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High refractive-index microspheres of optical cavity structure

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Microspheres of refractive index of $n_D>2$ have been investigated. The organic-inorganic hybrid microspheres of refractive index $n_D=1.70$–1.72 were prepared at room temperature by the vibrating orifice technique using titanium alkoxide and silane coupling reagents as starting materials. Subsequently heating the microspheres at 400–450 °C resulted in increasing their refractive indices to $n_D=2.10$–2.25 with keeping good spherical shape. Rhodamine 6G-doped microspheres of $n_D=1.72$ were also prepared at room temperature and the lasing from them was performed by pumping by second-harmonic pulses of Q-switched Nd–yttritium–aluminum–garnet laser.
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It is essential for micro-optical devices to enhance an interaction between light and materials to accomplish their optical performances. Recently spherical particles of micrometer size have attracted a stimulated interest for its potential uses such as a light source of multiwavelengths, probes for near-field scanning optical microscopy,[1] a low-threshold laser,[2] etc., along with their high quality factor Q,[3] and ultrafast response time.[4] The Q values of whispering-gallery-mode (WGM) depend on the sphere's diameter and relative refractive index $n_r=(n_{\mathrm{sphere}}/n_{\mathrm{medium}})$.[2] Thus, high n_r is inevitable to accomplish the spherical optical cavity structure in micrometer-sized particles. Lasing from dye-doped droplets,[5] plastic particles,[6] and organic-inorganic hybrid particles[7] have been reported. We developed the vibrating orifice technique for fabricating dye-doped spherical particles of highly controlled shape and diameter.[7] The lasing from these particles and high photostability of incorporated dyes have been demonstrated.[8] Since the refractive indices for these spherical particles were 1.37 (ethanol droplet),[5] 1.49 [(poly)methylmethacrylate],[6] 1.50 (hybrid material),[7] 1.58 (polystylene),[9] pumping of these particles were carried out in an air to meet the requirement of high index differences at the interface. From a practical point of view, the microspheres should be coated with clad materials of lower refractive index than those of particles. Supposing that we use available low-index materials for cladding (e.g., solvent or plastics of $n_{\mathrm{medium}}=1.3$–1.4), $n_{\mathrm{sphere}}>2.0$ are needed to satisfy the high index difference of nearly $n_r \geqq 1.5$.

In this letter, we report on the fabrication of micrometer-sized spherical particles of high-index of $n_D=1.72$ by the vibrating orifice technique at room temperature and the achievement of those of $n_D>2.0$ by subsequent heating.

Hybrid microspheres were prepared from diphenyldimethoxysilane (DPhDMS), 3-glycidoxy-propyltrimethoxysilane (GPTMS), and titanium tetra-n-butoxide (TTBu) as starting materials. The DPhDMS and GPTMS were dissolved in tetrahydrofuran and hydrolyzed in aqueous HCl solution of $p\mathrm{H}=2$ at room temperature for 3 days. After the reaction, the TTBu dissolved in isopropanol was titrated into the solution, and H_2O diluted with isopropanol was added to complete the hydrolysis of TTBu at 3 °C. Then the solution was stirred for 2 days at room temperature for aging. The resultant solution was diluted with ethanol and used as the starting sol solution for preparing spherical particles by the vibrating orifice technique.[7] For lasing demonstration, rhodamine 6G-doped spherical particles were also prepared by the similar procedures. A cylindrical liquid jet passing through the orifice of 20 μm in diameter broke up into equal-sized droplets by mechanical vibration of 50 kHz. The droplets were carried by air flow through a pipe, and during the process, alcohol solvent of these droplets was evaporated. Subsequently, these droplets were trapped and solidified in ammonium water. Surfactant dodecyl benzene sodium sulfonate was added into the ammonia water to avoid coagulation of particles. For increasing the refractive index, the microspheres were heated with a heating rate of 10 °C/h up to a certain temperature of 200–450 °C and kept for 2 h in an electric resistance furnace under oxygen atmosphere.

The rhodamine 6G-doped microspheres were set on a glass plate under an optical microscope in an air and one of them was pumped by a second harmonic pulse of Q-switched Nd–yttritium–aluminum–garnet (YAG) laser to perform the lasing in order to assure the cavity structure of the microspheres. Pulses were: 532 nm wavelength, 10 Hz repetition rate and 5 ns duration time. The emitted light was measured by an image-intensified charge coupled device array with an electric gate. This gate was synchronized with the Nd–YAG laser through the pulse generator controlled by a computer. The refractive index of microspheres was measured by the following two techniques. (1) Immersion method in various index matching oil was used for the microspheres of $n_D=1.52$–1.72. (2) The optical interference spectroscopy was also used to measure the samples of $n_D=1.52$–2.25. Using the same sol for the preparation of the microsphere, the thin films of 0.1–0.5 μm in thickness were prepared on glass substrates by the dip-coating technique. Optical reflection of the film samples was measured by a conventional ultraviolet-visible spectrometer to estimate the refractive indices. Using the same sol samples (both of the particles and the films), the results of the two techniques were crosschecked each other in the index range of 1.52–1.72.

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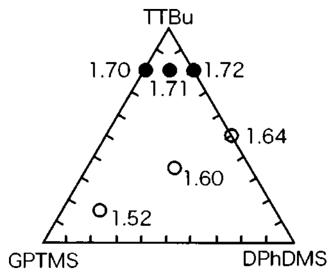

FIG. 1. Refractive indices in TTBu–DPhDMS–GPTMS system. The index increased with increasing the TTBu content, and n_D=1.72 was achieved at the composition 80TTBu–20DPhDMS. Closed circles show the compositions of high-index particles prepared successfully by the vibrating orifice technique.

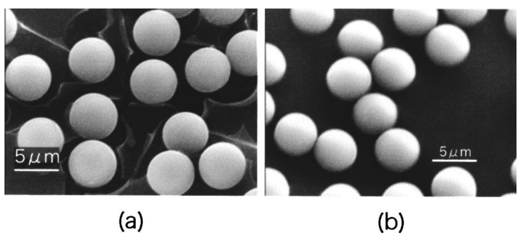

FIG. 2. SEM photographs of (a) 80TTBu–10DPhDMS–10GPTMS and (b) 80TTBu–20DPhDMS microspheres.

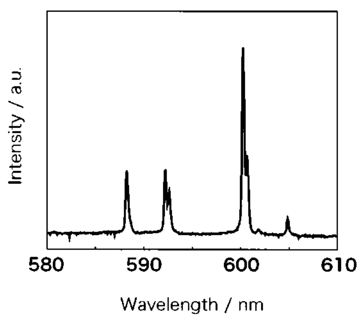

FIG. 3. Emission spectrum from R6G-doped 80TTBu–20DPhDMS microsphere pumped by second harmonic pulses of Q-swtched Nd:YAG laser.

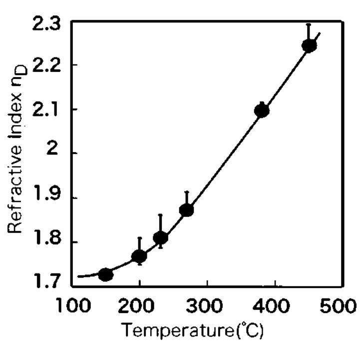

FIG. 4. Change of refractive index by heating. Initial composition of the sample is 80TTBu–20DPhDMS.

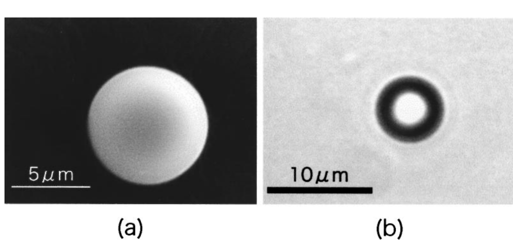

FIG. 5. Photographs of an 80TTBu–20DPhDMS microsphere after 400 °C heating. Observed by (a) SEM and (b) optical microscopy.

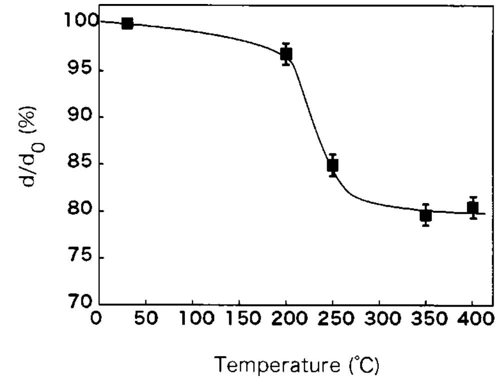

FIG. 6. Change in the diameter of microspheres by heating. Initial composition of the sample is 80TTBu–20DPhDMS. d_0 and d are the diameter of the initial sphere and the heat treated one, respectively.

Refractive indices measured by the optical interference spectroscopy for the samples prepared at room temperature in the TTBu–DPhDMS–GPTMS system are shown in Fig. 1. The refractive index increased with increasing the TTBu content, and n_D=1.72 was achieved in the composition 80TTBu–20DPhDMS. The microspheres of the compositions 80TTBu–20(DPhDMS–GPTMS), indicated as closed circles in the figure, were prepared and their refractive indices measured by the immersion method. There was no difference in index values, which was measured by two different techniques, within the experimental error.

Typical scanning electron microscopy (SEM) photographs of the microspheres (a) 80TTBu–10GPTMS–10DPhDMS and (b) 80TTBu–20DPhDMS are shown in Fig. 2. The microspheres have good spherical shape and smooth surface, and high optical transparency. The diameters of the particles were (a) 5.4 and (b) 5.2 μm and could be controlled within 0.1 μm. In Fig. 3, the laser emission spectrum from the rhodamine 6G-doped microspheres of refractive index 1.72 is shown. The peaks are attributed to the WGM resonances. The lasing performance from dye-doped spherical particles is the direct assurance of the spherical cavity for the encapsulation of light. Moreover, we confirmed that the diameter of microspheres agreed well with the results deduced from the theoretical formula for mode spacing.[3]

Figure 4 shows the refractive index change in the films of 80TTBu–20DPhDMS after heating at various temperatures. The photographs of an 80TTBu–20DPhDMS microsphere after heating at 400 °C are shown in Fig. 5. The refractive index increased dramatically above 200 °C, and n_D=2.10 and n_D=2.25 were achieved after heating at 400 and 450 °C, respectively. Such high indices after 400–450 °C heating were not surprising because the indices of TiO_2 (anataze) and TiO_2 (rutile) are known as high as n_D=2.493–2.554 and n_D=2.616–2.903.[10] The heating evolved solvents and fired the organic groups from hybrid matrix, and then resulted in $n_D>2.0$. From the DTA–TG measurement, the exothermic peak was observed at 250 °C along with the weight loss more than 10%, and slightly small loss continued with increasing temperature up to 450 °C. After heating at 450 °C, since no peak was observed in the x-ray diffraction pattern of the 80TTBu–20DPhDMS film, it still remained amorphous state. The change in diameter of the 80TTBu–20DPhDMS microspheres is shown in Fig. 6 as a function of temperature. Sizes of particles were estimated by SEM photograph. As shown in Fig. 6, the diameter decreased steeply at 250 °C, and 20% decrease was confirmed after heating at 450 °C. It is remarkable that the microspheres maintained their good shapes and high optical transparency as shown in Fig. 5, even after they were heated up to 400 °C. The fabrication of rare-earth-ion doped particles of high-index $n_D > 2.0$, and the laser emission from them is in progress.

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