

Optically Active Yb³⁺ Spin Defects in Cerium Oxide Nanocrystals

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ABSTRACT: Nanocrystalline CeO₂ is a chemically tunable wide-bandgap host lattice of interest for quantum information technologies due to its ability to accommodate optically- and spin-active defects. Here, we investigate CeO₂ nanocrystals as hosts for near-infrared-compatible Yb³⁺ ions as optically active spin quantum bits (qubits). We characterize the as-synthesized Yb³⁺-doped CeO₂ nanocrystals (0.01–10% Yb) by photoluminescence, which reveals short photoluminescence lifetimes dominated by nonradiative decay arising from surface and Ce³⁺-related defects. Thermal annealing at 700 °C increases crystalline domain sizes (from ~7 nm to ~20 nm) and reduces the concentration of Ce³⁺ defects, yielding an enhancement in excited-state lifetimes. Low-temperature optical spectroscopy reveals at least two distinct Yb³⁺ lattice sites with cubic and trigonal symmetries, and a ~5-fold difference in photoluminescence lifetimes between the two sites. Continuous-wave EPR measurements support these site assignments, while pulse EPR measurements further show that annealing the nanocrystals nearly doubles the spin–lattice relaxation time (T_1) from 33.9 to 62.7 μ s at 0.08% Yb. Phase memory times, however, remain relatively constant, indicating that coherence is limited by dephasing mechanisms (e.g., slowly fluctuating local fields) rather than by spin–lattice relaxation. Collectively, these results establish defect mitigation, rather than dopant identity alone, as a bottleneck in realizing nanocrystalline CeO₂ as a viable quantum host. This work provides quantitative benchmarks for optical and spin coherence in CeO₂:Yb³⁺ nanocrystals and highlights defect engineering as a critical pathway toward scalable rare earth-based qubits.

KEYWORDS: ceria, cerium oxide, spin defects, qubits, quantum information, ytterbium, colloidal nanocrystals, optical properties

INTRODUCTION

Quantum information technology is gaining significant momentum because of its promise to transform sensing,^{1–3} communications,^{4,5} and computing.^{6–9} Among the wide variety of potential qubit candidates, optically addressable spin defects in crystalline hosts are of particular interest due to their flexibility as robust qubits for scalable quantum systems.^{10–12} Nanoscale material platforms offer a high degree of control over facets, morphologies, surface-to-volume ratios, local electromagnetic environments, and processability. Atom-level tunability of both the core and surface, enabled by solution-phase chemistry, offers a unique approach to mitigating environmental decoherence while still allowing proximity to promote quantum sensing and integration into photonic platforms for optical addressability.^{12,13} However, nanoscale systems also exacerbate issues that are less severe in bulk crystals, such as a higher ratio of surface defects, proximity to those surfaces, or proximity to exogenous nuclear spins, all of which impact coherence.^{14,15}

Recent studies have demonstrated the potential of rare earth ions doped into inorganic solids for quantum information science, owing to their excellent photoluminescence properties

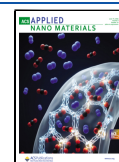
and spin coherence for spin-optical interfaces.^{9,16–20} Additionally, seminal studies on ensembles of lanthanide-doped nanocrystals and single crystals have demonstrated upconversion and single photon emission.^{21–23} Cerium oxide has attracted interest as a qubit host lattice due to its near-zero natural abundance of nuclear spins (Ce has no magnetic isotopes, and ¹⁷O has a natural abundance of 0.037–0.040%).^{10,16,24,25} Other requirements of an ideal qubit host lattice include low nuclear gyromagnetic ratios, the ability to control and mitigate crystal growth defects, and spatial separation of nonzero nuclear spin isotopes to prevent decoherence.¹⁰ In principle, stoichiometric CeO₂ offers a nonmagnetic electron-spin-free lattice since Ce⁴⁺ is diamagnetic. However, it is well-known that nanocrystalline CeO₂ is

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often nonstoichiometric (CeO_{2-x}), resulting in significant concentrations of paramagnetic Ce^{3+} due to its high tolerance to oxygen vacancy defects and the ease of reversible conversion of Ce^{4+} to Ce^{3+} .^{26–29}

Several studies of CeO_2 nanocrystals have aimed to understand how to control size, morphology, and concentrations of defects and dopants.²⁹ In the realm of catalysis, doped CeO_2 has long been studied to generate unique active-site environments by exploiting both the dopant properties and the balance of Ce^{4+} , Ce^{3+} , and oxygen vacancies.^{30–32} In the context of quantum technology, CeO_2 has only recently been investigated as a host lattice for lanthanide ions as spin qubits in both thin films and nanocrystals. Multiple studies of Er^{3+} -doped CeO_2 (via single crystalline thin films and nanocrystal ensembles) have demonstrated millisecond-long spin lifetimes and near microsecond-long coherence times at 3.2 K, experimentally supporting the promise of CeO_2 as a host lattice.^{9,16,33,34} However, the negative impact of surface and defect-related decoherence was identified as a significant challenge, prompting the need for further study and synthetic development. In pursuit of this goal, we investigated cerium oxide as a host for optically active Yb^{3+} spin qubits. Yb^{3+} was chosen because of its relatively simple electronic structure and its strong spectroscopic signature in the near-infrared. Previous studies on Yb^{3+} -doped CeO_2 have focused on its use as a catalyst in solid oxide fuel cells and electrolyzers,^{35,36} as a medium for identifying the hyperfine structure and luminescent properties of Yb^{3+} ,^{37–41} and applications in quantum cutting and upconversion nanomaterials.^{42–46} This work turns a unique lens on Yb^{3+} as an optically active spin qubit with an in-depth critique of CeO_2 as a host for Yb^{3+} emissive and spin properties. Varying the Yb^{3+} concentration, we characterize the dopant's optical response at room temperature and 4 K and demonstrate that annealing the nanocrystals at 700 °C significantly improves the excited-state lifetimes. Finally, we quantify the spin coherence via EPR spectroscopy and demonstrate that annealing the nanocrystals also improves the T_1 lifetime.

■ EXPERIMENTAL METHODS

General Methods and Materials

All synthetic preparations were performed in ambient air in a well-ventilated fumehood or on a benchtop unless otherwise stated. All chemicals listed below were used without further purification unless stated otherwise. Cerium(III) nitrate hexahydrate ($\geq 99\%$ trace metals basis), ytterbium(III) nitrate pentahydrate ($\geq 99.9\%$ trace metals basis), oleylamine (technical grade, 70%), 1-octadecene (technical grade, 90%), toluene (ACS reagent, $\geq 99.5\%$), hexanes (ReagentPlus, $\geq 99\%$), methanol (ReagentPlus, $\geq 99\%$) and acetone (ACS reagent, $\geq 99.9\%$) were all purchased from Millipore Sigma.

Synthesis of $\text{CeO}_2\text{:Yb}^{3+}$ Nanocrystals

As described by Lee et al.,⁴⁷ cerium(III) nitrate hexahydrate (1- x mmol) and ytterbium(III) nitrate pentahydrate (x mmol, $x = 0.1, 0.05, 0.01, 0.005, 0.001$) were added to a 50 mL 3-neck round-bottom flask equipped with a condenser, thermal probe, and stir bar. For the 0.005 and 0.001 mmol quantities, a stock solution of ytterbium(III) nitrate pentahydrate was prepared in a known volume of methanol, which was then transferred as a μL volume to the reaction flask according to the desired ytterbium concentration (109 and 22 μL of 0.045 M $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in MeOH for 0.005 and 0.001 mmol, respectively). Oleylamine (0.98 mL, 3 mmol) and 1-octadecene (4 g, 5.07 mL) were added to the mixture, forming a clear solution. The mixture was placed under nitrogen atmosphere, then heated to 80 °C while stirring, forming a clear yellow solution, and then held at 80 °C

for 30 min. Then, the temperature was quickly ramped to 260 °C and held for 2 h, turning into a dark brown solution, and then cooled to room temperature. The reaction mixture was purified by a series of centrifugation steps. First, the crude reaction mixture was transferred to a Falcon tube and precipitated using ~ 30 mL of acetone, followed by centrifugation at 8000 rpm for 10 min. The supernatant (typically a clear light brown on the first crash out) was poured off, and the pellet was redissolved in hexanes. The solution was crashed out twice more with additional acetone. The final pellet was redissolved in hexanes. The particle solution in hexanes is used for TEM sample preparation, XPS sample preparation, XRD sample preparation, and PL/PLE/TRPL sample preparation.

Instrumentation and Characterization Methods

Transmission electron microscopy (TEM) images were obtained with a FEI Tecnai G2 F20 SuperTwin microscope operated at 200 kV using bright field imaging. All samples were prepared by drop-casting 5 μL of sample dissolved in hexanes onto a suspended ultrathin carbon film on lacey carbon support film, 400 mesh, copper grids purchased from Ted Pella, Inc. The samples were allowed to dry in air for 5 min until the hexanes evaporated. All grids were placed under vacuum overnight to ensure complete dryness before imaging.

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Discover diffractometer at 50 kV with 1000 μA via a Cu anode microfocus X-ray source ($\lambda = 1.5406$ Å) and a Pilatus 100 K large-area detector. The beam for the measurement was collimated to a 1 mm beam diameter, and collection times were 30–90 s per step (5.5° 2θ step size). Raw diffraction data were processed using Bruker DIFFRAC.EVA software, and peaks were fitting with Pseudo-Voigt multipoint functions using Python.⁴⁸ As-synthesized samples were prepared by repeatedly drop-casting 5 μL of sample suspended in hexanes onto a Si wafer to build up a thick film of sample. Annealed samples were prepared by the same method as as-synthesized samples and then annealed under a furnace at 700 °C for 2 h.

Elemental analysis was performed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a PerkinElmer Optima 3000. Samples were digested for 48 h in a 1:1 conc H_2O_2 (30% w/w) to conc HNO_3 (67–70% w/w), and then filtered through a PTFE filter and diluted to 2% HNO_3 for analysis.

Thermogravimetric analysis (TGA) data were collected on a TA Instruments TGA Q5000 under ambient atmosphere at a scan rate of 10 °C/min.

Annealing was performed in a quartz tube using a Lindberg/Blue M Mini-Mite Tube Furnace with ambient air flow. The temperature was raised to 700 °C at a rate of 10 °C/min and kept at 700 °C for 2 h.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis-Ultra DLD spectrometer. This instrument has a monochromatized Al $K\alpha$ X-ray and a low energy electron flood gun for charge neutralization. X-ray spot size for these acquisitions was on the order of $700 \times 300 \mu\text{m}$. The electrostatic lens was used for data collection. Pressure in the analytical chamber during spectral acquisition was less than 5×10^{-9} Torr. Pass energy for survey spectra (composition) was 160 eV. Pass energy for the high-resolution spectra was 40 eV. The takeoff angle (the angle between the sample normal and the input axis of the energy analyzer) was 0° (0-degree takeoff angle ~ 100 Å sampling depth). The Kratos Vision2 software program was used to determine peak areas and to calculate the elemental compositions from peak areas. CasaXPS was used to peak fit the high-resolution spectra. For the high-resolution spectra, a Shirley background was used, and all binding energies were referenced to the C 1s C–C bonds at 285.0 eV. As-synthesized samples were prepared by repeatedly drop-casting 5 μL of sample suspended in hexanes onto a Si wafer to build up a thick film of sample. Annealed samples were prepared by the same method as as-synthesized samples and then annealed under a furnace at 700 °C for 2 h.

UV–visible (UV–vis) absorption measurements were collected on an Agilent Cary 5000 UV–Vis–NIR spectrophotometer in dual beam mode. All UV–vis data were collected by solid state measurements of samples drop-casted onto fused silica windows.

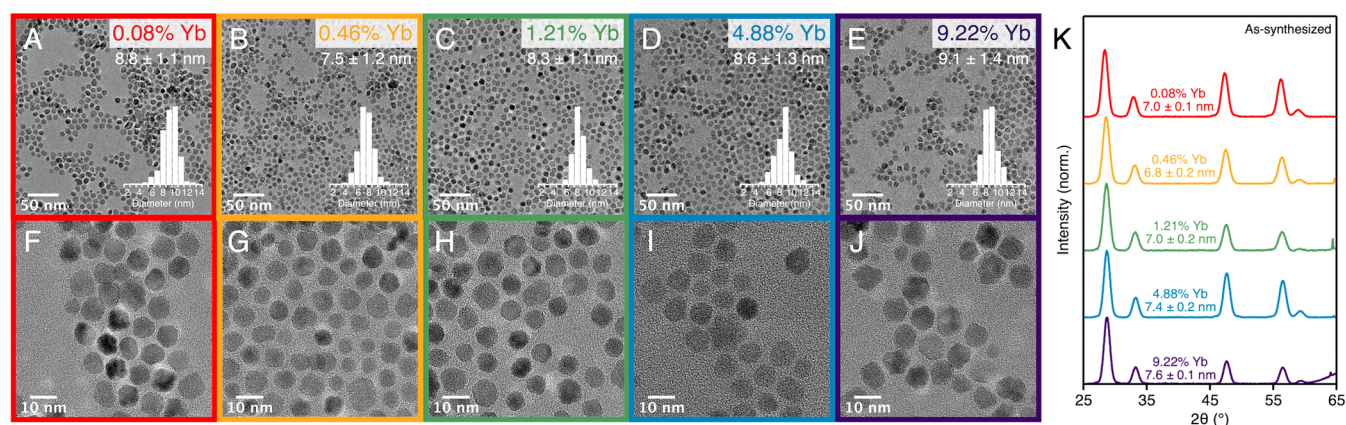


Figure 1. (A–E) TEM, (F–J) HR-TEM, and (K) PXRD of as-synthesized $\text{CeO}_2\text{:Yb}^{3+}$ nanocrystals.

Room temperature photoluminescence (PL), photoluminescence excitation (PLE), and time-resolved photoluminescence (TRPL) measurements were collected on an Edinburgh FLS1000 photoluminescence spectrometer equipped with a 450 W ozone-free Xenon arc lamp, a microsecond Xenon flashlamp, and an NIR PMT (PMT-1700). All PL, PLE, and TRPL data were collected using samples drop-cast onto fused silica substrates.

Variable temperature photoluminescence (PL) measurements were performed by drop-casting the samples onto a sapphire disk, which was covered by a secondary sapphire disk and loaded into a closed-cycle helium cryostat. The sample was brought under high vacuum (10^{-6} Pa) and cooled to 4 K. Sample emission was measured upon direct excitation of Yb^{3+} using a tunable continuous-wave Ti:sapphire laser with a spectral bandwidth of <0.01 nm, configured to lase in the 900–1000 nm range. The excitation wavelength was set to the $0 \rightarrow 2'$ transition (915 nm) as determined through PLE (see below). Sample emission was collected and focused into a monochromator with a spectral resolution of 0.02 nm. Spectra were recorded using a LN₂-cooled silicon CCD camera. All spectra were corrected for instrument response.

Variable-temperature time-resolved photoluminescence (TRPL) measurements were performed using the same general setup as described above for variable-temperature PL measurements. Indirect excitation of the samples was performed using the third harmonic of a Nd:YAG laser at 355 nm with a pulse duration of 20 ps and a repetition rate of 50 Hz. TRPL measurements using direct excitation of Yb^{3+} were performed by passing the Ti:sapphire laser beam through an acousto-optic modulator (AOM). The excitation wavelength was set to the $0 \rightarrow 0'$ transition (~ 965 nm) as determined through PLE (see below) and was optimized at every temperature point to account for shifts in the excitation peak position. A DS345 function generator was used to provide a custom square wave input signal to the AOM to control laser on- and off times. Pulses were configured with an on time of 100 μs and a 50 Hz repetition rate. For both excitation schemes, sample emission was focused onto a monochromator (10.7 nm spectral bandwidth), collected on a LN₂-cooled Hamamatsu InGaAs/InP NIR photomultiplier tube, and sent to an SR430 photon counter to generate the TRPL data. Emission was monitored at the $0' \rightarrow 4$ transition (1039 nm) and a time resolution of 1.28 μs was used for data binning.

Low temperature photoluminescence excitation (PLE) measurements were performed using the same general setup as described above for variable temperature PL measurements. Using the CCD camera, emission spectra were collected every 200 ms while the Ti:sapphire excitation wavelength was continuously scanned at a rate of approximately 0.15 nm/s. The excitation wavelength and sample emission were captured simultaneously on the CCD, using a 950 nm long-pass filter to reduce the laser intensity on the detector. For every spectrum, the excitation wavelength was extracted by fitting the laser peak with a Gaussian function. Sample emission in the 960–1050 nm range was integrated for every spectrum to provide the corresponding

PLE intensity. The resulting PLE spectrum was corrected for laser output power at every point.

Continuous-wave X-band (CW) electron paramagnetic resonance (EPR) spectra at 9.4 GHz and 5 K were collected on a Bruker EMX spectrometer equipped with a Bruker SHQE resonator and an Oxford Instruments ESR900 cryostat. Pulse X-band EPR experiments were performed at 9.7 GHz and 4 K on a Bruker ElexSys E580 spectrometer equipped with a 1 kW amplifier, a Bruker MD4 resonator, and an Oxford Instruments CF9350 cryostat. For both CW and pulse experiments, the cryostats were cooled with liquid helium, and the temperature was set with an Oxford Instruments ITC503 temperature controller. Pulse experiments used rectangular monochromatic 16 ns $\pi/2$ and 32 ns π pulses. Echo-detected field sweeps and Hahn echo decay experiments were done with $\pi/2$ - τ - π - τ -echo pulse sequences. Inversion recovery experiments were done with a π - T - $\pi/2$ - τ - π - τ -echo pulse sequence. As-synthesized samples were prepared by diluting a sample into toluene and freezing the sample in LN₂. Annealed samples were annealed as described above, the flakes/powder (few mg) were collected and dispersed with sonication to form a suspension in toluene, followed by freezing the sample in LN₂.

RESULTS AND DISCUSSION

Synthesis and Photoluminescence of Yb^{3+} -Doped CeO_2 Nanocrystals

Yb^{3+} -doped CeO_2 ($\text{CeO}_2\text{:Yb}^{3+}$) was synthesized by thermal decomposition of cerium(III) nitrate ($1-x$ eq), ytterbium(III) nitrate ($x = 0.001, 0.005, 0.01, 0.05, \text{ and } 0.1$ equiv), and oleylamine (3 equiv) in a bath of 1-octadecene, adapted from a previously reported method.⁴⁷ The resulting oleylamine-capped nanocrystals were colloiddally stable in nonpolar solvents and characterized via transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD), as shown in Figure 1. Yb^{3+} concentrations within the CeO_2 nanocrystals were measured by inductively coupled plasma–optical emission spectroscopy (ICP–OES) and are reported in Figure 1 for the corresponding nanocrystal samples, showing that Yb^{3+} is incorporated close to the intended doping percentage (0.1, 0.5, 1, 5, and 10%, respectively). High-resolution TEM (HR-TEM) images revealed spherical, highly crystalline particles with lattice fringes assigned to the (111) plane of the fluorite lattice (Figure S1). A comparison of the size distributions measured by manual TEM image analysis to the Scherrer analysis of the XRD using pseudo-Voigt fits indicated a small discrepancy between the observed nanocrystal diameters and nanocrystalline domain sizes for each $\text{CeO}_2\text{:Yb}^{3+}$ sample (Figure S2 for PXRD peak fittings).⁴⁸ For example, the

0.08% Yb sample appears to have an average measured diameter of 8.8 ± 1.1 nm by TEM but an average crystalline domain size of 7.0 ± 0.1 nm via Scherrer analysis. On average, the crystalline domain size is ~ 1.3 nm smaller than the measured nanocrystal size by TEM. This result suggests that the as-synthesized nanocrystals may have a defect-rich surface layer of Ce^{3+} and oxygen vacancies that reduce the overall crystalline domain. Prior literature has demonstrated that the (111) surface plane is prone to a reduced Ce^{3+} shell with an average thickness of ~ 0.8 nm, which may account for the discrepancy in TEM and XRD sizes.⁴⁹

We first investigated the optical properties of the as-synthesized nanocrystals as a function of Yb^{3+} concentration. We initially probed the CeO_2 -sensitized excitation of Yb^{3+} at 300 K using a broadband xenon arc lamp set at 320 nm (Figure S3), which falls at the tail end of the broad absorption band peaking at ~ 290 nm observed in the UV–vis absorption spectra. This band corresponds to the charge–transfer transition originating from the CeO_2 O^{2-} $2p$ valence band to Ce^{4+} $4f$ orbitals (Figure 2A).³⁹ Upon 320 nm excitation, we

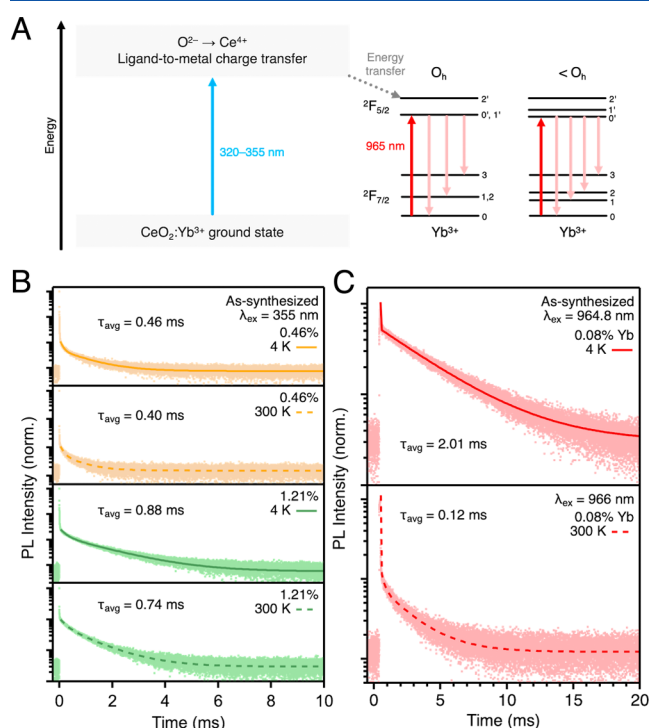


Figure 2. (A) Scheme of electronic transitions of Yb^{3+} -doped CeO_2 with arrows showing indirect (blue) and direct (red) excitation and Yb^{3+} emission (light pink). Comparison of Yb^{3+} TRPL by (B) indirect excitation ($\lambda_{\text{ex}} = 355$ nm, $\lambda_{\text{em}} = 1039$ nm) of as-synthesized **0.46% Yb** and **1.21% Yb** at 4 and 300 K, and (C) direct excitation ($\lambda_{\text{ex}} = 965$ – 966 nm, $\lambda_{\text{em}} = 1039$ nm) of **0.08% Yb** at 4 and 300 K.

observed characteristic emission of Yb^{3+} between 960–1100 nm, indicating successful energy transfer from the wide-bandgap CeO_2 (3.3–3.6 eV) to Yb^{3+} .^{50–52} Signal-to-noise improved with increasing Yb^{3+} concentration, consistent with an increase in energy capture by Yb^{3+} . Time-resolved photoluminescence (TRPL) measurements were collected at 300 K using a μs -pulsed xenon flash lamp and showed poor signal with an initial fast-decay component on the same time scale as the instrument response, as well as a low-intensity slow-decay component, making it difficult to extract accurate

lifetimes for comparison. An instrument response function collected under identical conditions confirmed that the initial fast decay is limited by the instrument (Figure S4). We observed a general trend of lengthening the slow-decay component as the Yb^{3+} concentration decreased from **9.22% Yb** to **0.08% Yb**.

When we cooled the as-synthesized **0.46% Yb** and **1.21% Yb** samples to 4 K, we observed that the Yb^{3+} emission line widths narrowed, but broad defect emission became more prominent between 700–1000 nm (Figure S5A,D). Additionally, we did not observe a significant increase in Yb^{3+} slow-decay component lifetimes nor a decrease in the fast-decay component at 4 K that would indicate freezing out of nonradiative decay pathways (Figure 2B, Table S1). This result suggests that defect states in the as-synthesized nanocrystals remain active even at low temperatures. To mitigate the effects of CeO_2 's native defects on the efficiency of energy transfer to Yb^{3+} , we switched to direct excitation of the Yb^{3+} with a tunable Ti:sapphire laser set to 965 nm (4 K) or 966 nm (300 K) to account for temperature-dependent changes in the Yb^{3+} absorption (Figure 2C, Table S2). We not only observed a reduction of the fast-decay component but also a lengthening of the slower component, which is reflected in an overall increase of the amplitude-weighted average lifetime (τ_{avg}) at both 4 and 300 K compared to indirect excitation. Nevertheless, a significant fraction of the total Yb^{3+} emission is released with a microsecond lifetime, much faster than the typical radiative decay times of Yb^{3+} (ms), likely indicating the presence of defects in close proximity to Yb^{3+} . To reduce defect density and improve overall crystal quality, we investigated the influence of sample annealing (see the Experimental Methods).

As mentioned above, it is well-known that cerium oxide is prone to oxygen vacancy defects when aliovalent dopants are introduced into the lattice, yielding nonstoichiometric CeO_{2-x} that is charge-compensated by Ce^{3+} ions.^{26–29,39} Previous studies have shown that annealing cerium oxide at 500 °C or higher in an oxidizing environment yields larger crystalline domains, reoxidizes Ce^{3+} to Ce^{4+} , and improves the rare earth's luminescence.^{41,53} Tracking these simple parameters allows us to investigate the extent to which annealing can improve the optical and, importantly, the spin coherence properties. After annealing, TEM and XRD measurements show that the nanocrystalline domain size and nanoparticle size both significantly increased for all concentrations from an average crystalline domain size of ~ 7 nm to ~ 20 nm (Figures 3A–C, S6 for PXRD peak fittings). Visually, the nanocrystal film, which appeared dark brown before annealing due to its high concentration of Ce^{3+} and associated oxygen vacancies (CeO_{2-x}), turned a lighter golden color after annealing.⁵⁴ This color change suggests a decrease in Ce^{3+} and oxygen vacancies and more stoichiometric CeO_2 . We note that the organic oleylamine ligands are burned off at this annealing temperature, leaving bare crystalline surfaces (Figure S7). We confirmed the decrease of Ce^{3+} by X-ray photoelectron spectroscopy, as shown in Figure 3D,E, where the high-resolution Ce $3d$ spectra indicate a smaller Ce^{3+} percentage (shaded area, Figure S8 for peak fitting) after annealing. On average, we observed a decrease in the relative Ce^{3+} content by approximately one-third.

Room-temperature PL data for the annealed nanocrystals as a function of Yb^{3+} concentration are shown in Figure S9. We repeated the CeO_2 -sensitized excitation of Yb^{3+} at 300 K using

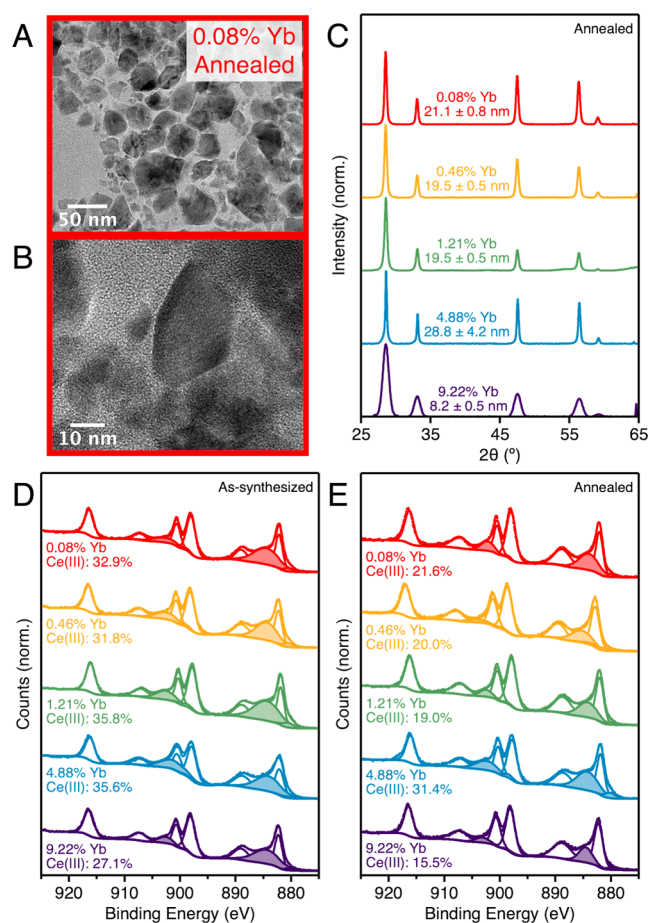


Figure 3. Representative (A) TEM and (B) HR-TEM of **0.08% Yb** showing morphology after annealing. (C) PXRD of $\text{CeO}_2:\text{Yb}^{3+}$ after annealing. High-resolution Ce 3d XPS spectra of $\text{CeO}_2:\text{Yb}^{3+}$ (D) as-synthesized and (E) after annealing (shaded area indicates Ce^{3+}).

a broadband xenon arc lamp set to 320 nm and confirmed the expected improvements in the signal-to-noise for both the PL and TRPL. We attribute these improvements to a reduction in defects, such as Ce^{3+} and oxygen vacancies, that cause unwanted nonradiative decay. In addition, it is suggested that Yb^{3+} ions migrate during annealing, decreasing the concentration of Yb^{3+} ions present in clusters and on the surface (*vide infra*).⁴¹

After confirming the improvements induced by annealing using indirect photoexcitation ($\lambda_{\text{ex}} = 320$ nm) at room temperature, we measured the Yb^{3+} TRPL with direct excitation ($\lambda_{\text{ex}} = 965\text{--}966$ nm, $\lambda_{\text{em}} = 1039$ nm) at 4 K (Figure 4A, Table S3). These data show significantly improved signal-to-noise and extended lifetimes, which fit well to monoexponential decay profiles up to **1.21% Yb^{3+}** . The variable temperature (VT) TRPL data in Figure 4B show that lowering the temperature from 300 to 4 K results in a substantial increase in the lifetime from 1.36 to 2.53 ms at the lowest dopant concentration, **0.08% Yb**. VT-TRPL data for the other Yb concentrations are shown in Figure S10.

Figure 5A shows low-temperature PL spectra of annealed $\text{CeO}_2:\text{Yb}^{3+}$ collected using 915 nm excitation. The spectra reveal an interesting trend: as the Yb^{3+} concentration increases, peak intensities at 965 and 972 nm decrease and increase, respectively. This observation suggests the presence of two emissive Yb^{3+} sites contributing to the spectrum. By varying

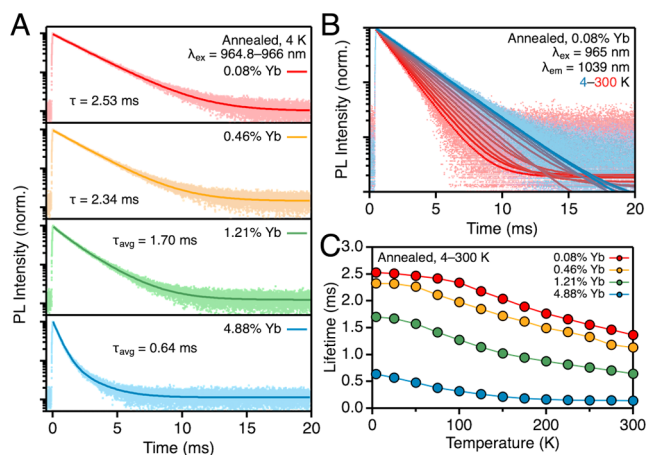


Figure 4. (A) TRPL of annealed $\text{CeO}_2:\text{Yb}^{3+}$ samples at 4 K using direct excitation at $\lambda_{\text{ex}} = 965\text{--}966$ nm ($\lambda_{\text{em}} = 1039$ nm). (B) Representative VT-TRPL of **0.08% Yb** using direct excitation at $\lambda_{\text{ex}} = 965$ nm ($\lambda_{\text{em}} = 1039$ nm) and (C) lifetimes of annealed $\text{CeO}_2:\text{Yb}^{3+}$ samples from 4 to 300 K.

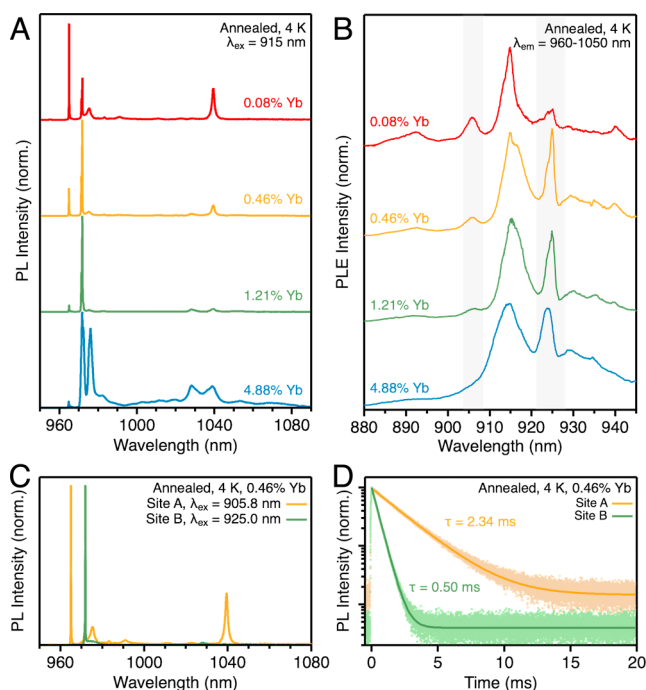


Figure 5. (A) PL and (B) PLE of annealed $\text{CeO}_2:\text{Yb}^{3+}$ at 4 K. Shaded regions show changes in the intensity of ~ 905 nm and ~ 925 nm PL features as the Yb^{3+} concentration changes. Overlay of (C) PL and (D) TRPL of Yb^{3+} **Site A** ($\lambda_{\text{ex}} = 965$ nm; $\lambda_{\text{em}} = 1039$ nm) and **Site B** ($\lambda_{\text{ex}} = 972$ nm; $\lambda_{\text{em}} = 1028$ nm) in **0.46% Yb**.

the Yb^{3+} density in the lattice, we can manipulate the ratio of PL from these two sites, yielding distinct emission spectra. Our observation was confirmed by measurement of PL excitation (PLE) spectra for these samples, which revealed changes in relative intensity around 905 and 925 nm, highlighted in gray in Figure 5B, that we attribute to the changing ratio of two different Yb^{3+} site populations within the CeO_2 lattice. When excited at 905 nm, assigned as **Site A**, the PL spectrum shows its highest intensity at 965 nm and a weaker peak at 1039 nm. Excitation at 925 nm gives the spectrum of **Site B**, which shows its highest intensity at 972 nm and two smaller features at 1028 and 1038 nm that overlap with the strong 1039 nm

Site A peak. Both spectra are isolated in Figure 5C. As for the as-synthesized samples, we see peaks corresponding to both **Site A** and **Site B**, however there is a broad signature with at least three peaks around where **Site B** emits, which may be due to variations in the orientation of the **Site B** Yb^{3+} that are resolved into a single **Site B** orientation after annealing (Figure S11).

When measuring TRPL of the lowest-energy $f-f$ transitions from each site (1039 and 1028 nm for **Site A** and **Site B**, respectively) in the 0.46% Yb sample, we observed that the **Site A** lifetime is approximately $5\times$ longer than the **Site B** lifetime (Figure 5D, Table S4). A similar $4\times$ lifetime difference between Yb^{3+} sites has been observed in Yb^{3+} -doped CeO_2 using parallel factor analysis.⁴¹ In that work, one site had dominant peaks at 965 and 975 nm. The 965 nm peak is prominently observed in the PL spectrum of **Site A** (Figure 5C). The 975 nm peak is also observed in our **Site A** spectra, but it is much less intense than the other two features at 965 and 1039 nm. The second site showed a dominant peak at 972 nm,⁴¹ closely aligning with our observations.

Additional studies have used the characteristic peaks of Yb^{3+} to identify the specific crystal-field symmetries of the two Yb^{3+} sites (Figure 6).^{41,55} Specifically, they assign the 968, 978, and

Given the similarity in positions and intensities of our spectra to theirs, we can associate our **Site A** spectrum (965, 975, and 1039 nm emission lines) with the O_h site and our **Site B** spectrum (971 and 1028 nm emission lines) with the C_{3v} site. We note that previous work differentiated between two types of C_{3v} sites, one formed by vacancy of the nearest O^{2-} anion proximal to the Yb^{3+} and one formed by an OH^- group substituting for an O^{2-} anion proximal to the Yb^{3+} , but these cannot be confidently differentiated in our PL spectra (*vide infra*). Finally, it is worth mentioning that tetragonal (C_{4v}) Yb^{3+} sites have also been reported in cerium oxide,³⁹ but this site is not observed in our samples.

Electron Paramagnetic Resonance Spectroscopy of $\text{CeO}_2:\text{Yb}^{3+}$

We investigated the spin properties of the lowest-lying Kramers doublet of the $^2F_{7/2}$ level using EPR spectroscopy. Continuous-wave (CW) EPR spectra of the 0.46% and 0.08% Yb samples before and after annealing are shown in Figure 7A,B. We observe a characteristic Yb^{3+} feature at ~ 200 mT ($g \sim 3.42$) attributable to a cubic Yb^{3+} site of nonmagnetic Yb^{3+} isotopes within the CeO_2 lattice, consistent with previous $\text{CeO}_2:\text{Yb}^{3+}$ EPR studies ($g \sim 3.43$).^{37,39,40} This line is flanked by hyperfine lines due to the magnetic isotopes ^{171}Yb (spin 1/2) and ^{173}Yb (spin 5/2).

Detailed EPR investigations of $\text{CeO}_2:\text{Yb}^{3+}$ have identified two types of trigonal sites that are formed by defects in bulk $\text{CeO}_2:\text{Yb}^{3+}$ crystals, trigonal site I ($g_{\perp} = 2.744$, $g_{\parallel} = 4.733$), due to an adjacent oxygen vacancy, and trigonal site II ($g_{\perp} = 3.060$, $g_{\parallel} = 4.152$), due to OH^- in place of an adjacent O^{2-} ion.^{37,38,40,56,57} The $g_{\perp}$ features are generally more pronounced than the $g_{\parallel}$ features. We observe the trigonal site I ($g \sim 2.76$) only in the 0.46% Yb sample, indicating a higher density of oxygen vacancies at increased Yb^{3+} concentrations. There is no clear evidence of Yb^{3+} in trigonal site II, but detection of trigonal site II is complicated by overlap with ^{171}Yb hyperfine lines. Simulated EPR spectra including trigonal sites I and II are shown in Figure S12. Previously, we noted that **Site B** cannot be assigned to a specific trigonal site based on our PL data. However, we see an increase in **Site B** intensity from 0.08% Yb to 0.46% Yb , similar to that of trigonal site I, suggesting that **Site B** is associated with trigonal site I.

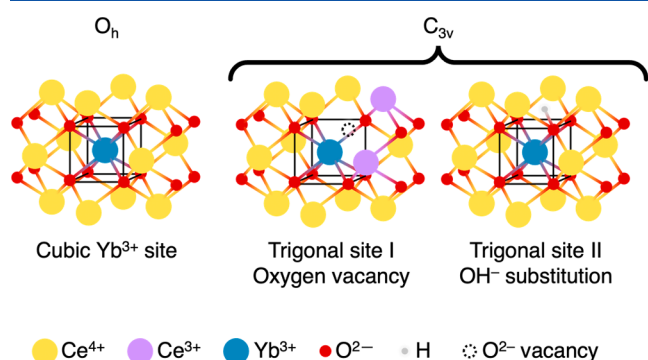


Figure 6. Schematic representation of local Yb^{3+} site geometries with possible arrangements demonstrating octahedral (O_h) and trigonal (C_{3v}) symmetries and associated distortions.

1041 nm emission lines to a site with O_h symmetry and the 975 and 1031 nm emission lines to a site with C_{3v} symmetry.³⁹

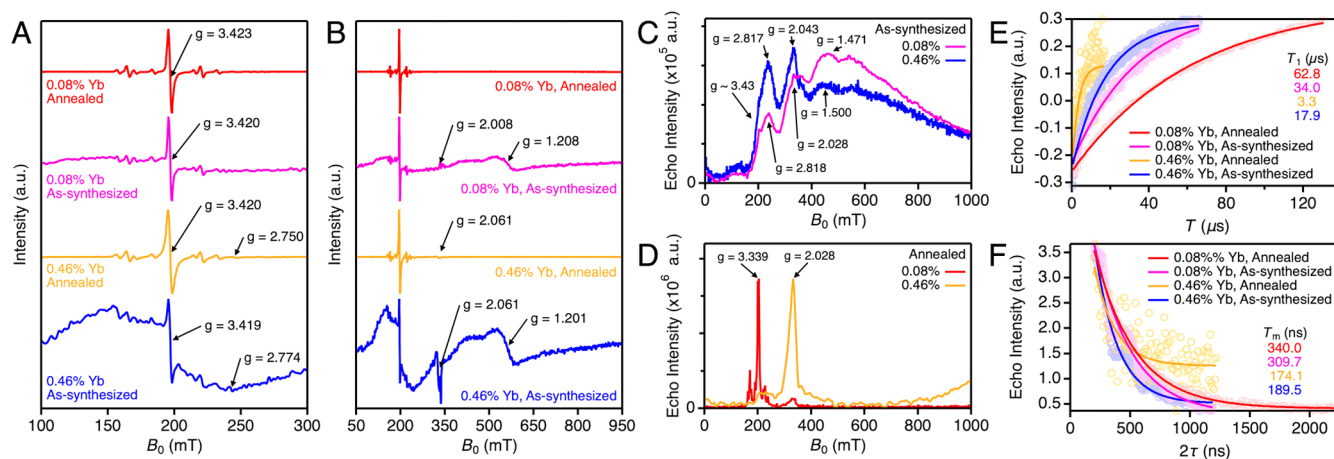


Figure 7. CW EPR (9.4 GHz, 5 K) spectra of (A) Yb^{3+} features and (B) CeO_2 defect features from as-synthesized and annealed 0.08% Yb and 0.46% Yb samples. Pulse EPR (9.7 GHz, 5 K) measurements including EDFS spectra of (C) as-synthesized and (D) annealed 0.08% Yb and 0.46% Yb samples, and (E) inversion recovery and (F) Hahn echo decay of 0.08% Yb and 0.46% Yb samples at 202 mT.

The feature at 335 mT ($g \sim 2$) in the **0.46% Yb** samples (Figure 7B) and the **0.08% Yb** as-synthesized sample is hypothesized to be indicative of adsorbed superoxo species, O_2^- , with one unpaired electron (g values ranging from 2.005–2.05), either adsorbing to Ce^{4+} ions or filling O^{2-} vacancies, as described by several prior studies.^{58–60} The other significant feature in Figure 7B at ~ 560 mT ($g \sim 1.20$) has been correlated to a nearly cubic Ce^{3+} site, with Constantini and co-workers demonstrating that the site symmetry has slight g -factor anisotropy and yields a range of g values from 1.14 to 1.44 due to the presence of distant defects (the homogeneous cubic site has $g = 1.266$ at 4.2 K).⁶¹ After annealing, the intensity of this feature is significantly reduced, in agreement with the observed decrease in Ce^{3+} concentration by XPS (Figure 3). It is worth noting that the Ce^{3+} resonance is often incorrectly associated with a feature at $g = 1.96$ – 1.97 due to an electron trapped in an oxygen vacancy.^{61,62} These observations are consistent with an increase in charge compensation from the charge mismatch created by the substitution of Yb^{3+} on the native Ce^{4+} sites. Annealing significantly reduces the concentrations of Ce^{3+} and O_2^- spin centers, while the signal of Yb^{3+} in cubic sites noticeably increases.

Echo-detected field-sweep (EDFS) spectra of the as-synthesized samples yield additional insight. We observed the characteristic Yb^{3+} feature at 202 mT ($g \sim 3.43$) as a shoulder of the second peak within a series of overlapping broad peaks at 110, 230, 350, 460, and 550 mT (Figure 7C). These broad peaks have not been fully identified in the literature, but we note them as possible defects that merit further investigation. Interestingly, as shown in Figure 7D, the difference between the annealed **0.08% Yb** and **0.46% Yb** samples becomes very prominent in the EDFs. The **0.08% Yb** has a sharp 201 mT peak ($g = 3.339$) while the **0.46% Yb** sample is dominated by a 350–360 mT peak with a small peak at 201 mT. The 360 mT feature is associated with the previously mentioned adsorbed superoxo species O_2^- (g values ranging from 2.005–2.05). We also note that the signal at 201 mT increased upon annealing in **0.08% Yb** but decreased with annealing in **0.46% Yb**. The decrease after annealing in **0.46% Yb** contrasts with the increase in the CW EPR signal, which is less limited by spin coherence and relaxation times.

For quantum applications, long electron spin coherence times are desired. We therefore probed the phase memory times (T_m) in these samples via Hahn echo decays and the longitudinal spin relaxation time T_1 via inversion recovery. The phase memory time is determined by several decoherence mechanisms and is ultimately limited by T_1 . Large T_1 and T_m are critical for qubit fidelity.⁶³ For the **0.08% Yb** samples, the annealed sample shows a longer T_1 (62.7 μ s) than the as-synthesized sample (33.9 μ s) (Figure 7E). However, comparable T_m values for the annealed (339 ns) and as-synthesized (309 ns) samples (Figure 7F) suggest that although T_1 doubles, annealing may not yield a corresponding improvement in coherence times. This result implies that the dominant decoherence pathway is dephasing due to fluctuating local fields, such as Yb–Yb interactions, residual paramagnetic surface defects, adsorbed superoxo species, local symmetry variations, or other sources of spectral diffusion, rather than T_1 relaxation of excited spins. Additionally, as the Yb^{3+} concentration increases to 0.46%, we see much shorter T_1 and T_m lifetimes for both as-synthesized and annealed samples. Due to the low signal-to-noise ratio of the data from the annealed **0.46% Yb** sample, no clear annealing effects are

observed in the T_1 or T_m at this Yb^{3+} concentration. In both the **0.08%** and **0.46%** as-synthesized samples, their echo decays show electron spin echo envelope modulation (ESEEM) oscillations of 8.6(2) MHz and 8.8(2) MHz, respectively (Figure S13); these modulations are ascribed to 1H , which has a Larmor frequency of 8.60 MHz at 202 mT. The 1H modulations disappear after annealing, suggesting that they originate from the oleylamine ligands that are burnt off during annealing. In comparison to previously reported $CeO_2:Er^{3+}$ nanocrystal studies, ensembles of ~ 7 nm nanocrystals doped with an estimated 13.2–0.3 Er^{3+} ions per nanocrystal were demonstrated to have T_m lifetimes of ~ 170 – 780 ns, and thin-films of $CeO_2:Er^{3+}$ at single ppm concentrations have reported T_m lifetimes of ~ 0.7 – 38.8 μ s or longer with different pulse sequences.^{9,33,34} While our **0.08% Yb** sample is significantly higher in Yb^{3+} concentration, our coherence lifetimes after annealing are similar to $CeO_2:Er^{3+}$ nanocrystal ensembles reported at ~ 3 dopants per nanocrystal.⁹ Our data thus point to the possibility of improving upon the current metrics by further decreasing the Yb^{3+} concentration to single-digit numbers of atoms within each nanocrystal (Table S5).

CONCLUSION

In conclusion, we report a systematic investigation of Yb^{3+} as an optically active and spin-bearing dopant within nanocrystalline CeO_2 . We observed that Yb^{3+} incorporation is near stoichiometric from 10% to 0.01% Yb; however, the accompanying oxygen vacancies, surface effects arising from the nanocrystal size, and the presence of Ce^{3+} result in poorly emitting nanocrystals in the as-synthesized state. Investigation of the Yb^{3+} PL revealed the presence of efficient nonradiative decay processes that compete with the desired PL, even at low temperatures. EPR measurements at 4–5 K indicate the presence of oxygen vacancies in close proximity to Yb^{3+} centers, which not only reduce the cubic site symmetry but may also facilitate unwanted nonradiative decay. After annealing at 700 °C for 2 h, the nanocrystal quality is significantly improved. We observed a decrease in Ce^{3+} concentration by XPS and improved signal-to-noise in the PL spectra, indicating that annealing helps mitigate the defects interacting with Yb^{3+} . However, pulse EPR measurements show that although annealing improves the spin lifetime (T_1), the coherence lifetime (T_m) is largely unaffected and may be limited by fluctuating local fields that dephase the electron spins. As CeO_2 gains increasing attention as a promising host lattice for quantum information processing, this work highlights several complicating aspects of its nanocrystalline structure and identifies annealing as one common experimental handle that can be used to control them. By combining low-temperature PL with CW and pulse EPR data on $CeO_2:Yb^{3+}$ nanocrystals, we directly connect dopant concentration and host-defect chemistry to qubit-relevant optical and spin-relaxation metrics, establishing quantitative benchmarks and a defect-engineering roadmap for scalable rare earth spin qubits in wide-bandgap colloidal hosts. To address the remaining challenges with limited coherence beyond low dopant concentrations, it is suggested that exploring alternative synthesis methods that yield CeO_2 with fewer paramagnetic Ce^{3+} sites, removal of surface species and defects with higher temperature annealing or additional encapsulation of the nanocrystals in a matrix or shell, and higher precursor purity are possible handles to improve the current benchmarks. While

these defects do not preclude the use of CeO₂ as a qubit platform, addressing the complexity within this system will require further investigation into defect formation and tunability to fully leverage CeO₂ for quantum applications.

■ ASSOCIATED CONTENT

Data Availability Statement

The original experimental data presented in this work is freely available at <https://doi.org/10.5281/zenodo.20532018>.

■ Supporting Information

This manuscript is available as a preprint on ChemRxiv at <https://chemrxiv.org/doi/full/10.26434/chemrxiv.15000731>. The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.6c01017>.

General experimental methods, instrumentation and characterization details, supplementary figures of XRD patterns and pseudo-voigt fittings, optical characterization at 300 and 4 K, XPS spectra and fittings, additional analysis of the EPR data (PDF)

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Notes

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