The effect of the size of raw Gd(OH)₃ precipitation on the crystal structure and PL properties of Gd₂O₃:Eu

Haiyong Chen a,b,*, Jiahua Zhang a, Xiaojun Wang a, Shiyong Gao b, Mingzhe Zhang b, Yanmei Ma b, Quanqing Dai b, Dongmei Li b, Shihai Kan b, Guangtian Zou b

a Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics, and Physics, Chinese Academy of Sciences, Changchun 130033, PR China
b State Key Laboratory of Super-Hard Materials, Jilin University, Changchun 130012, PR China

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Abstract

Our experiments show that cetyltrimethylammonium bromide (CTAB) has an obvious effect on the particle size of the precipitation of Gd(OH)₃. Without CTAB, the particle size of the Gd(OH)₃ precipitation is about 50 nm, whereas with CTAB, the particle size is less than 5 nm. We propose a mechanism where CTAB micelles work as a catalyst for the nucleation process and result in the precipitation of 5 nm particles. These small particles, after heat treatment at 1073 K, did not result in small Gd₂O₃ nanoparticles of the same size, but instead, forming crystals of 30–80 nm size in both cubic and monoclinic phases. When monitoring the photoluminescence (PL) peak at 610 nm, we found that the charge transfer state (CTS) absorption amplitude of Eu–O is reduced in the mixed structures. We speculate that the mixed structures modify the surface properties of the Gd₂O₃:Eu nanoparticles, leading to the reduction of Eu–O CTS absorption.

The subject of nanosize particles has been extensively studied and becoming a research focus due to its fundamental and technological importance [1,2]. This is particularly true in the case of luminescent materials because of their quantum confinement effect which leads to novel optoelectronic properties. For example, emission lifetime, luminescence quantum efficiency, and concentration quenching have been found to depend strongly on the particle size in the nanometer range [3–6]. These luminescent materials in nanosize crystal form, such as rare earth (RE) oxides, have been fabricated by sol-lyophilization [7], combustion [8], and polyol [9] methods. To control the size of raw precipitation particles, two common methods have been used, i.e., (1) homo-precipitations [10] which can evenly and continuously provide reactants, and (2) water/oil microemulsion method [11] which has a lot of homo-size microreactors limiting the growth of the precipitation. Here, we introduce a method in which small Gd(OH)₃ precipitation particles (several nm) can be obtained by simply adding CTAB in the reactants. We propose a mechanism for particle’s nucleation and growth which may account for this phenomenon.

Our experimental procedures were as follows: We prepared the Gd(NO₃)₃ solution by mixing 0.3625 g Gd₂O₃ (99.999%) and 0.0035 g Eu₂O₃ (99.999%) with 50 ml distilled water and adding appropriate HNO₃ to the mixture with proper stirring to form a clear solution. The solution was diluted to 100 ml by adding more distilled water. Two of such solutions were prepared, one marked as A (without CTAB), and the other one, with 3.3 g CTAB subsequently added in, marked as B (with CTAB). An additional 10 ml NaOH solution (0.006 M) was added into A and B solution. After being stirred for about 30 min, white precipitations, i.e., Gd(OH)₃, in A and B were separated out by centrifugation. They were washed by hot distilled water and were separated out by centrifugation again. The precipitations were then dried naturally.

As-prepared products were characterized by transmission electron microscope (TEM) (HITACHI TEM H-8100IV at 200 KV). Fig. 1a shows a high magnification TEM image of an as-prepared product from solution A (without CTAB). The size of the Gd(OH)₃ nanoparticles is about 50 nm. Fig. 1b shows a...
We propose the following scenario for the nucleation and growth process. At the beginning of the reaction, a large amount of Gd(OH)₃ monomers were formed. When the Gd(OH)₃ monomers concentration in the solution reached a critical value \( C_a \), they started to adhere to the surfaces of CTAB micelles which have a ball-like shape and a size about 10–100 nm. There were numerous CTAB micelles in the solution. As their surfaces started to take up the Gd(OH)₃ monomers, the concentration of Gd(OH)₃ monomers in the solution would be kept constant at the critical value \( C_a \). This is disadvantageous for new nuclei to form spontaneously. But the high population of Gd(OH)₃ monomers on the CTAB micelle surface created an environment where small nuclei were easily formed. As shown in Fig. 2, a nucleus could be formed from aggregates of Gd(OH)₃ monomers adsorbed on the surface of CTAB micelle. Since there were a large number of CTAB micelles, there would be numerous small Gd(OH)₃ nuclei as well. In addition, the above nucleation process would be repeated until most of the Gd(OH)₃ monomers were consumed and the concentration of Gd(OH)₃ monomers started to decrease below \( C_a \). At this condition, Gd(OH)₃ monomers would escape from the surface of CTAB micelle and grow evenly on Gd(OH)₃ nuclei. Just like Gd(OH)₃ monomers being absorbed on the surface of CTAB micelle, Gd(OH)₃ nuclei will absorb the CTAB molecules. This will slow the growth of the Gd(OH)₃ nuclei and lead more Gd(OH)₃ monomers to form new nuclei. As a result, the whole nucleation and growth process was largely dominated by the nucleation process, and leading to the formation of very small particles with a size less than 5 nm. During the whole process, the CTAB micelles acted like a catalyst, which could increase the speed of nucleation and decrease the rate of crystal growth.

The sample with and without CTAB were both heated to 1073 K and lasted for two hours. TEM, X-ray diffraction (XRD) and photoluminescence (PL) were used to characterize the samples. Figs. 1c and 1d are the images of the Gd₂O₃ from the precipitation without and with CTAB, respectively. They are all quasi-spherical nanoparticles with size of 30–80 nm. Thus, the small nanoparticles of size less than 5 nm from solution B with CTAB, after the heat treatment, now became particles of size 30–80 nm. Fig. 3 is a XRD spectrum (Mo Kα radial 0.707 Å) of Gd₂O₃ from the precipitation without and with CTAB. For the product from the precipitation without CTAB (curve a), the diffraction peaks correspond to a cubic structure with lattice constant of 10.81 Å (#760155), whereas for the one from the precipitation with CTAB (curve b), they correspond to a mixture of cubic (the same crystal structure as that in curve a) and...
monoclinic (with lattice constants: $a = 14.09 \, \text{Å}$, $b = 3.576 \, \text{Å}$, $c = 8.769 \, \text{Å}$, beta = 100.08 (421465)) structures. Fig. 4 is the excitation spectrum for 610 nm (Eu$^{3+}$: $5D_0 - 7F_2$) where (1) is from the cubic host’s absorption (232 nm); (2) is from the charge transfer state (CTS) absorption of Eu–O (256 nm); and (3) is from the absorption of Gd$^{3+}$ ions. For Gd$_2$O$_3$:Eu from the precipitation without CTAB (curve a), the cubic host’s absorption is lower than the CTS absorption of Eu–O, and this agrees with the conclusion that the CTS absorption of Eu–O is preponderant in nanoparticles. For Gd$_2$O$_3$:Eu from the precipitation with CTAB (curve b), the host’s absorption is almost equal to the absorption of Eu–O CTS. The CTS absorption of Eu–O is clearly reduced. The XRD spectrum indicates that the product is a mixture of cubic and monoclinic structures. If the mixture was composed of individually isolated cubic and monoclinic crystals it would be difficult to explain the reduction of Eu–O CTS absorption. We therefore speculate that the monoclinic structure is formed right on the surfaces of cubic nanoparticle similar to the twin crystals. This will remove part of the surfaces of both cubic and monoclinic phases where the Eu–O CTS absorption is most efficient, leading to the reduction of the CTS absorption. Research is currently being conducted to verify this hypothesis.

Fig. 5 is the emission spectrum of the two products from solutions A and B. For Gd$_2$O$_3$:Eu from the precipitation without CTAB (curve a), under the excitation of 256 nm, it shows a characteristic 4f–4f emission of Eu$^{3+}$ in cubic Gd$_2$O$_3$. The strong peak at 610 nm belongs to the $5D_0 \rightarrow 7F_2$ transition of Eu$^{3+}$ at the C$_2$ site. For Gd$_2$O$_3$:Eu from the precipitation with CTAB (curve b), under the same excitation (256 nm), there are two strong peaks at 613 and 623 nm besides the strong peak at 610 nm. These two peaks (613 and 623 nm) correspond to the emission of Eu$^{3+}$ in monoclinic Gd$_2$O$_3$. When the product from the precipitation with CTAB was excited by 232 nm (curve c), only one strong peak at 610 nm can be seen. This can be explained as follows: cubic and monoclinic Gd$_2$O$_3$:Eu coexist in the product from solution B. Under the excitation of 256 nm, according to the CTS absorption of Eu–O, Eu$^{3+}$ in cubic and monoclinic Gd$_2$O$_3$ are both excited, and a mixed emission spectrum containing characteristic emission of Eu$^{3+}$ in cubic (610 nm) and monoclinic (613 and 623 nm) Gd$_2$O$_3$ is obtained. When the same product was excited by 232 nm, according to the cubic host’s absorption, cubic Gd$_2$O$_3$ host will be excited and monoclinic Gd$_2$O$_3$ host will be ineffective, leading to the appearance of mainly the characteristic emission of Eu$^{3+}$ in cubic Gd$_2$O$_3$.

In conclusion, CTAB has an obvious effect on the particle size of Gd(OH)$_3$ precipitation. We propose a mechanism where CTAB micelles work as a catalyst for the nucleation process and result in the precipitation of less than 5 nm particles. These small particles, after heat treatment at 1073 K, did not result in small Gd$_2$O$_3$ nanoparticles of the same size, but instead, forming crystals of 30–80 nm size in both cubic and monoclinic phases. When monitoring the photoluminescence (PL) peak at 610 nm of the mixed structures, we found that the charge transfer state (CTS) absorption amplitude of Eu–O is reduced. We suggest that such reduction is due to the formation of nanosize...
monoclinic and cubic bicrystals removing part of the surfaces of both cubic and monoclinic crystals where the Eu–O CTS is most efficient.

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References


