Surface crystallization and second-order optical non-linearity in Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ glasses

Rie Ihara, Yasuhiko Benino, Takumi Fujiwara, Takayuki Komatsu*

Department of Chemistry, Nagaoka University of Technology, 1603-1 Kamitomioka-cho, Nagaoka 940-2188, Japan

Received 30 August 2004; revised 4 October 2004; accepted 10 November 2004

Abstract

Some ternary Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ glasses are prepared, and crystallization behavior and second harmonic intensity are examined to develop new non-linear optical crystallized glasses. The glasses with Gd$_2$O$_3$ contents of 8–14 mol% have large densities of over 6 g/cm$^3$ and large refractive indices of $n \approx 1.9$. Transparent surface crystallized glasses consisting of two kinds of crystalline phases with different morphologies, i.e. plate shape and needle shape crystals, are fabricated by heat-treatment at temperatures between glass transition and crystallization temperatures. From second harmonic generation microscope observations, micro-Raman scattering spectra and XRD analyses, plate shape crystals are determined to be non-linear optical Gd$_x$Bi$_{1-x}$BO$_3$ and needle shape crystals are Bi$_3$B$_5$O$_{12}$ having no second-order optical non-linearity. Since crystallized glasses consisting of Gd$_x$Bi$_{1-x}$BO$_3$ crystals exhibit relatively strong SHGs, they have a high potential for application to light control devices.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Bismuth borate glass; Crystallization; Second harmonic generation; Rare-earth ions; Micro-Raman spectra

1. Introduction

Crystallized glasses consisting of non-linear optical crystals have received much interest, because such materials have a high potential for laser host, tunable waveguide, tunable fiber gratings, and so on. For instance, transparent crystallized glasses consisting of LaBGeO$_5$, SrBi$_2$Ta$_2$O$_9$ and Ba$_2$TiGe$_2$O$_8$ which are noble optical non-linear and ferroelectric crystals have been fabricated [1–3]. In particular, it should be pointed out that the optical second-order non-linearity of $d_{33}$ for ferroelectric Ba$_2$TiGe$_2$O$_8$ crystals in transparent crystallized glasses is $\sim 10$ pm/V, being comparable to $d_{22}$ and $d_{11}$ of LiNbO$_3$ single crystal [3]. Very recently, Honma et al. [4,5] discovered the formation of new non-linear optical crystalline phases Ln$_x$Bi$_{1-x}$BO$_3$ in the crystallized glasses of Ln$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ (Ln=La, Gd, Sm) and found that the crystallized glasses of Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ show strong second harmonic (SH) intensities compared with the crystallized glasses consisting of La$_2$O$_3$ or Sm$_2$O$_3$. Furthermore, they found that some glasses such as 12.5Sm$_2$O$_3$·30Bi$_2$O$_3$·57.5B$_2$O$_3$ are crystallized by irradiations of a continuous Nd:YAG laser with a wavelength of $\lambda = 1064$ nm, giving the formation of non-linear optical crystalline dots and lines [4,5]. It is, therefore, of particular interest to clarify crystallization behaviors in the ternary glasses of Ln$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$.

In this study, we focus our attention on the crystallization behavior of ternary Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ glasses. The crystalline phases present at the surface of crystallized glasses have been clarified, and transparent surface crystallized glasses showing strong second harmonic generations (SHG) have been developed in the present study.

2. Experimental procedures

Glasses in the ternary system of Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ were prepared by using a conventional melt-quenching method. Commercial powders of reagent grade Gd$_2$O$_3$, Bi$_2$O$_3$ and B$_2$O$_3$ were mixed together and melted in a platinum crucible at 1150–1300 °C for 30 min in an electric furnace. The melts were poured onto an iron plate and pressed to a thickness of about 1.5 mm by another iron plate.
Glass transition, $T_g$, and crystallization onset, $T_s$, temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10 K/min. Densities of glasses were determined with the Archimedes method using kerosene as an immersion liquid. Refractive indices at a wavelength of 632.8 nm (He–Ne laser) were measured at room temperature with an ellipsometer (Mizojiri Optical, DVA-36 model).

Glasses were heat-treated at some temperatures, and crystalline phases present in the heat-treated samples were examined by X-ray diffraction (XRD) analysis at room temperature using Cu Kα radiation and from micro-Raman scattering spectra (Tokyo Instruments Co., Nanofinder operated at Ar$^+$ (488 nm) laser). The morphology of crystals was observed by scanning electron microscope (SEM) and polarization optical microscope. SH intensities of crystallized powders were evaluated using the Kurtz powder method [6]. A fundamental wave of a Q-switch Nd:YAG laser operating at a wavelength of $\lambda = 1064$ nm was used as the incident light. Crystallized powders with a different particle were used for the evaluation of SH intensity. The SH intensity of $\alpha$-quartz powders with a particle size of 20–25 $\mu$m was used as a reference.

### 3. Results and discussion

#### 3.1. Thermal and physical properties

The glass compositions in the Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ system examined in the present study are given in Table 1. The values of $T_g$ and $T_s$ for glasses were determined from DTA patterns are shown in Table 1. The values of $T_g$ and $T_s$ for the ternary glasses are 449–524 °C and 570–640 °C, respectively, and are higher than those for the binary 40Bi$_2$O$_3$–60B$_2$O$_3$ glass with no Gd$_2$O$_3$, meaning that the structure of Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ glasses is more rigid compared with the 40Bi$_2$O$_3$–60B$_2$O$_3$ glass. It is seen that the glass transition and crystallization temperatures increase with increasing Gd$_2$O$_3$ content. The thermal stability against crystallization, i.e. $\Delta T = T_s - T_g$, is, however, almost the same irrespective of Gd$_2$O$_3$ content, i.e. $\Delta T = 104–124$ °C. The values of density, $n$, and refractive index at 632.8 nm, $n$, of Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ glasses are given in Table 1. It is seen that both density and refractive index decrease by the substitution of Gd$_2$O$_3$ for Bi$_2$O$_3$. This would be partly due to the large difference in the molecular weight, $M$, between Gd$_2$O$_3$ ($M = 362$) and Bi$_2$O$_3$ ($M = 466$). The molar volumes, $V_m$, and molar polarizability, $\alpha_m$, evaluated using the Lorentz–Lorenz equation (Eq. (1)) are also given in Table 1.

$$R_m = \frac{((n_0^2 - 1)}{(n_0^2 + 2)} \frac{M}{d} = \frac{((n_0^2 - 1)}{(n_0^2 + 2)} \frac{V_m}{3}}{N_A}$$

(1)

$$\alpha_m = \left(\frac{3}{4\pi N_A}\right) R_m$$

(2)

where $R_m$ is the molar refraction and $N_A$ is Avogadro’s number. Honma et al. [7] examined the electronic polarizability and optical basicity ($\lambda$) of La$_2$O$_3$ and related glasses and clarified that the optical basicity for La$_2$O$_3$ oxide is $\lambda$(La$_2$O$_3$) = 1.07, being much larger compared with typical glass-forming oxides such as B$_2$O$_3$ ($\lambda = 0.42$). That is, the bonding character in the La$^{3+}$–O bond is an ionic (large electronic polarizability) [7]. The electronic polarizability of Gd$_2$O$_3$ has not been clarified, but it is considered that the bonding character in the Gd$^{3+}$–O bond would be similar to that in the La$^{3+}$–O bond. As seen in Table 1, the molar polarizability of Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ glasses increases by the substitution of Gd$_2$O$_3$ for Bi$_2$O$_3$, suggesting the order of $\lambda$(Gd$_2$O$_3$) > $\lambda$(B$_2$O$_3$). The electronic polarizability of Bi$_2$O$_3$ is large, giving a large optical basicity of $\lambda$(Bi$_2$O$_3$) = 1.19 [8,9]. As seen in Table 1, the molar polarizability of the glasses decreases by the substitution of Gd$_2$O$_3$ for Bi$_2$O$_3$, proposing the order of $\lambda$(Gd$_2$O$_3$) > $\lambda$(Bi$_2$O$_3$).

The structure of ternary Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ glasses has not been reported so far, but there are some reports on the structure of binary Ln$_2$O$_3$–B$_2$O$_3$ [10–12] and Bi$_2$O$_3$–B$_2$O$_3$ [13] glasses. It has been proposed that the network structures of Ln$_2$O$_3$–B$_2$O$_3$ glasses are basically similar to each other [12]. Chakraborty et al. [10] have proposed that the structure of Ln$_2$O$_3$–B$_2$O$_3$ glasses with near the metaborate (LnB$_2$O$_6$) composition consists of (B$_2$O$_3$)$_\infty$ ladder-type chains and those chains are composed of BO$_3$ triangles and BO$_4$ tetrahedral units. The ladder-type chains are interconnected by Ln$^{3+}$ ions, giving a three-dimensional network. In Bi$_2$O$_3$–B$_2$O$_3$ glasses, it is known that

### Table 1

| Glass composition (mol%) | $T_g$ (°C) | $T_s$ (°C) | $d$ (g/cm$^3$) | $n$ | $V_m$ (cm$^3$/mol) | $\alpha_m$ (Å$^3$) |
|--------------------------|-----------|-----------|----------------|-----|------------------|-------------------|
| Gd$_2$O$_3$ | Bi$_2$O$_3$ | B$_2$O$_3$ | | | | |
| 8 | 35 | 57 | 449 | 570 | 6.426 | 1.999 | 36.07 | 28.58 |
| 10 | 35 | 55 | 470 | 574 | 6.457 | 2.003 | 36.81 | 29.24 |
| 0 | 40 | 60 | 428 | 552 | 6.259 | 1.976 | 36.46 | 28.44 |
| 10 | 30 | 60 | 497 | 614 | 6.157 | 1.955 | 35.38 | 27.19 |
| 12 | 28 | 60 | 504 | 620 | 6.099 | 1.936 | 35.37 | 26.81 |
| 14 | 26 | 60 | 524 | 640 | 6.025 | 1.917 | 35.46 | 26.50 |
the addition of Bi$_2$O$_3$ to BO$_3$ induces the conversion of BO$_3$ to BO$_4$, resulting in the formation of rings with a BO$_4$ tetrahedron. Terashima et al. [13] clarified from Raman and $^{11}$B MAS NMR spectra that the maximum formation of BO$_4$ groups included in polyborate groups is established in the structure of the glass containing ~35 mol% Bi$_2$O$_3$ and the coordination number of Bi–O polyhedra does not change and remains high values of 5–6 independent of glass composition. These previous studies [10–13] suggest that the basic network structure of ternary Gd$_2$O$_3$–Bi$_2$O$_3$–B$_2$O$_3$ glasses consists of chains with BO$_3$ and BO$_4$ and the chains are partly interconnected by Gd$^{3+}$ and Bi$^{3+}$ ions. As seen in Table 1, the molar volumes of $x$Gd$_2$O$_3$·(40–$x$)Bi$_2$O$_3$·60B$_2$O$_3$ glasses with $x$=0–14 are almost the same irrespective of the Gd$_2$O$_3$/Bi$_2$O$_3$ ratio, supporting that the role of Gd$^{3+}$ and Bi$^{3+}$ ions in these ternary glasses are similar. The ionic radii of Bi$^{3+}$ and Gd$^{3+}$ ions with a six-oxygen coordination are 0.117 and 0.1078 nm, respectively.

3.2. Surface crystallization and second harmonic generation

In this study, the crystallization behavior and SHG for the sample of 10Gd$_2$O$_3$·30Bi$_2$O$_3$·60B$_2$O$_3$ were examined in detail. The 10Gd$_2$O$_3$·30Bi$_2$O$_3$·60B$_2$O$_3$ glass with $T_c=497$ °C and $T_m=614$ °C were heat-treated at various temperatures, and the crystalline phases and SH intensities for the crystallized samples were examined. The crystallized samples obtained by heat-treatments at 520–535 °C for 5 h keep a good transparency, and those at 540 and 550 °C for 5 h are translucent. All these samples showed a surface crystallization, and the thickness of crystalline layers at the surface determined by SEM observations was 1–30 μm, depending on heat-treatment temperature. The sample heat-treated at 650 °C for 3 h was opaque. We, therefore, focus our attention on the samples heat-treated at 520–550 °C.

Fig. 1 shows the polarization optical microscopy for the surface crystallized glass obtained by heat-treatment at 525 °C for 5 h in 10Gd$_2$O$_3$·30Bi$_2$O$_3$·60B$_2$O$_3$.

The micro-Raman scattering spectra at room temperature for the BiBO$_3$(I) and BiBO$_3$(II) phases formed in 50Bi$_2$O$_3$·50B$_2$O$_3$ crystallized glasses are shown in Fig. 2 together with the data for the plate shape and needle shape crystals in the crystallized glass of 10Gd$_2$O$_3$·30Bi$_2$O$_3$·60B$_2$O$_3$. It is found that the spectrum for plate shape crystals is almost the same as that for the BiBO$_3$(II) phase. Unfortunately, the crystal structure of the BiBO$_3$(II) phase has not been clarified at this moment, but our recent preliminary experiments suggest that this phase might have

Fig. 1. Polarization optical microscopy for the surface of the crystallized glass obtained by heat-treatment at 525 °C for 5 h in 10Gd$_2$O$_3$·30Bi$_2$O$_3$·60B$_2$O$_3$.

Fig. 2. Micro-Raman scattering spectra for the crystallized glasses. A and B are for BiBO$_3$(I) and BiBO$_3$(II) phases formed in 50Bi$_2$O$_3$·50B$_2$O$_3$. C and D are for plate shape and needle shape crystals in 10Gd$_2$O$_3$·30Bi$_2$O$_3$·60B$_2$O$_3$. 

$I^{2u}$(sample)/$I^{2u}$(α-quartz) = 4. The micro-Raman scattering spectra at room temperature for the BiBO$_3$(I) and BiBO$_3$(II) phases formed in 50Bi$_2$O$_3$·50B$_2$O$_3$ crystallized glasses are shown in Fig. 2 together with the data for the plate shape and needle shape crystals in the crystallized glass of 10Gd$_2$O$_3$·30Bi$_2$O$_3$·60B$_2$O$_3$. It is found that the spectrum for plate shape crystals is almost the same as that for the BiBO$_3$(II) phase. Unfortunately, the crystal structure of the BiBO$_3$(II) phase has not been clarified at this moment, but our recent preliminary experiments suggest that this phase might have
an orthorhombic structure [16]. As seen in Fig. 2, the micro-Raman scattering spectrum for the needle shape crystal is not consistent with those of the BiBO 3(I) and BiBO 3(II) phases, indicating that the needle shape crystal is not the BiBO3(I) phase and not the BiBO 3(II) phases.

The XRD patterns for the surface crystallized glass are shown in Fig. 3, in which the sample was polished from the initial surface and then the XRD patterns were taken for the polished bulk samples. The peaks corresponding to the BiBO3(II) phase [15] are clearly observed, supporting the results of the micro-Raman scattering spectra shown in Fig. 2. Some other XRD peaks are assigned to the Bi3B5O12 phase [17]. Since the Bi 3B5O12 phase has the inversion symmetry (Pnma) in its crystal structures (JCPDS: No. 29-228), we cannot expect a SHG in this crystal. As described in the above, the SHG was observed from the plate shape crystals, but not from the needle shape crystals. It is, therefore, concluded that the plate shape crystals correspond to the BiBO3(II) phase and the needle shape crystals are assigned to the Bi3B5O12 phase. As seen in Fig. 3, Bi1B3O12 crystals are formed mainly at the surface. The powder XRD pattern for the crystallized sample is also shown in Fig. 3, indicating a broad halo at around 2θ = 28°-29° together with some small peaks. This result also demonstrates that the crystallization at the heat-treatment condition of 550 °C and 5 h occurs only at the surface.

The XRD patterns for the crystallized glasses obtained by heat-treatment at around crystallization temperatures for 5 h in xGd2O3·(50−x)Bi2O3·50B2O3 glasses with x = 4 and 8 are similar to the BiBO3(II)-type phase. Since the d-spacing for the peak with the maximum intensity at 2θ = 28.5°-29° in Fig. 4 decreases with increasing Gd2O3 content, it is concluded that some amounts of Gd3+ ions are incorporated into BiBO3(II), i.e. the formation of the Gd,xBi1−xBO3 phase. Furthermore, as seen in Fig. 4, the intensity of the peak at around 2θ = 22.5° corresponding to the BiBO3(II) phase decreases with increasing Gd2O3 content. This result suggests that the Gd,xBi1−xBO3 (type-II) phase might be stabilized more compared with the BiBO3(II) phase containing no Gd3+ ions. It should be pointed out that there are many Bi–Ln oxide solid solutions because of similar ionic radii and the same valences of Bi3+ and Ln3+ [18]. Finally, from the above various experiments, it is concluded that the plate shape crystals showing SHGs are Gd,xBi1−xBO3.
as a function of particle size, where pulverized samples were heat-treated to get the fully crystallized state. It is seen that the SH intensity increases gradually with increasing particle size and saturates at the particle sizes over around 60 μm for the sample with x=0 and over around 40 μm for the sample with x=4. The maximum SH intensity for the sample with x=4 is approximately 150 times as large as α-quartz powders, i.e., $I^{2\omega}(\text{sample})/I^{2\omega}(\alpha\text{-quartz}) = 150$, again demonstrating that the Gd$_{4}$(Bi$_{1-x}$BO$_{3}$ phase is a non-linear optical crystal. Furthermore, it is found that the SH intensity of the BiBO$_{3}$(II) phase is enhanced by incorporation of Gd$^{3+}$ ions. The particle size dependence on SH intensity shown in Fig. 5 reveals that the Gd$_{4}$(Bi$_{1-x}$BO$_{3}$ phase has a phase matchable character [19].

4. Conclusions

The ternary Gd$_{2}$O$_{3}$–Bi$_{2}$O$_{3}$–B$_{2}$O$_{3}$ glasses were prepared, and crystallization behaviors and SH intensities were examined to develop new non-linear optical crystallized glasses. The glasses with Gd$_{2}$O$_{3}$ contents of 8–14 mol% have large densities of over 6 g/cm$^3$ and large refractive indices of ~1.9. Transparent surface crystallized glasses consisting of two kinds of crystalline phases with different morphologies, i.e., plate shape and needle shape crystals, were fabricated by heat-treatment at temperatures between $T_g$ and $T_x$. From SHG microscope observations, micro-Raman scattering spectra and XRD analyses, it was determined that plate shape crystals are non-linear optical Gd$_{4}$(Bi$_{1-x}$BO$_{3}$ and needle shape crystals are Bi$_3$B$_2$O$_{12}$ showing no second-order optical non-linearity. Since crystallized glasses consisting of Gd$_{4}$(Bi$_{1-x}$BO$_{3}$ crystals exhibit relatively strong SHGs, they might have a high potential for application to light control devices.

Acknowledgements

This work was supported from the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sport, and Culture, Japan, from the 21st Century Center of Excellence (COE) Program in Nagaoka University of Technology, and from the SCOPE (Strategic Information and Communications R&D Promotion Program) project by the ministry of Public Management, Home Affairs, Posts and Telecommunications, Japan.

References

[1] Y. Takahashi, Y. Benino, T. Fujiwara, T. Komatsu, Second harmonic generation in transparent surface crystallized glasses with stillwellite-type LaBGeO$_5$, J. Appl. Phys. 89 (2001) 5282–5287.
[2] G. Senthil, K.B.R. Varma, Y. Takahashi, T. Komatsu, Non-linear optic and ferroelectric lithium borate strontium bismuth tantalite glass-ceramic, Appl. Phys. Lett. 78 (2001) 4019–4021.
[3] Y. Takahashi, Y. Benino, T. Fujiwara, T. Komatsu, Large second order nonlinearities of Fresnoite and its related crystals in transparent crystallized glasses, J. Appl. Phys. 95 (2004) 3503–3508.
[4] T. Honma, Y. Benino, T. Fujiwara, R. Sato, T. Komatsu, New optical nonlinear crystallized glasses and YAG laser-induced crystalline dot formation in rare-earth bismuth borate system, Opt. Mater. 20 (2002) 27–33.
[5] T. Honma, Y. Benino, T. Fujiwara, T. Komatsu, R. Sato, Nonlinear optical crystal line writing in glass by yttrium aluminium garnet laser irradiation, Appl. Phys. Lett. 82 (2003) 892–894.
[6] S.K. Kurtz, T.T. Perry, A powder technique for the evaluation of nonlinear optical materials, J. Appl. Phys. 39 (1968) 3798–3813.
[7] T. Honma, Y. Benino, T. Fujiwara, T. Komatsu, R. Sato, V. Dimitrov, Electronic polarizability, optical basicity, and interaction parameter of La$_2$O$_3$ and related glasses, J. Appl. Phys. 91 (2002) 2942–2950.
[8] V. Dimitrov, T. Komatsu, Electronic polarizability, optical basicity and nonlinear optical properties of oxides, J. Non-Cryst. Solids 249 (1999) 160–179.
[9] T. Honma, Y. Benino, T. Komatsu, R. Sato, V. Dimitrov, Correlation among electronic polarizability, optical basicity, interaction parameter and XPS spectra in Bi$_2$O$_3$–B$_2$O$_3$ glasses, Phys. Chem. Glasses 43 (2002) 32–40.
[10] I.N. Chakraborty, D.E. Day, J.C. Lapp, J.E. Shelby, Structure–property relations in lanthanide borate glasses, J. Am. Ceram. Soc. 68 (1985) 368–371.
[11] I.N. Chakraborty, D.E. Day, Effect of R$^{3+}$ ions on the structure and properties of lanthanum borate glasses, J. Am. Ceram. Soc. 68 (1985) 641–645.
[12] K. Terashima, S. Tamura, S.H. Kim, T. Yoko, Structure and nonlinear optical properties of lanthanide borate glasses, J. Am. Ceram. Soc. 80 (1997) 2903–2909.
[13] K. Terashima, T.H. Shimoto, T. Yoko, Structure and nonlinear optical properties of PbO–Bi$_2$O$_3$–B$_2$O$_3$ glasses, Phys. Chem. Glasses 38 (1997) 211–217.
[14] R. Ibara, T. Honma, Y. Benino, T. Fujiwara, T. Komatsu, Second-order optical nonlinearities of metastable BiBO$_3$ phases in crystallized glasses, Opt. Mater. 27 (2004) 403–408.
[15] M.J. Potter, Mise en Evidence d’un compose BiBO$_3$ et de son polymorphisme par spectroscopie vibrationnelle, Bull. Soc. Chim. Belg. 83 (1974) 235–238.
[16] R. Ibara, T. Komatsu, unpublished data.
[17] E.M. Levin, C.L. McDaniel, The system Bi$_2$O$_3$–B$_2$O$_3$, J. Am. Ceram. Soc. 45 (1962) 355–360.
[18] P.D. Townsend, A.K. Jazmati, T. Karali, M. Maghrabi, S.G. Raymond, B. Yang, Rare-earth-size effects on thermoluminescence and second-harmonic generation, J. Phys.: Condens. Matter 13 (2001) 2211–2224.
[19] J. Goodey, J. Broussard, P.S. Halasyamani, Synthesis, structure, and characterization of a new second-harmonic-generating tellurite: Na$_2$TeW$_2$O$_9$, Chem. Mater. 14 (2002) 3174–3180.