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Emerging rare-earth doped material platforms for quantum nanophotonics

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Rare-earth dopants are arguably one of the most studied optical impurities in solids, with applications spanning from laser optoelectronics, biosensing, lighting to displays. Nevertheless harnessing rare-earth dopants’ extraordinary coherence properties for quantum information technologies is a relatively new endeavor, and has been rapidly advancing in recent years. Leveraging the state-of-the-art photonic technologies, on-chip rare-earth quantum devices functioning as quantum memories, single photon sources and transducers have emerged, often with performances unrivaled by other solid-state quantum technologies. These existing quantum devices, however, nearly exclusively rely on macroscopic bulk materials as substrates, which fundamentally limits the future scalability and potential functionalities of such quantum systems. Thus the development of new platforms beyond single crystal bulk materials has become a priority. In this review article, we summarize the latest progress towards nanoscale, low-dimensional rare-earth doped materials for enabling next generation rare-earth quantum devices. Different platforms with variety of synthesis methods are surveyed. Their key metrics measured to date are presented and compared. Special attention is placed on the connection between the topology of each platform to its target applications. Lastly, an outlook for near term prospects of these platforms are given, with a hope to spur broader interests in rare-earth doped materials as a promising candidate for quantum information technologies.

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INTRODUCTION

Solid-state quantum nanophotonics has emerged as one of the most active fields in quantum engineering. In particular, optically active atomic or atom-like defects in solids that simultaneously possess long-lived spin coherence and stable optical transitions play key roles in the development of quantum networks, quantum sensing and quantum information processing. Among numerous candidates, rare-earth doped materials have attracted significant interests in recent years, and is rapidly advancing. The emergent field of rare-earth nanophotonics inherits the rich history of rare-earth spectroscopy, and leverages the cutting-edge nanophotonic technologies to enable a new class of devices that are highly coherent, efficient and scalable. At the heart of this development is the fundamental science and engineering of rare-earth doped materials with wide variety of chemical compositions, physical behaviors, topologies and synthesis methods. The rich library of material properties offers nearly unlimited opportunities for quantum device engineering. At the same time, crucial device metrics also dictate the best combination of material topologies and growth technique to achieve those specifications.

Only recently the connection between material growths and quantum device engineering has been made, and the importance of material design and synthesis has been recognized. After decades of arduous efforts in perfecting bulk, single crystal hosts, newer platforms based on rare-earth doped nanocrystals, polycrystalline ceramics and films tailored for quantum technologies have been gaining momentum and begin to reap promising results. In this article, we summarize some of the most recent developments in emerging material platforms beyond bulk crystals for building next generation rare-earth quantum photonic devices. We attempt to establish a common ground for material chemists, spectroscopists and device engineers in this field by highlighting the relationship between material metrics and device functionalities. The hope is to spur further research in fundamental material science to understand, control and design better materials to meet the needs of fast-growing rare-earth quantum technologies. It should be pointed out that we do not intend to give a thorough review on rare-earth doped bulk crystals, nor the spectroscopic techniques used to characterize them. A number of works on those topics are already available to the interested reader [1–5].

This article is organized as follows: Section 2 gives a review of rare-earth quantum photonic device developed to date and highlight the trend in underlying material platforms. Section 3 surveys in more details the progress in several emerging material platforms. In Section 4, we give an outlook for future material development and elaborate several key metrics need to be accomplished in order to push forward the field of rare-earth nanophotonics.

RARE-EARTH QUANTUM PHOTONIC MATERIALS AND DEVICES

Rare-earth elements include lanthanides, scandium and yttrium. They are common dopants in host crystals
such as yttrium aluminum garnet (Y$_3$Al$_5$O$_{12}$ or YAG), Y$_2$SiO$_5$ (YSO), Y$_2$O$_3$, or YVO$_4$ (YVO). The 4f shell of rare-earth ions in crystals is partially occupied and is shielded from the interaction with the crystalline environment by 5s and 5p outer shells. The 4f electrons are highly localized and the 4f-4f intra-shell transitions are parity forbidden in free space, but become weakly allowed in the presence of crystal field, which result in sharp optical transitions with high quantum efficiency. Sharp optical transitions (equivalent quality factor over $10^{11}$) at cryogenic temperatures are correlated with long optical T$_1$ lifetimes (hundreds of $\mu$s to ms) but also weak oscillator strengths. Electronic Zeeman and hyperfine transitions in the radio-frequency or microwave regimes are abundant. When doped into host with small nuclear magnetic moments such as YSO, record long spin coherence times 6 hours in Eu:YSO [6] and 1.3 seconds in Er:YSO [7] have been achieved. Such long coherence times combined with a rich selection of spin levels (both electronic and nuclear) and optical addressability make rare-earth ions attractive candidates for qubits as a building block in quantum information science. Furthermore, optical transitions exhibit inhomogeneous broadenings that are typically $10^{5-6}$ times the homogeneous linewidths, indicating an excellent prospect for dense spectral multiplexing of qubits or memories to enable large data processing and storage bandwidths [8, 9].

One of the most successful application of rare-earth doped crystals in quantum technology is optical quantum memories. These memories which faithfully store a qubit encoded on a single photon have performances unmatched by any other solid-state system. For reviews on rare-earth quantum memories, readers are referred to ref. [10, 11]. Landmark ensemble experiments include storage of light up to a minute using electromagnetically induced transparency (EIT) in praseodymium doped yttrium orthosilicate (Pr$^{3+}$:YSO) [12, 13], quantum storage of photonic entanglement in neodymium (Nd) doped YSO (Nd$^{3+}$:YSO) [14, 15] and thulium-doped lithium niobate waveguides [16], optical memory at the single photon level in Nd doped yttrium orthovanadate (Nd:YVO) [17–19] and quantum level spin storage in Eu$^{3+}$:YSO [20], conditional phase shifts between two ensembles of europium (Eu) in YSO [21], up to 69% efficient quantum memory for light in Pr$^{3+}$:YSO [22–24], and a quantum optical connection between a cold atomic gas and Pr$^{3+}$ in YSO [25]. These ensemble-based memories provide natural interfaces between optical photons and spins at radio-frequency or microwave regimes, which can also be harnessed to realize quantum transducers interconnecting distant superconducting quantum circuits. Hybrid quantum systems based on rare-earth ensembles see the opportunities of microwave quantum storage [26] and microwave-to-optical conversion [27, 28]. To date, high cooperativity coupling of rare-earth spins to a superconducting resonator has been demonstrated [29, 30]. Unit efficiency microwave to optical conversion via magneto-optic coupling has been proposed [28], and its experimental implementation is being pursued [31–33].

Ultimately, the most powerful rare-earth quantum technologies will be devices operating on inindividual ions [34]. To that end, optical addressing of single ions is coming into focus of this research. Such a task, however, is not easy. The progress has been hindered by long optical lifetimes of rare-earth ions and resultant faint photoluminescence. So far, only a few experiments have succeeded in isolating individual praseodymium [35–37], cerium [38–40], neodymium [41] and erbium [42, 43] ions. It is worth noting that majority of these experiments were not probing ions via their highly coherent but weak 4f-4f optical transitions. Taking Pr and Ce as examples, bright 4f-5d transitions from high lying electronic levels were exploited to enhance the detection sensitivity of individual ions. To directly access the 4f-4f transitions of single ions, the emission rates of individual emitter need to be enhanced. Recent works by [41, 43] have been successful in that by coupling ions to nanophotonic cavities with sub-wavelength scale dimensions (more discussions on cavities in the next paragraph). Both experiments achieved Purcell enhancement of ions’ emission on the order of hundreds, allowing direct optical detection of individual ions with sufficient signal-noise performance using state-of-the-art superconducting nanowire detector technology. These results point at a viable approach to efficiently detect and coherently control individual ions in an on-chip nanophotonic platform.

The weak oscillator strengths of rare-earth emitters require significant enhancement of their atomic absorption cross-sections in order to strongly interact with light at the quantum level. One effective way to achieve such enhancement is to modify the local photonic density of states using nanophotonic structures including waveguides and cavities. Rare-earth doped photonic waveguides have been realized by ion-indiffusion in Tm or Er doped LiNbO$_3$ [16, 44, 45], laser written channels in Pr:YSO crystals [46], and high-index membranes deposited or transferred on top of doped oxide substrates [43, 47–49]. These waveguides provide transverse confinement of the optical field interacting with dopants, thus enhancing the coupling strengths. In the cases of ion-indiffused and laser written devices, the rare-earth emitters align with the peak field intensity in the waveguide. Whereas in systems based on high-index materials placed on top of doped crystals, the optical field evanescently couples to the dopants near the material interfaces. All of these designs have demonstrated enhanced light-matter interactions, and preserved optical coherence of the dopants comparable to bulk crystal hosts. The long coherence despite the fabrication processes highlights the remarkable robustness of rare-earth dopant as a quantum resource. The waveguide scheme has also been ex-
tended to cavities by forming a micro-ring [48, 49] or patterning photonic crystal lattices [43] along the waveguide. For cavity-based system, an important figure of merit is the Q/V ratio where Q is the quality factor and V is the normalized mode volume of the cavity in a unit of (λ/n)³ [50]. Focused ion beam-milled photonic crystal nanobeam resonator achieving Q/V on the order of 10⁴ have been fabricated [51, 52], which enabled first nanophotonic quantum memories [19, 53] based on mesoscopic ensemble of dopants and coherent optical addressing of individual ions. The photonic crystal cavities were proven effective to strongly enhance the spontaneous emission rate of rare-earth ions via the Purcell effect [41, 43]. When the enhancement is sufficient large compared to other optical dephasing processes of the emitter, radiatively-limited single photon emission from individual ions becomes feasible and has been demonstrated recently [41]. Besides waveguides and cavities, other techniques for controlling the rare-earth emission rates were also proposed. One example is a hybrid scheme in which the rare-earths are coupled to highly optically absorbing materials such as graphene via near field interactions [54].

Low dimensional host matrix

Nanocrystals and polycrystalline ceramic materials

A first approach to obtain these materials is to use chemical methods, the so-called bottom-up strategy. This has been first used to produce Eu³⁺:Y₂O₃ micro-size particles with 60 nm crystalline domains by a solvothermal method [56, 59]. These particles, as most of those studied so far by high-resolution and coherent spectroscopy, are polycrystalline, i.e. each particle is made of several crystallites. Optical properties were determined on samples in the form of a powder. Photon echoes, well known for providing an accurate measurement of homogeneous linewidths in transparent materials [60, 61], can also be observed in powders that strongly scatter light as first demonstrated by Beaudoux et al. [62] and recently theoretically analyzed [63]. Application of this technique to the above particles led to a homogeneous linewidth for Eu³⁺ ⁷F₀ →⁵D₀ transition at 581 nm of 86 kHz at 1.3 K [56]. This was about one to two orders of magnitude lower than previous results obtained on Eu:Y₂O₃ nanocrystals ([64]). It is however much larger than values obtained in the best single crystals (300 Hz [65]) or transparent ceramics (3.5 kHz) [66], although it should be noted that considerable dispersion of linewidths is found in single crystals grown by different methods [67].

Light scattering by particles introduces losses that are
very detrimental to cavities quality factor, and should be as small as possible. The particle diameter $d$ is a major factor to consider since the scattering cross-section varies as $d^6$ [58]. Moreover, to be able to use isolated particles, aggregation should be avoided. This was made possible using homogeneous precipitation, a technique that lead to low particle size dispersion and spherical shapes [68]. To obtain $\text{Y}_2\text{O}_3$ cubic phase, high temperature annealing of the precursor hydrocarbonates particles is required. It was shown that treatment at 1200 °C reduced inhomogeneous line-widths down to $\approx 10$ GHz for 0.5% Eu$^{3+}$ doping, a value comparable to bulk ones [69]. This was observed for particle and crystallite sizes in the ranges 150-540 nm and 90-120 nm respectively, suggesting that the decrease in line-widths was due to a decrease in defects, such as oxygen vacancies, in the volume of the nanocrystals. On particles of 400 nm diameter (130 nm crystallite diameter), an extensive study of homogeneous line-widths $\Gamma_h$ as a function of temperature, magnetic field and time was performed by 2 and 3-pulse photon echoes and spectral holeburning [70]. A surprising result was that magnetic fields up to 2.5 T had no effect on $\Gamma_h$, suggesting that dephasing from magnetic defects or impurities was not the main contribution to $\Gamma_h$. Indeed, it was concluded that for temperatures $< 12$ K, $\Gamma_h$ was due to interactions with two-level systems (TLS) and a temperature independent dephasing. While TLS effect has been previously identified in $\text{Y}_2\text{O}_3$ bulk crystals and nanoparticles [56, 67], it was not the case for the latter process. Based on a simple model, it was suggested that it can be due to electric field noise created by surface charges, a mechanism already observed in NV$^-$ centers in diamond for example [71]. Importantly, no sign of interaction between Eu$^{3+}$ and a modified phonon density of states, related to the crystallite sizes [64], was observed. This indicates that there is no intrinsic size-related contribution, which would be very difficult to overcome, to the homogeneous linewidth of the studied particles. The narrowest homogeneous line-widths reported were 45 kHz at 1.3 K with a broadening of $\approx 100$ kHz over 1 s [70]. Narrow line-widths were also demonstrated in smaller particles. Because of the required high temperature annealing that promote sintering, it can be challenging to directly obtain small particles that stay non-aggregated. An alternative approach was proposed in which large particles are reduced in size by wet chemical etching in a weak acid. Starting from dispersed and well crystallized particles of 450 nm diameter, particles down to 150 nm were obtained showing homogeneous line-widths of 34 kHz at 1.4 K, the smallest value reported so far for a nano-material [72]. The limited broadening induced by etching ($\approx 10$ kHz), while the particle size is reduced by 65% but the crystallite size remains unchanged, suggests that the latter is the relevant parameter for dephasing processes (Fig. 2). This was further supported by showing that etching proceeds by opening grain boundaries between crystallites in the particles. Single crystalline particles can therefore be produced, which may be useful when, for instance, a magnetic field should be applied in a specific direction or well defined Rabi frequencies are needed.

To assert the potential of rare-earth doped nanoparticles as quantum memories or processors, it is necessary to measure spin coherence lifetimes $T_2$ since qubits are usually defined within the energy level structure of ground state spins [73]. This was performed on 400 nm Eu$^{3+}$:Y$_2$O$_3$ particles using an all-optical technique for spin coherence manipulation and spin echo detection [74–76]. Powders cooled to 5 K showed nuclear spin echo signals for $^{151}$Eu$^{3+}$ with signal to noise ratio of about 10, proving that the technique actually works in a scattering medium, and sufficient for $T_2$ measurements [77]. Spin coherence lifetimes of 1.3 ms were recorded, increasing to about 3 ms under a 9 mT magnetic field (Fig. 3). These values, one order of magnitude lower than in transparent ceramics [78] but still the longest reported for any nanoparticle with optically addressable spins, provide valuable insight into dephasing mechanisms. First, the strong dependence of $T_2$ for very weak magnetic field suggests that the main dephasing is due to magnetic dipole-dipole interaction with electron spins carried by defects or impurities. Indeed, when the Zeeman interactions become larger than the dipole-dipole interaction, the effect of the latter is reduced. This magnetic noise also affect the optical transition, which can be expected to broaden to a similar level than the spin transition, i.e. $\approx 250$ Hz, based on the excited and ground state gyromagnetic ratios in other hosts [79–81]. This is much too small to account for the optical line-width of 45 kHz and supports the hypothesis of electric field perturbations as the main optical dephasing process. This is also in agree-
ment with Stark coefficient of the optical transition \[82\] being 4 to 5 orders of magnitude larger than the spin one \[83\]. Coherent spin control was further demonstrated by an all-optical dynamical decoupling (DD) technique that resulted in \(T_2\) up to 8 ms, limited by disorder and light scattering in the powders that prevent pulses with accurate area to be applied \[77\]. This highlights the interest of using single particles with single crystalline structure for optimal decoherence control. It was also shown that spin state phase is well preserved in echo and DD sequences, which is a requirement for quantum storage. Apart from experiment on powders, spectroscopy of single \(\text{Eu}^{3+}\):\(\text{Y}_2\text{O}_3\) nanoparticles has been studied using a fiber micro-cavity \[58\]. In this setup, the particles are placed on a flat mirror which faces a concave profile laser-machined in an optical fiber. It was found that \(\text{Eu}^{3+}\) in 90 nm particles had inhomogeneous linewidths identical to what had been measured on powders, and that the cavity allowed detecting about 10 ions taking advantage of the Purcell effect.

Similar results have also been reported in \(\text{Pr}^{3+}\):\(\text{Y}_2\text{O}_3\) nanoparticles \[D. Serrano et al., in preparation\], obtained by homogeneous precipitation, for optical and spin transitions. Compared to \(\text{Eu}^{3+}\), \(\text{Pr}^{3+}\) has generally stronger optical transitions and more favorable branching ratios that could be beneficial for coupling to a cavity. Hyperfine splittings are however smaller \[2\], which limits the minimal pulse duration that can be applied to a specific transition between hyperfine levels and therefore operation fidelity. Homogeneous linewidths of between 100 and 300 kHz were observed for the \(^3\text{H}_4 \rightarrow ^1\text{D}_2\) transition at 619 nm and particles between 400 and 150 nm (crystallite size 120 and 80 nm). Interestingly, spin coherence lifetimes reached nearly 1 ms, longer than reported so far in bulk \(\text{Pr}^{3+}\) doped crystals, like YSO \[84, 85\]. This could be explained by lower gyromagnetic ratios for \(\text{Pr}^{3+}\) in \(\text{Y}_2\text{O}_3\) according to calculations based on crystal field modeling of electronic levels \[86, 87\].

Pioneering experiments on high resolution spectroscopy of rare earth doped nanomaterials used a top-down approach, laser ablation, to produce \(\text{Y}_2\text{O}_3\) nanocrystals with a monoclinic phase \[64, 88\]. Spectral hole burning was used to probe \(\text{Eu}^{3+}\) homogeneous linewidths, which were found in the several MHz range for crystals of 10s of nm, likely to be highly agglomerated. Interactions with modified phonon density of states were proposed to explain the broadening.

Other top-down approaches have also been investigated, in which a single crystal is ground to nanoparticles. In \(\text{Pr}^{3+}\):\(\text{YSO}\), optical homogeneous linewidths of a few MHz for single crystals were reported for particles between 100s of nm and a few microns, as well as spectral diffusion of 10 MHz over minutes for the larger particles \[36, 89\]. Strain induced by grinding and associated TLS could be the source of this significant broadening compared to the 80 kHz linewidth in the bulk crystal. Such mechanisms were also put forward in studies on \(\text{Tm}^{3+}\) doped crystals ground to micron size powders and probed by spectral hole burning \[90\]. The main effect of strain was observed on spectral hole lifetimes that strongly shortened under milling (several hours down to 10s of minutes) and could be partially recovered with high-temperature annealing. Homogeneous linewidths, that can be estimated from hole widths, followed the same trends although the already broad values of several MHz for bulk crystals do not allow studying very narrow linewidths. Milled, micron-size powders of \(\text{Er}^{3+}\):\(\text{LiNbO}_3\) were also studied by spectral hole burning and photon echoes, and showed that even low energy milling impacts kHz range homogeneous linewidths \[91\]. For powders with 1-100 µm crystals, annealing was able to recover close to bulk properties.

Another class of polycrystalline materials are transparent ceramics, which are usually obtained by sintering cubic phase nanoparticles under high temperature and high isostatic pressure (HIP). This results in the growth of micron size crystals with random orientation and a strong decrease of the material porosity, ultimately leading to negligible scattering losses \[92\]. Thanks to their high flexibility in composition, shape, and ability to build composite materials, transparent ceramics are thus an alternative to single crystals in a variety of photonic applications like lasers or scintillators, and could also allow obtaining new high performance materials in quantum technologies \[93–95\]. \(\text{Eu}^{3+}\) in \(\text{Y}_2\text{O}_3\) transparent ceramic properties have been investigated in details, as a function of doping concentration, post-synthesis treatment and co-doping with sintering aids. Optical transition inhomogeneous linewidths down to 9 GHz were observed.
for 1000 ppm Eu$^{3+}$ doping [95, 96], comparable to bulk values, while co-doping with Zr$^{4+}$ (5000 ppm), a common sintering aid, increased the linewidth to 100 GHz [97]. Homogeneous linewidths were also studied as a function of temperature, magnetic field and delay in 3 pulse experiments to reveal spectral diffusion processes [66]. This revealed complex behaviors, that could be in some cases analyzed by taking into account the dependence of perturbation correlation times on temperature and magnetic field. The narrowest homogeneous lines were 3.2 kHz for ceramics post-annealed under air and are due to several contributions, including TLS and possibly magnetic perturbations. Dephasing was more pronounced in samples without post-annealing, underlining the role of oxygen in controlling defects concentration and nature. This was further investigated by comparing high resolution spectroscopy with photoluminescence, electron paramagnetic resonance and thermo-luminescence, showing that defects related to oxygen vacancies, like F centers, seem to be correlated to optical linewidth [97]. Nuclear spin properties of $^{151}$Eu$^{3+}$ and $^{153}$Eu$^{3+}$ were also measured by the all-optical technique described above and showed remarkably long coherence lifetimes, up to 16 ms under a 3 mT magnetic field [78], close to values measured in Eu$^{3+}$:Y$_2$SiO$_5$ single crystal [98, 99]. As in the nanoparticles, spin transitions are much less sensitive to perturbations than optical transitions, pointing to a possible role of electric noise.

Very narrow inhomogeneous lines, as low as 442 MHz, have also been observed in Er$^{3+}$ in Y$_2$O$_3$ transparent ceramics. This indicates the very high crystalline quality of the samples. Homogeneous linewidths measured at 2.5 K and under 0.65 T magnetic field vary between 10 and 50 kHz, depending on Er$^{3+}$ concentration. In the case of paramagnetic ions, interaction between ground state spins themselves can cause strong dephasing, which can explain the observed dependence on Er$^{3+}$ concentration [100]. At low Er$^{3+}$ concentration, temperature dependence of $\Gamma_h$ under magnetic field suggests that TLS contribution dominates the homogeneous linewidth. This suggests a low concentration in defects or impurities carrying electron spins, that could induce significant broadening by coupling to Er$^{3+}$ electron spin.

*Rare-earth doped films*

Atomic layer deposition (ALD) is a common technique for obtaining Y$_2$O$_3$ films with well controlled thickness and good crystalline quality [101]. A study of Eu$^{3+}$ and Er$^{3+}$ doped ALD films in the context of applications in quantum technologies was reported [102]. It showed that optimized growth followed by high temperature annealing resulted in Eu$^{3+}$ luminescence spectra corresponding mainly to the Y$_2$O$_3$ cubic phase. In a 100 nm thick sample doped with 5% Eu$^{3+}$ and deposited on (100) silicon wafers, $^5$D$_0$ level lifetimes reached 0.8 ms, close to bulk values. The $^7$F$_0 \rightarrow ^5$D$_0$ inhomogeneous linewidth was about 200 GHz, a factor of 2 larger than expected from studies on transparent ceramics [96]. This could be due to stress in the film induced by differences in thermal expansion coefficients between silicon and Y$_2$O$_3$, which would also explain the shift of the line with the annealing temperature. It may also stem from the presence of defects at grain boundaries since grain size in such polycrystalline thin films is of the order of 30 nm. Ultra-thin films, which are of interest for dopant localization and hybrid devices [54], have also been investigated [102]. In films as thin as 7 nm, Er$^{3+}$ luminescence at 1.5 μm showed decay times of about 1.5 ms, a long value for Er$^{3+}$ nanoparticles, although still shorter than the 7.7 ms of bulk Er$^{3+}$:Y$_2$O$_3$. Further studies on coherent properties are needed to assert the potential of these systems for quantum technologies, which may require specific setups such as waveguides to deal with film/substrate geometries and the low number of active ions in very thin layers [103]. The simple chemical composition and stable cubic phase of Y$_2$O$_3$ makes it possible to grow wafer-scale, epitaxial thin films. Indeed, single crystal, epitaxial Y$_2$O$_3$ have been synthesized using molecular beam epitaxy (MBE) on silicon wafers for high-k dielectric gate in MOSFET [104, 105]. Recently, this process has been improved to achieve exceptional qualities of Y$_2$O$_3$ films doped with Er$^{3+}$ [106]. Controls of doping concentrations in the range of 1 to 100 parts per millions can be achieved. The thickness of the film up to 1.5 μm is also controllable with a precision down to a monolayer of atoms. The growth occurs via a two-dimensional layer-by-layer growth mode, resulting in smooth, uniform films, which offers several
distinct advantages: first, the epitaxial film has significantly less optical loss and suggests better coherence for dopants; second, it allows atomic precision placement of rare-earth dopants via delta doping; third, the wafer-size film allows scalable top-down device patterning using standard lithography and etching techniques. The photoluminescence of Er$^{3+}$ was measured, which clearly showed two distinct transitions corresponding to two crystal symmetry sites: C2 site at 1532 nm and C3i at 1542 nm. The wavelengths of the peaks agree with that in bulk Er$^{3+}$:Y$_2$O$_3$ [107], confirming the correct Y site occupancies. Optical lifetimes and ground-state electron paramagnetic resonance were measured [106]. The photoluminescence decay gives a $T_1$ of 8.7 ms for C2 site, in excellent agreement with bulk Er$^{3+}$:Y$_2$O$_3$ measurement [107]. Optical and spin coherence are next experiments to fully characterize this epitaxial film material.

Hybrid rare-earth materials

Other hybrid architectures have been considered, based on thin films or nanoparticles. A first example is the electrical control of coupling between rare-earth ions and a graphene layer [54]. Depending on the Fermi level in graphene, rare-earth can decay through photon emission, non-radiatively by creation of electron-hole pairs in the graphene layer or by excitation of graphene plasmons. This process however is only efficient at distances below 10 nm and is therefore maximized for very thin rare-earth doped films. This effect was observed in a Er$^{3+}$:Y$_2$O$_3$ thin film of about 60 nm thickness obtained by the metal organic decomposition method on a Si substrate [108]. A graphene layer was placed on top of the film and covered by a transparent solid polymer electrolyte to allow tuning of graphene Fermi level by a gate voltage. Comparing Er$^{3+}$ emission below or outside the graphene sheet as a function of the voltage applied to the device, it was possible to identify a regime of low emission in which Er$^{3+}$ is quenched by the graphene, a stronger emission when electron hole pair creation becomes reduced and finally a low emission again when Er$^{3+}$ is able to excite plasmon in the graphene layer [54]. This demonstrates a unique capability of electrically controlling the local density of optical states of an emitter. The on-demand coupling of emitters with plasmons opens promising possibilities for quantum optoelectronics, which could take advantage of the coherence properties of rare-earth transitions. This will require large couplings that could be obtained with thinner films, provided that rare-earth properties can be preserved (see above, [102]).

A second example is the incorporation of rare-earth ions in diamond, one of the major material for quantum technologies. Such a system could combine the excellent properties of diamond such as high purity and crystalline quality with the narrow lines of rare-earth ions. Moreover, diamond can host a variety of defects with strong emissions and/or carrying spins with long coherence lifetimes that could also interact with rare-earths in hybrid quantum systems. Incorporating rare-earth ions, which have a large ionic radius, into the diamond lattice is however difficult. One approach is to chemically self-assemble rare-earth complexes on bulk or nano-diamonds before growing a new diamond layer by CVD [109, 110]. Another one consist in implanting rare-earth into bulk or nano diamond [111, 112]. Rare-earth ions luminescence has been observed with these different methods, with long lifetimes in the case of Eu$^{3+}$ ions [109]. The lack of well resolved crystal field structure in the spectra however prevents a detailed analysis of the rare-earth local environment and comparison with simulations [109–111], which could unambiguously confirm their incorporation into diamond, still under debate [110]. High-resolution or coherent spectroscopy has not yet been reported on these systems.

OUTLOOK

Future advances in rare-earth nanophotonics hinges on breakthroughs in material synthesis, control and engineering. A set of material properties forms the key metrics for guiding this material development and optimization. For nanocrystals, the particle size should be small enough for precise localization of the emitter with respective to the optical field it couples to, while large enough to suppress unwanted decoherence due to proximity to particle surfaces. For thin films, well controlled thickness and surface roughness are important for high quality photonic devices. The dopant spectroscopic properties, including narrow optical and spin inhomogeneous line widths, optical lifetimes, homogeneous linewidth, long spin $T_1$ and $T_2$, will continue to be the qualifying parameters that drive the growth optimization process. Some of these parameters are less restrictive than others for specific applications. For instance, for single ion devices, inhomogeneous broadening is of secondary concern as long as individual ion exhibits long-lived coherence.

One decisively enabling capabilities for rare-earth nanophotonics is the deterministic control of doping concentration and placement in host matrices. The former is notoriously difficult in bulk, yttrium-based doped crystals, because the background doping of all sorts of rare-earth elements is at ~ppm level in the raw yttrium material. This limitation might be overcome with less common growth techniques such as floating zone growth or molecular beam epitaxy in which elements of rare-earths and yttrium can be better separated by their disparate vapor pressures or other physical properties. In terms of dopant placement, ALD and MBE offers powerful delta-doping options to precisely control the distance of dopant...
to material interfaces, and in principle could result in a mono layer thickness of the doped material. The mastery of 2D film growth technique will further spur new ways to control dopant placement in 3D, for instance, by combining delta-doping with aperture-masked doping at prescribed locations on the substrate. With nanocrystals containing one or a few rare-earth ions, its placement can be controlled by functionalizing the substrate surface and chemically docking the nanocrystal to the desired location.

Once the above metrics and capabilities are realized, they open up powerful tools to nanoscopically control and tailor interactions of rare-earth ions with other quantum degrees of freedoms. With regard to nanophotonics, such controls will enable unprecedented enhancement of light-matter interaction at single rare-earth ion level, and potentially unlock new coupling modalities such as rare-earth-phonon, rare-earth-electric field interactions at varying length and energy scales. Together, these new rare-earth materials and accompanying processing techniques present an exciting prospect of engineering highly coherent quantum systems with on demand functionality and performance.

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