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Spatially selective Er/Yb-doped CaF_2 crystal formation by CO_2 laser exposure☆

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ABSTRACT

We report the glass–ceramic precipitation on the oxyfluoride glass surface by spatially selective annealing with a CO_2 laser and a heat gun exposure. X-ray diffraction analysis showed the formation of major CaF_2 and miner Ca_2SiO_4 nanoparticles. We observed ~100 nm nanoparticle aggregation by tunneling electron microscopy and element distribution in glass and crystal phases. Spatial distribution of glass ceramics near the glass surface was probed by confocal fluorescence microscope by using much enhanced emission from the Er ions in the laser-treated area. Strong emissions at 365 nm excitation and visible up-conversion emissions at 980 nm excitation also indicated well incorporation of Er and Yb ions into a crystalline environment.

1. Introduction

Oxyfluoride glass ceramics have been paid much attention due to their combined advantages of oxide glasses and fluoride glasses [1,2]. They are fabricated using controlled heat treatments in an electric furnace, and nanocrystals are formed in the interior of glass [3]. Rare-earth ion doped glass ceramics may become potentially useful for optoelectronic applications. 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 [4]. We applied the CO_2 laser-induced crystallization technique to a multi-component SiO_2–Al_2O_3–CaF_2 oxyfluoride glass. CaF_2 is a non-toxic optical material with wide transparent spectral region and high solubility of rare earth ions [5], and gives a better matching of refractive index with the alumino-silicate glass [6]. It also has the advantage of not only high chemical and mechanical stabilities [7], but also much less phonon energy (~400 cm^{-1}) [8], yielding large quantum efficiency. Er^{3+} ions have been well known rare-earth ions for optical communication and Yb^{3+} ions are widely used for infrared-to-visible upconversion applications [9]. In this work, we report the precipitation of spatially selective glass–ceramics containing CaF_2 nanocrystals doped with Er^{3+} and Yb^{3+} ions and compared their emission characteristics with traditional electric-furnace heated glass–ceramics.

2. Experimental

The nominal composition of precursor glass (as-melted) used in this study was $45SiO_2$–$15Al_2O_3$–$35CaF_2$–$4Yb_2O_3$–$1Er_2O_3$ (mol%). The raw materials used for preparation were fine grained powders from high purity (3 N) commercial chemicals. Starting batches were thoroughly mixed and melted at 1450 °C for 1 h in a covered platinum crucible under normal atmosphere. Then, the melt was cast into an iron mold before being annealed at 530 °C for 10 h to release inner stress. The glass transition temperature were measured as 622 °C by Differential Thermal Analysis (DTA, SDT2960). Finally, the glass was cut and polished into the glass samples with thickness of 1 mm. For thermal treatment to induce CaF_2 nanocrystals, we used both a heat gun at 500 °C and a 1.5 W

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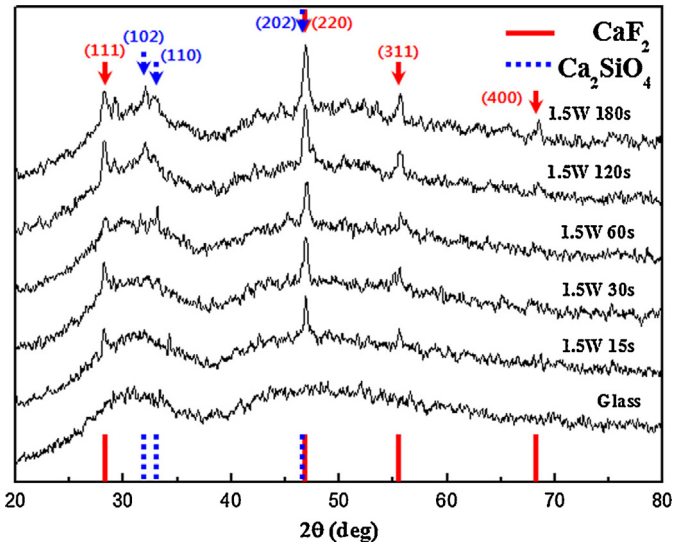

Fig. 1. XRD patterns of the glass and glass–ceramics prepared by space-selective CO_2 laser annealing with various exposure times.

CO_2 laser with various exposure times of 15–180 s. The laser beam passed an aperture and was focused on the glass of 1 mm thickness by a silicon lens. The selective area had a ~200 μm diameter.

We employed micro-X-ray diffraction (μ-XRD, D/MAX RAPID-S) analysis for the irradiated and unirradiated regions to testify the formation of CaF_2 crystals. Furthermore, to clarify the size and crystallization of nanocrystals, we performed transmission electron microscopy (TEM, Titan G2 60-300) analysis for the laser-treated surface. Photoluminescence and upconversion emission spectra for Er^{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, and compared with those for the glass–ceramics precipitated by electric furnace treatment. Besides, confocal fluorescence microscope was employed to know the depth of crystal formation region inside the laser-treated glass.

3. Results and discussion

Fig. 1 shows the micro-XRD patterns for the glass samples treated by the same CO_2 laser power of 1.5 W with different laser exposure times (0–180 s). In contrast to the electric-furnace annealed glass–ceramics containing nanocrystals in a larger volume portion of host studied previously [10], the laser heated samples showed weak and broad diffraction signals in the XRD pattern. The broadened XRD line width may be due to an inhomogeneous stress distribution in the crystals [11]. Diffraction angels slightly shifting toward left indicates increased interplanar crystal spacing because an interstitial ion is associated to each Er or Yb ion to insure the charge balance and should lead to the increase of the lattice parameter [12]. The XRD peaks were observed only in the CO_2 laser exposed area. Although the X-ray beam has a slightly smaller than the laser beam size on the surface and penetrates the sample, the laser thermal treatment is applied only to the surface. The broad humps are due to its amorphous structure in the untreated volume, and almost the same as those from the untreated glass sample. The sharp diffraction peaks at 28°, 47°, 56°, and 69° are easily assigned to the diffractions from (1 1 1), (2 2 0), (3 1 1), and (4 0 0) planes of cubic CaF_2 phase (PDF-No. 00-035-0816) respectively. We estimated the CaF_2 nanocrystal size by using the Sherrer's equation,

$$D(h\ k\ l) = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D ($h\,k\,l$) is the crystal size in the direction of ($h\,k\,l$), λ is the wavelength of X-ray, θ is the angle of diffraction, β is the full width at half maximum (FWHM) of the diffraction peak, and K is the instrument constant. The estimated size range of CaF_2 nanocrystal from the XRD data is 15–20 nm.

Extra peaks observed at 31.8°, 33.0°, and 46.5° for the samples treated longer than 30 s are assumed to be originated from (1 0 2), (1 1 0), and (2 0 2) planes of γ-Ca_2SiO_4 (PDF-No. 00-023-1042).

The area under the CaF_2 peaks is proportional to the crystalline CaF_2 concentration and increases with exposure temperature. In oxyfluorides, the rare earth ions in the glass act as nucleation sites for crystallization [13]. Thus, the spectral properties of precipitated crystalline CaF_2 are similar to those of CaF_2 single crystals.

In order to confirm the XRD identification of crystalline phases, a high-resolution transmission electron microscopy (HRTEM) combined with the selected area electron diffraction was employed. The HRTEM images of the glass ceramic containing CaF_2 crystals doped with Er and Yb ions are presented in Fig. 2a and b. The size of fine crystals are varied from 100 to 700 nm. Fig. 2b shows the result of observations of the crystallite (bright and dark line images)

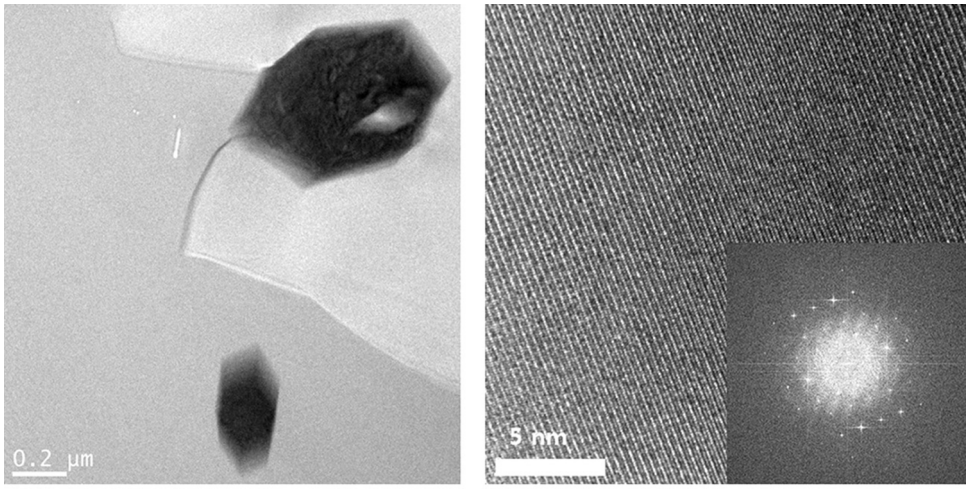

Fig. 2. (a) TEM micrograph of crystallites, and (b) high-resolution image of crystalline area in the Er/Yb co-doped glass–ceramics (insert shows its Fourier transform) precipitated by exposure to CO_2 laser for 3 min.