Spectroscopic characterizations of Er doped LaPO₄ submicron phosphors prepared by homogeneous precipitation method

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Abstract: Hexagonal shaped LaPO₄ submicron particles doped with various concentrations of Er were successfully prepared by homogenous precipitation method using metal nitrates and ammonium phosphate. Particles of approximate particle size 125 nm and size distribution of 85 nm are obtained with good crystallinity. After heat treatment at 1200 °C for 2 hrs, the particles are characterized for their various optical properties such as absorption, emission, fluorescence decay and optical band gap. Optical absorption and emission data are numerically analyzed with the help of Judd-Ofelt model to evaluate various radiative spectral properties such as radiative decay rates, radiative quantum yield, emission cross-section and fluorescence branching ratios of various emission transitions. Though the radiative quantum yield of 1554 nm emission approaches the theoretical limit of 100%, the experimentally measured quantum yield is only 11% at 12 W/cm² at 980 nm excitation power density in 2% Er doped LaPO₄.

Keywords: phosphor, orthophosphate, Judd-Ofelt, emission cross-section and quantum yield

1. Introduction

The introduction of nanotechnology has had profound influence in ceramic materials and their applications in various areas such as medical, military, lighting etc. [1–3]. The area of nanotechnology has advanced to such a level, that it is now possible to manipulate the size, shape, dopant profile and several other parameters in a customized way which has ultimately resulted in several advanced technological innovations. One of the most obvious advantages of ceramic technology is the large scalability of the nanoceramic structure compared to their single crystal form. The last century has witnessed one such notable invention by researchers who developed the first fully transparent Nd doped ceramic YAG that is 100% equivalent to single crystalline material [4,5]. The ceramic technology has several advantages compared to single crystal technology such as, low cost of production, large scalability, different size/shape, homogeneity, control of the dopant profile, fabrication of composite structures etc. By controlling the synthesis chemistry and processing methods, it is possible to tailor the ceramic technology for any kind of materials.

Several inorganic phosphor compositions have been reported in the past among which, rare earth doped LaPO_4 is considered as a potential candidate in display applications [6,7]. Metal orthophosphates (MPO_4 , where M is a metal) have several favorable properties, such as high thermal stability of (at about) 2300°C , low water solubility [8–11], high refractive index ($\text{YPO}_4 = 1.76$, $\text{LaPO}_4 = 1.85$, $\text{GdPO}_4 = 1.97$), high density ($\text{YPO}_4 = 4.22$, $\text{LaPO}_4 = 5.0$, $\text{GdPO}_4 = 6 \text{ g/cc}$), which makes them suitable candidates for variety of applications, such as lasers, catalyst, magnets and in medicine. Bulk lanthanum phosphate crystals have been extensively used as host for lanthanide ions [12]. Lanthanum phosphates offer phonon energy of 1050 cm^{-1} which is higher than halides ($250\text{--}350 \text{ cm}^{-1}$) and chalcogenides ($400\text{--}520 \text{ cm}^{-1}$). High rare earth solubility and weak ion-ion interactions have been previously reported [13,14]. Bulk MPO_4 ($\text{M} = \text{La}, \text{Gd}, \text{Y}$) is usually prepared by solid-state reactions at temperatures above 1000°C [15]. With the introduction of nanotechnology in the past decade, several

solution methods have been reported for synthesizing pure and rare-earth-doped metal phosphates [16–21].

Here we report a detailed spectroscopic characterization of Er doped LaPO_4 submicrometer size phosphor prepared by homogeneous precipitation method. Optical properties such as absorption, optical band gap, refractive index, near infrared emission (NIR) and fluorescence decay are measured. By using the Judd-Ofelt procedure, quantitative estimates of the radiative spectral properties of various emission channels are obtained. In addition, quantum yield of the NIR emission at 1550 nm was measured as a function of the Er concentration and compared with the theoretical radiative quantum yield.

2. Experimental

2.1. Synthesis

$\text{LaPO}_4\text{:Er}$ phosphor particles are prepared by homogeneous precipitation method using La and Er nitrates (99.9%, GFS Chemicals, NJ) as the metal precursors and water as the solvent. To explore the concentration dependence of the spectroscopic properties, four different Er concentrations viz. 0.5, 1, 2 and 5 mol% were prepared. Appropriate amounts of $\text{La}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ were dissolved into 50 ml of de-ionized water and 13 gm of $(\text{NH}_4)_2\text{HPO}_4$ was dissolved into 100 ml of de-ionized water. The resulting two solutions were then mixed slowly and NH_4OH was added drop wise, to adjust the pH of combined solutions to 8-9. The resulting precipitate was centrifugally separated (Z323, Labnet, U.S.) and then washed 4 times each, in ethanol followed by de-ionized water, by repeatedly dispersing the centrifuge cake with a sonifier (Cell Disruptor 200, Branson, U.S.) and subsequently centrifuging the suspension at a speed of 10,000 rpm for 10 min. The precipitate was dried at 80°C for 1 hr to obtain the amorphous $\text{LaPO}_4\text{:Er}$. In order to remove the unreacted chemicals, water residues, and to improve the emission properties the phosphor particles were heat treated at 1200°C for 2 hr in a muffle furnace (KSL 1500, MTI, U.S.).

2.2. Characterizations

The obtained powders were characterized by X-ray diffraction analysis (XRD), Field Emission Scanning Electron microscopy (FESEM), and various experimental and theoretical spectroscopic techniques. The powder diffraction profiles were collected with an automated diffractometer (Ultima IV, Rigaku, Japan) using Ni-filtered Cu K α radiation at 44 KeV and 30 mA. The data were collected in the 20° to 60° range using a step size of 0.05° and a count time of 0.15 seconds. The morphology and size were examined with a Field Emission Scanning Electron Microscope (STEM-5500, Hitachi, Japan). Optical absorption spectrum was collected using a spectrophotometer (Perkin Elmer Lambda 19, U.S.). NIR fluorescence measurements were done by exciting the samples using 980 nm laser (Spectra Physics, Model 3900S) and the emission of the sample was recorded by the Quanta Master 51 spectrofluorimeter (Photon Technology International Inc. NJ, U.S.) with an InGaAs detector (Teledyne Judson Technologies, 062-8451, U.S.). Photoluminescence decay curves of 1550 nm emission were measured on a Quanta Master 40 system (Photon Technology International Inc. NJ, U.S.) using the single shot transient digitizer technique with a Nitrogen pumped Dye Laser (Photon Technology International part GL-3300 + GL-302) as excitation source. The Nitrogen laser, with 800 ps pulse width, pumps a high resolution dye chamber to give 523 $\pm$ 0.04 nm light. The collected decay curve was analyzed by Origin 8 software (Origin lab, U.S.). For the quantum yield (QY) measurements, we employed a barium sulfate coated 203 mm diameter integrating sphere (Oriel, Model 70451) mounted on the side of the spectrofluorimeter sample chamber and excited by the 980 nm laser. More details about the QY measurements can be seen in our previous publications [22].

3. Results and discussion

3.1. Phase and morphology

Fig. 1 shows the XRD pattern of the heat treated LaPO₄:Er where all the peaks are indexed with

respect to the monoclinic lanthanum phosphate (JCPDS No. 01-083-0657) with no evidence of secondary phases, suggesting that the dopant distribution was uniform. The strongest peak at 29° was used to estimate the crystallite size by the Scherrer equation [23]. Using this procedure an average crystallite size of about 129 nm was obtained for the prepared phosphor particles.

Fig. 1. X-ray diffraction pattern of LaPO₄:Er (2%) in comparison with the standard monoclinic lanthanum phosphate (JCPDS No. 01-083-0657) shown as vertical lines.

(a)

(b)

Fig. 2. (a) FESEM image of LaPO₄:Er (2%), (b) particle size distribution.

Fig. 2 shows a typical FESEM image of prepared $\text{LaPO}_4\cdot\text{Er}$ with particle size distribution. The phosphor particles show nearly hexagonal shape with an average particle size of 125 nm and a particle size distribution of 85 nm. The average size of the phosphor particles observed from FESEM images is well in agreement with XRD data.

3.1 Band gap and refractive index

Optical band gap of a powder sample can be obtained from the reflectance spectra using the Kubelka-Munk relationship [24], according to which, the absorption coefficient (α) and scattering coefficient (S) are related to the reflectance (R) by the relationship

$$F(R_\infty) = \frac{\alpha}{S} = \frac{(1 - R_\infty)^2}{2R} \quad (1)$$

$$R_\infty = \frac{R_{\text{sample}}}{R_{\text{PTFE}}}$$

where α is the absorption coefficient, S the scattering coefficient, R_∞ is the Kubelka-Munk (KM) function for reflectance, R_{sample} is the reflectance of the sample and R_{PTFE} is the reflectance of the standard Polytetrafluoroethylene (PTFE). The photon energy (E) and the absorption coefficient (α) are related by the expression [25]

$$\alpha E = K(E - E_g)^n \quad (2)$$

where E_g is the band gap energy, K is a constant and $n = 1/2, 3/2, 2, 3$ respectively for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions. In the case of reflectance spectra KM function can be replaced by α for the estimation of band gap using Eq. (2) [24]. At $E = E_g$, a plot of E vs $(\alpha E)^{2n}$, Fig. 3, results in a straight line with the X-intercept value equal to the band gap. According to this procedure the direct allowed optical band gap of LaPO_4 was estimated to be 3.6 eV.

With the calculated band gap energy, we determined the refractive index (n_0) by solving the

following expression [26]

$$\frac{n_0^2-1}{n_0^2+1} = 1 - \sqrt{\frac{E_g}{20}} \quad (3)$$

where E_g is the band gap energy and n_0 is the index of refraction of the material. The result of the calculation yielded $n_0 = 1.94$.

Fig. 3. Plot of absorption band energy vs. $[F(R)E]^2$

3.2 Judd-Ofelt analysis

The room temperature absorption spectrum of 2% Er doped LaPO_4 is shown in Fig. 4 with all spectral band assignments. All the absorption bands and their barycenters are found to be almost identical to Er doped LaPO_4 single crystal except with some differences in the band intensities [27]. The absorption bands of Er^{3+} ion corresponds to transitions from the $^4\text{I}_{15/2}$ ground state to the various excited levels. By fitting the absorption spectral data with Judd-Ofelt model [28,29], we can predict various radiative spectral properties such as radiative transition probability, fluorescence branching ratio and radiative decay time. According to this procedure, the experimental electric dipole strength of an absorption band can be mathematically expressed as

$$S_{meas}(J \rightarrow J') = \frac{3ch(2J+1)n}{8\pi\bar{\lambda}e^2N_0} \left[\frac{9}{(n^2+2)^2} \right] \Gamma \quad (4)$$

where $\Gamma = \int \alpha d\lambda$, the integrated absorbance, and J' , J are, respectively, the ground and excited state angular momentum quantum number, c is the speed of light, h is plank's constant, n is the refractive index, $\bar{\lambda}$ is the peak absorption band wavelength, e is the charge of an electron in units, N_0 is the dopant ionic concentration in ions/cc.

By Judd-Ofelt procedure, the calculated dipole line strength can be obtained using the expression,

$$S_{calc}(J \rightarrow J') = \sum_{t=2,4,6} \Omega_t \left| \langle (S, L)J \| U^{(t)} \| (S', L')J' \rangle \right|^2 \quad (5)$$

where Ω_2 , Ω_4 , Ω_6 are the Judd-Ofelt phenomenological parameters and the $\|U^{(t)}\|$ factor represent the doubly reduced matrix elements of rank t ($t=2,4,6$) between ground state ($^4I_{15/2}$) to various excited states of Er^{3+} and are obtained from standard reported values [30].

Fig. 4. Optical absorption spectrum of $LaPO_4:Er$ (2%) with spectral band notations for various observed bands.

The best set of Ω parameters are determined by a standard least square fitting of the theoretical line strength (S_{calc}) values to the experimental ones (S_{meas}) and the values obtained are $\Omega_2 = 2.93 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 3.85 \times 10^{-20} \text{ cm}^2$, $\Omega_6 = 0.39 \times 10^{-20} \text{ cm}^2$. Results of the calculations are summarized in Table 1. The quality of the fit was determined from the RMS deviation obtained from

$$RMS = \sqrt{\frac{\sum_1^q (\Delta S)^2}{q-3}} \quad (6)$$

where q is the number of absorption bands considered for calculation and $\Delta S = S_{\text{meas}} - S_{\text{calc}}$

Once the three Judd-Ofelt parameters are obtained it is possible to calculate the radiative transition probability (A) of any emission transitions by using the expression [30],

$$A(J' \rightarrow J) = A_{JJ'}^{ed} + A_{JJ'}^{md} = \frac{64 \pi^4 e^2}{3h(2J+1)\lambda^3} \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right] \quad (7)$$

where, S_{ed} and S_{md} represent the calculated dipole line strength for the electric and magnetic dipole transition respectively. S_{ed} , is calculated using Eq. (5) by using the transition matrix elements for the-

Table 1. Observed absorptions bands with band wavelengths, integrated absorbance (Γ), measured electric dipole line strength (S_{meas}) and calculated electric dipole line strength (S_{calc}).

Transition (from $^4\text{I}_{15/2}$)	λ (nm)	Γ (nm cm^{-1})	S_{meas} (10^{-20} cm^2)	S_{calc} (10^{-20} cm^2)	ΔS (10^{-20} cm^2)
$^4\text{I}_{11/2}$	974.0	57.70	0.49	0.24	0.25
$^4\text{I}_{9/2}$	807.5	45.13	0.46	0.67	-0.21
$^4\text{F}_{9/2}$	655.0	173.99	2.19	2.24	-0.05
$^2\text{H}_{11/2}$ + $^4\text{S}_{3/2}$ + $^4\text{F}_{7/2}$	522.0	347.61	5.49	4.61	0.88
$^2\text{H}_{9/2}$	413.5	18.04	0.36	0.19	0.17
$^4\text{G}_{11/2}$	377.0	187.14	4.09	4.76	-0.67
Er concentration = $1.06 \times 10^{21} \text{ ions cm}^{-3}$			Density (g cm^{-3}) = 5.2		RMS = $0.65(10^{-20} \text{ cm}^2)$

various emission transitions and the magnetic dipole line strength S_{md} can be calculated using the expression [30]

$$S_{md} = \frac{h^2}{16\pi^2 m^2 c^2} \left| \langle (S, L)J \| L + 2S \| (S', L')J' \rangle \right|^2 \quad (8)$$

where the terms inside the bracket represents the transition matrix elements for magnetic dipole transitions, which are identified by applying the selection rules $\Delta S=\Delta L=0$, $\Delta J=0$ and ± 1 but not $0 \rightarrow 0$ transitions. A simpler approach, for determining $A_{md}^{JJ'}$, is by comparing the A_{md} value of LaF_3 with respect to the host, using the equation [26]

$$A_{JJ'}^{md} = \left[\frac{n}{n'} \right]^3 A'_{md} \quad (9)$$

where n and n' are the refractive index of LaPO_4 (1.85) and LaF_3 (1.60) and A'_{md} is the reported magnetic dipole-transition probability of LaF_3 [31].

Adding the radiative transition probability of every transition, running over all final state J , results in the total radiative transition probability $A_T = \sum A(J \rightarrow J')$ that is related with the fluorescence branching ratio, β_{JJ} , by the expression [30]

$$\beta(J \rightarrow J') = \frac{A(J \rightarrow J')}{\sum A(J \rightarrow J')} \quad (10)$$

The total radiative transition probability, A_T , permits us to calculate the radiative decay time τ_r for an excited state J by using the expression [30]

$$\tau_r = \frac{1}{\sum A(J \rightarrow J')} \quad (11)$$

The predicted values of the transition probabilities, radiative decay time and fluorescence branching ratio of several common emission transitions are tabulated in Table 2. It should be noted that the calculated radiative decay time of 7.5 ms is almost in good agreement with previous reported value of 6.7 ms in $\text{LaPO}_4:\text{Er}$ single crystal [27]. It should be noted that in performing these calculations two absorption transitions viz. $^4I_{15/2} \rightarrow ^4F_{5/2}$ and $^4I_{15/2} \rightarrow ^4I_{13/2}$ have to be avoided because of the larger RMS deviation between experimental and calculated dipole strength values. By excluding these two transitions the RMS deviation was reduced to $0.63 \times 10^{-20} \text{ cm}^2$.

Table 2. Calculated radiative spectral properties of LaPO₄:Er for various emission transitions.

Transition		$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$	$A_{ed}(s^{-1})$	$A_{md}(s^{-1})$	$A_{J'J''}(s^{-1})$	$\beta_{J'J''}$	$\tau_{rad}(ms)$
$^4I_{13/2} \rightarrow ^4I_{15/2}$		0.0195	0.1173	1.4316	113.47	19.93	133.40	1.000	7.50
$^4I_{11/2} \rightarrow ^4I_{13/2}$		0.0331	0.1708	1.0864	440.47	4.45	444.93	0.833	1.87
	$^4I_{15/2}$	0	0	0.3953	89.35		89.35	0.167	
$^4I_{9/2} \rightarrow ^4I_{11/2}$		0.003	0.0674	0.1271	273.25	0.64	273.88	0.231	0.84
	$^4I_{13/2}$	0.0004	0.0106	0.7162	378.40		378.40	0.319	
	$^4I_{15/2}$	0	0.1732	0.0099	535.58		535.58	0.451	
$^4F_{9/2} \rightarrow ^4I_{9/2}$		0.1279	0.0059	0.0281	481.00	1.38	482.37	0.077	0.16
	$^4I_{11/2}$	0.0704	0.0112	1.2839	1427.39	3.13	1430.52	0.228	
	$^4I_{13/2}$	0.0101	0.1533	0.0714	955.57		955.57	0.152	
	$^4I_{15/2}$	0	0.5354	0.4619	3407.95		3407.95	0.543	
$^4S_{3/2} \rightarrow ^4I_{9/2}$		0	0.0788	0.2542	3307.08		3307.08	0.531	0.16
	$^4I_{11/2}$	0	0.0042	0.0739	440.53		440.53	0.071	
	$^4I_{13/2}$	0	0	0.3462	1515.92		1515.92	0.243	
	$^4I_{15/2}$	0	0	0.2211	968.14		968.14	0.155	
$^2H_{11/2} \rightarrow ^4F_{9/2}$		0.3629	0.0224	0.0022	2199.25	0.11	2199.36	0.150	0.07
	$^4I_{9/2}$	0.2077	0.0662	0.2858	2169.43	0.00	2169.43	0.148	
	$^4I_{11/2}$	0.0357	0.1382	0.0371	1532.35	50.25	1582.60	0.108	
	$^4I_{13/2}$	0.023	0.0611	0.0527	769.99	33.60	803.59	0.055	
	$^4I_{15/2}$	0.7125	0.4123	0.0925	7864.95		7864.95	0.538	
$^4F_{7/2} \rightarrow ^4F_{9/2}$		0.121	0.0342	0.0151	1807.31		1807.31	0.124	0.05
	$^4I_{9/2}$	0.0163	0.0954	0.4277	2883.06		2883.06	0.197	
	$^4I_{11/2}$	0.0035	0.2648	0.1515	4864.50		4864.50	0.333	
	$^4I_{13/2}$	0	0.3371	0.0001	5641.37		5641.37	0.386	
	$^4I_{15/2}$	0	0.1468	0.6266	4105.64		4105.64	0.281

Figure 5. 980 nm excited NIR emission of LaPO₄:Er for various Er concentrations.

3.3. Near infrared Fluorescence

The 980 nm excited near infrared fluorescence spectrum of the samples as a function of the Er concentration is shown in Fig. 5. The emission spectra consist of the characteristic band originating from the $^4I_{13/2}$ meta-stable level to the terminal $^4I_{15/2}$ level and are peaked at 1554 nm with several Stark level structures in all compositions. Observation of the emission intensity shows a linear increment in the emission intensity with Er concentration. The FWHM of the emission band was estimated to be 81-92 nm, which is comparable to other Er doped crystalline materials [35–38]. The emission spectra were used to estimate all the stimulated emission parameters. The stimulated emission cross-section (σ_e) for 1554 nm transition was evaluated from the measured emission line shape using the expression [30]

$$\sigma_{em} = \frac{\lambda^4 A_{jj'}}{8\pi n^2 \Delta\lambda} \quad (12)$$

where λ is the peak fluorescence wavelength, $A_{jj'}$ is the radiative transition probability of the transition and $\Delta\lambda_{eff}$ is the effective line width, determined using the expression

$$\Delta\lambda_{eff} = \frac{\int I d\lambda}{I_{peak}} \quad (13)$$

where I_{peak} is the peak fluorescence intensity corresponding to 1554 nm. The calculated values of the emission cross-section for different Er content are summarized in Table 3, along with reported emission cross-sections for other crystalline materials [32–35].

Table 3. NIR emission spectral properties of LaPO₄:Er as a function of Er concentrations.

Concentration	λ (nm)	$\Delta\lambda_{eff}$	σ_{em} (10^{-21} cm ²)	Q_m	Q_r	Ref
LaPO ₄ :Er (0.5%)	1554	81.57	3.68	2.67	96	Present work
LaPO ₄ :Er (1%)	1554	81.06	3.70	3.40	95	
LaPO ₄ :Er (2%)	1554	89.76	3.35	11.39	89	
LaPO ₄ :Er (5%)	1554	92.04	3.26	3.50	80	
GGG	1554	81.1	1.55			[33]
Ca ₉ Y(VO ₄) ₇	1533	55	9.43			[32]
YAG	1571	49	5.2		56	[35]
LiLa(MoO ₄) ₂	1530	107.2	0.58			[34]

In order to measure the radiative quantum yield (Q_r) of the 1554 nm emission, fluorescence decay time of the emission was measured as a function of Er concentration and is shown in Fig. 6. All the decay curves can be well fitted with a double exponential fit to extract the decay time. The values of the decay times obtained are 7.24, 7.12, 6.65 and 6.0 ms for 0.5, 1, 2 and 5 mol% Er concentrations. As usual, the fluorescence decay time decreases with the Er^{3+} concentration and is a consequence of various non-radiative energy transfer processes.

The most commonly known fluorescence quenching phenomena in Er^{3+} doped systems are concentration quenching by energy transfer between neighboring ions, upconversion and cross-relaxation [36]. In addition to the concentration quenching process, OH content and multiphonon relaxation could also contribute to the non-radiative processes [37]. With the measured decay values, radiative quantum efficiency was calculated as the ratio of the measured fluorescence decay time to the calculated radiative decay time and the results are summarized in Table 3.

Fig. 6. Fluorescence decay curve of 1554 nm emission as a function of Er concentration.

A theoretical maximum of 96 % quantum yield was obtained at 0.5 mol% Er and it decreases to 80% at 5 mol% Er content. Though the radiative quantum yield shows the upper limit of the efficiency,

a more quantitative way to analyze the result is to measure the quantum efficiency (Q_m) with an integrating sphere with $12\text{W}/\text{cm}^2$ excitation power density at 980nm and the results are shown in Fig. 7 along with the calculated radiative quantum yield. According to this measurement, the measured quantum yield shows a highest value of 11% at 2% Er and after that it decreases continuously. The obtained quantum yield is comparable to several other near infrared emitting rare earths in similar host [38].

In our present quantum yield measurements, the sample was excited using the 980 nm excitation which populate the $^4I_{11/2}$ from where it rapidly decay to the meta-stable state $^4I_{15/2}$ giving rise to the emission band at 1554 nm. However, a better quantum yield can be expected under excitation of the upper level of the $^4I_{15/2}$ state due to the fact that there are no non-radiative losses under this excitation. Because of the lack of a high power laser sources at this wavelength this experiment was a part of our future studies.

Fig. 7. Measured and calculated quantum yield of 1554 nm emission in LaPO_4 for various Er concentrations.

6. Conclusion

Homogeneous precipitation is a more viable synthesis method for rare earth doped metal orthophosphates whose optical properties are matching with phosphor particles synthesized by solvothermal and other solution based methods. Radiative spectral properties of the $\text{LaPO}_4\text{:Er}$ phosphor particles show good correlation with its single crystalline structure. Though the radiative quantum yield shows a theoretical limit of 96 % in 0.5 mol % Er the experimentally measured quantum yield shows a highest value of 11 % in 3 mol% Er doped sample at 1554 nm under 12 W/cm² excitation power density. This slower value is due to the non-radiative losses between the $^4\text{I}_{11/2}$ and the meta-stable emitting state $^4\text{I}_{15/2}$. A higher quantum yield can be expected under direct pumping of the $^4\text{I}_{13/2}$ level.

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