Fluorescence MDR features of Eu^{3+} doped sol-gel TiO_2 hydrate microspheres

H. Ikari,[1*] K. Okanishi,[2] M. Tomita,[2] and T. Ishidate[2]

[1]Faculty of Education, Shizuoka University

[2]Department of Physics, Shizuoka University

, Shizuoka, 422-8529, Japan

Single particle fluorescence of Eu^{3+}-doped TiO_2 hydrate microsphere formed in sol-gel process has been studied, where TiO_2 hydrate spheres are characterized by the relatively high refractive index of 1.8. Observed fluorescence spectra display a structure that consists of narrow peaks of varing height superimposed on the familiar broad band emission from europium ions. Such emission peaks result from spherical cavity resonances, and resonance mode positions were assigned from Lorenz-Mie theory calculation. We have also directly measured the lifetime of the MDR peaks of the fluorescence spectra from 8-μm diameter Eu^{3+} doped TiO_2 hydrate microsphere.

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*Corresponding author.

E-mail address: edhikar@ipc.shizuoka.ac.jp.

There has been considerable interest in studies of optical resonators having dimensions comparable to the wavelength of light[1]. Among the resonators of these micrometer sized spheres, of particular interest are the modes localized at the surface. Light in such modes is trapped near the surface by repeated total internal reflections and travels in a great circle around the sphere with virtually no loss except for residual absorption and scattering in the dielectric. Emission from dielectric spheres containing fluorescing dyes shows sharp line structure superimposed on the normal broadband emission. These spectral features result from cavity QED enhancement of the emission rate at specific spherical cavity resonance wavelengths[2-7]. The broad off-resonant spectral components resemble the free-space spectrum.

The resonant emission rate is enhanced, leading to the formation of a spectral peak which decays more rapidly than the usual free space rate[8]. Significant lifetime modification of 610-620 light spontaneously emitted by chelated europium ions has been observed from successive time frames of the Eu emission spectrum for 10μ -diameter droplet[3,4]. Most of the experimental observations of the QED effect have been carried out in liquid microdroplets[2-4]. Experiments with droplets, however, suffer from their short lifetime since the droplet evaporates and is often free fall. For extensive observations of QED effects and practical applications in microcavities, measurements for solid spheres are desired.

A silica microsphere laser doped with any number of rare-earth ions was reported to have an extremely low threshold[9]. One of the

intriguing qualities of silica glass microspheres is their optical and structural compatibility with telecommunication optical fiber[10,11]. Kerr nonlinearities in a silica microcavities with very low optical power have been observed at 2K[12] and room temperature[13].

The Q values of whispering-gallery-mode(WGM) depend on the sphere's diameter and the refractive index m, high m is inevitable to accomplish the spherical optical cavity structure in microspheres. As the refractive index is increased, the density of resonances increases and their linewidth decreases as a function of size parameter. A small increment in refractive index actually shifts the resonance positions of each mode. In the present work, we qualitatively illustrate the index effect in TiO_2 hydrate microspheres by demonstrating cavity mode assignments of optical resonances of fluorescence, where our TiO_2 hydrate microspheres formed in sol-gel process have the relatively high refractive index of 1.8[14].

Titanium tetra-butoxide has been hydrolyzed in mixing solvent of n-octanol and acetonitrile. The synthesized microspheres consist of titanium oxide hydrate with amorphous structure, which is shown in Fig.1. The TiO_2 hydrate spheres were soaked in an europium nitrate pentahydrate 0.4mol/L aqueous solution and doped with Eu^{3+} ions[15]. The Eu^{3+} concentration in the hydrate sphere has not been known. We don't know whether or not the europium ions are uniformly distributed in the sphere. These TiO_2 hydrate spheres doped with Eu^{3+} are not heat-treated. For estimation of the refractive index, the microspheres have been immersed in refractive index liquids(Cargille Laboratory Inc.),

and the index of the spheres was estimated at about 1.78 by microscope immersion method. The diameters of the microspheres were measured with the laser microscope or SEM.

A cw argon laser beam with wavelength 457nm is focused by an objective lens and introduced on to the microsphere which is placed at a thin glass plate mounted on a two-dimensional adjuster. An optical fiber is positioned under the sphere by operating a three-dimentional adjuster. Fluorescence from the excited sphere is collected with the optical fiber and sent into a 0.3m spectrometer(resolution ~ 0.15nm) with CCD detectors. The life-times of the excited state population of the Eu ions have been investigated by chopping the intensity of the pump beam with Acousto-Optic Modulator and measuring the exponential decay of MDR emission peaks superimposed on the broadband bulk fluorescence. The pulse duration in these life-time measurements is 100 μs and the repetition rate is about 600Hz.

Figure 2 and 3 show the Eu^{3+} emission spectra for 5 and 8μm diameter Eu^{3+} doped TiO_2 hydrate microspheres, respectively. The broad band spectrum for Eu^{3+} shown in Fig.2 and 3 has been modified by the microcavity density of photon states. The spectral peaks in Fig.2 and Fig.3 are due to cavity enhanced emission. It has been known that these spectral features result from cavity QED enhancement of the emission rate at specific spherical cavity resonance wavelengths. Spherical cavity resonators, often called morphology dependent resonances (MDR's), occur at numerous discrete wavelengths throughout the visible in micrometer sized dielectric spheres.

For a given microsphere, resonances occur at specific values of $x_{n,l}$. Here x is the size parameter given by $2\pi a/\lambda$, where a is the microsphere radius, λis the wavelength and n and l are integers. The mode number n indicates the order of the spherical Bessel and Hankel functions describing the radial field distribution and the order l indicates the number of maxima in the radial dependence of the internal field distribution. Both discrete transverse electric, TEn, and transverse magnetic, TMn, resonances exist. We compare the observed resonance energies with the calculated values by adjusting the refractive index and size. With the proper choice of these parameters, the resonance frequencies are approximately reproduced. The initial values of the parameters for the 8μm diameter sample have been the measured refractive index of 1.78 and the measured diameter of 8μm. Reproduction of the observed resonance modes requires higher accuracy than a few digits. Best matches were obtained with the index of 1.777, and the diameter of 7.778μm.

Another concern in matching experimental spectra to calculated resonance peaks is the effect of dispersion in the microsphere medium. A simple linear dispersion of $m=1.78-(\lambda-\lambda_0)\times 2\times 10^{-4}\ \mathrm{nm}^{-1}$ from 605nm to 630nm provides a sufficient fit to the observed resonance positions. The dispersion coefficient is smaller than that for rutile ($6\times 10^{-4}\ \mathrm{nm}^{-1}$). The mode-indices to the observed lines are labeled in this way, which are shown in Fig.2 and 3.

On the other hand, when atoms are placed in a microcavity, fluorescence may be alternatively enhanced or inhibited depending on

whether or not the emission spectrally coincides with a cavity resonance. Lin et.al.[3] observed significant lifetime modification of 610-620nm light spontaneously emitted by chelated europium ions in 10μm diameter dimethylformamide-alcohol (DMFA) solution droplets. The size of the droplet relative to the spectral bandwidth of the fluorophore is critical to whether or not lifetime changes occur. The spontaneous emission rate enhancement simply reduces to approximately $\Delta\nu_{MDR}/\delta_{HB}$ [3], where δ_{HB} and $\Delta\nu_{MDR}$ are the spectral widths of the emission (homogeneously broadened) and cavity modes, respectively. $\Delta\nu_{MDR}$ is the spectral spacing between modes of the same order. This quantity is inversely proportional to the sphere radius and is approximated[16] by $\{\arctan[(m^2-1)^{1/2}]\}/[2\pi a(m^2-1)^{1/2}]$, where m is the refractive index of the sphere and a is the sphere radius. The homogeneous line width δ_{HB} of E^{3+} in various glasses [17-20] has been investigated at high temperatures, which is ranging from 1 to $10^2 cm^{-1}$. If the homogeneous width is also assumed to be roughly $50cm^{-1}$, $\Delta\nu_{MDR}/\delta_{HB}$ for the 8μm diameter Eu^{3+} doped TiO_2 hydrate microsphere is calculated to be about 4, which is approximately the same as that for 10μm-diameter DMFA solution droplets [3]. The effect on lifetime for 10μm-diameter droplets was observed from successive time frames of the Eu^{3+} emission spectrum[3]. We intended to observe the emission lifetime modification for a single solid Eu^{3+} doped microsphere. The decay of the fluorescence MDR emission peak was directly observed in this work.

Figure 4 shows the Eu^{3+} emission spectrum for the crushed Eu^{3+} doped TiO_2 hydrate microsphere, which, absence of MDR features, resembles

the characteristic bulk emission spectrum. Figure 5 shows the $^5D_0 \rightarrow {}^7F_2$ flourescence decays at 615nm for the crushed microsphere and at 615nm of the MDR emission peak for the 8μm diameter microsphere. The fluorescence light at 615nm in the crushed microsphere is observed to decay in 270μs[21-26], which is expected to yield an observed lifetime close to that of the free-space europium lifetime. The fluorescence MDR emission at 615nm in the 8μm diameter microsphere appears to be an admixture of components displaying both enhanced and free space lifetime, which is shown in Fig.5. The MDR emission feature in the 8μm diameter microsphere is observed to decay in less than 100μs(τ_2). The observed spontaneous emission rate enhancement is about 3(~ 270μs /100μs), which is comparable to the rough estimation($\Delta\nu_{MDR}/\delta_{HB}$) of about 4. This feature is qualitatively consistent with the observed lifetime modification for liquid microdroplets[3]. However, we could not observe the inhibited lifetime due to weak intensities presumably emitted from inhibited locations.

In summary, we have studied the single particle fluorescence of Eu^{3+}-doped TiO_2 hydrate microsphere formed in sol-gel process with the relatively high refractive index. The emission peaks result from spherical cavity resonances, and resonance mode positions were assigned from Lorenz-Mie theory calculations. These results show that the sol-gel TiO_2 hydrate microspheres have good spherical shapes and high optical transparency. Water-soluble rare earth ions can easily be doped in these spheres. Heating the spheres at 550℃ resulted in increasing their refractive indices with keeping good spherical shapes. These heat

treated TiO_2 microspheres also show some nonlinear effects. The use of the sol-gel TiO_2 spheres provides an useful vehicle for measuring QED effects in dielectric microspheres.

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Figure captions:

Figure 1.

A scanning electron micrograph of the prepared Eu^{3+} doped TiO_2 hydrate microsphere.

Figure 2.

Emission spectrum observed from Eu^{3+} in TiO_2 hydrate microsphere with diameter of 5μm. The spectral peaks superimposed on the usual broadband Eu^{3+} emission are due to cavity QED enhancement of the emission and their positions correlate well with spherical-cavity-resonance wavelengths. Open circles refer to TE modes and filled circles to TM modes.

Figure 3.

Emission spectrum observed from Eu^{3+} in TiO_2 hydrate microsphere with the 8μm diameter. Resonance mode assignments are indicated.

Figure 4.

Emission spectrum observed from Eu^{3+} in the crushed TiO_2 hydrate microsphere, corresponding to the usual broadband Eu^{3+} emission.

Figure 5.

Temporal profiles of the fluorescence at 615nm in the crushed microsphere(circles) and at 615nm in the MDR emission peak for the 8μm diameter microsphere(crosses). The emission from the crushed sphere has a measurable 1/e lifetime(τ_1) of about 270μs, close to the slow decay(τ_1) in the lifetime of the MDR peak for the 8μm diameter microsphere. The rapid decay(τ_2) is estimated at about 100μs, suggesting lifetime shortening due to the effects of cavity QED.

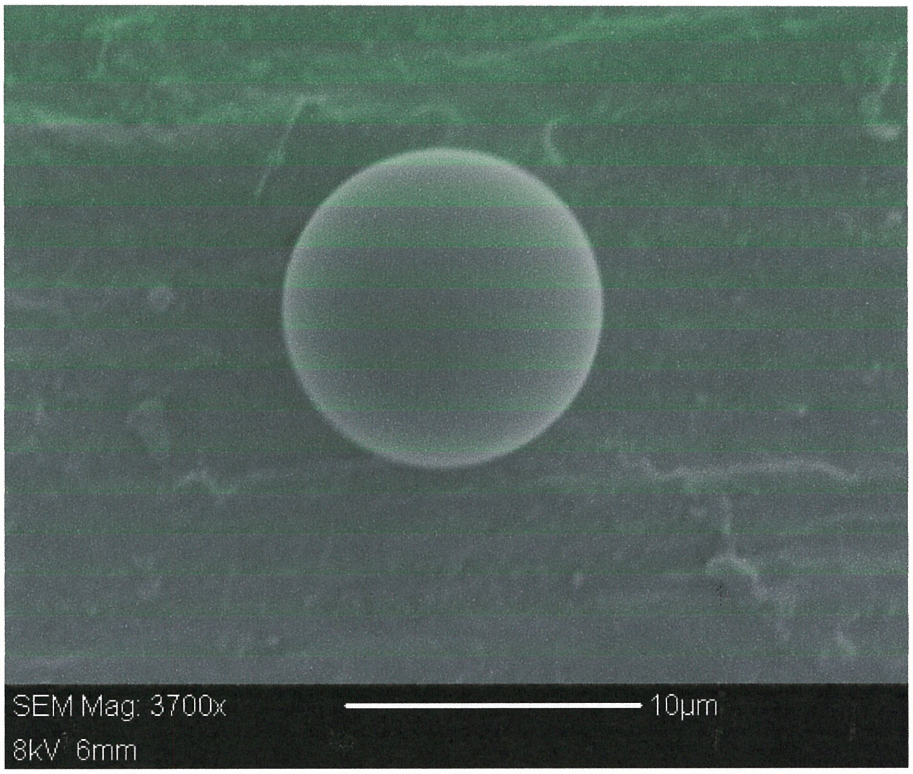

Figure 1 :

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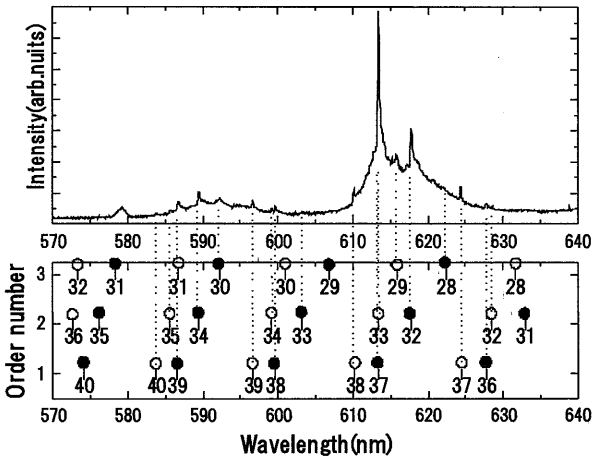

Figure 2:

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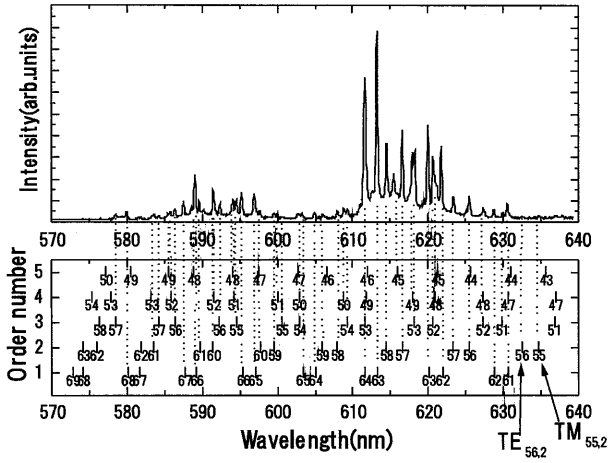

Figure 3 :

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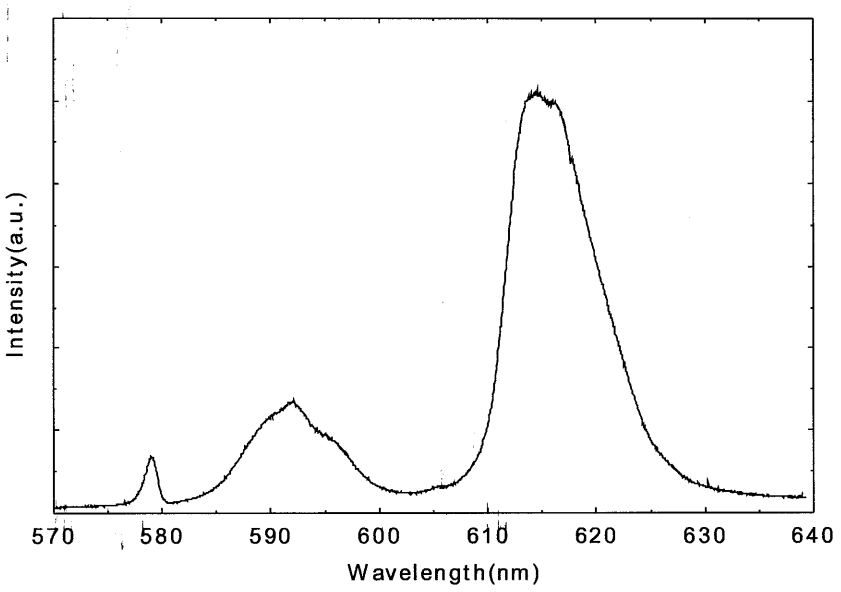

Figure 4 :

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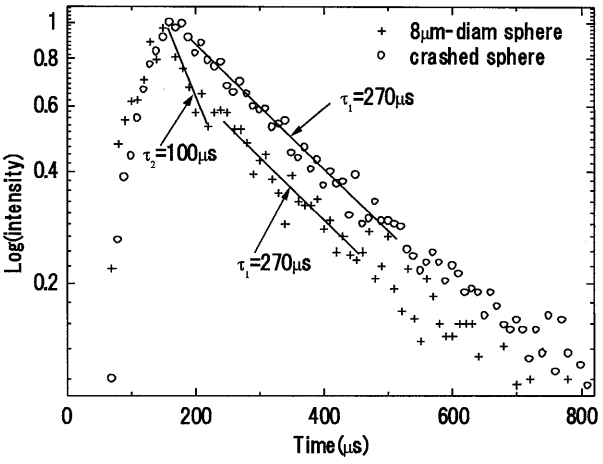

Figure 5 :

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