EuO Nanocrystal Formation under ArF Laser Irradiation

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(Received April 14, 2003; CL-030315)

EuO (Europium(II) oxide) nanocrystals are prepared under irradiation by means of an ArF excimer laser. The formation of EuO nanocrystals with the clear lattice fringes was confirmed by TEM image. The crystal growth was monitored by the emission spectra.

EuO has attracted considerable interest because of some physical features such as optical, magnetic and electronic properties.[1] Recently, we successfully prepared EuO nanocrystals (average diameter: 3.4 nm) by photochemical reduction of $Eu(NO_3)_3$ in the presence of urea and methanol as solvent.[2] The EuO nanocrystals exhibited two unconventional photophysical properties; strong photoluminescence and dramatic increase in magnetization under UV irradiation at room temperature. The EuO nanocrystals would lead to novel plastic photo-isolators for optical fiber and future photomagnetic devices.[3–5]

UV light irradiation at the charge transfer band between an oxygen atom of methanol and the Eu(III) ion induces photoreduction to give EuO nanocrystals at room temperature.[1] The EuO prepared with a 500 W high-pressure mercury arc lamp, however, dose not give nanocrystals with clear lattice fringes. Formation of EuO with high crystallinity is desirable for optomagnetic application. Recently, molecular crystal growth using laser flash has been reported.[6] Crystal structure can be made by irradiating a supersaturated solution with laser light. Here, we attempted to prepare the EuO nanocrystals using ArF excimer laser pulse. In this paper, we report the formation of EuO nanocrystals with high crystallinity for the first time.

In a quartz vessel, $Eu(NO_3)_3$ (37.5 mM) and urea (112.5 mM) were dissolved in methanol (4 mL), and then the solution with mechanical stirrer was irradiated with a ArF excimer laser (193 nm, 130 mJ, 1 Hz) at 25 °C under N_2 atomsphere. After 1000 shots, white nanocrystals of EuO in methanol were obtained. The TEM image is shown in Figure 1a.[7] We successfully observed the clear lattice fringes of the EuO nanocrystals. The average size of the EuO nanocrystals was found to be 4.7 nm (Figure 1d). The electron diffraction patterns of the nanocrystals revealed responses at 2.95, 2.43, 1.78, and 1.51 dA, corresponding to (111), (200), (220) and (222) planes of NaCl-type EuO nanocrystals, in agreement with those of the previous report (Figure 1c). In contrast, the TEM images of EuO nanocrystal prepared with a 500 W high-pressure mercury arc lamp did not give clear lattice fringes (Figure 1b).[1] We suggest that the laser-irradiation is advantageous in nanocrystal growth. Garetz has reported that the laser-induced crystal growth depends on the electric-field-induced effect in saturated solution. The laser-induced electric field aids in organizing the existing prenucleating cluster, increasing the fast nucleation and growth of the nanocrystals.[6] However, we could not observe the fast formation of EuO nanocrystals when KrF excimer laser (248 nm) was employed. These results indicate that the direct laser excitation at the charge-transfer bands (ca. 195 nm) between the oxygen atom of methanol and the Eu(III) ion needs effective laser reduction of Eu(III) to give an Eu(II).[8]

The crystal growth using a laser system is also advantageous in observation of the growth process. We carried out the measurements of emission spectra for monitoring of the crystal growth process. The emission spectra in each laser shot were shown in Figure 2. The shorter emission area (Eu(II): 310–500 nm) and longer emission area (Eu(III): 500–650 nm) were excited at 290 and 395 nm, respectively. In Figure 2a, the emission intensities at 345 nm increased with small decreasing those of Eu(III) at 590 and 615 nm. After 20 laser shots, the emission

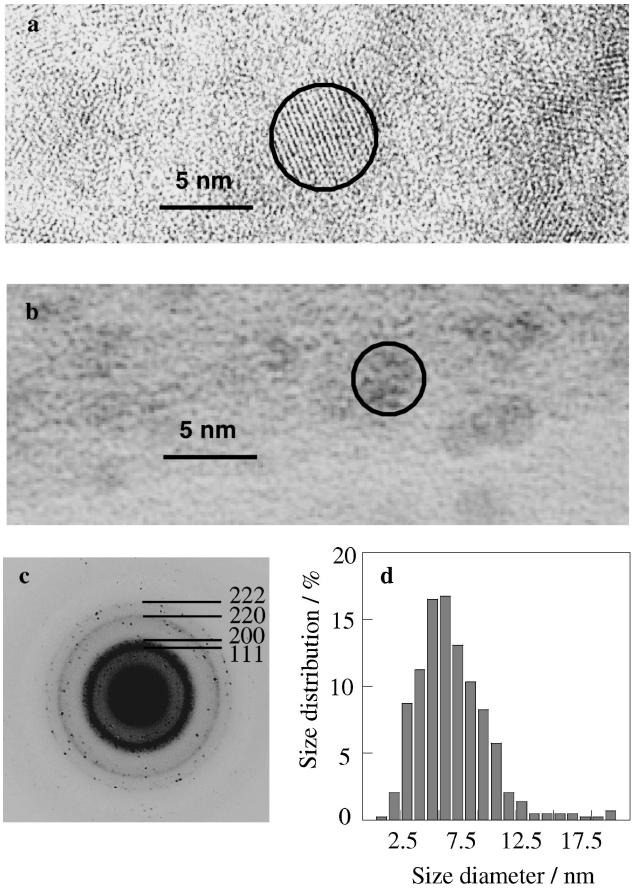

Figure 1. TEM image of the EuO nanocrystals. (a) Bright-field image of EuO nanocrystals prepared from ArF laser irradiation. (b) Bright-field image of EuO nanocrystals prepared from 500 W high-pressure mercury arc lamp. (c) Electron diffraction pattern of Figure 1a. (d) Size distribution of Figure 1a.

intensity decreased with shifting to longer wavelength (Figure 2b). We also observed the dramatic decrease of emission intensities at 590 and 615 nm. These observations indicate reduction of Eu(III) and the resulting formation of EuO nanocrystals.

The simple scheme of the EuO formation was shown as follows.

$$[\mathrm{Eu(III)\bullet CH_3OH}]_{CT} \xrightarrow{h\nu} \text{precursor Eu(II)} \xrightarrow[\text{crystal growth}]{OH^-} \text{EuO nanocrystals}$$

In this scheme, hydroxide ions come from by the reaction of nitrate ions with methanol radical.[3] Formation of Eu(II) ions is indispensable as a precursor of EuO nanocrystals. The precursor Eu(II) ions in solution would emit at 345 nm. The decrease of the precursor Eu(II) that start at around 20 laser shots might be due to nucleation and growth of EuO nanocrystals.[9]

On the other hand, the emission peak-top of EuO nanocrystals after 1000 laser shots was found at 377 nm. The peak-top wavelength of the EuO nanocrystals (4.7 nm) is longer than that of previously reported EuO (3.4 nm). These emission processes are originated in the electron transition between conduction band (5d orbitals of Eu(II)) and degeneracy level of 4f orbitals.[10] The energy level of conduction band in laser-induced EuO nanocrystals should be lower than that in previously reported EuO, because 4f orbitals are intrinsic and never affected by the morphology like crystal size.

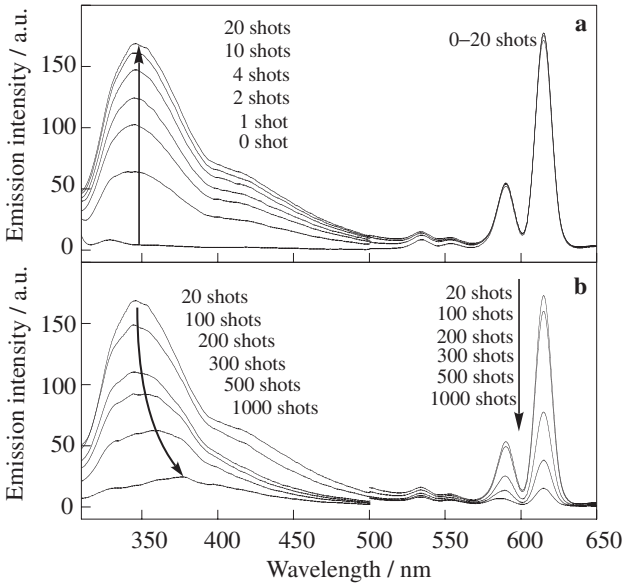

Figure 2. Emission spectra of the experimental solution in each laser shots. The shorter emission area (Eu(II): 310–500 nm) and longer emission area (Eu(III): 500–650 nm) were excited at 290 and 395 nm.

We succeeded in a preparation of EuO nanocrystals using ArF excimer laser. Laser-induced synthetic method is of advantage in preparation of EuO nanocrystals with clear lattice fringes, and the nucleation of the crystal growth can be successfully monitored by the laser-induced emission of the system.

This work was supported partly by NEDO (New Energy Industrial Technology Development Organization) and Grant-in-Aid for Scientific Research No. 13740397 from the ministry of Education, Science, Sports and Culture. Furthermore, A part of this work was supprted by "Nanotechnology Support Project" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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Published on the web (Advance View) July 14, 2003; DOI 10.1246/cl.2003.708