The Progress of Photoluminescent Properties of Rare-Earth-Ions-Doped Phosphate One-Dimensional Nanocrystals

Lixin Yu and Hai Liu

Department of Materials Science and Engineering, Nanchang University, Nanchang 330031, China

Correspondence should be addressed to Lixin Yu, yulixin72@yahoo.com.cn

Received 5 November 2009; Accepted 3 March 2010

One-dimensional (1D) nanostructures, such as tubes, wires, rods, and belts, have aroused remarkable attentions over the past decade due to a great deal of potential applications, such as data storage, advanced catalyst, and photoelectronic devices. On the other hand, in comparison with zero-dimensional (0D) nanostructures, the space anisotropy of 1D structures provided a better model system to study the dependence of electronic transport, optical and mechanical properties on size confinement and dimensionality. Rare earth (RE) compounds, were intensively applied in luminescent and display devices. It is expected that in nanosized RE compounds the luminescent quantum efficiency (QE) and display resolution could be improved. In this paper, we systematically reported the research progress of luminescent properties of RE-doped 1D orthophosphate nanocrystal, including the synthesis of 1D nanostructures doped with RE ions, local symmetry of host, electronic transition processes, energy transfer (ET), and so forth.

1. Introduction

It is well known that the reduction of particle size of crystalline system can result in remarkable modification of their properties which are different from those of microsized hosts because of surface effect and quantum confinement effect of nanometer materials. In 1994, Bhargava et al. reported that radiative transition rate of ZnS:Mn nanocrystals increased five orders in comparison with bulk one [1]. Although this result was strongly criticized later, the studies on nanosized luminescent semiconductor attracted great interests [2–6]. RE compounds were extensively applied in luminescence and display, such as lighting, field emission display (FED), cathode ray tubes (CRT), and plasma display panel (PDP) [7–11]. Lanthanide orthophosphate (LnPO₄) belongs to two polymorphic types, the monoclinic monazite type (for La to Gd) and quadratic xenotime type (for Tb to Lu). Due to its high QE, bulk lanthanide phosphate as an ideal host in fluorescent lamps, CRT and PDP, has been extensively investigated [12–14]. It is expected that nanosized RE compounds can increase luminescent QE and display resolution. To improve luminescent properties of nanocrystalline phosphors, many preparation methods have been used, such as solid state reactions, sol-gel techniques, hydroxide precipitation, hydrothermal synthesis, spray pyrolysis, laser-heated evaporation, and combustion synthesis. Currently, the luminescent RE-doped 1D nanocrystals such as LaPO₄:RE nanowires [15–19], Y₂O₃:RE and La₂O₃:Eu nanotubes/nanowires [20–25], and YVO₄: Eu nanowires/nanorods [26–28] have also attracted considerable interests. 1D structures, such as tubes, wires, rods, and belts, have aroused remarkable attentions over past decade due to a great deal of potential applications, such as data storage [29], advanced catalyst [30], and photoelectronic devices [31]. On the other hand, in comparison with 0D structures, the space anisotropy of 1D structures provided a better model system to study the dependence of electronic transport and optical and mechanical properties on size confinement and dimensionality [32]. To develop 1D phosphors, a basic question should be answered: could the photoluminescent properties for 1D nanocrystals be improved than 0D ones as well as the micrometer materials, the so-called bulk materials? In this review, we concentrated...
on the study progress of photoluminescent properties of RE ions in phosphate 1D nanocrystals.

2. The Synthesis of Phosphate 1D Nanocrystals Doped with RE

In 1999, Meyssamy et al. reported the preparation of LaPO₄:Eu³⁺/Tb³⁺ nanowires by a hydrothermal method and studied their luminescent properties for the first time [15]. After then, researchers prepared phosphate 1D nanocrystals doped with RE ions by different synthesis techniques, such as hydrothermal method to prepare LaPO₄:Ce³⁺/Eu³⁺ nanofibers [33], CePO₄:Tb³⁺ colloidal nanocrystals [34], CePO₄:Tb³⁺/LaPO₄ nanowires core-shell structures [35, 36], and LnPO₄ (Ln = RE) nanowires and nanosheets [19]. It should be noted that these reports mainly emphasize the morphology control through changing synthesis conditions. To our knowledge, although LnPO₄ 1D nanocrystals doped with RE ions with different shapes were prepared by the wet chemistry method by many groups, the luminescent properties, especially electronic transition processes and ET processes, were not further studied. Our group systematically reported luminescent characteristics of LnPO₄:RE (Ln = La, Gd) nanowires and nanorods. Song and Yu et al. investigated the microstructures of Eu³⁺ doped 1D LaPO₄ nanowires in contrast with 0D nanoparticles and corresponding micrometer hosts (micrometer particles and rods) [16, 18, 41]. The LaPO₄ nanoparticles, nanowires, and bulk materials were synthesized by the same synthesis technique, a hydrothermal method. All samples were at monazite phase and no additional phases were observed. The size of LaPO₄:Eu³⁺ nanoparticless is ranging from 10 to 20 nm. The diameter of LaPO₄:Eu³⁺ nanowires ranges from 10 to 20 nm, and the length is about several hundreds nanometer. They observed that the Eu³⁺ ions locate new site in nanowires due to shape effect. Figure 1 shows the high-resolution spectra of LaPO₄:Eu³⁺ nanomaterials and bulk materials at 266 nm pulsed laser excitation at 10 K. The emission associated with 5D⁰-7F¹ transitions is quite different between nanoparticles and nanowires at 10 K. In the nanoparticles, three additional lines 4–6 were observed. However, the relative intensity of lines 4–6 becomes weaker in comparison with that in nanowires. 7F₁ associated with one site symmetry can split into three

YBO₃ nanoparticles through high-resolution spectra at low temperature [37–40]. They contributed the origin of additional sites of Eu³⁺ doped nanoparticles to the surface effect because the disorder of atoms at the surface of nanoparticles increased on comparison with the inside atoms. Although LnPO₄:Eu³⁺ 1D nanowires/nanorods were prepared and their basic spectra were researched, the dependence of local symmetry on shape was not studied. Song and Yu et al. investigated the microstructures of Eu³⁺ doped 1D LaPO₄ nanowires in contrast with 0D nanoparticles and corresponding micrometer hosts (micrometer particles and rods) [16, 18, 41]. The LaPO₄ nanoparticles, nanowires, and bulk materials were synthesized by the same synthesis technique, a hydrothermal method. All samples were at monazite phase and no additional phases were observed. The size of LaPO₄:Eu³⁺ nanoparticless is ranging from 10 to 20 nm. The diameter of LaPO₄:Eu³⁺ nanowires ranges from 10 to 20 nm, and the length is about several hundreds nanometer. They observed that the Eu³⁺ ions locate new site in nanowires due to shape effect. Figure 1 shows the high-resolution spectra of LaPO₄:Eu³⁺ nanomaterials and bulk materials at 266 nm pulsed laser excitation at 10 K. The emission associated with 5D⁰-7F₁ transitions is quite different between nanoparticles and nanowires at 10 K. In the nanoparticles, three additional lines 4–6 were observed. However, the relative intensity of lines 4–6 becomes weaker in comparison with that in nanowires. 7F₁ associated with one site symmetry can split into three
Stark lines in the crystal field. The results in Figure 1 indicate that in nanoparticles and microrods, the $^5D_0-^7F_1$ transitions are from one crystalline site, A, while in nanowires and microrods, the $^5D_0-^7F_1$ transitions come from the same site (L1–L3), A, and an additional site (L4–L6), B. The relative number of Eu$^{3+}$ at site B decreases as the powders vary from the nanowires to the microrods. In the present case, from the microparticles to the nanoparticles, the ratio of surface to volume increases greatly, but no additional site is observed. From the microparticles to the nanowires, the ratio of surface to volume do not increase so much; however, the additional site B appears and the relative number of Eu$^{3+}$ at site B changes greatly. We thus believe that the appearance of the additional site B is not caused by the surface effect, but by the shape anisotropy. This is the first time to report that the shape effect affects the local structures of Eu$^{3+}$ doped 1D nanocrystals.

4. Electronic Transition Processes and QE of Eu$^{3+}$ in LaPO$_4$ 1D Nanocrystals

In 0D nanoparticles, many groups reported that the QE and luminescent intensity of Eu$^{3+}$ ions decreased in comparison with the bulk materials due to higher nonradiative transition rate in nanoparticles [42, 43]. An important problem should be answered: does the QE of Eu$^{3+}$ in 1D nanocrystals increase in contrast with nanoparticles and bulk materials? Song and Yu et al. systematically studied the electronic transition processes of Eu$^{3+}$ in LaPO$_4$ nanowires [16, 18, 41]. The luminescent QE of $^5D_1$ level of Eu$^{3+}$ was determined by the following equation:

$$\tau(T) = \frac{1}{W_1 + W_{10}(T)},$$  \hspace{1cm} (1)

where $W_1$ is the radiative transition rate of $^5D_1 - \sum_j F_j$, $W_{10}(T)$ is nonradiative transition rate at a certain temperature, $T$. According to the theory of multiphonon relaxation, $W_{10}$ can be written as

$$W_{10}(T) = W_{10}(0)(1 + (n)\Delta E_{10}/\hbar\omega),$$  \hspace{1cm} (2)

where $W_{10}(0)$ is nonradiative transition rate at 0 K, $\Delta E_{10}$ is the energy separation between $^5D_1$ and $^5D_0$, $\hbar\omega$ is the phonon energy, $k$ is Boltzmann constant, and $(n) = 1/(e^{\hbar\omega/kT} - 1)$ is the phonon occupation number. According to (1) and (2), the lifetime of $^5D_1$ can be expressed as

$$\tau = \frac{1}{W_1 + W_{10}(0)[1 - \exp(-\hbar\omega/kT)]^{-\Delta E_{10}/\hbar\omega}}.$$  \hspace{1cm} (3)

They measured the lifetime of $^5D_1$ level of Eu$^{3+}$ ions at different temperatures and obtained the radiative and nonradiative transition rate by fitting according to (3). The results were listed in Table 1. It is obvious that the radiative transition rate and QE of $^5D_1$ level in nanowires were higher than that in nanoparticles and bulk crystals. This result indicates that the 1D nanocrystal-doped RE ions is ideal phosphors. After then, they also studied the electronic transition processes of Eu$^{3+}$ ions in Y$_2$O$_3$ and La$_2$O$_3$ nanowires [24, 25]. The results indicate that the radiative transition rate of Eu$^{3+}$ in oxide nanowires hardly changes in comparison with the bulk hosts.

5. ET between RE Ions in LaPO$_4$ 1D Nanowires

Ce$^{3+}$ and Tb$^{3+}$ ions are important RE ions, which have been applied in blue and green phosphors. The ET processes between Ce$^{3+}$ and Tb$^{3+}$ in some micrometer-sized materials, such as lanthanum oxybromide [44], aluminate [45], alkaline earth sulphate [46], and so on, were intensively investigated. As efficient green phosphors, Ce$^{3+}$ and Tb$^{3+}$ coactivated LaPO$_4$ bulk powders were extensively applied to fluorescent lamps, cathode ray cube (CRT), and plasma display panel (PDP) due to the high ET efficiency between Ce$^{3+}$ and Tb$^{3+}$ ions [13]. To obtain the efficient green phosphors of 1D LaPO$_4$:Ce$^{3+}$/Tb$^{3+}$ nanowires, the electronic transition and ET processes in 1D nanowires should be studied, and compared with the corresponding bulk powders. However, the studies on ET processes between Ce$^{3+}$ and Tb$^{3+}$, even between different RE impurity centers, are rather rare. Song and Yu et al. fabricated Ce$^{3+}$ and Tb$^{3+}$ coactivated LaPO$_4$ nanowires as well as the micrometer-sized rods by the same hydrothermal method [17, 47]. They systematically studied and compared their electronic transition and ET processes by the luminescent spectra and dynamics analysis. Figure 2 shows the excitation and emission spectra of LaPO$_4$:Ce$^{3+}$/Tb$^{3+}$ nanowires and microrods. It is obvious and important that the luminescent intensity of Tb$^{3+}$ in LaPO$_4$:Ce$^{3+}$/Tb$^{3+}$ nanowires is much stronger than that in

### Table 1: A list of parameters $W_1$, $W_{10}(0)$ and the internal luminescent QE at 0 K in different powders.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Nanoparticles</th>
<th>Nanowires</th>
<th>Microparticles</th>
<th>Microrods</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_1$ (ms$^{-1}$)</td>
<td>14.9</td>
<td>28.9</td>
<td>17.6</td>
<td>16.5</td>
</tr>
<tr>
<td>$W_{10}$ (ms$^{-1}$)</td>
<td>24.1</td>
<td>19.7</td>
<td>17.8</td>
<td>18.5</td>
</tr>
<tr>
<td>QE (%)</td>
<td>38%</td>
<td>59%</td>
<td>49%</td>
<td>47%</td>
</tr>
</tbody>
</table>
microrods corresponding to the excitation of Ce$^{3+}$ ions. It should be noted that the emission of Ce$^{3+}$ or Tb$^{3+}$ in single-doped nanowires is lower than that in microrods. The dynamic results were listed in Table 2. The dynamic measurements and analysis indicate that the electronic transition rate of Ce$^{3+}$ and Tb$^{3+}$, the ET rate from Ce$^{3+}$ to Tb$^{3+}$ in Ce$^{3+}$-Tb$^{3+}$ codoped LaPO$_4$ nanowires, is lower than that in microrods. They attributed the increased intensity of Tb$^{3+}$ in nanowires to the lower ET efficiency from Tb$^{3+}$ to other quench centers, shown in Figure 3. According to the Eu$^{3+}$ and Tb$^{3+}$ doped LaPO$_4$ nanowires, we suggested that the RE-doped 1D nanowires were ideal nanophosphors. In addition, we also observed the ET from Gd$^{3+}$ to Tb$^{3+}$ in GdPO$_4$:Tb$^{3+}$ nanorods [48].

### 6. The Core Shell Nanostructures of LaPO$_4$

**Nanowires Doped with RE**

Due to the increased disorder of surface atoms for nanomaterials, the nonradiative transition rate of RE-doped nanocrystals will increase. The surface modification can effectively eliminate the quenching centers at surface of nanocrystal. In 1999, Li et al. prepared Y$_2$O$_3$:Eu$^{3+}$@SiO$_2$/Al$_2$O$_3$ nanoparticles heterostructures and observed the increase of Eu$^{3+}$ luminescence [49]. In 2003, Haase prepared the CePO$_4$:Tb$^{3+}$/Eu$^{3+}$@LaPO$_4$ nanoparticles core-shell structures and observed that the quantum yield of Tb$^{3+}$ was increased from 43% to 70% [50, 51]. Lin group systematically studied 0D nanoparticles doping with RE coated with SiO$_2$ [52–67]. Recently, 1D nanosized core-shell structures doped with RE have been reported. Bu et al. reported uniform CePO$_4$@LaPO$_4$ and CePO$_4$:Tb$^{3+}$@LaPO$_4$ 1D single-crystalline nanocable heterostructures with highly enhanced photoluminescent emission [36]. The resulting 1D single-crystalline nanocable heterostructures have smooth and uniform LaPO$_4$ sheaths, which is of great significance in effectively eliminating surface trap-states and suppressing the energy quenching in ET processes. The photoluminescence results for these 1D nanocable heterostructures illustrate that the uniform LaPO$_4$ sheaths remarkably increase the luminescent efficiency. Figure 4 shows the emission spectra of (ex = 278 nm) the dilute colloidal solutions of the Ce$_{0.9}$Tb$_{0.1}$PO$_4$ 1D nanocrystals (dashed line) and the Ce$_{0.9}$Tb$_{0.1}$PO$_4$@LaPO$_4$ 1D nanocable heterostructures (solid lines). It is obvious that the emission intensity of Tb$^{3+}$ and Ce$^{3+}$ in LaPO$_4$:Ce$^{3+}$, Tb$^{3+}$, Tb$^{3+}$ nanowires coated with LaPO$_4$ is much higher than that in noncoated samples.

Fang et al. also reported that CePO$_4$:Tb$^{3+}$/LaPO$_4$ core/shell nanowires synthesized by a simple hydrothermal method, and the resulting 1D core/shell nanostructures have high photoluminescence efficiency [35]. Until recently, it has been considered difficult to obtain a nanocrystal phosphor material with the quantum yield being close to that of the corresponding bulk material. The novel core/shell nanostructures, which are more robust than organically passivated nanowires, may be used as building blocks for optoelectronic nanodevice applications. CePO$_4$:Tb/LaPO$_4$ core/shell nanowires with high quantum yield would also be a new class of biomedicinal labels for ultrasensitive, multicolor, and multiplexing applications owing to their nontoxicity and biocompatibility.

In summary, we introduced the recent progresses of phosphate 1D nanowires doped with RE. We suggest that the research focus should be the application of 1D nanowires in biological probe, photonic crystals, optical communication, etc in future.

### References


Submit your manuscripts at http://www.hindawi.com