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

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Abstract

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 varying height superimposed on the familiar broadband 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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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 10 μ-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 2 K [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

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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 0.4 mol/L aqueous solution and doped with Eu^{3+} ions [15]. The Eu^{3+} concentration in the hydrate sphere has not been known. We do not 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 457 nm 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-dimensional adjuster. Fluorescence from the excited sphere is collected with the optical fiber and sent into a 0.3 m spectrometer (resolution ~ 0.15 nm) 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 600 Hz.

Figs. 2 and 3 show the Eu^{3+} emission spectra for 5 and 8 μm diameter Eu^{3+} doped TiO_2 hydrate microspheres, respectively. The broad band spectrum for Eu^{3+} shown in Figs. 2 and 3 has been modified by the microcavity density of photon states. The spectral peaks in Figs. 2 and 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

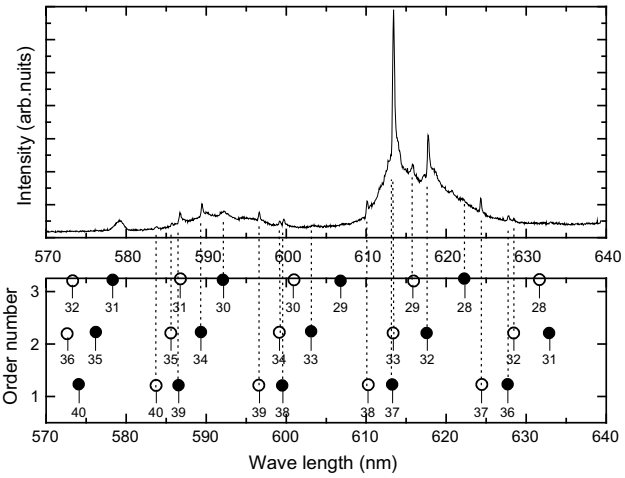

Fig. 2. Emission spectrum observed from Eu^{3+} in TiO_2 hydrate microsphere with diameter of 5 μm. The spectral peaks superimposed on the usual broadband Eu^{3+} emission are due to cavity QED enhancement of the emission and their positions correlate well with spherical-cavity-resonance wavelengths. Open circles refer to TE modes and filled circles to TM modes.

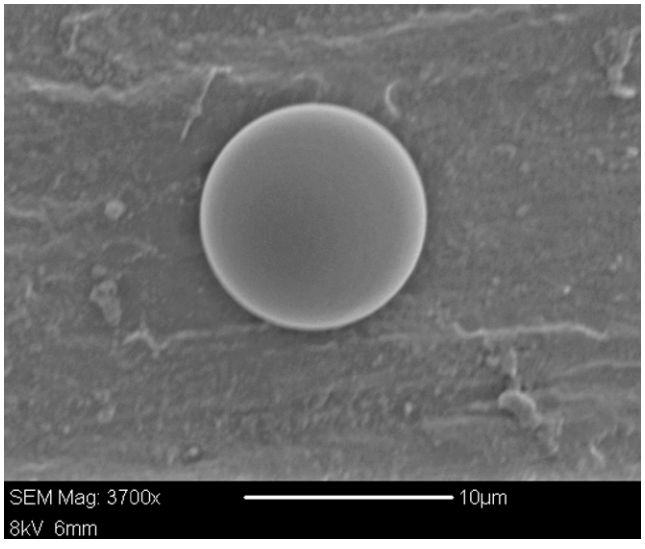

Fig. 1. A scanning electron micrograph of the prepared Eu^{3+} doped TiO_2 hydrate microsphere.

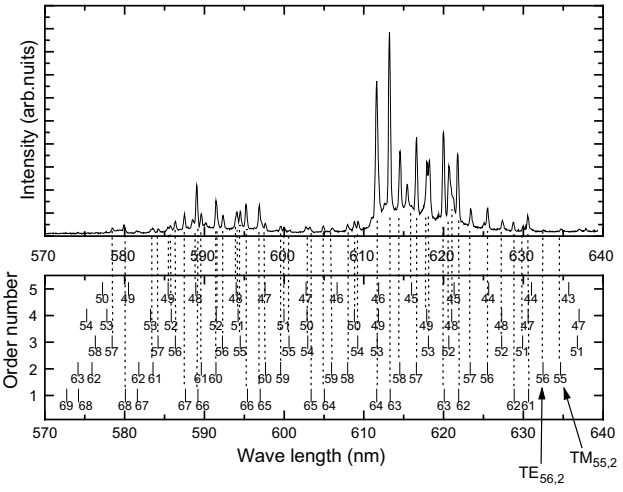

Fig. 3. Emission spectrum observed from Eu^{3+} in TiO_2 hydrate microsphere with the 8 μm diameter. Resonance mode assignments are indicated.