Colloidal Nanoparticles of Ln\textsuperscript{3+}-Doped LaVO\textsubscript{4}: Energy Transfer to Visible- and Near-Infrared-Emitting Lanthanide Ions

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Received February 25, 2005. In Final Form: May 16, 2005

Colloidal, organic solvent-soluble Ln\textsuperscript{3+}-doped LaVO\textsubscript{4} nanoparticles have been synthesized by a precipitation reaction in the presence of (C\textsubscript{18}H\textsubscript{37}O\textsubscript{2})\textsubscript{2}PS\textsubscript{2} as ligand, that coordinates to the surface of the nanoparticles. The materials are well soluble in chlorinated solvent such as chloroform. Energy transfer of excited vanadate groups has been observed for Ln\textsuperscript{3+} ions that emit in the visible and the near-infrared (Eu\textsuperscript{3+}, Tb\textsuperscript{3+}, Nd\textsuperscript{3+}, Er\textsuperscript{3+}, Ho\textsuperscript{3+}, Dy\textsuperscript{3+}, Sm\textsuperscript{3+}, Pr\textsuperscript{3+}), thus making it a very generic sensitization mechanism. The LaVO\textsubscript{4} nanoparticles have a different crystal structure than bulk LaVO\textsubscript{4} ones (xenotime instead of perovskite), thus making it very stable against photooxidation. The high stability is a result, luminescent materials based on lanthanide ions doped in the nanoparticles show luminescence properties that are very similar to those of the bulk materials.\textsuperscript{1-5} The lanthanide ions in these nanoparticles are shielded from the organic environment, and as a result high quantum yields and long luminescence lifetimes are observed. This is particularly important for Ln\textsuperscript{3+} ions that emit in the near-infrared, because the energy involved in the transitions is smaller, and thus the quenching by OH and to a lesser extent CH groups is much more pronounced. The luminescence of lanthanide ions originates from intra-4f transitions and does not involve valence electrons; as a result, luminescent materials based on lanthanide ions are very stable against photooxidation. The high stability is especially useful for applications that require high pump powers, such as lasers and optical amplifiers. These lanthanide-doped nanoparticles make it possible to study processes that need high laser power excitation in these organic host materials. Haase et al. showed that nanoparticles of LaPO\textsubscript{4} and NaYP\textsubscript{4} doped with Yb\textsuperscript{3+}, Er\textsuperscript{3+} and Yb\textsuperscript{3+} can show up-conversion in solution.\textsuperscript{6,7} We have focused on soluble core and core-shell nanoparticles based on Ln\textsuperscript{3+}-doped LaF\textsubscript{3} and LaPO\textsubscript{4} that emit in the near-infrared (NIR).\textsuperscript{3-5} Furthermore, we showed that surface modification can be done by ligand-exchange reactions in solution, and in case of LaPO\textsubscript{4}, covalent reactions are also possible between the surface phosphate groups and alcohols.\textsuperscript{8} Ligand-exchange reactions in solution are usually fast and quantitative if the new ligand binds more strongly to the surface than the original. In our group we showed that nanoparticles of La\textsubscript{3} doped with Nd\textsuperscript{3+} can be used in polymer waveguide amplifiers that operate in the 1.33 μm band of the telecommunication window.\textsuperscript{9} A recent publication by us discusses the optical properties of surface versus “bulk” Eu\textsuperscript{3+} ions in colloidal nanoparticles through a systematic study of Eu\textsuperscript{3+} concentration, ligand-exchange reactions, and core and core-shell nanoparticles.\textsuperscript{10}

The direct excitation of the lanthanide ions is a relatively inefficient process, due to the forbidden character of the 4f transitions (extinction coefficient are typically 1–10 M\textsuperscript{-1} cm\textsuperscript{-1}). Energy transfer from a host material or other ion with a higher absorption coefficient could lead to much more efficient materials. Eu\textsuperscript{3+} and Yb\textsuperscript{3+} ions doped in the LaPO\textsubscript{4} nanoparticles can be excited using a charge-transfer transition in the Ln–O bond, because Eu\textsuperscript{2+} and Yb\textsuperscript{2+} are stable oxidation states. Tb\textsuperscript{3+} ions can be excited using energy transfer from excited co-doped Ce\textsuperscript{3+} ions, which have an allowed 4f–5d absorption in the UV. This sensitization with Ce\textsuperscript{3+} is only efficient with Tb\textsuperscript{3+}, not markedly efficient with Sm\textsuperscript{3+} and Dy\textsuperscript{3+}, and not effective with Eu\textsuperscript{3+}, the latter probably because of reox processes. LaF\textsubscript{3} nanoparticles doped with Ln\textsuperscript{3+} ions can, in general, emit in the near-infrared, because the energy involved in the transitions is smaller, and thus the quenching by OH and to a lesser extent CH groups is much more pronounced. The luminescence of lanthanide ions originates from intra-4f transitions and does not involve valence electrons; as a result, luminescent materials based on lanthanide ions are very stable against photooxidation. The high stability is especially useful for applications that require high pump powers, such as lasers and optical amplifiers. These lanthanide-doped nanoparticles make it possible to study processes that need high laser power excitation in these organic host materials. Haase et al. showed that nanoparticles of LaPO\textsubscript{4} and NaYP\textsubscript{4} doped with Yb\textsuperscript{3+}, Er\textsuperscript{3+} and Yb\textsuperscript{3+} can show up-conversion in solution.\textsuperscript{6,7} We have focused on soluble core and core-shell nanoparticles based on Ln\textsuperscript{3+}-doped LaF\textsubscript{3} and LaPO\textsubscript{4} that emit in the near-infrared (NIR).\textsuperscript{3-5} Furthermore, we showed that surface modification can be done by ligand-exchange reactions in solution, and in case of LaPO\textsubscript{4}, covalent reactions are also possible between the surface phosphate groups and alcohols.\textsuperscript{8} Ligand-exchange reactions in solution are usually fast and quantitative if the new ligand binds more strongly to the surface than the original. In our group we showed that nanoparticles of La\textsubscript{3} doped with Nd\textsuperscript{3+} can be used in polymer waveguide amplifiers that operate in the 1.33 μm band of the telecommunication window.\textsuperscript{9} A recent publication by us discusses the optical properties of surface versus “bulk” Eu\textsuperscript{3+} ions in colloidal nanoparticles through a systematic study of Eu\textsuperscript{3+} concentration, ligand-exchange reactions, and core and core-shell nanoparticles.\textsuperscript{10}

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only be excited via direct excitation of the Ln³⁺ ions. However, Yb³⁺ can be used as sensitizer of Er³⁺; nevertheless, even though Yb³⁺ is more efficient than direct Er³⁺ excitation, the extinction coefficient of Yb³⁺ is still low. Therefore, it would be advantageous to have a more general and more efficient approach to excite the other lanthanide ions as well. Doping of lanthanide ions in semiconductor nanoparticles is a possible option, but it proved difficult to dope the lanthanide ion in the nanoparticle cores of several of these materials. We did report the successful doping of lanthanide ions in TiO₂ nanoparticles and showed that energy transfer between the semiconductor host to several lanthanide ions takes place, but the quantum yields of these materials were low.

With direct excitation being rather inefficient and energy transfer from excited Ce³⁺ working well for Tb³⁺ only and the charge-transfer band involving oxygen only operable with Eu³⁺ and Yb³⁺, there is a clear need to have general excitation methods for the luminescent Ln³⁺ ions, in particular the ones that emit in the NIR. Procedures to synthesize lanthanide-doped YVO₄ nanoparticles in aqueous solution have been described in which the energy transfer from excited VO₄ groups is being exploited. Most of these efforts focus on Eu³⁺; the only other lanthanide ions that were used were the visible-emitting ions Dy³⁺ and Sm³⁺. In this paper we describe the synthesis of LaVO₄ nanoparticles that are soluble in organic solvents, through the coordination of negatively charged ligands on the surface of the nanoparticles. These nanoparticles provide the possibility to excite most of the lanthanide ions via the charge-transfer transition within the vanadate group, followed by energy transfer to the emissive Ln³⁺. They offer a unique crystal site to the doping ion with very low symmetry, which increases the radiative rate constant, thus giving quenching processes less chance.

Experimental Section

General. TEM images were collected on a Philips CM 30 Twin FTEM, operating at 300 kV. Samples were prepared by evaporating a drop of a diluted nanoparticle dispersion in dichloromethane on a carbon-coated 200 mesh copper grid. X-ray fluorescence was carried out on a Philips PW 1489 spectrometer using LaF₃, Li₃PO₄, and Eu₂O₃ as the standards. Elemental analyses were performed on a Carlo Erba EA 1106 apparatus. For the XRD measurements approximately 40–50 mg of a sample was gently stirred in an alumina Ehrbach EA 1106 apparatus. The XRD analyses were performed on a Siemens D5000 Bragg–Brentano 0–2θ diffractometer equipped with a detector with a graphite monochromator crystal, 2 mm (1°) divergence and anti-scatter slits, 0.6 mm receiving slit, and incident beam Soller slit. The scanning step size was 0.04° and with a counting time of 2 s/step. Data are presented from 2θ = 12–100°, because there are no features below 12°. The X-ray powder diffraction pattern of LaVO₄ was refined in space group D₃h₃ with the Rietveld program Topas 3.0.

Results and Discussion

The synthesis of these LaVO₄ nanoparticles is very similar to a procedure described earlier for LaF₃ nanoparticles. This procedure involves the precipitation of the lanthanide salts and vanadate ions in the presence of a dithiophosphate ligand (Ligand 1) shown in Figure 1. In other words, the process can be characterized as an arrested precipitation because of the presence of ligands that coordinate to the surface of the nanoparticles.

This ligand is present to control the growth of the nanocrystalline particles and to give the nanoparticles solubility in organic solution after their synthesis. Using the same procedure, YVO₄ nanoparticles could also be made, but the dispersibility of these particles was much lower. This is probably a result of increased Ln³⁺–ligand interaction of the smaller Y³⁺ ion compared to that of La³⁺.

Figure 1. Dithiophosphate ligand used in the synthesis of LaVO₄:Ln nanoparticles.

(Bruker AXS 2003) using the fundamental parameters approach (Cheary and Coelho, 1992). The lanthanide salts were purchased from Aldrich or Acros in the highest purity available (at least 99.9%). All chemicals were used as received without further purification. CH₂Cl₂ and hexane were distilled from CaCl₂, ethyl acetate was distilled from K₂CO₃.

Ln³⁺-Doped LaVO₄ Nanoparticles. The ligand was synthesized as reported previously. The LaVO₄ nanoparticles were prepared by heating a solution of 0.95 mmol ligand 1 (618 mg) and 184 mg (1 mmol) sodium orthovanadate in 35 mL of ethanol/water at 75 °C. A solution of La(NO₃)₃·6H₂O and Ln(NO₃)₃·6H₂O (1.33 mmol total of which 5 mol % was of the luminescent ion, unless otherwise stated) in 2 mL of water was added dropwise, and the solution was stirred at 75 °C for 2 h and then cooled to room temperature. The precipitate was separated by centrifugation and was washed subsequently with water and ethanol. The nanoparticles were further purified by dispersing in 2 mL of dichloromethane and precipitating by the addition of 20 mL of ethanol. After separation by centrifugation the nanoparticles were dried in a vacuum over P₂O₅ for 2 days. After drying, the nanoparticles are soluble in apolar solvents such as chloroform, dichloromethane, and toluene.

Methods. Photoluminescence measurements in the visible were done with an Edinburgh Instruments FS/FL instrument with a 450 W Xe arc lamp, and for the time-resolved measurements, a micro-flashlamp as the excitation source. The excitation light was fed to a monochromator (single grating, 1800 lines/mm) and focused on a square quartz cuvette (1 × 1 cm²) containing the nanoparticle solution. The emitted visible light was fed to a second monochromator (1800 lines/mm grating) and collected on a red-sensitive Peltier element cooled Hamamatsu R955 PMT. The emission spectra were corrected for the detector response, and the excitation spectra were corrected for the lamp intensity. The NIR spectra were measured with the same instrument using a liquid nitrogen-cooled Ge detector and a monochromator equipped with a 600 lines/mm grating. The luminescence lifetime of Nd³⁺ was measured using a liquid nitrogen-cooled Hamamatsu R5509 NIR-PMT. Luminescence quantum yields were determined by comparing the luminescence intensity of a particle solution with a solution of quinine bisulfate in 1 M H₂SO₄ with approximately the same absorption at the excitation wavelength, taking the quantum yield of quinine bisulfate as 54.4%.²⁰

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Colloidal Nanoparticles of Ln$^{3+}$-Doped LaVO$_4$

A similar problem was observed previously by us in the synthesis of YF$_3$ nanoparticles.

A typical transmission electron micrograph (TEM) picture of the LaVO$_4$:Eu nanoparticles is shown in Figure 2.

This TEM picture shows particles with a size between 6 and 10 nm of mostly irregular shapes. The lattice fringes are clearly visible in the magnification of a single nanoparticle, demonstrating the high crystallinity of these nanoparticles.

The elemental composition of the nanoparticles was determined using X-ray fluorescence and combustion elemental analysis. The results of these measurements are summarized in Table 1.

It can be seen that the ratio of lanthanide ions that is found in the nanoparticles is very similar to the ratio applied in the synthesis. This is consistent with a homogeneous, i.e. completely statistical, doping in the nanoparticles. We have shown this in detail in a recent paper.\(^9\) The organic ligand makes up a large part of the total weight. Figure 3 shows the X-ray diffraction (XRD) pattern of LaVO$_4$:Eu nanoparticles.

The X-ray powder diffraction pattern of LaVO$_4$ was refined in space group D194h with the Rietveld refinement observed for bulk LaVO$_4$. This different crystal structure in contrast to the monazite structure that is generally LaVO$_4$ is most likely a result of the increased amount of structure between the nanocrystalline LaVO$_4$ and bulk material.\(^10\) The difference in crystal of this nanomaterial was observed before for a nanocrystalline LaVO$_4$ material.\(^21\) The pattern fits well with the xenotime crystal structure of LaVO$_4$,\(^22\) which offers the Y$^{3+}$ ions a crystal site with D$^{1S}_{4h}$ symmetry. Luminescent lanthanide ions doped in the crystal will replace Y$^{3+}$ ions, which gives the luminescent ions a site without inversion symmetry. This lack of inversion symmetry has a significant advantage on the optical properties of the lanthanide ions. In general the lack of inversion symmetry around the lanthanide ions makes the electric dipole transitions more allowed than in a site with inversion symmetry; as a consequence, the rates of absorption and emission are higher, resulting in higher absorption coefficients and higher radiative rates. The higher radiative rates reduce the probability of quenching, which can result in higher quantum yields.

An example where this crystal structure is advantageous is the well-known red-emitting phosphor, YVO$_4$: Eu. Due to the lack of inversion symmetry around the Eu$^{3+}$ ion, most of the emission is in the hypersensitive $^5D_0 \rightarrow ^7F_2$ electric dipole transition at 617 nm, which gives the material an intense red emission. Eu$^{3+}$ materials that show emission primarily in the $^5D_0 \rightarrow ^7F_2$ transition are especially useful for display applications.

YVO$_4$:Nd is another example. This material is being studied widely for use in high-power solid-state lasers.\(^23\) The absorption coefficient of the Nd$^{3+}$ ion is about 8 times higher than in the often used YAG crystal, which could lead to much more efficient lasers. This difference in absorption strength is mainly caused by the difference in symmetry around the lanthanide ion.

The increase in the electric dipole transition is demonstrated in the emission spectrum of, for instance, the Eu$^{3+}$ ion. The luminescence spectrum of LaVO$_4$:Eu nanoparticles shown in Figure 4 clearly shows the dominating peak at 617 nm of the $^5D_0 \rightarrow ^7F_2$ electric dipole transition.

The similarity of this emission spectrum with the emission spectra found for bulk YVO$_4$:Eu confirms that the crystal structure of these LaVO$_4$ nanoparticles

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Table 1. Elemental Composition of LaVO$_4$:Eu Nanoparticles (wt %)

<table>
<thead>
<tr>
<th>Particle</th>
<th>La$^a$</th>
<th>Eu$^a$</th>
<th>P$^b$</th>
<th>V$^a$</th>
<th>C$^b$</th>
<th>H$^b$</th>
<th>S$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaVO$_4$:Eu</td>
<td>18.46</td>
<td>1.17</td>
<td>4.48</td>
<td>9.24</td>
<td>44.62</td>
<td>7.88</td>
<td>6.70</td>
</tr>
</tbody>
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$^a$ Measured with XRF. $^b$ Measured with combustion elemental analysis.

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is tetragonal instead of the usual monazite phase. This has clear advantages for some applications such as displays, because most of the Eu$^{3+}$ light is at 617 nm, which gives this material an intense red emission color. A high radiative rate is desirable for displays etc. because of the good emission properties. The broad absorption band of the VO$_4$ groups can be seen in both the excitation spectrum and the absorption spectrum. The excitation spectrum is recorded by scanning the excitation wavelength at a fixed emission wavelength and thus recording those absorptions that lead to a specific emission. The absorption is caused by a charge-transfer transition in the V–O bond, and the energy is subsequently transferred to the Eu$^{3+}$ ion, as expected. The absorption spectrum shows an additional band below 250 nm due to absorption by the ligand, which does not lead to excited Eu$^{3+}$ ions. At this low nanoparticle concentration the 4f absorption lines of the Eu$^{3+}$ ion cannot be observed, which shows that the Eu$^{3+}$ ions are only excited through energy transfer from the vanadate groups.

The inset of Figure 4 shows the luminescence decay. The luminescence lifetimes were fitted using a biexponential decay, and lifetimes of 670 μs (59%) and 190 μs (41%) were obtained. A multiexponential decay is generally observed in these nanoparticles, which can be attributed to an increased chance of quenching of Eu$^{3+}$ ions close to or at the surface of the nanoparticle by the organic ligand and/or coordinated water. These lifetimes are significantly shorter than the lifetimes measured for LaF$_3$:Eu and LaPO$_4$ nanoparticles synthesized with similar procedures, which is a direct result of the increase in the radiative rates due to the reduced symmetry around the Eu$^{3+}$ ion. For a more elaborate model that describes the decay please refer to our previous work.

The quantum yield of these LaVO$_4$:Eu nanoparticles with different concentrations of Eu$^{3+}$ ions was determined by comparing the emission intensity with the emission intensity of quinine bisulfate with the same absorption at the excitation wavelength of 280 nm. The results are summarized in Table 2.

Table 2. Quantum Yields of LaVO$_4$:Eu Nanoparticles Doped with Different Concentrations of Eu$^{3+}$

<table>
<thead>
<tr>
<th>Eu$^{3+}$ content</th>
<th>quantum yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.4</td>
</tr>
<tr>
<td>10</td>
<td>5.6</td>
</tr>
<tr>
<td>15</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The quantum yield at 5% doping level is clearly lower than the quantum yield of 70% of bulk YVO₄. The decreased quantum yield can be a result of increased quenching due to the small particles size or due to a reduced efficiency of energy transfer in the LaVO₄ host. The larger size of the La³⁺ ion compared to that of the Y³⁺ ion increases the distance between adjacent vanadate groups, and this could lead to a reduced efficiency of the energy-transfer processes. It can be seen that the quantum yield increases with increasing Eu³⁺ concentration. For the bulk YVO₄:Eu phosphor the maximum quantum yield is observed at a Eu³⁺ concentration of 5%. The quantum yield of this material is determined by how effective the energy transfer of the vanadate groups to the Eu³⁺ ion is; therefore, a higher concentration of Eu³⁺ would lead to a higher quantum yield, but high concentrations of Eu³⁺ lead to self quenching of the Eu³⁺ ions by cross relaxation. These counteracting processes lead to an optimum Eu³⁺ concentration of 5% for the bulk material. Quenching of surface vanadate groups is generally observed in nanocrystals of YVO₄; as a result, the optimum Eu³⁺ can be as high as 15%, and the quantum yield of 70% of the bulk material is not observed.14 Probably the same applies to our LaVO₄:Eu nanoparticles, which leads us to conclude that quenching of surface vanadate groups is an important quenching path in our materials. The synthesis of core-shell structures, in which a layer of inert inorganic material is grown over the LaVO₄ core, could prevent most of this surface quenching. Improved optical properties have been shown for LaF₃ and LaPO₄ core-shell nanoparticles. A possible shell material could be LaPO₄ that has similar lattice parameters, for it would allow an epitaxial growth of the shell on the surface of the core. An epitaxial growth generally requires that the lattice mismatch of the two materials is usually not larger that a few percent.

Emission of most other luminescent lanthanide ions could also be observed after excitation in the charge-transfer band of the vanadate group, which is demonstrated in Figure 5 with the emission spectrum of LaVO₄: Tm.

These nanoparticles emit intense blue light, which is clearly visible under irradiation with a hand-held UV lamp. The blue emission originates from the 1G₄ → 3H₅ transition, but emissions from the 1G₄ → 3H₆ and 3F₄ → 3H₅ transitions at 650 and 790 nm, respectively, are also observed. Emission spectra of other visible-emitting lanthanide ions, such as Dy³⁺, Pr³⁺, Sm³⁺, and Ho³⁺ all excited at 280 nm, can be found in the Supporting Information. All excitation spectra are very similar to the excitation spectrum of the Eu³⁺ ion shown in Figure 4, which demonstrates that energy transfer from the vanadate host to all these ions is also possible.

Several NIR-emitting lanthanide ions could also be excited using the charge-transfer band of the VO₄ group. Figure 6 shows the emission spectrum of LaVO₄:Nd nanoparticles after excitation at 280 nm.

The emission spectrum shows the typical emissions of Nd³⁺ ion at 880, 1060, and 1330 nm of the transitions from the 4F₃/2 level to the 4I₁₅/2, 4I₁₁/2, and 4I₉/2 levels, respectively. The inset of Figure 6 shows the luminescence...
decay. The lifetimes could be fitted using a biexponential decay, and lifetimes of 6.2 (21%) and 14.6 (79%) μs were found. The bottom of Figure 6 shows a comparison of the absorption spectra of LaVO₄:Nd nanoparticles and LaF₃:Nd nanoparticles with identical Nd³⁺ ion concentrations. It can be seen that the absorption of the Nd³⁺ ions in the LaVO₄ host are a little red-shifted and in general much stronger than the absorptions of the Nd³⁺ ion in the LaF₃ host. This could have significant advantages in applications such as lasers and optical amplifiers, in which the lanthanide ions are excited directly, for instance, with diode lasers.

The NIR emission spectra of Er³⁺ and Ho³⁺ after excitation of the VO₄ absorption band are shown in Figure 7. These spectra show the typical emissions of the Er³⁺ ion at 980 and 1530 nm from the 4I_{11/2} to the 4I_{15/2} transition and the 4I_{13/2} to the 4I_{15/2} transition, respectively, and the emissions of Ho³⁺ at 960 and 1460 nm from the 5F₅ level to the 5I₇ and 5I₆ level, respectively.

Conclusions

The emission properties of colloidal lanthanide-doped nanoparticles that are soluble in organic solvents are mainly determined by the crystal properties of the host material. The possibility to make nanoparticles of different crystal structures is therefore very important for tuning the luminescent properties of these kind of materials. Energy transfer of excited vanadate groups in Ln³⁺-doped LaVO₄ nanoparticles has been demonstrated for visible- and NIR-emitting Ln³⁺ ions, thus making it a generic sensitized emission mechanism. The LaVO₄ nanoparticles reported in this work show a different crystal structure than that of the bulk material, and as a result not all the knowledge of bulk crystalline materials can be applied directly to this class of nanocrystalline materials.

Acknowledgment. NWO-CW (The Netherlands) is gratefully acknowledged for financial support of the majority of the work. NSERC (Canada) is acknowledged for the financial support of a small part of this research. CFI and BCKDF (Canada) are acknowledged for financial support of the infrastructure.

Supporting Information Available: Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

LA0505162