

RESEARCH ARTICLE | MARCH 27 2024

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J. Appl. Phys. 135, 124302 (2024)

<https://doi.org/10.1063/5.0188938>



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Cite as: J. Appl. Phys. **135**, 124302 (2024); doi: [10.1063/5.0188938](https://doi.org/10.1063/5.0188938)

Submitted: 25 November 2023 · Accepted: 12 March 2024 ·

Published Online: 27 March 2024



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ABSTRACT

This work presents the influence of host defect centers on the photoluminescence characteristics of $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01$, and 0.03) nanocrystals under UV and near-infrared (NIR) excitations. The spinel-structured nanocrystals are synthesized through the combustion method. The Rietveld refinement and nuclear magnetic resonance analyses estimated the Er^{3+} ion occupancy at octahedral and other random sites of the MgAl_2O_4 lattice, and the existence of various lattice defects. Diffuse reflectance spectra showed broad bands attributed to oxygen vacancies as well as antisite defects and sharp peaks attributed to $f-f$ transitions of Er^{3+} ions. The upconversion luminescence spectra consisted of sharp emission lines, ascribed to Er^{3+} ions, in the green and red wavelength regions, which overlapped over the broad curve attributed to intrinsic defects. Further, the UV excited downconversion luminescence spectra showed two broad emission bands in blue-violet and red-NIR regions with a very weak Er^{3+} ion emission feature. This up- and downconversion emission revealed energy transfer between host and Er^{3+} ions via intrinsic defects. As a result, the emission color changes from bluish purple to white by varying the excitation wavelength from UV to NIR. This rare earth activated luminescence from MgAl_2O_4 nanocrystals would exhibit potential applications in display devices and solid-state lighting.

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I. INTRODUCTION

Recently, trivalent rare earth (RE) doped nanocrystals have evoked enormous interest owing to their unique luminescence properties, such as sharp emission bandwidths, large Stokes shifts, low auto-fluorescence, long emission lifetimes, high signal-to-noise ratio, as well as low light scattering under near-infrared (NIR) excitation.^{1–3} Their NIR triggered upconversion and UV/Vis/NIR triggered downconversion photoluminescence exhibited promising applications in solid-state lighting,^{2,4} optical thermometry,^{5,6} fiber lasers,⁷ bioimaging,⁸ etc. Considering the luminescence properties, the erbium (Er^{3+}) ion acts as an outstanding activator for

NIR (at $1.5\ \mu\text{m}$) and visible light (in green and red regions) emission because of its favorable electronic energy level structure with equally spaced long-lived excited states. Additionally, the Er^{3+} doped systems can be easily pumped by a low-cost and high-power NIR diode laser and find applications in various photonic devices.^{3,4,9–12} Further, the fluoride based upconversion nanoparticles have gained more interest in recent years due to their low phonon energy. The important luminescent fluoride host is NaYF_4 . However, the poor chemical stability may result in environmental issues due to toxicity. Thus, oxide-based hosts are preferred over fluorides due to their high mechanical strength, low-cost, high chemical, and temperature stability.^{13–15}

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The MgAl_2O_4 spinel may exhibit compositional deviation from the standard stoichiometry attributed to the presence of structural vacancies and cation disorder. Thus, it can provide room for the doping of RE ions.^{16–18} The high thermal and chemical stability, wide energy bandgap, and easy and low-temperature synthesis make it a suitable matrix to tailor its optical properties with RE ion doping.¹⁹ Moreover, the comparatively lower phonon frequency of the MgAl_2O_4 host ($\sim 670\text{ cm}^{-1}$) than other oxide-based phosphors will lead to efficient up- and downconversion photoluminescence with reduced non-radiative relaxation probability.²⁰ The Er^{3+} ion with a large ionic radius can either substitute the octahedral (M)/tetrahedral (T) sites occupied by $\text{Al}^{3+}/\text{Mg}^{2+}$ ions or free lattice interstices by inducing lattice strain and distortion in the host lattice. Van den Hoven *et al.* reported that 70% of the Er reside on displaced, free octahedral sites, while some at tetrahedral and random sites of the $\alpha\text{-Al}_2\text{O}_3$ crystal.²¹ The octahedral site of the Er^{3+} ion was the dominant luminescent site. Similar occupancy of Er^{3+} ion at the displaced Li octahedral site is reported by Rebouta *et al.* for LiNbO_3 crystals.²² According to the available research analysis, it is found that there is no prior research of the host's influence on the Er^{3+} dopant emission in the MgAl_2O_4 matrix. Thus, Er^{3+} substitution is expected to influence the inversion parameter, cation disorder, and native defects of the MgAl_2O_4 host. In this research, the impact of Er^{3+} doping concentration and excitation wavelength on energy transfer between host and dopant ions and, hence, the up- and downconversion photoluminescence from the Er^{3+} doped MgAl_2O_4 host are studied.

II. EXPERIMENTAL SECTION

The nanocrystals of $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01, \text{ and } 0.03$) were synthesized through the solution combustion method using the precursors, magnesium nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Loba Chemie; 99%], aluminum nitrate nonahydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich; >98%] and erbium nitrate pentahydrate [$\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Sigma Aldrich; 99%], and monoethanolamine ($\text{C}_2\text{H}_7\text{NO}$, Sigma Aldrich; >99%) as a fuel. The amount of the precursors was calculated from the stoichiometric substitution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. The synthesized nanocrystals with the Er^{3+} doping concentrations of 0.5, 1 and 3 mol. % were labeled as E0.5, E1, and E3, respectively. The combustion of the redox mixture occurred at 500°C in a muffle furnace and annealing of the obtained powder was done at 900°C for an hour. The detailed description of the procedure followed for the combustion reaction is given in earlier work.²³

The structural-phase analysis was performed by x-ray diffraction data measured from PANalytical X'pert PRO x-ray diffractometer using $\text{Cu K}\alpha_1$ ($\lambda = 1.5406\text{ \AA}$) radiation source in the 2θ range of 10° – 90° . The morphological features were studied from high resolution transmission electron microscopy (HR-TEM) (Hitachi H-7500 TEM, Japan). The Fourier transform infrared (FTIR) spectra were obtained using Agilent Cary 630 FTIR spectrometer in 400 – 1800 cm^{-1} . The ^{27}Al solid-state nuclear magnetic resonance (NMR) spectra were recorded at a photon frequency of 400 MHz and a magnetic field strength of 9.389 T using a JEOL ECX400 NMR spectrometer. The diffuse reflectance spectra (DRS) were recorded on an UV–VIS–NIR spectrophotometer (SHIMADZU

UV-2600) in the 200 – 1000 nm wavelength range. The electron spin resonance (ESR) spectra were recorded on a JES-FA200 ESR spectrometer (JEOL, Japan) with X-band frequency (9.44 GHz) at room temperature. The upconversion (UC) emission spectra were recorded using a 976 nm diode laser on a micro-Raman spectrometer (LabRAM HR, Horiba Scientific, France). The down-shifted (DC) emission spectra measurements were carried out with a modular RI PL spectrofluorometer equipped with a 280 nm LED. Thermoluminescence (TL) study was done after irradiating the pre-annealed samples with ^{60}Co γ rays (at GAMMA CHAMBER 1200, IUAC, New Delhi) at 1 kGy radiation dose. TL measurements were performed in the 50 – 400°C temperature range through a Harshaw TL reader (Model 3500) at a heating rate of 5°C .

III. RESULTS AND DISCUSSION

The XRD patterns of Er^{3+} (0.5, 1, and 3 mol. %) doped MgAl_2O_4 samples are depicted in Fig. 1(a). All the diffraction peaks are indexed according to the ICDD (International center for diffraction data) card 00-021-1152. Figure 1(b) presents the Rietveld refined XRD patterns with Fullprof program²⁴ using the pseudo-Voigt profile function. The diffraction peak positions are consistent with the spinel phase of space group $Fd\bar{3}m$. The absence of extra peaks corresponding to any impurity or secondary phase inferred the successful incorporation of Er^{3+} dopant into the lattice sites of the spinel structure. Table I revealed the crystal structure and fitting parameters. The fitting was performed with Er^{3+} ion occupying the octahedral sites of the spinel structure as tetrahedral site occupancy is least expected due to valence mismatch of Er^{3+} ion with the Mg^{2+} cation at the tetrahedral site. The relatively lower values of R_p (unweighted profile R-factor), R_{wp} (weighted profile R-factor), R_{exp} (expected R-factor), and GOF (goodness of fit) parameters, and matching of observed and calculated profiles confirmed the goodness of Rietveld refinement. The lattice parameter (a) increases as expected with the doping concentration due to the substitution of Er^{3+} ions of large ionic radii ($0.88\text{ \AA}$) with $\text{Al}^{3+}/\text{Mg}^{2+}$ ions of small ionic radii ($0.53\text{ \AA}/0.57\text{ \AA}$).^{17,25} The observed decrease in the oxygen fractional coordinate (u), along with a significant decrease in the T–O bond length and an increase in the M–O bond length, is associated with the structural distortion induced by the incorporation of Er^{3+} ions.²⁶ Further, the ion occupancy values inferred the formation of cation (Al^{3+} , Mg^{2+}), oxygen vacancies, and antisite defects by swapping of Mg^{2+} and Al^{3+} ions at T and M sites. For E1 and E3 samples, the calculated values for Er^{3+} occupancy at octahedral sites are 0.007 and 0.027, respectively, which are found to be lower than their substituted concentrations ($x = 0.01$ for E1 and $x = 0.03$ for E3). Thus, Er^{3+} ion is supposed to occupy the octahedral sites as well as some random sites (can be tetrahedral sites or other vacant interstitial sites) with an increase in the doping concentration.

The diffraction peak positions of the E1 sample [the intense (311) peak is shown in Fig. S1(a) in the [supplementary material](#)] show a slight positive shift as compared to that for the E0.5 sample and then a slight negative shift for the E3 sample, which is attributed to the occupation of larger size Er^{3+} ions at octahedral sites as well as other random lattice sites at higher doping concentrations. The Williamson–Hall (W–H) plots for all the samples are depicted

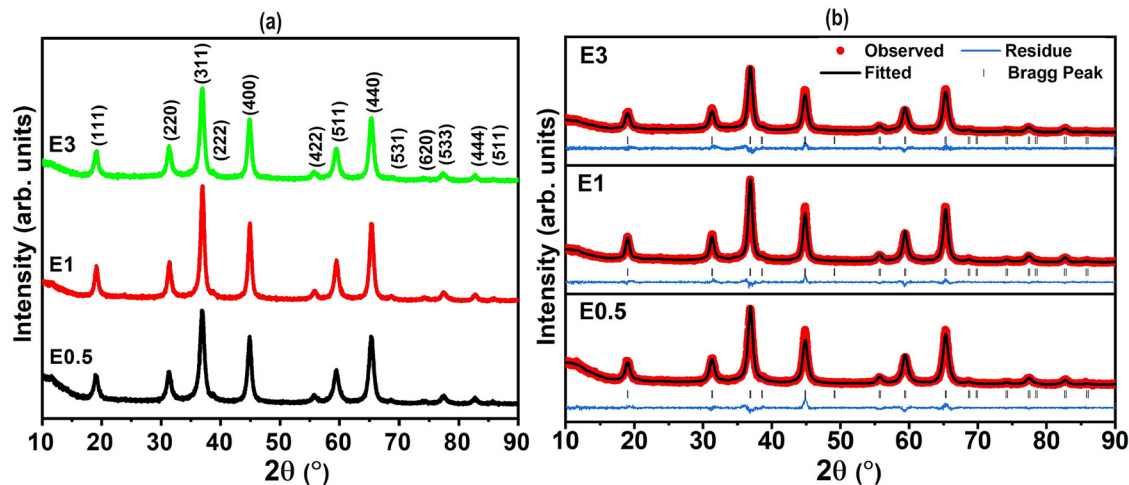


FIG. 1. (a) X-ray diffraction patterns and (b) Rietveld refined x-ray diffraction patterns of $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01, \text{ and } 0.03$) samples.

in Fig. S1(b) in the [supplementary material](#). Table II presents the average crystallite size estimated from Scherrer's formula and Williamson–Hall equation²⁷ as well as lattice strain from W–H plots. The crystallite size increases for 1 mol. % Er^{3+} doped nanocrystals and then decreases at 3 mol. % concentration. The lattice strain values are negative for E0.5 and E1 samples, indicating lattice compression, while positive for the E3 sample, indicating lattice expansion. The lattice expansion at 3 mol. % doping content can be explained in two ways. First, it may be attributed to the increased substitution of larger Er^{3+} ions at octahedral sites occupied by Al^{3+} ions, tetrahedral sites occupied by Mg^{2+} ions, or even at free interstitial sites. Second, it could be due to the increased concentration of the point defects with decreasing particle size.^{28,29}

Figures 2(a) and 2(b) show the HR-TEM images taken for E0.5 and E3 samples. The images revealed the formation of agglomerated irregular polygon shaped particles. Figures 2(c) and 2(d) depict the particle size variation in 6–22 nm, with the average particle size ~ 15 and 12 for E0.5 and E3 samples, respectively. The selected area electron diffraction patterns in Figs. 2(e) and 2(f) present various concentric circles of different radii corresponding to (111), (220), (311), (440), (422), and (511) lattice diffraction planes of spinel phase. Further, at a higher resolution of 2 nm, the lattice fringes are observed [shown in Figs. 2(g) and 2(h)] corresponding to (220) diffraction plane of the cubic spinel structure. Thus, HR-TEM images reveal a polygon shaped morphology, confirming the spinel phase of synthesized nanocrystals.

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TABLE I. Rietveld refined structural and quality of fit parameters for $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01, \text{ and } 0.03$) nanocrystals.

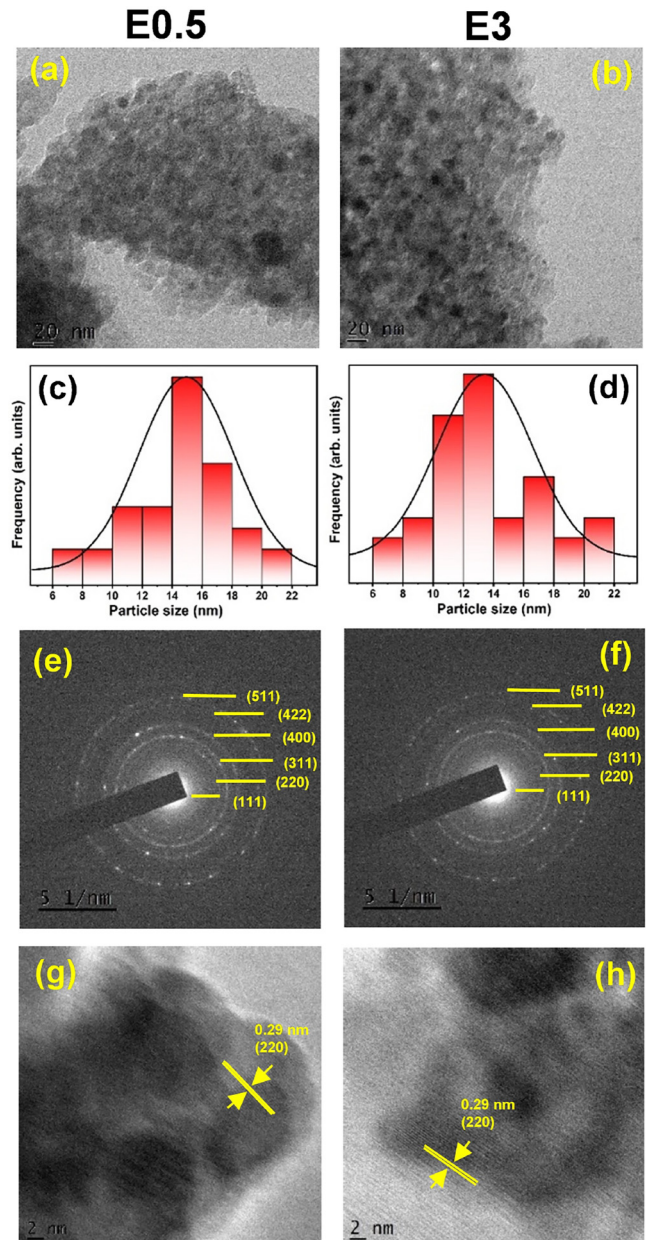
Sample	E0.5	E1	E3
Crystal phase	MgAl_2O_4	MgAl_2O_4	MgAl_2O_4
Lattice constant, a (Å)	8.081 676	8.083 474	8.083 680
Bond length (Å)	T–O : 1.8633 M–O : 1.9571	T–O : 1.8527 M–O : 1.9634	T–O : 1.8521 M–O : 1.9638
Oxygen position, u	0.258 12	0.257 33	0.257 28
Occupancy	Mg(T) : 0.554 Mg(M) : 0.432 Al(M) : 1.543 Al(T) : 0.409 Er(M) : 0.005 O : 4.000	Mg(T) : 0.559 Mg(M) : 0.430 Al(M) : 1.550 Al(T) : 0.366 Er(M) : 0.007 O : 4.000	Mg(T) : 0.551 Mg(M) : 0.420 Al(M) : 1.534 Al(T) : 0.402 Er(M) : 0.027 O : 4.000
Quality of fit	R_p : 5.95 R_{wp} : 7.95 R_{exp} : 7.02 GOF : 1.08	R_p : 5.56 R_{wp} : 7.20 R_{exp} : 7.14 GOF : 1.01	R_p : 5.42 R_{wp} : 6.83 R_{exp} : 6.76 GOF : 1.01

TABLE II. Average crystallite size and lattice strain evaluated from Scherrer's formula and Williamson-Hall (W-H) equation for $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01$, and 0.03) nanocrystals.

Sample	Sample ID	Scherrer's formula Crystallite size (nm)	W-H plot	
			Crystallite size (nm)	Lattice strain (10^{-4})
$\text{Mg}_{0.995}\text{Er}_{0.005}\text{Al}_2\text{O}_4$	E0.5	10.18	9.76	-3.75
$\text{Mg}_{0.99}\text{Er}_{0.01}\text{Al}_2\text{O}_4$	E1	12.06	11.70	-2.22
$\text{Mg}_{0.97}\text{Er}_{0.03}\text{Al}_2\text{O}_4$	E3	10.21	10.50	0.36

The spinel structure is further confirmed by metal-oxygen bond vibrations in FTIR spectra. Figure 3 presents the FTIR spectra of Er^{3+} doped MgAl_2O_4 nanocrystals in $1800\text{--}400\text{ cm}^{-1}$. The spectra consist of two prominent broad bands around ~ 670 and 470 cm^{-1} in the $800\text{--}400\text{ cm}^{-1}$ range, which are characteristic of Mg-O-Al vibrations of the MgAl_2O_4 spinel.^{30,31} Further, the weak absorption around 830 cm^{-1} is due to the stretching vibrations of Al^{3+} cations at tetrahedral sites and hence cation inversion in all the samples. The weak bands observed in $1600\text{--}1400\text{ cm}^{-1}$ are ascribed to C-O stretching vibrations of the carbonate groups due to residual carbonaceous content left from fuel employed in the combustion process.^{32,33}

In $\alpha\text{-Al}_2\text{O}_3$ single crystals, the octahedral sites were reported as dominant optically active site for Er^{3+} ion occupation.²¹ Here, the Rietveld analysis revealed the cation inversion of Mg^{2+} and Al^{3+} ions at T and M sites and estimated the occupancy of Er^{3+} ions at octahedral lattice sites. Thus, for a clearer understanding of cation occupancies with Er^{3+} ion doping, the Al^{3+} ion distribution at T and M sites of the spinel structure is examined from ^{27}Al solid-state NMR spectra presented in Fig. 4. The two broad resonance peaks and a spinning sideband (SSB) are observed, corresponding to the isotropic chemical shifts (δ) lying in $(-40)\text{--}40$, $40\text{--}80$, and $80\text{--}140\text{ ppm}$, respectively. The two peaks with maxima around ~ 10 and 70 ppm are attributed to six and four-coordinated aluminum in the spinel structure, respectively.^{34,35} The value of inversion parameter (i) determined from the intensity ratio (r) of the resonance peaks corresponding to aluminum occupying the octahedral and tetrahedral sites is given by $i = \frac{2-r}{1+r}$. This becomes $i = \frac{2-\mu}{1+r}$ for the $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ system, if μ amount of the Er^{3+} ions are assumed to substitute Al^{3+} ions occupying octahedral sites.³⁶ Here, the estimated value of r after deconvoluting the main resonance peaks and their sidebands for E0.5, E1, and E3 samples are 3.342, 3.489, and 3.464, respectively. The significant increase in the relative occupancy of Al^{3+} ions at octahedral sites than at tetrahedral sites in E1 and E3 samples than in E0.5 samples inferred that Er^{3+} may have started to occupy some tetrahedral or interstitial sites (can be free octahedral sites) too, in addition to the Al octahedral sites with an increase in Er^{3+} ion concentration. The inversion parameter values for E0.5, E1, and E3 samples are 0.461, 0.445, and 0.448 by considering no substitution of Er^{3+} ions at M sites occupied by Al^{3+} ions and 0.459, 0.443, and 0.441 by considering entire Er^{3+} ions substituting Al^{3+} ions at M sites, respectively. The cation inversion estimated through Rietveld analysis from Al

**FIG. 2.** (a) and (b) High resolution transmission electron microscopy (HR-TEM) images, (c) and (d) particle size distribution, (e) and (f) selected area electron diffraction patterns, and (g) and (h) HR-TEM fringe patterns for 0.5 and 3 mol. % Er^{3+} doped MgAl_2O_4 nanocrystals.

distribution at T as well as M sites and Er^{3+} at M sites using the above expression is 0.418, 0.380, and 0.410 for E0.5, E1, and E3 samples, respectively.

Furthermore, increasing the Er^{3+} ion concentration to 3 mol. % causes a noticeable broadening and slight negative chemical shift of

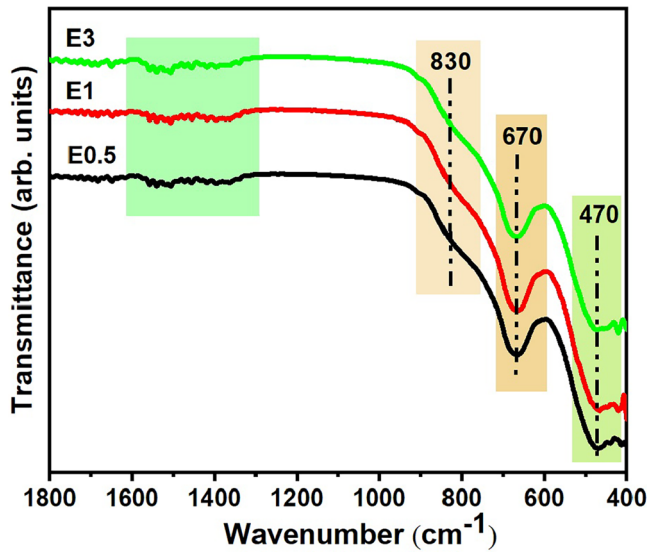


FIG. 3. Fourier transform infrared spectra of $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01$, and 0.03) nanocrystals.

the NMR spectral lines, alluding to the changes induced in the local atomic environment and electric field gradient distribution at octahedral as well as tetrahedral sites occupied by aluminum ions.^{23,37} These changes could be brought about by induced defects or Er^{3+} ion substitution near the aluminum sites.¹⁷ Further, the increase in the intensity of SSB with Er^{3+} doping is the result of increased

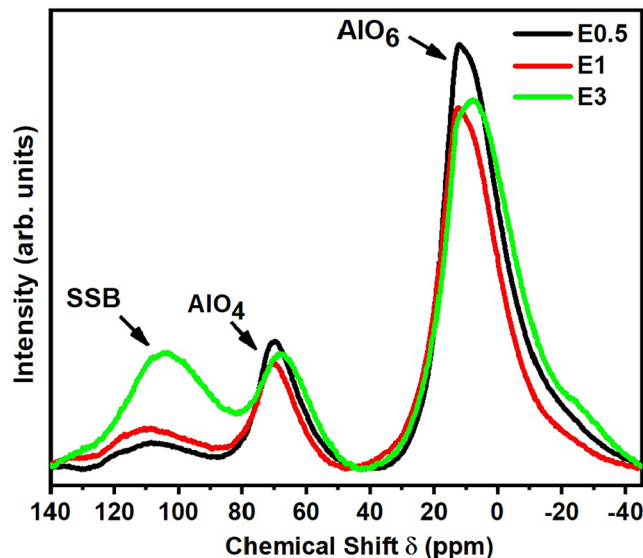


FIG. 4. ^{27}Al nuclear magnetic resonance spectra of $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01$, and 0.03) nanocrystals.

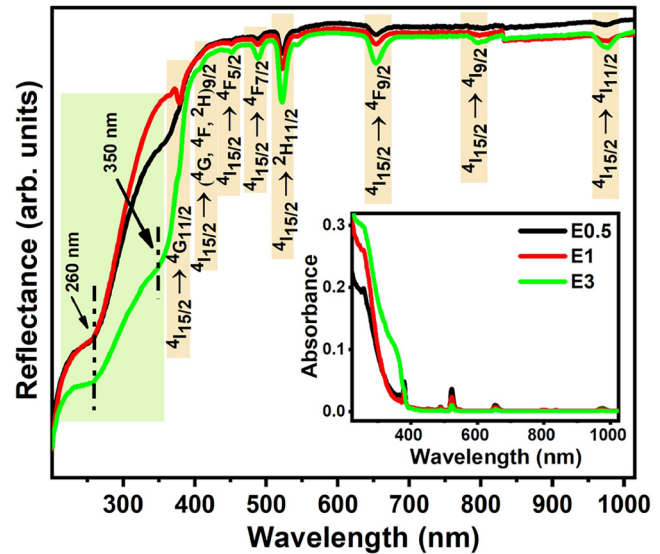


FIG. 5. Diffuse reflectance spectra of $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01$, and 0.03) nanocrystals. The inset shows the absorbance spectra of the respective samples.

strength of pseudo-scalar interactions of ^{27}Al nuclei with unpaired f -electrons of Er^{3+} ions.³⁸ Thus, concluding the quantitative NMR and Rietveld analysis, we observe a significant decrease in cation inversion at 1 mol. % Er substitution. This decrease is expected, considering the Er ions occupying the octahedral sites. This pseudo-linear dependence between Er content and expected parameters would have continued if Er remained solely in octahedral sites, as indicated from cation inversion calculations (from NMR) for entire Er^{3+} ions occupying the M sites only. The observed increase in cation inversion at 3 mol. % content anticipated that Er^{3+} ions might be occupying the random sites (tetrahedral or free interstitial sites) in addition to octahedral Al sites.

The DRS spectra of Er^{3+} doped samples, scanned between 200 and 1000 nm, is shown in Fig. 5 with the inset showing the absorbance spectra of respective samples. The spectra show broad absorption bands in 250–360 nm attributed to intrinsic host defects such as oxygen vacancies (F , F^+ , etc.) and antisite defects (Mg_{Al} and Al_{Mg}).^{17,39} The absorption peaks around 380, 406, 450, 488, 522, 654, 796, and 976 nm are attributed to the f - f transitions, $^4I_{15/2} \rightarrow ^4G_{11/2}$, $^4I_{15/2} \rightarrow (^4\text{F}, ^2\text{H})_{9/2}$, $^4I_{15/2} \rightarrow ^4F_{5/2}$, $^4I_{15/2} \rightarrow ^4F_{7/2}$, $^4I_{15/2} \rightarrow ^4H_{11/2}$, $^4I_{15/2} \rightarrow ^4F_{9/2}$, $^4I_{15/2} \rightarrow ^4I_{9/2}$, and $^4I_{15/2} \rightarrow ^4I_{11/2}$ of Er^{3+} ions, respectively.^{40,41} The increase in reflectance or decrease in the absorbance of the Er^{3+} associated peaks is observed with the increase in Er^{3+} doping concentration from 0.5 to 3 mol. %. The decreased absorption of the Er^{3+} associated peaks and increased absorption for host associated bands might be due to the increased lattice defect absorption at higher Er^{3+} content that may have hindered the absorption by increasing Er^{3+} ions.

To investigate the paramagnetic defect centers, the ESR spectra of E0.5 and E3 samples are shown in Fig. 6. The spectra

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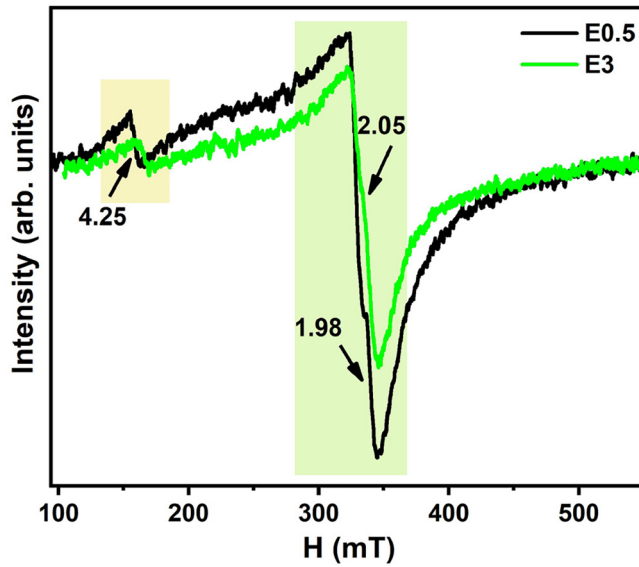


FIG. 6. Electron spin resonance spectra of $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005$ and 0.03) nanocrystals.

consist of two prominent broad signals having g -values ~ 2.05 and ~ 1.98 in both samples. These resonance signals may be linked to F^+ and V^- centers which are interacting with the nearby cations. The broadness of the ESR signal indicates the delocalization of electron spin at neighboring defect centers. In MgAl_2O_4 host, the resonance signal at g -value ~ 4.25 is attributed to the isolated ions in distorted octahedral sites.^{42–44}

The above DRS analysis revealed host defects and Er^{3+} dopant absorption in the MgAl_2O_4 lattice. To observe the photoluminescence response, two excitation wavelengths, 280 nm corresponding

to defect absorption and 976 nm corresponding to Er^{3+} ion absorption, are chosen. Figure 7(a) presents upconversion photoluminescence spectra upon excitation at 976 nm, while Fig. 7(b) presents the room temperature down-shifted photoluminescence spectra upon excitation at 280 nm.

The UC emission spectra of 0.5, 1, and 3 mol. % Er^{3+} doped MgAl_2O_4 samples upon 976 nm laser excitation consist of three narrow emission peaks located around 525, 550 (in green region), and 660 nm (in red region) overlapped over the broad spectra spanning 400–800 nm wavelength region. The UC emission spectrum of the E1 sample, depicted in Fig. 7(a), has been deconvoluted using Fityk software.⁴⁵ The Gaussian fitting is provided in the supplementary material (Fig. S2). Following Gaussian fitting, the spectrum revealed nine emission components peaking around 440, 485, 525, 550, 605, 660, 705, 740, and 780 nm, labeled as P1, P2, P3, P4, P5, P6, P7, P8, and P9, respectively. The components P3 (525 nm), P4 (550 nm), and P6 (660 nm) are ascribed to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ions, respectively.^{46,47} The emission around 440 nm (P1) may originate from F_2^+ centers, while the green emission around 485 nm (P2) may be due to the transition of an electron to a hole trapped at V_{Mg} . The yellow–orange emission around 605 nm (P5) may be attributed to oxygen vacancies formed with the creation of Mg_{Al} antisite defects. The longer-wavelength emission components (P7, P8, and P9) could be due to the transitions from shallow to deep oxygen vacancy states ($\text{V}_{\text{O}}^{\bullet\bullet}$, $\text{V}_{\text{O}}^{\bullet}$) or between two deep oxygen vacancy states ($\text{V}_{\text{O}}^{\bullet\bullet}$, $\text{V}_{\text{O}}^{\bullet}$) linked to distorted octahedra.^{17,48,49}

The red to green emitting ratio (R/G), corresponding to Er^{3+} assisted emission, for E0.5, E1, and E3 samples is calculated to be 0.633, 0.729, and 1.104, respectively. The reason behind the increase in the R/G ratio with the increase in doping concentration is explained below. Figure 8 illustrates the proposed schematic band model revealing the emission from defect and Er^{3+} ion associated energy levels. The Er^{3+} ion emission excited via two photon absorption is explained below. The green emission from $^2\text{H}_{11/2}$ and

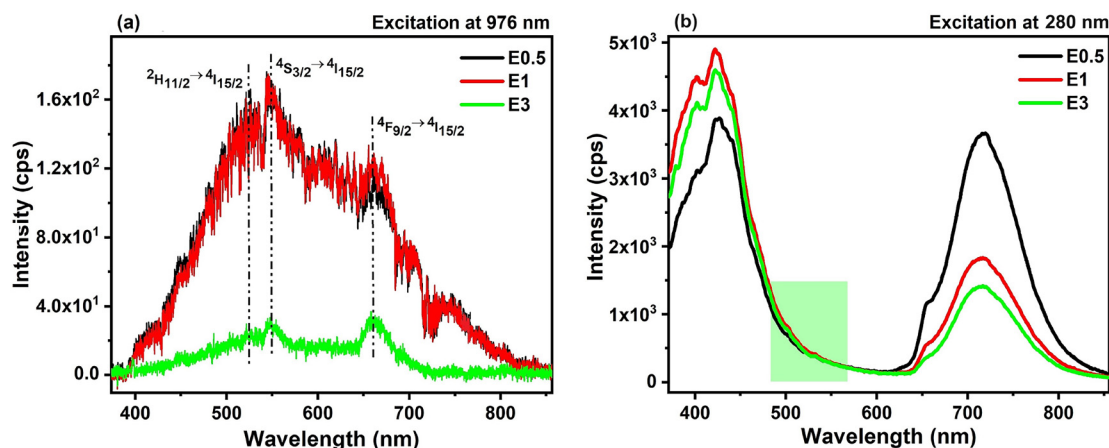


FIG. 7. (a) Upconversion photoluminescence spectra upon excitation at 976 nm and (b) down-shifted photoluminescence spectra upon excitation at 280 nm for $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01$, and 0.03) nanocrystals.

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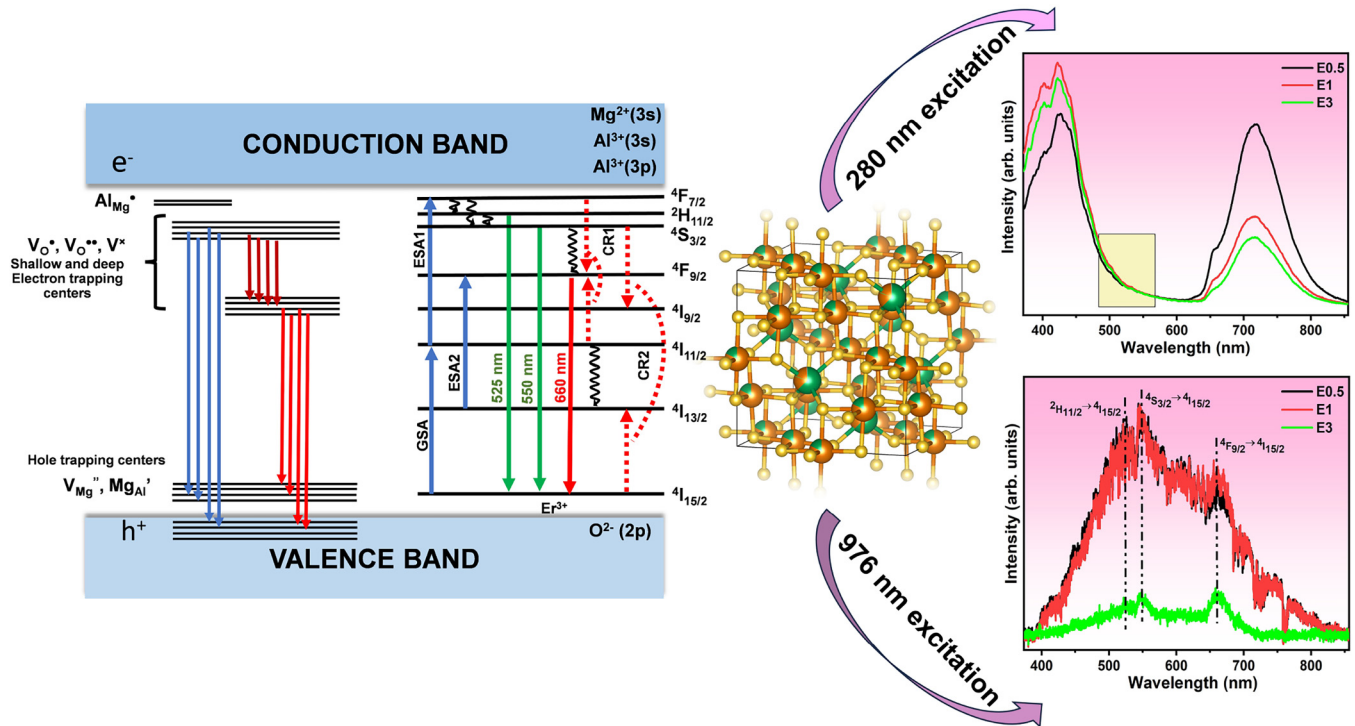


FIG. 8. Schematic band model illustrating the defect and Er³⁺ ion associated emission upon UV and NIR excitations (the depicted energy states are arbitrary, shown just to reveal the phenomenon).

⁴S_{3/2} states occur *via* population of the ⁴F_{7/2} state where the ground state absorption (GSA: ⁴I_{15/2} → ⁴I_{11/2}) is followed by excited state absorption (ESA1: ⁴I_{11/2} → ⁴F_{7/2}). The direct non-radiative relaxations from green emitting ²H_{11/2} and ⁴S_{3/2} states populate the red emitting ⁴F_{9/2} state. Further, the non-radiative relaxation from the ⁴I_{11/2} state to ⁴I_{13/2} and excited state absorption (ESA2: ⁴I_{13/2} → ⁴F_{9/2}) leads to population of ⁴F_{9/2} state. Another important process behind this increased R/G ratio may be the cross-relaxation mechanism (CR1: ⁴F_{7/2} + ⁴I_{11/2} → ⁴F_{9/2} + ⁴F_{9/2} and CR2: ⁴S_{3/2} + ⁴I_{15/2} → ⁴I_{9/2} + ⁴I_{13/2}), which directly or indirectly populates ⁴F_{9/2} level. Further, the rate of cross-relaxation processes vary as 1/R⁶, where R is the distance between two neighboring ions. As the distance between two neighboring Er³⁺ ions shorten with increasing Er³⁺ ion concentration, the cross-relaxation probability increases at higher doping content. Thus, the increased probability of CR1 and CR2 processes at higher Er³⁺ ion content might have enhanced the R/G emission ratio with the increase in the Er³⁺ doping concentration.^{50,51} The UC emission spectra exhibited similar dopant and defect assisted emission features across all samples. However, the slight increase in UC emission intensity at a 1 mol.% doping concentration and a significant decrease at a 3 mol.% doping concentration indicate that the optimum concentration for upconversion emission is 1 mol.%. The decrease in emission intensity at 3 mol.% content may be due to the cross-relaxation, energy transfer processes, or concentration quenching among the Er³⁺ ions.⁵²

The luminescence spectra upon 280 nm excitation show broad emission bands ranging in 370–550 (blue–violet) and 600–840 nm (red–NIR) as observed for MgAl₂O₄ host, reported earlier.¹⁷ The emission in the blue–violet region strongly peaks around 400, 420, and 440 nm while a weak green emission is observed around 532 nm. This blue–violet emission may be attributed to transitions originating from shallow oxygen vacancy related defect centers (F⁺ (400 nm), F (415–420 nm), and F₂⁺ (440 nm) centers to shallow hole trapping defect centers (V_{Mg}[•] and Mg_{Al}[•]) or to valance band.^{17,23,53} The very weak emission around 532 nm (indicated by green colored contour) is ascribed to ²H_{11/2} → ⁴I_{15/2} transitions of Er³⁺ ions. Further, the red emission around 650 nm may be ascribed to transitions from deep (V_O^{••}, V_O[•], and V_O^x) to shallow defect states (V_{Mg}[•] and Mg_{Al}[•]), while NIR emission around 715 nm may be ascribed to transitions from shallow to deep or between two deep oxygen vacancy states, as mentioned earlier.^{17,49} The NIR emission intensity decreases with the increase in doping concentration, indicating a reduction in the concentration of oxygen vacancies. This decrease in oxygen vacancies is also observed from the decrease in the ESR signal intensity corresponding to F⁺ centers. The reduction is also confirmed from the thermoluminescence response of Mg_{1-x}Er_xAl₂O₄ (x = 0.005, 0.01, and 0.03) nanocrystals under γ-irradiation at a 1 kGy radiation dose, as shown in [supplementary material](#) (Fig. S3). The broad TL glow curves exhibited an incomplete peak centered at 400 °C (673 K), ascribed to deep F⁺ centers.^{31,54,55} The decrease in the TL intensity of this

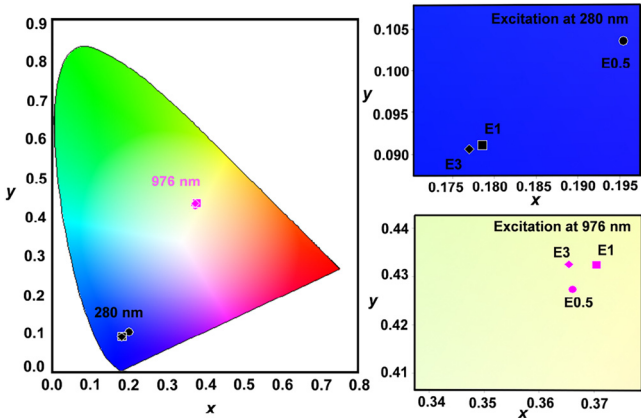


FIG. 9. Chromaticity diagram showing the emission color of $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01, \text{ and } 0.03$) nanocrystals at 976 and 280 nm excitation wavelengths.

peak from E0.5 to E1 and then to E3 sample indicates a decrease in TL exhibiting F^+ centers with an increase in doping concentration. Thus, upon 280 nm excitation, a weak emission attributed to Er^{3+} ions overlaps with the broad spectrum attributed to host defects. This Er^{3+} ion and host defects assisted emission upon UV excitation revealed some of the excitation energy transfer from intrinsic defects to Er^{3+} ions occupying the lattice sites.

The overall color emitted from the nanocrystals is estimated from Commission Internationale de l'Éclairage (CIE) 1931 chromaticity diagram analysis shown in Fig. 9. The CIE coordinates and corresponding emission colors at various excitation wavelengths are reported in Table III. The emission color is found to tune from bluish purple to white upon varying the excitation wavelength from 280 to 976 nm, respectively. A slight color variation is observed by varying the Er^{3+} doping concentration. Additionally,

TABLE III. CIE coordinates and color emitted from $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01, \text{ and } 0.03$) nanocrystals at various excitation wavelengths.

Sample	Sample ID	Excitation wavelength	CIE coordinates	Color
$\text{Mg}_{0.995}\text{Er}_{0.005}\text{Al}_2\text{O}_4$	E0.5	280 nm	(0.1955, 0.1036)	Bluish purple
$\text{Mg}_{0.99}\text{Er}_{0.01}\text{Al}_2\text{O}_4$	E1		(0.1786, 0.0911)	Bluish purple
$\text{Mg}_{0.97}\text{Er}_{0.03}\text{Al}_2\text{O}_4$	E3		(0.1770, 0.0906)	Bluish purple
$\text{Mg}_{0.995}\text{Er}_{0.005}\text{Al}_2\text{O}_4$	E0.5	976 nm	(0.3661, 0.4272)	White
$\text{Mg}_{0.99}\text{Er}_{0.01}\text{Al}_2\text{O}_4$	E1		(0.3704, 0.4324)	White
$\text{Mg}_{0.97}\text{Er}_{0.03}\text{Al}_2\text{O}_4$	E3		(0.3654, 0.4325)	White

the correlated color temperature (CCT) corresponding to the up-converted white emission for E0.5, E1, and E3 samples is calculated as 4644, 4560, and 4679 K, while the color rendering index (CRI) as 84, 83, and 85, respectively. This cool white light upon 976 nm excitation suggests its applicability in white light emitting diodes for outdoor illumination.

Thus, the color tuning in the bluish purple and white region *via* host and dopant assisted emission is the consequence of excitation energy transfer between host and Er^{3+} ions occupying the lattice sites *via* intrinsic defects. This high and low energy excited luminescence from Er^{3+} doped MgAl_2O_4 nanophosphors offers potential applications in WLEDs and display technologies. Furthermore, as NaYF_4 host is characterized by its efficient upconversion properties albeit at a higher cost and requirement of stabilization measures for UC applications,⁵⁶ the MgAl_2O_4 can emerge as a promising alternative with its ability to yield commendable UC emission, along with lower cost, straightforward synthesis, and comparable stability by employing sensitizer and optimizing dopant concentrations in future.

IV. CONCLUSION

The $\text{Mg}_{1-x}\text{Er}_x\text{Al}_2\text{O}_4$ ($x = 0.005, 0.01, \text{ and } 0.03$) nanocrystals were synthesized through the combustion method. The site preference of the Er^{3+} ion in MgAl_2O_4 host and the emission exhibited is analyzed as per the structural and luminescence characteristics. Various host lattice defects, viz., antisite defects, cation, and oxygen vacancies, were inferred from Rietveld refinement, nuclear magnetic resonance, and electron spin resonance analyses. The emission spectra are studied at various excitation wavelengths, corresponding to host defect absorption and f - f transitions of the Er^{3+} ion. Upon direct excitation of the Er^{3+} ions at 976 nm, the upconversion emission spectra showed features in green and red regions attributed to Er^{3+} ions, which are overlapped over the broad curve ascribed to lattice defects. Further, the down-shifted emission spectra upon UV excitation showed a weak green emitting feature, due to f - f transitions of the Er^{3+} ion, over the emission spectra consisting of two broad bands in blue-violet and red-NIR regions, attributed to intrinsic defects. This high and low energy excited emission spectra reveal non-radiative energy transfer between host and Er^{3+} ions *via* lattice defect centers. The above luminescence spectra result in the emission color tuning from the bluish purple to white region and hence, making spinel the host ideal for WLEDs and display applications.

SUPPLEMENTARY MATERIAL

The supplementary material includes the x-ray diffraction peak shift corresponding to the (311) plane, the Williamson–Hall plots, Gaussian fitting of the UC luminescence spectrum, and the TL glow curves.

ACKNOWLEDGMENTS

The authors are grateful to acknowledge the financial support from the Inter University Accelerator Centre (IUAC), New Delhi through Project No. IUAC/XIII.7/UFR-63307 and University Grant Commission (UGC), India (NTA Ref. No.: 191620066754). The authors are also thankful to Sophisticated Analytical Instrument

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Facility, IIT Bombay for ESR analysis and Sophisticated Instruments Facility, IISc Bangalore for NMR analysis.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Savita: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Madan Murari Upadhyay:** Data curation (supporting); Formal analysis (supporting). **Priyanka Bishnoi:** Data curation (supporting); Formal analysis (supporting). **Sanjay Kumar:** Data curation (supporting); Formal analysis (supporting). **Kaushal Kumar:** Data curation (supporting); Formal analysis (supporting). **Ankush Vij:** Conceptualization (lead); Formal analysis (lead); Supervision (lead); Visualization (lead). **Anup Thakur:** Conceptualization (lead); Formal analysis (lead); Supervision (lead); Visualization (lead).

DATA AVAILABILITY

The data that supports the findings of this study are available within the article and its [supplementary material](#).

REFERENCES

- ¹J. Zhao, Y. Sun, X. Kong, L. Tian, Y. Wang, L. Tu, J. Zhao, and H. Zhang, *J. Phys. Chem. C* **112**, 15666 (2008).
- ²S. Sinha, M. K. Mahata, V. Rai, and K. Kumar, *AIP Conf. Proc.* **1728**, 020476 (2016).
- ³C. Dlamini, M. R. Mhlongo, L. Koao, T. Motaung, T. Hlatshwayo, Y. Dwivedi, and S. V. Motloung, *Mater. Res. Express* **7**, 106302 (2020).
- ⁴V. Tikhomirov, V. Rodríguez, J. Méndez-Ramos, J. Del-Castillo, D. Kirilenko, G. Van Tendeloo, and V. Moshchalkov, *Sol. Energy Mater. Sol. Cells* **100**, 209 (2012).
- ⁵S. Tabanlı and G. Eryurek, *Sens. Actuators A Phys.* **285**, 448 (2019).
- ⁶I. Kumar, A. Kumar, S. Kumar, G. B. Nair, H. Swart, and A. K. Gathania, *Phys. Scr.* **98**, 105532 (2023).
- ⁷W. Liu, T. Shi, M. Liu, Q. Wang, X. Liu, Q. Zhou, M. Lei, P. Lu, L. Yu, and Z. Wei, *Opt. Express* **29**, 29402 (2021).
- ⁸N. Venkatachalam, T. Yamano, E. Hemmer, H. Hyodo, H. Kishimoto, and K. Soga, *J. Am. Ceram. Soc.* **96**, 2759 (2013).
- ⁹I. Kumar, A. Kumar, S. Kumar, H. Thakur, N. Dhiman, and A. K. Gathania, *Ceram. Int.* **49**, 36979 (2023).
- ¹⁰Y. Cheng, K. Sun, and P. Ge, *Optik* **170**, 1 (2018).
- ¹¹S. Thakur and A. K. Gathania, *J. Mater. Sci. Mater. Electron.* **27**, 1988 (2016).
- ¹²T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida, *Opt. Mater.* **106**, 110028 (2020).
- ¹³M. F. Torresan and A. Wolosiuk, *ACS Appl. Bio Mater.* **4**, 1191 (2021).
- ¹⁴J. Shi, W. Ge, M. Xu, and J. Zhu, *J. Lumin.* **213**, 15 (2019).
- ¹⁵R. T. Parayil, S. K. Gupta, M. M. Upadhyay, K. Sudarshan, and M. Mohapatra, *New J. Chem.* **47**, 20286 (2023).
- ¹⁶S. Sawai and T. Uchino, *J. Appl. Phys.* **112**, 103523 (2012).
- ¹⁷S. Wadhwa, M. Jain, M. Bhatia, A. Kumar Sinha, F. Singh, A. Vij, and A. Thakur, *J. Appl. Phys.* **129**, 125111 (2021).
- ¹⁸U. Schmock, H. Boesch, and F. Waldner, *Phys. Lett. A* **40**, 237 (1972).
- ¹⁹I. Ganesh, *Int. Mater. Rev.* **58**, 63 (2013).
- ²⁰A. Choudhary, A. Dwivedi, A. Bahadur, T. Yadav, and S. Rai, *Ceram. Int.* **44**, 9633 (2018).
- ²¹G. Van den Hoven, A. Polman, E. Alves, M. Da Silva, A. Melo, and J. Soares, *J. Mater. Res.* **12**, 1401 (1997).
- ²²L. Rebouta, M. Da Silva, J. Soares, D. Serrano, E. Diéguez, F. Agulló-López, and J. Tornero, *Appl. Phys. Lett.* **70**, 1070 (1997).
- ²³Savita, P. Vashishtha, G. Gupta, A. Vij, and A. Thakur, *J. Phys.: Condens. Matter* **35**, 115303 (2023).
- ²⁴L. McCusker, R. Von Dreele, D. Cox, D. Louër, and P. Scardi, *J. Appl. Crystallogr.* **32**, 36 (1999).
- ²⁵Y. Tian, Y. Tian, P. Huang, L. Wang, Q. Shi, and C. Cui, *Chem. Eng. J.* **297**, 26 (2016).
- ²⁶F. Bosi, *Acta Crystallogr. B Struct. Sci. Cryst.* **75**, 279 (2019).
- ²⁷P. Bindu and S. Thomas, *J. Theor. Appl. Phys.* **8**, 123 (2014).
- ²⁸C. R. Fell, D. Qian, K. J. Carroll, M. Chi, J. L. Jones, and Y. S. Meng, *Chem. Mater.* **25**, 1621 (2013).
- ²⁹P. M. Diehm, P. Ágoston, and K. Albe, *Chem. Phys. Chem.* **13**, 2443 (2012).
- ³⁰M. O'horo, A. Frisillo, and W. White, *J. Phys. Chem. Solids* **34**, 23 (1973).
- ³¹Savita, S. Dani, S. Kumar, F. Singh, A. Vij, and A. Thakur, *J. Phys. D: Appl. Phys.* **54**, 335303 (2021).
- ³²K. Morita, B.-N. Kim, H. Yoshida, K. Hiraga, and Y. Sakka, *J. Eur. Ceram. Soc.* **36**, 2961 (2016).
- ³³Savita, S. Kumar, A. Vij, and A. Thakur, *J. Phys. D: Appl. Phys.* **56**, 075301 (2023).
- ³⁴M. Jain, Manju, M. Kumar, H. H. Lee, S. O. Won, K. H. Chae, A. Vij, and A. Thakur, *Dalton Trans.* **49**, 9336 (2020).
- ³⁵C. Jagadeeshwaran, K. Madhan, and R. Murugaraj, *J. Mater. Sci. Mater. Electron* **29**, 18923 (2018).
- ³⁶G. Gobbi, R. Christoffersen, M. Otten, B. Miner, P. Buseck, G. Kennedy, and C. Fyfe, *Chem. Lett.* **14**, 771 (1985).
- ³⁷V. Šepelák, I. Bergmann, S. Indris, A. Feldhoff, H. Hahn, K. D. Becker, C. P. Grey, and P. Heitjans, *J. Mater. Chem.* **21**, 8332 (2011).
- ³⁸T. S. Goncalves, R. J. M. Silva, M. de Oliveira Junior, C. R. Ferrari, G. Y. Poirier, H. Eckert, and A. S. de Camargo, *Mater. Chem. Phys.* **157**, 45 (2015).
- ³⁹V. Gritsyna, Y. G. Kazarinov, A. Moskvitin, and I. Reimanis, *Phys. Rad. Dam. Rad. Mater. Sci.* **95**, 28-31 (2010); available at <http://dspace.nbuv.gov.ua/handle/123456789/14946>.
- ⁴⁰A. S. S. de Camargo, L. A. D. O. Nunes, J. Silva, A. Costa, B. Barros, J. Silva, G. De Sá, and S. Alves, *J. Phys.: Condens. Matter* **19**, 246209 (2007).
- ⁴¹S. Mondal, S. Park, J. Choi, L. H. Tran, M. Yi, J. H. Shin, C.-Y. Lee, and J. Oh, *Ceram. Int.* **46**, 16020 (2020).
- ⁴²N. Pathak, P. S. Ghosh, S. Saxena, D. Dutta, A. K. Yadav, D. Bhattacharyya, S. N. Jha, and R. M. Kadam, *Inorg. Chem.* **57**, 3963 (2018).
- ⁴³E. A. Raja, S. Menon, B. Dhabeekar, N. Rawat, and T. G. Rao, *J. Lumin.* **129**, 829 (2009).
- ⁴⁴V. Singh, V. K. Rai, S. Watanabe, T. Gundu Rao, I. Ledoux-Rak, and H.-Y. Kwak, *Appl. Phys. A* **100**, 1123 (2010).
- ⁴⁵M. Wojdyr, *J. Appl. Crystallogr.* **43**, 1126 (2010).
- ⁴⁶T. B. Ivetić, Y. Ding, M. Cvetinov, J. Petrović, O. R. Klisurić, and S. R. Lukić-Petrović, *Ceram. Int.* **47**, 17778 (2021).
- ⁴⁷R. K. Kunchala, R. Kalia, B. S. Naidu *et al.*, *RSC Adv.* **10**, 14525 (2020).
- ⁴⁸P. Borges, J. Cott, F. Pinto, J. Tronto, and L. Solfaro, *Mater. Res. Express* **3**, 076202 (2016).
- ⁴⁹N. Pathak, P. S. Ghosh, S. K. Gupta, S. Mukherjee, R. M. Kadam, and A. Arya, *J. Phys. Chem. C* **120**, 4016 (2016).
- ⁵⁰V. Mahalingam, C. Hazra, R. Naccache, F. Vetrone, and J. A. Capobianco, *J. Mater. Chem. C* **1**, 6536 (2013).
- ⁵¹L. Shi, Q. Shen, and Z. Qiu, *J. Lumin.* **148**, 94 (2014).
- ⁵²L. Vijayalakshmi, K. N. Kumar, K. S. Rao, and P. Hwang, *J. Mol. Struct.* **1155**, 394 (2018).
- ⁵³B. Choudhury, P. Basyach, and A. Choudhury, *J. Lumin.* **149**, 280 (2014).
- ⁵⁴A. Ibarra, D. Mariani, and M. J. De Castro, *Phys. Rev. B* **44**, 12158 (1991).
- ⁵⁵A. Lorincz, M. Puma, F. J. James, and J. Crawford, Jr., *J. Appl. Phys.* **53**, 927 (1982).
- ⁵⁶C. M. Jones, A. Gakamsky, and J. Marques-Hueso, *Sci. Technol. Adv. Mater.* **22**, 810 (2021).