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 h, 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.

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1. Introduction

The introduction of nanotechnology has had profound influence in ceramic materials and their applications in various areas such as medical, military and lighting [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, and fabrication of composite structures. 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 LaPO₄ is considered as a potential candidate in display applications [6,7]. Metal orthophosphates (MPO₄ 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 (YPO₄ = 1.76, LaPO₄ = 1.85, GdPO₄ = 1.97), high density (YPO₄ = 4.22, LaPO₄ = 5.0, GdPO₄ = 6 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 (250–350 cm⁻¹) and chalcogenides (400–520 cm⁻¹). High rare earth solubility and weak ion–ion interactions have been previously reported [13,14]. Bulk MPO₄ (M = La, Gd, 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 LaPO₄ 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

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of the Er concentration and compared with the theoretical radiative quantum yield.

2. Experimental

2.1. Synthesis

LaPO₄: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 La(NO₃)₃ and Er(NO₃)₃ were dissolved into 50 ml of de-ionized water and 13 g of (NH₄)₂HPO₄ was dissolved into 100 ml of de-ionized water. The resulting two solutions were then mixed slowly and NH₄OH was added drop wise, to adjust the pH of combined solutions to 8–9. The resulting precipitate was centrifugally separated (Z232, Labecon, 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 h to obtain the amorphous LaPO₄: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 h 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 Kα radiation at 44 keV and 30 mA. The data were collected in the 20–60° range using a step size of 0.05° and a count time of 0.15 s. 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 camera (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 ± 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 spectrophotometer 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) shown as vertical lines.

![Fig. 1. X-ray diffraction pattern of LaPO₄:Er (2%) in comparison with the standard 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.](image)

Fig. 2 shows a typical FESEM image of prepared LaPO₄: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.

3.2. 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

\[ F(R_a) = \frac{2}{\pi} \left( \frac{1 - R_a}{R_a} \right)^{1/2} \]

where α is the absorption coefficient, S the scattering coefficient, \( R_a \) 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],

\[ \alpha E = K(E - E_g)^n \]

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 (αE)^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 LaPO₄ was estimated to be 3.6 eV.

With the calculated band gap energy, we determined the refractive index (n₀) by solving the following expression [26]

\[ \frac{n_0^2 - 1}{n_0^2 + 1} = 1 - \sqrt{\frac{E_g}{20}} \]

where \( E_g \) is the band gap energy and n₀ is the index of refraction of the material. The result of the calculation yielded \( n_0 = 1.94 \).
3.3. Judd–Ofelt analysis

The room temperature absorption spectrum of 2% Er doped LaPO₄ 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 LaPO₄ single crystal except with some differences in the band intensities [27]. The absorption bands of Er³⁺ ion corresponds to transitions from the ⁴I₁₅/₂ 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

$$S_{\text{meas}}(J \rightarrow J_0) = \frac{3ch}{8\pi^2e^2N_0} \left[ \frac{9}{(n^2 + 2)} \right] \Gamma$$

(4)

where \( \Gamma = \int \alpha dl \), the integrated absorbance, and \( J, J_0 \) 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, \( \lambda \) 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,

$$S_{\text{calc}}(J \rightarrow J_0) = \sum_{t=2,4,6} \Omega_t |\langle S, L | f U | S', L' f' \rangle|^2$$

(5)

where \( \Omega_2, \Omega_4, \Omega_6 \) are the Judd–Ofelt phenomenological parameters and the \( |\langle U | f \rangle| \) factor represent the doubly reduced matrix elements of rank \( t \) (\( t = 2,4,6 \)) between ground state (⁴I₁₅/₂) to various excited states of Er³⁺ and are obtained from standard reported values [30].

The best set of \( \Omega \) parameters are determined by a standard least square fitting of the theoretical line strength \( (S_{\text{calc}}) \) values to the experimental ones \( (S_{\text{meas}}) \) 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

$$\text{RMS} = \sqrt{\frac{\sum_{q}(A_{\text{calc}} - A_{\text{meas}})^2}{q - 3}}$$

(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],

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

(7)

where \( S_{\text{ed}} \) and \( S_{\text{md}} \) represent the calculated dipole line strength for the electric and magnetic dipole transition respectively, \( S_{\text{ed}} \) is calculated using Eq. (5) by using the transition matrix elements for the various emission transitions and the magnetic dipole line strength \( S_{\text{md}} \) can be calculated using the expression [30].
The predicted values of the transition probabilities, radiative decay time and fluorescence branching ration 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 LaPO4:Er single crystal [27]. It should be noted in performing these calculations two absorption transitions viz. 4I15/2 → 4F5/2 and 4I13/2 → 4I11/2 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 × 10⁻²⁰ cm².

3.4. 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 4I13/2 meta-stable level to the terminal 4I15/2 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

\[ S_{md} = \frac{\hbar^2}{16\pi^2 n^2 c^2} \left| \langle (S, L) | J | L + 2S \rangle \right|^2 \]  

(8)

where the terms inside the bracket represents the transition matrix elements for magnetic dipole transitions, which are identified by applying the selection rules ΔS = ΔL = 0, ΔJ = 0 and ±1 but not 0 → 0 transitions. A simpler approach, for determining the total radiative transition probability \( A_{rad} \), by the expression [26].

\[ A_{rad} = \sum_{J} A_{J} \] 

(9)

where \( n \) and \( n' \) are the refractive index of LaPO4(1.85) and LaF3 (1.60) and \( A_{md} \) is the reported magnetic dipole-transition probability of LaF3 [31].

Adding the radiative transition probability of every transition, running over all final state \( J \), results in the total radiative transition probability \( A_{rad} = \sum_{J} A_{J} \) that is related with the fluorescence branching ratio, \( \beta_{J} \) by the expression [30].

\[ \beta_{J} = \frac{A_{J}}{\sum_{J} A_{J}} \] 

(10)

The total radiative transition probability, \( A_{rad} \), permits us to calculate the radiative decay time \( \tau_{r} \), for an excited state \( J \) by using the expression [30].

\[ \tau_{r} = \frac{1}{\sum_{J} A_{J}} \] 

(11)
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 ($\sigma_{em}$) for 1554 nm transition was evaluated from the measured emission line shape using the expression [30]

$$\sigma_{em} = \frac{A_{pp} \lambda^3}{8 \pi n^2 \Delta \lambda}$$  \hspace{1cm} (12)$$

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

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. 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 W/cm$^2$ excitation power density at 980 nm 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 $^4I_{15/2}$ from where it rapidly decay to the meta-stable state $^4I_{11/2}$ 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. 5. 980 nm excited NIR emission of LaPO$_4$:Er for various Er concentrations.](image)

![Table 3](image)

NIR emission spectral properties of LaPO$_4$:Er as a function of Er concentrations.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\lambda$ (nm)</th>
<th>$\Delta \lambda_{eff}$</th>
<th>$\sigma_{em}$ ($10^{-21}$ cm$^2$)</th>
<th>$Q_m$</th>
<th>$Q_r$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPO$_4$: Er</td>
<td>1554</td>
<td>8.15</td>
<td>3.68</td>
<td>2.67</td>
<td>96</td>
<td>Present work</td>
</tr>
<tr>
<td>LaPO$_4$: Er (0.5%)</td>
<td>1554</td>
<td>8.16</td>
<td>3.70</td>
<td>3.40</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>LaPO$_4$: Er (1%)</td>
<td>1554</td>
<td>8.76</td>
<td>3.35</td>
<td>11.39</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>LaPO$_4$: Er (2%)</td>
<td>1554</td>
<td>9.04</td>
<td>3.26</td>
<td>3.50</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>GGG</td>
<td>1554</td>
<td>8.11</td>
<td>1.55</td>
<td></td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td>Ca$_2$X(VO$_4$)$_2$</td>
<td>1533</td>
<td>55</td>
<td>9.43</td>
<td></td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td>YAG</td>
<td>1571</td>
<td>49</td>
<td>5.2</td>
<td>56</td>
<td></td>
<td>[35]</td>
</tr>
<tr>
<td>LiLa(MoO$_4$)$_2$</td>
<td>1530</td>
<td>107.2</td>
<td>0.58</td>
<td></td>
<td></td>
<td>[34]</td>
</tr>
</tbody>
</table>

![Fig. 6. Fluorescence decay curve of 1554 nm emission as a function of Er concentration.](image)

![Fig. 7. Measured and calculated quantum yield of 1554 nm emission in LaPO$_4$ for various Er concentrations.](image)
4. 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 LaPO₄: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 ⁴I₁₁/₂ and the meta-stable emitting state ⁴I₁₃/₂. A higher quantum yield can be expected under direct pumping of the ⁴I₁₃/₂ level.

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