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Effect of chemical etching on the surface morphology of laser-patterned lines with Er^{3+}-doped CaF_2 nanocrystals in oxyfluoride glass

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ABSTRACT

The chemical etching behavior for the lines consisting of Er^{3+}-doped CaF_2 nanocrystals patterned on the surface of an oxyfluoride glass by using a laser-induced crystallization technique (laser: Yb-doped YVO_4; wavelength: 1080 nm; power: 1.7 W; a scanning speed: 2 μm/s) in a nitric acid solution (1N HNO_3) is examined, and the morphology change in the lines due to the etching is characterized from confocal laser microscope observations and photoluminescence (PL) spectrum measurements of Er^{3+} ions. The higher and wider bumps compared with the bump of the original line (no etching) are observed in etched lines, and in particular, the surrounding of lines is etching away preferentially, forming the groove in both sides of line. PL spectra of Er^{3+} ions with strong intensities are observed from etched lines, suggesting that Er^{3+}-doped CaF_2 nanocrystals are largely present just at the surface of etched lines. It is found that the chemical etching rate (1.2×10^{-2} μm/min) of the crystallized bulk sample is smaller than that (5.4×10^{-2} μm/min) of the precursor bulk glass, suggesting that CaF_2 nanocrystals formed have a high resistance against the chemical attack.

1. Introduction

Transparent oxyfluoride-based crystallized glasses (glass-ceramics) consisting of fluoride nanocrystals have received much attention [1–6]. In such materials, for instance, rare-earth (RE^{3+}) ions are incorporated into fluoride nanocrystals embedded in SiO_2-based oxide glass matrices with high thermal/chemical stabilities, and photoluminescence (PL) spectra with strong intensities are observed from RE^{3+}-doped fluoride nanocrystals with low phonon energies. Usually, oxyfluoride-based crystallized glasses are fabricated through well-controlled heat treatments in an electric furnace. Recently, a laser-induced crystallization technique has been applied to oxyfluoride glasses, and lines consisting of LaF_3 or CaF_2 nanocrystals have been patterned [7–9]. Spatially selected crystallization of fluoride crystals in oxyfluoride glasses would give a high potential for optical device applications such as waveguide-type amplifications, and it is of interest to characterize morphologies and properties of fluoride crystal lines patterned by lasers.

Very recently, Hirokawa et al. [10] and Honma et al. [11] applied a combination technique of laser irradiation and chemical etching (e.g., 1N HNO_3 solution) to nonlinear optical $Ba_2TiGe_2O_8$ crystal dots and lines on the glass surface and proposed that its technique is effective in constructing the micro-architecture of crystal dot array and patterned line. The key-point in their studies is that chemical etching rates of the precursor glass and crystallized part in an acid solution are different largely [10,11]. It is of interest and importance to clarify the chemical etching behavior in oxyfluoride glasses and crystallized glasses with fluoride nanocrystals for their device applications. There have been, however, no reports on chemical etching of oxyfluoride glasses and their ceramics so far.

The purpose of this study is to examine the chemical etching behavior for laser-induced crystal lines consisting of Er^{3+}-doped CaF_2 nanocrystals in oxyfluoride glasses and to clarify the change in the surface morphology and PL spectra after chemical etching. In this study, it has been clarified that the chemical etching rate for the patterned lines in a nitric acid solution (1N HNO_3) is smaller than that for the precursor oxyfluoride glass (non-irradiated part). A combination technique of laser-induced crystallization and simple chemical etching is proposed to be effective in designing the micro-architecture of lines with CaF_2 nanocrystals in oxyfluoride glasses. Lines consisting of Er^{3+}-doped CaF_2 nanocrystals in oxyfluoride glasses have been already successfully patterned using a laser-induced crystallization technique by our research group [7,9].

2. Experimental

In this study, an oxyfluoride glass with the composition of $41.5SiO_2$–$21.3Al_2O_3$–$4.8CaO$–$12.6NaF$–$16.4CaF_2$–$2.9NiO$–$0.5ErF_3$ (mol.%) (designated here as Glass A) was examined [9]. The glasses were prepared using a conventional melt quenching method. Commercial powders of raw materials of SiO_2, Al_2O_3, $CaCO_3$, NaF,

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CaF_2, NiO, and ErF_3 were mixed and melted in a platinum crucible with a lid at 1400 °C for 1.5 h in air in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness of ~2 mm with another iron plate. The glass transition, T_g, crystallization onset, T_x, and crystallization peak, T_p, temperatures for the glasses (bulk samples) were determined using differential thermal analyses (DTA) at a heating rate of 20 K/min. The formation of CaF_2 crystals in the crystallized samples was examined from X-ray diffraction (XRD) analyses (Cu Kα radiation) at room temperature. The incorporation of Er^{3+} ions into CaF_2 crystals was confirmed from PL spectra of Er^{3+} ions by using a micro-PL spectrum apparatus (Tokyo Instruments Co., Nanofinder; Ar^+ laser with a wavelength of λ = 488 nm).

The glasses were mechanically polished to a mirror finish with CeO_2 powders. Continuous-wave (cw) Yb:YVO_4 fiber lasers with λ = 1080 nm were irradiated onto the surface of the glasses using an objective lens (magnification: 50×; numerical aperture: NA = 0.8). The sample was put on the stage and mechanically moved during laser irradiations to construct crystal lines. After laser irradiation, wet chemical etchings with a nitric acid (HNO_3) solution (concentration: one normality, 1N) and different etching times at room temperature were carried out. The surface morphology of etched crystal lines was observed with a confocal scanning laser (CSL) microscope (Olympus-OLS 3000). The PL spectra of Er^{3+} ions in the crystal lines were measured by using a micro-PL spectrum apparatus.

3. Results and discussion

3.1. Chemical etching rates of bulk precursor glass and crystallized samples

The DTA pattern showed that the glass prepared in this study gives the values of T_g = 575 °C, T_x = 620 °C, and T_p = 635 °C [9]. It was confirmed from the XRD patterns and PL spectra that Er^{3+}-doped CaF_2 nanocrystals are formed in the samples obtained by heat treatments at T_x and T_p for 2 h, as already reported in previous paper [9]. That is, the average particle size, d, of CaF_2 crystals was estimated to be d = 17 nm for the sample heat-treated at T_x = 620 °C and d = 20 nm for the sample heat-treated at T_p = 635 °C from the peak width of the (2 2 0) plane in the XRD patterns by using Scherrer's equation [9].

Prior to the study of the chemical etching behavior for laser-induced crystal lines consisting of Er^{3+}-doped CaF_2 nanocrystals, the chemical etching rate of the bulk precursor oxyfluoride glass and the crystallized (T_p = 635 °C, 1 h) glass was examined. Some parts of the surfaces of glass and crystallized samples were masked by using an epoxy resin and were immersed into a solution of 1N HNO_3 for 30, 60, 90, and 120 min. After removing the epoxy resin, the etching depth was measured from CSL microscope observations. The results are shown in Fig. 1. It is found that the etching thickness increases almost linearly with increasing etching time. Furthermore, it is seen that the chemical etching rate of the crystallized sample, i.e., 1.2×10^{-2} μm/min, is smaller than that (5.4×10^{-2} μm/min) of the precursor glass. This new information would be very important for practical applications of aluminosilicate-based oxyfluoride glass-ceramics with RE^{3+}-doped nanocrystals. To the best of our knowledge, there have been no reports on mechanical properties and chemical durability for oxyfluoride glass-ceramics, although numerous studies on optical properties of RE^{3+} ions in oxyfluoride glass-ceramics have been reported.

Kiczenski and Stebbins [12] examined the fluorine sites in calcium aluminosilicate oxyfluoride glasses by using a ^{19}F magic-angle spinning nuclear magnetic resonance (MAS NMR) technique and proposed that most of the F bonding is to Al, i.e., the formation of Al–F–Ca bonds, with roughly 0–30% Si–F–Ca bonds. Therefore,

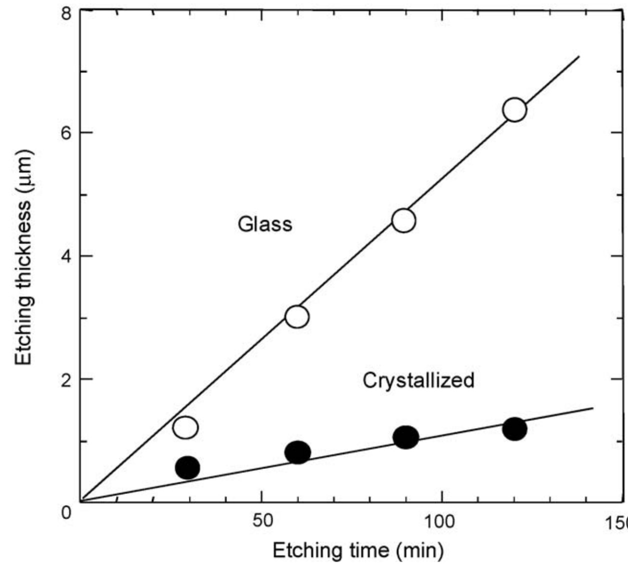

Fig. 1. Chemical etching thickness of the crystallized (635 °C, 2 h) bulk sample and the precursor bulk glass in a solution of 1N HNO_3 as a function of etching time.

Ca^{2+} ions with the high field strength can more effectively compete with Al^{3+} for bonding with F^- in aluminosilicate oxyfluoride glasses [12]. It is known that the viscosity of Al-free silicate melts decreases with the partial substitution of $2F^-$ for O^{2-} [13], where the mobile fluoride anion may serve to catalyze network bond breaking [12]. On the other hand, as demonstrated in the dental science and technology, calcium fluoride (CaF_2) at the surface of teeth can act as protecting layers, reducing acid dissolution of teeth [14]. It is, therefore, considered that the formation of CaF_2 crystals in oxyfluoride glasses would decrease the amount of F^- ions acting as anions for the breaking of Si–O–Si bonds in the glassy phase and would increase the chemical resistance against the attack of acids such as HNO_3. From these reasons, it is expected that the chemical etching rate of the crystallized sample with CaF_2 nanocrystals is much smaller than that of the precursor oxyfluoride glass, as obtained in the present study (Fig. 1).

3.2. Chemical etching of crystal lines with Er^{3+}-doped nanocrystals

As reported in previous papers [7–9], lines consisting of fluoride crystals such as LaF_3 or CaF_2 are patterned in aluminosilicate oxyfluoride glasses by laser irradiations. The CSL micrograph for the sample obtained by irradiations of Yb:YVO_4 fiber lasers (λ = 1080 nm) with a power of P = 1.7 W and a scanning speed of S = 2 μm/s in Glass A is shown in Fig. 2(a). The bump is observed in the laser-irradiated parts, and the values of height (h) and width (w) are $h \sim 1$ μm and $w \sim 3$ μm. The formation of bump at the surface is a typical feature in the laser-induced crystallization in oxide and oxyfluoride glasses, indicating that at least the temperature in the laser-irradiated region is going up over the glass transition temperature [15,16].

The CSL micrographs for the samples obtained by chemical etchings in a nitric acid solution (1N HNO_3) for the etching times of t = 30 and 60 min at room temperature are shown in Fig. 2(b) and (c). The higher and wider bumps compared with the bump of the original line (no etching) are observed. Furthermore, in particular, the surrounding of the lines is etching away preferentially, forming the groove in both sides of the lines. The height and width of the bumps evaluated from CSL measurements for the etched lines are summarized in Fig. 3. The results shown in Figs. 2 and 3 clearly indicate that the chemical etching rate in the lines changes largely depending on the position of line. Very recently, Kanno et al. [9]