PLuminescence properties of Er^{3+} doped SiO_2-ZrO_2 prepared using Er–Zr double alkoxide

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In optical telecommunications systems, Er^{3+} doped fiber amplifiers (EDFAs) have been used to recover the transmitted light signals near 1.5 μm but they still occupy a large space due to their structures and are not allowed for the integration of several functions on one chip. Recently, in order to reduce the size and cost of optical devices, Er^{3+} doped waveguide amplifiers (EDWAs) have been developed and fabricated by various techniques [1, 2]. However, the shorter path length of Er^{3+} doped waveguide amplifiers, compared with the long interaction lengths in the Er^{3+} doped fiber amplifiers, requires higher Er doping levels to obtain acceptable gain. Eventually these doping levels result in the clustering of Er^{3+} and the nonradiative or radiative upconversion effect, which degrade the performance of Er^{3+} doped waveguide amplifiers by decreasing the fluorescence emission and lifetime of Er^{3+} [3, 4].

In order to improve luminescence performance of Er^{3+} doped waveguide amplifiers reducing the clustering of Er^{3+}, the studies about materials used for the fabrication of these optical devices have been implemented actively. Er^{3+} doped silica based sol–gel materials co-doped with Al_2O_3, TiO_2, P_2O_5, and Ge_2O_3 were reported by a lot of researchers. It was found that those co-dopants play important role in enhancing the solubility of Er^{3+} ion in the glass matrix, improving its dispersion and reducing the possibility of ion–ion interaction in Er^{3+} ion-rich system [5].

In the present work, for the application to Er^{3+} doped waveguide amplifiers with high gain, incorporating a large amount of Er^{3+} without clustering of Er^{3+}, we prepared Er^{3+} doped SiO_2–ZrO_2 sol–gel materials using Er–Zr double alkoxide, which was synthesized to prevent the optically harmful Er^{3+} clustering by the selective coordination of Zr^{4+} around Er^{3+} ions. Luminescence properties of Er^{3+} doped SiO_2–ZrO_2 sol–gel materials prepared from different Er^{3+} concentrations were investigated from their fluorescence spectra and corresponding metastable level lifetimes.

The preparation of Er^{3+} doped SiO_2–ZrO_2 solution was carried out using tetraethylorthosilicate (TEOS) and Er–Zr isopropoxide as starting materials. First of all, Er–Zr isopropoxide was synthesized. All synthesis processes of Er–Zr isopropoxide were performed in an inert atmosphere to avoid hydrolysis of the double alkoxide. The synthesis reaction of Er–Zr isopropoxide was represented simply as follows: [6]

$$\mathrm{ErCl_3} + 3\mathrm{KZr(OPr^i)_5} \rightarrow \mathrm{Er\{Zr(OPr^i)_5\}_3} + 3\mathrm{KCl} + \mathrm{Pr^iOH/C_6H_6}$$

Prepared Er–Zr isopropoxide was added to partially hydrolyzed TEOS solution (the molar ratio of Er–Zr isopropoxide/TEOS=0.005, 0.01, 0.02, and 0.03) and sufficient amount of water was added for full hydrolysis of partially hydrolyzed TEOS. And then Er^{3+} doped SiO_2–ZrO_2 gel powders were obtained by pouring the solutions into Petridishes and drying them in the oven. After that, the samples were annealed at 700, 900 and 1100 °C for 1 hr, respectively, under O_2 atmosphere.

The thermogravimetric analysis was performed on the gel powder, with a heating rate of 5 °C/min up to 900 °C under oxygen flow. The phase of Er^{3+} doped SiO_2–ZrO_2 powders with different annealing temperatures was identified by XRD (Rigaku, D/MAX-2200V) with CuKα radiation. To determine the content of residual OH groups, FT-IR transmittance spectra were investigated using Bio-RAD Ltd., FTS-165 spectrometer. The fluorescence emission was measured using 980 nm laser diode as an excitation source, mechanically chopped at 80 Hz. The emission

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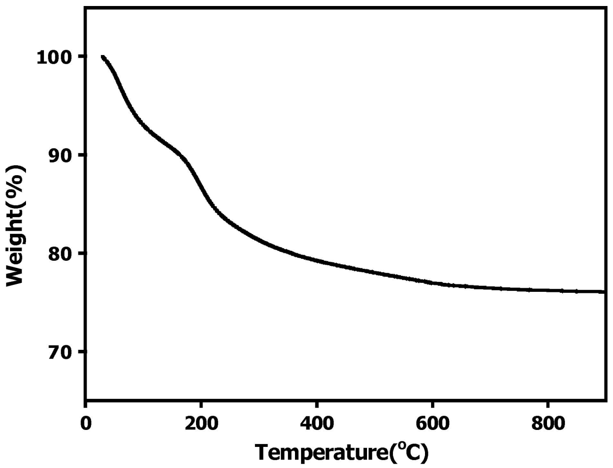

Figure 1 Thermogravimetric analysis data of Er^{3+} doped SiO_2–ZrO_2 gel powder.

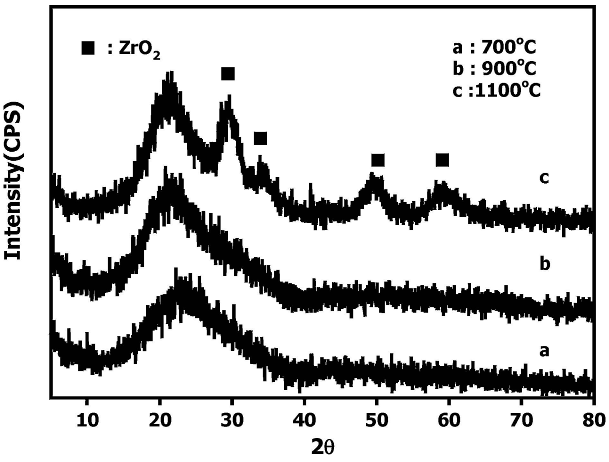

Figure 2 X-ray diffraction curves of Er^{3+} doped SiO_2–ZrO_2 powders annealed at different temperatures.

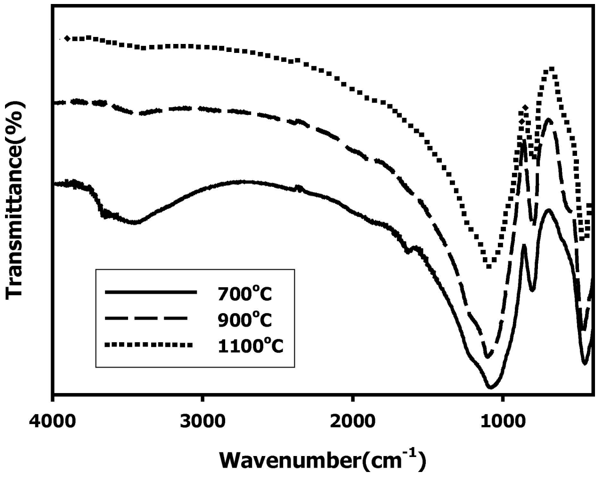

Figure 3 FT-IR spectra of Er^{3+} doped SiO_2–ZrO_2 powders annealed at different temperatures.

was projected onto the entrance slits of a monochromator and detected with a PMT detector. The photoluminescence spectra at 1.55 μm were recorded at the room temperature. The measurement of fluorescence lifetime for the emission at 1.55 μm was performed by monitoring the fluorescence decay. A digital oscilloscope was used to average the decay curves.

Fig. 1 shows the thermogravimetric analysis result of the gel powder obtained after drying Er^{3+} doped SiO_2–ZrO_2solution. According to this figure, there is a large change in weight between room temperature and 600 °C. The weight loss below 200 °C is believed to the evaporation of water and the thermal decomposition of remaining organic solvent. Between 200 and 600 °C, the weight loss is attributed to the removal of water formed by sol–gel condensation reaction and the combustion of organic compounds.

Fig. 2 shows the X-ray diffraction curves of Er^{3+} doped SiO_2–ZrO_2 powders annealed at different temperatures. The samples were prepared by annealing gel powders at 700, 900, and 1100 °C for 1 hr, respectively, under O_2 atmosphere. Er^{3+} doped SiO_2–ZrO_2 samples annealed below 900 °C have an amorphous structure but small diffraction peaks were observed on the curve of 1100 °C annealed sample, indicating the beginning of crystallization of ZrO_2. From these XRD profiles, it can be presumed that the crystallization of ZrO_2 will be more increased in Er^{3+} doped SiO_2–ZrO_2 annealed at higher than 1100 °C, which will make the distribution of Er^{3+} ions in SiO_2–ZrO_2 system not to be achieved homogenously.

Fig. 3 shows FT-IR transmittance spectra measured in order to investigate the amount of OH groups retained in Er^{3+} doped SiO_2-ZrO_2 powder. In the spectral range of 4000 $cm^{-1}\sim$ 3000 cm^{-1}, the broad band where OH group stretching vibrations are located was found. The amount of OH content was gradually reduced with an increment of the annealing temperature. After annealing at 1100 °C, the OH groups were completely removed within the sensitivity range of the FT-IR spectrometer. Therefore, for the effective removal of OH groups, which affect the luminescence quenching by non-radiative energy transfer process in sol–gel derived materials, high temperature annealing is generally required.

Fig. 4 shows the fluorescence spectra of Er^{3+} doped SiO_2–ZrO_2 powders with different Er concentrations. The samples were obtained by annealing them at 1100 °C, after drying the solutions prepared from various Er^{3+} concentrations. As can be seen in this figure, the emission peak was observed at 1.55 °C corresponding to the $^4I_{13/2} \rightarrow ^4 I_{15/2}$ transition of Er^{3+} ion. Emission band structure is very typical and is attributed to the stark splitting of Er^{3+} embedded in an amorphous structure. As Er^{3+} concentration increased, the fluorescence intensity of Er^{3+} doped SiO_2–ZrO_2 was enhanced without the concentration saturation. The full width at half maximum (FWHM) measured for 2 mol% Er^{3+} doped SiO_2–ZrO_2 is about 120 nm and this value is much broader than those observed in Er^{3+} doped silica-based systems prepared by the other method [7, 8]. The relatively wide FWHM implies that optical waveguide amplifiers or lasers made from this material can cover a wider wavelength range.

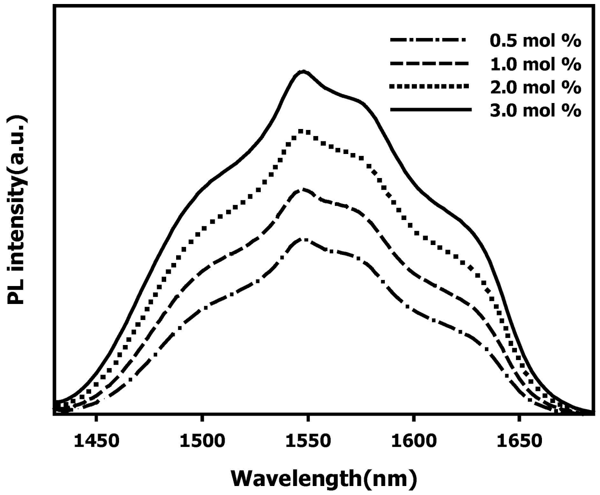

Figure 4 Fluorescence spectra of E^{3+} doped SiO_2–ZrO_2 powders annealed at 1100 °C with different Er^{3+} concentrations.

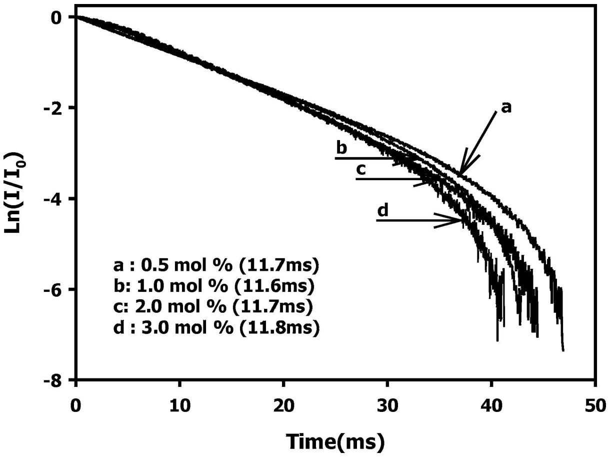

Figure 5 Fluorescence decay curves and lifetimes of Er^{3+} doped SiO_2–ZrO_2 powders.

Fig. 5 shows the fluorescence decay curves and lifetimes of Er^{3+} doped SiO_2–ZrO_2 powders containing same compositions as those of Fig. 4. When an isolated Er^{3+} ion is considered in the $^4I_{13/2}$ metastable state, the fluorescence decay is purely exponential, with a time constant τ, according to Einstein's law:

$$I(t) = I(0)\exp\left(\frac{-t}{\tau}\right)$$

where $I(t)$ is the intensity of the light emitted at 1.5 μm as a function of time [9]. In the present work, for Er^{3+} doped SiO_2–ZrO_2 with the Er^{3+} concentration of 0.5 mol% and 1.0 mol%, purely exponential fluorescence decay was observed. However, the fluorescence decay at the Er^{3+} concentration of 2.0 mol% and 3.0 mol% was no longer purely exponential. This indicates that there are the nonradiative energy exchange processes, dependent on the distances between the emitting Er^{3+} ion and neighboring Er^{3+} ions.

For Er^{3+} amount of 0.5, 1.0, 2.0, and 3.0 mol%, the lifetimes were found to be equal to 11.7, 11.6, 11.7, and 11.8 ms, respectively. The lifetime of the $^4I_{13/2}$ excited state is almost constant although the content of Er^{3+} increases. Additionally, the lifetime of Er^{3+} doped SiO_2–ZrO_2 prepared using Er–Zr double alkoxide is long in comparison with that of Er^{3+} doped silica-based systems prepared by other methods. It means that the introduction of Er–Zr double alkoxide in which the environmental structure around Er^{3+} ions is controlled orderly at precursor stage, makes Er^{3+} ions be distributed more homogeneously in the matrix. This fact suggests that optically active Er^{3+} doped silica-based sol–gel materials with higher Er^{3+} concentration can be prepared by the present method, without significant shorting of fluorescence decay lifetime.

In the summary, Er^{3+}doped SiO_2–ZrO_2 sol–gel materials were prepared using Er–Zr double alkoxide, in an attempt to incorporate a large amount of Er^{3+} in silica system without the clustering of Er^{3+}. Strong photoluminescence emission and long lifetime due to homogenous distribution of Er^{3+} ions were obtained in Er^{3+} doped SiO_2–ZrO_2 system. It was found that the optically active Er^{3+} doped silica-based sol–gel materials with relatively high Er^{3+} concentration were prepared by using Er–Zr double alkoxide, without significant shorting of fluorescence decay lifetime. Those results give the possibility that Er^{3+} doped SiO_2–ZrO_2 can be applied to Er^{3+} doped waveguide amplifiers with high gain.

Acknowledgments

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