Photo-induced valence-number changes and defects in Eu$_2$O$_3$ fine particle films

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Abstract. Different Eu$_2$O$_3$ fine particle films were prepared by the laser ablation method. Under a continuous wave (CW) 325 nm laser light irradiation, their photoluminescence spectra are measured both in vacuum and in O$_2$ gas atmosphere. All the specimens display reversible spectral change and clear luminescence colour changes (red luminescence ↔ white luminescence) for changing specimen atmosphere. Moreover, the white-luminescent state is stored for more than several years at room temperature in air under room light. The obtained results suggest that the spectral changes arise from both the photo-induced valence (Eu$^{3+}$ → Eu$^{2+}$) change of europium ions and the photo-generated oxygen defect structure at Eu$_2$O$_3$ particle surfaces in vacuum, which is expressed by the following reaction, Eu$_2$O$_3$ in lattice + CW 325 nm photon → (Eu$^{2+}$-oxygen vacancy-Eu$^{2+}$) complex + $\frac{1}{2}$O$_2$. The obtained results are discussed in the light of the exciton theory.

1. Introduction

Europium sesquioxide Eu$_2$O$_3$ exhibits five crystal phases designated by X, H, A, B and C at normal pressure in the order of decreasing temperature [1]. Cubic X form transforms into hexagonal H form at about 2553 K, to hexagonal A form at about 2413 K, to monoclinic B form at about 2313 K, to cubic C form at about 1373 K. The B form contains six formulae per unit cell of which space group is C2/m. The body-centered cubic C form contains 32 europium ions and 48 oxygen ions per unit cell of which space group is Ia3. Several years ago, we found reversible photo-induced spectral change in Eu$_2$O$_3$ at room temperature [2, 3]. When Eu$_2$O$_3$ powder compacts, films and particles are irradiated with a 325 nm laser light in vacuum, their photoluminescence (PL) spectra change from a red sharp-line structure to a white broad band, which can be clearly seen with the naked eye. After removing the UV laser light, the white PL state is stored for more than several years at room temperature under room light, regardless of any changes of atmosphere. By irradiating with the same UV laser light at room temperature under oxygen gas atmosphere, the original red PL state re-appears. Such reversible phenomenon may well yield materials for white-light-emitting devices and erasable optical storage. Especially, Eu$_2$O$_3$ fine particles are thought to have potential application for high-density luminescent device and they lead to important modifications of some of the bulk properties. For example, particle-size reduction may give rise to the confinement of Eu$^{3+}$ excitation and long-wavelength phonon modes

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in the particle [4, 5]. In the present paper, we report upon the structural and optical studies on Eu₂O₃ fine particle films and we arrive at a view on the photo-induced spectral change.

2. Specimen preparation and characterization
The laser ablation target was prepared by compressing Eu₂O₃ powder 99.98 % in purity under a pressure of 0.2 GPa for 1 h at room temperature and then by sintering at 1273 K for 24 h in air. Eu₂O₃ fine particle production and deposition were carried out in oxygen atmosphere of different pressures with a pulsed Nd³⁺-YAG laser light (wavelength λ=355 nm, pulse width=3 ns, repetition =10 Hz). The temperature of the silica glass substrate was room temperature. After deposition, the half of the as-deposited film specimens was annealed at 873 K in air for 24 h. The conditions of the specimen preparation are listed in table 1.

| Specimen | Laser ablation atmosphere | Comments |
|----------|--------------------------|----------|
| #1α      | 0.00                     | as deposited |
| #1β      | 0.00                     | annealed at 873 K in air |
| #2α      | 1.26                     | as deposited |
| #2β      | 1.26                     | annealed at 873 K in air |
| #3α      | 2.54                     | as deposited |
| #3β      | 2.54                     | annealed at 873 K in air |
| #4α      | 5.10                     | as deposited |
| #4β      | 5.10                     | annealed at 873 K in air |

Table 1. Summary of Eu₂O₃ films investigated.

As standard specimens, the B-form and C-form specimens were also prepared by sintering Eu₂O₃ powder compacts at 1823 K and 1273 K in air, respectively. The films were characterized by the x-ray diffraction (XRD) analysis with Cu Ka₁ radiation at 300 K. Distribution maps of europium and oxygen atoms in the films were obtained by using a scanning electron microscope (SEM) with an energy dispersive x-ray (EDX) fluorescence spectrophotometer (Shimadzu SSX-550). Figures 1(a), (b), (c) and (d) show the room-temperature XRD patterns of Eu₂O₃ specimens listed in table 1. Gray bold and black solid curves correspond to as-deposited film and annealed one, respectively. The XRD lines of the B-form and C-form Eu₂O₃ crystals [6] are given as histograms in figures 1(e) and (f), respectively. As seen in these figures, the as-deposited films display halo XRD pattern. The halo XRD pattern is reproduced by rescaling and broadening these B-form- and C-form XRD lines and then by superposing them. This suggests that the as-deposited films consist of very small crystallites or that the as-deposited films are amorphous. As-deposited films were fully transformed to crystalline Eu₂O₃ ones by heating at 873 K in air for 24 h. The crystalline Eu₂O₃ films are mixtures of a lot of C-form crystallites and few B forms. The EDX fluorescence map of europium atoms coincides well with that of oxygen atoms. Both the XRD patterns and the EDX fluorescence maps indicate that the produced films are chemically uniform Eu₂O₃. The film morphology was analyzed by the SEM and an optical microscope with a charge-coupled device camera system. As typical results, the SEM images of the as-deposited Eu₂O₃ film (#4α) and annealed film (#4β) are shown in figures 2(a) and (b), respectively. The uniform particle layer consists of particles smaller than several ten nanometers. Few particles with size larger than several hundred nanometers are seen. These particles may be explosively spouted out
from Eu$_2$O$_3$ target. As seen in figure 2(b), annealing gives rise to many crevices in the uniform layer and divide into large number of domains of several micronmeter sizes.

3. Results and discussion

Figures 3(a), (b), (c) and (d) show the PL spectra of the as-deposited and annealed Eu$_2$O$_3$ films. The measurements were carried out at room temperature in air under CW 325 nm photoexcitation. These specimens show the $^5$D$_0 \rightarrow ^7$F$_J$ (J=0, 1, 2, 3, 4) emissions at wavelengths between 570 and 720 nm [7]. With increasing oxygen pressure for the pulsed laser ablation, the $^5$D$_0 \rightarrow ^7$F$_0$ emission band becomes sharpen. At wavelengths shorter than 550 nm, these specimens show also broad band emission. The large PL intensity ratio of the broad band emission to the $^5$D$_0 \rightarrow ^7$F$_2$ one is observed for the $^5$D$_0 \rightarrow ^7$F$_0$ films which were fabricated in vacuum or extremely low oxygen pressure. Except for the #1 specimen fabricated under vacuum, annealing depresses considerably the PL intensity and makes the spectrum to resolve clearly into several emission bands. Since crystallites grows in size and transform to predominant C-form film by annealing, the selection rule may become rigorously effective to depress PL intensity. In figure 4, the room-temperature PL spectra of different Eu$_2$O$_3$ specimens are compared. Although the spectra are rescaled to each maximum intensity value, the C-form bulk specimen shows more intense emission than the B-form bulk one. These $^5$D$_0 \rightarrow ^7$F$_J$ emission lines appear at almost the same wavelength in every specimen, but the bandwidths in the as-deposited fine particle films are larger than those in annealed films. Such broadening may arise from both random arrangement of crystallites and finite size of crystallites at which surfaces the electronic excitations of Eu$^{3+}$ ions are scattered. It is also found that the PL spectra of the as-deposited and annealed fine particle films consist of the emission lines observed at both the B-form and C-form crystals. More high resolution measurements indicate that there are, at least, three distinct $^5$D$_0 \rightarrow ^7$F$_0$ emissions in the annealed films, while there is a very broad $^5$D$_0 \rightarrow ^7$F$_0$ emission in the as-deposited
films. In addition, the presence of the $^5D_0 \rightarrow ^7F_{0,3}$ emissions and the J-degeneracy of $^7F_{1,2}$ level suggest that the local site environments of these Eu$^{3+}$ ions may be described by different point groups, for example, $C_1$, $C_2$, $C_s$ and $C_{2v}$ [8]. The effects of surface reconstruction of constituent atoms and surface defects have been frequently pointed out for fine particle specimens.

As shown in figure 4(b), the B-form (monoclinic crystalline phase) with $C_s$ point group can exist at room temperature, as a metastable state. Moreover, Eu$_2$O$_3$ tends to be structurally degenerated at room temperature. Therefore, some local structural mixture of the B and C forms may occur in Eu$_2$O$_3$ fine particles, as seen in figure 1. This is compatible with the results obtained for Eu$^{3+}$ doped Y$_2$O$_3$ nanocrystals and Eu$_2$O$_3$ nanocrystals [9, 10].

The as-deposited and annealed films were irradiated with the 325 nm laser light in oxygen gas of $1.01 \times 10^5$ Pa or in air, the specimens showed red emission which can be seen with the naked eye. When the specimen chamber was evacuated, the PL colour changes from red to white. The intensity of the white emission increases with increasing irradiation time, which can be clearly seen with the naked eye. Oxygen gas of $1.01 \times 10^5$ Pa was again introduced in the chamber. The red PL colour appeared again, while the white-colour PL decreased in intensity with increasing irradiation time. Such PL colour change took place repeatedly with sufficient reproducibility, when the kind of atmosphere about specimen was exchanged. After removing the 325 nm laser light irradiation, each PL-state is stored for more than several years at room temperature under room light, regardless of any change of atmospheres ($1.01 \times 10^5$ Pa O$_2$ gas and air). The change to white PL occurs only as a result of the CW 325 nm laser light irradiation in vacuum, while we have not observed the colour change in any other reducing atmosphere; for example, Ar-H$_2$ mixture gas. The change to white PL can be observed at different temperatures from 7 K to room temperature. This indicates the observed spectral changes are purely electronic phenomena and are not phonon-assisted.

By irradiating with the same 325 nm laser light, we have then measured the PL spectral change of all of the films listed in table 1 at room temperature under both vacuum of $1.33 \times 10^{-4}$ Pa and
atmospheric O₂ gas, as a function of irradiation time. As typical results, the spectra obtained for the specimens (#1α and #1β) and the specimens (#3α and #3β) are shown figures 5 and 6, respectively. The spectral change for 30 minutes is shown in the figures at intervals of 2 minutes for each specimen. The arrows indicate progress of irradiation time. The kind of atmosphere is given in each figure.

The speed of the spectral change is increased with increasing laser fluence. The annealed films (#2β, #3β, #4β) show larger PL-intensity change than the as-deposited films (#2α, #3α, #4α). Specimen fabricated under higher oxygen pressure shows more structure-less white luminescence. We also studied the spectral transition in all the specimens for more than four hours. The results for the #3α- and #3β specimens are shown in the insets in figures 6(b) and (d), as typical results. In the insets, V and O indicate vacuum and oxygen atmosphere, respectively. The irradiation time was about 120 minutes for each atmosphere. It is noted that the white PL band increases in intensity with depressing 5D₀ → 7F₃ emissions. Then, the structure of the white band becomes pronounced.

4. Mechanism of the photo-induced spectral transition

The results given in the section 3 suggest that the reversible spectral transition observed in the Eu₂O₃ fine particle films arises from photo-activated oxidation and reduction near particle surfaces. Since the 325 nm laser light cannot dissociate directly free O₂ molecules as atmospheric gas, the photo-induced oxidation indicates that the photo-dissociation energy of O₂ is considerably decreased at the particle surfaces by the interactions between O₂ and Eu₂O₃. The photo-activated reduction of Eu₂O₃ fine particle is accompanied both by a valence-number change of europium ions (Eu³⁺ → Eu²⁺) and by oxygen defect formation. Broad band emission may be connected with Eu²⁺ ions and local structural changes arising from oxygen defects. We prepared also a EuO film by reducing Eu₂O₃ powder compact at 1273 K in vacuum. The EuO film shows a broad PL band centred at about 1.03 μm. This centre wavelength is far away from that of the observed white PL. Therefore, the photo-generated Eu²⁺ ions and oxygen defects do not form any structure based on EuO crystal, but they may form (Eu²⁺-
oxygen vacancy-Eu$^{2+}$) complex. Therefore, the observed photo-induced phenomena can be described
the following reaction:

$$\text{Eu}_2O_3 \text{ in lattice} \xrightleftharpoons{\text{CW 325 nm laser photon}} (\text{Eu}^{2+} - \text{oxygen vacancy} - \text{Eu}^{2+}) \text{ complex} + \frac{1}{2} O_2 \quad (1)$$

In the complex, the Eu$^{2+}$ ions act as hole traps (S_h), while the oxygen vacancy do as electron traps
(S_e). Toyozawa [11] proposed three types of symmetry-breaking instabilities of excitons in the phonon
field and when the electron and the hole have deformation potentials of opposite sign, the
decomposition into a pair of self-trapped particles occurs. In other word, the instability of an exciton
leads to lattice decomposition into an electron centre (an anion vacancy) S_e and a hole centre (an anion
interstitial) S_h, if the exciton is formed in the bulk. On surfaces, the hole centre is emitted from
the surface, thus leaving only the electron centre. Therefore, such exciton instability may result in oxygen
desorption at Eu$_2$O$_3$ surfaces. Unlike alkali halides, a single interband excitation never induces the
desorption of surface atom in semiconductors, since the binding energy of atoms is larger than the
energy gap. In such semiconductor case, only atom around crystal defect at the surfaces can be
released for single photoexcitation [12]. In the present Eu$_2$O$_3$ specimens, the seeds of the observed
photo-induced spectral change may be the defects which had already existed at particle surfaces. It has
been said that the desorption via such excited state occurs within $10^{-13}$ s after a laser pulse incidence.
However, considerable time is taken to complete the spectral change in Eu$_2$O$_3$, as seen in figures 5 and
6. This indicates that the photo-induced oxygen desorption probability is very low at the Eu$_2$O$_3$ particle
surfaces. The saturation tendency observed at further increasing irradiation time suggests that photo-
duced oxygen defect structure increases the lattice potential energy of the light irradiated surface. In
such case, equilibrium may be realized in a system composed of a matter (Eu$_2$O$_3$ particles) and a
radiation (laser photon) field.

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