

Study on the preparation of erbium ion doped oxide films by the sol-gel method and their fluorescence properties

Nobuko Maeda

Since heavy metal oxides of ZrO_2 and Ta_2O_5 have low phonon energies, they can enhance fluorescence of rare earth ions, such as the erbium ion (Er^{3+}), doped in a host matrix of such oxides. A sol-gel method makes it possible to disperse rare earth ions homogeneously in a host matrix, which is useful for strengthening their fluorescence. In the present study, Er^{3+} doped ZrO_2 , Ta_2O_5 , and Al_2O_3 - Ta_2O_5 films were prepared by a sol-gel method. Downconversion and upconversion fluorescence due to the 4f electronic transitions of Er^{3+} ions were measured by using a high-resolution Raman spectroscopic equipment, and then analyzed by the Judd-Ofelt theory.

In a $0.5\text{Er}_2\text{O}_3$ - 100ZrO_2 film, green (515-570 nm) and red (640-680 nm) fluorescence bands were split widely into two bands. This is probably caused by a large distribution of Er^{3+} sites in the film. Green upconversion fluorescence was weak in the tetragonal ZrO_2 , and strengthened with the phase transition from tetragonal to cubic. It is certainly because that excited state absorption (ESA), an excitation mechanism for upconversion fluorescence, decreased due to a more ionic Er-O bond in the tetragonal ZrO_2 , whereas ESA increased due to its more covalent bond in the cubic ZrO_2 .

In $1\text{Er}_2\text{O}_3$ - $100\text{Ta}_2\text{O}_5$ films, the effects of hydrolysis inhibitor added in a starting solution, 2-ethanolamine or 2-isopropylamine, on the film thickness, crystallization, and fluorescence properties were investigated. In amorphous films prepared from the former, downconversion fluorescence was not observed because organic residues remained in the films, while in such films prepared from the latter, the reverse occurred. On the other hand, downconversion fluorescence was observed more strongly in crystallized films prepared from the former than those from the latter, because the former makes the films more thick (*ca.* 1 μm). By crystallization, downconversion fluorescence increased, whereas upconversion fluorescence decreased. This is because that ESA decreased when the site symmetry for the Er^{3+} was increased and the Er-O bond became more ionic with crystallization.

In $1\text{Er}_2\text{O}_3$ - $x\text{Al}_2\text{O}_3$ -($100-x$) Ta_2O_5 films, increasing x value raised the crystallization temperature from 800 to 1000 $^\circ\text{C}$. In a crystallized film of $x = 4$ heat treated at 1000 $^\circ\text{C}$, downconversion fluorescence was enhanced because the solubility of the Er^{3+} increased with increasing the content of $\text{Ta}=\text{O}^\delta$. In an amorphous film of $x = 75$ heat treated at 800 $^\circ\text{C}$ upconversion fluorescence became strong because organic residues remained little and ESA was easy to occur in amorphous Ta_2O_5 . When Ta_2O_5 was crystallized, Er^{3+} infrared downconversion fluorescence around 1500 nm became very broaden (FWHM; 95 nm), which is expected for application to waveguide amplifiers.