Laser Precipitation of Eu and Yb co-doped CaF_2 Nanocrystals on the Surface of Glass and Emission Characteristics

Dong-Seon Kim, Chang-hyuck Bae, and Ki-Soo Lim*

Department of Physics, Chungbuk National University, Cheongju, Republic of Korea

*kslim@chungbuk.ac.kr

ABSTRACT

We precipitated spatially selective Eu/Yb doped CaF_2 nanocrystals on the surface of glass by CO_2 laser irradiation. Because of inhomogeneous thermal energy dstribution on the surface, nanocrystal formation depended on the surface position, which was studied by micro–X-ray diffraction analysis. Confocal fluorescence microscopy analysis revealed the nanocrystal distribution along the depth from the surface. We also confirmed Eu and Yb ions are mainly confined inside CaF_2 nanocrystals by transmission electron microscope and electron dispersion spectroscpy analysis. Emission intensities from Eu ions are much enhanced in both down-shift and upconversion transitions.

Keywords: CO_2 laser, Eu, Yb, CaF_2, nanocrystal

1. INTRODUCTION

Glass ceramics (GCs) are polycrystalline ceramic matrices formed through the controlled nucleation and growth of crystalline phases in the precursor glass. The GC is usually made in two steps. First, the precursor glass is made by normal melt quenching technique. Then, a structural phase transition is thermally induced to transform it into a composite material formed by at least one crystalline phase dispersed within the glass matrix [1]. Such GC matrices have been intensively studied, and have shown potential optical applications as liquid crystal displays, solar concentrator cells, and photonic devices [2]. The oxyfluoride glass-ceramics doped with rare earth ions were researched widely in the past decades, as they provide a desirable low phonon energy fluoride environment for active ions while maintaining the advantages of an oxide glasses, such as high mechanical strength, chemical durability and thermal stability [1]. In such materials, fluoride nanocrystals were embedded in oxide glass matrices homogeneously. Due to much smaller size of the precipitated crystals than the wavelength of visible and near-infrared light as well as the matching of the refractive index between nanocrystals and the glassy host, these glass ceramics containing CaF_2 doped with rare-earth ions with low phonon energy have been studied owing to their possible applications in optical materials [3-4]. Among all the rare-earth ions, Yb^{3+} ion is recognized as one of the most popular and efficient ions for obtaining upconversion emission [5]. Eu-doped nanoparticles are quite popular because of the efficient red emission [6] and used as excellent single-molecule labels and display no blinking, in contrast to quantum dots [7]. Abundant energy level structure of rare-earth ions allow efficient energy transfer between Eu and Yb ions doped in CaF_2 nanocrystals. The present work reports on the detailed spatial and spectral properties of 1.0 mol. % Er^{3+} and 1.0 mol. % Yb^{3+} co-doped oxyfluoride transparent glass ceramics containing CaF_2 nanocrystals precipitated by CO_2 laser irradiation [8].

2. EXPERIMENTAL

We have synthesized precursor glass with nominal composition of high purity $48SiO_2 + 20Al_2O_3 + 20CaF_2 + 10NaF + 1EuF_3 + 1YbF_3$ (mol. %). The raw materials used for preparation were fine grained powders from high purity commercial chemicals. Glasses were synthesized by the conventional melt quenching technique at a temperature of 1450°C for 1 h in a covered alumina crucible under normal atmosphere. The melt was cast into an iron mold before being annealed at 530℃ for 10 h to release inner stress. For glass ceramics preparation, CO_2 laser heating method instead of an electric furnace was employed. To find optimized condition for precipitation of CaF_2 nanocrystals, we controled CO_2 laser power and exposure time. The beam width was about 300 μm. We employed micro-x-ray diffraction (μ−XRD)to find spatial distribution of nanocrystals on the surface, and transmission electron microscopy (TEM) to confirm the formation and morphology. In addition, we used energy-dispersive spectroscopy (EDS) mapping to find the atomic distribution in nano-crystal and glass domain. We also measured microscopic spatial emission distribution along the depth from the surface by employing confocal fluorescence microscopy. Besides, we obtained the down-shift Eu^{3+} emission under 365 nm excitation and the upconverted emission under 980 nm excitation to testify the enhancement of emissions due to nanocrystal formation.

3. RESULTS AND DISCUSSION

The XRD patterns of glass and glass ceramics are shown in Fig. 1(a). As expected the XRD pattern of the glass contains broad structures. For the GCs, there are a number of narrow and relatively intense peaks that show diffraction pattern of crystalline phases. With the fixed 30 s exposure, the 2.3 W focused CO_2 laser beam produced CaF_2 nanocrystals mainly with the (111) plane, including additional phases of Ca_2SiO_4 and $(Na,Ca)(Si,Al)_4O_8$ structures. The sample treated with 1.8 W shows peaks at 47° and 49°, indicating SiO_2 phase. The lower power irradiation with much longer exposure time produced mainly CaF_2 phase as shown in Fig. 1(b). From the measured XRD pattern peak width, the average size of the nanocrystals can be calculated using the Scherrer formula,

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

where *D(hkl)* is the crystal size in the vertical direction of (*hkl*), λ is the wavelength of X-ray, θ is the angle of diffraction, β is the full width at half maximum of the diffraction peak [9].

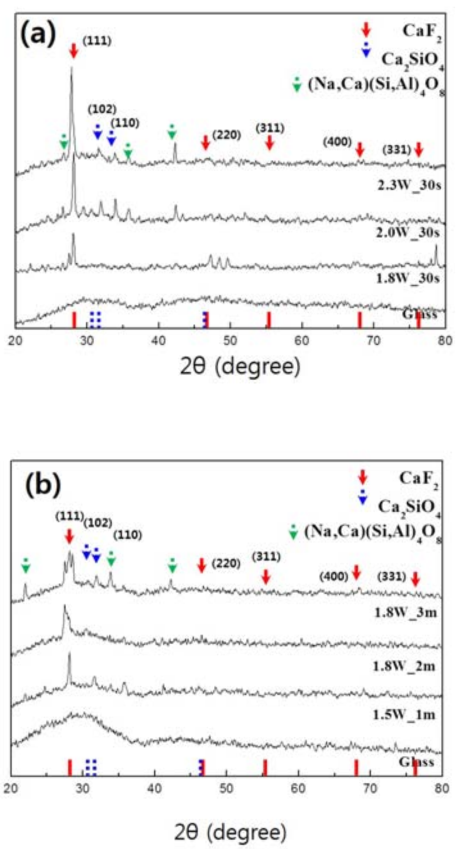

Figure 1: XRD patterns of laser irrated glass ceramics with (a) varius powers and (b) exposure times.

The size was estimated as 10~100 nm, and increases gradually with laser power and exposure time as expected from the patterns in Fig. 1.

Figure 2(a) shows fluorescence image on the glass ceramics precipitated by CO_2 laser irradiation employing obtained from a confocal microscope. The diameter of the area is about 30 μm. The μ-XRD patterns from the three selected area shown in Fig.2(b) implies that crystalline phases depend on temperature variation due to the Gaussian beam shape and thermal boundary condition. Thus, CaF_2 nanocrystals are formed mainly in the focused region of CO_2 laser beam which is expected at the highest temperature. Existance of extra peaks at 22° and 24° which did not appear in Fig. 1 originates from $(Na,Ca)(Si,Al)_4O_8$ phase, indicating its complicate structure.

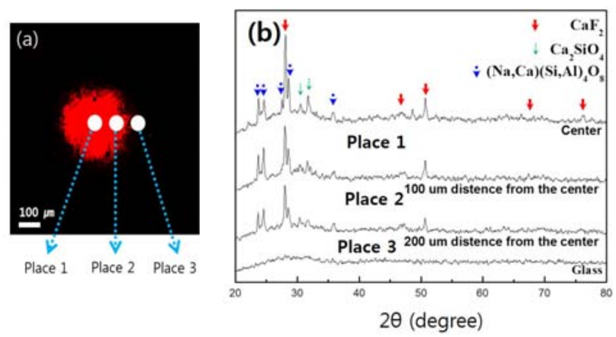

Figure 2: (a) Emission from glass-ceramic area and (b) XRD patterns from three positions

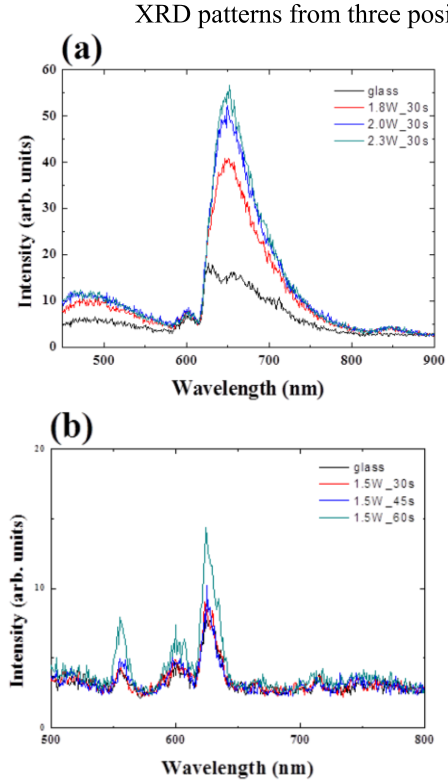

Figure 3: (a) Down-shift and (b) upconversion emission obtained under 365 nm and 980 nm excitation for glass and glass ceramics prepared with different laser conditions.

Down-shifting spectra of glass-ceramics under 365 nm excitation showed three times enhancement of emission efficiency in the GC treated by 2.3 W for 30 s as shown in Fig. 3(a). The emission consists of the $^5D_0$ - $^7F_{1-4}$ transitions and indicates inhomogenity of Eu sites. The up-conversion emissionin Fig. 3(b) shows an additional peak of $^5D_0$ - $^7F_0$ at 550 nm due to the energy transfer [10] from from Yb^{3+} to Eu^{3+} ions. Upconversion emission were slightly enhanced with exposure time. Confocal fluorescence microscope image reveals the distributed region of nanocrystals doped with Er and Yb ions along CO_2 laser direction as shown in Fig. 4. Emission obtained under 405 nm excitation shows that the nanocrystals are precipitated down to 50 μm from the surface, because each image was collected with 2 um step along the depth direction from the surface.

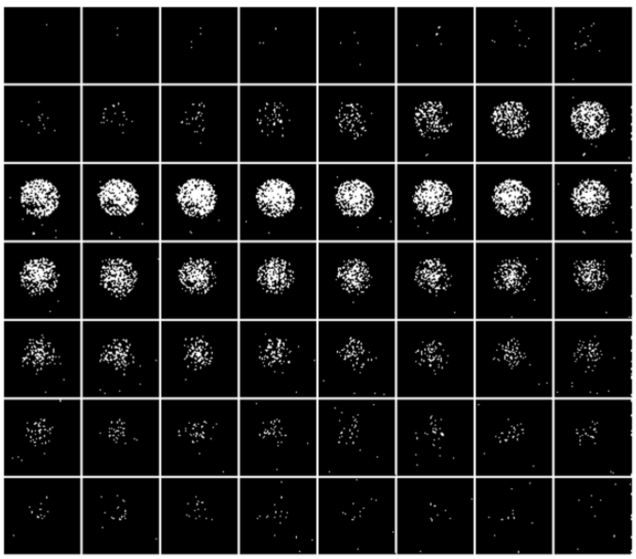

Figure 4: Emission profile obtained along the depth direction from the glass-ceramic surface by a confocal microscope with 2 μm step.

Figure 5 shows TEM and EDS images [11] of nanocrystals formed in the central part irradiated by CO_2 laser. The size is about 100 um, but varies depending on positions because of thermal distribution and sustaining time during irradiation. We can notice that Eu and Yb dopants are mainly located inside CaF_2 nanocrystals. Rare-earth ions give clean images because of heavy atoms.

4. CONCLUSIONS

Our approach to produce glass-ceramics containg CaF_2 nanocrystals did not require an electric furnace for thermal diffusion of composite materials in glass. It needs only a few minutes instead of several hours to precipitate nanocrystals. We controlled CO_2 laser power and exposure time to optimize the condition. We obsrved spatial distribution of nanocrystals on the surface and in the depth by μ-XRD and confocal microscope. We also nanocrystals and dopant distributions in and outside CaF_2 nanocrystals.

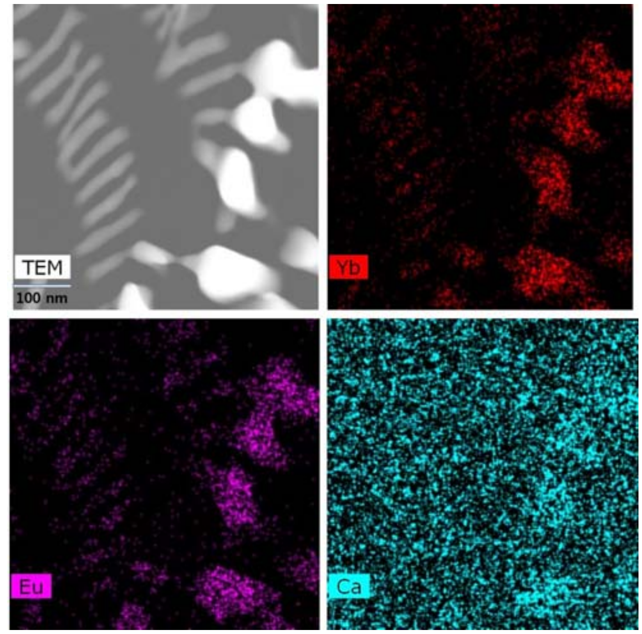

Figure 5: TEM and EDS images of CaF_2 nanocrystals precipitated by CO_2 laser irradiation on the glass doped with Eu and Yb ions.

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