Infrared-Laser Precipitation of $ZnAl_2O_4$ Nanocrystals doped with Eu^{3+} and Yb^{3+} and Efficient Upconversion Emission

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ABSTRACT

We present a novel and simple method to enable spatially selective $ZnAl_2O_4$ nanocrystal formation on the surface of oxide glass prepared by a melt-quenching technique. Optimized precipitation of glass-ceramics containing nanocrystals doped with Eu^{3+} and Yb^{3+} ions were performed by controlling CO_2 laser power and scan speed. Micro-x-ray diffraction and transmission electron microscopy revealed the mean nano-crystal size. We also report much enhanced down-shift visible emission due to nanocrystals and Yb^{3+} as efficient sensitizer for red upconversion emission from Eu^{3+} in glass ceramics under 980 nm excitation.

Keywords: CO_2 laser, Eu, Yb, $ZnAl_2O_4$, nanocrystal

1. INTRODUCTION

Over the past few decades, nanostructure materials have been the subject of much interest due to their remarkable physical properties such as decreased size, increased surface to volume ratio and novel morphologies. $ZnAl_2O_4$ is well-known spinel oxide as a wide band gap (3.8 eV) semiconductor [1]. It is of interest due to its properties such as high mechanical resistance, high thermal stability, low temperature sinter ability, low surface acidity, and good diffusion.

Glass-ceramics [2] bring advantages to the low phonon energy as well as their physical and chemical stability. It is expected that the rare-earth-ion doping in $ZnAl_2O_4$ crystals may improve the emission properties of doped ions. Among lanthanides, Eu^{3+} ion is widely investigated as it is one of the favorite rare earth for display devices due to its intense and sharp 4f–4f transition in orange/red regions [3]. Yb^{3+}ions are also widely used for infrared-to-visible upconversion applications [4]. They are fabricated using controlled heat treatments in an electric furnace, and nanocrystals are formed in the interior of glass. Recently, laser irradiation of glass has been reported as an alternative method for glass ceramic formation with an advantage of spatially selected structural modification and crystallization inside glass [5]. We applied the CO_2-laser-induced crystallization technique to a multi-component B_2O_3–Al_2O_3–ZnO-CaO-K_2O glass. In this work, we report the precipitation of spatially selective glass–ceramics containing $ZnAl_2O_4$ nanocrystals doped with Er^{3+} and Yb^{3+} ions.

2. EXPERIMENTAL

The nominal component of precursor glass (as-melted) used in this study was ZnO–H_3BO_3-Al_2O_3–K_2O-$CaCO_3$-Yb_2O_3–Er_2O_3. The raw materials used for preparation were fine grained powders from high purity commercial chemicals. Starting batches were thoroughly mixed and melted at 1350℃ for 1 h in a covered alumina crucible under normal atmosphere. Then, the melt was cast into an iron mold before being annealed at 530℃ for 10 h to release inner stress. Finally,the glass was cut and polished into the glass samples with thick-ness of 1 mm. For thermal treatment to induce $ZnAl_2O_4$ nanocrystals, we scanned a 1.4-1.8 W CO_2 laser beam with various speeds of 0.1-0.3 mm/s. The beam width ~200 μm diameter. We employed micro-X-ray diffraction (D/MAX RAPID-S) analysis for the irradiated and unirradiated regions to testify the nanocrystal formation. Furthermore, to clarify the size and crystallization, we performed transmission electron microscopy (TEM, Titan G2 60-300) analysis for the laser-treated surface. Photoluminescence and upconversion emission spectra for Eu^{3+} ions under 365 nm LED and 980 nm LD excitations were measured respectively for both unirradiated and irradiated glass area to clarify if the ions are doped inside the nanocrystals.

3. RESULTS AND DISCUSSION

Micro- x-ray diffraction patterns of glass and glass-ceramic were shown in Fig. 1. Glass does not show any apparent diffraction peaks. In contrast, the glass ceramics show several narrow and relatively intense peaks indicating the diffraction pattern of $ZnAl_2O_4$ crystalline phase. The broad humps are due to its amorphous structure in the untreated volume, and almost the same as those from the untreated glass sample as shown in the lower one [6]. The XRD peaks were observed only in the CO_2 laser exposed

area. Although the x-ray beam has a slightly smaller size than the laser beam on the surface and penetrates the sample, the laser thermal treatment is effective only on the surface because of low thermal conductivity of glass. Thus, most of the sample volume exposed to x-ray beam produces amorphos feature in the XRD pattern. The sharp diffraction peaks are easily assigned to the diffractions from (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (5 1 1), (4 4 0), (6 2 0), and (5 3 3) planes of spinel $ZnAl_2O_4$ phase (PDF-No. 01-070-8209 and JCPDS No. 05–0669) respectively. The average size of the nanocrystals have been calculated using the Scherrer formula [7] for XRD peaks, using the full width at half maximum β, diffraction angle θ, and x-ray wavelength λ Of the lattice plane (*hkl*),

$$D(hkl) = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

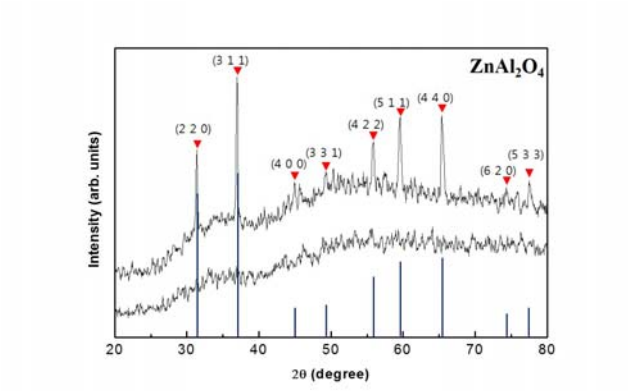


Figure 1: XRD patterns of $ZnAl_2O_4$. The lower and upper patterns correspond to glass and glass-ceramic respectively.

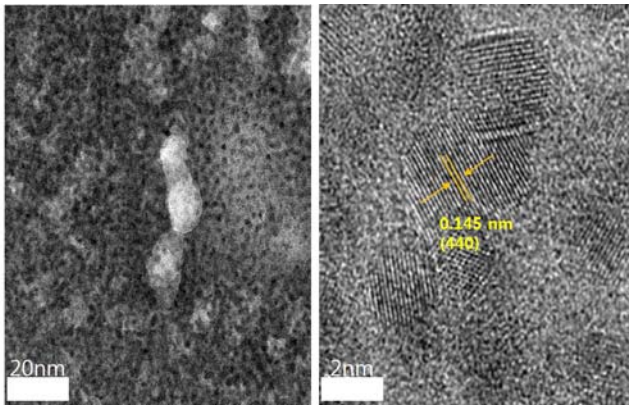
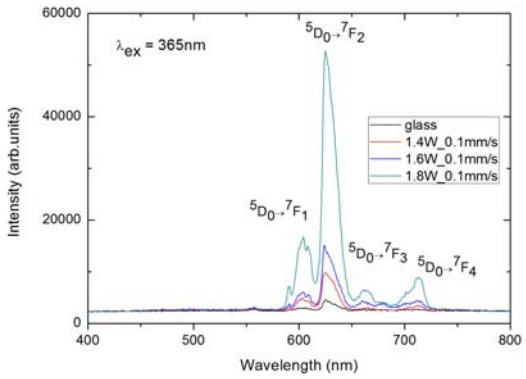


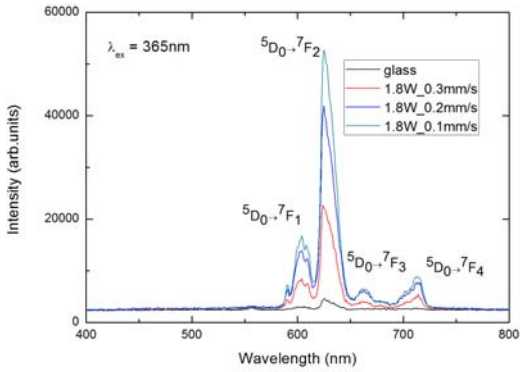
Figure 2: TEM images of $ZnAl_2O_4$ nanocrystals.

It was estimated as 5 nm. Thus, the spectral properties of precipitated crystalline of $ZnAl_2O_4$ are similar to those of zinc aluminate spinel single crystals. In order to confirm the XRD identification of crystalline phases, a high-resolution transmission electron microscopy (HRTEM) was employed. The HRTEM images of the glass ceramics are presented in Fig. 2. It can be seen that most of the particles are almost in the size range estimated from XRD analysis. The lattice spacing of the chosen nanoparticle in the HRTEM image was measured as 0.145 nm, corresponding the (440) plane of $ZnAl_2O_4$. It has been also reported that rare-earth ions are highly populated in the nanocrystals in EDS mapping [8].

Down-shifting spectra of glass-ceramics under 365 nm excitation showed enhanced emissions of Eu^{3+} ions for higher laser power up-to 1.8 W at speed of 0.1 mm/s as shown in Fig. 3(a). In contrast, the emission decreases with higher scan speed in Fig. 3(b), because the exposure energy needed to provide thermal energy for crystallization reduces. Thus, the glass-ceramics showed ~ 10 times emission enhancement compared to the emission from glass in our exposure conditions. The emission indicate the $^5D_0$ - $^7F_{1\text{-}4}$ transitions of Eu^{3+} ions.



(a)

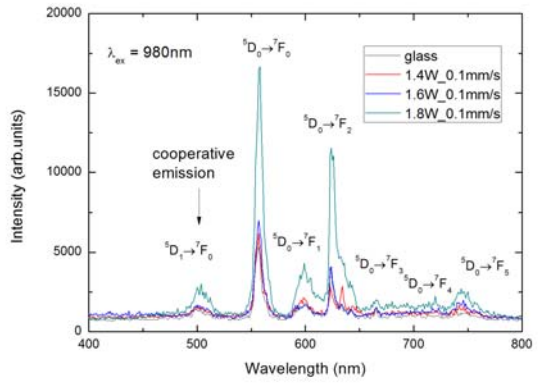


(b)

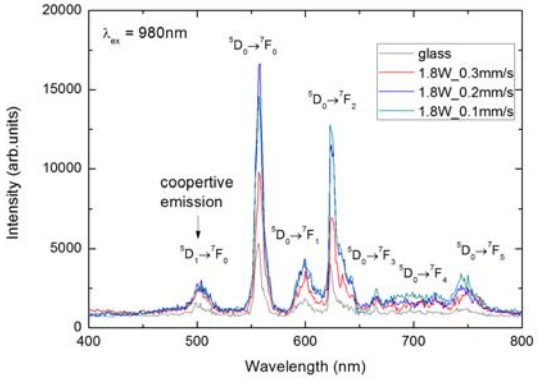
Figure 3: Down-shift emissions from Eu^{3+} and Yb^{3+} co-doped glass-ceramics treated by (a) various laser intensities and (b) scan speeds.

However, the up-conversion emission spectra, Fig. 4(a) and 4(b), obtained by the excitation at 980 nm show additional peaks of $^5D_0 \rightarrow {}^7F_{0,5}$ and $^5D_1 \rightarrow {}^7F_0$ which were not observed in down-shift emissions. As the case of down-shift emissions, the glass ceramics treated by higher laser power showed several times stronger up-conversion

emissions. New emission from the $^5D_1$ state can be explained by good energy matching of $^5D_1$ state and a virtual state at 490 nm [9]. Efficient energy transfer from Yb^{3+} to Eu^{3+} ions enable the emission at 490 nm as shown in Fig. 5. The glass-ceramics precipitated by slower laser scan produces stronger emissions. However, scan speed or exposure time does not give stronger effect than CO_2 laser power. The narrower bands in the up-conversion emission compared to those in the down-shift emission implies that the two-step excitation and energy transfer are effective only at a few sites of Eu^{3+} and Yb^{3+} ions. Because of nonlinear process, the overall intensity is much weaker than down-shift emission intensity.



(a)



(b)

Figure 4: Upconversion emissions from Eu and Yb co-doped glass-ceramics treated by (a) various laser intensities and (b) scan speeds.

A large temperature gradient in the laser-treated region can produces various sizes of nanocrystals. Enhancement of Eu emission in down-shift emission is an evidence of Eu-doped $ZnAl_2O_4$ crystal formation, because it can be described to suppressed nonradiative relaxation of rare-earth ions incorporated into nanocrystals with low phonon energy of 840 cm^{-1} [10]. Besides, the enhancement of Eu emission in the up-conversion emission is originates from effective energy transfer from Yb^{3+} to Eu^{3+} ions, indicating the formation of Eu^{3+} and Yb^{3+} co-doped $ZnAl_2O_4$ crystals. Strong emissions can be explained not only by doped nanocrystal formation but ion diffusion into the crystals resulting in higher ion density in them. However, the inhomogeneous thermal distribution due to Gaussian beam shape can produce crystal size variations.

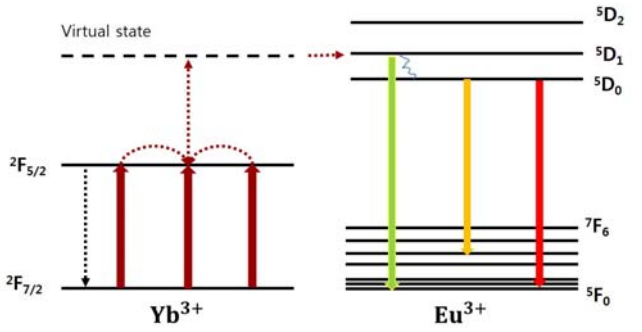


Figure 5: Energy diagram to explain upconversion originated from energy transfer and two-step excitation in Eu and Yb co-doped nanocrystals.

4. CONCLUSIONS

The glass-ceramics containing Eu and Yb ion doped $ZnAl_2O_4$ crystals on the glass surface were prepared by focused CO_2 laser beam irradiation. We provided thermal energy to reach crystallization temperature by controlling the laser power in the range of 1.4-1.8 W and the laser scan speed in 0.1 – 0.3 mm/s. The laser beam diameter was about 200 μm. Formation of doped nanocrystals were confirmed by XRD and TEM analysis. More than 30 times enhanced red emission from the glass ceramics treated by 1.8 W and 0.1 mm/s also gives the evidence of Eu ion-doped nanocrystal formation.

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