Morphology Design of Crystals and Mechanical Behavior in Glass-ceramics

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**Morphology Design of Crystals and Mechanical Behavior in Glass-ceramics**

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Chapter I

Introduction

1.1. General introduction

According to Zachariasen [1], glass is a substance can form extend three-dimensional networks lacking periodicity with an energy content comparable with that of the corresponding crystal network. In essence, the density and mechanical properties of glasses are solid-like; however, the atoms form a continuous random network such that the unit cell is infinitely large, containing an infinite number of atoms. Thus a working definition of glass is that a solid with a liquid-like structure.

Because of a liquid-like structure, glasses show excellent transparency and have high formability at high temperature like a starch syrup. So, glasses are desirable materials for the use of photonic realms, such as optical fiber, lens, prism, and wave-guide. Glass is a key material for the telecommunication technique. However, glass cannot have ferroelectricity, second-order non-linearity, and many desirable properties because of their non-periodic structure.

Crystallization of glass is one of the effective methods for fabrication of periodic part in glass. Glass-ceramics have been developed for over forty years and numerous commercial products have been developed using this technique. Typically, base glass is prepared by the usual melt-quench method; it is then formed in desired shape and size. Subsequently, the product is subjected to two-step heat-treatments at the temperatures of maximum nucleation and controlled growth to yield desired microstructure. Previously, various optical transparent glass–ceramics (crystallized glasses) consisting of nanocrystals have been designed by controlling nucleation and crystal growth in corresponding glasses. For instance, glass–ceramics based on the Li2O–Al2O3–SiO2 glass system, which show several distinctive properties such as excellent optical transparency, thermal shock resistance, and mechanical properties, have been widely used in various practical applications [2,3]. Recently, transparent glass–ceramics consisting of nonlinear optical/ ferroelectric nanocrystals have been developed, because
such materials have high potentials for applications in photonic devices such as optical switch [4,5].

Recently, the patterning of oriented/ nano-crystals on the glass surface by laser irradiations has been proposed as a new design of spatially controlled crystallization [6-9]. Spatially selected crystallization of crystals in glasses would give a high potential for optical device applications such as waveguide-type amplifications, optical switches, and wavelength converters and it is of interest to characterize morphologies and properties of crystal lines patterned by lasers. To fabricate such crystal line is one of the most important techniques of fabrication of novel morphology of the glass-ceramics.

Glass has desirable nature for many applications such as telecommunications, electronics, medical care, architecture, automobile, bottle, and so on. For such applications, the demand for lightweight and thin glass continues to rise. However, glasses have the characteristics of being brittle and easily broken, unlike metals and plastics, when subjected to thermal or mechanical stresses. On theoretical grounds, these parameters are directly related to Young’s modulus, which, in turn, is influenced predominantly by the glass’ chemical composition. However, in practice, strength of glass is controlled by surface flaws, or Griffith flaws, on the glass surface [10]. For example, the strength of silica glass fiber without any surface flaws, i.e., pristine fiber is approximately 10–15 GPa at liquid nitrogen temperature [11] and 5–6 GPa at room temperature [12], while the strength of bulk silica glass is approximately two orders of magnitude lower. The difference is due to the surface flaws on the bulk glass. Although great amounts of research on glass strength and glass strengthening have been widely reported over the years, brittleness of glass products has still been the main problem in applications.

The flaws develop easily on the glass surface because of the brittle nature of the glass. Brittleness was defined by Lawn and Marshall [13] using the parameter $B=H/K_C$, where $H$ is hardness and $K_C$ is fracture toughness. The hardness represents resistance to deformation and the fracture toughness represents resistance to fracture. Thus, a glass with easier plastic deformation and higher toughness is expected to exhibit a lower brittleness. Under deformation, glass deforms in elastic and plastic deformation in room temperature. Plastic deformation can be classified as plastic flow and densification. In general, the ratio of densification/ flow has a tendency to increase with decreasing of density of glass [14]. Sehgal and Ito [15,16] investigated the brittleness of various
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glasses in a silicate system and developed a unique ‘less brittle glass’. The glass has a similar glass composition to the commercial window glass yet it exhibits remarkable features such as greater crack initiation load under indentation and cleaner scratch patterns. This difference is caused by difference of deformation behavior. It should be point out in here brittleness largely depends on their surface deformation behavior.

On the other hand, mechanical behavior for glass-ceramics is not clarified yet. There are many studies for fracture of glass-ceramics for the application of bioactive ceramics such as apatite or for architecture. According to these studies, fracture of glass-ceramics are largely decreasing due to the effects of crystals inhibiting the straight propagation of cracks, causing them to turn or branch out. In addition to it, the difference of thermal expansion between glass matrix and crystal particle makes internal stress. If thermal expansion coefficients of the glass is smaller than of crystal, compressive stress are formed in glass matrix and brittleness should decrease.

Most these researches are only glass-ceramics having the large crystal (several micrometers in diameter). In the case of the nanocrystals, the effect of inhibiting the crack propagation is not so large and the effect to the deformations behavior should be different from both glasses and glass-ceramic with large crystals. It is necessary to clarify the effect of the crystal on the deformations and fracture behavior in the viewpoints of applications and developing the novel glass materials. Especially, the chemical composition and morphology of crystals has a large effect on the deformation behavior.

For the new application in photonics/ electronics realms, it is strongly required to upgrade a morphology control technique of crystallization. In this study, I proposed development of morphology control technique for; (1) crystal line obtained by laser irradiation technique and (2) conventional heat-treatment technique to form nanocrystal. In this study, morphology of crystals in glass has been trying to control by novel technique and investigated in nano-scale. The morphology of nanocrystals should largely affect to the mechanical behavior such as fracture and derormation. In this study, relationship between crystal morphology in two types of glass-ceramics, i.e. fresniote glass-ceramics and oxyfluoride glass-ceramics, are discussed. Fresnoite glass-ceramics has fresnoite type nanocrystals in stoichiometric composition of glass matrix. The interface between crystals and glass matrix consider to be strong. By contrast, in oxyfluoride glass-ceramics, strong ionic crystals dispersed in covalent oxide glass
matrix. So, it is interested in the viewpoint of effect their structure in mechanical behavior.

In chapter 1, the outline and propose of this thesis are described. The investigated materials and technique for evaluation of materials, glass and transparent crystallized glass, are also presented. Fresnoite nanocrystallized glass and oxyfluoride glass and glass-ceramics investigated in this thesis and estimation methods of elastic and mechanical properties are described here. For the measurement of elastic properties such as Young’s modulus and Poisson’s ratio, cube resonance method (for bulk) and nanoindentation techniques (for surface) are employed. Nanoindentation is measured in two types, i.e. standard type and continuous stiffness measurement (CSM) mode. Mechanical properties such as Vickers hardness and Fracture toughness are evaluated by Vickers indentation.

In chapter II, elastic and mechanical behaviors of the glass with a composition of 40BaO-20TiO$_2$-40SiO$_2$ corresponding to Ba$_3$TiSi$_2$O$_8$ and transparent glass-ceramics with Ba$_3$TiSi$_2$O$_8$ nanocrystals have been evaluated. In the viewpoint of volume fraction of nanocrystals and surface/bulk properties, the effects of nanocrystals have been discussed.

In chapter III, elastic and mechanical behavior of an oxyfluoride glass and glass-ceramics with CaF$_2$ nanocrystals are described from the viewpoint of the size and morphology of CaF$_2$ nanocrystals. Crystal morphology and crack propagation behavior are observed by atomic force microscopy (AFM) and TEM. It has been suggested that the chemical bonding between CaF$_2$ nanocrystals and oxide glass matrix is weak. It has been discussed about the effect of such weakness of interface.

In chapter IV, surface crystal morphology of transparent glass-ceramics with CaF$_2$ nanocrystal have been clarified using TEM observations combined with focused ion beam (FIB). It was demonstrated that a fluorine deficient layer was observed and no crystal are appeared in the region. The mechanism of this crystallization behavior and the effect on their surface mechanical properties have been discussed.

In chapter V, the morphology and spatial distribution state of CaF$_2$ nanocrystals in transparent oxyfluoride glass-ceramics based on the ErF$_3$-CaF$_2$-Al$_2$O$_3$-SiO$_2$ system with different ErF$_3$ contents and addition of AlN have been examined. The effect of rare earth ion and AlN in elastic properties and the morphology of CaF$_2$ nanocrystals in oxyfluoride glass is clarified.
Chapter I - Introduction

In chapter VI, the optical properties and crystallization behavior of the glass with a composition of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ corresponding to BaAlBO$_3$F$_2$ have been examined. A crystal line composed by BaAlBO$_3$F$_2$ oxyfluoride single crystal having optical non-linearity was fabricated on the surface of new oxyfluoride glass with large fraction of fluorine, i.e. F/(F + O). Crystal line was investigated using transmission electron microscope (TEM). Optical properties such as luminescence, refractive index, transmittance and crystallization behavior of the glass were also investigated.

In summary, the main results and discussions through the whole of this thesis are summarized.

1.2. Introduction to Investigated Materials

1.2.1. Optical Application of Glass and Glass-ceramics

Because of the development of information technology, such as Cloud computing and video on demand, explosive in recent years, optical communications is strongly required to be higher speed and higher capacity. Silica glass fiber, extremely high transmittance, is widely used in transmission of the information of light. It has been achieved that the loss in silica glass fiber about 0.2 dB/km closes as theoretical value of 0.1 dB/km in the communication wavelength 1.55µm [18].

Because of the transmission of large-capacity and long-distance, this small transmission loss cannot be ignored. It is necessary to amplify the signal by the optical amplifier. Erbium-doped fiber amplifier is typically used as an optical amplifier to amplify the signal using the stimulated emission of Er$^{3+}$ in the silica glass. Rare-earth doped fiber amplifier has been proposed not only silica glass, but also fluoride and tellurite glasses with Pr$^{3+}$, Tm$^{3+}$, and Er$^{3+}$ ions in accordance with the amplification wavelength of the desired [17]. Not only glass, but also glass-ceramics have been investigated as the rare earth doped amplifier so far. Since a large amount of rare earth ions are dissolved in the calcium fluoride crystals (fluorite), with low phonon energy, and showing excellent luminescence, calcium fluoride nanocrystals in glass host investigated in this study have been developed for the novel amplifier [19].

Glass-ceramics with nanocrystals have been investigated as not only passive devices,
such as the transmission of information in optical communications, but also an optical active device such as optical switch and photonic modulation [20]. Nonlinear optical materials are key materials of the optical technology in the devices as applied optical switches, photonic modulators, high-speed optical shutter, optical memory, wavelength convertors, and light sensors. Currently, LiNO$_3$ or organic crystals having large optical nonlinearity have been investigated as optical modulators and optical switches [20]. Recently, Fresnoite crystallized glass investigated in this study is known to exhibit ferroelectricity and large second-order nonlinearity [21].

1.2.2. Fresnoite Glass-ceramics

Fresnoite is the mineral name of the crystal described as the chemical formula Ba$_2$TiSi$_2$O$_8$ and it named after discovered place, Fresno Country, California, United States [22]. Fresnoite Ba$_2$TiSi$_2$O$_8$ has the fresnoite structure, shown in Fig. 1 [23]. Fresnointe structure is composed of a stacked layered structure in which a layer composed of Ba ion and a layer formed vertex shared [Si$_2$O$_7$] two tetrahedral units and [TiO$_5$] pyramid units. Then, spontaneous polarization in [TiO$_5$] unit is the origin of the various functions. Thus, the polarization direction of the crystal will be [001]. Several types of fresnoite crystal using other cation such as Ba$_2$TiGe$_2$O$_8$, Sr$_2$TiSe$_2$O$_8$ have been proposed so far. Since these crystals consisted by only relatively large typical element of the Clarke numbers, it has also attracted attention from the viewpoint of elemental strategy. These fresnoite crystals show various optical and electric properties such as blue-white emission without dopant, dielectricity, optical nonlinearity, piezoelectricity, pyroelectricity and so on [24-31]. Because of the large optical nonlinearity of fresnoite crystal close to LiNbO$_3$, typically used for various optical devices, the crystal is expected as a wave control device materials [20].

The glass with the composition of stoichiometric composition of Ba$_2$TiSi$_2$O$_8$ crystal, i.e. 40BaO-20TiO$_2$40Si$_2$O$_3$ is vitrified. The glass-ceramics with Ba$_2$TiSi$_2$O$_8$ nanocrystals is obtained by heat-treatment for the glass in suitable condition. This glass-ceramics shows high optical transparency, and has optical and electrical properties as described above further. Recently, Takahashi et al. reported that the intensity of the blue-white light emitting and second harmonic generation in Fresnoite based nano-crystallized glass increases with the heat-treatment temperature [32]. The
researches such as the following have been carried out so far in this laboratory. Enomoto et al. fabricated the nanocrystallized glass fiber with the composition of $40\text{BaO}-20\text{TiO}_2-40\text{SiO}_2$ and succeeded in sharpening of the fiber by Meniscus etching method [33]. Toyohara et al. proposed that the optical secondary non-linearity and ferroelectricity is improved by heat-poling for the BTS nano-crystallized glass [34]. Takahashi et al. proposed that the transparent surface crystallized glasses with the composition of $30\text{BaO}-15\text{TiO}_2-55\text{GeO}_2$ show a high secondary optical non-linearity, resulting from $\text{Ba}_2\text{TiGe}_2\text{O}_8$, as large as the single crystal of $\text{LiNbO}_3$ [35-40].

Based on this background, various studies have been carried out in crystallized glass containing Fresnoite crystal [41-45]. All these study show the potential as practical photonic material.

Fig. 1. Crystal structure of fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$).
1.2.3. Oxyfluoride Glass and Glass-ceramics

Fluoride crystal and glass show high transparency in a wide range to the infrared to ultraviolet region and have less lattice vibration as 500-600 cm\(^{-1}\) compared to 1100 cm\(^{-1}\) in silicate glass. There are numerous studies for the application of lenses and low loss optical fiber. In particular, after the discovery of ZrF\(_4\)-BaF\(_2\) based glass [46], many new fluoride glasses have been developed. Fluoride glasses with the composition of many have been found so far, ZrF\(_4\)-BaF\(_2\)-LaF\(_3\)-AlF\(_3\)-NaF-based glass (ZBLAN) [17] is particularly well-known because of their excellent transparency and luminescence. AlF\(_3\)-based fluoride glass have been used as energy transmission fiber for Er:YAG laser (medical laser) because of their wide transmission range and high efficiency of energy convection. Fluoride glass is not only investigated as optical transmitter, but also phosphor due to their low phonon energy. Rare earth doped fluoride glass and crystal shows excellent high efficiency because of less non-radiation decay. Further, fluoride crystal of fluorite therefore can be added a large amount of rare earth ions, it is a promising material as a laser host and rare-earth doped fiber amplifier.

Although the fluoride glasses and crystals have an excellent optical function, there is a limit to the practical use because it shows thermally unstable, much brittle, and poor water resistance. Wang et al. proposed that the oxyfluoride glass-ceramics with CaF\(_2\) nanocrystals obtained by heat-treatments for the glass with the composition of CaF\(_2\)-NaF-Al\(_2\)O\(_3\)-SiO\(_2\) to solve these problems [19]. The glass-ceramics shows a high transparency due to the particle size is reduced by the control of an appropriate heat-treatment process. Moreover, it is often well researched in the ternary CaF\(_2\)-Al\(_2\)O\(_3\)-SiO\(_2\) system in recent years. In this material, Fluoride nanocrystals (CaF\(_2\)) act as excellent phosphor and oxide glass matrix mainly composed of aluminosilicate (Al\(_2\)O\(_3\)+SiO\(_2\)) have excellent heat resistance, chemical resistance and mechanical strength. Furthermore, strontium fluoride (SrF\(_2\)) and barium fluoride (BaF\(_2\)) having larger lattice space have been investigated because larger amount of rare earth can be dissolved. Rare earth doped oxyfluoride nanocrystallized glass have been proposed as laser host and fiber amplifier so far [47-57]. Recently not only used in fiber shape, but also used in a waveguide, crystal line on glass have been fabricated using femtosecond laser irradiation and laser-induced crystallization method [58-62].
1.3. Evaluation methods for Elastic and Mechanical Properties

1.2.1. Elastic Properties of Bulk: Cube Resonance Method

In the subject of the stress $\sigma$ on the glass, strain $\varepsilon$ is formed. When the strain is small, Hooke’s law is confirmed as $\sigma=E\varepsilon$ where $E$ is Young’s modulus. In order to brittle fracture in the high strain region, Hooke law always true unless such hydrostatic deformation glass material.

Young's modulus of the glass varies greatly depending on the packing factor and the bond strength [69]. Young’s modulus and Poisson’s ratio of most oxide glass is 50-90 GPa and 0.16-0.28, respectively [17,63,70]. There are two methods to measure the elastic properties, i.e. static method and dynamic method and static method (JIS R 1602-1995). In static method, isothermal modulus are obtained due to the stress is applied slowly in the sample. On the other hand, dynamic modulus is obtained in dynamic method doe to stress changes adiabatically. It is known that the differences of the values are small at room temperature. Three-point bending and four-point bending as a dynamic elastic modulus measurement method are well-known [64,74]. It is a technique for obtaining the elastic modulus from the relationship between stress and strain using Hooke’s law, but the amount of deformation is small for low stress fracture in the glass, the measurement accuracy is not sufficient. Further, since it takes a relatively large test piece uniform and is not suitable. In this study, a cubic resonance method, one of the dynamic elastic modulus measurement method, was used [65-67]. This method is possible to measure a small sample piece of 2mm square. Thus this method is suitable for the measurement of a sample preparation of large specimen is difficult.

Vibration modes in cube samples under free vibration are illustrated in Fig. 2. It can be classified into twist (EV), deflection (EV), shear (OS), expansion stretching (OD) mode. In isotropic materials such as glass, vibration mode is degenerate resonance spectrum like Fig. 3. Non-dimensional frequency is calculated using following equation [68];

$$a_n = \frac{f_n}{f_{EV-1}} a_{EV-1}$$  \hspace{1cm} (1)
where $f_n$ are resonance frequency ($n$ is vibration mode) and $a_{EV-1}$ is constant as 1.4285. After assigned the vibration mode for each $a_n$, Poisson's ratio $\nu$ can be estimated using Fig. 4 [65]. Shear sound velocity ($V_s$) can be estimated by following equation;

$$V_s = \frac{f_n}{a_n} L \pi$$  \quad (2)

where $L$ is length of the sample [65-67]. Longitudinal sound velocity ($V_l$), Young’s modulus ($E$), bulk modulus ($K$), and shear modulus ($G$) are calculated by the equations summarized in Table 1.

<table>
<thead>
<tr>
<th>Young’s modulus, $E$</th>
<th>Shear modulus, $G$</th>
<th>Bulk modulus, $K$</th>
<th>Poisson’s ratio, $\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{9KG}{3K+G}$</td>
<td>$\frac{E}{2+2\nu}$</td>
<td>$\frac{E}{3(1-2\nu)}$</td>
<td>$\frac{3K-2G}{2(3K+G)}$</td>
</tr>
<tr>
<td>$2G(1+\nu)$</td>
<td>$\frac{3KE}{9K-E}$</td>
<td>$\frac{2(1+\nu)}{3(1-2\nu)}$</td>
<td>$\frac{3K-E}{6K}$</td>
</tr>
<tr>
<td>$3K(1-2\nu)$</td>
<td>$\frac{3K(1-2\nu)}{2+2\nu}$</td>
<td>$\frac{3(3G-E)}{EG}$</td>
<td>$\frac{E}{2G-1}$</td>
</tr>
<tr>
<td>$\frac{\rho V_s^2(3V_l^2-4V_s^2)}{V_l^2-V_s^2}$</td>
<td>$\rho V_s^2$</td>
<td>$\rho \left(V_i^2 - \frac{4}{3} V_s^2\right)$</td>
<td>$\frac{1}{2} \left(1 - \frac{V_s^2}{V_l^2-V_s^2}\right)$</td>
</tr>
</tbody>
</table>
Fig. 2. Typical vibrating mode of a cubic specimen in cube resonance method [65].

Fig. 3. A typical degenerated cubic resonance spectra [65].
Fig. 4. Normalized frequency as the function of Poisson’s ratio [65].
1.2.2. Mechanical Properties: Vickers Test

Vickers test is widely used as a practical test method to measure the hardness of glass (JIS Z 2251-1992). The Vickers test is a method for determining the hardness of projected area of the indentation as shown in Fig. 5. Vickers indenter, pyramid indenter diamond face angle 136°, penetrate into the sample and permanent deformation is formed. Because the shape of the indentation is similar always mutually comparable without depending on the sample size and load versatility is high. Using the diagonal length of an indentation, Vickers hardness is determined from the following equation[78-81];

\[
H_v = 0.1891 \frac{P}{a^2}
\]

where P is maximum load during penetration. Because the Vickers test is convenient and important industrial parameters, this test is widely used in polymer, metal, ceramics, and so on. Furthermore, it is only as industrial parameter, but also reflecting strong physical properties of the material [71-73,75-77]. It is extremely important to approach scientifically respect material.

Fig. 5. Sketch of the impression made by Vickers indenter.
The theoretical strength of the glass reaches 10GPa in typical glass and that is one of the materials with the highest strength [11]. However, the strength of glass is only 100 MPa in practical, i.e. 2-3 orders less than the theoretical strength [12]. The reason of this is stress concentration occurring in the cracks present in the inner or surface of glass. According to the failure criterion of Griffith, stress $\sigma$ needed to break a brittle material containing cracks is represented by the following equation [82];

$$\sigma = \frac{1}{Y} \left( \frac{2 \gamma E}{C(1 - \nu^2)} \right)^{\frac{1}{2}}$$  \hspace{1cm} (4)

where $C$ is crack length, $Y$ is shape of crack or sample, $\gamma$ is surface fracture energy, and $\nu$ is Poisson’s ratio. In here, surface fracture energy means the energy required to make a new surface by crack propagation. In linear fracture mechanics, it is represented by the stress intensity factor $K$ in the stress field of the crack tips. $K_{IC}$ is a critical value leading to destruction of the crack opening (tension), i.e. mode I. Using the fracture toughness $K_{IC}$, fracture strength $\sigma_f$ is given as follows;

$$\sigma_f = \frac{1}{Y} \frac{K_{IC}}{a^{1/2}}$$  \hspace{1cm} (5)

From eq. (4) and (5), the relationship of the surface fracture energy and fracture toughness are described as the follow;

$$K_{IC} = \left( \frac{2 \gamma E}{1 - \nu^2} \right)^{\frac{1}{2}}$$  \hspace{1cm} (6)

As described above, the fracture strength of the glass is indicated by tensile stress value acting on the fracture origin. However, tensile test from the issue of support of the specimen is difficult in brittle materials such as normal glass, bending test of a flat plate or prism. Chevron-notch method, Double Cleavage Drilled Compression (DCDC) method, and Indentation Fracture (IF) method using a Vickers hardness tester has been carried out well. IF method is semi-empirical measurement method for determining the fracture toughness of development of cracks produced by indentation test using a cube corner indenter and Vickers indenter. IF method is conveniently measured fracture toughness $K_{IC}$ in small specimens. Using the 2C crack length of an indentation surrounding, using the fracture toughness test method of fine ceramics have been employed in the Japanese Industrial Standards (JIS R 1607), was determined by the following equation [77-80];
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\[ K_{IC} = 0.18 \left( \frac{E}{H_V} \right)^{1/2} \left( \frac{P}{C^{3/2}} \right) \] (7)

where \( E \) is the Young’s modulus and \( C \) is the characteristic crack length in Vickers indenter test.

Method of calculates the Brittleness \( B \) of the glass from the fracture toughness \( K_{IC} \) and hardness \( H \) have been proposed. Lawn and Marshal proposed following equation is widely used for glass materials [13]. However, it is an expression that targets a median crack, because it is not possible length median cracks employed be at least three times the diagonal length of the indentation.

\[ B = \frac{H_V}{K_{IC}} \] (8)

Furthermore, Ito et al. extend the equation and proposed more convenient equation as follow [15,16]:

\[ B = \gamma P^{-1/4} \left( \frac{C}{a} \right)^{3/2} \] (9)

where \( \gamma = 2.39 \text{N}^{1/4} / \text{\mu m}^{1/4} \). Brittleness of glass which represents well fragility in practical use at the time, the ease of cracking. For example, as an indicator of the ease caused the crack, is often used Crack Initiation Load (CIL), has a good relationships between the brittleness and crack initiation load [15,16,75,76]. Thus, brittleness is a useful indicator of good abrasion resistance in practical use of the glass.
1.2.3. Elastic and Mechanical Properties in Surface of The Sample: Nanoindentation Technique

1.2.3.1. Quasi-static Nanoindentation

Vickers hardness is calculated from the shape of the imprint. On the other hand, in nanoindentation (instrumented indentation) technique, the penetration depth is continuously obtained during applying a load to the tip [82-85]. Then, the hardness, Young's modulus etc. are carried out by the load - displacement curves. To distinguish the Young's modulus materials nature such as the values obtained by resonance method, in this paper, the Young's modulus measured by indentation method is denoted as the elastic modulus. Since it is possible to have a displacement control resolution of 0.01 nm or less, to know the characteristics of the infinitesimal area outermost surface, nanoindenter (Agilent, G-200) was used in this study. Berkovich tip is normally used because the shape workability is good to the indenter and projected area is same as the Vickers indenter of it [85]. In the nanoindentation technique, because it is possible to know the detailed deformation behavior of the material by not only the properties of the thin film material, the use of load-displacement curve as shown in Fig. 6, it is also very effective in the material bulk. In general, the elastic-plastic material such as glass shows a deformation as shown in Fig. 7. The universal hardness \( H_U \) stands for resistance to all deformed and is calculated using the following formula;

\[
H_U = \frac{P_{\text{max}}}{24.5h_t^2} \tag{11}
\]

where \( h_t \) is maximum indentation depth and \( P_{\text{max}} \) is maximum load.

Generally, at room temperature, about 50% of deformation (impression) on glass is elastic recovered after unloading. It is much important to clarify the elastic deformation behavior. Vickers test does not include the information of the elastic deformation due to the imprint is composed by only plastic deformation (viscous flow and plastic deformation). By contrast, it is possible to obtain information of the elastic deformation of the displacement curve by nanoindentation technique. By conventional nanoindentation (quasistatic nanoindentation), the load-displacement curve are obtained as Fig. 8. Contact projection area \( A \) and contact depth \( h_c \) are calculated by following equation;
\[ h_c = h_i - \epsilon \frac{P_{\text{max}}}{S} \]  

\[ A = 24.56 h_c^2 + \sum_{i=0}^{7} C_i h_i^{2i} \]

where S=dP/dh is a unloading slope of the curve and \( \epsilon \) is intercept factor depends on the shape of the tip and the case of Berkovich tip, \( \epsilon = 0.75 \) [85]. In Eq(13), the second term in the right side is a correction function due to the indenter is not theoretical trigonal pyramid in practice. Further, it is possible to use the contact area A obtained, to determine the indentation hardness \( H_{\text{in}} \) as following equation;

\[ H_{\text{IN}} = \frac{P_{\text{max}}}{A} \]  

Since the recovery of unloading is elastic completely, it conform to the rule of Hook’s law (E=\( \sigma/\epsilon \)). It is possible to estimate elastic modulus \( E_r \) using the stiffness \( S=dP/dh \) as follow;

\[ S = \frac{2}{\sqrt{\pi}} E_r \beta \sqrt{A} \]

where, \( \beta \) is the Geometry factor of the indenter, in here, \( \beta \) is 1.034 for the Berkovich tip. Because \( E_i \) contains the characteristics of the indenter, elastic modulus of the sample \( E_s \) was calculated by following equation;

\[ E_r = \left[ \frac{1-v_i^2}{E_s} + \frac{1-v_i^2}{E_i} \right]^{-1} \]

where \( E_i \) and \( v_i \) is the Young’s modulus and Poisson’s ratio for the indenter, respectively.

Deformation energy can be determined from the integral value of the load-displacement curves. Plastic deformation energy, \( A_p \), elastic deformation energy, \( A_e \), and total deformation energy, \( A_t \), are obtained by the following equation [86-89];

\[ A_p = A_t - A_e = \int_0^{h_t} Pdh - \int_{h_i}^{h_t} Pdh \]  

\[ A_e = \int_{h_i}^{h_t} Pdh \]  

\[ A_t = \int_0^{h_t} Pdh \]

Elastic recovery, the ratio of the elastic and plastic deformation energy, is calculated
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by the following equation [86];

\[
ER = \frac{A_e}{A_i}
\]  

(20)

Deformation energy per mole or per volume is evaluated by deformation energy and deformation volume calculated using indentation depth. Plastic deformation energy per mole, \(U_p\), elastic deformation energy, \(U_e\), and total deformation energy, \(U_t\), are calculated by the following equation;

\[
U_p = \frac{A_p}{V_p} \frac{M.W.}{d} = \frac{A_p}{\frac{1}{3} 24.5h_i^3} \frac{M.W.}{d}
\]  

(21)

\[
U_e = \frac{A_e}{V_e} \frac{M.W.}{d} = \frac{A_e}{\frac{1}{3} 24.5(h_i^3 - h_c^3)} \frac{M.W.}{d}
\]  

(22)

\[
U_t = U_e + U_p
\]  

(23)

where \(M.W.\) is the molecular weight and \(d\) is the density of the sample. Deformation energy per mole is the important parameter in order to infer the deformation behavior of the sample [92,93]. For instance, Suzuki et al. demonstrated that the deformation energy per mole of the silica glass is significantly less than single bond strength of Si-O [91]. It suggests the plastic deformation of silica glass is mostly composed by densification, only the change of packing, without bond breaking [32]. As described above, conventional nanoindentation is a useful approach to investigate the deformation behavior of the material in under deformation.
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Fig. 6. Typical load-unload curve in glass materials obtained by quasi-static nanoindentation.

Fig. 7. Deformation pattern of elastic-plastic body typical, such as glass
1.2.3.2. Continuous Stiffness Measurement (CSM)

As described above, quasi-static nanoindentation is the effective approach for the elastic and mechanical behaviors. By contrast continuous stiffness measurement (CSM) nanoindentation makes it possible to measure the contact stiffness, \( S \), can be alternatively measured during the loading portion. The concept of device configuration is shown in Fig. 8.. The CSM is accomplished by imposing a harmonic force, which is added to the nominally increasing load, \( P \), on the indenter [82,83]. Phase difference, \( \phi \), between the load, \( P \), and the displacement, \( h \), is produced during applying a frequency \( \omega \) as following equation;

\[
P = P_0 \exp(i\omega t) \tag{24}
\]
\[
h = h_0 \exp(i\omega t + \phi) \tag{25}
\]

Since CSM is represented by harmonic oscillator model, the stiffness, \( S \), is calculated from phase difference, \( \phi \), by the following equation;

\[
\left| \frac{P_0}{h(\omega)} \right| = \sqrt{ \left( \frac{1}{S^{-1} + K_f^{-1}} \right)^{-1} + K_s - m\omega^2 }^2 + \omega^2 C_f^2 \tag{27}
\]

or from the phase difference between the force and displacement signals, the phase angle, \( \phi \), is

\[
\tan(\phi) = \frac{\omega D}{(S^{-1} + K_f^{-1})^{-1} + K_s - m\omega^2} \tag{26}
\]

where the relevant components are the mass, \( m \), of the indenter, the spring constant, \( K_s \), of the leaf springs that support the indenter, the stiffness of the indenter frame \( K_f = 1/C_f \), where \( C_f \) is the compliance of the load frame and the damping coefficient, \( C \), due to the air in the gaps of the capacitor plate displacement sensing system. The contact stiffness, \( S \), can be given by following equation;

\[
S = \frac{P}{h} \cos \phi \tag{27}
\]

It is possible to determine the hardness, \( H_{IN} \), elastic modulus, \( E \), by the contact stiffness, using eq. (14)-(16). In quasi-static nanoindentation can obtain the hardness and elastic modulus at just maximum penetration depth. By contrast, CSM makes it possible to determine the hardness and elastic modulus continuously indentation depth for which it is possible to determine the stiffness \( S \) at all points in penetration. Therefore, it has attracted attention as a method to investigate the elastic properties of the surface of the materials.
Fig. 8. The harmonic oscillator model of continuous stiffness measurement (CSM).
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Chapter II
Micro- and Nano-Scale Deformations and Elastic Properties in Optically Transparent Glass-Ceramics with Fresnoite Ba$_2$TiSi$_2$O$_8$ Nanocrystals

2.1. Introduction

Recently, transparent glass–ceramics consisting of nonlinear optical/ferroelectric nanocrystals have received much attention, because such materials have high potentials for optical/electric applications such as microwave tunable application and optical switching devices [1,2]. Glass-ceramics based on the BaO-TiO$_2$-SiO$_2$ system have been extensively studied so far, [2-12] because fresnoite Ba$_2$TiSi$_2$O$_8$ (designated here as BTS) crystals exhibit good dielectric and nonlinear optical properties. Halliyal et al. [3] prepared grain-oriented glass-ceramics of BTS and proposed that those glass-ceramics are attractive candidate materials for hydrophones and several piezoelectric devices. It is also known that a glass with the composition corresponding to the fresnoite Ba$_2$TiSi$_2$O$_8$ crystalline phase, i.e., 40BaO-20TiO$_2$-40SiO$_2$ (mol%), show a prominent nanocrystallization, forming BTS nanocrystals (~100 nm). For instance, Enomoto et al. [9] succeeded in fabricating transparent glass-ceramic fibers with BTS nanocrystals showing second harmonic generations (SHGs). Maruyama et al. [11] reported the enhanced quantum yield of yellow luminescence of Dy$^{3+}$ ions incorporated into BTS nanocrystals formed in glasses. Very recently, the patterning of BTS crystals on the glass surface by laser irradiations has been proposed as a new design of spatially controlled BTS crystallization. [13-16] All these previous studies reported so far propose that transparent glass-ceramics with BTS nanocrystals have high potentials for...
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practical device applications. It is strongly required to clarify their elastic/mechanical properties, because glass-ceramics would be cut mechanically to get desired shapes and joined with other kinds of materials for device fabrications, but such studies have not been reported so far.

In this study, we focus our attention on micro- and nano-scale elastic and mechanical properties of glass-ceramics consisting of BTS nanocrystals. We approached these properties using cube resonance, usual Vickers indentation, and Berkovich nanoindentation (standard-type and continuous stiffness measurements (CSM)-type) methods, and the correlation between elastic/mechanical properties and BTS nanocrystallization, in particular micro- and nano-scale deformation behaviors, was discussed.

2.2. Experimental Procedure

A glass with the composition of $40\text{BaO}-20\text{TiO}_2-40\text{SiO}_2$ (mol%) was prepared using a conventional melt-quenching method. The composition of $40\text{BaO}-20\text{TiO}_2-40\text{SiO}_2$ corresponds to that of the $\text{Ba}_2\text{TiSi}_2\text{O}_8$ crystalline phase. Commercial powders of reagent grade $\text{BaCO}_3$, $\text{TiO}_2$, and $\text{SiO}_2$ were mixed, and a well-mixed batch was melted in a platinum crucible at 1500°C for 1 h in an electric furnace. The batch weight was 20 g. The melts were poured onto an iron plate heated at ~200°C and pressed with another plate. Two types of samples with different thicknesses of 1.2 mm and ~4.0 mm were prepared. The glass transition ($T_g$), crystallization onset ($T_x$), and crystallization peak ($T_p$) temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10K/min in air. Thermal expansion for the glass and glass-ceramics were carried out using thermomechanical analyzer (TMA-100). Sample size was 10x5x1.5mm and heating rate was 5 K/min for each sample.

The glasses were annealed at $T_g$ to release internal stresses and mechanically polished to a mirror finish with $\text{CeO}_2$ powders. The annealed glasses were heat-treated at different temperatures for 1 h in an electric furnace in air. The crystalline phase present in the heat-treated samples was examined by X-ray diffraction (XRD) analyses at room temperature using CuKα radiation. The morphology of crystals in the
crystallized glasses was observed by TEM and HR-TEM observations using JEM-2100F microscope (JEOL, Tokyo, Japan) working at 200 kV.

Densities (d) of the base glass and crystallized glasses at room temperature were determined with the Archimedes method using distilled water as an immersion liquid. The volume fraction of BTS nanocrystals (f) in the heat-treated samples were evaluated from the density of samples using the following equation:

\[ d_{\text{sample}} = (1 - f)d_{\text{glass}} + f d_{\text{crystal}} \]  

where \( d_{\text{sample}} \) is the density of heat-treated sample, \( d_{\text{glass}} (=4.294) \) is the density of BTS glass, and \( d_{\text{crystal}} (=4.446) \) is the density of \( \text{Ba}_2\text{TiSi}_2\text{O}_8 \) crystal. [20]

Bulk elastic properties such as Young’s modulus and Poisson’s ratio at room temperature in air for the glass and crystallized samples were determined from measurements of longitudinal (\( V_l \)) and shear (transvers) (\( V_s \)) ultrasonic velocities. The values of \( V_l \) and \( V_s \) were measured using a cube resonance method with the frequency of 0.2–1 MHz, in which the sample size was 3.5 mm × 3.5 mm × 3.5 mm. [16,17] The values of Young’s modulus (\( E \)), shear modulus (\( G \)), bulk modulus (\( K \)), and Poisson’s ratio (\( \nu \)) were calculated from the values of \( V_l \) and \( V_s \) using the following equations:

\[ E = 2dV_s^2(1 + \nu) \]  
\[ G = dV_s^2 \]  
\[ K = d\left(V_l^2 - \frac{4}{3}V_s^2\right) \]  
\[ \nu = \frac{1}{2}\left(1 - \frac{V_l^2}{V_l^2 - V_s^2}\right) \]

Eqs. (2) to (5) have been applied to various glasses and glass-ceramics with nanocrystals for evaluations of elastic properties. [21-24] Usual Vickers indentations (loads: 1~19.6 N) at room temperature (\( \sim25^\circ\) C) in air (relative humidity\( \sim48\%\)) were applied to the samples using Akashi HM-114, and Vickers hardness (\( H_v \)) and indentation fracture toughness (\( K_c \)) at room temperature were measured ten times and calculated the average and standard deviation. From deformation patterns in Vickers indentation tests, the values of Vickers hardness \( H_v \) were evaluated using Eq. (9):

\[ H_v = \frac{P}{\alpha_o a^2} \]

where \( P \) is an applied load, \( a \) is a characteristic indentation diagonal, and \( \alpha_o \) is an
indenter constant of 2.157 in the present experiment used a diamond pyramid indenter. The values of characteristic crack length, $C$, in Vickers indenter test give information on the resistance to fracture, and many models for the estimation of $K_c$ have been proposed. The following equation has been recommended by Japanese Industrial Standards (JIS) for ceramics. [25]

$$K_c = 0.018 \left( \frac{E}{H_v} \right)^{1/2} \left( \frac{P}{C^{3/2}} \right)$$  \hspace{1cm} (10)

where $E$ is the Young’s modulus estimated from the cube resonance method. Eq. (10) is almost the same as that proposed by Anstis et al. [26]

Nanoindentation measurements at room temperature (22°C) in air (relative humidity ~45%) were carried out using a nanoindentation apparatus (Agilent Tech., Nano Indenter G-200), in which load/unload displacement curves, i.e., the relation between load ($P$) and indentation depth ($h$), are obtained. A Berkovich diamond indenter was used. In this study, two methods were used. One is the standard nanoindentation test (quasi-static indentation), in which monotonic loading and unloading with a constant speed of 10 mN/s were applied, and the contact stiffness (S) was determined from the slope of the unloading curve. The maximum load was 50–500 mN. The other is the continuous stiffness measurement (CSM) test, in which a small oscillating excitation with an amplitude equal to about 1 nm was superimposed to the loading that allows us to continuously measure the contact stiffness during the experiment and, consequently, to analyze the totality of the loading curve, i.e., to capture the evolution of the contact pressure with the depth in one experiment. [27-30] In CSM experiments carried out in the present study, strain rate was 0.05/s and the frequency of the oscillation was 75 Hz for the DCM head and 45 Hz for XP head. CSM tests for each sample were conducd ten times at different positions and average values were evaluated. The Berkovich indenter was calibrated on fused silica before and after all experiments. All nanoindentation tests obeyed the International Organization for Standardization (ISO 14577).
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2.3. Results and Discussion

2.3.1. Ba$_2$TiSi$_2$O$_8$ Nanocrystals: Formation and Volume Fraction

A glass with the composition of 40BaO-20TiO$_2$-40SiO$_2$ (mol%) prepared in this study is designated here as BTS glass. DTA curves for the BTS glass are shown in Fig. 1. The BTS glass shows the values of $T_g$=730˚C, $T_x$=816˚C, and $T_p$=832˚C. The glass plates with polished surfaces were heat-treated at temperatures of 750, 760, 770, 780, and 790˚C for 1 h in air and cooled to room temperature at a cooling rate of 1 K/min in an electric furnace. As demonstrated in previous papers, [6-12] the glass of 40BaO-20TiO$_2$-40SiO$_2$ (mol%) shows the crystallization of fresnoite Ba$_2$TiSi$_2$O$_8$ nanocrystals (designated here as BTS crystals) with diameters of ~100 nm through a homogeneous nucleation. The XRD patterns at room temperature for some heat-treated samples prepared in this study are shown in Fig. 2. All XRD peaks are assigned to the so-called fresnoite Ba$_2$TiSi$_2$O$_8$ crystalline phase with a space group $P4bm$ (JCPDS: No. 022-0513). The size of BTS crystals was also estimated to be ~100 nm in all heat-treated samples using Scherrer’s equation from the peak position and the peak-width at half-maximum, collected from the instrumental broadening, irrespective of the heat treatment temperature, as similar to the previous papers. [6-12] It is also confirmed that all heat-treated samples have a good optical transparency. The optical photographs for the glass and some heat-treated samples are also shown in Fig. 2.

Morphology of nanocrystals was observed by TEM. TEM images for the glass-ceramics (760˚C and 790˚C) are shown in Fig. 3. Ellipsoidal nanocrystals with the size of ~200 nm were observed in both samples. A high resolution TEM image for the glass-ceramics (790˚C for grain boundary) are shown in Fig. 4. Lattice fringe of Ba$_2$TiSi$_2$O$_8$ were observed. The distance between the crystals in the glass-ceramics obtained at 760˚C and 790˚C were found to be several tens or hundreds nanometers in inside region and several nanometers, respectively. The distance of Ba$_2$TiSi$_2$O$_8$ nanocrystals in the glass-ceramics (790˚C) are too close for the volume fractions. Volume factions can be underestimated due to the density decreased by strain.

The density of the samples heat-treated at 750~790 ˚C are shown in Fig. 5. The volume fractions ($f$) of BTS nanocrystals in the heat-treated samples were evaluated
from the density \(d\) of samples using eq. (1), and the volume fraction for the samples are also shown in Fig. 5. For instance, the samples heat-treated at 760°C and 790°C give the values of \(f=7.9\%\) and \(f=54.5\%\), respectively. It is found that the BTS nanocrystals are formed rapidly at temperatures of around 770°C below the crystallization temperature of \(T_c=816°C\).

TMA curves for the glass and glass-ceramics (770°C and 790°C) are shown in Fig. 6. The temperatures of glass transition and softening for the glass and for glass-ceramics (770°C) were almost same. It indicated that the structure of remaining glass in glass-ceramics were same as the precursor glass. The glass transition Coefficients of thermal expansion obtained using slope in 50-350°C are shown in Fig. 7. CTE of precursor glass was \(\alpha=107\times10^{-7}\) (K\(^{-1}\)). CTE were linearly decreased with increased with increasing volume fraction of BTS nanocrystals. CTE of the BTS single crystal is reported as much smaller value than the crystals value, i.e., \(\alpha_1=87\times10^{-7}\) (K\(^{-1}\)) in \(a, b\)-axis and \(\alpha_3=9.3\times10^{-7}\) (K\(^{-1}\)) in \(c\)-axis. [51]

![Fig. 1. Differential thermal analyses patterns for the powdered and bulk samples of the BTS glass. The heating rate was 10 K/min.](image-url)
**Fig. 2.** XRD patterns at room temperature for the precursor BTS glass and crystallized (at 770 and 790°C for 1 h) samples. All XRD peaks are assigned to the fresnoite Ba$_2$TiSi$_2$O$_8$ crystalline phase. The optical photographs for the samples are included.
Fig. 3. TEM image (bright field) of the glass-ceramics (at 760°C and 790°C for 1h).
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Fig. 4. High resolution TEM image of the glass-ceramics (at 790°C for 1h).

Fig. 5. Density and volume fraction of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals for the samples heat-treated at 730~790°C for 1 h as a function of heat-treatment temperature.
Fig. 6. TMA curves for the glass and glass-ceramics (at 770°C and 790°C for 1h).

Fig. 7. Coefficients of thermal expansion (CTE) in 50-350°C for the glass and glass-ceramic (at 770°C and 790°C for 1h).
2.3.2. Bulk Elastic Properties: Cube Resonance Method

The values of longitudinal sound velocity \( (V_l) \) and shear sound velocity \( (V_s) \) obtained using a cube resonance method for the BTS glass and glass-ceramics are shown in Table 1. It is seen that both velocities increase with increasing the volume fraction of BTS nanocrystals. The data obtained for BTS glass and glass-ceramics are summarized in Table 1. It is seen that all values of \( E \), \( G \), and \( K \) increase with increasing the volume fraction of BTS nanocrystals. For instance, the BTS glass show the values of \( E=79.9 \text{ GPa} \), \( G=31.1 \text{ GPa} \), and \( K=61.3 \text{ GPa} \). On the other hand, the glass-ceramic with the volume fraction of 54.5% of BTS nanocrystals has the values of \( E=105.6 \text{ GPa} \), \( G=41.1 \text{ GPa} \), and \( K=82.4 \text{ GPa} \). That is, elastic properties of BTS glass are largely enhanced due to the nanocrystallization. The Young’s modulus is plotted as a function of the volume fraction of BTS nanocrystals in Fig. 8, indicating the presence of the linear relation between them.

According to lattice dynamics, [32] the Debye temperature, \( \theta_D \), can be calculated from the mean sound wave velocity, \( V_m \), using Eq. (11):

\[
\theta_D = \frac{h}{k} \left( \frac{9Npd}{4\pi M} \right)^{1/3} V_m
\]

where \( h \) is the Planck’s constant, \( k \) is the Boltzmann’s constant, \( M \) is the molecular weight, and \( r \) is the number of atoms in the chemical formula. The mean sound wave velocity is obtained using the values of \( V_l \) and \( V_s \). Eq. (11) has been applied to evaluate Debye temperatures in various glasses and glass-ceramics. [17,22,23] The Debye temperatures estimated using Eq. (11) for BTS glass and glass-ceramics are given in Table 1 and are plotted as a function of the volume fraction of BTS nanocrystals in Fig. 9, indicating the presence of the linear relation between them as similar to Young’s modulus.

As can be seen in Table 1, the BTS glass and crystallized samples give the Poisson’s ratio of 0.28~0.29, almost irrespective of the volume fraction of BTS nanocrystals. Poisson’s ratio depends on the dimensionality of the structure and cross-link density. [34] Typical three-dimensional glasses like SiO\(_2\) or GeO\(_2\) have \( \nu \sim 0.15 \), whereas B\(_2\)O\(_3\) including two-dimensional structure have \( \nu \sim 0.3 \). Many oxide glasses including both network formers such as SiO\(_2\) and network modifiers such as Na\(_2\)O have the value of \( \nu \sim 0.2 \), because addition of network modifier oxide results in creation of non-bridging oxygen and hence reduction in dimensionality. It is, therefore, considered from the
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Poisson’s ratio that even in the BTS glass with SiO$_2$ of 40 mol% the three-dimensional network structure of SiO$_4$ tetrahedra is largely broken due to the additions of BaO (40 mol%) and TiO$_2$ (20 mol%).

Bergman and Kantor [35] proposed a new parameter $F_d$ for network connectivity for an inhomogeneous random mixture of fluid and a solid backbone near the percolation limit, and it is expressed by Eq. (12):

$$F_d = \frac{4C_{44}}{K}$$  \hspace{1cm} (12)

where $C_{44}$ is an adiabatic second-order elastic stiffness tensor component and is evaluated from the relation of $C_{44}=dV_s^2$ for isotropic materials such as glass. This new parameter $F_d$ is called the fractal bond connectivity and gives information on effective dimensionality of materials; $F_d=3$ for three-dimensional coordination polyhedra, $F_d=2$ for two-dimensional layer structures, and $F_d=1$ for one-dimensional chains. [33] The $F_d$ values of the BTS glass and glass-ceramics were estimated using Eq. (12), and the results are shown in Table 1. The values of $F_d=1.98~2.03$ are obtained for all samples, almost irrespective of the nanocrystallization. The values of fractal bond connectivities ($F_d=1.98~2.03$) also suggest that three-dimensional network structures consisting of SiO$_4$ units are largely broken due to the presence of a large amount of BaO (40 mol%) and TiO$_2$ (20 mol%).

The structure of 40BaO-20TiO$_2$-40SiO$_2$ glass, in particular the valence and coordination states of Ti ions, has been studied by using various techniques. Markgraf et al. [36] examined the structure of BTS glass from Raman scattering spectrum measurements and reported that most of Ti$^{4+}$ ions are five-fold coordination. Schneider et al. [37] reported from X-ray photoelectron spectroscopy measurements that Ti$^{4+}$ ions possess ~25% four-fold, ~60% five-fold and ~15% six-fold coordinations in BTS glass. On the other hand, in the structure of fresnoite Ba$_2$TiSi$_2$O$_8$ crystals, corner-linked TiO$_5$ pentahedra and pyrosilicate groups Si$_2$O$_7$ comprise flat sheets perpendicular to the [001] direction, and these sheets are interconnected by tenfold barium ions. [38] These structural features in fresnoite Ba$_2$TiSi$_2$O$_8$ crystals would give the values of the Poisson’s ratio of $\nu=0.29$ and the fractal bond connectivity of $F_d=1.99$ for the glass-ceramics with the volume fraction of 54.5% of BTS nanocrystals.

As can be seen in Figs. 8 and 9, the values of Young’s modulus and Debye temperature increase linearly with increasing the volume fraction of BTS nanocrystals.
in the glass-ceramics. Such linear correlations were confirmed for other elastic properties of shear modulus and bulk modulus as shown in Table 1. Poisson’s ratio of the base glass and glass-ceramics are almost the same ($\nu=0.28-0.29$), and Bulk elastic properties of the glass-ceramics with BTS nanocrystals are expressed as a simple (parallel) composite model of the glassy phase and nanocrystals. The Young’s modulus of the glass-ceramics ($E_{\text{sample}}$) would be expressed as follows:

$$E_{\text{sample}} = (1 - f)E_{\text{glass}} + fE_{\text{nanocrystal}}$$  \hspace{1cm} (13)$$

where $E_{\text{glass}}$ and $E_{\text{nanocrystal}}$ are Young’s moduli of the base glass and BTS nanocrystals, respectively. Similar relations would be proposed for other elastic properties of $G$, $K$, and $q_0$. We estimated the bulk elastic properties of BTS nanocrystals using Eq. (13), and the following values were obtained, i.e., $E_{\text{nanocrystal}}=125$ GPa, $G_{\text{nanocrystal}}=48$ GPa, $K_{\text{nanocrystal}}=101$ GPa, and $q_0$ (nanocrystal)$=656$ K. It is noted that the ratio of $E_{\text{glass}}/E_{\text{nanocrystal}}=1.56$. These results, therefore, suggest that fresnoite $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals with a diameter of $\sim100$ nm formed in 40BaO-20TiO$_2$-40SiO$_2$ glass have much higher bulk elastic properties compared with the corresponding precursor glass. It is desired to compare elastic properties of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals estimated using Eq. (13) with properties of bulk fresnoite $\text{Ba}_2\text{TiSi}_2\text{O}_8$ single crystal, although elastic properties of fresnoite $\text{Ba}_2\text{TiSi}_2\text{O}_8$ single crystal have not been reported so far.

The elastic properties of optical transparent GeO$_2$-based (15K$_2$O-25Nb$_2$O$_5$-50GeO$_2$) and TeO$_2$-based (15K$_2$O-15Nb$_2$O$_5$-68TeO$_2$-2MoO$_3$) nanocrystallized glasses have been examined using a cube resonance method, and it has been found that the elastic properties of the precursor glasses are largely improved due to the nanocrystallization. [23,24] The values of elastic constants reported for their glass-ceramics are given in Table 2 together with the data for the glass-ceramics with BTS nanocrystals obtained in this study. It is seen that glass-ceramics with SiO$_2$-based nanocrystals show much higher elastic properties compared with glass-ceramics with TeO$_2$-based or GeO$_2$-based nanocrystals. For instance, Young’s moduli are 69.7 GPa for TeO$_2$-based sample, 85.5 GPa for GeO$_2$-based sample, and 105.6 GPa for SiO$_2$-based sample. It should be pointed out that the single bond strength ($B_{\text{M-O}}$) of SiO$_2$, GeO$_2$, and TeO$_2$ oxides is in the order of $B_{\text{Si-O}}$ (443 kJ/mol) $> B_{\text{Ge-O}}$ (343 kJ/mol) $> B_{\text{Te-O}}$ (284 kJ/mol). [39,40] It is considered that the chemical bond strength of main constituent oxides SiO$_2$, GeO$_2$, and TeO$_2$ has a large contribution on elastic properties even in the glass-ceramics with
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nanocrystals.

**Fig. 8.** Values of the Young’s modulus evaluated using a cube resonance method as a function of the volume fraction of Ba$_2$TiSi$_2$O$_8$ nanocrystals for the glass-ceramics.

**Fig. 9.** Debye temperature evaluated using a cube resonance method as a function of the volume fraction of Ba$_2$TiSi$_2$O$_8$ nanocrystals for the glass-ceramics.
**Table 1**

Elastic properties evaluated using a cube resonance method for the BTS (40BaO-20TiO₂-40SiO₂) glass and heat-treated samples. $d$ is the density, $V_m$ is the molar volume, $f$ is the volume fraction of BTS (Ba₂TiSi₂O₈) nanocrystals, $V_s$, $V_l$, and $V_m$ are shear, longitudinal, and mean sound velocities, respectively, $E$ is the Young’s modulus, $G$ is the shear modulus, $K$ is the bulk modulus, $\nu$ is the Poisson’s ratio, $\theta_D$ is the Debye temperature, and $F_d$ is the fractal bond connectivity.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Glass</th>
<th>Heat-treated sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>760°C</td>
<td>770°C</td>
</tr>
<tr>
<td>$d$ (g/cm³)</td>
<td>4.294</td>
<td>4.306</td>
</tr>
<tr>
<td>$V_m$ (cm³/mol)</td>
<td>23.60</td>
<td>23.54</td>
</tr>
<tr>
<td>$f$ (%)</td>
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<td>7.9</td>
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<tr>
<td>$V_s$ (m/s)</td>
<td>2693</td>
<td>2744</td>
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<tr>
<td>$V_l$ (m/s)</td>
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<td>4955</td>
</tr>
<tr>
<td>$V_m$ (m/s)</td>
<td>3002</td>
<td>3059</td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>79.9</td>
<td>83.2</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>31.1</td>
<td>32.4</td>
</tr>
<tr>
<td>$K$ (GPa)</td>
<td>61.3</td>
<td>64.2</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.28</td>
<td>0.28</td>
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<tr>
<td>$\theta_D$ (K)</td>
<td>522</td>
<td>532</td>
</tr>
<tr>
<td>$F_d$</td>
<td>2.03</td>
<td>2.02</td>
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</table>
Table 2

Elastic properties evaluated using a cube resonance method for optical transparent glass-ceramics consisting of nanocrystals. The data for BTS (40BaO-20TiO₂-40SiO₂) glass-ceramics were obtained in this study. The data for KNbGeO₅ (25K₂O-25Nb₂O₅-50GeO₂) and KNbTeMo (15K₂O.15Nb₂O₅.68TeO₂.2MoO₃) glasses were taken from Ref. [29,30], respectively. \(d\) is the density, \(E\) is the Young’s modulus, \(G\) is the shear modulus, \(K\) is the bulk modulus, \(\nu\) is the Poisson’s ratio, \(\theta_D\) is the Debye temperature, and \(F_d\) is the fractal bond connectivity.

<table>
<thead>
<tr>
<th>Properties</th>
<th>KNbTeMo</th>
<th>KNbGeO₅</th>
<th>BTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d) (g/cm³)</td>
<td>4.903</td>
<td>3.906</td>
<td>4.377</td>
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<tr>
<td>(E) (GPa)</td>
<td>69.7</td>
<td>85.5</td>
<td>105.6</td>
</tr>
<tr>
<td>(G) (GPa)</td>
<td>28.6</td>
<td>35.0</td>
<td>41.1</td>
</tr>
<tr>
<td>(K) (GPa)</td>
<td>41.5</td>
<td>50.9</td>
<td>82.4</td>
</tr>
<tr>
<td>(\nu)</td>
<td>0.22</td>
<td>0.215</td>
<td>0.29</td>
</tr>
<tr>
<td>(\theta_D) (K)</td>
<td>447</td>
<td>575</td>
<td>597</td>
</tr>
<tr>
<td>(F_d)</td>
<td>2.75</td>
<td>2.75</td>
<td>1.99</td>
</tr>
</tbody>
</table>
2.3.3. Micro-scale Deformation: Vickers Indentation

In order to clarify the feature in deformation behaviors in the glass-ceramics consisting of BTS nanocrystals, usual Vickers indentation tests were carried out in this study. Two photographs for the BTS glass and glass-ceramics (heat-treated at 790°C for 1h: the volume fraction of BTS nanocrystals \( f = 54.5\% \)) obtained by Vickers indentation with a load of 9.8N are shown in Fig. 10. In both samples, radial cracks are observed.

The values of Vicker hardness \( (H_v) \) for the BTS glass and glass-ceramics were evaluated using Eq. (9) and summarized in Table 3. For instance, the BTS glass show the values of \( H_v = 4.97 \text{ GPa} \pm 0.02 \), and the heat-treated sample with the volume fraction of 54.5% of BTS nanocrystals has the values of \( H_v = 5.93 \text{ GPa} \pm 0.05 \). The Vickers hardness is plotted as a function of the volume fraction of BTS crystals in Fig. 11, indicating that the Vickers hardness increases with increasing the volume fraction.

The values of \( K_c \) for the samples were evaluated using Eq. (10), and the following values were obtained; \( K_c = 0.48 \text{ MPam}^{1/2} \pm 0.07 \) or the BTS glass and \( K_c = 1.04 \text{ MPam}^{1/2} \pm 0.04 \) for the heat-treated sample with the volume fraction \( (f) \) of 54.5% of BTS nanocrystals. The values of \( K_c \) were plotted as a function of the volume fraction of BTS crystals in Fig. 12, indicating that the indentation fracture toughness of the BTS glass is largely enhanced due to the nanocrystallization.

According to the fracture mechanics, the relationship between fracture toughness and Young’s modulus is expressed by the following equation; [41]

\[
K_c = \frac{2E\gamma_f}{\sqrt{1-v^2}}
\]

(14)

where \( \gamma_f \) is the fracture surface energy. The fracture surface energy is termed as the energy associated with surface formation during fracture, and thus it controls the fracture process and is important in understanding the underlying mechanism affecting the fracture of solid materials. [42] The values of \( \gamma_f \) for the BTS glass and glass-ceramics were estimated using Eq. (11), and the results are shown in Table 3. For instance, the values of 1.3 J/m² for the BTS glass and 4.7 J/m² for the heat-treated sample with the volume fraction of 54.5% of BTS nanocrystals were obtained, indicating the fracture surface energy is largely enhanced due to the nanocrystallization. Todd et al. [47] and Kotoul et al. [48] discussed increase fracture toughness with increase alumina reinforced glass matrix caused by increase Young’s modulus and other toughening mechanism, such as compressive residual stress and crack deflection.
Increase fracture surface energy can be caused by increase compressive residual stress and crack deflection.

The evaluation of brittleness of glass and ceramics is important for materials design and applications. [43] The brittleness, $B$, defined as the ratio of hardness and fracture toughness, which was proposed by Lawn and Marshall [44] and is expressed by Eq. (15), is used in this study.

$$B = \frac{H}{K_C} \quad (15)$$

Brittleness of the glass and glass-ceramics are shown in Fig. 13. BTS glass and crystallized (54.5% of BTS nanocrystals) sample give the values of $B=10.4$ and $B=5.7$ $\mu m^{-1/2}$, respectively, indicating that the brittleness of BTS glass is largely improved by nanocrystallization. The relationship between the fracture surface energy and brittleness is shown in Fig. 13. As expected from Eqs. (14) and (15), the brittleness decreases with increasing the fracture surface energy.

The values of $H_v$, $K_C$, $\gamma_f$, and $B$ estimated in this study for the BTS and glass-ceramics with BTS nanocrystals are summarized in Table 3. As can be seen in Figs. 11 and 12, the change of $H_v$, $K_C$, and $B$ is not monotonous against the volume fraction of BTS nanocrystals. It should be pointed out that this behavior is in contrast with the behavior of elastic properties (e.g., Fig. 8) estimated from the cube resonance method. Torres et al. [45] evaluated the values of $K_C$, $\gamma_f$, and $B$ using Eqs. (13) to (15) for TeO$_2$-based glass (15K$_2$O-15Nb$_2$O$_5$-70TeO$_2$) and nanocrystallized glasses and reported that poor mechanical properties of the precursor TeO$_2$-based glass are improved through the sufficient nanocrystallization.
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Fig. 10. Photographs for the precursor BTS glass and glass-ceramics (heat-treated at 790°C for 1h: the volume fraction of BTS nanocrystals $f=54.5\%$) obtained by Vickers indentation with a load of 9.8N.
**Fig. 11.** Values of the Vickers hardness evaluated using a Vickers indentation technique as a function of the volume fraction of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals for the glass-ceramics. The measurement was carried out in air atmosphere at room temperature.

**Fig. 12.** Values of the Fracture toughness evaluated using a Vickers indentation technique as a function of the volume fraction of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals for the glass-ceramics. The measurement was carried out in air atmosphere at room temperature.
Fig. 13. Values of the brittleness evaluated using a Vickers indentation technique as a function of the volume fraction of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals for the glass-ceramics. The measurement was carried out in air atmosphere at room temperature.

Fig. 14. Relationship between the fracture surface energy and brittleness evaluated using a Vickers indentation technique for the glass and glass-ceramics with $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals.
### Table 3.
Elastic and mechanical properties of the BTS (40BaO-20TiO₂-40SiO₂) glass and heat-treated samples evaluated from usual Vickers indentation and nanoindentation (standard-type) methods. $H_v$ is Vickers hardness, $K_c$ is the fracture toughness, $\gamma_f$ is the fracture surface energy, $B$ is the brittleness, $E_{IT}$ is the elastic modulus, $H_{IT}$ is the indentation hardness, $H_M$ is Marten hardness, and $E_R$ is the elastic recovery. Errors are ±0.05 GPa for $H_v$, ± 0.01 MPa m$^{-1/2}$ for $K_c$, ± 0.5 µm$^{1/2}$ for $B$.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Glass</th>
<th>Heat-treated sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>760°C   770°C 780°C 790°C</td>
</tr>
<tr>
<td>Vickers (P=0.98 N for $H_v$, P=10-20 N for $K_c$ and $B$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_v$ (GPa)</td>
<td>4.97</td>
<td>5.40    5.66    5.95    5.93</td>
</tr>
<tr>
<td>$K_c$ (MPa m$^{-1/2}$)</td>
<td>0.48</td>
<td>0.62    0.68    0.84    1.04</td>
</tr>
<tr>
<td>$\gamma_f$ (J/m²)</td>
<td>1.3</td>
<td>2.1     2.4     3.2     4.7</td>
</tr>
<tr>
<td>$B$ (µm$^{1/2}$)</td>
<td>10.4</td>
<td>8.8     8.3     7.0     5.7</td>
</tr>
<tr>
<td>Nanoindentation ($P_{max}$=500 mN, Loading/unloading speeds=10 mN/s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{IT}$ (GPa)</td>
<td>88.5</td>
<td>93.0    98.4    108.3   113.4</td>
</tr>
<tr>
<td>$H_{IT}$ (GPa)</td>
<td>6.71</td>
<td>7.02    7.64    8.28    8.36</td>
</tr>
<tr>
<td>$E_R$ (%)</td>
<td>42.9</td>
<td>43.7    44.9    45.3    45.3</td>
</tr>
</tbody>
</table>
2.3.4. Nano-scale Deformation: Standard Nanoindentation

The load/unload displacement curves at the maximum load of 500 mN in air for the BTS glass and heat-treated (760 and 790°C) samples are shown in Fig. 15, as examples. In these standard-type nanoindentation tests, monotonic loading and unloading with a constant speed of 10 mN/s were applied, and the contact stiffness (S) was determined from the slope of the unloading curve. Furthermore, the load in Fig. 15 was held at 500 mN for 10 s to avoid the creep affecting the unloading behavior. The maximum load was changed in the range of 10~500 mN. The curves shown in Fig. 15 demonstrate that the BTS glass and nanocrystallized glasses with BTS nanocrystals show both elastic and plastic deformations during nanoindentations with a Berkovich indenter.

The indentation Young’s modulus, $E_{IT}$, for a given sample is calculated from the load/unload displacement curves following the method given by Oliver and Pharr. [29] The elastic modulus is given by the following equation:

$$\frac{1}{E_r} = \frac{(1-\nu)}{E_{IT}} + \frac{(1-\nu_i^2)}{E_i}$$  \hspace{1cm} (2)

where $\nu$ is Poisson’s ratio for the sample, and $E_i$ and $\nu_i$ are Young’s modulus and Poisson’s ratio for the indenter. In this study, a Berkovich diamond indenter was used, and the elastic parameters for diamond are $E_i=1140$ GPa, $\nu_i=0.07$. [49] $E_r$ is the reduced modulus for the sample, which is found from indentation test data and is given by the following equation:

$$S = \frac{dP}{dh} = \frac{1}{\beta \sqrt{\pi}} \frac{2}{E_r \sqrt{A}}$$  \hspace{1cm} (3)

where $S$ is the initial unloading contact stiffness, $h$ is the penetration depth, $\beta$ is a constant of the geometry of indenter tip, i.e., $\beta=1.034$ for the Berkovich tip, and $A$ is the projected area of contact at the load. Furthermore, the indentation hardness, $H_{IN}$, is defined by the following equation:

$$H_{IN} = \frac{P}{A}$$  \hspace{1cm} (4)

The values of the indentation Young’s modulus ($E_{IT}$) and hardness ($H_{IN}$) at $P=500$ mN were evaluated using Eqs. (2) to (4) for the BTS glass and heat-treated samples. The results are given in Table 4, and the values of $E_{IT}$ are shown in Fig. 16 as a function of the volume fraction of BTS nanocrystals. It is found that both values of $E_{IT}$ and $H_{IT}$
increase with increasing the volume fraction. That is, the indentation elastic properties in the BTS glass are also enhanced due to the formation of BTS nanocrystals.

Since the product of load \( P \) (N) and displacement \( h \) (m) has a dimension of energy (J), it is possible to estimate consumed energies for elastic deformation and plastic deformation from load/unload displacement curve. The total consumed deformation energy, \( U_t \), elastic deformation energy, \( U_e \), and plastic deformation energy, \( U_p \), are given by the following equations:

\[
U_t = \frac{\int_0^{h_p} Pdh}{V} \frac{M}{d}
\]

\[
U_e = \frac{\int_{h_p}^{h_f} Pdh}{V} \frac{M}{d}
\]

\[
U_p = U_t - U_e
\]

where \( h_p \) and \( h_f \) are the indenter displacement at peak load and the final depth of the contact impression after unloading, respectively, \( V \) is the volume of indent, \( M \) and \( d \) are the molecular weight and density of the sample, respectively.

The values of \( U_e \) and \( U_p \) at different maximum loads for the BTS glass and nanocrystallized glasses were estimated from load/unload displacement curves using Eqs. (5) to (7) and are shown in Figs. 17 and 18. It is seen that the crystallized samples with BTS nanocrystals have larger elastic and plastic deformation energies compared with the precursor BTS glass. The values of \( U_e \) and \( U_p \) at the maximum load of 500 mN for the glass and crystallized samples are shown in Fig. 19 as a function of the volume fraction of BTS nanocrystals. It is seen that both values increases with increasing the volume fraction. It is noted that the plastic deformation energy \( U_p \) is in the range of 115~140 kJ/mol, which is close to the single bond strength (\( B_{Ba-O}=138 \) kJ/mol) of BaO oxide, and the elastic deformation energy \( U_e \) is in the range of 80~100 kJ/mol. The elastic recovery during unload displacement is calculated as a ratio of elastic and plastic deformation energies, i.e., \( E_R = U_e/U_t \), and the results at the maximum load of 500 mN for the glass and crystallized samples are shown in Fig. 20 and summarized in Table 3. It is found that the values of the elastic recovery are 0.43~0.46 and tend to increase very slightly with the crystallization of BTS nanocrystals.

The deformation energies for some glasses (e.g., \( SiO_2, 10La_2O_3-90P_2O_5 \)) and nanocrystallized glasses (10BaO-10Er_2O_3-80TeO_2) have been also evaluated from
load/unload displacement curves in standard-type nanoindentation tests, and the deformation mechanism during applied load has been discussed from the points of view of single bond strength. [50-52]

![Berkovich Nanoindentation](image)

**Fig. 15.** Load and unload displacement curves at room temperature in air obtained using the Berkovich standard-type nanoindentation technique for the precursor BTS glass and crystallized (at 770 and 790°C for 1 h) samples.
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**Fig. 16.** Values of the elastic modulus evaluated using the Berkovich standard-type nanoindentation technique as a function of the volume fraction of Ba$_2$TiSi$_2$O$_8$ nanocrystals for the glass-ceramics. The maximum load was 500 mN.

**Fig. 17.** Values of the elastic deformation energy evaluated using the Berkovich standard-type nanoindentation technique as a function of the applied maximum load for the precursor BTS glass and crystallized (at 770 and 790 °C for 1 h) samples.
Fig. 18. Values of the plastic deformation energy evaluated using the Berkovich standard-type nanoindentation technique as a function of the applied maximum load for the precursor BTS glass and crystallized (at 770 and 790 °C for 1 h) samples.

Fig. 19. Values of the plastic deformation energy evaluated using the Berkovich standard-type nanoindentation technique as a function of volume fraction of crystals for the precursor BTS glass and crystallized samples.
Fig. 20. Values of the Young’s modulus evaluated using the Berkovich CSM-type nanoindentation technique as a function of the displacement (penetration depth) of indenter for fused glass. The correlation between the contact stiffness and displacement is included.
Table 4

Elastic and mechanical properties of the BTS (40BaO-20TiO2-40SiO2) glass and heat-treated samples evaluated from nanoindentation. $E_{IT}$ is the elastic modulus, $H_{IT}$ is the indentation hardness, and $E_R$ is the elastic recovery.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Glass</th>
<th>Heat-treated sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>760°C</td>
</tr>
<tr>
<td>$V_f$ (%)</td>
<td>23.60</td>
<td>23.54</td>
</tr>
<tr>
<td>$E$ (GPa)</td>
<td>79.9</td>
<td>83.2</td>
</tr>
<tr>
<td>$H_{IT}$ (GPa)</td>
<td>6.71±0.04</td>
<td>7.02±0.07</td>
</tr>
<tr>
<td>$E_{IT}$ (GPa)</td>
<td>88.5±0.4</td>
<td>93.0±0.4</td>
</tr>
<tr>
<td>$E_R$ (%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nanoindentation at 500 mN

| $H_{IT}$ (GPa) | 93.393 | 96.985 | 106.481 | 113.631 | 114.973 |
| $E_{IT}$ (GPa) | 7.302  | 7.702  | 8.249   | 8.511   | 8.318   |
| $E_R$ (%)     |       |       |       |       |       |
2.3.5. Nano-scale Deformation: CSM Experiments

In continuous stiffness measurement (CSM) experiments, the material being in contact with the oscillating force responds with a displacement phase and amplitude. [27-30,53] The material stiffness ($S$) under indentation loading can be calculated using the following equation [28]:

$$\tan \phi = \frac{\omega D}{(S^{-1} + C_f^{-1})^{-1} + K_s - m\omega^2}$$

(8)

where $\phi$ is the phase angle between the force and displacement response (signal), $C_f$ is the compliance of the load flame, $K_s$ is the stiffness of the column support springs, $\omega$ is the frequency of the oscillation, $D$ is the damping coefficient, and $m$ is the mass of the indenter column. For a Berkovich indenter, the projected contact area ($A$) is a function of contact depth ($h_c$), i.e., $A = 24.5h_c^2$, and thus the contact stiffness can be expressed by the following equation [30,53]:

$$S = 2\sqrt{\frac{24.5}{\pi}} E_r h_c$$

(9)

In the CSM-type technique, the contact stiffness is measured continuously using Eq. (9), and thus the reduced modulus ($E_r$) is calculated as a function of $h_c$. That is, the indentation Young’s modulus, $E_{IT}$, for a given sample is estimated using Eq. (2). It should be, therefore, pointed out that the contact stiffness $S$ in CSM-type tests is not estimated from the slope in initial unloading curves and is different from the standard-type nanoindentation technique. Furthermore, it should be pointed out that for a non-uniform material, $E_r$ changes with indentation depth and thus the linear relationship between $E_r$ and $h_c$ does not exist. [30,54]

Prior to the measurement for the BTS glass and glass-ceramics with BTS nanocrystals, CSM-type measurements were applied to fused silica with a homogeneous structure, and the data are shown in Fig. 21. It is seen that the contact stiffness increases linearly with increasing contact depth (displacement), indicating that the relation expressed by Eq. (9) is well held. It is also seen that the indentation Young’s modulus calculated is almost constant in the displacement range of $h_c=100$-300 nm, giving the value of $E_{IT}=77$ GPa. This value is close to the Young’s modulus of 72 GPa reported by Wiederhorn in 1969. [55]

The results on CSM-type measurements for the BTS glass are shown in Figs. 22 and
23, in which the Young’s modulus and hardness are plotted as a function of displacement. It is seen that a good linear relation is held between the contact stiffness and displacement. The BTA glass shows the values of $E_{IT}=98$ GPa at $h_c >100$ nm and $H_{IT}=8.8$ GPa at $h_c=100$ nm. The value of $E_{IT}=98$ GPa at $h_c=100-300$ nm determined from CSM-type measurements is much larger compared with the value of $E=80$ GPa evaluated from the cube resonance method and the value of $E_{IT}=88.5$ GPa evaluated from the standard-type nanoindentation (Table 4).

The results on CSM-type measurements for the glass-ceramics (crystallized at 790°C) BTS glass are shown in Figs. 24 to 26. It is found that in the relation between the contact stiffness and displacement, a deviation from the linearity is observed at $h_c >150$ nm. It should be pointed out that the glass-ceramics is a composite of BTS nanocrystals with a diameter of ~100 nm and the glassy phase. As can be seen in Fig. 25, the Young’s modulus tends to increase gradually with increasing displacement, and the values are $E_{IT}=110$ GPa at $h_c =100$ nm and $E_{IT}=118$ GPa at $h_c =200$ nm. The glass-ceramics shows the value of $H_{IT}=8.6$ GPa at $h_c=100$ nm. The CSM-type measurements also demonstrate that the Young’s modulus of the BTS glass is largely enhanced due to the nanocrystallization. It is also noted that the degree of the scattering of the data in the glass-ceramics is quite large compared with the glass. This indicates that CSM-type measurements are very sensitive in the nano-scaled homogeneity in a given sample. It is noted that the value of $E_{IT}=110$ GPa at $h_c =100$ nm determined from CSM-type measurements is close to the value of $E=106$ GPa evaluated from the cube resonance method and the value of $E_{IT}=113$ GPa evaluated from the standard-type nanoindentation (Table 4).
Fig. 21. Values of the Young’s modulus evaluated using the Berkovich CSM-type nanoindentation technique as a function of the displacement of indenter for fused glass. The correlation between the contact stiffness and displacement is included.
Fig. 22. Values of the elastic modulus evaluated using the Berkovich CSM-type nanoindentation technique as a function of the displacement (penetration depth) of indenter for the precursor BTS glass measured by XP head (above graph) and DCM head (below graph) in different penetration depth.
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Fig. 23. Values of the Hardness evaluated using the Berkovich CSM-type nanoindentation technique as a function of the displacement (penetration depth) of indenter for the precursor BTS glass measured by XP head (above graph) and DCM head (below graph) in different penetration depth.
Fig. 24. Correlation between the contact stiffness and displacement evaluated using the Berkovich CSM-type nanoindentation technique for the crystallized (at 790°C for 1 h) sample.
Fig. 25. Values of the Young’s modulus evaluated using the Berkovich CSM-type nanoindentation technique as a function of the displacement (penetration depth) of indenter for the crystallized (at 790°C for 1 h) sample measured by XP head (above graph) and DCM head (below graph).
Fig. 26. Values of the hardness evaluated using the Berkovich CSM-type nanoindentation technique as a function of the displacement (penetration depth) of indenter for the crystallized (at 790°C for 1 h) sample.
2.3.6. **Mechanism of Micro-scale Deformations**

As can be seen in Fig. 11, the Vickers hardness does not change linearly against the volume fraction of BTS nanocrystals. That is, the hardness changes largely at around $f=20$–$30\%$, and over $f=40\%$, its value is almost constant, irrespective of the volume fraction. In previous papers, [22,46] such a percolation-like behavior has been observed for elastic properties in transparent crystallized glasses in $25\text{K}_2\text{O}-25\text{Nb}_2\text{O}_5-50\text{GeO}_2$ glass. The glass-ceramics prepared in this study are considered as homogeneous composites consisting of the glassy phase and $\text{Ba}_2\text{TiSi}_2\text{O}_8$ nanocrystals with a particle size of $\sim100$ nm. In other words, the present results demonstrate clearly that BTS nanocrystals themselves induce a high resistance against deformation during indenter loadings. It is considered that deformation in glass containing no crystals consists of elastic deformation and plastic deformation. In the plastic deformation during indenter loading in glass, both densification and plastic flow would be possible depending on glass system, composition, indenter load, and so on. Densification has been considered to be a more close-packed rearrangement of atoms without breaking molecular bonds. On the other hand, plastic flow (shear flow) occurs probably through breaking of chemical bonds. In materials with large free volumes, stress concentration would be relaxed more easily through movement or displacement of constituent ions or structural units into open spaces (free volume). In this case, materials can deform easily under a given applied load, and consequently hardness and Young’s modulus would be small. On the other hand, in composite materials with compact structure (small free volume) and nanocrystals, relaxation of stress concentration due to movement of constituent ions or structural units would be more difficult and contacts or collisions of nanocrystals would resist against deformations, giving large hardness and Young’s modulus. On this basis, the glass-ceramics containing BTS nanocrystals would show much larger hardness and Young’s modulus compared with the precursor BTS glass, as obtained experimentally in the present study.
2.3.7. Mechanism of Nano-scale Deformations

It is considered that deformation in glass consists of elastic deformation and plastic deformation, irrespective of the deformation scale, i.e., irrespective of the micro-scale deformation and nano-scale deformation. In the plastic deformation during indenter loading in glass, both densification and plastic flow would be possible depending on glass system, composition, indenter load, and so on. Densification has been considered to be a more close-packed rearrangement of atoms without breaking molecular bonds. [56] On the other hand, plastic flow (shear flow) occurs probably through breaking of chemical bonds. [56] As reported by Sun, [57] single-bond strengths of network modifier BaO and former SiO$_2$ are 138 and 444 kJ/mol, respectively. The single bond strength of network intermediate TiO$_2$ is estimated to be 364 kJ/mol, if the oxygen coordination number of Ti$^{4+}$ is assumed to be five. It is obvious that the single bond strength is the order of Ba-O << Ti-O < Si-O. This order suggests that the weakest bond in BaO-TiO$_2$-SiO$_2$ glasses would be Ba-O bonds. Indeed, as can be seen in Fig. 19, the plastic deformation energy $U_p$ in BTS glass is in the range of 115–140 kJ/mol kJ/mol, being close to the single bond strength of Ba-O. It is, therefore, considered that the plastic deformation in BTS glass might proceed mainly together with the breaking of Ba-O bonds. Since a stress concentration is considered to be present at the front of indenter tip during loading, some breakings of Ti-O and also Si-O bonds would not be neglect.

As can be seen in Figs. 11, 16, and 19, the Vickers hardness, elastic modulus evaluated by nanoindentation (standard-type), and deformation energies do not change linearly against the volume fraction of BTS crystals. That is, such parameters change largely at around $f=20$–$30\%$, and over $f=40\%$, those values are almost constant, irrespective of the volume fraction. In previous papers, [22,46] such a percolation-like behavior has been observed for elastic properties in transparent crystallized glasses in 25K$_2$O-25Nb$_2$O$_5$-50GeO$_2$ glass. In other words, the present results demonstrate clearly that BTS nanocrystals themselves induce a high resistance against deformation during indenter loadings. In materials with large free volumes, stress concentration would be relaxed more easily through movement or displacement of constituent ions or structural units into open spaces (free volume). In this case, materials can deform easily under a given applied load, and consequently hardness and Young’s modulus would be small. On the other hand, in materials with compact structure (small free volume), relaxation
of stress concentration due to movement of constituent ions or structural units would be more difficult, giving large hardness and Young’s modulus. On this basis, the glass-ceramics containing BTS nanocrystals would show much larger hardness and Young’s modulus compared with the precursor BTS glass, as obtained experimentally in the present study.

In the present study, for the glass-ceramics containing BTS nanocrystals (the volume fraction is 54.5%), it is found that the Young’s modulus of $E_{IT}=110$ GPa at $h_c=100$ nm determined from CSM-type nanoindentation measurements is almost the same as that of $E_{IT}=113$ GPa at $h_c\sim1700$ nm (Fig. 16) evaluated from the standard-type nanoindentation. On the other hand, for the BTS glass, the different values were obtained, i.e., $E_{IT}=98$ GPa at $h_c=100-300$ nm in the CSM-type nanoindentation and $E_{IT}=88.5$ GPa at $h_c\sim1700$ nm in the standard-type nanoindentation. At this moment, the origin of these behaviors is not clear. It is desired to evaluate Young’s modulus using both standard-type and CSM-type nanoindentation methods for various glasses. Such studies are now under consideration.
2.4. Conclusions

The optically transparent glass-ceramics (composition: 40BaO-20TiO2-40SiO2) consisting of nonlinear optical Ba2TiSi2O8 (BTS) nanocrystals (diameter: ~100 nm) were fabricated, and their elastic and mechanical properties were examined as a function of the volume fraction of BTS nanocrystals using cube resonance, Vickers indentation, and Berkovich nanoindentation technique (standard-type and continuous stiffness measurement (CSM)-type) in order to clarify micro- and nano-scale deformation behaviors in glass/nanocrystal composite materials. The volume fractions of BTS nanocrystals were estimated from density changes.

The elastic properties such as Young’s modulus ($E$) increased linearly with increasing the volume fraction of nanocrystals, e.g., $E=84$ GPa for $f=0\%$ (glass) to $E=107$ GPa for $f=54.5\%$. The Vickers hardness ($H_v$) and indentation fracture toughness ($K_c$) increased from 5.0 to 6.0 GPa for $H_v$ and 0.48 to 1.05 MPa m$^{-1/2}$ for $K_c$ with increasing the volume fraction (from $f=0\%$ to $f=54.5\%$), but they do not change linearly against the volume fraction of nanocrystals.

It was found from nanoindentation measurements that the deformation energy increased with increasing volume fraction. In particular, the plastic deformation energy was found to be 114-136 kJmol$^{-1}$, which is close to the Ba-O single bond energy (~138 kJmol$^{-1}$), suggesting that the breaking of Ba-O bonds might be important for the plastic deformation in this glass. The Young’s modulus in a deformation scale of about 100 nm was evaluated from CSM-type nanoindentation measurements and compared with the values obtained by the cube resonance method. It was clarified that elastic/mechanical properties of the glass are largely improved by nanocrystallization.
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Chapter III - Morphology of CaF$_2$ Nanocrystals and Elastic Properties in Transparent Oxyfluoride Crystallized Glasses

3.1. Introduction

Optically transparent oxyfluoride-based crystallized glasses (glass-ceramics) containing fluoride nanocrystals such as CaF$_2$ have received much attention [1-7]. In such materials, for instance, rare-earth (RE$^{3+}$) ions are incorporated into fluoride nanocrystals, giving excellent photoluminescence (PL) properties of RE$^{3+}$ ions, because fluoride crystals have low phonon energies compared with oxide materials. Furthermore, fluoride nanocrystals are dispersed homogeneously in oxide glass matrices such as Al$_2$O$_3$-SiO$_2$ based glasses, giving the decrease in the drawbacks of low mechanical properties of fluoride materials themselves. Usually, oxyfluoride-based crystallized glasses are fabricated through well-controlled heat treatments in an electric furnace and desired fluoride nanocrystals are formed in the interior of glasses. Numerous studies on fabrications and PL properties of RE$^{3+}$ ions in fluoride nanocrystals in crystallized glasses have been reported so far [1-7]. Recently, the laser patterning of fluoride crystals such as LaF$_3$ and CaF$_2$ on the surface of oxyfluoride glasses has been proposed as a new design of spatially controlled crystallization [8-13].

It is of interest and important to clarify the morphology of fluoride nanocrystals in oxyfluoride crystallized glasses, because PL properties of RE$^{3+}$ ions would depend on the quality (e.g., size and shape) of fluoride nanocrystals. It should be pointed out that the morphology of fluoride nanocrystals has not been well studied so far, although there have been some reports on the morphology of fluoride nanocrystals using transmission electron microscopy (TEM) [4-7]. It is also strongly required to examine elastic
properties such as Young’s modulus and Vickers hardness in oxyfluoride crystallized glasses, because they would be processed mechanically to get desired shapes and joined with other kinds of materials for optical device applications. However, there have been no reports on elastic properties of oxyfluoride crystallized glasses so far.

In this study, we focus our attention on the morphology of fluoride nanocrystals in oxyfluoride crystallized glasses and elastic properties of oxyfluoride crystallized glasses. The oxyfluoride crystallized glasses containing CaF$_2$ nanocrystals and Al$_2$O$_3$-SiO$_2$ based oxide glass matrices are prepared as model materials. The morphology of CaF$_2$ nanocrystals is examined using atomic force microscopy (AFM) and TEM, and elastic properties such as Young’s modulus are evaluated from the values of longitudinal and shear (transverse) ultrasonic velocities measured using a cube resonance method. The present study demonstrates that oxyfluoride crystallized glasses containing CaF$_2$ nanocrystals have good elastic (mechanical) properties, being available in practical device applications from the mechanical point of view.

### 3.2. Experimental Procedure

A glass with the nominal composition of 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ (mol%) was prepared using a conventional melt-quenching method. For the comparison, a glass of 30CaO-20Al$_2$O$_3$-50SiO$_2$ (mol%) containing no CaF$_2$ was also prepared. Commercial powders of reagent grade CaF$_2$, CaCO$_3$, Al$_2$O$_3$, and SiO$_2$ were used. The batch of 20 g was mixed and melted in a platinum crucible at 1400°C for 20 min in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness of ~1.5 mm by another iron plate. The glasses with a cubic shape for a cube resonance method were also prepared by pouring melts into a graphite mold. The glass transition ($T_g$) and crystallization peak ($T_p$) temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10K/min in air.

The glasses were annealed at $T_g-30^\circ$C for 3 h to release internal stresses. The glasses were heat-treated at 660-760°C in an electric furnace in air, and the crystalline phase present in the heat-treated samples was examined by X-ray diffraction (XRD) analyses at room temperature using CuK$\alpha$ radiation. Densities ($d$) of the glasses and
crystallized samples were determined with the Archimedes method using distilled water as an immersion liquid. The morphology of CaF$_2$ crystals in the crystallized glasses was observed with a contact mode in AFM (SII, SPA300-type, Tokyo, Japan), and TEM observations were conducted for pulverized particles using FE-TEM (JEM-2100F, JEOL).

Bulk elastic properties at room temperature in air for the glasses and crystallized samples were determined from measurements of longitudinal ($V_l$) and shear (transverse) ($V_s$) ultrasonic velocities. The values of $V_l$ and $V_s$ were measured using a cube resonance method with the frequency of 0.2~1.5 MHz, in which the sample size was 4.5 mm $\times$ 4.5 mm $\times$ 4.5 mm [14,15]. The values of Young’s modulus ($E$), shear modulus ($G$), bulk modulus ($K$), and Poisson’s ratio ($\nu$) were calculated from the values of $V_l$ and $V_s$ using the following equations:

$$E=2dV_s^2(1+\nu) \quad (1)$$

$$G=dV_s^2 \quad (2)$$

$$K = d\left(V^2_l - \frac{4}{3}V^2_s\right) \quad (3)$$

$$\nu = \frac{1}{2}\left(1 - \frac{V^2_s}{V^2_l - V^2_s}\right) \quad (4)$$

Eqs.(1) to (4) have been applied to various glasses and crystallized glasses with nanocrystals for evaluations of elastic properties so far [15-22].

Usual Vickers indentations (loads: 1~19.6 N, holding time: 15 s) at room temperature (~20°C) in air (relative humidity~55%) were applied to the samples using Akashi HM-114, and Vickers hardness ($H_v$) at room temperature was measured. The load was 1 N and the holding time was 15 s. From deformation patterns in Vickers indentation tests, the values of $H_v$ were evaluated using the following equation:

$$H_v = \frac{P}{\alpha_0 a^2} \quad (5)$$

where $P$ is an applied load, $a$ is a characteristic indentation diagonal, and $\alpha_0$ is an indenter constant of 2.157 in the present experiment used a diamond pyramid indenter. The values of indentation fracture toughness ($K_c$) at room temperature were evaluated using the following equation recommended by Japanese Industrial Standards (JIS) for ceramics [23]:

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\[ K_c = 0.018 \left( \frac{E}{H_v} \right)^{1/2} \left( \frac{P}{C^{3/2}} \right) \]

where \( C \) is the characteristic crack length in Vickers indenter test. Eq. (6) is almost the same as that proposed by Anstis et al. [24]. The load was 10 N and the holding time was 15 s. In the estimation of \( H_v \) and \( K_c \), measurements were carried out ten times, and the average value and standard deviation were evaluated.

### 3.3. Results and Discussion

#### 3.3.1. Thermal and Elastic Properties of the Glasses

The melt-quenched samples of \( x \text{CaF}_2-(30-x)\text{CaO-20Al}_2\text{O}_3-50\text{SiO}_2 \) (mol\%) \((x=0, 25)\) prepared in this study showed only halo patterns in XRD patterns. The DTA curve for the obtained glass with a composition of \( 25\text{CaF}_2-5\text{CaO-20Al}_2\text{O}_3-50\text{SiO}_2 \) is shown in Fig. 1. The endothermic peak due to the glass transition and exothermic peaks due to the crystallization are observed. The values of the glass transition and the first crystallization peak temperatures were determined to be \( T_g=590^\circ\text{C} \) and \( T_p=651^\circ\text{C} \). In the DTA curve for \( 30\text{CaO-20Al}_2\text{O}_3-50\text{SiO}_2 \) glass with \( x=0 \) (no \( \text{CaF}_2 \)), the glass transition \((T_g=775^\circ\text{C}) \) was detected, but any clear exothermic peak corresponding to the crystallization was not observed. The glass transition temperatures for the glasses with the compositions of \( x\text{CaF}_2-(30-x)\text{CaO-20Al}_2\text{O}_3-50\text{SiO}_2 \) are shown in Fig. 2. Glass transition temperatures are largely decreasing with addition of \( \text{CaF}_2 \). The densities were found to be \( d=2.723 \text{ g/cm}^3 \) for the glass with no \( \text{CaF}_2 \) and \( d=2.707 \text{ g/cm}^3 \) for the glass with 25\( \text{CaF}_2 \). It is known that the melting temperature \((T_m) \) and density of \( \text{CaO} \) and \( \text{CaF}_2 \) crystals are \( T_m=2570^\circ\text{C} \) and \( d=3.25 \text{ g/cm}^3 \) and \( T_m=1418^\circ\text{C} \) and \( d=3.18 \text{ g/cm}^3 \), respectively. That is, it is considered that the strength of \( \text{Ca-O} \) bonds in \( \text{CaO} \) crystals is much larger than that of \( \text{Ca-F} \) bonds in \( \text{CaF}_2 \) crystals. The difference in the chemical bond strength between \( \text{CaO} \) and \( \text{CaF}_2 \) would be a main reason for the large decrease in the glass transition temperature due to the substitution of \( \text{CaF}_2 \) for \( \text{CaO} \) in \( x\text{CaF}_2-(30-x)\text{CaO-20Al}_2\text{O}_3-50\text{SiO}_2 \) glasses. On the other hand, the density of \( \text{CaF}_2 \) is close to that of \( \text{CaO} \), and this would give similar values in the density of the glasses with the \( \text{CaF}_2 \) content of 0 and 25. The large decrease in the glass transition temperature
due to the addition of CaF$_2$ have been reported in other Al$_2$O$_3$-SiO$_2$ based oxyfluoride glasses [25,26].

Bocker et al. [27] reported that fluorine is lost due to an unavoidable evaporation during melting. For instance, for the melting of (100-x)(2Na$_2$O-16K$_2$O-8Al$_2$O$_3$-74SiO$_2$)–xBaF$_2$ (mol%) with x=0-5 at 1590°C for 1.5 h, on the average about 34% of fluorine was lost during melting. In the present study, the glass of 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ (mol%) was melted at 1400°C for 20 min. That is, the melting temperature is low and the melting time is short compared with the case reported by Bocker et al. [27]. As shown in the above, 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ glass has a much lower glass transition temperature ($T_g$=590°C) compared with 30CaO-20Al$_2$O$_3$-50SiO$_2$ glass ($T_g$=775°C), indicating that a large amount of fluorine is still present in the oxyfluoride glass prepared in this study. The nominal composition of 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ is used through the present study.

The values of $E$, $G$, $K$, and $v$ evaluated using Eqs. (1) to (4) are shown in Table 1 and Young’s modulus, $E$, for the glasses are shown in Fig. 3. The glass with no CaF$_2$ content shows the values of $E$=94.6 GPa, $G$=37.1 GPa, and $K$=70.3 GPa. On the other hand, the glass with 25CaF$_2$ content has the values of $E$=88.4 GPa, $G$=34.8 GPa, and $K$=64.4 GPa. Elastic properties such as Young’s modulus of glass would be determined from the glass structure and chemical bonding strength of constituent ions. At this moment, the structure of the oxyfluoride glasses (xCaF$_2$-(30-x)CaO-20Al$_2$O$_3$-50SiO$_2$ with x=0-30) prepared in the present study has not been clarified. It should be, however, pointed out that the content of Al$_2$O$_3$ and SiO$_2$ is the same in both glasses with x=0 and 25. As described in the above, the large decrease in the glass transition temperature due to the substitution of CaF$_2$ for CaO in the glasses supports strongly that the strength of bonds related to F$^-$ ions such as Ca–F, Al–F, and Si–F would be much smaller than that of bonds related to O$^{2-}$ ions such as Ca–O, Al–O, and Si–O. This would be one of the main reasons why the substitution of CaF$_2$ for CaO in the glasses induces the decrease in elastic constants such as Young’s modulus. The role of F$^-$ in the structure of Al$_2$O$_3$-SiO$_2$ based glasses have been studied by several researchers [27,28]. Stamboulis et al. [28] proposed from $^{29}$Si, $^{27}$Al, and $^{19}$F magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra that incorporating F$^-$ into calcium aluminosilicate glasses such as xCaF$_2$-(40-x)CaO-20Al$_2$O$_3$-40SiO$_2$ results in the formation of F-Ca bonds at low F$^-$ contents and both F-Ca and Al-F-Ca bonds at higher F$^-$ contents.
As shown in Table 1, the oxyfluoride glasses give the Poisson’s ratio of \( \nu = 0.27 \sim 0.28 \), almost being independent on the content of CaF\(_2\). Poisson’s ratio depends on the dimensionality of the structure and cross-link density [29]. Typical three-dimensional glasses like SiO\(_2\) or GeO\(_2\) have \( \nu \sim 0.15 \), whereas B\(_2\)O\(_3\) including two-dimensional structure have \( \nu \sim 0.3 \). Many oxide glasses including both network formers such as SiO\(_2\) and network modifiers such as Na\(_2\)O have the value of \( \nu \sim 0.2 \), because addition of network modifier oxide results in creation of non-bridging oxygen and hence reduction in dimensionality. The value of \( \nu = 0.27 \) in the oxyfluoride glass with 25CaF\(_2\) suggests that CaF\(_2\) might act as network modifier as similar to CaO.

It is well known that fluoride glasses are excellent transparent materials from the near ultra-violet to the middle infrared region and have low phonon energies. However, their thermal, chemical and mechanical properties are poor compared with SiO\(_2\)-based oxide glasses, giving the difficulty in handling. For instance, a fluoride glass with the composition of 65ZrF\(_4\)-25BaF\(_2\)-10LaF\(_3\) shows the values of \( E = 62.0 \) GPa, \( K = 46.9 \) GPa, \( G = 24.2 \) GPa, and \( \nu = 0.280 \) [30]. Usually, ZrF\(_4\)-based glasses have the values of \( T_g \sim 300^\circ \) C [31]. On the other hand, an oxide glass with the composition of 25CaO-25Al\(_2\)O\(_3\)-50SiO\(_2\) (anorthite: CaAl\(_2\)Si\(_2\)O\(_8\)) shows the values of \( E = 94.3 \) GPa, \( K = 65.2 \) GPa, \( \nu = 0.261 \), and \( T_g = 852^\circ \) C [31,32]. As observed in the present study, therefore, it is expected that the addition of fluoride such as CaF\(_2\) into Al\(_2\)O\(_3\)-SiO\(_2\) based oxide glasses induce the decrease in elastic constants and glass transition temperature.
Fig. 1. DTA curve for 25CaF₂-5CaO-20Al₂O₃-50SiO₂ glass. Heating rate was 10K/min.

Fig. 2. Glass transition temperature as a function of contents of CaF₂ in the glass composition of xCaF₂-(30-x)CaO-20Al₂O₃-50SiO₂.
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Fig. 3. Young’s modulus as a function of contents of CaF$_2$ in the glass composition of xCaF$_2$-(30-x)CaO-20Al$_2$O$_3$-50SiO$_2$.

Table 1
Elastic properties as a function of contents of CaF$_2$ in the glass composition of xCaF$_2$-(30-x)CaO-20Al$_2$O$_3$-50SiO$_2$.

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<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
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<tr>
<td>Share velocity, $V_s$ (km/s)</td>
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<td>3.69</td>
<td>3.59</td>
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<td>6.58</td>
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<td>6.40</td>
<td>6.28</td>
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<td>4.11</td>
<td>4.00</td>
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<td>117.4</td>
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<tr>
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<td>37.1</td>
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<td>33.0</td>
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<td>33.0</td>
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<td>68.0</td>
<td>64.2</td>
<td>64.4</td>
<td>62.2</td>
</tr>
<tr>
<td>Poisson’s ratio, $\nu$ (-)</td>
<td>0.276</td>
<td>0.269</td>
<td>0.269</td>
<td>0.271</td>
<td>0.274</td>
</tr>
<tr>
<td>Debye temperature, $\theta_D$ (K)</td>
<td>838</td>
<td>784</td>
<td>748</td>
<td>732</td>
<td>703</td>
</tr>
<tr>
<td>Network connectivity, $F_d$ (-)</td>
<td>2.11</td>
<td>2.18</td>
<td>2.18</td>
<td>2.16</td>
<td>2.12</td>
</tr>
</tbody>
</table>
3.3.2. Formation of CaF$_2$ Nanocrystals

The polished and annealed glasses with $x=25$ were heat-treated at temperatures of 660-760°C for 3 h in air. The XRD patterns for these heat-treated samples are shown in Fig. 4. All peaks are assigned to the fluorite-type CaF$_2$ crystalline phase (ICDD: 035-0816). The samples obtained by heat treatments at 660–720°C keep a good optical transparency, but the samples heat-treated at 740 and 760°C were opaque. The size of CaF$_2$ crystals in the crystallized samples was estimated using Scherrer’s equation, in which the peak position and the peak-width at half-maximum corrected from the instrumental broadening were used. The values of the crystal size obtained (660-760°C, 3 h) are shown in Fig. 5. It is seen that the crystal size increases monotonously with increasing heat treatment temperature. For example, the transparent sample heat-treated at 680°C gives the value of ~20 nm, and opaque sample heat-treated at 760°C show the value of ~70 nm. In the DTA pattern shown in Fig. 1, another exothermic peak is observed at ~860°C. This peak would be due to the crystallization of the Al$_2$O$_3$-SiO$_2$ based oxide glassy phase remained after the formation of CaF$_2$ [8].

The values of the density for the crystallized (660-730°C, 3 h) samples are shown in Fig. 6. It is noted that the density decreases slightly due to the formation of CaF$_2$ nanocrystals. Usually, the density of oxide glasses increases due to the formation of oxide nanocrystals [20,33]. Considering that the densities of the glass (25CaF$_2$) and CaF$_2$ crystal are $d=2.707$ and $d=3.18$ g/cm$^3$, respectively, the oxide glass network structure based on Al$_2$O$_3$ and SiO$_2$ might also change due to the formation of CaF$_2$ nanocrystals.

The glass transition temperature was measured for the crystallized samples with 25CaF$_2$ from DTA curves, and the results are shown in Fig. 7. It is seen that the value of $T_g$ increases largely with increasing heat treatment temperature. It is known that crystallization of glass proceeds through two steps of nucleation and crystal growth. The temperature dependence of nucleation and crystal growth rates in oxyfluoride glasses prepared in this study has not been clarified at this moment. However, as shown in Fig. 4, CaF$_2$ nanocrystals are formed as an initial crystalline phase. This means that the temperature dependence of nucleation and crystal growth rates for CaF$_2$ nanocrystals is largely different from that for the host Al$_2$O$_3$-SiO$_2$ based oxide glassy part [8]. Furthermore, even for the crystallized glass obtained by a heat treatment at 760°C, the formation of only CaF$_2$ crystals is detected (Fig. 4). That is, Al$_2$O$_3$-SiO$_2$ based oxide
glassy parts in $25\text{CaF}_2\text{-}5\text{CaO}\text{-}20\text{Al}_2\text{O}_3\text{-}50\text{SiO}_2$ are very stable thermally against the crystallization. Indeed, it is known that glasses based on the ternary CaO-Al$_2$O$_3$-SiO$_2$ system have high glass transition temperatures [31,32] and are difficult to crystallize [34,35]. Duán et al. [34] reported that some Al$^{3+}$ ions in $20\text{CaO}\text{-}17\text{Al}_2\text{O}_3\text{-}63\text{SiO}_2$ glass enter as network former. Rüssel et al. [26,36] also observed the increase in the glass transition temperature due to the formation of fluoride nanocrystals in oxyfluoride glasses.

Fig. 4. XRD patterns at room temperature for the crystallized (at 660-760 °C for 3 h) samples with $25\text{CaF}_2$. All XRD peaks are assigned to the fluorite-type CaF$_2$ crystalline phase (ICDD: 035-0816).
Fig. 5. Size of CaF$_2$ crystals estimated using Scherrer’s equation in crystallized glasses with 25CaF$_2$ obtained by heat treatments at different temperatures.

Fig. 6. Density for the crystallized samples with 25CaF$_2$ obtained by heat treatments at different temperatures.
**Fig. 7.** Glass transition temperature for the crystallized samples with $25\text{CaF}_2$ obtained by heat treatments at different temperatures.
3.3.3. TEM and AFM Observations of CaF\textsubscript{2} Nanocrystals

TEM photographs for the sample obtained by a heat treatment at 700°C for 3 h are shown in Fig. 8. It is seen that small particles with a diameter of about 30 nm are dispersed homogeneously in the matrix. The TEM photograph for the sample heat-treated at 740°C for 3 h is shown in Fig. 9. The formation of particles with a diameter of ~60 nm was detected. It is noted that particles are dispersed homogeneously even in the sample obtained by a heat treatment at a high temperature of 740°C. It should be pointed out that these particle sizes obtained from TEM observations for the samples heat-treated at 700 and 740°C are very close to the values estimated using Scherrer’s equation (Fig. 5).

The AFM photograph for the fracture surface of the sample heat-treated at 700°C for 3 h is shown in Fig. 10. The formation of small particles with a diameter of about 30 nm and a smooth surface are observed. Furthermore, it is noted that many holes with a diameter of about 30 nm are present at the fracture surface. From the size of particles, it is considered that the particles observed in the AFM photograph would be CaF\textsubscript{2} nanocrystals. That is, at the fracture surface shown in Fig. 10, some CaF\textsubscript{2} nanocrystals formed in the heat-treatment at 700°C are remained and others are removed. The interface between CaF\textsubscript{2} nanocrystals and the glass matrix is seemed to be clear. This might be a reason for the removal (i.e., holes) of CaF\textsubscript{2} nanocrystals from the fracture surface. In other words, the chemical bonding state between CaF\textsubscript{2} nanocrystals and Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} based glass matrix might be weak. The AFM photograph for the fracture surface of the sample heat-treated at 740°C for 3 h is shown in Fig. 11. It is seen that more large particles and holes compared with the sample heat-treated at 700°C (Fig. 10) are formed at the fracture surface. Sroda et al. [37] also succeeded in observing LaF\textsubscript{3} nanocrystals formed in Na\textsubscript{2}O-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-LaF\textsubscript{3} glasses using AFM. As a preliminary result, we found that 30CaO-20Al\textsubscript{2}O\textsubscript{3}-50SiO\textsubscript{2} glass shows a linear thermal expansion coefficient of $\alpha$ (50~300°C)=72 x 10^{-7} K^{-1}. On the other hand, it is known that CaF\textsubscript{2} crystal has the value of $\alpha$=187 x 10^{-7} K^{-1} [38], which is 2.6 times larger than that of the glass. Such a large difference in the thermal expansion between CaF\textsubscript{2} crystal and Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} based glass matrix might lead to the removal of CaF\textsubscript{2} nanocrystals in the fracture surface (Figs. 10 and 11).

Scanning transmission electron microscopy (STEM) is used for electron tomography experiments in nanocrystallized glass ($T_{HT} = 740$ °C) and the image is
shown in Fig 11. The imaging mode is the HAADF (high angle annular dark field) or Z-contrast. This technique enables not only sub-nanometric resolution but provides chemical information because the scattered electrons are collected via an annular detector giving images whose intensity is proportional to $\rho \cdot t \cdot Z^{1.7}$, with $\rho$ the material density, $t$ the thickness and $Z$ the atomic number. Thereby STEM-HAADF gives images whose intensities correspond directly to the atomic number of the elements within the materials and this technique does not require some energy selectivity as for electron energy loss spectroscopy or electron-filtered TEM. In here, the material is composed of Ca, Al, Si, O, and F. Atomic number, $Z$, of Ca is the largest and should show the highest contrast in this material. EDX mapping image is shown in Fig. 13. The image of the glass-ceramics including the crack in Fig. 12 and 13. The image also suggests that the crack is developed along the interface between CaF$_2$ nanocrystal and glass matrix.

Fig. 8. TEM photographs for the sample obtained by a heat treatment at 700°C for 3 h.
Fig. 9. TEM photographs for the sample obtained by a heat treatment at 740°C for 3 h.
Fig. 10. AFM photograph for the fracture surface of the sample obtained by a heat treatment at 700°C for 3 h.

Fig. 11. AFM photograph for the fracture surface of the sample obtained by a heat treatment at 740°C for 3 h.
Fig. 12. STEM-HAADF image for the fracture surface of the sample obtained by a heat treatment at 740°C for 3 h.
Fig. 13. STEM-EDS mapping for the fracture surface of the sample obtained by a heat treatment at 740°C for 3 h.
3.3.4. Elastic Properties and Vickers Hardness of Crystallized Oxyfluoride Glasses

The values of $E$, $G$, $K$, and $\nu$ evaluated using Eqs.(1) to (4) for the crystallized glasses with CaF$_2$ nanocrystals are shown in Table 2. Young’s modulus ($E$) for the crystallized glass are shown in Fig. 14. It is seen that all values of $E$, $G$, and $K$ increase due to the formation of CaF$_2$ nanocrystals. For instance, the base glass show the values of $E=88.4$ GPa, $G=34.8$ GPa, and $K=64.4$ GPa. On the other hand, the crystallized glass (heat-treated at 700°C) with CaF$_2$ nanocrystals has the values of $E=93.3$ GPa, $G=36.7$ GPa, and $K=65.4$ GPa. That is, elastic properties of oxyfluoride glass (25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$) are enhanced due to the CaF$_2$ nanocrystallization. However, it should be pointed out that the degree in the change in the elastic properties among crystallized glasses obtained by different heat treatments of 660~760°C is not so large (Table 2 and Fig.14). It is also noted that the Poison’s ratio of the oxyfluoride glass and crystallized glasses is almost the same, being independent on the formation CaF$_2$ nanocrystals, i.e., $\nu=0.26$~0.27. Ladison et al. [39] have reported the values of $E=146$ GPa for the [100] direction, $E=90$ GPa for the [111] direction, and $\nu=0.26$ for CaF$_2$ single crystal.

In order to clarify the feature in the deformation behavior in the crystallized glasses containing CaF$_2$ nanocrystals, usual Vickers indentation tests were carried out, and the values of Vickers hardness $H_v$ and indentation fracture toughness $K_c$ were evaluated using Eqs.(5) and (6). The values obtained for the crystallized glasses are shown in Fig. 15 for $H_v$ and Fig. 16 for $K_c$. In the indentation for $H_v$, the load was 1 N and holding time 15 s. As shown in Fig. 15, Vickers hardness increases with increasing heat treatment temperature, i.e., $H_v=5.6$ GPa for the base glass and $H_v=6.1$ GPa for the crystallized glass obtained by a heat treatment at 740°C. The results clearly indicate that crystallized glasses with CaF$_2$ nanocrystals have higher resistance against the deformation during Vickers indentation compared with the base oxyfluoride glass.

In the indentation for $K_c$, the load was 10 N and holding time 15 s. As an example, an optical photograph for the crystallized (660°C, 3 h) sample is shown in Fig. 17, indicating the formation of cracks. Although the scattering in the value of $K_c$ is large, the oxyfluoride glass and crystallized glasses show $K_c=0.75$~1.1 MPam$^{1/2}$, and the indentation fracture toughness tends to increase due to the formation of CaF$_2$ nanocrystals.
nanocrystals. The data of $K_c$ shown in Fig. 16 suggest that crystallized glasses with CaF$_2$ nanocrystals would have higher resistance against the crack growth compared with the base oxyfluoride glass.

The oxyfluoride crystallized glasses prepared in the present study are regarded as composite (hybrid) materials containing CaF$_2$ nanocrystals and thermally stable Al$_2$O$_3$-SiO$_2$ based oxide glassy parts. In other words, it is considered that CaF$_2$ nanocrystals are dispersed in the strongly bonded glass network consisting of Al$_2$O$_3$ and SiO$_2$. In particular, the glass network strength would increase with the formation of CaF$_2$ nanocrystals, because the content of F$^-$ ions in the glassy parts would decrease. These structural features would give the increase in elastic constants ($E$, $G$, and $K$) and Vickers hardness ($H_v$) due to the formation of CaF$_2$ nanocrystals. Rüssel et al. [26] examined the nanocrystallization of CaF$_2$ in oxyfluoride glasses (SiO$_2$ content: 62 mol%) based on the Na$_2$O-K$_2$O-CaO-CaF$_2$-Al$_2$O$_3$-SiO$_2$ system and reported that a highly viscous layer enriched in SiO$_2$ is formed during the crystallization of CaF$_2$, which acts as a diffusion barrier and hinders further crystal growth.

At this moment, the amount of CaF$_2$ nanocrystals formed in the crystallized glasses has not been determined experimentally. If all of the CaF$_2$ component (25 mol%) in the 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ glass are assumed to be taken part in the formation of CaF$_2$ nanocrystals, the maximum volume fraction of CaF$_2$ nanocrystals is estimated to be 23.9%, where the densities of CaF$_2$ nanocrystals and Al$_2$O$_3$-SiO$_2$ based glasses are assumed to be 3.18 and 2.72 g/cm$^3$, respectively. This value of ~24% is small compared with the threshold of 0.3~0.4 in the so-called percolation in properties of composite materials [40]. Indeed, as observed in TEM and AFM, CaF$_2$ nanocrystals are dispersed homogeneously in the glassy matrices, and significant connections among CaF$_2$ nanocrystals are not observed. Consequently, considering the volume fraction of CaF$_2$ nanocrystals, the content of SiO$_2$ and Al$_2$O$_3$ in oxyfluoride glasses would be extremely important not only for the control (morphology and size) of CaF$_2$ nanocrystals but also for the design of elastic and mechanical performances. Commercially available float glasses have, for instance, the values of $E$=70~75 GPa, $H_v$~5.4 GPa, and $K_c$~0.76 MPam$^{1/2}$ [41]. The present study demonstrates that oxyfluoride crystallized glasses containing CaF$_2$ nanocrystals have good elastic (mechanical) properties (i.e., $E$=90~95 GPa, $H_v$=5.6~6.1 GPa, and $K_c$~0.9 MPam$^{1/2}$), being available in practical device applications even from the mechanical point of view.
Table 2

Values of Young’s modulus (\(E\)), shear modulus (\(G\)), bulk modulus (\(K\)), and Poisson’s ratio (\(\nu\)) for the crystallized glasses obtained by heat treatments at different temperatures for 1 h in 25CaF\(_2\)-5CaO-20Al\(_2\)O\(_3\)-50SiO\(_2\) glass.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E) (GPa)</th>
<th>(G) (GPa)</th>
<th>(K) (GPa)</th>
<th>(\nu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>88.4</td>
<td>34.8</td>
<td>64.4</td>
<td>0.27</td>
</tr>
<tr>
<td>Heat-treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>660(^\circ)C</td>
<td>92.0</td>
<td>36.4</td>
<td>65.3</td>
<td>0.26</td>
</tr>
<tr>
<td>680(^\circ)C</td>
<td>93.3</td>
<td>36.7</td>
<td>68.2</td>
<td>0.27</td>
</tr>
<tr>
<td>700(^\circ)C</td>
<td>93.3</td>
<td>37.0</td>
<td>65.4</td>
<td>0.26</td>
</tr>
<tr>
<td>720(^\circ)C</td>
<td>96.6</td>
<td>38.1</td>
<td>69.7</td>
<td>0.27</td>
</tr>
<tr>
<td>740(^\circ)C</td>
<td>92.2</td>
<td>36.3</td>
<td>67.0</td>
<td>0.27</td>
</tr>
<tr>
<td>760(^\circ)C</td>
<td>94.2</td>
<td>37.0</td>
<td>68.7</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Fig. 14. Elastic modulus for the samples obtained by heat treatments at different temperatures.
Fig. 15. Vickers hardness for the samples obtained by heat treatments at different temperatures. The indentation load was 1 N and holding time 15 s.

Fig. 16. Indentation fracture toughness for the samples obtained by heat treatments at different temperatures. The indentation load was 10 N and holding time 15 s.
Fig. 17. Optical micrographs of the imprints and cracks of the glass and glass-ceramics ($T_{HT}=660^\circ$C). The indentation load was 10 N and holding time 15 s.
3.4. Conclusions

The oxyfluoride glass with the composition of 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ (mol%) and glass-ceramics containing CaF$_2$ nanocrystals were fabricated. The size and morphology of CaF$_2$ nanocrystals was examined using transmission electron microscope (TEM) and atomic force microscope (AFM), and elastic properties of glass-ceramics were evaluated using a cube resonance method. It was suggested from AFM observations that the chemical bonding between CaF$_2$ nanocrystals and oxide glass matrix is weak. Young’s modulus ($E$) increased with increasing heat treatment temperature, i.e., $E=88.4$ GPa for the glass and $E=93.3$ GPa for the sample (CaF$_2$: ~30 nm) heat-treated at 700°C for 3 h. The change in the elastic properties due to the formation of CaF$_2$ nanocrystals were discussed from the viewpoint of the microstructure change in the glass-ceramics.
Chapter III - Morphology of CaF$_2$ Nanocrystals and Elastic Properties in Transparent Oxyfluoride Crystallized Glasses

References


Chapter III - Morphology of CaF$_2$ Nanocrystals and Elastic Properties in Transparent Oxyfluoride Crystallized Glasses


[37] M. Sroda, C. Paluszkiewicz, M. Reben, B. Handke, “Spectroscopic study of
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Chapter IV
Fluorine Deficient layer at the Surface of Transparent Glass-Ceramics with CaF$_2$ Nanocrystals

4.1. Introduction

Rare earth (RE) ion doped oxyfluoride glass-ceramics containing fluoride nanocrystals have been considered to be promising materials for photonic devices such as optical fiber amplifier, laser, and planer optical waveguide, because fluoride crystals have low phonon energies for RE environments and oxide glass matrices have high mechanical resistances and high thermal/chemical stabilities. Many studies have been reported from the view point of microstructure and spectroscopic properties such as fluorescence, upconversion, and quantum cutting for RE$^{3+}$-doped transparent glass-ceramics containing fluorite-type CaF$_2$ nanocrystal based on the CaF$_2$-Al$_2$O$_3$-SiO$_2$ system and CaF$_2$-NaF-Al$_2$O$_3$-SiO$_2$ system [1-4]. Usually, oxyfluoride-based glass-ceramics are fabricated through well-controlled heat treatments in an electric furnace and desired fluoride nanocrystals are formed in the interior of glasses. Recently, locally crystallized lines consisting of CaF$_2$ nanocrystals were patterned on the glass surface by laser irradiations [5-7].

It is of interest and important to clarify the morphology and dispersion state of fluoride nanocrystals in oxyfluoride glass-ceramics for their practical applications. In particular, optically transparent oxyfluoride glass-ceramics would be used mainly as bulk plate form or fiber form in devices applications, and thus the dispersion state of fluoride nanocrystals at the surface would be extremely important. Very recently, Shinozaki et al. [8] found from atomic force microscope (AFM) observations that the chemical bonding between CaF$_2$ nanocrystals and oxide glass matrix in transparent
Chapter IV - Fluorine Deficient layer at the Surface of Transparent Glass-Ceramics with CaF₂ Nanocrystals

glass-ceramics based on the CaF₂-CaO-Al₂O₃-SiO₂ system is weak. They also demonstrated that oxyfluoride glass-ceramics containing CaF₂ nanocrystals have good elastic (mechanical) properties, being available in practical device applications even from the mechanical point of view [8].

In this study, we focus our attention on the dispersion state of CaF₂ nanocrystals at the surface of transparent glass-ceramics in 25CaF₂-5CaO-20Al₂O₃-50SiO₂. From transmission electron microscope (TEM) observations combined with focused ion beam (FIB) sample preparations, it was demonstrated that CaF₂ nanocrystals are not present at the surface of ~150 nm in the bulk glass-ceramics obtained by heat treatments in an electric furnace. We also found from nanoindentation measurements that the surface with no CaF₂ nanocrystals has higher indentation elastic modulus and hardness compared with the surface with CaF₂ nanocrystals. Generally, it has been considered that fluoride nanocrystals are dispersed (distributed) homogeneously over the whole part of a given sample. The present study gives new and important information for device applications and for the crystal growth mechanism of fluoride nanocrystals in oxyfluoride glass-ceramics.

4.2. Experimental Procedure

A glass with the composition of 25CaF₂-5CaO-20Al₂O₃-50SiO₂ (mol%) was prepared using a conventional melt-quenching method. A batch of 20 g was mixed and melted in a platinum crucible at 1400°C for 20 min in an electric furnace. Commercial powders of reagent grade CaF₂, CaCO₃, Al₂O₃ and SiO₂ were used. The melts were poured onto an iron plate and pressed into ~1.4 mm thick with another plate. The glass transition, \( T_g \), and crystallization peak, \( T_p \), temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10 K/min in air. A mass change of the glass powder of 20 mg during heat treatments was measured by thermogravimetric (TG) analysis. The glasses were annealed at 560°C (=\( T_g-30°C \)) for 1 h to release internal stresses. The annealed glasses were mechanically polished into 1 mm of thick and a mirror finish with CeO₂ powders and re-annealed at 560°C (=\( T_g-30°C \)) again for 1 h to release strains induced in the polishing. The glasses were heat-treated at 700°C for 3h in
an electric furnace in air. The crystalline phase present in the heat-treated samples was examined by X-ray diffraction (XRD) analyses at room temperature using CuKα radiation.

The heat-treated sample was sputtered with Ag target to a thickness of about several decades of nanometers. A foil of the heat-treated sample around the surface was fabricated using a focused Ga ion beam (JEOL, JIB-4500) method, i.e., FIB method, and set onto a molybdenum grid. The cross-section of the surface of the heat-treated sample was observed using field emission transmission electron microscopy (FE-TEM, JEOL, JEM-2100F) operating at 200 kV. A compositional analysis was operated using energy dispersive X-ray spectroscopy with scanning transmission electron microscopy (STEM-EDS) mode of the FE-TEM.

Nanoindentation measurements at room temperature (25°C) in air (relative humidity ~45%) were carried out to measure the hardness and elastic modulus of the glass and heat-treated samples using a nanoindentation apparatus (Agilent Tech., Nano Indenter G-200) with a Berkovich diamond tip. Nanoindentation tests were performed for 16 times with the loading speed of 0.1 mN/s and the contact stiffness (S) determined from the slope of the unloading curve. The maximum load (P) was 100 and 500 µN and the load was held for 10 s. The indentation elastic modulus, $E_{IT}$, is calculated from the load/unload displacement curves following the method given by Oliver and Pharr [9]:

$$\frac{1}{E_r} = \frac{(1 - \nu^2)}{E_{IT}} + \frac{(1 - \nu_i^2)}{E_i}$$

(1)

where $\nu$ is Poisson’s ratio for the sample, and $E_i$ and $\nu_i$ are elastic modulus and Poisson’s ratio for Berkovich diamond indenter, i.e., $E_i=1140$ GPa and $\nu_i=0.07$ [10]. $E_r$ is the reduced modulus for the sample, which is found from indentation test data and is given by the following equation:

$$S = \frac{dP}{dh} = \frac{1}{\beta \sqrt{\pi}} \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$

(2)

where $S$ is the initial unloading contact stiffness, $h$ is the penetration depth, $\beta$ is a constant of the geometry of indenter tip, i.e., $\beta=1.034$ for the Berkovich tip, and $A$ is the projected area of contact at the load. Furthermore, the indentation hardness, $H_{IT}$, is defined by the following equation:

$$H_{IT} = \frac{P}{A}$$

(3)
4.3. Results and discussion

4.3.1. Sample Preparation and Observation of Surface of the Glass-ceramics with CaF$_2$ Nanocrystals

A glass sample with the composition of 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ (mol%) shows the values of $T_g=590^\circ$C and $T_p=651^\circ$C, as already reported in the chapter III and the previous paper [8]. The XRD pattern for the sample obtained by a heat treatment at 700°C for 3 h in air is shown in Fig. 1. All peaks appeared are assigned to fluorite-type CaF$_2$ crystals (ICDD: 00-035-0816). The size of CaF$_2$ crystals in the heat-treated (700°C) sample was estimated to be ~30 nm using Scherrer’s equation, in which the peak position and the peak-width at half-maximum corrected from the instrumental broadening were used.

In order to clarify the dispersion state of CaF$_2$ nanocrystals at the surface of the heat-treated (700°C) sample using TEM observations, the heat-treated bulk sample was processed to a thin foil shape using a FIB method. In usual sample preparation for TEM observations in oxyfluoride glass-ceramics, plate shape sample is pulverized and edge (thin part) of powders is observed. Consequently, information on the dispersion state and morphology of fluoride nanocrystals in the interior of a given glass-ceramics is obtained by TEM observations. Contrary, by using FIB sample preparation, the dispersion state and morphology of fluoride nanocrystals at the original surface of a given bulk glass-ceramics are examined.

The TEM image for the edge part of a thin foil (heat-treated at 700°C for 3 h) prepared by a FIB method is shown in Fig. 2(a). The sphere particles with a diameter of ~30 nm are observed at the interior. The diameter of ~30 nm evaluated from TEM observations is almost the same as that evaluated from XRD pattern. It should be pointed out that, however, at the surface of ~150 nm, any particle is not observed. These results suggest that the crystallization behavior of CaF$_2$ nanocrystals at the surface is different from that in the interior. The high resolution images for the surface and a particle are shown in Fig. 2(b) and Fig. 2(c), respectively. It is confirmed that the surface is amorphous and the particles are crystals, i.e., CaF$_2$. The STEM-EDS data for the thin foil are shown in Fig. 3. The peaks are attributed for the elements of Ca, Al, Si, O, and F, which are constituents in the sample of 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$, and
the peaks assigned to the elements of Ga and Mo are also detected, which are coming from the FIB sample preparation (Ga ion beam and Mo grid). It is seen that the peak intensities for Ca, Al, Si, and O elements in the near edge region of the thin foil (the original surface of the bulk heat-treated sample) are almost the same as those in the inside region. However, it is found that the peak intensity of F in the near edge region is smaller than that in the inside region. To confirm this phenomenon more clearly, the line analysis in STEM-EDS experiments was carried out from the surface to the inside region, and the relative intensity ratio of F and O, i.e., F/(F+O), is shown as a function of the distance from the surface in Fig. 4. It is seen that the concentration of F changes gradually depending on the distance from the surface. The results shown in Figs. 3 and 4 indicate clearly that the concentration of F at the surface is small compared with the interior. That is, in the transparent oxyfluoride glass-ceramics containing CaF$_2$ nanocrystals obtained by a heat treatment at 700°C for 3 h in air, a fluorine deficient layer is formed at the surface. This would be a main reason why CaF$_2$ nanocrystals are not formed at the surface of bulk glass-ceramics as shown in Fig. 2.
Fig. 1. XRD pattern for the sample obtained by a heat treatment at 700°C for 3 h in air. All XRD peaks are assigned to the fluorite CaF$_2$ crystalline phase.
Fig. 2. TEM image (a) for the edge part of a thin foil (heat-treated at 700°C for 3 h) prepared by a FIB method. (b) and (c) are the high resolution TEM images for the surface and a particle of a thin foil, respectively.
Fig. 3. STEM-EDS spectra for the inside region and near edge region of a thin foil (heat-treated at 700°C for 3 h) prepared by a FIB method.
Fig. 4. Intensity ratio of the peaks of F and O obtained from STEM-EDS spectra as a function of the distance from the surface for a thin foil (heat-treated at 700°C for 3 h) prepared by a FIB method.
4.3.2. Weight Loss of the Oxyfluoride Glass

TG measurements in air were carried out for 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ glass ($T_g$=590°C and $T_p$=651°C), in which the glass was held at temperatures of 500, 600, and 700 °C for 12 h. The results are shown in Fig. 5. It is seen that the glass weight decreases gradually during the heating at 600 and 700°C. For instance, the heating at 600°C and 700°C for 12 h gives the weight losses of ~1.20wt% and ~1.56wt%, respectively. It was confirmed from XRD analyses that any crystal is not formed in the heating at 600°C for 12 h. Combined with the data shown in Figs. 3 and 4, it is concluded that some amount of fluorine is removed from the glass during the heating at temperatures above the glass transition temperature. The chemical composition of 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ glass corresponds to the weight of fluorine of ~13wt%. If the weight loss of ~1.56wt% observed is assumed to be due to the removal of only fluorine, the amount of 12% of fluorine present in the glass must be removed from the surface.

Fig. 5. Mass changes at the temperatures of 500, 600, and 700°C obtained by TG curves as a function of holding time for the powder of the base glass.
4.3.3. Mechanical Properties of the Oxyfluoride Glass and Glass-ceramics in the Surface

The deformation behavior of the transparent oxyfluoride glass-ceramics containing CaF$_2$ nanocrystals obtained by a heat treatment at 700°C for 3 h was examined using a nanoindentation technique in order to clarify the effect of the fluorine deficient layer on elastic properties. Two samples were prepared; one is the heat-treated sample without any polishing, i.e., the sample with a fluorine deficient layer, and the other is the surface polished sample, i.e., the sample without any fluorine deficient layer. The load and displacement curves obtained for these samples in the condition of the maximum load of $P=100$ $\mu$N are shown in Fig. 6, and the values of elastic modulus ($E_{IT}$) and hardness ($H_{IT}$) evaluated from the curves (Fig. 6) and using Eqs. (1) to (3) are presented in Table 1. In the calculation, the value of the Poisson’s ratios, $\nu=0.26$, was used [8]. It is seen that the values of $E_{IT}=140$ GPa and $H_{IT}=9.5$ GPa for the un-polished sample are larger than those ($E_{IT}=117$ GPa and $H_{IT}=8.5$ GPa) for the polished sample. That is, the sample with a fluorine deficient layer show a high resistance against a Berkovich indentation compared with the sample with no fluorine deficient layer. As reported in the previous paper [8], the oxide glass of 30CaO-20Al$_2$O$_3$-50SiO$_2$ with no CaF$_2$ shows larger elastic properties compared with the oxyfluoride glass of 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$. The data shown in Fig. 6 and Table 1 are, therefore, support the formation of a fluorine deficient layer at the surface of oxyfluoride glass-ceramics.

The present study gives new information on the crystallization behavior of oxyfluoride glass (25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$). That is, a fluorine deficient layer of about 150~200 nm is formed during the heating at temperatures above $T_g$ in the surface region and thus fluoride nanocrystals (CaF$_2$) are not present in the surface region. The reason for the formation of such fluorine deficient layers is due to the removal of some fluorine from the surface of bulk glass during heating. This new finding would be extremely important for practical applications of transparent oxyfluoride glass-ceramics containing fluoride nanocrystals, because it is expected that transparent oxyfluoride glass-ceramics would be used as the bulk shape of plate or fiber.
Fig. 6. Load/unload and displacement curves obtained for the original (not surface polished) and surface polished samples obtained by a heat treatment at 700°C for 3 h in air. The maximum load was $P=0.1$ mN.

Table 1

Values of hardness ($H_{IT}$) and Elastic modulus ($E_{IT}$) estimated from the load and displacement curves obtained by a nanoindentation method for the transparent oxyfluoride glass-ceramics (heat-treated at 700°C for 3 h in air).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum penetration depth (nm)</th>
<th>$H_{IT}$ (GPa)</th>
<th>$E_{IT}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load: 0.1 mN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Un-polished</td>
<td>21</td>
<td>9.5±0.5</td>
<td>140±3</td>
</tr>
<tr>
<td>Polished</td>
<td>22</td>
<td>8.5±0.4</td>
<td>117±4.</td>
</tr>
<tr>
<td>Load: 0.5 mN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Un-polished</td>
<td>53</td>
<td>10.2±0.2</td>
<td>131±2</td>
</tr>
<tr>
<td>Polished</td>
<td>58</td>
<td>8.3±0.6</td>
<td>113±2</td>
</tr>
</tbody>
</table>
4.3.4. Mechanism of Formation of Fluorine Deficient Layer

The fluorine removal observed at the glass surface in the temperatures of 600 and 700°C would be closely related to the bonding and coordination states of fluoride ion F⁻ in oxufluoride glasses. As suggested in the previous paper [8], the difference in the chemical bond strength between CaO (the melting temperature, \( T_m = 2570°C \)) and CaF₂ (\( T_m = 1418°C \)) would be a main reason for the large decrease in the glass transition temperature due to the substitution of CaF₂ for CaO in xCaF₂-(30-x)CaO-20Al₂O₃-50SiO₂ glasses, i.e., \( T_g = 775°C \) for the glass with x=0 and \( T_g = 590°C \) for the glass with x=25. Bocker et al. [11] reported that the viscosity of Na₂O-K₂O-Al₂O₃-SiO₂ glasses with BaF₂ additions decreases with increasing BaF₂ content, being due to a weakened network caused by the incorporation of F⁻, and the diffusion coefficient of F⁻ is around two orders of magnitude larger than that of Ba²⁺. Stamboulis et al., [12] proposed from \( ^{29} \text{Si}, ^{27} \text{Al}, \) and \( ^{19} \text{F} \) magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra that the addition of CaF₂ to xCaF₂-(40-x)CaO-20Al₂O₃-40SiO₂ glasses results in the formation of F-Ca bonds at low fluoride ion content and both F-Ca and Al-F-Ca bonds at higher fluoride ion content. From these previous reports [8,11,12], it is reasonable to conclude that the mobility of F⁻ ions in oxyfluoride glasses is much larger than those of O²⁻ ions and other cations.

Persson et al., [13] examined the kinetics of fluoride evaporation from CaF₂-CaO-Al₂O₃-SiO₂ slags in the temperature range of 1400-1600°C using thermogravimetric analysis and proposed the following reaction as a mechanism:

\[
2\text{CaF}_2(\text{slag}) + \text{SiO}_2(\text{slag}) \rightarrow \text{SiF}_4(\text{g}) \uparrow + 2\text{CaO}(\text{slag}) \quad (4)
\]

\[
\text{CaF}_2(\text{slag}) + \text{H}_2\text{O} \rightarrow \text{CaO} + 2\text{HF}(\text{g}) \uparrow \quad (5)
\]

It is noted that the direct evaporation of CaF₂ according to the following reaction is negligible [13]:

\[
\text{CaF}_2(\text{slag}) \rightarrow \text{CaF}_2(\text{g}) \quad (6)
\]

In the present study, a fluorine deficient layer was formed in the heating at much low temperatures of 600 or 700°C as shown in Fig. 5. Therefore, the model (Eq.(4)) proposed by Persson et al.[13] might not be applied to the present study. In order to clarify the mechanism of the formation of a fluorine deficient layer in oxyfluoride glasses, further study will be required.
4.4. Conclusions

The transparent glass-ceramics with CaF$_2$ nanocrystals (diameter: ~30 nm) for 25CaF$_2$-5CaO-20Al$_2$O$_3$-50SiO$_2$ were fabricated using a conventional glass crystallization method in an electric furnace in air and the dispersion state of CaF$_2$ nanocrystals at the surface was examined from transmission electron microscope observations combined with focused ion beam sample preparations. It was demonstrated that a fluorine deficient layer of about 150~200 nm is formed during the heating at temperatures above the glass transition temperature in the surface region and thus CaF$_2$ nanocrystals are not present in the surface region. The reason for the formation of such fluorine deficient layers is due to the removal of some fluorine from the surface of bulk glass during heating. It was found that the indentation elastic modulus and indentation hardness measured by a nanoindentation technique for the surface with a fluorine deficient layer are larger than those for the inside region. The present study gives new information for device applications and for the crystal growth mechanism of fluoride nanocrystals in oxyfluoride glass-ceramics.
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References


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Chapter V

Effect of AlN and Er$^{3+}$ Addition on Morphology of CaF$_2$ Nanocrystals in Oxyfluoride Glass-ceramics

5.1. Introduction

Optically transparent oxyfluoride glass-ceramics containing rare-earth (RE$^{3+}$)-doped fluoride nanocrystals such as Er$^{3+}$-doped CaF$_2$ have received much attention for use of optical devices such as laser and phosphor [1-3]. In such materials, RE$^{3+}$ ions are incorporated into fluoride nanocrystals having low phonon energies and consequently excellent photoluminescence (PL) properties of RE$^{3+}$ ions are obtained. Furthermore, host oxide glassy matrices such as Al$_2$O$_3$-SiO$_2$ having strong glass network structures guarantee mechanical and chemical stability in oxyfluoride glass-ceramics [4,5]. Usually, oxyfluoride glass-ceramics are fabricated through well-controlled heat treatments in an electric furnace and desired fluoride nanocrystals are formed in the interior of glasses.

Besides heat treatment condition, the design of glass system and chemical composition is also important for controlling the size and morphology of fluoride nanocrystals in oxyfluoride glass-ceramics. The most well-known and familiar system in oxyfluoride glass-ceramics is CaF$_2$ (or BaF$_2$, SrF$_2$)-Al$_2$O$_3$-SiO$_2$, and the content of CaF$_2$ is around 15-30 mol%. The doping amount of RE$^{3+}$ ions in oxyfluoride glass-ceramics shows strong PL intensities. From the point of view of practical device applications, although the problem so called concentration quenching, a large amount doping of RE$^{3+}$ into fluoride nanocrystals would be desirable, especially luminescence for infrared region or upconversion laser for Er$^{3+}$[6, 7]. Furthermore, a deep understanding of the morphology and spatial distribution state of fluoride nanocrystals...
in oxyfluoride glass-ceramics with a large amount of RE$^{3+}$ ions would be also important [4,5]. Although it has been reported that the formation behavior of fluoride nanocrystals in oxyfluoride glasses is largely affected by the addition of RE$^{3+}$ ions [8-10], the morphology of fluoride nanocrystals has not been well understood.

The purpose of this study is to clarify the morphology and spatial distribution state of CaF$_2$ nanocrystals in oxyfluoride glass-ceramics based on the ErF$_3$-CaF$_2$-Al$_2$O$_3$-SiO$_2$ system with different ErF$_3$ contents of 1-3 mol% from transmission electron microscope (TEM) observations. We found that the addition of a small amount (2 mol%) of AlN has a remarkable effect on the spatial uniform distribution (i.e., disappearance of assembly) of CaF$_2$ nanocrystals. The present study proposes a new method for the design of composition in rare-earth doped oxyfluoride glass-ceramics.

### 5.2. Experimental Procedure

Glasses with the nominal compositions of $x$ErF$_3$-(30-x)CaF$_2$-20Al$_2$O$_3$-50SiO$_2$ ($x$=0, 1, 3) and 2AlN-3ErF$_3$-27CaF$_2$-19Al$_2$O$_3$-50SiO$_2$ (mol%) were prepared using a conventional melt-quenching method. Commercial powders of reagent grade ErF$_3$, CaF$_2$, AlN, Al$_2$O$_3$, and SiO$_2$ were used. The batch of 20 g was mixed and melted in a platinum crucible or an aluminum crucible with a cover at 1350°C for 1 h in an electric furnace. The melts were poured onto an iron plate and pressed by another iron plate. The glass transition ($T_g$) and crystallization peak ($T_p$) temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10K/min in air. The glasses were annealed at the temperature of $T_g-30$°C for 3 h to release internal stresses. The glasses were heat-treated at 700°C for 3 h in an electric furnace in air. The crystalline phase present in the heat-treated samples was examined by X-ray diffraction (XRD) analyses at room temperature using CuK$\alpha$ radiation. TEM and scanning transmission electron microscope (STEM) observations in the high angle annular dark-field imaging mode (STEM-HAADF) with an energy dispersive spectrometry (EDS) were conducted for pulverized particles on molybdenum mesh using JEM-2100F microscope (JEOL, Tokyo, Japan). Young’s modulus and Poisson’s ratio at room temperature for the samples were determined by cube resonance method (same as Chapter II and III).
Chapter V - Effect of AlN and Er$^{3+}$ Addition on Morphology of CaF$_2$ Nanocrystals in Oxyfluoride Glass-Ceramics

5.3. Results and Discussion

5.3.1. Optical Properties and Crystallization of Er$^{3+}$-doped Oxyfluoride Glass

All of the samples obtained by a melt-quenching were optically transparent and their amorphous state was confirmed from XRD analyses. The glass with the addition of 2 mol% AlN and 3 mol% of ErF$_3$ keeps a good optical transparency, but some bubbles are present in the inside of the glass. The formation of bubbles suggests that the following reaction is taking place during melting at 1350°C in air:

$$4AlN + 3O_2\text{(inair)} \rightarrow 2Al_2O_3 + 2N_2 \uparrow$$  \hspace{1cm} (1)

All the melt-quenched samples showed similar DTA curves shown in Fig. 1 with endothermic peaks due to the glass transition and exothermic peaks due to the crystallization. The glass with no ErF$_3$ has the values of $T_g=576^\circ$C and $T_p=647^\circ$C. Other glasses showed the following values: $T_g=603^\circ$C and $T_p=701^\circ$C for the glass with 1 mol% ErF$_3$, $T_g=600^\circ$C and $T_p=717^\circ$C for 3 mol% ErF$_3$, and $T_g=601^\circ$C and $T_p=647^\circ$C for 2 mol% AlN. It is found that the crystallization temperature increases slightly with the addition of ErF$_3$.

The XRD patterns for the samples obtained by heat-treatments at 700°C for 3 h are shown in Fig. 2. All peaks are assigned to the fluorite-type CaF$_2$ crystalline phase (ICDD: 00-035-0816). The peak positions of CaF$_2$ crystal shifted to a lower angle with the addition of ErF$_3$, indicating the increase in the lattice constant. This result suggests that Er$^{3+}$ ions are incorporated into Ca$^{2+}$ sites in CaF$_2$ crystals. In the glass with the addition of 2 mol% AlN and 3 mol% of ErF$_3$, the formation of CaF$_2$ crystals are clearly confirmed, indicating that the small addition of AlN does not depress the crystallization of CaF$_2$ crystals in alunimosilicate-based oxyfluoride glasses.

The optical photographs for the crystallized samples are also shown in Fig. 2 and transmittance spectra for no doped and 3ErF$_3$-doped sample are shown in Fig.3. It is seen that the crystallized glass with no ErF$_3$, i.e., 30CaF$_2$-20Al$_2$O$_3$-50SiO$_2$, is colorless, suggesting that nano-scaled CaF$_2$ crystals are formed. The crystallized glass with 1 mol% ErF$_3$ still keeps a good optical transparency. The crystallized glass with 3 mol% ErF$_3$, however, loses an optical transparency and is becoming a translucent sample. The crystallized glass with the addition of 2 mol% AlN and 3 mol% of ErF$_3$ keeps a good
optical transparency, although some bubbles are still present in the inside of the sample.

![Fig. 1. DTA curves for the obtained oxyfluoride glasses with the compositions of $x\text{ErF}_3-(30-x)\text{CaF}_2-20\text{Al}_2\text{O}_3-50\text{SiO}_2$ ($x=0-3$) and $2\text{AlN}-3\text{ErF}_3-27\text{CaF}_2-19\text{Al}_2\text{O}_3-50\text{SiO}_2$.](image)
Fig. 2. XRD patterns at room temperature for the heat-treated (700°C, 3 h) samples in xErF<sub>3</sub>-(30-x)CaF<sub>2</sub>-20Al<sub>2</sub>O<sub>3</sub>-50SiO<sub>2</sub> (x=0-3) and 2AlN-3ErF<sub>3</sub>-27CaF<sub>2</sub>-19Al<sub>2</sub>O<sub>3</sub>-50SiO<sub>2</sub> glasses (mol%). All XRD peaks are assigned to the fluorite-type CaF<sub>2</sub> crystalline phase (ICDD: 035-0816).
Fig. 3. Transmittance of 1-mm thick of (top) no dope and (bottom) 3mol% of ErF₃-doped glass and glass-ceramics.
5.3.2. Morphology of Er$^{3+}$-doped Oxyfluoride Glass-ceramics

The TEM images for the crystallized (700°C, 3 h) samples containing CaF$_2$ crystals are shown in Fig. 4. The samples with no ErF$_3$ and 1 mol% ErF$_3$ show the formation of sphere particles with the size of ~30 nm for no ErF$_3$ and ~40 nm for 3 mol% ErF$_3$ and the particles are distributed homogeneously. In the sample with 3 mol% ErF$_3$, however, star-like particles with a size of ~50 nm or assembly of particles are formed. The HAADF image for the crystallized (700°C, 3 h) samples with 3 mol% ErF$_3$ is shown in Fig. 5. Many particles with a size of ~50 nm and with a square morphology are observed, and some of them are assembled. The HAADF image shown in Fig. 5 means that the white color particles contain heavy elements such as Ca and Er. The EDS spectra for a white color particle and a grey color region are shown in Fig. 4. It is seen that elements of Ca, Er, and F are enriched in the white color particle compared with the grey color region enriching Al, Si, and O. These results indicate that the white color particle is a CaF$_2$ crystal containing Er$^{3+}$ ions.

The present study indicates the following three features in the crystallization of CaF$_2$ nanocrystals in a ErF$_3$ added aluminosilicate-based oxyfluoride glass: 1) the addition of a large amount (~3 mol%) of ErF$_3$ induces the increase in the size of CaF$_2$ crystals and also their assembly, 2) Er elements are incorporated into CaF$_2$ nanocrystals, 3) the addition of an amount (2 mol%) of AlN depresses the increase in the size of CaF$_2$ crystals and also their assembly.

Barros et al. [8] studied the effect of ErF$_3$ addition on the crystallization behavior of BaF$_2$ nanocrystals in aluminosilicate-based oxyfluoride glasses and reported that small amount of ErF$_3$ addition promotes droplet-type phase separations. It has been also suggested that Er$^{3+}$ ions act as nucleating agents in the formation of fluoride nanocrystals in oxyfluoride glasses [9]. Hu et al. [8] studied the effect of ErF$_3$ content on the crystallization behavior of 41.2SiO$_2$-29.4Al$_2$O$_3$-17.6Na$_2$O-11.8LaF$_3$-xErF$_3$ glasses (x=0-6) (mol%) and reported that the size of LaF$_3$ nanocrystals increases with increasing ErF$_3$ content. These studies [8-10] suggest that the increase in Er$^{3+}$ content in oxyfluoride glasses induces the increase in the size and the assembly of fluoride nanocrystals, and thus the maximum concentration of ErF$_3$ in oxyfluoride glasses is generally limited to ~2 mol% in order to keep a good optical transparency and also to avoid the concentration quenching.

The results obtained in this study, i.e., the addition of an amount (2 mol%) of AlN
depresses the increase in the size of CaF$_2$ crystals and also their assembly, strongly suggest that the size of phase separation in the aluminosilicate-based oxyfluoride glasses with an amount of 3 mol% ErF$_3$ prepared by the addition of AlN is becoming small. At this moment, the amount of nitrogen remained in the oxyfluoride glass prepared in this study is unclear. If all AlN added are converted to Al$_2$O$_3$ and N$_2$ gas followed by the reaction (1), the composition of 2AlN-3ErF$_3$-27CaF$_2$-19Al$_2$O$_3$-50SiO$_2$ (mol%) corresponds to 3ErF$_3$-27CaF$_2$-20Al$_2$O$_3$-50SiO$_2$. That is, the content of Al$_2$O$_3$ in both glasses, i.e., the ratio of Al$_2$O$_3$/SiO$_2$, is the same. It is recognized that the rigid network structure constructed by Al$_2$O$_3$ and SiO$_2$ has a key role for the formation of fluoride nanocrystals in aluminosilicate-based oxyfluoride glasses. Recently, Raghuwanshi et al. [11] studied that the crystallization of the oxyfluoride glass-ceramics having narrow crystallite size distribution with the composition of 69.6SiO$_2$-7.5Al$_2$O$_3$-15.0K$_2$O-1.9Na$_2$O-6BaF$_2$. They proposed that the BaF$_2$ nanocrystals having narrow size distribution are formed due to the SiO$_2$-enriched high viscosity barrier formed around the BaF$_2$ nanocrystals and it prevents crystal growth and Ostwald ripening. It indicates the viscosity around the nanocrystals is largely affects for the crystal size. The present study suggests that the network structure in oxyfluoride glasses changes depending on the use of Al$_2$O$_3$ or AlN. It is required to clarify the coordination state of Al in oxyfluoride glasses prepared by using AlN.
Fig. 4. TEM image (bright field) for the heat-treated (700°C, 3 h) samples in xErF\(_3\)-(30-x)CaF\(_2\)-20Al\(_2\)O\(_3\)-50SiO\(_2\) (x=0-3) and 2AlN-3ErF\(_3\)-27CaF\(_2\)-19Al\(_2\)O\(_3\)-50SiO\(_2\) glasses (mol%).
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Fig. 5. STEM-HAADF image for the heat-treated (700°C, 3 h) samples in 3ErF$_3$-27CaF$_2$-20Al$_2$O$_3$-50SiO$_2$ glass.
Fig. 6. EDS spectra in the crystal (bright) region and glass matrix (dark) region measured by STEM-EDS for the heat-treated (700°C, 3 h) samples in 3ErF₃-27CaF₂-20Al₂O₃-50SiO₂ glass.
5.3.3. Elastic Properties of Er$^{3+}$-doped Oxyfluoride Glass-ceramics

All glass-ceramics obtained by heat-treatments were formed CaF$_2$ nanocrystals. Densities of the glasses and glass-ceramics are shown in Fig. 7. Densities increased with increasing ErF$_3$ content due to high molar weight. Packing densities were also increased with increasing Er content. Young’s modulus, shown in Fig. 8, is evaluated by cube resonance method. 3 mol% of ErF$_3$ doped glass and glass ceramics showed higher Young’s modulus relative to no doped glass and glass-ceramics. Elasticity depends on the bonding energy and packing density. Er$^{3+}$ ion is consider to make increase Young’s modulus due to Er$^{3+}$ has larger bonding energy and higher cationic field and packing density than Ca$^{2+}$. Poisson’s ratio, $\sigma$, is shown in Fig. 9. Poisson’s ratio was decreased with adding ErF$_3$ or crystallization. As referred in Chapter 11, Poisson’s ratio depends on the dimensionality of the structure and cross-link density. Typical three-dimensional glasses like SiO$_2$ or GeO$_2$ have $\sigma=0.15$, whereas B$_2$O$_3$ including two-dimensional structure have $\sigma=0.3$. Many oxide glasses including both network formers such as SiO$_2$ and network modifiers such as Na$_2$O have the value of $\sigma=0.2$, because addition of network modifier oxide results in creation of non-bridging oxygen and hence reduction in dimensionality. It is known that the oxide having lower bonding energy forms non-bridging oxygen and the oxide having higher bonding energy act as glass network. ErF$_3$ has higher bonding strength than CaF$_2$. It is, therefore, considered that ErF$_3$ makes smaller amount of non-bridging oxygen and ErF$_3$-doped glass has higher dimension structure.
Chapter V - Effect of AlN and Er$^{3+}$ Addition on Morphology of CaF$_2$ Nanocrystals in Oxyfluoride Glass-ceramics

Fig. 7. Densities for the glass and heat-treated (660 or 700°C, 3 h) samples in xErF$_3$-(30-x)CaF$_2$-20Al$_2$O$_3$-50SiO$_2$ (x=0-3) (mol%).

Fig. 8. Young’s modulus for the glass and heat-treated (660 or 700°C, 3 h) samples in xErF$_3$-(30-x)CaF$_2$-20Al$_2$O$_3$-50SiO$_2$ (x=0-3) (mol%).
Fig. 9. Poisson’s ratio for the glass and heat-treated (660 or 700°C, 3 h) samples in xErF₃-(30-x)CaF₂-20Al₂O₃-50SiO₂ (x=0-3) (mol%).
5.4. Conclusions

The morphology and spatial distribution state of CaF$_2$ nanocrystals in oxyfluoride glass-ceramics in the system of xErF$_3$-(30-x)CaF$_2$-20Al$_2$O$_3$-50SiO$_2$ (x=0-3) and 2AlN-3ErF$_3$-27CaF$_2$-19Al$_2$O$_3$-50SiO$_2$ (mol%) with different ErF$_3$ contents of 1-3 mol% and the addition of AlN were examined from TEM and STEM-HAADF observations. The content of 3 mol% ErF$_3$ induced the growth of CaF$_2$ nanocrystals with star-like morphologies and their assemblies with the size of ~70 nm. The addition of a small amount (2 mol%) of AlN has a remarkable effect on the spatial uniform distribution (i.e., disappearance of assembly) of CaF$_2$ nanocrystals. The glasses with ErF$_3$ of Young’s modulus are increased and Poisson’s ratio are decreased with addition of ErF$_3$. The present study suggests that the network structure in oxyfluoride glasses changes depending on the use of Al$_2$O$_3$ or AlN and thus proposes a new method for the design of rare-earth doped oxyfluoride glass-ceramics.
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References


Chapter VI

Novel Oxyfluoride Glass-ceramics with BaAlBO$_3$F$_2$ Nanocrystals and Fabrication of Single Crystal Line

6.1. Introduction

Oxyfluoride glass and ceramics are desirable materials for photonics uses because of their phonon energy, chemical and mechanical durability, and thermal stability. This makes them attractive for up-conversion laser, fiber amplifier, and phosphor. Recent decades, glass-ceramics containing fluoride nanocrystals such as fluorite type CaF$_2$ are proposed [1-3]. Usually, oxyfluoride-based glass-ceramics are fabricated through well-controlled heat treatments in an electric furnace and desired fluoride nanocrystals are formed in the interior of glasses. Recently, fabrication of wave-guide consisted of CaF$_2$ nanocrystals are proposed [4-7]. Kanno et al. reported that spatially controlled crystallized crystal line consisting of CaF$_2$ nanocrystals fabricated on the glass with the composition of ErF$_3$-NiO-NaF-CaF$_2$-Al$_2$O$_3$-SiO$_2$ system by laser irradiations [6, 7]. Such glass has the strong network consisted of Al$_2$O$_3$-SiO$_2$ strong glass network. Such strong glass network prevents crystal growth and, therefore, nano-sized crystals are formed. Ihara et al. reported that the single crystal or highly oriented non-linear optical (NLO) crystal lines, i.e. BaB$_2$O$_4$ and BiBO$_3$, fabricated on the glass having related composition to crystal phase [8, 9]. Such NLO crystal line on glass surface is a candidate material of photoregulation devices. Such precursor glass has weak glass network, such as B$_2$O$_3$ network, and related composition of crystal phase. Therefore, crystal growth is easily and not demanded large diffusion of ions. It is interesting for the use of photonic devices such as wave-guide laser to fabricate the wave-guide consisted of single crystal oxyfluoride glass containing large amount of fluorine. However, fabrication of oxyfluoride crystal line and the crystallization of oxyfluoride crystals from the glass
BaAlBO$_3$F$_2$ (BABF) is new oxyfluoride crystal and attractive material first demonstrated high efficiency SHG laser generation by Z.G. Hu et al. in 2002 [10]. After that, BABF crystal is the excellent candidate for high power UV laser because of its high SHG and THG efficiency, about two times large as SHG efficiency of KH$_2$PO$_4$ (KDP), deep UV absorption edge and high thresholds for laser-induced damage [10-13]. We focused our attention on fabrication of high orientation NOL BABF line on glass surface. We first succeeded for SHG observation in novel oxyfluoride glass-ceramics having large amount of fluorine up to 40% for anions with the composition of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ containing BaAlBO$_3$F$_2$ nanocrystal and fabrication of single crystal line.

6.2. Experimental Procedure

A glass with the composition of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ (in mol%) and 1Eu$_2$O$_3$, 3NiO, 3NiO-1ErF$_3$ -doped sample were prepared using a conventional melt-quenching method. 10 g of batches were well mixed and melted in a platinum crucible with a caver at 1200°C for 20 min in an electric furnace. Commercial powders of reagent grade BaF$_2$, Al$_2$O$_3$, B$_2$O$_3$, Eu$_2$O$_3$, NiO, ErF$_3$ were used. The melts were poured onto iron plate and pressed into ~1mm thick using another iron plate. The glass transition, $T_g$, crystallization onset, $T_x$, and crystallization peak, $T_p$, temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10 K/min in air. The glasses were annealed at $T_g$ for 1 h to release internal stresses. The glasses were heat-treated at 500°C for 10 h and 560°C for 3 h in an electric furnace in air. The crystalline phase present in the heat-treated samples was examined by X-ray diffraction (XRD) analyses at room temperature using CuKα radiation. Density of the samples was obtained by Archimedes method. Refractive index of the glass samples was measured by ellipsometry. Optical absorption spectra for the samples with a thickness of 1mm were taken in the wavelength range of $\lambda$=180–1000 nm on a Shimadzu UV-3150 spectrometer. The PL quantum efficiencies in the visible region of Eu$^{3+}$ ions were measured with a PL spectrometer with an integrating sphere (Hamamatsu Photonics:...
Absolute PL Quantum Yield Measurement System (C9920-20) at room temperature was used. The structure of the investigated slags was analyzed by FT-IR spectroscopy (Nicolet, IMP-410). FT-IR transmitting spectra were recorded in the 4000–400 cm\(^{-1}\) range. Each sample of 2.0 mg was mixed with 200 mg of KBr, and then pressed into pellets of 13 mm diameter. The spectrum for each sample represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet. The FT-IR spectra have been analyzed by computer software. XPS measurements were carried out with a JEOL JPS-9010TR electron spectrometer, which has Al conical anode for charge control. Non-monochromatic 240 W MgK\(_{α}\) X-ray provided the excitation radiation. During experiments the pressure inside the analyzer chamber was about 10 \(^{-7}\) Pa. The drift of the electron binding energy due to surface charging effect was calibrated by utilizing the C\(_{1s}\) peak (binding energy = 284.6 eV) of the contamination of the pumping oil at the sample introduction chamber. Transparent electron microscopy (TEM) for the heat-treated sample was observed by FE-TEM (JEM2100F, JEOL). SHG of samples were observed by SHG microscopy with \(\lambda=1064\) nm of Q-switch Nd: YAG laser. Yb: YVO\(_4\) fiber laser with \(\lambda=1080\) nm was irradiated to the NiO doped glass surface in the power of 1.1 W for laser-inducing crystallization. The glass sample was put on the stage and mechanically moved with the speed of 8 \(\mu\)m/s and formed crystallized line [5]. The crystalline phase in the laser-irradiated regions was examined with micro-Raman scattering spectra (Tokyo Instruments Co., Nanofinder; Ar\(^{+}\) laser \(\lambda=488\) nm).
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6.3. Results and Discussion

6.3.1. Thermal Properties of the Oxyfluoride Glass

A clear transparent melt-quenched sample was obtained for the composition of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$, and the amorphous state was confirmed from the XRD analysis. The DTA curves for the bulk and powdered samples are shown in Fig. 1. One sharp exothermic peak is observed for the bulk sample. The values of glass transition and crystallization peak temperatures for the bulk sample were determined to be $T_g$=488 °C and $T_p$=566°C, respectively. For the powder sample, a small and broad exothermic peak is observed, and it is noted that the peak position (temperature) is almost the same as for the bulk sample. These results demonstrate that a glass with the composition of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ (mol%) with a high fluorine content which corresponds to the stoichiometric composition of BaAlBO$_3$F$_2$ crystal, is prepared using a conventional melt-quenching method.
**Fig. 1.** DTA curves for the bulk and powdered samples for 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ glass. The glass transition temperature ($T_g$) and crystallize peak ($T_p$) temperatures were defined for the bulk sample. The heating rate was 10 K/min.
6.3.2. Crystallization of the Glass in the Furnas

The XRD patterns for the samples obtained by heat treatments at 500°C (near $T_g=488^\circ$C) for 10 h and 550°C (near $T_p=566^\circ$C) for 3 h in air are shown in Fig. 2. All peaks observed are assigned to the BaAlBO$_3$F$_2$ crystal (ICDD: 01-071-2773). The lattice constants of BaAlBO$_3$F$_2$ crystals formed in the heat-treated samples were evaluated from XRD patterns using a least-square fitting method, and the values of $a=0.4853$ nm and $c=0.9438$ nm were obtained. These values are close to those ($a=0.48770$ and $c=0.93824$ nm) for BaAlBO$_3$F$_2$ single crystal [16]. The density of the sample heat-treated at 550°C for 3 h was $d_{\text{sample}}=4.29$ g/cm$^3$. The volume fraction ($f$) of BaAlBO$_3$F$_2$ crystals formed was calculated from the values of $d_{\text{glass}}=4.02$ g/cm$^3$ for the base glass and $d_{\text{crystal}}=4.47$ g/cm$^3$ for BaAlBO$_3$F$_2$ single crystal by using the following equation;

$$d_{\text{sample}} = f d_{\text{crystal}} + (1-f)d_{\text{glass}}$$

and the value of $f=0.58$ was obtained.

Second harmonic generations (SHGs) were clearly observed for the heat-treated samples (the data are not shown here), indicating that BaAlBO$_3$F$_2$ crystals formed are nonlinear optical crystals. The sample heat-treated at 550°C for 3 h is optically translucent. This would be due to the large difference in refractive index between the host glass ($n=1.564$) and BaAlBO$_3$F$_2$ crystal ($n_o=1.6284$) and also due to the relatively large particle size of 50-100 nm (TEM observations).

A TEM photograph for the sample heat-treated at 550°C for 3 h is shown in Fig. 3. The particles with a size of ~50-100 nm were observed. A high resolution TEM image for a particle is also shown in Fig. 3, indicating the formation of BaAlBO$_3$F$_2$ crystal. It should be emphasized that the morphology of particles are not spherical, but ellipsoidal.

BaAlBO$_3$F$_2$ crystal has a hexagonal structure ($P\overline{6}2c$) and is built of the (001) layers of corner-sharing AlO$_3$F$_2$ triangular bipyramids and BO$_3$ triangles. The F atoms and O atoms are fully ordered on the axial and equatorial positions of AlO$_3$F$_2$ bipyramids, respectively, and the layer stacking in BaAlBO$_3$F$_2$ yields as 12-fold coordination of the Ba atoms by 6 fluorine and 6 oxygen atoms [11,12,16]. BaAlBO$_3$F$_2$ is, therefore, an anisotropic crystal. It is considered that such a structural anisotropy provides the ellipsoidal morphology in BaAlBO$_3$F$_2$ crystals formed in oxyfluoride glass-ceramics. Indeed, Yamazawa et al. [26] reported the formation of ferroelectric Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$
nanocrystals with the ellipsoidal morphology in glass-ceramics based on the SrO-BaO-Nb_2O_5-B_2O_3 system. Very recently, Shinozaki et al. [27] also observed the crystallization of nano-scaled Ba_2TiSi_2O_8 particles with the ellipsoidal morphology in glass-ceramics with the composition of 40BaO-20TiO_2-40SiO_2 (i.e., stoichiometric to Ba_2TiSi_2O_8 crystal).

Fig. 2. XRD patterns at room temperature for the samples heat-treated at 500°C for 10 h and 550°C for 3 h of 50BaF_2-25Al_2O_3-25B_2O_3 glass. All XRD peaks are assigned to the BaAlBO_3F_2 crystalline phase.
Fig. 3. TEM image (bright field image) for the sample heat-treated at 550°C for 3 h of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ glass. A high resolution TEM image for a particle is also shown.
6.3.3. Optical Properties of the Oxyfluoride Glass and Glass-ceramics

The refractive index spectrum for BABF glass was measured by ellipsometry and fitted by following Sellmeier equation:

\[ n^2 = A + \frac{B}{\lambda^2 - C} - D\lambda^2 \]  

(2)

where \( A, B, C, D \) are constant. The refractive index for obtained value for BABF glass and BABF single crystal (literature value [12]) are shown in Fig. 4. The glass has large dispersion and the Abbe’s number for BABF glass was calculated as 25. The refractive index \( (n) \), measured by prism coupler, of the base BABF glass at \( \lambda = 632.8 \text{ nm} \) was estimated to be \( n = 1.564 \). It is known that a linear relationship between the refractive index and Abbe’s number. A diagram of relation between the refractive index and Abbe’s number of typical glasses are shown in Fig. 5 and the value of this glass is also included in the graph. Abbe’s number of this glass is to small relative from other glasses. The refractive index of the glass is much smaller than those of nonlinear optical BaAlBO\( _3 \)F\( _2 \) single crystal, i.e., \( n_o = 1.6284 \) and \( n_e = 1.5850 \) [12]. The value of refractive index of glasses is closely related to the electronic polarizability and optical basicity of glasses [21,22]. Duffy [23] reported that the optical basicities (\( \Lambda \)) of binary fluorides are one half those of the corresponding oxides, for example, \( \Lambda (\text{CaF}_2) = 0.50 \) compared with \( \Lambda (\text{CaO}) = 1.00 \) and \( \Lambda (\text{BaF}_2) = 0.62-0.72 \) compared with \( \Lambda (\text{BaO}) = 1.15 \). It is, therefore, expected that oxyfluoride glasses containing a large amount of \( F^- \) ions would show low refractive indices, as in 50BaF\( _2 \)-25Al\( _2 \)O\( _3 \)-25B\( _2 \)O\( _3 \) (mol%) glass.

The optical transmittance spectrum for the base BABF glass with a thickness of 1 mm is shown in Fig. 6. The UV cutoff wavelength is \( \sim 200 \text{ nm} \) and the absorption edge is \( \sim 290 \text{ nm} \). Hu et al. [12] reported that the UV cutoff wavelength of BaAlBO\( _3 \)F\( _2 \) single crystal is 165 nm. The density \( (d) \) of the base BABF glass was estimated to be \( d_{\text{glass}} = 4.02 \text{ g/cm}^3 \), which is much smaller (i.e., about 10%) compared with the value of \( d_{\text{crystal}} = 4.47 \text{ g/cm}^3 \) for BaAlBO\( _3 \)F\( _2 \) single crystal. At this moment, there is no information on the structure of the base BABF glass. But, it is obvious that the base BABF glass has a large open structure compared with BaAlBO\( _3 \)F\( _2 \) crystal.

The PL properties for Eu\(^{3+}\)-doped BABF glass, i.e., 1Eu\( _2 \)O\( _3 \)-50BaF\( _2 \)-25Al\( _2 \)O\( _3 \)-25B\( _2 \)O\( _3 \) (mol), and glass-ceramics were measured. The PL
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spectrum at an excitation of $\lambda_{ex}=397$ nm is shown in Fig. 7. The spectra are normalized by intensity of absorbance. The shapes and intensity ratios of each peak were not changed by heat-treatment. It indicates that the environment of rare earth in the glass and glass-ceramics are similar. The PL peaks due to the $^5D_0 \rightarrow ^7F_J$ transition ($J=0, 1, 2, 3,$ and $4$) in Eu$^{3+}$ ions are clearly observed, and the broad peaks indicate that the site environment of Eu$^{3+}$ ions are largely distributed, being a typical for glasses. The total quantum yield of the emissions of Eu$^{3+}$ ions at the bands of $^5D_0 \rightarrow ^7F_J$ transition ($J=0, 1, 2, 3,$ and $4$) in the visible region for the base BABF glass was measured and the value of 97% was obtained. Quantum yield of the glass as a function of content of Eu$_2$O$_3$ on the glass with the composition of xEu$_2$O$_3$-50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ is shown in Fig. 8. It is clear that the quantum yield did not decreased with increasing Eu$^{3+}$ concentration to show about 97% up to x=3 mol%, whereas further increasing the Eu$^{3+}$ concentration led to decrease in the quantum yield. Quantum yields of some important materials are summarized in Table 1 [24-28]. Su et al. reported that Ca$_{1-2x}$(Eu, Na)$_{2x}$WO$_4$ doped with about 5% of Eu$^{3+}$ showed 92% of quantum yield in maximum and the values are significantly decreased with Eu$^{3+}$ content, for instance only ~45% of quantum yield at 12% of Eu$^{3+}$ content. [25]. By contrast, this glass showed the matchable value of quantum yield and the less concentration quenching, i.e. 70% of quantum yield at 10 mol% of Eu$_2$O$_3$ (~20 mol% of Eu$^{3+}$) content, than these typical phosphors in spite of the glass. It is known that the PL quantum yield of RE ions in glasses depends on the maximum phonon energy of a given matrix. That is, in glasses having high maximum phonon energies, the emission intensity tends to decrease due to the multi-phonon relaxation process. On the contrary, in glasses having low maximum phonon energies, the probability of multi-phonon relaxations decreases, and consequently the emission intensity tends to increase. In the oxyfluoride glass of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ examined in this study, B$_2$O$_3$ has a high maximum phonon energy of ~1350 cm$^{-1}$ [29]. On the contrary, BaF$_2$, which is a main constituent of this glass, has a low maximum phonon energy of ~350 cm$^{-1}$ [30]. The high quantum yield of 97% suggests that Eu$^{3+}$ ions in this oxyfluoride glass are surrounded largely by F$^-$ ions.
Fig. 4. The wavelength dependence of refractive index obtained by ellipsometry for 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ glass.

Fig. 5. The relationship of refractive index and Abbe’s number and present work.
Fig. 6. Optical absorption spectrum at room temperature for 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ glass.

Fig. 7. Photoluminescence spectrum at room temperature for 1Eu$_2$O$_3$-50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ glass. The excitation light of the wavelength of $\lambda$=397nm was used.
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Fig. 8. Quantum yield as a function of content of $Eu_2O_3$ in the glasses with the composition of $xEu_2O_3$:50$BaF_2$:25$Al_2O_3$:25$B_2O_3$ ($x=0.5$-10). The excitation light of the wavelength of $\lambda=397\text{nm}$ was used.

Table 1
Quantum yield (QY) of some important red phosphors doped with $Eu^{3+}$ excited by ultraviolet at room temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample Origin</th>
<th>QY (%)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_2O_3$: Eu$^{3+}$</td>
<td>--</td>
<td>92</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>Philips</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>$YVO_4$: Eu$^{3+}$</td>
<td>--</td>
<td>89</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>Derbi</td>
<td>95</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>G. Blasse</td>
<td>70</td>
<td>[27]</td>
</tr>
<tr>
<td>$Y_3Al_5O_12$:Eu$^{3+}$ (YAG)</td>
<td>--</td>
<td>90</td>
<td>[26]</td>
</tr>
<tr>
<td>$Y_2O_2S$</td>
<td>Hitachi</td>
<td>95</td>
<td>[27]</td>
</tr>
<tr>
<td>$LaPO_4$:Eu</td>
<td>--</td>
<td>59</td>
<td>[28]</td>
</tr>
<tr>
<td>$Ca_{1-x}(Na_xEu_x)WO_4$</td>
<td>--</td>
<td>92</td>
<td>[25]</td>
</tr>
<tr>
<td>$50BaO-25Al_2O_3-25B_2O_3$ (Glass): Eu$^{3+}$</td>
<td>--</td>
<td>97</td>
<td>This Work</td>
</tr>
</tbody>
</table>
6.3.4. Structure of the Oxyfluoride Glass

FT-IR spectra for the glass and glass-ceramics are shown in Fig. 9. Typical IR bands and its vibration type are summarized in Table 2 [34,35]. In glass-ceramics shows three main peaks around 1380 cm\(^{-1}\). The BaAlBO\(_3\)F\(_2\) crystal is composed by AlBO\(_3\)F\(_2\) units consisted by BO\(_3\) (B\(_3\)) and AlO\(_2\)F\(_2\) (Al\(_5\)) units. That is, large peak in 1380 cm\(^{-1}\) are suggested as a possible cause of bending vibration of the BO\(_3\) Glass sample shows broad peaks in same 530, 760, 890, 1040, 1250, 1380, 1460 cm\(^{-1}\). The peaks around 1250, 1330, and 1460 cm\(^{-1}\) are attributed to stretching vibration in B\(_3\) tetrahedron. The peaks around 890 and 1040 cm\(^{-1}\) are attributed to stretching vibration in B\(_4\) tetrahedron (BO\(_4\): 1010–1050 cm\(^{-1}\), BO\(_4\)O\(_2\): 1050 cm\(^{-1}\) and 1400 cm\(^{-1}\)). The peaks around 530 and 760 cm\(^{-1}\) are attributed to Al\(_4\), Al\(_6\). These results indicate the glass is including lots of B as BO\(_3\) unit and Al as AlO\(_4\), AlO\(_5\) and AlO\(_6\) units.

XPS spectra for the glass and glass-ceramics are shown in Fig. 10. F\(_{1s}\) peak position is largely depends on the environment. Typical F\(_{1s}\) peak of various fluoride glasses and fluoride crystals are shown in Fig. 11 and the values are summarized in Table 3 [42]. F\(_{1s}\) binding energy is considered to shift higher energy with higher polarizability. F\(_{1s}\) peak in the glass and glass-ceramics was appeared in 685.0 eV. The value is less than AlF\(_3\) (686.8 eV) and larger than BaF\(_2\) (683.9 eV). In BABF crystal, F is surrounded by three Ba and one Al and the structural model is shown in Fig. 12. That is, the binding energy of F in glass-ceramics showed the value between AlF\(_3\) and BaF\(_2\). Peak position and shape of F of glass is almost same as glass-ceramics. It indicates that the environment of F in the glass is similar as in glass-ceramics. That is, the most fluoride ions are bonding with Ba in BABF glass and showed prominent luminescence by addition of Eu\(^{3+}\).
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![FT-IR spectra for the KBr disc shaped sample of the glass and glass-ceramics sample.](image)

**Fig. 9.** FT-IR spectra for the KBr disc shaped sample of the glass and glass-ceramics sample.

**Table 2**

IR absorption bands and its vibration type [34,35].

<table>
<thead>
<tr>
<th>Absorption bands (cm$^{-1}$)</th>
<th>Vibration types</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-600</td>
<td>Stretching vibration in [AlO$_6$] (Al$_6$ units) triangle</td>
</tr>
<tr>
<td>550-630</td>
<td>Bending vibration of the isolated BO$_3^-$ ion</td>
</tr>
<tr>
<td>650-730</td>
<td>Bending vibration in [BO$_3$] (B$_3$ units) triangle</td>
</tr>
<tr>
<td>~670</td>
<td>Stretching vibration in [AlO$_5$] (Al$_5$ units)</td>
</tr>
<tr>
<td>778-800</td>
<td>Bending vibration in [AlO$_4$] (Al$_4$ units) tetrahedron</td>
</tr>
<tr>
<td>850-1100</td>
<td>Stretching vibration in [BO$_4$] (B$_4$ units) tetrahedron</td>
</tr>
<tr>
<td>1200-1400</td>
<td>Stretching vibration in [BO$_3$] (B$_3$ units) tetrahedron</td>
</tr>
</tbody>
</table>
**Fig. 10.** XPS peak profiles of the glass and glass-ceramics.
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**Fig. 11.** $F_{1s}$ XPS peak profiles of ZnF$_2$, AlF$_3$, GaF$_3$, InF$_3$, ScF$_3$, ZrF$_4$, HfF$_4$, BaF$_2$ and ErF$_3$ crystals quoted from literature [42].
Table 3

$F_{1s}$ binding energies and full widths at half maximum, FWHM, of $F_{1s}$ XPS peaks in fluoride glasses and fluoride crystals, quoted from literature [42].

<table>
<thead>
<tr>
<th></th>
<th>$F_{1s}$ binding energy (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluoride glass</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn glass</td>
<td>684.9±0.1</td>
<td>2.0±0.1</td>
</tr>
<tr>
<td>Al glass</td>
<td>685.2±0.1</td>
<td>2.5±0.1</td>
</tr>
<tr>
<td>Ga glass</td>
<td>685.0±0.1</td>
<td>2.2±0.1</td>
</tr>
<tr>
<td>In glass</td>
<td>684.6±0.1</td>
<td>2.0±0.1</td>
</tr>
<tr>
<td>Sc glass</td>
<td>685.0±0.1</td>
<td>2.1±0.1</td>
</tr>
<tr>
<td>Zr glass</td>
<td>685.1±0.1</td>
<td>2.1±0.1</td>
</tr>
<tr>
<td>Hf glass</td>
<td>685.1±0.1</td>
<td>2.2±0.1</td>
</tr>
<tr>
<td><strong>Fluoride crystal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnF$_2$</td>
<td>685.1±0.1</td>
<td>1.4±0.1</td>
</tr>
<tr>
<td>AlF$_3$</td>
<td>686.8±0.1</td>
<td>1.6±0.1</td>
</tr>
<tr>
<td>GaF$_3$</td>
<td>685.8±0.1</td>
<td>1.8±0.1</td>
</tr>
<tr>
<td>InF$_3$</td>
<td>685.0±0.1</td>
<td>1.4±0.1</td>
</tr>
<tr>
<td>ScF$_3$</td>
<td>685.4±0.1</td>
<td>1.5±1.0</td>
</tr>
<tr>
<td>ZrF$_4$</td>
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</tr>
<tr>
<td>HfF$_4$</td>
<td>685.8±0.1</td>
<td>2.3±0.1</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>683.9±0.1</td>
<td>1.9±0.1</td>
</tr>
<tr>
<td>ErF$_3$</td>
<td>684.9±0.1</td>
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</tr>
<tr>
<td>LiF$^a$</td>
<td>684.8</td>
<td></td>
</tr>
<tr>
<td>NaF$^a$</td>
<td>683.5</td>
<td></td>
</tr>
<tr>
<td>KF$^a$</td>
<td>683.6</td>
<td></td>
</tr>
<tr>
<td>RbF$^a$</td>
<td>683.4</td>
<td></td>
</tr>
<tr>
<td>CsF$^a$</td>
<td>682.2</td>
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Fig. 12. Model of BaAlBO$_3$F$_2$ crystal and F site.
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6.3.5. Fabrication of Single Crystal Line of BaAlBO$_3$F$_2$

For the patterning of BaAlBO$_3$F$_2$ crystals by laser irradiation, NiO-doped glass, i.e., 3NiO-50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ (mol) with $T_p=574^\circ$C, was used. Laser light absorbed by Ni$^{2+}$ ions is transferred to thermal energy due to the non-radiative relaxation in Ni$^{2+}$ ions, and consequently spatially selected crystallization is induced [32,33]. The optical absorption coefficient at $\lambda=1080$ nm was 4.55 cm$^{-1}$. The polarized optical microphotograph (POM) for the sample patterned by Yb:YVO$_4$ laser ($\lambda=1080$ nm) irradiations with a power of $P=1.1$ W and scanning speed of $S=8$ $\mu$m/s is shown in Fig. 13. It is seen that a line with a homogeneous color (retardation) is patterned.

The micro-Raman scattering spectrum at room temperature for the line patterned by laser irradiations is shown in Fig. 14 together with the spectra for the glass-ceramics heat-treated at 550$^\circ$C for 3 h and the base BABF glass. The laser-patterned line provides the Raman spectrum similar to the glass-ceramics containing BaAlBO$_3$F$_2$ crystals, indicating that BaAlBO$_3$F$_2$ crystals are formed in the laser patterned line. There has been no report on the Raman scattering spectrum for nonlinear optical BaAlBO$_3$F$_2$ single crystal. According to the Raman scattering spectra for Al$_2$O$_3$-B$_2$O$_3$ based materials reported so far, [34,35] all Raman bands observed at $\sim 357, 469, \text{and} 982$ cm$^{-1}$ are considered to be related to the bending or stretching modes of BO$_3$ units in BaAlBO$_3$F$_2$ crystal.

Micro-PL spectrum at room temperature for the line obtained by irradiations of Yb:YVO$_4$ fiber lasers with $P=1.1$ W and $S=8$ $\mu$m/s in the NiO,ErF$_3$-doped glass, i.e., 3NiO-1ErF$_3$-50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$, is shown in Fig. 15 together with the data for the glass-ceramics and the base BABF glass. The clear emissions corresponding to the $f-f$ transitions of $^2$H$_{11/2}$ $\rightarrow$ $^4$I$_{15/2}$ at $\sim 525$ nm, $^4$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$ at 540-570 nm, and $^4$F$_{9/2}$ $\rightarrow$ $^4$I$_{15/2}$ at $\sim 660$ nm for Er$^{3+}$ ions are observed. As can be seen in Fig. 15, in the $f-f$ transition of $^4$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$, the peak at $\sim 540$ nm (the dotted line in Fig. 15) is clearly observed for the line part and the glass-ceramics, but is not clear for the base BABF glass. The appearance of the sharp peak at $\sim 540$ nm indicates that the site environment of Er$^{3+}$ ions in the line part is defined more clearly compared with the glass part. That is, it is considered that the PL peak at $\sim 540$ nm would be used as a probe peak to examine the coordination environments of Er$^{3+}$ ions in the laser-irradiated part. [18-20] The PL spectra shown in Fig. 15, therefore, suggest that Er$^{3+}$ ions are incorporated into BaAlBO$_3$F$_2$ crystals patterned by laser irradiations. The most probable site of Er$^{3+}$ ions
in BaAlBO$_3$F$_2$ crystals would be Ba$^{2+}$ sites [18,19].

In order to observe the orientation of BaAlBO$_3$F$_2$ crystals in the line (Fig. 13, $P=1.1$ W and $S=8$ µm/s) by using TEM observations, the line part was processed to thin foil shapes using a FIB method, i.e., (a) a cross-section of the line and (b) a parallel-section of the center of the line. In TEM observations, the center part of the thin films was concerned. A bright field image for the thin foils (a) and (b) is shown in Fig. 16. The foil (a) shows a bell-shaped crystal with a height of ~2 µm and a width of ~2 µm. The selected area electron diffraction (SAED) patterns in the area of a circle with a diameter of 1 µm at the center of the crystal line are shown in Fig. 17 (The surface dark region is the deposited W layer). The clear diffraction spots were observed and any diffuse rings were not observed, demonstrating that the line consists of a crystal. By using a simulation technique, it was clarified that the electron diffraction patterns are assigned to BaAlBO$_3$F$_2$ crystal. That is, the diffraction patterns for the cross-section thin foil (a) and the parallel-section thin foil (b) are for the zone axis of [0001] and [1120] of BaAlBO$_3$F$_2$ crystal, respectively. High resolution TEM image of the thin foil (b) is shown in Fig. 18. The lattice of BaAlBO$_3$F$_2$ crystal was observed. The whole region of the image (~100 nm square) having a homogeneous lattice fringe indicates that there is no crystal grain boundary and also no large planer defects. The distances of the lattice in the scanning direction and in the direction toward the surface were assigned to {0001} and {1100}, respectively. Therefore, the results shown in Figs. 17 and 18 indicate that BaAlBO$_3$F$_2$ crystal being present in the line is consisted to be single crystal.

Furthermore, TEM observations indicate that the direction of crystal growth along the laser scanning direction is the $c$-axis and the direction toward a surface direction is the [1100] axis. The structure of BaAlBO$_3$F$_2$ crystal is shown in Fig. 19. It is noted that the layers of corner-sharing AlO$_3$F$_2$ triangular bipyramids and BO$_3$ triangles are stacked along the $c$-axis.

The laser-induced crystallization method has been applied to various oxide glasses, and highly oriented nonlinear optical oxide crystals such as β-BaB$_2$O$_4$, LiNbO$_3$, and Li$_2$SiO$_3$ have been patterned on the glass surface. [32,33,36-40] It should be pointed out that the direction of crystal growth along the laser scanning direction is basically $c$-axis, i.e., preferential crystal growth direction. On the contrary, in aluminosilicate (Al$_2$O$_3$-SiO$_2$)-based oxyfluoride glasses, it is known that laser irradiations induce the formation of fluoride nanocrystals such as CaF$_2$. [17-20,31] In such oxyfluoride glasses,
the network structure constructed by Al₂O₃ and SiO₂ is rigid and stable thermally and consequently depress the large growth of fluoride crystals [8,41]. In the present study, however, the chemical composition of the oxyfluoride glass (50BaF₂-25Al₂O₃-25B₂O₃) is the same as that of BaAlBO₃F₂ crystal. This would be an important point for the patterning of highly oriented BaAlBO₃F₂ crystals. Finally, it should be emphasized that the present study is the first demonstration for the patterning of nonlinear optical oxyfluoride (BaAlBO₃F₂) crystals in oxyfluoride glasses.
Fig. 13. Polarized optical microphotograph for the line patterned by laser irradiations (Yb:YVO₄ fiber laser with λ=1080 nm, power of P=1.1 W, and scanning speed of S=8 µm/s) in 3NiO-50BaF₂-25Al₂O₃-25B₂O₃ glass.
Fig. 14. Micro-Raman scattering spectra at room temperature for the line patterned by laser irradiations (Fig. 13), the sample heat-treated at 550°C for 3 h, and the base glass.

Fig. 15. Photoluminescence spectra at room temperature of Er^{3+} ions for the line patterned by laser irradiations (Fig. 13), the sample heat-treated at 550°C for 3 h, and the base glass. The excitation wavelength was 488 nm.
**Fig. 16.** Bright field image for the cross-section thin foil (a) and the parallel-section thin foil (b) prepared by a focused ion beam method for the original line was patterned by laser irradiations (Yb:YVO₄ fiber laser with $\lambda=1080$ nm, power of $P=1.1$ W, and scanning speed of $S=8$ $\mu$m/s) in 3NiO-1ErF₃-50BaF₂-25Al₂O₃-25B₂O₃ glass.
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Fig. 17. Selected area electron diffraction (SAED) patterns for the cross-section thin foil (a) and the parallel-section thin foil (b) in the center region of crystal (Fig. 16) with the circle with the diameter of ~1 µm. Bright field image in same angle for the patterns are also included.
Fig. 18. High resolution TEM (HRTEM) image for the parallel-section thin foil (b) (Fig.16).
Fig. 19. Structure of BaAlBO$_3$F$_2$ crystal.
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6.4. Conclusions

A novel glasses with the compositions, having large amount of fluorine content up to 40% for anion, of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ (in mol%) and 1Eu$_2$O$_3$, 3NiO, and 1ErF$_3$-3NiO -doped glass fabricated. The glass-ceramics were obtained by heat-treatments at 500°C for 10 h and 560°C (~$T_x$) for 3 h. Crystal phase was determined with BaAlBO$_3$F$_2$ crystal using X-ray diffraction. The crystal size was found to be 50-100 nm by TEM observation. Second harmonic generation (SHG) of green light ($\lambda$=532 nm) was demonstrated from the glass-ceramics by Q-switch Nd: YAG laser ($\lambda$=1064 nm). The $x$Eu$_2$O$_3$-doped ($x$=0.5-10) glasses and glass-ceramics were measured fluorescent spectra and quantum yield. The quantum yields of Eu$^{3+}$ in visible region were evaluated to 97% for Eu$_2$O$_3$-doped glass. It indicated the glass is excellent material for phosphor. FT-IR and XPS spectra indicate Ba sites are surrounded by large amount of F. Rare earth ion is considered to place in Ba site, surrounded by large amount of F having low phonon energy.

A homogeneous single-crystal line on 3mol% of NiO doped glass surface was fabricated using laser-induced crystallization by $\lambda$=1080 nm of cw Yb: YVO$_4$ fiber laser. Crystal line was identified as BABF crystal. The crystal line was observed homogeneous retardation and suggested to have high orientation. TEM image and electron diffraction pattern of the line were obtained. The line is considered to be composed single crystal. The crystal grew along (0001) zone axis. Fluorescence spectrum in line was clearly different from the glass and showing Stark splitting. It suggested the Er$^{3+}$ incorporated in crystal phase. These results indicate the highly oriented line of BABF crystal and glass-ceramics with BABF nanocrystals are attractive materials for the use of photonic devices.
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Summary

In chapter I, the outline and propose of this thesis are described. The investigated materials and technique for evaluation of materials, glasses and transparent crystallized glasses, are presented. Evaluation methods of elastic and mechanical properties are described. For the measurement of elastic properties such as Young’s modulus and Poisson’s ratio, cube resonance method (for bulk) and nanoindentation techniques (for surface) are employed. Nanoindentation is measured in two types, i.e. standard type and continuous stiffness measurement (CSM) mode. Mechanical properties such as Vickers hardness and Fracture toughness are evaluated by Vickers indentation.

In chapter II, optically transparent glass–ceramics with the composition of 40BaO-20TiO2-40SiO2 (mol%) consisting of nonlinear optical Ba2TiSi2O8 (BTS) nanocrystals (diameter: ~100 nm) are fabricated, and their elastic and mechanical properties are examined as a function of the volume fraction of BTS nanocrystals using cube resonance, Vickers indentation, and Berkovich nanoindentation technique (standard-type and continuous stiffness measurement (CSM)-type) in order to clarify micro- and nano-scale deformation behaviors in glass/nanocrystal composite materials. In the early stage of crystallization, BTS crystalline layers with a thickness of ~ 120 nm were formed at the surface and ellipsoid-shaped crystallites with a diameter of 100–200 nm were dispersed in the glass matrix. In the late stage, BTS crystals with a diameter of 200–400 nm were formed densely, but a glassy phase was present between BTS crystals. The cube resonance method shows that the Young’s modulus increases from 84 to 107 (GPa) with increasing the volume fraction of nanocrystals and the Poisson’s ratio was almost constant of 0.28-0.29. The Vickers hardness (HV) and fracture toughness (Kc) increase from 5.0 to 6.0 (GPa) for HV and 0.48 to 1.05 (MPa m^−1/2) for Kc with increasing the volume fraction. It is found from nanoindentation measurements that the deformation energy increases with increasing volume fraction. In particular, the plastic deformation energy is found to be 114-136 kJmol^−1, which is close to the Ba-O single bond energy (~138 kJmol^−1), suggesting that the breaking of Ba-O bonds might be important for the plastic deformation in this glass. The Young’s modulus evaluated from CSM-type nanoindentation measurements for a deformation scale of about 100
Summary

nm shows the values of 98 GPa for the glass and 110 GPa for the glass-ceramics with nanocrystals. It is clarified that elastic/mechanical properties of the glass are largely improved due to the nanocrystallization.

In chapter III, an oxyfluoride glass with the composition of 25CaF$_2$–5CaO–20Al$_2$O$_3$–50SiO$_2$ (mol%) and crystallized glasses containing CaF$_2$ nanocrystals (10–70 nm) are prepared. The size and morphology of CaF$_2$ nanocrystals is examined using transmission electron microscopy and atomic force microscopy (AFM), and elastic properties of crystallized glasses are evaluated using a cube resonance method. The large increase in the glass transition temperature in crystallized glasses suggests that the Al$_2$O$_3$–SiO$_2$ based glass network having a high thermal stability is created due to the formation of CaF$_2$ nanocrystals. It is suggested from AFM observations that the chemical bonding between CaF$_2$ nanocrystals and oxide glass matrix is weak. Young’s modulus ($E$) increases with increasing heat treatment temperature, i.e., $E = 88.4$ GPa for the glass and $E = 93.3$ GPa for the sample heat-treated at 700 °C for 1 h. The present study demonstrates that oxyfluoride crystallized glasses containing CaF$_2$ nanocrystals have good elastic (mechanical) properties, being available in practical device applications even from the mechanical point of view.

In chapter IV, optically transparent glass-ceramics with CaF$_2$ nanocrystals (diameter: 30 nm) for 25CaF$_2$–5CaO–20Al$_2$O$_3$–50SiO$_2$ were prepared using a conventional glass crystallization method in an electric furnace in air and the dispersion state of CaF$_2$ nanocrystals at the surface was examined from transmission electron microscope (TEM) observations combined with focused ion beam sample preparations. It was demonstrated that a fluorine deficient layer of about 150–200 nm is formed during the heating at temperatures above the glass transition temperature in the surface region and thus CaF$_2$ nanocrystals are not present in the surface region. The reason for the formation of such fluorine deficient layers is due to the removal of some fluorine from the surface of bulk glass during heating. The present study gives new information on the crystal growth behavior of fluoride nanocrystals in oxyfluoride glass-ceramics.

In chapter V, the morphology and spatial distribution state of CaF$_2$ nanocrystals in oxyfluoride glass-ceramics based on the ErF$_3$–CaF$_2$–Al$_2$O$_3$–SiO$_2$ system with different ErF$_3$ contents of 1-3 mol % and the addition of AlN were examined from transmission electron microscope (TEM) observations. The content of 3mol% ErF$_3$ induced the
growth of CaF$_2$ nanocrystals with star-like morphologies and their assemblies with the size of ~70 nm. The addition of a small amount (2 mol %) of AlN has a remarkable effect on the spatial uniform distribution (i.e., disappearance of assembly) of CaF$_2$ nanocrystals. The present study proposes a new method for the design of composition in rare-earth doped oxyfluoride glass-ceramics.

In chapter VI, a new oxyfluoride glass of 50BaF$_2$-25Al$_2$O$_3$-25B$_2$O$_3$ (mol. %) with a large fraction of fluorine, i.e., F/(F + O) = 0.4, was prepared using a conventional melt-quenching method in order to synthesize new glass-ceramics containing nonlinear optical oxyfluoride crystals. The refractive index at 632.8 nm and ultra-violet cutoff wavelength of the glass were 1.564 and 200 nm, respectively. Eu$^{3+}$ ions in the glass showed a high quantum yield of 97% in the photoluminescence spectrum in the visible region. BaAlBO$_3$F$_2$ crystals (size: 50–100nm) showing second harmonic generations were formed through the crystallization of the glass. Lines consisting of BaAlBO$_3$F$_2$ crystals were patterned successfully on the glass surface by laser irradiations (Yb:YVO$_4$ laser with a wavelength of 1080 nm, laser power of 1.1 W, scanning speed of 8 lm/s). High-resolution transmission electron microscope observations combined with a focused ion beam technique indicate that BaAlBO$_3$F$_2$ crystals are highly oriented just like a single crystal. The present study proposes that the new oxyfluoride glass and glass-ceramics prepared have a high potential for optical device applications.

In this study, fabrication of the glass with the crystal having new design and highly controlled morphology are succeeded. To design crystal morphology is most important for crystallization of glass and should open the new possibility of glass materials. The relationships between crystal morphology and their elastic and mechanical properties are clarified. From the points of view, brittleness is considered to be one of most important scientific and practical issues for developing the glass. In this study, principle of the material design of glass-ceramics is given and the realization of glass-ceramics device is proceeded toward.
Publications and Awards

【Publication Papers】


【Presentation in International Conference】

**Oral Presentation**


**Poster Presentation**


【Presentations in Domestic Conference】

〇Oral Presentation
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