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Photoluminescence from surfactant-assembled Y₂O₃:Eu nanotubes

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 Y_2O_3 : Eu nanotubes were fabricated by a surfactant assembly mechanism. The tubular structure was characterized by transmission electron microscopy. Under an ultraviolet-light excitation, the nanotubes show a relatively intense emission peak at 618 nm besides the 610 nm peak, different from that of single Y_2O_3 : Eu nanocrystallites. The results of laser-selective excitation indicate that the emission centers near the surface of nanotube walls exhibit inhomogenously broadened spectra without spectral structures while the two sites (sites B and C) inside the nanotube walls present legible spectral structures. It is concluded by the number and peak positions of Stark levels that the sites B and C possess different site symmetries. © 2003 American Institute of Physics. [DOI: 10.1063/1.1542685]

One-dimensional structures, such as nanotubes, are attracting a great deal of attention in both fundamental and applied studies.^{1–3} They could be used to study the physical and chemical properties of molecules confined in their inner and outer spaces. They could find potential applications in fields such as photoelectronics, advanced catalysis, and energy storage/conversion, and also could be designed to mimic biological channels. The interests in nanotubular materials thus stimulated researchers to extensively expand the family of inorganic nanotubes from carbon-based substances to sulfides,^{4,5} nitrides,⁶ and oxides.^{7–9}

Rare earth compounds have been extensively applied to high-performance magnets, luminescence devices, catalysts, and other functional materials. Most of these functions depend strongly on the composition and structure. Recently Yada et al.³ reported the synthesis of rare earth (Er, Tm, Yb, Lu) oxide nanotubes templated by dodecylsulfate assemblies. The nanotubes have small inner diameters of 3 nm and single thin inorganic walls of about 1 nm. However, except for the four oxides, no nanotubular structures were obtained with yttrium and the other lanthanides. The reason was attributed to the differences in ionic radii of their trivalent forms responsible for their coordination numbers and basicities. In this letter, Y_2O_3 : Eu nanotubes were prepared by a similar but a little different method. Y2O3:Eu phosphor is commonly used as a red emitting material for field emission display technology, so we focus our attention on the luminescence properties of Y₂O₃:Eu nanotubes. In addition, we believe that single nanotubes can be converted into a composite structure for particular applications by filling and coating the tubes with functional molecules, which cannot be expected for bulk materials.

The method for fabricating $Y_2O_3:2\%$ Eu nanotubes is as follows: surfactant such as sodium dodecylsulfate selforganizes into rodlike micelles when its concentration is about 0.09 mol/L in a water solution at 40 °C. After a certain amount of yttrium and europium chlorides at a molar ratio of 98:2 were added in, the mixtrure was stirred to be a transparent solution. Urea was used to adjust the pH of the solution in order that precipitation occurred. The precipitate was separated, washed thoroughly, and dried in air. The resulting solid was put into a furnace. The temperature was gradually raised to 500 °C and maintained at that temperature for 3 h. After cooling to room temperature, the sample was annealed again at 800 °C for 2 h to decompose the surfactant molecules. The tubular structure was observed using a JEM-2010 (JEOL) transmission electron microscope (TEM). The samples were mounted in the helium exchange gas chamber of a closed cycle refrigeration system and their temperature maintained at 10 K. A Rodamine 6G dye laser pumped by a second harmonic of a Nd:yttrium-aluminum-garnet pulsed laser was used as the excitation source. The fluorescence spectra were obtained with a Spex 1403 spectrometer. Photoluminescence signals were detected by a photomultiplier, averaged with a boxcar integrator, and processed by a computer. Room-temperature emission spectra were recorded with a Hatachi F-4500 fluorescence spectrometer using a Xe lamp as the excitation source.

TEM image confirms the formation of Y_2O_3 :Eu nanotubes. As shown in Fig. 1, the central part of the cylindrical sample is white and the two peripheries are black, suggesting the formation of single nanotubes. A bundle aggregate of several nanotubes is also observed in the TEM image. The typical outer diameters of the nanotubes are in the range of 20–30 nm and the walls are estimated to be several nanometers in thickness. The inset shows the electron diffraction pattern recorded perpendicular to the nanotube long axis, which reveals that the nanotubes are in crystal phase and also stable enough to withstand the irradiation of convergent high-energy electron beam.

Figure 2 presents the room-temperature emission spectra of Y_2O_3 :Eu nanotubes and nanocrystalline powders under 394 nm excitation. The Y_2O_3 :Eu powders with an average size of 20 nm were obtained by combustion synthesis.¹⁰ The peak at 610 nm is due to the forced electric dipole transition

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FIG. 1. TEM image of Y_2O_3 :Eu nanotubes. The inset shows the electron diffraction pattern recorded perpendicular to the nanotube long axis.

 $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$, which is allowed on condition that the europium ion occupies a site without an inverse center. Its intensity is hypersensitive to crystal environments. The peaks near 590 nm derive from the allowed magnetic dipole transition $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$. The relative intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions in $Y_{2}O_{3}$:Eu nanotubes decreases compared with that in $Y_{2}O_{3}$:Eu nanotubes. Furthermore, a comparatively intense peak at 618 nm appears in the emission spectrum of $Y_{2}O_{3}$:Eu nanotubes. It is known that the Eu³⁺ ions occupy the S₆ and C₂ symmetry sites in cubic yttria.¹¹ The tubular $Y_{2}O_{3}$:Eu material has different structure from the nanocrystalline powders, so site selective excitation was performed to distinguish the different sites occupied by the Eu³⁺ ions in the nanotubes.

Figure 3 gives the low-temperature excitation spectra of the nanotubes, where the excitation peaks correspond to the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ transition. The dashed line was taken at the emission wavelength of 610 nm. An intense peak (marked A) with two weak peaks (marked B and C, respectively) in the low-energy wing was observed. The solid line was measured by monitoring the emission wavelength of 618 nm, and only peaks B and C were observed. This means that the 610 and 618 nm peaks derive from different emission centers. The site-selective emission spectra were measured at 10 K by using different resonant excitation wavelengths into the ${}^{7}F_{0}$ $\rightarrow {}^{5}D_{0}$ absorption bands. The excitation positions are labeled with numbers 1–5, as indicated by the arrows in Fig. 3. The corresponding emission spectra are shown in Fig. 4. Peak A



FIG. 3. Excitation spectra of Y_2O_3 :Eu nanotubes. The solid and dashed lines were taken at the emission wavelength of 618 and 610 nm, respectively. The arrows indicate different excitation positions. The corresponding emission spectra were listed in Fig. 4.

has a long tail extending to the high-energy side, and also its linewidth is broader than those of peaks B and C. Spectra 1, 2, and 3 were obtained by exciting different positions of peak A. No Stark splittings can be discerned from the spectra. We propose that peak A may originate from the emission centers near the surface of the nanotube walls. Qualitatively, in view of the coexistence of outer surface and inner surface, the Y₂O₃:Eu nanotubes have a high ratio of surface to volume which enhances the number of surface states. As a result, the Eu³⁺ ions near the surface may locate at various symmetry sites because the surface states modify the site symmetry irregularly. Therefore, no spectral structure is observed from the three emission spectra broadened inhomogeneously. Spectrum 4 was measured by exciting the peak position of peak B. The three Stark splittings for ${}^{7}F_{1}$ multiplets and five for ${}^{7}F_{2}$ multiplets can be clearly discerned. Spectrum 5 was taken by exciting the peak position of peak C. The spectrum exhibits three Stark splittings for both ${}^5D_0 \rightarrow {}^7F_1$ transition and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition. The number of ${}^{7}F_{2}$ multiplets and the peak positions of ${}^{7}F_{1}$ multiplets in spectrum 5 are different from those of spectrum 4. Spectra 4 and 5 present clear spectral structure, which indicates that peaks B and C originate from the emission centers in a crystalline rather than disordered environment. Interfacial models of nanocrystalline materials consist of a crystalline core with a slightly disordered surface layer.^{12,13} Accordingly, we suggest that peaks B and C derive from two different sites (labeled as



FIG. 2. Comparison of emission spectra between Y_2O_3 : Eu nanotubes and Y_2O_3 : Eu nanocrystallites.



FIG. 4. Emission spectra of Y_2O_3 : Eu nanotubes corresponding to different excitation positions in Fig. 3.

sites B and C, respectively) inside the Y_2O_3 :Eu nanotube walls. It can be concluded by the number and peak positions of the Stark levels that the sites B and C possess different site symmetries, although their symmetries are not definitely determined.

In conclusion, Y_2O_3 : Eu nanotubes were synthesized by a surfactant assembly mechanism. TEM image confirms the formation of the tubular structures. Under the excitation of ultraviolet light, the nanotubes show luminescence properties different from that of Y_2O_3 : Eu nanocrystallites. The results of laser selective excitation indicate that the emission centers near the surface exhibit inhomogenously broadened spectra while the two different symmetry sites inside the nanotubewalls present legible spectral structures.

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