

Observation of whispering gallery modes in cathode luminescence in $\text{TiO}_2:\text{Eu}^{3+}$ microspheres

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We report cavity enhanced periodic structures in cathode luminescence spectra in $\text{TiO}_2:\text{Eu}^{3+}$ microspheres ranging from 6.2 to 12.2 μm in diameter. The spectral structures observed at the accelerating voltage below 10 kV are attributed to the lower order whispering gallery modes, while the additional components appearing at 20 kV are to the higher order modes within the microsphere. These observations illustrate that the basic properties of phosphors can be advanced from the point of view of cavity quantum electrodynamics by fabricating a microcavity structure onto a single phosphor crystal. © 2006 American Institute of Physics. [DOI: 10.1063/1.2335578]

In the study of cathode phosphors, a lot of materials have been synthesized and their basic characteristics have been fully examined.¹ Rare-earth and transition metals are widely used as practical phosphors in modern light emitting devices, while the rapidly developing technologies demand more sophisticated phosphors. For example, since the accessible voltage and current in field emission displays are restricted by several factors, a cathode phosphor with a low working voltage is desired. Along with the traditional method based on solid state reactions, an alternative approach based on sol-gel process has also been applied to fabricate highly pure nanopowders or homogeneous thin film from organic precursors.^{2,3}

Most of the previous investigations on phosphors have been devoted to the material research. On the other hand, the emission property is relevant not only to the material but also to the radiation fields interacting with the emission center. This quantum-electrodynamic (QED) effect is known as the Purcell effect,⁴ that is, the luminescence from rare-earth atoms or molecules may be alternatively enhanced or inhibited, depending on whether or not the emission spectrally coincides with the cavity resonances.⁵⁻⁷ Here, we discuss a novel concept of cathode phosphor in order to improve the basic properties, such as emission efficiency, color purity, and lifetime from point of view of the QED effect by fabri-

cating a microcavity structure onto a single phosphor crystal. Specifically, we prepared high quality Eu^{3+} doped TiO_2 dielectric spheres and observed cavity enhanced periodic structures in the cathode luminescence (CL) spectra, which are attributed to whispering gallery modes^{5,6,8,9} (WGMs) within the spheres. The spherical cavity enhanced effects in photoluminescence,^{5,10} light scattering, and nonlinear optics or the effects associated with other morphological cavity structures¹¹⁻¹³ have widely been observed in optical experiments. Although these effects have potentialities to develop phosphors, such an effect has not been reported so far in cathode luminescence.

The Eu^{3+} doped TiO_2 microspheres were prepared by a hydrolysis process of alkoxide droplets.^{14,15} First, $\text{Ti}(\text{OC}_4\text{H}_9)_3$ was dissolved at 0.1 mol/l in a mixed solvent of *n*-octanol and acetonitrile, which contained hydroxy propyl cellulose as the surface stabilizer. Water dissolved in ethanol was added into the mixed solvent, and the subsequent hydrolysis process of alkoxied droplets resulted in hydroxide particles. The sphere size was controlled through the concentration of hydroxy propyl cellulose. In order to dope Eu^{3+} ion, the microsphere was dipped in aqueous solution of europium nitrate [$\text{Eu}(\text{NO}_3)_3$]. The doped spheres were then crystallized into a stable phase. The cathode luminescence was measured by an experimental setup based on a scanning electron microscope. The $\text{TiO}_2:\text{Eu}^{3+}$ microsphere was placed on a metal substrate and set at one of the focal points of the elliptical

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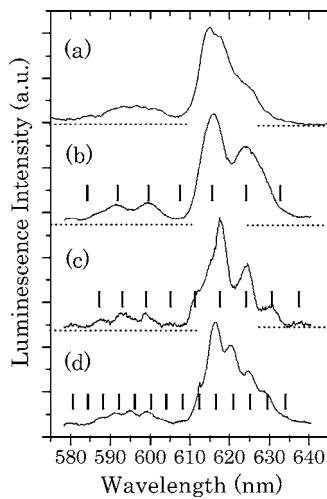


FIG. 1. Cathode luminescence spectra from $\text{TiO}_2:\text{Eu}^{3+}$ (a) in the form of agglomerated irregular powders; (b), (c), and (d) are from microspheres of $d=6.2$, 8.1, and $12.2 \mu\text{m}$ in diameter, respectively. The vertical lines in (b), (c), and (d) indicate the free spectral range of $\Delta\nu=6.5$, 5.0, and 3.3 THz, respectively.

mirror, while the emitted light from the single microsphere was collected from another focal point by using an optical fiber. The luminescence from the fiber was led into a 30 cm polychromator and the spectra were measured by a cooled charge-coupled device camera. The spectral resolution was 0.5 nm and the accelerating voltage was varied from 6 to 20 kV.

Figure 1 shows CL spectra from $\text{TiO}_2:\text{Eu}^{3+}$ observed at the accelerating voltage of 10 kV. Figure 1(a) is the spectrum from agglomerated irregular shaped powders, where the peaks at 595 and 620 nm correspond to the transitions of 5D_0 to 7F_1 and 5D_0 to 7F_2 in Eu^{3+} , respectively. Figs. 1(b)–1(d) are CL spectra from well shaped microsphere. In contrast to the irregular powders, these spectra show periodic structures superimposed over the normal broadband emission. The vertical lines in Figs. 1(b)–1(d) indicate the free spectral range of $\Delta\nu=6.5$, 5.0, and 3.3 THz, respectively. When the sphere size is increased from 6.2 to $12.2 \mu\text{m}$, the free spectral range between peaks decreases. We consider that these spectral features arise from cavity enhancement effect in the spontaneous emission by WGM resonance in the microspheres. The WGMs are assigned by radial order number n , angular number l , azimuth number m , and polarization indices, TE or TM,^{8,9} similar to those used in a simple atomic system. For the large mode numbers, the spacing between TE or TM modes with the same order number and with the differing mode number by 1 is approximated as $\Delta\nu \sim (c \tan^{-1} \rho)/(2\pi a \rho)$, where $\rho = (\eta^2 - 1)^{1/2}$, a is radius, η is refractive index of the sphere, and c is the speed of light,⁹ which explains the experimental observation. In order to see the absolute mode numbers, we calculated the mode positions for the sphere of $d=8.1 \mu\text{m}$ with $\eta=2.48$ and represented by a series of vertical lines in Fig. 2. In the notation, such as $\text{TE}_{91,1}$, the first and second subscripts represent the mode ($l=91$) and order ($n=1$) numbers, respectively. The spectral peaks observed show good correlations with the predicted positions for the lower order modes.

While the cavity enhanced effects have widely been observed in optical experiments, such an effect has not been reported in cathode luminescence. Several differences could

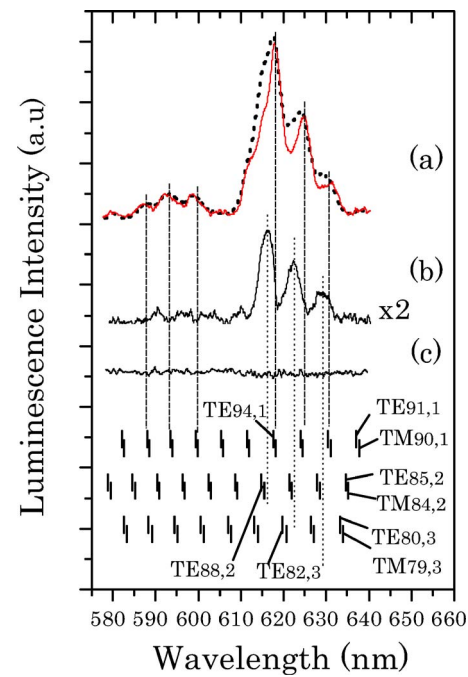


FIG. 2. Cathode luminescence spectra from $\text{TiO}_2:\text{Eu}^{3+}$ microsphere of $8.1 \mu\text{m}$. (a) Solid and dotted lines are normalized spectra observed at 10 kV (multiplied by 2.3) and 20 kV. Differential spectra: (b) $\Delta\text{CL}=\text{CL}(20 \text{ kV}) - 2.3 \times \text{CL}(10 \text{ kV})$ and (c) $\Delta\text{CL}=\text{CL}(10 \text{ kV}) - 4.8 \times \text{CL}(6 \text{ kV})$. A series of vertical lines (combs) represents the resonance wavelength of WGMs calculated for the microsphere of $d=8.1 \mu\text{m}$ with refractive index of $\eta=2.48$. The order numbers are $n=1, 2$, and 3 from top to bottom combs, while the mode number increases in a step of 1 from the long wavelength side to the short wavelength side.

appear between photoluminescence experiments and CL experiments. First, the CL experiment has the advantage that the electron beam can be focused below the optical wavelength and the local emission characteristics can be probed.¹⁶ Secondly, in the CL experiment, the depth dependent emission profiles can be examined through the control of the accelerating voltage.¹⁷ In order to demonstrate this advantage, we examined the dependence of CL spectra on the accelerating voltage. Figure 2(a) shows normalized spectra observed at 10 and 20 kV. We calculated the differential spectrum by subtracting the normalized spectrum of 10 kV (multiplied by 2.3) from that of 20 kV (multiplied by 1.0). It is seen that additional components appear when the voltage is increased up to 20 kV. Similar analysis was carried out for the spectra observed at 6 kV (multiplied by 4.8) and 10 kV. In this case, the spectra at 6 and 10 kV are essentially the same as shown in Fig. 2(c).

Figure 3 shows the luminescence intensity as a function of the accelerating voltage. From this figure, the dead voltage of luminescence quenching can be estimated as 5 kV. The corresponding penetration depth of electron beam through TiO_2 at 5 kV is estimated to be of the order of $0.1 \mu\text{m}$ on the basis of the Feldman formalism,¹⁸ while this length increases up to $4 \mu\text{m}$ at 20 kV. We can also calculate the spatial intensity distribution within the WGMs on the basis of Mie theorem.¹⁹ For WGMs around 620 nm with $n=1, 2$, and 3 and $\text{TE}_{94,1}$, $\text{TE}_{88,2}$, and $\text{TE}_{82,3}$ in Fig. 2, the radial positions of the intensity maximum from the sphere surface are calculated as 0.19, 0.44, and $0.65 \mu\text{m}$, respectively. These values, together with the estimated penetration depth, suggest that at the accelerating voltage below 5 kV, the electron beam pen-

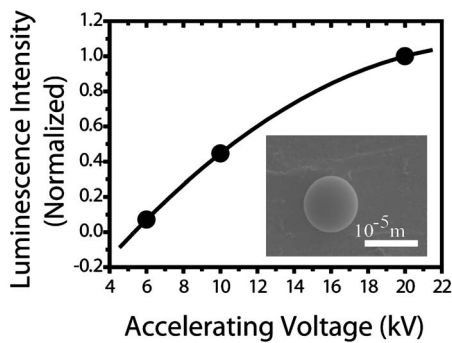


FIG. 3. Solid circles are normalized luminescence intensity in $\text{TiO}_2:\text{Eu}^{3+}$ microsphere of $8.1 \mu\text{m}$ as a function of the accelerating voltage. The inset shows a scanning microscope photograph of a typical $\text{TiO}_2:\text{Eu}^{3+}$ microsphere.

etrates only the dead layer and does not excite the WGM efficiently, while at 6 or 10 kV, the beam excites the lower order number WGMs and shows the periodic structures in the CL spectra. When the accelerating voltage is further increased up to 20 kV, the beam excites the deep inner region of the sphere and additional components appear as shown in Fig. 2(b). The possible origin of the dead layer may be the surface defects or the charging up during the excitation of the TiO_2 spheres.

In summary, we have observed WGM resonance modes in CL spectra in $\text{TiO}_2:\text{Eu}^{3+}$ microsphere. In the present experiment, we employed TiO_2 microsphere, since the synthesis technique has well been developed. From the point of view of practical cathode phosphors, other host crystals such as $\text{Y}_2\text{O}_3\text{S}:\text{Eu}^{3+}$ are interesting. Since the size of spheres synthesized by alkoxide method matches well with the typical size of fine display pixels, it is also interesting to design a microsphere laser array relevant to WGMs pumped by the field electron emitters. Such a coherent flat panel display

could have potentiality in three dimensional displays or multidirectional displays.

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