lifetimes are much shorter in the nanoparticles than in macroscopic samples. This happens primarily due to the strong contribution of surface defects in the case of nanoparticles, which confirms a general phenomenon of luminescence dynamics of rare earth ions in nanocrystals.

5. Conclusions

Research and development of nanoscale upconversion materials are part of the rapidly advancing nanoscience and nanotechnology. Experimental observations have imposed new challenges on theoretical interpretation of the marked variations in the dynamics of upconversion luminescence with respect to that of the bulk materials. Because of the localized electronic states and relatively weak ion-phonon interactions, the electronic properties of the trivalent rare earth ions in nanocrystals do not differ significantly from those in bulk crystals. Therefore, theories established for rare earth ions in bulk crystal apply in general to rare earth ions in nanostructures. Most of the observed nano-effects appearing in the upconversion luminescence from rare earth doped nanophosphors originate primarily from changes in materials properties, which include structure distortion, vibration frequencies and surface layer defects. These changes lead to modifications in electronic transitions and ion-phonon interactions, and therefore, to variations in electronic transition intensities and excited state relaxation that are critical to upconversion performance.

We have reviewed the theoretical principles and empirical models that provide quantitative interpretations of the spectra and emission intensities of rare earth doped upconversion materials. Depending strongly on synthesis procedures and conditions, the lattice structure often varies more or less in nanocrystals with respect to their bulk analogs. The structure distortion in most cases break down site symmetries. It does not result in significant changes in electronic energy levels with which upconversion is achieved, but may substantially change transitions probabilities and relaxation rates. In small nanostructures, ion-lattice interaction may induce stronger configuration mixing, especially between the $4f^N$ and $4f^{n-}$-5d configurations than that in bulk crystals, thus increase the cross section of electronic transitions and the luminescence efficiency. The most recognized changes occur between the cubic phase and hexagonal phase of $NaYF_4$ which is known as one of the most efficient upconversion host when doped with the Yb^{3+}-Er^{3+}(Tm^{3+}) pairs. Crystal-field induced configuration coupling provides a theoretical interpretation to the differences between the two $NaYF_4$ structures and explains a series of experimental studies aimed at controlling the particle size or modifying the surface of the cubic phase of $NaYF_4$ nanocrystals to improve upconversion performance.

Numerous studies have shown that nanoscale size variation impacts the excited state dynamics including radiative and nonradiative lifetimes, energy transfer, and thermalization phenomena. Many of the observed effects can be interpreted as the consequences of modified ion-phonon interactions. It is shown that in nanocrystals, the PDOS is no longer continuous, and the low-energy phonon modes are absent. As a result, size reduction imposes confinement on electron-phonon interactions of rare earth ions in nanocrystals. Such a size confinement has a direct impact on the nonradiative phonon relaxation and phonon-assisted energy transfer processes. The effects of size confinement on upconversion can be quantitatively evaluated using the theories established for bulk crystals with a modification of PDOS and domain restriction in energy transfer. For evaluation energy transfer in doped upconversion nanophosphors, except the Inokuti-Hirayama model not effective for nanocrystals, no analytical functions are available. Using the PDOS modified energy transfer rate and Monte Carlo method, predictive simulation of experimental results can be effectively achieved.

In addition to nano-phenomena induced by modified PDOS, luminescence decay time and efficiency of rare earth ions in nanomaterials are also influenced by variation of local environments that affect the spontaneous photon emission and index of refraction. It has been shown that the variation of index of refraction and the coherent interference of local electric fields at the boundary of nanoparticles must be considered in the evaluation of luminescence intensity and radiative lifetime.

Although, the effects of surface defects cannot be addressed theoretically in detail, inhomogeneous line broadening and non-radiative phonon relaxation are generally anticipated to increase in the optical spectra of rare earth ions in nanoparticles because of structural defects. Surface modification of nanophopshors, in many cases via coating and construction of core-shell structures, enables control of upconversion performance and improving upconversion efficiency and changing luminescence color. Accordingly, separated treatments of ions in the surface layer and core of a nanoparticle may facilitate using of empirical models and accomplish a theoretical understanding of experimental results.

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Figure captions

Fig. 1 Energy levels of trivalent rare earth ions Ln^{3+} in LaF_3. The $4f^N$ (N=1 to 13) energy levels are calculated using a parameterized Hamiltonian and the $4f^{N-1}5d$ energy levels are estimated from systematic analysis. Anticipated emitting states in the visible, near IR and UV region are marked with dots.

Fig.2 Upconversion emission intensity versus dopant concentration of Gd^{3+} (0–60 mol%) in $NaY_{1-x}Gd_xF_4$ nanocrystals doped with Er^{3+} and Yb^{3+}. The emission intensities were calculated by integrating the spectral intensity of the emission spectra over wavelength in the range 400–700 nm. (Data from Wang *et al. Nature* **463**, 1061-1065 (2010))

Fig. 3 Spectral profile of vibronic sidebands in absorption spectrum calculated using Franck-Condon model of electron-phonon coupling. Multi-phonon progressions arise from electronic coupling to two vibration modes with frequency ν_1=150 cm^{-1} and ν_2 = 210 cm^{-1}. A value of Huang-Rhys parameter S=0.8 and line width σ =10 cm^{-1} are assumed.

Fig. 4 Selected absorption spectra of Cs_2NaErF_6. (a) 6475 −6900 cm^{-1} at different temperatures; (b) 18 300 −18 800 cm^{-1} at 10 K; and (c) 19 200−19 900 cm^{-1} at 10 K. S_i are various vibrational modes. The vibrational energies from the zero phonon line (ZPL) at 0 cm^{-1} are marked in (b). The assigned ZPLs in (c) are Γ_8 (1) at 19212 cm^{-1}, Γ_7 (2) at 19219 cm^{-1} , Γ_8(10) at 19351 cm^{-1}, and Γ_7 at 19413 cm^{-1}. (Copied with permission from Xianju Zhou; Peter A. Tanner; Michèle D. Faucher; *J. Phys. Chem. C* **2007,** 111, 683-687 DOI: 10.1021/jp0660482)

Fig. 5 (a) Main radiative/nonradiative transitions and energy transfer processes relevant to the upconversion luminescence in $NaYF_4$:Yb-Er nanocrystals. (b) Room-temperature upconversion emission spectra of $NaYF_4$:Yb-Er nanocrystals with varying size from 6 nm to 45 nm (IR excitation intensity 5W/cm^2). The spectrum was normalized to Er3+ emission at 540 nm. (c and d) Evolution of lifetime decays for a series of $NaYF_4$:Yb-Er nanocrystals at the green (c) and red (d) upconversion emission bands, respectively. Insets indicate the lifetime variation of green (c) and red (d) upconversion luminescence for 31 nm nanocrystals after coating with a 10 nm-thick silica layer. (Copied with permission from Zhua et al., Nanoscale, 2013, 5, 944-952)

Fig. 6 Reduction of PDOS in nanocrystals and its effect on Er^{3+} absorption and emission. (a) Calculated PDOS of a 20-nm Y_2O_2S crystal. PDOS is discrete and low frequency modes are cut off. (b) Anomalous hot bands appear in the excitation spectrum of Er^{3+} (2 mole%) in 20-nm Y_2O_2S anaocrystals in comparison with the spectrum from bulk crystals. Spectra were recorded when both nano- and bulk-crystals were cooled in liquid helium (T=4K). Hot bands appear due to the absence of low-frequency phonons in the lattice. Relaxation from the upper levels in the ground state is eliminated. (c)Temperature dependence of the fluorescence excitation intensity of Er^{3+} in the nano crystals. The hot band at 20288 cm^{-1} are shown in (b). Laser selectively excitation of Er^{3+} from an upper level (45 cm^{-1}) above the ground level to the lowest level of the excited state $^4F_{7/2}$ at 20333 cm^{-1} with emission from the $^4S_{3/2}$ excited state at 18248 cm^{-1} was monitored (Ref. 97). As a result of diminished phonon relaxation, the excitation intensity anomalously increases below a critical temperature Tc = 9 K. Using the calculated PDOS and including one- and two-phonon coupling to electronic states, the solid line is a theoretical fitting to the experimental data.

Fig.7 Fluorescence decay of Er^{3+} from the $^4S_{3/2}$ state in 20-nm Er^{3+}:Y_2O_2S nanocrystals with different doping concentration recorded at 295K. The scattering points are experimental results and the lines are theoretical fitting.

Fig.8 Phonon-assisted energy transfer efficiency as a function of particle size in 2% Er^{3+}:Y_2O_2S at 295K. For comparison, the efficiency is normalized to the bulk sample. The inset shows the calculated and observed luminescence decay of Er^{3+} $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition in Er^{3+}:Y_2O_2S of bulk and 20-nm crystals respectively at room temperature.

Fig. 9 Photon upconversion in KYb_2F_7 nanocrystals codoped with Er^{3+} and Yb^{3+}. **a**, Room-temperature emission spectra of KYb_2F_7:Er (2 mol%) (top) and KYb_2F_7:Er-Lu (2/0–80 mol%; bottom) nanocrystals recorded in cyclohexane solutions (0.2 wt%). The emission spectra were normalized to Er^{3+} emission either at 558 nm or 545 nm, whichever is stronger. The inset is a typical micrograph showing the luminescence of KYb_2F_7:Er (2 mol%) nanocrystals. **b**, Proposed four-photon upconversion mechanisms in KYb_2F_7:Er nanocrystals following excitation with a 980-nm laser. The $^4S_{3/2}$ state of Er^{3+} is first populated by sequential energy transfer of two photons from an excited Yb^{3+} ion. The $^4I_{13/2}$ state of Er^{3+} is then populated by back-energy-transfer from the $^4S_{3/2}$ state of Er^{3+} to the ground state of a neighbouring Yb^{3+} ion. Subsequently, localized energy transfer within the Yb tetrad cluster provides two additional photons to the Er^{3+} ion, thereby leading to the population of the $^2H_{9/2}$ state. The dashed–dotted, dashed, dotted and full arrows represent photon excitation, energy transfer, multiphonon relaxation, and emission processes, respectively. The sequential multiphoton pumping processes are numbered. **c**, Energy transfer confinement in the Yb tetrad clusters of orthorhombic-phase KYb_2F_7. The probability of energy transfer within the Yb cluster (*P*intra) is calculated to be more than 10 times higher than that of inter-cluster energy transfer (*P*inter). **d**,**e**, The probability of excitation plotted against migration distance using Monte Carlo simulations for a KYb_2F_7 crystal (**d**) and a simple cubic structure (**e**). (Copied with permission from Wang et al., Nature Materials, 13, 157-162 (2014))

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