# Highly efficient low-voltage cathodoluminescence of $LaF_3:Ln^{3+}$ ($Ln=Eu^{3+}, Ce^{3+}, Tb^{3+}$) spherical particles

Zhen-Ling Wang,[1,2] H. L. W. Chan,[1] Hiu-Ling Li,[1] and J. H. Hao[1,a)]
[1]*Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, People's Republic of China*
[2]*Analytical and Testing Center, Zhoukou Normal University, Zhoukou 466000, People's Republic of China*

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Spherical particles of rare-earth doped $LaF_3$ are synthesized through refluxing in glycerol/water media. The low-voltage cathodoluminescence of $LaF_3:Eu$ due to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions was found to be sensitive to the site that $Eu^{3+}$ ions occupied. The luminous efficiency of $LaF_3:Ce^{3+}$, $Tb^{3+}$ with green emission is improved from 1.53 to 2.02 lm/W compared with $LaF_3:Tb^{3+}$, due to the energy transfer processes from $Ce^{3+}$ to $Tb^{3+}$ ions. Our results suggest that the obtained spherical particles of rare-earth doped $LaF_3$ are promising as highly efficient low-voltage cathodoluminescent phosphors, which have received considerably less attention. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2998582]

The phenomenon of cathodoluminescence (CL) is related to the emission of light in response to the excitation of matter with accelerated electrons. As an electron-beam excitation may produce orders-of-magnitude greater carrier generation rates than optical excitation, it is especially advantageous in studies of wide bandgap materials. Moreover, the CL properties of materials are critical for field-emission displays (FEDs), which are promising emissive displays realizing high resolution and low consumption of electric power.[1] Phosphors used in FEDs require several new properties that the traditional cathode-ray tube (CRT) display phosphors may not possess, such as high CL efficiency under low excitation voltage ($\leq$5 kV) and specific surface conditions.[2] Much work has been done to explore low-voltage cathodoluminescent phosphors for FED application.[3–5]

Fluorides are advantageous as luminescent host materials owing to their wide bandgap, low vibrational energies, and the subsequent minimization of the quenching of the excited state of the rare-earth ions.[6] Rare-earth doped fluorides have extensively been studied in the applications of vacuum ultraviolet optics, upconverters, biological fluorescent labels, and so on.[7–9] However, a few papers has been reported on the CL of fluorides, limited to $CeF_3$ crystals, rare-earth-activated binary fluoride crystals and Zr–Ba–La–Al–Na fluoride glass.[10–12] In particular, the characteristic of low-voltage CL in fluorides is unknown. The $LaF_3$ compound has the photochemical stability and its phonon energy is as low as 350 $cm^{-1}$. In this letter, the low-voltage CL properties of $LaF_3:Eu^{3+}$, $LaF_3:Tb^{3+}$, and $LaF_3:Ce^{3+}$, $Tb^{3+}$ spherical particles are reported. Excellent performance of low-voltage CL for the phosphors is determined.

$LaF_3:20\%\ Eu^{3+}$, $LaF_3:10\%\ Tb^{3+}$, and $LaF_3:20\%\ Ce^{3+}$, $10\%\ Tb^{3+}$ spherical particles were prepared by mixing lanthanide trichlorides with $NH_4F$ in glycerol/water media and refluxing at boiling state (110 °C) for 2 h. The solid was separated by centrifugation, cleaned, and dried at 90 °C for 12 h. Then the as-prepared samples were annealed at 600 °C for 4 h. The commercial CRT phosphors $Y_2O_2S:Eu$ (red) and ZnS:Cu (green) were provided by Shanghai Yuelong New Materials Co. for comparison. The details of measurements were described in our recent work.[13]

After annealing at 600 °C, the x-ray diffraction (XRD) patterns indicate that $LaF_3:Eu^{3+}$, $LaF_3:Tb^{3+}$, and $LaF_3:Ce^{3+}$, $Tb^{3+}$ particles are basically in agreement with the hexagonal structure known from bulk $LaF_3$ (Fig. 1). The rare-earth ions ($Eu^{3+}$, $Ce^{3+}$, $Tb^{3+}$) were doped into the $LaF_3$ lattice and occupied the site of $La^{3+}$ ions, with the formation of a $La_{1-x}Ln_xF_3$ solid solution even at relatively higher $Ln^{3+}$ doping concentration, except those two very weak peaks arising from $CeO_2$ (Ref. 15) for $LaF_3:20\%\ Ce^{3+}$: $10\%Tb^{3+}$ sample [denoted as * in Fig. 1(d)]. The typical scanning electron microscopy (SEM) image of $LaF_3:Eu^{3+}$ sample is shown in Fig. 2. $LaF_3:Eu^{3+}$ powders annealed at 600 °C are composed of spherical or near spherical particles with size around 300 nm (Fig. 2, inset). The morphologies of $LaF_3:Tb^{3+}$ and $LaF_3:Ce^{3+}$, $Tb^{3+}$ particles are similar to that of $LaF_3:Eu^{3+}$ particles, which indicated that the spherical morphology was not evidently affected by categories of doping lanthanide ions. Phosphors with submicron-scale spherical morphology are important for displays because they offer higher packing density, lower scattering of light, brighter lu-

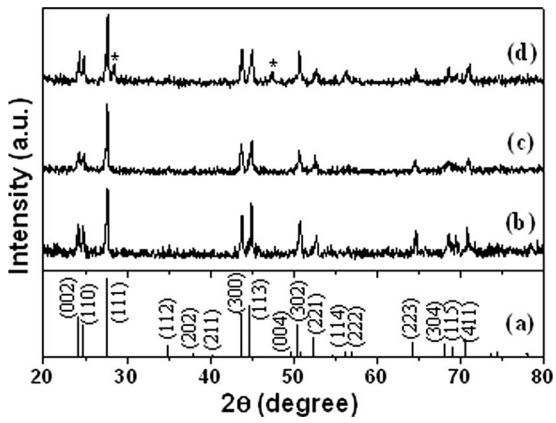


FIG. 1. XRD patterns of (b) $LaF_3:Eu^{3+}$, (c) $LaF_3:Tb^{3+}$, (d) $LaF_3:Ce^{3+}$, $Tb^{3+}$ particles, and (a) the standard data for bulk $LaF_3$ (Ref. 14).

a)Author to whom correspondence should be addressed. Electronic mail: apjhhao@polyu.edu.hk.

 

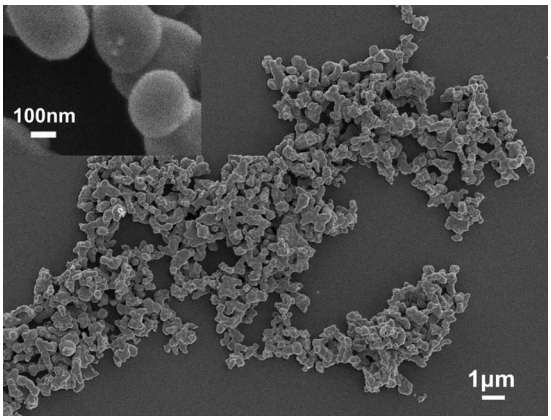


FIG. 2. SEM images of $LaF_3:Eu^{3+}$ particles annealed at 600 °C (inset is the enlarged image of the same sample).

minescent performance, and more improved screen packing.[5,13]

Under the excitation of low-voltage electron beam, $LaF_3:Eu^{3+}$ particles exhibit orange-red emission of $Eu^{3+}$ ions. The CL spectra are composed of the characteristic line emissions arising from the $^5D_0 \rightarrow {}^7F_J$ and $^5D_1 \rightarrow {}^7F_J$ transitions of the $Eu^{3+}$ ions [Fig. 3(a)]. The relative intensities of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ emissions were found to be very sensitive to the site that $Eu^{3+}$ ions occupied. As for $LaF_3:Eu^{3+}$ particles, the $Eu^{3+}$ ions occupy the $La^{3+}$ ion lattice and are at a site with inversion symmetry in the $LaF_3$ matrix; thus the dominating emission centered at 590 nm corresponds to the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition.[16] The CL spectrum of the sample annealed at 600 °C [solid line in Fig. 3(a)] is markedly strengthened compared with that of the as-prepared sample [dotted line in Fig. 3(a)]. At 4.0 kV and 91.6 $\mu A/cm^2$, the luminance values of the as-prepared and annealed samples are 25 and 835 $cd/m^2$, respectively. The luminous efficiency is improved from 0.02 to 0.72 lm/W after annealing treatment, which is still poorer than 9.20 lm/W of commercial $Y_2O_2S:Eu$ phosphor. Annealing treatment at high temperature makes the crystallite size increase and the number of atoms in the grain boundaries and on the surface decrease, leading to an increase in the number of radiative recombination sites and therefore a higher probability of radiative recombination.

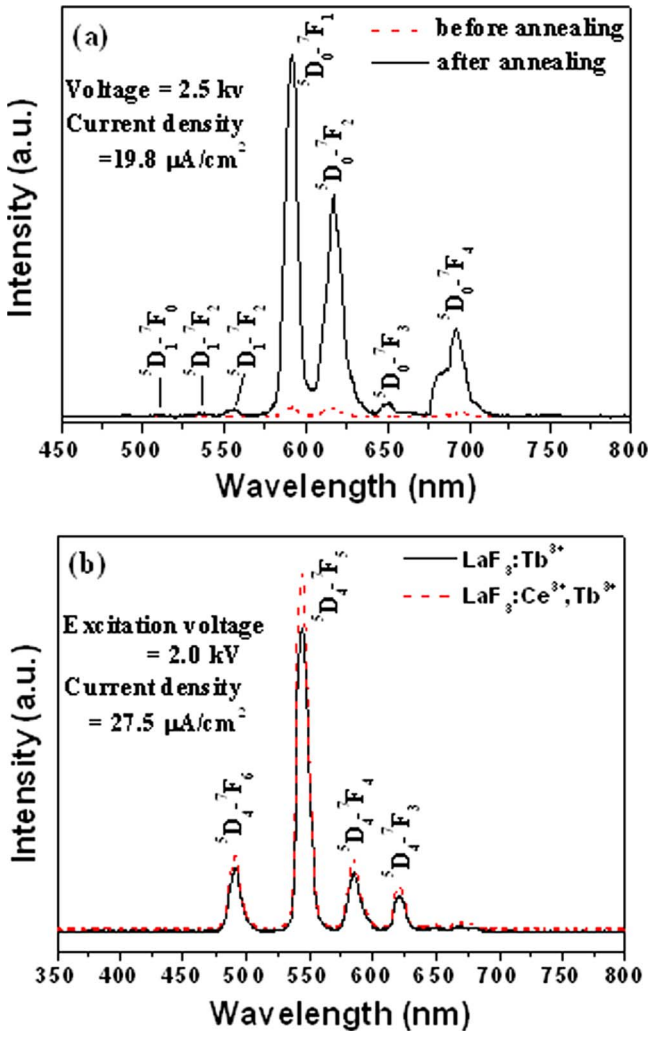


FIG. 3. (Color online) CL spectra of (a) $Eu^{3+}$ and (b) $Tb^{3+}$ ions in $LaF_3$ particles.

$LaF_3$ particles doped with $Tb^{3+}$ and codoped with $Ce^{3+}$, $Tb^{3+}$ ions show green emission under the excitation of low-voltage electron beam. The CL spectra of these two samples annealed at 600 °C are similar in profile, which are arising from the transitions between the excited $^5D_4$ state and the $^7F_J$ $(J=6-3)$ ground states of $Tb^{3+}$ ions [Fig. 3(b)]. However, the CL intensity of $LaF_3:Ce^{3+}$, $Tb^{3+}$ particles (dotted line) is improved by 17% with respect to that of $LaF_3:Tb^{3+}$ particles (solid line). Correspondingly, the luminance value is increased from 2300 to 3036 $cd/m^2$, and the luminous efficiency is improved from 1.53 to 2.02 lm/W (4.0 kV, 117.5 $\mu A/cm^2$). This indicates that the $Tb^{3+}$ green emission in $LaF_3:Ce^{3+}$, $Tb^{3+}$ particles can be enhanced by the energy transfer processes from $Ce^{3+}$ to $Tb^{3+}$ ions. For cursory comparison, the following data of luminance or luminous efficiency from other hosts are presented: (a) 171 $cd/m^2$ at 3 kV and 500 $\mu A/cm^2$ for YAG:Tb (YAG denotes yttrium aluminum garnet) powder prepared by combustion synthesis and annealed at 1600 °C,[17] (b) 0.70 lm/W at 5 kV and 57 $\mu A/cm^2$ for $ZnAl_2O_4:Tb$ prepared by spray pyrolysis and annealed at 1600 °C,[18] (c) 0.54 lm/W at 5 kV for $Ba_2B_5O_9Cl:Tb$ prepared by spray pyrolysis and annealed at 630 °C,[19] and (d) 9.19 lm/W at 4 kV and 110 $\mu A/cm^2$ for commercial product ZnS:Cu. Some works deserve to be done in order to improve the luminous efficiency of these fluoride phosphors, such as increasing crystallinity, controlling particle size, altering doping concentration, optimizing the synthesis procedure, etc.[20,21]

The CL intensity is dependent on measurement conditions such as current density and excitation voltage. The CL intensities of the $LaF_3:Eu^{3+}$ particles (annealed at 600 °C) increased linearly with the applied voltage from 1.5 to 3.5 kV at a current density of 12.3 $\mu A/cm^2$ [Fig. 4(a)]. According to an empirical formula,[22] the electron penetration depths of $LaF_3:Eu^{3+}$ phosphors at the anode voltage of 1.5, 2.0, 2.5, 3.0, and 3.5 kV are estimated to be 6.1, 13.2, 24.2, 39.8, and 60.5 nm, respectively. Hence, the increase in intensity with increasing applied voltage is due to an increase in the number of excited luminescence centers resulting from an increase in electron penetration depth. The CL intensities also increase with the increasing current density from 9.9 to 26.9 $\mu A/cm^2$ under fixed excitation voltage of 2.5 kV [Fig. 4(b)]. This indicates that $LaF_3:Eu^{3+}$ particles are resistant to the current saturation, which is of benefit to FEDs.

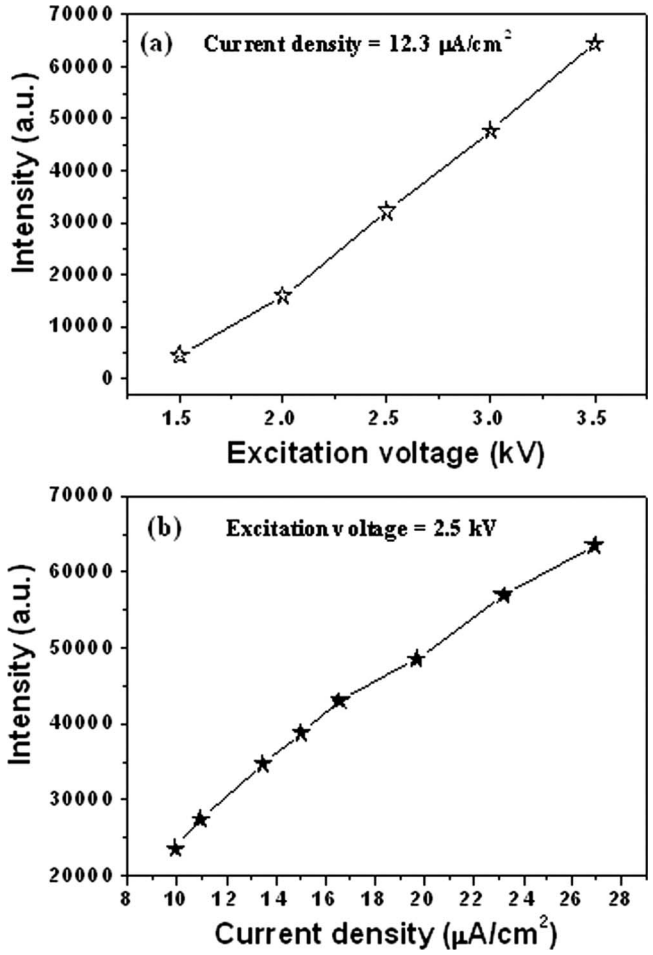


FIG. 4. The dependence of CL intensity (592 nm) of $LaF_3:Eu^{3+}$ particles on the (a) excitation voltage and (b) current density.

In summary, rare-earth doped $LaF_3$ spherical particles were prepared by soft-chemistry method. The effect of annealing treatment, codoping, and measurement conditions on CL properties was investigated as well. The particles excited at low-voltage electron beam (4.0 kV) show high efficiencies of 0.72 and 2.02 lm/W for $LaF_3:Eu^{3+}$ and $LaF_3:Ce^{3+}$, $Tb^{3+}$, respectively. Our work indicates that rare-earth doped $LaF_3$ is promising for low-voltage CL applications.

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