High Efficiency Near-IR Emission of Nd(III) Based on Low-Vibrational Environment in Cages of Nanosized Zeolites

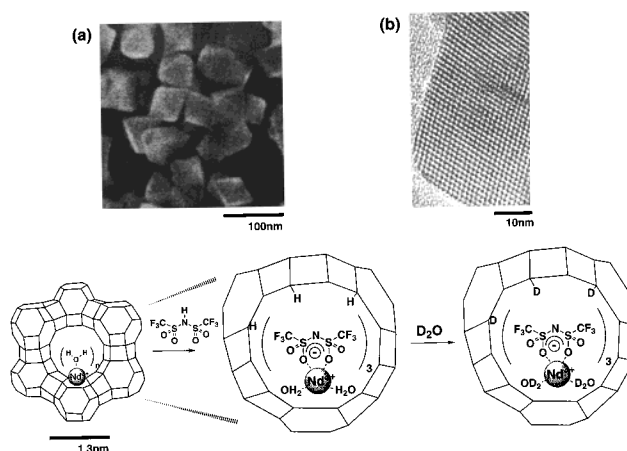Yuji Wada,[†] Tatsuya Okubo,[‡] Munenori Ryo,[†] Toru Nakazawa,[§] Yasuchika Hasegawa,[†] and Shozo Yanagida*,[†]

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This contribution describes observation of the strong emission from Nd^{3+} complex immobilized within the cages of a nanocrystalline Faujasite-type zeolite, which is dispersed in deuterated dimethylsulfoxide. Developing a strongly luminescent Nd^{3+} center in organic media has been an attractive target because of its applicability to organic liquid lasers, optical-fiber polymers, organic electroluminescent devices, and near-IR immunoassays. However, Nd^{3+} rarely emits in fluid media due to the fast relaxation of its excitation energy through nonradiative vibrational excitation[1] and the energy migration at collisions (cross relaxation).[2,3] Despite these limitations, very weak emission of Nd^{3+} has been observed from systems that exclude chemical bonds having low vibration quanta, for example, C–H and O–H,[3–5] and by separating the distance between the emitting centers by ligating with long perfluoroalkyl chains.[3] Recently, we observed the quantum efficiency (3×10^{-2}) of the Nd^{3+} emission using a complex with bis(perfluorooctylsulfonyl)aminate as ligand in acetone containing C–H bands.[5]

On the other hand, zeolites possessing pore structures as a host of photochemically or optically active guest have attracted scientists' interests for constructing novel materials designed at nanosized levels.[6] Luminescence of rare earth cation-exchanged zeolites has been investigated as luminescent materials and as a probe to obtain information on the structure and the environment inside the cages in which the cations are located.[7–9] A series of

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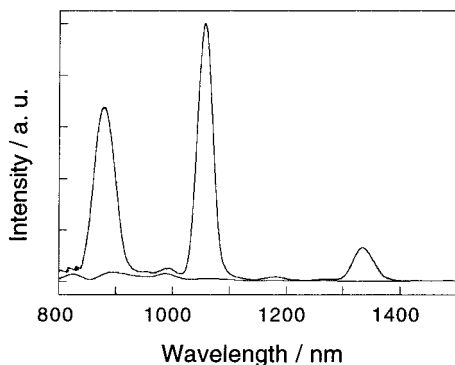
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Figure 1. FE-SEM (a) and TEM (b) views of the nanosized zeolite prepared. The scheme displayed below the photos shows the conceptual process of the ship-in-bottle synthesis and the treatment with D_2O.

zeolites should be one of the most suitable host materials for the efficient near-IR emission of rare earth cations, because their wall consists of Si–O–Al and Si–O–Si framework with low vibration quanta and their pores can be used for separately locating the cations. However, there had been no successful reports on it, probably because of the existence of hydroxyl groups in cages, causing excitation energy relaxation through vibrational excitation as pointed out for the emission of Eu^{3+}-exchanged zeolites.[8]

Here we have succeeded in drastically enhancing the near-IR emission of Nd^{3+} by ligating it with bis(perfluoromethylsulfonyl)aminate in cages of a nanocrystalline, large-pore zeolite (Faujasite type). The nanosized zeolite powder containing the Nd^{3+} complex is stably dispersed in dimethylsulfoxide-d_6 (DMSO-d_6), constituting a transparent dispersion, by which we have achieved the highest quantum efficiency in its emission in organic media.

Synthesis of nanosized Faujasite was carried out according to a recipe reported in the literature[10] using a clear solution containing a composition of 3.4 SiO_2: 1.7 Al_2O_3: 2.3 $(TMA)_2O$: 0.1 NaCl: 300 H_2O. FE-SEM and TEM views are shown in Figure 1. The shape of each particle was an octahedron (Figure 1a), and the fine structure of the zeolite cage was clearly observed (Figure 1b). The particle sizes of the crystallites were 50–80 nm. This sample is denoted as n-FAU, hereafter, although it contained A-type (LTA) by 10%. LTA has pores too small to allow the access of the ligand molecule employed in the present work.

The n-FAU was placed in an aqueous solution containing an excess $NdCl_3$·$6H_2O$. The solution was then heated at 373 K for 24 h. The Nd-exchanged n-FAU was washed with deionized water. After centrifugation and re-dispersion by two times, the Nd-exchanged n-FAU powder was dried in air at 358 K. Chemical compositions of Nd-exchanged zeolite were determined by ICP-MS: Si/Al = 2.8, the exchange degree of Na^+ by Nd^{3+} = 85–95%.

As displayed in Figure 1, the resulting Nd-exchanged n-FAU was degassed at 423 K for 1 h and was kept in contact with vapor of bis(perfluoromethylsulfonyl)amine (PMS-H) at 373 K for 1 h (denoted as Nd(PMS)–n-FAU, hereafter).[11] Furthermore, it was exposed to D_2O vapor for 10 min at 423 K three times to convert –OH with high vibrational frequency ($\sim$3600 cm^{-1}) to –OD with low vibrational frequency ($\sim$2600 cm^{-1}) and degassed at the same temperature for 30 min, since high vibrational –OH

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Figure 2. Emission spectra of Nd(PMS)−n-FAU (above) and Nd-exchanged n-FAU treated with D_2O alone (below) measured by a reflectance method of their powders under vacuum. The samples were excited at 585 nm.

Figure 3. Emission spectrum of the dispersion of Nd(PMS)−n-FAU in DMSO-d_6. The sample was excited at 585 nm. The inset is emission decay.

groups in remaining water molecules coordinated to Nd^{3+} and on the wall of the cages should induce rapid de-excitation of the excited state of Nd^{3+}. The differential scanning calorimetry analysis showed an endothermic peak above the decomposition temperature of the neodymium with PMS, supporting the formation of the complex inside the cages.[12] The number of the complexes was estimated to be 1−2 per one supercage from the elemental analysis of Nd(PMS)−n-FAU, when it was assumed that the three ligands were coordinated to Nd^{3+}.

Figure 2 shows the emission spectra of Nd(PMS)−n-FAU as a powder excited at 585 nm ($^4I_{9/2} \rightarrow {}^2G_{7/2}$) under vacuum.[13] The three peaks in the emission spectrum were attributed to the f−f transitions; $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$, and $^4F_{3/2} \rightarrow {}^4I_{13/2}$. In contrast to the poor emission of Nd-exchanged n-FAU treated only with D_2O, Nd(PMS)−n-FAU showed remarkably strong emission. The observation has led us to a conclusion that ligation of Nd^{3+} with PMS in the cages of n-FAU enhances the emission. PMS should play important roles (1) to replace D_2O coordinating to Nd^{3+} and (2) to retard the vibrational excitation of −OD groups existing on the wall of the cages. The negative effect of coordinating H_2O molecules and hydroxyl groups on the emission of Eu^{3+} in zeolites was already reported[8,9] and should be more serious for that of Nd^{3+} than Eu^{3+} because of the matching of the emitting level at low vibration quanta.[3]

To characterize Nd(PMS)−n-FAU powder, the powder was dispersed in DMSO-d_6. The transparent dispersion showed the seven peaks in absorption spectrum, which were attributed to the typical transitions of Nd^{3+}. Using the peak intensity at 526 nm ($^4I_{9/2} \rightarrow {}^2G_{9/2}$) as a standard because of its insensitiveness to the environment, the apparent concentration of Nd^{3+} cations was determined to be 8.5 mM in the DMSO-d_6 dispersion.

The transparent dispersion of Nd(PMS)-n-FAU showed remarkable emission when excited at 585 nm (Figure 3),[14] while the dispersion of Nd-exchanged n-FAU without treatment with
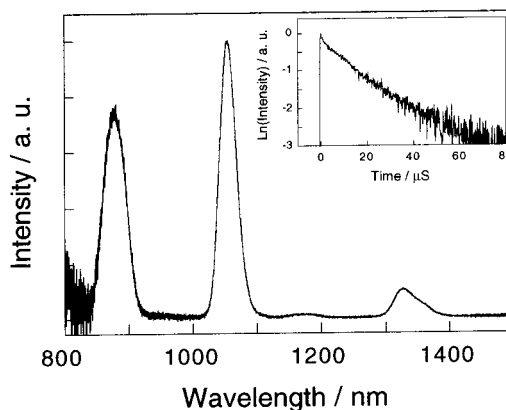
PMS gave no detectable emission.[15] The quantum yield for the emission of Nd(PMS)−n-FAU was determined to be $(9.5 \pm 1.0) \times 10^{-2}$ under excitation at 585 nm.[16,17] This is the highest value ever observed for Nd^{3+} emission in organic media. The time decay of the emission seemed to consist of the two components at least, but was fitted by one-main-component exponential. The lifetime was determined as 22 μs (Figure 3, inset).[18] The quantum efficiency was much larger than that of Nd(PMS)$_3$ in DMSO-d_6 (3.3×10^{-2}). Interestingly, dynamic light scattering (DLS) analysis of the Nd(PMS)−n-FAU dispersion revealed that the Nd-(PMS)−n-FAU particles aggregate to some extent, giving the particle size distribution ranging between 100 and 175 nm. This fact indicates that 2−3 particles of Nd(PMS)−n-FAU aggregate in DMSO-d_6 without undergoing cross relaxation of the excited states of Nd^{3+}.

The success in obtaining the strong emission in this work should be attributed to suppression of the relaxation of the excitation energy of Nd^{3+} through the vibrational excitation by the low-vibrational zeolite cage wall and the energy migration at collisions by locating Nd^{3+} separately in the cages. Furthermore, ligation of the emitting Nd^{3+} center with PMS in the zeolite cages should play an important role in retarding the vibration excitation caused by −OD groups surrounding the emitting centers. Detailed work is in progress for obtaining structural information for Nd-(PMS)−n-FAU and for extending this system to other rare earth cations emitting in the near-IR region.

(11) After the Nd-exchanged nano-FAU was degassed at 423 K, Nd^{3+} cation should be still coordinated by water molecules. The authors have already synthesized the complex, Nd(III)(PMS)$_3$ and isolated it. This complex was found to be coordinated by three PMS ligands and two water molecules. The similar coordination of PMS and water molecules should occur to Nd^{3+} cation in the pore structure. However, the real structure of the complex formed in the zeolite pore is still in veil.

(12) The preliminary investigation of Nd(PMS)−n-FAU and Nd(PMS)−FAU of the conventional size (about 1−10 mm) with neutron diffraction analysis, X-ray diffraction analysis, and solid NMR suggested the formation of the complex inside the cages. The detailed analysis of the structure is in progress.

(13) A photoelectron multiplier and a Ge detector were used as a detector for the region of 400−1000 nm and 800−1500 nm, respectively.

(14) Nd(PMS)−nano-FAU was prepared under vacuum without exposure to air as described in the text. The mixture of Nd(PMS)−nano-FAU and DMSO-d_6 was degassed by freeze−pump thaw cycles and sealed in a quartz cell (optical length: 10 mm) for optical measurements. The dispersion was ultrasonicated and kept still overnight. The transparent supernatant of the dispersion was supplied for the measurements of the absorption spectra.

(15) The amount of dispersed Nd-exchanged n-FAU without treatment with PMS in DMSO-d_6 could be estimated only roughly as 20 times lower than that of Nd(PMS)−n-FAU from very weak absorption of Nd^{3+}. Therefore, the present success in observing the emission of the dispersion of Nd(PMS)−n-FAU should be attributed to both (1) intrinsic enhancement in the emission and (2) enhancement in the dispersibility.

(16) Quantum yield was determined by the standard procedure using an integral sphere (diameter 9 cm) and a cell of optical path length, 1 mm.

(17) There is no doubt in that the strong emission is attributed to that of the complex in the cages of n-FAU, not to the complex which might be dissolved from the cages into the DMSO-d_6 solution, because the solution of the complex gave the lower quantum efficiency (3.3×10^{-2}) than that obtained for the dispersion solution of Nd(PMS)−nano-FAU.

(18) The measurements were performed by using Q switch Nd:YAG laser, and Si photodiode (time response < 1ns). Nanosecond pulse for sample excitation ($\lambda = 532$ nm, power 300 mW, diameter = 56 mm) was obtained by second harmonic generation with KDP crystal. Emission from the sample was filtered by low-cut optical filters placed in front of the detector. The response of the photodiode was monitored by a digital oscilloscope synchronized to single-pulse excitation.