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Flux-solvothermal preparation of dispersible LiLa$_{0.4}$Nd$_{0.6}$(PO$_3$)$_4$ microcrystals with regular morphology and superior fluorescence

Zhongyue Wang, a Weikuan Duan, a Xiaokai Cui, c Chen Liang, b Ruilin Zheng, b Wei Wei bc*

A flux-solvothermal method was firstly used to grow a kind of novel dispersible LiLa$_{0.4}$Nd$_{0.6}$(PO$_3$)$_4$ microcrystals with high Nd$^{3+}$ ions concentration of 2.63×10$^{21}$ cm$^{-3}$ and excellent fluorescence properties for the first time. By optimizing experimental conditions, the microcrystals with the sizes in the region of 1.5~5 μm, strong emission intensity and long lifetime of 107 μs were obtained. The results show that their transparent dispersion in the mixed solvents of DMSO and CHBr$_3$:CHBr$_2$ had strong absorption at 800 nm, low solvent quenching ratio of 6.5%, high quantum yield of 32.17% and large emission cross section of 4.39×10$^{20}$ cm$^2$ when Nd$^{3+}$ ions concentration is 1×10$^{20}$ cm$^{-3}$, which imply the microcrystals is of potential application in transparent glass-ceramics, dispersion amplifiers and lasers.

**Introduction**

Lithium-neodymium tetraphosphate [LiNd(PO$_3$)$_4$, LNP] crystal, as a result of its high Nd$^{3+}$ ions concentration, strong absorption coefficient, low pump threshold and high conversion efficiency, is regard as an extraordinary promising miniature laser material. In LNP crystal, the Nd$^{3+}$ ions concentration (N) can reach 4.39×10$^{21}$ cm$^{-3}$, [1] which is approximately ca.32 times higher in commercial 1.0 at% Nd:YAG crystal. Although it has so high concentration of Nd$^{3+}$ ions, the fluorescence quenching effect of LNP crystal is particularly weak due to weakening of the dipole interaction between Nd$^{3+}$ ions separated by the group of —O—P—O—. [2] Therefore, the fluorescence lifetime of LNP crystal still keeps special long under high Nd$^{3+}$ concentration, and the cross relaxation rate (Q) is only about 0.5×10$^{-43}$ cm$^6$, it is about 20 times smaller than that of Nd:YAG. [3] At the same time, the absorption cross section ($\sigma_a$) and emission cross section ($\sigma_e$) are equivalent to these of Nd:YAG while the lifetime (τ) is about half of that of Nd:YAG (Table 1). Then the gain coefficient of LNP crystal proportional to $\frac{\sigma_a \sigma_e N}{N}$ [4] is about 20 times larger than that of Nd:YAG, all these imply that LNP crystal can obtain higher optical gain in short optical path. Up to now, LNP crystal has the lowest saturation parameter ($I_s$) of 49 Wmm$^{-2}$ [3] and the lowest measured pump threshold energy of 0.14 mw. [5] Besides, LNP possesses no ferroelastic twinning domains and doesn’t have the pronounced cleavability of NdP$_2$O$_{14}$ (NPP). [6]

As a high quality laser material, LNP crystal was investigated in the early 1970s, but it hasn’t been applied widely so far. One of the most important reasons is that large size of LNP crystal is too difficult to grow. In past 40 years, two methods, including high-temperature solution method [9-11] and flux method, [12-14] were used to grow LNP single crystal. Compared to high-temperature solution method, flux method has many outstanding advantages, such as wider applicability, simpler device, lower growing temperature and higher crystalline quality, so it become the main method for preparing LNP crystal. However, low growing temperature means slow growth rate and long growth cycle, and more importantly, it will cause small crystal size.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Nd:YAG (1.0 at %)</th>
<th>LNP</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(10$^{20}$cm$^{-3}$)</td>
<td>1.38</td>
<td>43.9</td>
</tr>
<tr>
<td>$\sigma_a$(10$^{20}$cm$^{-2}$)</td>
<td>12</td>
<td>12.5</td>
</tr>
<tr>
<td>$\sigma_e$(cm$^{-1}$)</td>
<td>16.56</td>
<td>548.75</td>
</tr>
<tr>
<td>$\sigma_e$(10$^{-20}$cm$^2$)</td>
<td>280</td>
<td>32</td>
</tr>
<tr>
<td>τ(μs)</td>
<td>230</td>
<td>120</td>
</tr>
<tr>
<td>$\sigma_a \sigma_e N$(10$^{15}$ cm$^{-1}$μs)</td>
<td>1.066</td>
<td>21.072</td>
</tr>
<tr>
<td>ref</td>
<td>7.8</td>
<td>1.3,4</td>
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</table>

Scientists had investigated the structure, morphology and optical properties of nanoparticles for many years, [15-17] and many people began to focus their attentions on neodymium ultraphosphate micro- and nano-crystals in past few years. H.Naili investigated the synthesis, structural, IR spectroscopy and conductivity of AgGd(PO$_3$)$_3$ powder in 2006, [18] and T. Shalapska studied the luminescence properties of Ce$^{3+}$-doped LiGdP$_2$O$_{12}$ microcrystals in 2009. [19] Since the growing temperature of melt solution technique was over 550°C, it results in fast-growing of crystals and irregular morphology with the sizes in the region of 5~100 μm. Almost at the same
time, NdP2O14, LiLnP2O12 (Ln=La/Nd, Yb) [20-21] and LiLn(PO4)3 (Ln=La/Nd, Eu) [22-23] nanocrystals were reported. Yet the work by using flux method to make LiNd(PO4)3 microcrystals have never been reported.

In this paper, a flux-solvothermal method was utilized to prepare LiLa0.4Nd0.6(PO4)3 microcrystals. We investigated the influence of the preparation conditions containing growth temperature, growth time and solvothermal on its fluorescence intensity and lifetime at first. Under the optimal conditions, LiLa0.4Nd0.6(PO4)3 microcrystals have perfect crystallization with relatively small size of 1.5-5 μm. What’s more, they can be dispersed in a mixed solvent of DMSO/CHBr3/CH2Br2 to form a transparent dispersion, and has particularly low solvent quenching rate. Besides, the emission quantum yield and the emission cross section of the dispersion with Nd3+ ions concentration of 1×10−3 mol/L were calculated as 32.17% and 4.39×10−20 cm2 respectively based on the Judd-Ofelt theory.

**Experimental**

**Materials**

HNO3 (GR, 65-68%), CH3CH2OH (AR) and H3PO4 (GR, ≥85%) were obtained from Aladdin Chemistry Co., Ltd. Urea while Li2CO3 (99%), Nd2O3 (99.9%), La2O3 (99%), DMSO (99.9%) and CHBr3/CH2Br2 (97%) were provided by Alfa Aesar.

**Preparation of LiLa0.4Nd0.6(PO4)3 microcrystals**

In a typical synthesis, 25 ml of phosphoric acid (85%) containing 0.6 mmol Nd2O3, 0.4 mmol La2O3, 8.5 mmol Li2CO3 were added to a 50 ml glassy carbon crucible under agitation. The reaction was controlled at 250 °C for 24 h to evaporate the free water first, then rise the temperature to 330 °C and keep it for 3h. Follow on, the crucible was cooled to room temperature in the air, and the product were washed by boiled water, 0.1 mol/L HNO3, cold water and ethanol for 3 times orderly. The collected product was put in a 100 mL Teflon-lined autoclave with 70 mL ethanol and treated at 180°C for 12 h. After solvothermal treatment, the reactor was cooled to room temperature, and the products were centrifuged and washed by water and ethanol for 3 times. Finally, the residual precipitation was dried at 60°C for 48 h at vacuum.

**Preparation of LiLa0.4Nd0.6(PO4)3 microcrystals dispersion**

The dispersion was prepared by adding 0.5 mL mixed solvents of DMSO and CHBr3/CH2Br2 under definite volume proportion in quartz cuvette containing 67 mg LiLa0.4Nd0.6(PO4)3 microcrystals powder and treated by ultrasonic finally.

**Characterization**

The fluorescence spectra of all LiLa0.4Nd0.6(PO4)3 microcrystals were recorded by ZolixOmini-k 300 spectrophotometer pumped by a laser diode at 800 nm, and the luminescence decay times were measured by a 300 MHz Tektronix oscilloscope (Model 3032B). The quantum yield of LiLa0.4Nd0.6(PO4)3 microcrystals dispersion was tested on full-featured steady state/transient fluorescence spectrometer FLS920 from Edinburgh Instruments. The X-ray diffraction (XRD) patterns were measured on a Rigaku Dmax-2400 X-ray powder diffractometer with graphite monochromatized Cu Kα radiation (kα=0.154 nm). The morphologies were characterized by a JEOI JEM-2100F field emission transmission electron microscope (TEM) under a 200 kV working voltage. The transmissivity and absorption spectrum of dispersion were recorded using a UV-vis-NIR spectrophotometer (Shimadzu UV-3600) at room temperature.

**Results and discussion**

The fluorescence intensity and lifetime of as prepared LiLa0.4Nd0.6(PO4)3 microcrystals are mainly affected by growth temperature, growth time and solvothermal, which have been discussed in detail as follows.

**Effect of growth temperature on fluorescence properties**

It is well-known that growth temperature plays the leading role on growing crystals by flux method. Generally, phosphoric acid (H3PO4) will lose water into pyrophosphate (H2PO4) at about 250°C, then turns into metaphosphate (HPO3) at 280°C, which is the cause of that flux method is often carried out at above 300°C on growing LNP crystals. Therefore, three temperatures of 300°C, 330°C and 360°C were chose as the growth temperature of LiLa0.4Nd0.6(PO4)3 microcrystals.

![Fig.1](image-url) Fig.1 Fluorescence spectra of LiLa0.4Nd0.6(PO4)3 microcrystals prepared at (A)300°C, (B)330°C and (C)360°C for 2 h. The inset is the fluorescence decay curves of corresponding samples.

Fig.1 is the fluorescence spectra and fluorescence decay curves of LiLa0.4Nd0.6(PO4)3 microcrystals prepared at different temperature for 2h. Obviously, three fluorescence spectra are consistent and the lifetimes are longer than LaPO4: Nd (5 mol%) (90μs). [24] By increasing the growth temperature from 300°C to 330°C, the fluorescence intensity and lifetime improved markedly. The main reason is that higher temperature prolonged the effective growth time and quickened the growth rate. In fact, high temperature process of 2 h can be divided into two parts, including the water evaporation from H3PO4 to HPO3 and the effective growth of LiLa0.4Nd0.6(PO4)3. Higher temperature will speed up the evaporation of water and
prolonged the effective growth time indirectly, as well as quickened the growth rate.

Nevertheless, higher temperature is not always better. On one hand, it will increase the number of nuclei and the range of particle distribution. On the other hand, exorbitant temperature often associated with a variety of crystal types and defect, which will affect the optical properties seriously. The weaken of fluorescence properties of LiLa_{0.4}Nd_{0.6}(PO_4)_4 is probably the main cause of crystal defects by further increasing the temperature from 330 °C to 360 °C.

Effect of growth time on fluorescence properties

![Fluorescence spectra of LiLa_{0.4}Nd_{0.6}(PO_4)_4 microcrystals prepared at 330 °C for 4h, following by (A) solvothermal treatment at 180 °C for 12h and (B) without solvothermal treatment.](image)

In determining 330 °C as the optimal growth temperature, the influence of growth time on fluorescence spectra and fluorescence decay curves of LiLa_{0.4}Nd_{0.6}(PO_4)_4 microcrystals was shown in Fig.2.

By prolonging reaction time from 2h to 8h, both the fluorescence intensity and lifetime were improved to some extent, but the increase rate reduced gradually. It is well known that the specific surface area will reduce slowly while the size of the microcrystals increases rapidly with the extension of growth time. So the fluorescence performance will be proportional to the increases of effective active ions ratio caused by specific surface area decreasing, which can match the Fig.2 very well. But, the fluorescence performance enhancement is limited in extending the growth time, and 4h was designated as the best growth time.

Effect of solvothermal treatment on fluorescence properties

As a broad synthesis method of inorganic semiconducting nanostructures, hydrothermal treatment is not only an effective approach on optimizing the crystallization for more complete, but also a way to remove impurities to a certain degree. Herein we added a solvothermal process to expect better fluorescence performance. As it can be seen from the fluorescence spectra and fluorescence decay curves of LiLa_{0.4}Nd_{0.6}(PO_4)_4 microcrystals by different treatments (Fig.3), the fluorescence properties of the microcrystals treated at 180 °C for 12h in ethanol were improved markedly, which was roughly correspondent with our wishes.

![Fluorescence spectra of LiLa_{0.4}Nd_{0.6}(PO_4)_4 microcrystals prepared at 330 °C for 4h following by (A) solvothermal treatment at 180 °C for 12h and (B) without solvothermal treatment. The inset is the fluorescence decay curves of corresponding samples.](image)

Morphology and crystal phase of LiLa_{0.4}Nd_{0.6}(PO_4)_4 microcrystals

![XRD patterns (A) and TEM images (B and C) of LiLa_{0.4}Nd_{0.6}(PO_4)_4 microcrystals prepared at 330 °C for 4h, following by solvothermal treatment at 180 °C for 12h. The inset is HRTEM of LiLa_{0.4}Nd_{0.6}(PO_4)_4 microcrystals.](image)

By the optimal experimental conditions, LiLa_{0.4}Nd_{0.6}(PO_4)_4 microcrystals with perfect crystallization and relatively small size were obtained, as shown in Fig.4. All the diffraction peaks can match with the standard card (JCPDS 34-0003) perfectly (Fig.4A), which means the product crystallizes in pure monoclinic-phase of LiNd(PO_4)_4. The sharp diffraction peaks illustrated that the size of LiLa_{0.4}Nd_{0.6}(PO_4)_4 is a little big, it was proved by the TEM images of the microcrystals, which had regular shape and a size range of 1.5~5 μm (Fig.4B and C). Besides, HRTEM (the inset of Fig.4C) reveal that these...
microcrystals are single-crystalline, and they mainly show the lattice fringes of (3 1 -1) plane and (0 0 2) plane.

As everyone knows, an oblique crystal surface is the biggest feature of monoclinic system. All the LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals observed in the TEM images have oblique crystal surface, illustrating that the microcrystals crystallized in monoclinic-phase. What’s more, all the angles signed in the TEM image are about 126°, consistent with the cell parameters ($\beta=126.46^o$) of LiNd(PO$_4$)$_3$. It is another evidence of monoclinic LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals.

Optical properties of LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals dispersion

A noteworthy phenomenon is that LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals can be dispersed in a mixed solvents of DMSO and CHBr$_2$CHBr$_2$ in a certain volume ratio to form a transparent purple dispersion (the inset of Fig.5). Generally, the scattering phenomenon of particles dispersion will rise sharply with increasing the particles size, embodying in serious muddy performance of the dispersion.

Besides, another factor affected the transmittance of the dispersion is the matching degree of refractive index between particles and solvents. In view of the particles of LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ in micron level, we identified that adjusting the refractive index of solvents to match that of LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals is the only way to get a transparent dispersion. Finally, CHBr$_2$CHBr$_2$ and DMSO were chose as the main solvent.

By fitting the fluorescence decay curves of LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals and their dispersions with different Nd$^{3+}$ ions concentrations (Fig.6) by using single exponential function, four lifetimes of 107 μs, 100 μs, 99 μs and 95 μs were obtained respectively. Based on the equation of ($\tau_{\text{powder}}$-$\tau_{\text{dispersion}}$)/$\tau_{\text{powder}}$, particular low quenching rates of solvents on LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals were calculated as 6.54%, 7.48% and 11.2% for three kinds of Nd$^{3+}$ ions concentrations, which confirmed above conjecture.

Fig.5 Fluorescence spectra of LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals and their dispersions in DMSO/CHBr$_2$CHBr$_2$ with different Nd$^{3+}$ ions concentrations. The inset is the photograph of LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals dispersion with Nd$^{3+}$ ions concentration of 1×10$^{20}$ cm$^{-3}$ in quartz utensil (2 mm×10 mm×45 mm) and upconversion spectrum.

Fig.6 Fluorescence decay curves of LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals (A) and their dispersions in DMSO/CHBr$_2$CHBr$_2$ with different Nd$^{3+}$ ions concentrations: (B)1×10$^{20}$ cm$^{-3}$, (C)0.5×10$^{20}$ cm$^{-3}$ and (D)0.1×10$^{20}$ cm$^{-3}$.

Fig.7 Transmittance(A) and Absorption coefficient (B) spectra of LiLa$_{0.4}$Nd$_{0.6}$(PO$_4$)$_3$ microcrystals dispersion with Nd$^{3+}$ ions concentration of 1×10$^{20}$ cm$^{-3}$.
In addition, the transmittance and absorption coefficient spectra of LiLa_{0.6}Nd_{0.4}(PO_3)_4 microcrystals dispersion with Nd^{3+} ions concentration of 1×10^{20} cm^{-3} were measured (Fig. 7). Five absorption peaks can be observed obviously, and the special sharp peak at 800 nm means strong absorption of the excitation light, which can be seen in Fig. 7B. However, the transmittance of the dispersion was very low in the visible region below 550 nm, which is mainly caused by scattering of relatively large particles size.

**Judd-Ofelt analysis**

According to the Judd-Ofelt theory and the absorption coefficient spectrum of LiLa_{0.6}Nd_{0.4}(PO_3)_4 microcrystals dispersion (Fig. 7B), some optical parameters were calculated to evaluate the laser performance of the dispersion. Under reference to the refractive index of LNP single crystal, [28] five experimental oscillator strengths (f_{exp}) of electronic transitions of Nd^{3+} ions from ground state (\(^4I_{\frac{11}{2}}\)) to various excited states can be calculated by Equation 1.

\[ f_{\text{exp}} = \frac{m e^2}{4\pi \varepsilon_0 N \hbar^2} \int \alpha(\lambda) d\lambda \]  

(1)

Where \(m\) and \(e\) are electron mass and charge, \(c\) is the velocity of light, \(N\) is the number density of Nd^{3+} ions, and \(\alpha(\lambda)\) is the absorption coefficient.

Based on Equation 2, the calculated oscillator strengths (f_{cal}) of electronic transitions from the ground state (\(aJ\)) to the excited state (\(bJ'\)) level are obtained.

\[ f_{\text{cal}}(aJ, bJ') = \frac{8 \pi^2 m c \chi}{3h(2J+1)} S \]  

(2)

Where \(\chi\) is the local field correction factor expressed as \(\chi = n(n^2-2)^{\frac{1}{2}}/\hbar\), \(n\) is the Planck constant, \(2J+1\) is the degeneracy of the ground state, and \(S\) is the spectral line intensity of the electronic dipole transitions, which can be expressed as the following equation:

\[ S = \sum_{i=2,4,6} \Omega_i \langle aJ \| U^{(i)} \| bJ' \rangle^2 \]  

(3)

Here \(|\langle aJ \| U^{(i)} \| bJ' \rangle|^2\) represents the reduced matrix elements given by Carnall et al. [29] The J-O parameters \(\Omega_i(2, 4, 6)\) are calculated by a least-squares fitting of \(f_{\text{exp}}\) to \(f_{\text{cal}}\).

The absorption bands, absorption coefficient, experimental and theoretical oscillator strengths and Judd-Ofelt parameters \(\Omega_i(2, 4, 6)\) obtained for LNP nanocrystals dispersion with Nd^{3+} ions concentration 1×10^{20} cm^{-3} were presented in Table 2.

On the basis of \(\Omega_i(2, 4, 6)\) parameters, the emission line strengths corresponding to transitions from the upper multiplet manifolds \(2S^+1L_{\frac{1}{2}}\) to the lower manifolds \(2S^+1L'_{\frac{1}{2}}\) can be calculated.

\[ S_{\text{in}}(J, J') = \frac{3hc(2J+1)}{8\pi^2 \varepsilon_0^2 \lambda^3} \int k(\lambda) d\lambda \]  

(4)

<table>
<thead>
<tr>
<th>Transition</th>
<th>Absorption peak (nm)</th>
<th>Absorption coefficient (\bar{\alpha}(\lambda)d\lambda) ((1^0))</th>
<th>Oscillator strength (f_{\text{exp}}) ((10^4 \text{cm}^2))</th>
<th>Oscillator strength (f_{\text{cal}}) ((10^4 \text{cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^4\text{G}<em>{5/2} \rightarrow ^4\text{S}</em>{7/2})</td>
<td>522</td>
<td>10.93717</td>
<td>3.18898</td>
<td>5.16737</td>
</tr>
<tr>
<td>(^4\text{G}<em>{7/2} \rightarrow ^4\text{S}</em>{7/2})</td>
<td>577</td>
<td>13.50392</td>
<td>7.19509</td>
<td>10.9464</td>
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<tr>
<td>(^4\text{F}<em>{7/2} \rightarrow ^4\text{S}</em>{7/2})</td>
<td>748</td>
<td>36.19294</td>
<td>5.13935</td>
<td>7.48763</td>
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<tr>
<td>(^4\text{F}<em>{9/2} \rightarrow ^4\text{S}</em>{7/2})</td>
<td>800</td>
<td>43.77406</td>
<td>5.4205</td>
<td>7.39324</td>
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<tr>
<td>(^4\text{I}_{11/2})</td>
<td>871</td>
<td>16.66125</td>
<td>1.74485</td>
<td>2.45756</td>
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</tbody>
</table>

Then the radiative decay rates \(A(J \rightarrow J')\) for transitions between the upper manifold \(J\) and the corresponding lower multiplet manifolds \(J'\) is obtained by the following expression.

\[ A(J \rightarrow J') = \frac{64\pi^4 e^2 \chi}{3\hbar(2J+1)\lambda^3} S_{\text{in}}(J \rightarrow J') \]  

(5)

The quantum efficiency (\(\varphi\)) of the emission bands can be evaluated from function 8.

\[ \varphi = \frac{A_{\text{em}}}{A_{\text{rad}}} \]  

(8)

The fluorescence branching ratios \(\beta(J \rightarrow J')\) for transitions originating from the \(^4\text{F}_{5/2}\) manifold are determined from the radiative decay rates by Equation 7.

\[ \beta(J \rightarrow J') = A(J \rightarrow J')/\tau_i \]  

(7)

Besides, the stimulated emission cross section \(\sigma\) for \(^4\text{F}_{5/2} \rightarrow ^4\text{I}_{1/2}\) transition is calculated by Equation 9.

\[ \sigma = \frac{\lambda_{\text{eff}}^3}{8\pi n^2 c \Delta \lambda_{\text{eff}}} A_{\text{em}}(a,b) = \frac{1}{8\pi n^2 c \Delta \lambda_{\text{eff}}} A_{\text{em}}(a,b) \]  

(9)

Where \(\Delta \lambda_{\text{eff}}\) is the effective fluorescence line width at the peak wavelength (\(\lambda_{\text{p}}\)) for \(^4\text{F}_{5/2} \rightarrow ^4\text{I}_{1/2}\) transition and is equal to

\[ \Delta \lambda_{\text{eff}} = \frac{\int I(\lambda) d\lambda}{I_{\text{max}}} \]  

(10)

The radiative decay rates \(A_{\text{rad}}\), fluorescence branching ratios \(f_{\text{exp}}\), radiative lifetime \(\tau_i\) of the excited state \(^4\text{F}_{5/2}\) \((J=3/2)\), quantum yield and emission cross section of the \(^4\text{F}_{5/2} \rightarrow ^4\text{I}_{11/2}\) were listed in Table 3.
This work was financially supported by the National Basic Research Program of China (No. 2012CB933301) and National Natural Science Foundation of China (No.60977023, 61077070, 61107015 and 61177086).

Notes and references


Table 3 Observed emission bands, their measured and calculated radiative properties of LiLa\(_{0.4}\)Nd\(_{0.6}\)(PO\(_4\))\(_3\) microcrystals dispersion.

<table>
<thead>
<tr>
<th>n</th>
<th>λ(_{\text{ex}}) (nm)</th>
<th>(A_{\text{rad}}) (% (\times 10^{-5}))</th>
<th>(\beta_{\text{np}})</th>
<th>(\tau_{\text{rad}}) (μs)</th>
<th>(\eta) (%)</th>
<th>(\sigma) (10(^{-20}) cm(^2))</th>
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<tbody>
<tr>
<td>1</td>
<td>780</td>
<td>3.01 × 10(^{-5})</td>
<td>50</td>
<td>311</td>
<td>33.18</td>
<td>3.09 × 10(^{-20})</td>
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<td>2</td>
<td>859</td>
<td>8.12 × 10(^{-5})</td>
<td>42.23</td>
<td>311</td>
<td>33.18</td>
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<tr>
<td>3</td>
<td>1049</td>
<td>15.51 × 10(^{-5})</td>
<td>48.22</td>
<td>311</td>
<td>33.18</td>
<td>3.09 × 10(^{-20})</td>
</tr>
<tr>
<td>4</td>
<td>1318</td>
<td>30.74 × 10(^{-5})</td>
<td>9.56</td>
<td>311</td>
<td>33.18</td>
<td>3.09 × 10(^{-20})</td>
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In order to validate the reliability of quantum yield we calculated, a test quantum yield of LiLa\(_{0.4}\)Nd\(_{0.6}\)(PO\(_4\))\(_3\) microcrystals dispersion in DMSO/CHBr\(_2\)CHBr\(_2\) was taken, as shown in Fig. 8. By integrating the emission intensity and excitation intensity, we can obtain the photon counts emitted and absorbed by LiLa\(_{0.4}\)Nd\(_{0.6}\)(PO\(_4\))\(_3\) microcrystals dispersion. Then the test quantum yield, the quotient of emitted photon counts divided by absorbed photon counts, was determined to be 35.51%, which is a little higher than the value by Judd-Ofelt calculation.

Conclusions

In summary, LiLa\(_{0.4}\)Nd\(_{0.6}\)(PO\(_4\))\(_3\) microcrystals with the sizes of 1.5–5 μm were grown via flux–solvothermal method by optimizing growth temperature and time, and solvothermal process. They can be dispersed in mixed solvents of DMSO and CHBr\(_2\)CHBr\(_2\) to form a transparent purple dispersion, which had high quantum yield of 32.17%, large emission cross section of 4.39*10\(^{-20}\) cm\(^2\) and low quenching ratio of 6.5%. It is a potential gain medium for transparent glass-ceramics, dispersion amplifiers and lasers.

Acknowledgements

Acknowledgements

Notes and references

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