Effect of Ultrasonic Surface Treatment on the Transparency and Orientation of Fresnoite Surface Crystallization

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Effect of Ultrasonic Surface Treatment on the Transparency and Orientation of Fresnoite Surface Crystallization

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Abstract. Surface crystallized glass ceramics with fresnoite ($Ba_2TiSi_2O_8$) phase were prepared by conventional heat treatment of 30BaO-20TiO_2-50SiO_2 glass together with ultrasonic surface treatment (UST) technique. The precursor glass was fully crystallized in a bulk form without any cracks, and the optical transparency and crystallographic orientation of the crystalline layers were evaluated by UV-Vis spectroscopy and XRD diffraction analyses, respectively. These properties were both enhanced significantly by applying UST using fresnoite/water suspension before the crystallization process, which is advantage for nonlinear optical applications of bulk glass ceramics. The effects of UST on the crystallization behavior were investigated by applying UST with various conditions.

1. Introduction

Glass ceramic materials with including fresnoite $Ba_2TiSi_2O_8$ phase are of interest because of their excellent nonlinear optical (NLO) functions induced by the crystalline phase formation, and a number of researches on the preparations and NLO evaluations of the glass ceramic materials in BaO-TiO_2-SiO_2 glass system were reported so far. Among them a transparent glass ceramic with oriented fresnoite crystalline layer was one of the most remarkable approaches to realize an optical device application for second harmonic conversion by NLO glass ceramics in a bulk form. Fresnoite glass ceramics with optical transparency and crystallographic orientation were only fabricated in a narrow region near a specific composition of 30BaO-20TiO_2-50SiO_2 and by a well-controlled heat treatment [1]. The morphology control of glass ceramics via controlling crystallization behavior is expected for the development of transparent glass ceramics with NLO function, and it is also necessary to improve morphological aspects of the fresnoite glass ceramics. A novel technique of ultrasonic surface treatment (UST) is known to be effective for controlling surface crystallization. In this technique precursor glass surface is exposed to ultrasonic wave through suspensions before heat treatment, and then the nucleation and following crystallization growth are affected by physical and/or chemical changes on the surface. The mechanism of UST is not clear at present but it would be useful for fabricating fresnoite glass ceramics with a practical level of optical and nonlinear optical quality.

The main purpose of the present study is to enhance both of the transparency and the *c*-axis orientation of the fresnoite crystalline layer using UST technique. The optical transparency and the crystallographic orientation were evaluated by UV-Vis spectroscopy and X-ray diffraction analyses,

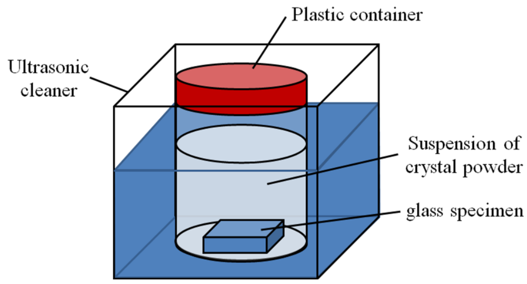

Figure 1. Schematic illustration of UST.

respectively. The effects on the crystallization behavior were investigated by considering both physical and chemical changes induced by UST just below the glass surfaces.

2. Experimental procedure

The glass with a composition of 30BaO-20TiO_2-50SiO_2 (mol%) was prepared by a conventional melt-quenching method. Commercial powders of reagent grade $BaCO_3$, TiO_2 and SiO_2 were mixed and melted in a platinum crucible in an electric furnace at 1500°C for 1 h. The melt was quenched onto a preheated steel plate and then annealed at the glass transition temperature for 1 h. The glass thus formed was cut into plates with ~1 mm in thickness and they were mechanically polished to obtain mirror surfaces with aqueous suspension of alumina powder (~ 1μm).

UST was carried out by exposing the polished glass samples to an ultrasonic energy transmitted through fresnoite/water suspension held in an ultrasonic cleaning bath (VS-100 II SUNPAR 100W Velvo Clear Co.) for various conditions of exposure times, 1-60 min and ultrasonic waves, 28, 45 and 100 kHz (see Figure 1). The fresnoite powder was prepared by firing and pulverizing the stoichiometric mixture of reagent grade $BaCO_3$, TiO_2 and SiO_2 at 1100°C for 120 h and 1200°C for 20 h in an electric furnace, and it was also confirmed to be a single phase of fresnoite (JCPDS 22-513) by the X-ray diffraction measurement at room temperature. The weight concentration of fresnoite particle in the suspensions was fixed 1 wt%. Alumina suspension with the same condition was also used for comparison. After the UST for as-polished surfaces the glass samples were heat-treated at 840°C for 48 h to complete the surface crystallization of fresnoite phase.

The crystalline phases on the surface were examined by XRD with Cu Kα radiation at room temperature. The polar orientation of them was evaluated by Lotgering factor (L.F.) for (00*l*) lines from the surface XRD patterns as well as FWHM from fresnoite-(004) rocking curve analyses. The optical transparency of the fully crystallized bulk glass ceramics was measured by using a spectrophotometer in a range of 380-800 nm in wavelength. In order to investigate the change in the morphologies of the glass surface after UST as well as the powders in suspensions, SEM observations were carried out.

3. Results and discussion

3.1. Transparency of fresnoite crystals

Figure 2 shows the transmittance spectra of the glass ceramics after heat treatment at 840°C for 48 h. In the case that UST was applied to the precursor glass surfaces before the heat treatment the transmittance values in visible region were significantly enhanced, for example 5% (without UST) to 35% (with UST) at 532 nm in wavelength. It is considered that inhomogeneous nucleation at the surface was accelerated by applying UST, resulting in small domain size of fresnoite crystallites and smooth surface of the sample. Consequently light scattering origins created by crystallization were remarkably decreased. UST was found to be a quite effective technique for the transparency of the fresnoite-oriented glass ceramics.

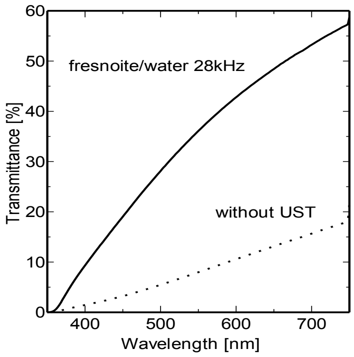

Figure 2. Transmittance spectra of fresnoite glass ceramics obtained after heat treatment with UST of 28 kHz and without UST.

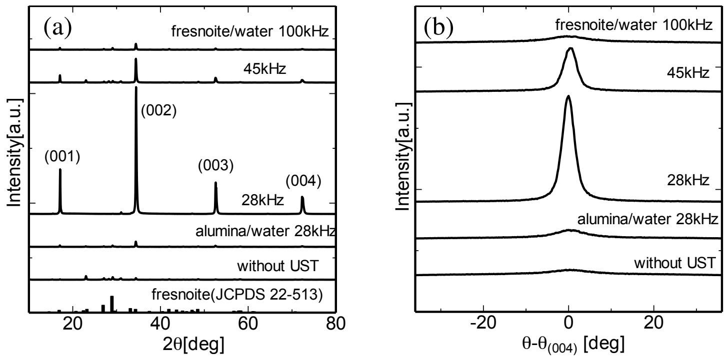

Figure 3. XRD analyses of surface orientation of fresnoite layer, (a) surface XRD patterns and (b) fresnoite-(004) rocking curves for various UST conditions.

3.2. Orientation of fresnoite crystalline layer

The orientation of the fresnoite crystalline layer was confirmed by the XRD measurements. The surface XRD patterns for the samples without UST (as control) and with USTs using fresnoite/water and alumina/water suspensions are shown in Fig. 3(a). The definite effect on the (00*l*) orientation was found for all the samples with UST. Among them the *c*-axis orientation obtained by fresnoite/water suspension and ultrasonic wave of 28 kHz was remarkable, where the L.F. for (00*l*) diffraction lines was maximized to be 0.991. On the other hand the L.F. for alumina/water suspension was very low 0.456. This result supports the existence of some effects of the corresponding crystalline powders in suspension, but further discussion must be done based on the detection of nucleation sites imprinted by fresnoite powder.

The dependence on the ultrasonic frequencies was also found, that is, the (00*l*) diffraction for fresnoite/water with 28 kHz was maximized and the FWHM of fresnoite-(004) rocking curve was minimized. As for the present equipments of UST the ultrasonic powers are not constant between these frequencies, so it cannot be concluded that UST with lower frequency is effective. However, fresnoite/water suspension with 28 kHz should be selected as a standard condition of UST hereafter.

Figure 4 shows the dependence of the *c*-axis orientation on the ultrasonic exposure time from 0 (without UST) to 60 min. The L.F. shown in Fig. 4(c) was saturated after 15 min exposure. On the other hand the FWHM of fresnoite-(004) rocking curves shown in Fig. 4(b) and (d) seemed to include some experimental errors but similar tendency of the saturation. The effective parameters of UST conditions were determined as follows: fresnoite/water suspension, 28 kHz, 15 min exposure.

3.3. SEM observations of glass surface

Figure 5(a) shows the SEM image of the surface and cross section edge of the glass sample just after UST using fresnoite/water suspension. Although the fresnoite powders in suspension, shown in Fig. 5(b), were carefully removed by water before the SEM observation, a clear and flat surface was found on the glass sample. In other words any expected changes, for example fine particle residues, embedded particles, micro-cracking or damages, and chemical corrosion, cannot be detected in micrometer scale. The size and shape of fresnoite powder in suspension did not show significant change after UST. The effect and mechanism of UST was discussed in terms of seeding, pseudo-epitaxy and surface corrosion [4]. Even if some of these effects are substantial, they maybe happened in smaller scale so that we could not detect by the present observation techniques. In order to confirm any physical and/or chemical effects on the surface submicro- or nano-scale techniques other than the present observation must be applied in the future.

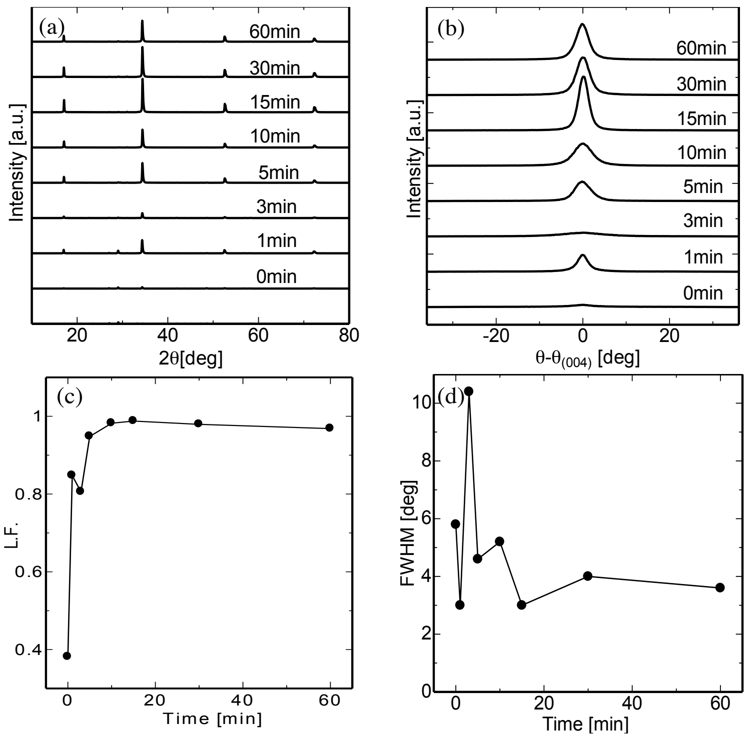

Figure 4. XRD analyses of surface orientation of fresnoite layer by UST exposure times, (a) surface XRD patterns, (b) fresnoite-(004) rocking curves, (c) L.F. for (00l) lines and (d) FWHM of (004) rocking curves.

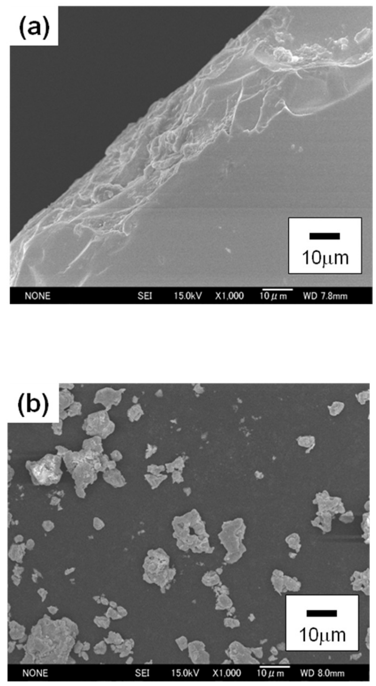

Figure 5. SEM observations of (a) UST applied glass surface and edge and (b) fresnoite powders in suspension for UST.

The authors have already performed non-aqueous UST experiments using fresnoite/kerosene and fresnoite/hexane suspensions, and it was confirmed that they were also effective for the orientation of surface crystalline layers. This fact does not deny any mechanisms associated with water such as glass surface corrosion by water but implies the validity of physical effects.

4. Conclusion

Transparency and *c*-axis orientation of surface crystallized glass-ceramics with fresnoite were investigated in terms of UST effects. They were successfully enhanced by applying UST before the conventional heat treatment and the effective parameters of UST conditions were determined. However, the SEM observation of the glass surface after UST did not show any significant changes. The effect and mechanism of UST resulting in the enhancement of transparency and *c*-axis orientation are not yet explained at present, but the practical importance should be emphasized in order to develop new series of transparent glass ceramics with oriented crystals.

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