Formation of fresnoite-type $\text{Ba}_2\text{TiGe}_2\text{O}_8$ crystallites in $\text{BaO-TiO}_2\text{-GeO}_2$ glass thin film and its optical nonlinearity

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We report on fabrication of the $\text{BaO-TiO}_2\text{-GeO}_2$ glass thin films on a fused silica substrate by RF sputtering, and investigation of the crystallization behavior, surface texture and the optical non-linearity in the glass thin film by means of AFM, XRD, Raman and Maker fringe techniques. Although the $\text{Ba}_2\text{TiGe}_2\text{O}_8$, hereafter abbreviated to BTG, phase with second-order optical nonlinearity was mainly crystallized, the precipitation of the sub-phase of BaGe_4O_9 was also confirmed in the heat-treated glass thin films. In the glass thin film heat-treated at heat-treatment temperature (T_{HT}) = 730–750°C, the (211) preferential orientation of BTG phase and an upheaval about 300–400 nm were confirmed at the surface. These transparent crystallized glass thin films indicated a clearly Maker fringe patterns, demonstrating a second-order optical nonlinearity, and the effective second-order nonlinear optical constant, d_{eff} , was estimated to be ~0.8 pm/V.

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1. Introduction

In the area of photonics, nonlinear optical crystals, e.g., LiNbO_3 and KTiOPO_4 with large optical non-linearity, are significant materials because they enable us to switch an optical signal and convert the fundamental laser light into the light with twice frequency. On the other hand, the transparent glass-ceramics consisting of nonlinear optical crystals have been also considered to be a candidate for the photonic material because precursor glass possesses high formability, which is a characteristic of amorphous material, and the optical functional crystal can be crystallized by a selecting glass-system and its composition. For example, reported the transparent LiNbO_3 and BaTiO_3 -crystallized glasses showing second-order harmonic generation (SHG) are fabricated in the $\text{Li}_2\text{O-Nb}_2\text{O}_5\text{-SiO}_2$ and $\text{BaO-TiO}_2\text{-TeO}_2$ system, respectively.^{1),2)}

Fresnoite-type $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (BTS), $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (BTG) and $\text{Sr}_2\text{TiSi}_2\text{O}_8$ (STS) crystals indicate an excellent piezoelectric property, which is appropriate for surface-acoustic wave devices.^{3)–6)} Recently, the transparent fresnoite-type BTS, BTG, and STS-crystallized glasses with high orientation from the corresponding glasses were successfully fabricated, and large second-order optical nonlinearity was confirmed in these materials.^{7)–12)} Moreover, Honma et al. succeeded in patterning BTG crystal line with a width of approximately 5 μm in the $\text{BaO-TiO}_2\text{-GeO}_2$ system glass by transition metal atom heat (TMAH) processing.¹³⁾ Thus, the transparent BTG glass/glass-ceramics have a great potential for the advanced photonic device component. However, in practical use of this material as the device component, e.g., photonic circuit, fabrication of the thin film of the precursor glass/glass-ceramics should be demanded for the purpose of its miniaturization and integration.

Very recently, Ogawa et al. succeeded for the first time in fabricating the $\text{BaO-TiO}_2\text{-GeO}_2$ glass thin films using an RF

magnetron sputtering and the BTG crystalline thin film showing a clear second-harmonic generation (SHG) was obtained by crystallization of the glass thin film.¹⁴⁾ In addition, the thin film possesses a possibility for the form of novel glass composition because it has high flexibility of the glass composition compared to the bulk glass. Since Takahashi et al. reported that the crystal morphology and second-order optical nonlinearity of the BTG-crystallized glasses are considerably affected by their glass compositions,¹⁵⁾ it is quite important to examine those issues in the $\text{BaO-TiO}_2\text{-GeO}_2$ glass thin films in order to apply them to the photonic devices with high optical performance. Therefore, the aim of this study is to clarify the crystallized phase, surface texture and estimation of its nonlinear optical constant in the $\text{BaO-TiO}_2\text{-GeO}_2$ glass thin film.

2. Experimental procedures

The $\text{BaO-TiO}_2\text{-GeO}_2$ glass thin film was fabricated by RF magnetron sputtering (ULVAC MNS-2000-RF2F) on a fused silica substrate. A detail procedure for preparation of the thin film is described in elsewhere.¹⁴⁾ After sputtering, the as-prepared glass thin films were heat-treated at various temperatures, T_{HT} , for 3 h in order to obtain the transparent BTG-crystallized glass thin films

The thickness of as-prepared thin films were measured by a surface texture measuring instruments (Tokyo Seimitsu SURFCOM-480A) and surface roughness of crystallized glass thin films were examined using an atomic force microscope (SII NanoTechnology Nanopics2100). After heat-treatment, the identification of the crystalline phase in the heat-treated thin films were characterized by X-ray diffraction (XRD) analysis (Rigaku RINT 2000) and Raman spectroscopy (Horiba Jobin Yvon T64000). Second-harmonic (SH) intensities of the crystallized thin film were measured by the Maker fringe technique.¹⁶⁾ The fundamental wavelength of a Q-switched Nd^{3+} :yttrium-aluminum-garnet (YAG) laser at a wavelength of 1064 nm was used as the incident light. Z-cut α -quartz with a thickness of 0.6 mm was used as a reference. As the polarization condition in

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Maker fringe measurements, the combination of *p*-excitation and *p*-detection was used.

3. Results and discussion

Although the glass thin films subjected to heat-treatment were slightly opaque, they possessed a sufficient transparency and homogeneity for optical measurements. **Figure 1** shows the AFM image of the surface of the as-deposited thin film and the thin films heat-treated at $T_{HT} = 730$ – 750°C . One can see that heat-treated samples have an upheaval of approximately 300–400 nm, implying the formation of crystallites at the surface. The relationship between the heat-treatment temperature, T_{HT} and the root-mean-square value (RMS) for the surface of the thin film, which is a criterion of surface roughness, is shown in **Fig. 2**. The value of RMS in the as-deposited thin film was estimated to be 1.41 nm, indicating a smooth surface of the thin film. Although the values of RMS were almost constant (~ 50 nm) in the $T_{HT} = 700$ – 740°C , the sudden increase in the RMS was observed in the $T_{HT} = 750^\circ\text{C}$. This is probably due to an abnormal growth of crystallites by higher heat-treatment temperature. It is also suggested that the decrease in transparency is due to the scattering of light by the large crystallites presented in the heat-treated glass thin films.

Fig. 1. AFM images of the as-deposited glass thin film and thin film heat-treat at $T_{HT} = 730$ – 750°C .

Fig. 2. Relationship between heat-treatment temperatures, T_{HT} and RMS.

Figure 3 shows XRD patterns of the surface region in the as-deposited thin film and the samples heat-treated at $T_{HT} = 730$ – 750°C for 3 h, together with the diffraction pattern of $\text{Ba}_2\text{TiGe}_2\text{O}_8$, referred to the ICDD data (No. 000440560). Although the diffraction peaks could not be observed (i.e., a halo pattern) in the glass thin film heat-treated at $T_{HT} = 700^\circ\text{C}$, indicating the amorphous state, the thin film heat-treated at higher temperature, i.e., $T_{HT} = 710$ – 750°C revealed sharp diffraction peaks associated with the crystalline phase, meaning that nucleation and crystal growth occurred in the BaO – TiO_2 – GeO_2 glass thin film by the heat-treatment technique. By comparison with the ICDD data, the diffraction peaks at $2\theta \sim 26.6^\circ$, 28.6° and 32.6° are attributed to the BTG phase, and these peaks are assigned to the (201), (211), and (420) planes. In addition, it is found that the crystallized glass thin film obtained by heat-treatment shows the (211) preferential orientation of the BTG phase. This crystallization behavior is quite different from that of the 30BaO – 15TiO_2 – 55GeO_2 , which is hereafter called BTG55, bulk glass, i.e., the *c*-orientation.⁸⁾ On the other hand, the additional diffraction peaks also appeared at $2\theta \sim 24.0^\circ$ and 30.8° . According to the Takahashi et al., it is difficult to distinguish the formation of the $\text{BaTiGe}_3\text{O}_9$ phase and the BaGe_4O_9 phase in the BTG55 glass because the crystal structure of both phases and their lattice constants are similar.¹⁰⁾ Although it is considered that either of the crystalline phases is formed in the crystallized thin films, it was necessary to check the formation crystalline phase by another technique in this study.

Raman spectroscopy for the as-deposited thin film and the thin film heat-treated at $T_{HT} = 730^\circ\text{C}$ are shown in **Fig. 4**, together with the $\text{Ba}_2\text{TiGe}_2\text{O}_8$, $\text{BaTiGe}_3\text{O}_9$ and BaGe_4O_9 phases synthesized by a solid state reaction. It is observed that two Raman peaks e.g., 490 , 600 cm^{-1} attributed to a fused silica substrate are confirmed (solid triangle in Fig. 4) in the as-deposited thin film.¹⁷⁾ On the other hand, the glass thin film heat-treated at $T_{HT} = 730^\circ\text{C}$ indicates the additional bands, e.g., 250 , 710 , 845 , and 910 cm^{-1} . These Raman bands could be assigned to the BTG phase by comparison with Raman spectrum of the BTG phase (solid circle in Fig. 4). Markgraf et al. reported that Raman peaks around 290 cm^{-1} and 518 cm^{-1} are due to $\nu(\text{Ba-O})$ and $\nu_s(\text{Ge-O-Ge})$ modes, respectively. The bands in the range of 700 – 900 cm^{-1} are assigned to the stretch of the short Ti-O^* (apical oxygen of the pyramidal TiO_5 unit) bond, the Ti-O^- (non-bridging oxygen) bond, and terminal GeO_3 groups. The Raman band observed at 911 cm^{-1} is attributed to the anti-symmetric stretch of the pyrogermanate groups.^{19),20)} The position of Raman bands observed in the crystallized thin film at $T_{HT} = 730^\circ\text{C}$ also correspond to that of Markgraf's report. In addition, the shoulder peak around 550 cm^{-1} , weak and broad bands at 844 and 882 cm^{-1} are also observed in the spectrum. By comparison with the spectra of the $\text{BaTiGe}_3\text{O}_9$ and BaGe_4O_9 phase, the position of this shoulder is close to that of the main bands of the BaGe_4O_9 phase. Furthermore, weak and broad bands correspond to that of the BaGe_4O_9 phase. Therefore, it is considered that the BaGe_4O_9 phase is precipitated in the glass thin film. Thus, we have concluded that the peaks at $2\theta \sim 24.0$ and 30.8° in the Fig. 3 could be ascribed to the BaGe_4O_9 phase. In the previous study,¹⁰⁾ the formation of the $\text{BaTiGe}_3\text{O}_9$ crystallite is necessary for homogeneous crystallization of the BTG phase in the BTG55 glass. However, we already confirmed that the glass thin film heat-treated firstly crystallized the BTG phase at $T_{HT} = 710^\circ\text{C}$, and then the sub-phase of BaGe_4O_9 was formed at higher temperature. It was demonstrated that crystallization mechanism of BTG phase in the thin film was different from that in the BTG55 glass

Fig. 3

Fig. 4

Fig. 5

Fig. 3. XRD patterns in the surface region of the as-deposited glass thin film and the BTG-crystallized thin films heat-treated at $T_{HT} = 730$ – 750°C for 3 h and Ba₂TiGe₂O₈ (JCPDS No 000440560).

Fig. 4. Raman scattering spectra for the as-deposited thin film, crystallized thin films heat-treated at $T_{HT} = 730^\circ\text{C}$ with BaGe₄O₉ and BaTiGe₃O₉ prepared by solid state reaction. Closed triangle is associated with the fused silica¹⁴⁾ and closed circle is attributed to Ba₂TiGe₂O₈.^{15),16)}

Fig. 5. Maker fringe pattern for heat-treated glass thin films prepared by heat-treated at $T_{HT} = 730$ – 750°C in electro furnace.

composition.

The Maker fringe patterns for the BTG-crystallized thin film obtained by heat treatment at $T_{HT} = 730$ – 750°C for 3 h are shown in Fig. 5. One can see a clear fringe patterns in these heat-treated glass thin films, meaning that these samples have the optical nonlinearity. The SH intensity is increased with increasing the heat-treatment temperature. It is probably due to increase of the volume fraction of BTG phase in the glass thin film. According to Lu et al.,²⁰⁾ effective second-order nonlinear optical constant, d_{eff} , in the crystalline thin film is expressed by following formula:

$$d_{eff} \sim \frac{l_{c,Q}}{l_s} \left(\frac{n^2(2\omega)n(\omega)}{n_Q^2(2\omega)n_Q(\omega)} \frac{I_{S,Max}}{(I_{Q,Max})T} \right)^{1/2} d_{11,Q} \quad (1)$$

where l_s is the film thickness, $l_{c,Q}$ is the coherence length of the quartz ($\sim 20 \mu\text{m}$), $n(\omega)$ and $n(2\omega)$ are the refractive indices of ω and 2ω , respectively (the subscript of Q and S denotes the values for the quartz and sample, respectively), I is the maximal value of SH intensity, T is transmittance of sample, and $d_{11,Q}$ is the d_{11} of the quartz ($0.55 \text{ pm}\cdot\text{V}^{-1}$). Figure 6 shows the relation between the value of d_{eff} and the heat-treatment temperature, T_{HT} . It is found that the value of d_{eff} is increased with increasing the heat-treatment temperature, T_{HT} . Although the d_{33} value of transparent BTG surface-crystallized glass is estimated to be $24 \text{ pm}\cdot\text{V}^{-1}$,¹¹⁾ the thin film obtained in this study showed the considerably lower optical nonlinearity ($d_{eff} \sim 0.8 \text{ pm}\cdot\text{V}^{-1}$) compared to the surface crystallized glass (i.e., the BTG55 glass ceramics).

It is considered that the d value is largely affected by the (1) volume fraction, (2) homogeneity and (3) orientation of the BTG phase in the corresponding glass. For example, Takahashi et al. reported that the BTG crystalline layer in the crystallized glass is $\sim 10 \mu\text{m}$ of thickness,¹⁰⁾ and the second-order nonlinear optical constant, d_{33} , of the BTG-crystallized glasses is increased as the surface-crystalline layer of BTG phase on the glass phase

Fig. 6. d_{eff} value estimated by Eq. (1) against heat-treatment temperature.

became homogeneous.¹⁵⁾ On the other hand, the as-deposited film has about 500–600 nm of thickness. Therefore, the volume fraction of the BTG phases in the crystallized thin film is smaller than that of surface-crystallized glass in the BTG55 reported so far. In addition, the results from the AFM observation in the crystallized thin film samples (refer to Fig. 1), we can see an upheaval at the surface of samples, which is caused by the heat-treatment, indicating the inhomogeneity of BTG phase due to crystallization. Furthermore, the formation of the sub-phase of BaGe₄O₉ was confirmed by XRD and Raman spectroscopy in the heat-treated glass thin films. This crystallization tendency is quite different from the case of surface-crystallized glasses with BTG55 composition, i.e., precipitation of BaTiGe₃O₉ phase and subsequent crystallization of BTG phase. In fact, although, the obtained fringe pattern was clear with increasing heat-treatment temperature, the estimated d_{eff} value in this study was low com-

pared to bulk glass ceramics. It is considered that crystallized glass thin film heat-treated at $T_{HT} = 750^{\circ}\text{C}$ shows clear fringe pattern is caused by the volume fraction of the BTG phase in the thin film increases with increasing heat-treatment temperature. However, the impurity phase, such as BaGe_4O_9 also increases. Takahashi et al. estimated the SH intensity for the BTG crystalline and the $\text{BaTiGe}_3\text{O}_9$ crystalline by Kurtz method (powder state),¹⁰⁾ and as a result, the SH intensity of the BTG phase was approximately 130 times as large as that of the $\text{BaTiGe}_3\text{O}_9$ phase. Since the structure of the $\text{BaTiGe}_3\text{O}_9$ phase is similar to that of the BaGe_4O_9 phase, the BTG crystal should have a large optical nonlinearity compared to BaGe_4O_9 phase. Thus, it is considered that the decrease of the estimated d_{eff} value in the thin film compared to the bulk glass ceramics is caused by two reasons. One of them is low crystal volume in the thin film compared to the bulk glass ceramics. Another one is the precipitation of the sub phase, i.e. the BaGe_4O_9 phase.

Moreover, it is known that $30\text{BaO}\cdot 15\text{TiO}_2\cdot 55\text{GeO}_2$, $33.3\text{BaO}\cdot 16.7\text{TiO}_2\cdot 50\text{GeO}_2$, and $40\text{BaO}\cdot 20\text{TiO}_2\cdot 40\text{GeO}_2$ glass compositions show surface crystallization with high orientation to c -axis, which is the polarization axis in the crystalline phase.^{8)-12),15)} Masai et al. examined the relation between the d_{33} value and degree of orientation of BTG phase in the surface-crystallized glasses. It was found that the d_{33} value was increase with increasing the ratio of the diffraction peak intensity of (002) plane, I_{002} , to that of the (311) plane, I_{311} , in the XRD patterns, i.e., I_{002} / I_{311} , (degree of orientation).¹¹⁾ This result indicates that the nonlinear optical coefficient depends on the c -axis orientation. On the other hand, the crystallized glass thin film in this study showed the preferential (211) orientation. Therefore it might be expected that the large optical nonlinear constant is achieved by increase of the volume fraction of BTG, decrease of impurities such as BaGe_4O_9 in the thin film and growth of the strongly c -axis oriented crystallites in the glass thin film.

4. Conclusion

The thin film of $\text{BaO-TiO}_2\text{-GeO}_2$ glass was fabricated by RF sputtering and the fersnoite-type $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (BTG) crystallized glass was obtained by proper heat-treatment in glassy thin film. Surface roughness of the glass thin films heat-treated at $T_{HT} = 700\text{--}750^{\circ}\text{C}$ was examined by AFM. Crystallization behavior of BTG in the glass thin film was investigated by means of XRD analyses and Raman spectroscopy. The second order optical nonlinearity was examined by Maker fringe method and their effective non-linear optical constant d_{eff} was estimated. The heat-treated glass thin films showed several different aspects in morphology and crystallization behavior from the bulk glass ceramics. The (211) preferential orientation of the BTG phase and an upheaval about 300–400 nm were observed. Although the $\text{BaTiGe}_3\text{O}_9$ phase is indeed important factor as a nucleation site for the growth of fersnoite-type BTG phase in case of the bulk glass, the precipitation of BaGe_4O_9 phase was confirmed in the thin film. Moreover the BTG phase was grown involving with

precipitation of the BaGe_4O_9 phase. The SH generation in the crystallized glass thin film heat-treated at $T_{HT} = 730\text{--}750^{\circ}\text{C}$ was clearly observed and their effective optical non-linearity (d_{eff}) was estimated to be $\sim 0.8 \text{ pm}\cdot\text{V}^{-1}$.

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