This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Synthesis and luminescent properties of La$_{1-x}$Nd$_x$P$_5$O$_{14}$ nanocrystals

L. Marciniak,$^{a,*}$ W. Strek,$^a$ Y. Guyot$^b$ and D. Hreniak$^c$,

La$_{1-x}$Nd$_x$P$_5$O$_{14}$ nanocrystals were synthesized by coprecipitation method. Their structure and morphology were determined. The luminescence and excitation spectra of La$_{1-x}$Nd$_x$P$_5$O$_{14}$ nanocrystals were measured in the entire range of Nd$^{3+}$ concentration. It was found that the relative intensities of absorption transitions increased significantly with concentration due to the cooperative interactions. The effect of concentration on fluorescence transitions was investigated. It was found the intensity of the $^4F_{3/2} ightarrow ^4I_{11/2}$ transition significantly increased with concentration relative to the resonant $^4F_{3/2} ightarrow ^4I_{9/2}$ transition almost three times due to strong reabsorption. The concentration quenching of fluorescence was discussed in terms of the Yokota-Tanimoto model.

Moreover, a significantly lower threshold of the laser action reported for NdP$_5$O$_{14}$ crystal around 0.45mW classifies those materials, together with LiNdP$_5$O$_{14}$ (threshold around 0.36mW), as one of the most important hosts for laser oscillation$^5$. Crystals of neodymium pentaphosphates reveal tendency to twinning due to their ferroelastic properties, which becomes a problem for laser crystals preparation with reduced defects. Spectroscopic properties of neodymium phosphates crystals and glasses have been reported by many authors$^{15-22}$. Recently we have reported on optical properties of LiLa$_{1-x}$Nd$_x$P$_5$O$_{14}$ nanocrystals$^{14,19-26}$ and LiLa$_{1-x}$Dy$_x$P$_5$O$_{14}$ nanocrystals$^{23}$. In this paper we report synthesis, structural and spectroscopic properties of the La$_{1-x}$Nd$_x$P$_5$O$_{14}$ nanocrystals. Despite the fact that the spectroscopic properties and laser engineering of La$_{1-x}$Nd$_x$P$_5$O$_{14}$ crystals have been thoroughly investigated$^{11,15-13}$ no spectroscopic studies of respective nanocrystals have been performed. In particular our interest was focused on the concentration quenching of the Nd$^{3+}$ luminescence and the mechanism of cooperative interactions.

Experimental

Nanocrystals of lanthanum pentaphosphates doped with neodymium ions (La$_{1-x}$Nd$_x$P$_5$O$_{14}$) were synthesized by a coprecipitation method. Lanthanum oxide (La$_2$O$_3$ 99.99% from...
Stanford Materials Corporation), neodymium oxide (Nd$_2$O$_3$ 99.95% from Stanford Materials Corporation) and diammonium phosphate ((NH$_4$)$_2$HPO$_4$ from Sigma Aldrich) were used as starting materials. Appropriate amounts of lanthanum oxides were diluted in nitric acid in order to obtain nitrates. Afterwards, water solution of nitrates was combined with water solution of diammonium phosphates and the obtained solution was stirred using magnetic stirrer for 7 h and dried at 90°C for 48 h. Obtained precursor was ground in a mechanical mill for 2 h in order to achieve homogenization followed by sintering for 6 h in 550°C.

The X-ray diffraction measurements (XRD) of La$_{1-x}$Nd$_x$P$_2$O$_{14}$ nanocrystalline powders were measured in Bragg-Brentano geometry on PANalytical X'Pert Pro diffractometer with a beta-filtered Cu Kalpha radiation ($\lambda = 0.15418 \text{ nm}$). Transmission electron microscopy (TEM) images were taken with a JEM-2100F microscope under an operating voltage of 200 kV. The back scattering absorption spectra of nanocrystalline powders were measured using Varian Cary 5 UV-VIS Spectrophotometer.

The emission spectra were measured in the 800-1700 nm range with a CCD IDUS near-infrared InGaAs camera from ANDOR equipped with a 900 line/mm grating blazed at 1300 nm under 808 nm excitation line of a laser diode.

Decay profiles were measured using digital oscilloscope LeCroy WaveSurfer 400 and 532 nm excitation line of pulsed Nd:YAG (2$\text{nd}$ harmonic) and Horiba Jobin–Yvon HR1000 monochromator supplied with a Hamamatsu R5108 photomultiplier tube. Low temperature measurements were performed using a HC2 cryostat from APD Cryogenics equipped with a 330 Autotuning Temperature Controller from Lake Shore. The low temperature measurements were carried out in a closed flow cryostat.

**Results and discussion**

There are three types of crystallographic groups into which Ln$_5$P$_3$O$_{14}$ structure can crystallize: monoclinic P21/c, monoclinic C2/c and orthorhombic Pncm$^{28-30}$. However, at room temperature the monoclinic P21/c phase is dominant. The ferroelastic phase transition was observed at $\sim$426 K$^3$. The structure of Nd$_5$P$_3$O$_{14}$ is presented in Fig. 1a. One can notice characteristic ribbons of (PO$_4$)$^3-$ tetrahedrons and well separated Nd$^{3+}$ ions.

The cell parameters are as follows $a = 8.771 \text{ Å}$, $b = 9.012 \text{ Å}$, $c = 13.057 \text{ Å}$, $\beta = 89.58^\circ$ with $V = 1032.05 \text{ Å}^3$ and $Z = 4$. In Fig. 1b, a dodecahedron of the first coordination sphere with distance lengths between ions emphasis can be observed. It is clearly seen that the length of the Nd$^{3+}$-O$^2-$ distance changes in the range of 2.28-2.50 Å while the distance between the neighboring Nd$^{3+}$ ions is relatively large (5.19 - 6.62 Å).

The phase purity of the La$_{1-x}$Nd$_x$P$_2$O$_{14}$ nanocrystals was confirmed by the X-ray diffraction (XRD) measurements (Fig. 2a). All of the observed reflections correspond to the reference profile of a monoclinic Nd$_5$P$_3$O$_{14}$ phase with a space group P1 21/c1 (ISCD 2035). From the Rietveld analysis, the average grain size of the La$_{1-x}$Nd$_x$P$_2$O$_{14}$ nanocrystals was determined to be 45 nm. This result was confirmed by transmission electron microscopy (TEM) images (Fig. 2b). More TEM images can be found in the Supporting Information. However it is important to mention that the resolution of the images was limited due to low stability of phosphates crystals under high voltage of the electron beam. One can see a number of agglomerates composed of nanocrystals due to ferroelasticity of the pentaphosphate crystals$^3$.

![Figure 1](image1.png)

**Figure 1.** Structure visualization of a Nd$_5$P$_3$O$_{14}$ crystal; with specified Nd$^{3+}$-Nd$^{3+}$ and Nd$^{3+}$-O$^2-$ distances b.

![Figure 2](image2.png)

**Figure 2.** The X-ray diffraction patterns of the La$_{1-x}$Nd$_x$P$_2$O$_{14}$ nanocrystals - a; and transmission electron microscopy (TEM) image of Nd$_5$P$_3$O$_{14}$ nanocrystals - b.
For high dopant concentration, the population of the \(^4\)I\(_{11/2}\) state becomes more efficient due to the \(^4\)F\(_{5/2}\)\(\rightarrow\)^\(^4\)I\(_{11/2}\) luminescence.

After populating the \(^4\)I\(_{11/2}\) state, the absorption both from \(^4\)I\(_{9/2}\) and \(^4\)I\(_{11/2}\) terms can occur leading to the cooperative absorption process. The intensity of the cooperative absorption transition \(I_{coop}\) is proportional to a square of the dopant concentration \(x\) so that the relative intensity of the absorption transitions shown in Fig. 3 b results in a linear plot \(I_{coop} / I \sim x\), where \(I\) is the absorption intensity for non-interacting ions. The cooperative absorption transitions were reported previously for LiLa\(_{x}\)Pr\(_x\)P\(_2\)O\(_{12}\) bulk crystals by Strek\(^{32}\), for PrCl\(_3\) crystals by Varsanyi and Dieke\(^{33,34}\) and for EuO\(_2\)S by Tanner and Pei\(^{35}\). A detailed discussion of the mechanism responsible for the cooperative absorption transitions in LiLa\(_{x}\)Nd\(_x\)P\(_2\)O\(_{12}\) nanocrystals was recently presented by us\(^{27}\).

The emission spectra of La\(_{1-x}\)Nd\(_x\)P\(_2\)O\(_{14}\) nanocrystals were measured at room temperature using the 808 nm laser diode excitation line (see Fig. 4a). Three characteristic luminescence bands located at around 890 nm, 1060 nm and 1350 nm are associated with transitions from the excited \(^4\)F\(_{3/2}\) state to the \(^4\)I\(_{9/2}\), \(^4\)I\(_{11/2}\) and \(^4\)I\(_{13/2}\) multiplets. One can notice that in all presented spectra the so-called ‘laser transition’ \(^4\)F\(_{3/2}\)\(\rightarrow\)^\(^4\)I\(_{11/2}\) is dominant. However with the increase of the dopant concentration the ratio of the transition intensities between particular bands changes. The emission branching ratio of the fluorescent transition intensities \(\beta_j\) from the \(^4\)F\(_{3/2}\) state to the \(^4\)I\(_j\) terminal states is

\[
\beta_j = \frac{I_j}{\sum I_j}
\]

(1)

Where \(I_j\) is the emission intensity of the \(^4\)F\(_{3/2}\)\(\rightarrow\)^\(^4\)I\(_j\) transition and the sum in the denominator is taken over all the states into which a radiative depopulation of \(^4\)F\(_{3/2}\) takes a place.

The effect of concentration on the intensity branching ratios is shown in Fig. 4b. One can see that the value of \(\beta_{11/2}\) remains stable (\(\sim 0.09\)) in the entire range of concentrations while \(\beta_{9/2}\) as well as \(\beta_{11/2}\) are strongly affected by the concentration. For the most diluted sample (\(x = 0.01\)) the band intensities are almost comparable (\(\beta_{9/2}=0.45\) while \(\beta_{11/2}=0.55\)). However, with the increase of the Nd\(^{3+}\) concentration \(\beta_{9/2}\) gradually decreases, while \(\beta_{11/2}\) increases. The mechanism responsible for such behavior is associated with the fast diffusion of excitation energy corresponding to the resonant \(^4\)F\(_{3/2}\)\(\rightarrow\)^\(^4\)I\(_{9/2}\) transition. It is clearly seen (Fig. 4a) that with the increase of the dopant concentration the short wavelength part of the \(^4\)F\(_{3/2}\)\(\rightarrow\)^\(^4\)I\(_{9/2}\) transition band decreases. These components of the emission band are associated with the transition from \(^4\)F\(_{3/2}\) to the \(I_3\) and \(Z_2\) Stark levels of \(^4\)I\(_{9/2}\). The energy diagram of Nd\(^{3+}\) ions in NdP\(_2\)O\(_{14}\) host is presented in Fig. 5 with emphasis of two types of energy transfer which can takes place in this host. First of them is cross-relaxation \{\(^4\)F\(_{3/2}\), \(^4\)I\(_{9/2}\)\}\(\rightarrow\)\{\(^4\)I\(_{15/2}\), \(^4\)I\(_{13/2}\)\} (blue arrows) and fast energy diffusion between \(^4\)F\(_{3/2}\) states (dark yellow arrows). Detailed analysis on probabilities of both of these processes will be given below.

According to the Judd-Ofelt theory\(^{36,37}\) the transition probability of an electric dipole transition is given by

\[
P_{\ell\lambda J} = \frac{64\pi^2}{3h(2J+1)} \chi \sum_{\ell=2,4}\Omega_{\ell} \left| (\ell L J|\ell' S L J) \right|^2
\]

(2)

where \(e\), \(h\) and \(\lambda\) are the elementary charge, the Planck constant and the emission wavelength, respectively. \(\chi\) is the correction parameter depending on the refractive index \(n\). Table 1 presents the \(\left| (\ell L J|\ell' S L J) \right|^2\) elements of the \(^4\)F\(_{3/2}\)\(\rightarrow\)^\(^4\)I\(_j\) transitions of Nd\(^{3+}\) and the \(\Omega_{\ell}\) parameters of the NdP\(_2\)O\(_{14}\) matrix.

| Transition     | \(\left| (\ell L J|\ell' S L J) \right|^2\) | \(\Omega_{\ell}\)  |
|---------------|--------------------------------|-----------------|
| \(^4\)I\(_{9/2}\) | 0                              | 0.0258          |
| \(^4\)I\(_{11/2}\) | 0                              | 0.0285          |
| \(^4\)I\(_{13/2}\) | 0.01136                        | 0.4104          |
| \(^4\)I\(_{15/2}\) | 0.0293                         | 0.0548          |

The fluorescent \(^4\)F\(_{3/2}\)\(\rightarrow\)^\(^4\)I\(_{15/2}\) transition was neglected due to a low probability related to a remarkably low value of \(\left| (\ell L J|\ell' S L J) \right|^2\).
The change of $\beta_3$ is probably associated with the reabsorption process of the $^4F_{9/2} \rightarrow I_{13/2}$ emission for which the absorption cross-section is relatively high (see Fig.3). The confirmation of this explanation can also be found in the changes in the shape of the $^4F_{9/2} \rightarrow I_{12}$ transition within the entire range of Nd$^{3+}$ concentrations. In the case of an insignificant contamination by an active ion, one can observe relatively intense lines around 863 nm and 870 nm related to the transitions from two Stark components ($^4F_{9/2} \rightarrow R_2$ and $R_1$, respectively) to the ground component of $^{4}I_{13/2}(Z_1)$. Nevertheless, with the increase of the number of active ions, a consistent decrease of the relative intensity of those two bands can be observed. Those bands correspond to the fundamental absorption to the first emitting process of the one can notice that for low concentration of the Nd$^{3+}$ ions the dopant concentration. From the decay curves presented in Fig. 6a one can notice that for low concentration of the Nd$^{3+}$ ions the distance between them is sufficiently large to prevent the impact of ion-ion interactions so that exponential dependencies are observed.

For the Nd$^{3+}$ concentration above $x = 0.1$, the luminescence decay profiles reveal a nonexponential shape due to the cooperative donor-acceptor interactions. However, for the higher concentration, the decay exhibits an exponential profile due to the energy diffusion process through the Nd$^{3+}$ sublattice. The donor-acceptor interaction between the excited Nd$^{3+}$ ions is responsible for the excited state energy migration (diffusion). In the case of coexistence of the donor-acceptor and donor-donor interactions, the fluorescence decay kinetics may be described by the Yokota-Tanimoto model. The temporal evolution of the intensity can be expressed as follows

$$I(t) = I_0 \exp \left( -\frac{t}{\tau_D} - \alpha \left( \frac{t}{\tau_D} \right)^{3/2} \frac{1+10.866Z+15.502Z^2}{1+8.749Z} \right) + b$$

where

$$\alpha = \frac{4}{3} \Gamma \left( 1 - \frac{3}{S} \right) N_D R_0^3$$

and

$$Z = D C_{DD}^{-2/S} t^{1-2/S}$$

Here $S$ defines the character of the ion-ion interaction ($S = 6, 8, 10$ for the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively), $\tau_D$ is the radiative life time (for La$_{1-x}$Nd$_x$P$_2$O$_{14}$, the value of $\tau_D = 330$ µs was adopted), $N_D$ is the dopant concentration (for NdP$_2$O$_{14}$, $N_D = 4 \cdot 10^{21}$ ions/cm$^3$), $\Gamma$ is Euler gamma function, $I_0$ is the initial intensity and $b$ is the fitting offset. The numerical coefficients preceding $Z$ are the Padée parameters derived for the dipole-dipole interaction. $D$ and $C_{DD}$ – are the diffusion rate and the donor-donor interaction constant, respectively. The critical distance $R_0$ can be recast as

$$R_0 = \sqrt{\frac{\alpha}{\frac{4}{3} \Gamma \left( 1 - \frac{3}{S} \right) N_D}}$$

The most accurate approximation presented in Fig. 6b was obtained for the $S = 6$ value which points to the dipole-dipole interaction. Using $R_0$, the donor-acceptor interaction parameter $C_{DA}$ is given by
of the R2 state becomes significant and emission from this state – possible. In the 10 K emission spectra (black line) only a transition from the R1 state can be observed while emission from R2 is absent. However, in the 100 K emission spectra (red line), an increase of the relative intensity from R3 can be observed (especially for R2 – R3 at about 863 nm). On the other hand, the highest absorption cross-section can be observed precisely for the Z1 – R2 transition. Hence, one can conclude that for temperatures above 80 K, a fast diffusion is much more probable due to the energy resonance having an impact on the increase of the decay constant. However, above 200 K the lifetime decreases slightly again. At 200 K (kBT ≈ 150 cm⁻¹) – the thermal energy is sufficient for bridging the cross-relaxation transition [R(11583 cm⁻¹), Z(0 cm⁻¹) + h(150 cm⁻¹)→(W(5872 cm⁻¹), W(5872 cm⁻¹)]. For the La1-xNdP0.35O14 nanocrystals, the cross-relaxation is strongly reduced and the energy migration process becomes dominant.

Conclusions

The novel method of La1-xNdP0.35O14 nanocrystals synthesis was described. The average grain sizes were determined to be 45 nm using Rietveld analysis and transmission electron microscopy. The impact of Nd³⁺ concentration on the spectroscopic properties of the La1-xNdP0.35O14 nanocrystals have been investigated. It was found that the Nd³⁺ concentration strongly affects the intensities of the absorption transitions, whereby intense cooperative absorption transitions were observed. The distribution of emission intensities of particular 4F₃/2 – 2I emissions is strongly affected by the concentration of the Nd³⁺ ions. It was shown that β₂/₂ decreases from 0.45 to 0.35 whereas β₂₁/₂ demonstrated quite an opposite behavior and increases from 0.55 to 0.65. It was concluded that a reabsorption process is responsible for this behavior. Following the Judd-Ofelt theory the calculation of the emission branching ratios of fluorescence intensities βᵢ from 4F₃/2 to 2I was performed. In particular, the process of concentration quenching of the Nd³⁺ fluorescence was investigated. It was found that the concentration quenching in the La1-xNdP0.35O14 nanocrystals is strongly reduced due to the relatively large distance between the neighboring Nd³⁺ ions in this host. The kinetics of the Nd³⁺ fluorescence was measured and discussed in terms of the Yokota-Tanimoto model. It was observed that the role of the donor-acceptor interaction responsible for the cross-relaxation is significant and leads to a nonexponential fluorescence decay dependencies in the intermediate concentration range 0.1 < x < 0.9. For a fully concentrated crystal NdP0.35O14, corresponding to x = 1, the decay profiles became exponential again due to the large donor-donor interaction responsible for energy migration that prevails the donor-acceptor interaction between the Nd³⁺ ions.

Acknowledgements

L. M. acknowledges support from the NCN under grant no. 2012/05/N/ST5/02327. Authors would like to acknowledge dr Yuri Strzhemechny for critical reading of this manuscript.

Notes and references

Figure 7. Temperature dependence of the decay time for the NdP0.35O14 nanocrystals (a); and comparison of 10K, 100K emission spectra with 300K absorption spectra of NdP0.35O14 (b).

The spectra have been limited only to the resonant 4F₃/2 – 2I₂ transition. The energy difference between the two Stark components R₁ and R₂ of the excited 4F₃/2 multiplet in the NdP0.35O14 lattice is about 110 cm⁻¹. Therefore, above 80 K (kBT ≈ 55 cm⁻¹) a population of the R₂ state becomes significant and emission from this state – possible. In the 10 K emission spectra (black line) only a transition from the R₁ state can be observed while emission from R₂ is absent. However, in the 100 K emission spectra (red line), an increase of the relative intensity from R₃ can be observed (especially for R₂ – R₃ at about 863 nm). On the other hand, the highest absorption cross-section can be observed precisely for the Z₁ – R₂ transition. Hence, one can conclude that for temperatures above 80 K, a fast diffusion is much more probable due to the energy resonance having an impact on the increase of the decay constant. However, above 200 K the lifetime decreases slightly again. At 200 K (kBT ≈ 150 cm⁻¹) – the thermal energy is sufficient for bridging the cross-relaxation transition [R(11583 cm⁻¹), Z(0 cm⁻¹) + h(150 cm⁻¹)→(W(5872 cm⁻¹), W(5872 cm⁻¹)]. For the La1-xNdP0.35O14 nanocrystals, the cross-relaxation is strongly reduced and the energy migration process becomes dominant.

Conclusions

The novel method of La1-xNdP0.35O14 nanocrystals synthesis was described. The average grain sizes were determined to be 45 nm using Rietveld analysis and transmission electron microscopy. The impact of Nd³⁺ concentration on the spectroscopic properties of the La1-xNdP0.35O14 nanocrystals have been investigated. It was found that the Nd³⁺ concentration strongly affects the intensities of the absorption transitions, whereby intense cooperative absorption transitions were observed. The distribution of emission intensities of particular 4F₃/2 – 2I₂ transitions is strongly affected by the concentration of the Nd³⁺ ions. It was shown that β₂/₂ decreases from 0.45 to 0.35 whereas β₂₁/₂ demonstrated quite an opposite behavior and increases from 0.55 to 0.65. It was concluded that a reabsorption process is responsible for this behavior. Following the Judd-Ofelt theory the calculation of the emission branching ratios of fluorescence intensities βᵢ from 4F₃/2 to 2I₁ was performed. In particular, the process of concentration quenching of the Nd³⁺ fluorescence was investigated. It was found that the concentration quenching in the La1-xNdP0.35O14 nanocrystals is strongly reduced due to the relatively large distance between the neighboring Nd³⁺ ions in this host. The kinetics of the Nd³⁺ fluorescence was measured and discussed in terms of the Yokota-Tanimoto model. It was observed that the role of the donor-acceptor interaction responsible for the cross-relaxation is significant and leads to a nonexponential fluorescence decay dependencies in the intermediate concentration range 0.1 < x < 0.9. For a fully concentrated crystal NdP0.35O14, corresponding to x = 1, the decay profiles became exponential again due to the large donor-donor interaction responsible for energy migration that prevails the donor-acceptor interaction between the Nd³⁺ ions.

Acknowledgements

L. M. acknowledges support from the NCN under grant no. 2012/05/N/ST5/02327. Authors would like to acknowledge dr Yuri Strzhemechny for critical reading of this manuscript.

Notes and references

Figure 7. Temperature dependence of the decay time for the NdP0.35O14 nanocrystals (a); and comparison of 10K, 100K emission spectra with 300K absorption spectra of NdP0.35O14 (b).

The spectra have been limited only to the resonant 4F₃/2 – 2I₂ transition. The energy difference between the two Stark components R₁ and R₂ of the excited 4F₃/2 multiplet in the NdP0.35O14 lattice is about 110 cm⁻¹. Therefore, above 80 K (kBT ≈ 55 cm⁻¹) a population of the R₂ state becomes significant and emission from this state – possible. In the 10 K emission spectra (black line) only a transition from the R₁ state can be observed while emission from R₂ is absent. However, in the 100 K emission spectra (red line), an increase of the relative intensity from R₃ can be observed (especially for R₂ – R₃ at about 863 nm). On the other hand, the highest absorption cross-section can be observed precisely for the Z₁ – R₂ transition. Hence, one can conclude that for temperatures above 80 K, a fast diffusion is much more probable due to the energy resonance having an impact on the increase of the decay constant. However, above 200 K the lifetime decreases slightly again. At 200 K (kBT ≈ 150 cm⁻¹) – the thermal energy is sufficient for bridging the cross-relaxation transition [R(11583 cm⁻¹), Z(0 cm⁻¹) + h(150 cm⁻¹)→(W(5872 cm⁻¹), W(5872 cm⁻¹)]. For the La1-xNdP0.35O14 nanocrystals, the cross-relaxation is strongly reduced and the energy migration process becomes dominant.


D. Petrov, B. Angelov, V. Lovchinov, J Rare Earth, 2013, 31, 485.


