Effect of SnO addition on optical absorption of bismuth borate glass and photocatalytic property of the crystallized glass

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We have found that an addition of SnO in a bismuth-borate glass, $CaO-B_2O_3-Bi_2O_3-Al_2O_3-TiO_2$, decreases the optical absorption coefficient in the visible region, in which selective crystallization of TiO_2 was observed after heat treatment. Since selective crystallization of TiO_2 was also attained in the SnO-containing glass, the transparency of TiO_2 crystallized glass can be improved independently of selective crystallization of TiO_2. We have also demonstrated that the rutile-nanocrystallized glass with SnO addition shows a higher photocatalytic activity than the glass without SnO, indicating that this crystallized glass has a large potential for application as transparent photocatalytic materials. © *2008 American Institute of Physics*.
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Crystallized glass consists of both glassy regions and crystalline regions, and this hybrid material can show both glassy and crystalline characteristics below the glass transition temperature. Conventional crystallized glass, which is obtained by heat treatment of the precursor glass, is generally superior to the precursor glass in terms of strength, heat resistance, and thermal shock resistance. If precipitated crystallites in a glass material show unique physical properties,[1–3] the obtained crystallized glass can also possess not only merits of glass materials but also unique properties originating from the crystallites.

Titanium dioxide, TiO_2, has attractive characteristics, such as chemical stability and high refractive index, and it is used in electronic devices or as a photocatalyst.[4] There are, however, only a few reports on the crystallization from a glass matrix by a heat treatment.[5,6] Although addition of TiO_2 is sometimes used to enhance the nucleation of other crystals[7] due to the role of TiO_2 working as a nuclei forming agent for other crystal phases but not for TiO_2 itself, it is difficult to achieve selective crystallization of TiO_2 from a glass matrix. Moreover, it is also difficult to obtain a transparent glass matrix containing TiO_2 crystallites because of a large difference of refractive index (Δn) between the precipitated TiO_2 crystallites and the glass matrix. These are the reasons why the shape of photocatalytic materials containing TiO_2 crystallites has been restricted to either thin film, microparticles, or an opaque bulk material.

Recently, our group has fabricated a TiO_2 crystallized glass in which about 10 nm TiO_2 crystallites were precipitated.[8] The obtained $CaO-B_2O_3-Bi_2O_3-Al_2O_3-TiO_2$ (CaBBAT) glass showed a selective crystallization of TiO_2, and precipitation of no other crystallites was observed. It is also worth noting that the obtained glass showed a high transparency despite a large Δn between rutile crystallites and glass matrix, approximately 0.8 or larger, because the size of the precipitated crystallites was much smaller than the incident light wavelength in the visible region. The advantage of the glass containing TiO_2 crystallites in bulk form, a slab shape, in particular, is that the initial catalytic property can be repeatedly recovered by surface polishing. Moreover, since glass can be easily shaped, complicated shapes of a catalyst possessing a photocatalytic property are feasible.

However, the photocatalytic property of the CaBBAT glass was not measured because there was a strong absorption band in the visible region. Although several authors have reported that the absorption coefficient is correlated with the bismuth content,[9,10] the detail of the absorption band remains to be clarified. To understand the absorption band, we attempted to see how the optical absorption changes with chemical composition. Since bismuth oxide is an essential starting material for both a transparent glass and the crystallized glass obtained by heat treatment, we cannot drastically change the bismuth content. For example, if the amount of Bi_2O_3 is decreased, the obtained sample becomes opaque because of the crystallization of TiO_2. Therefore, addition of a small amount of other elements should be considered. In this paper, we investigated possible improvement of transparency in the $CaO-B_2O_3-Bi_2O_3-Al_2O_3-TiO_2$ glass by an addition of SnO and its effect on the photocatalytic property of the TiO_2 crystallized glass together with the crystalline phase and the size of TiO_2 crystallites.

The SnO-containing CaBBAT precursor glass was prepared using $CaCO_3$ (5 mol %), Bi_2O_3 (10 mol %), TiO_2 (20 mol %), B_2O_3 (65 mol %), and SnO. These starting chemicals were placed into an alumina crucible that can provide Al_2O_3 into the glass melt. The batches were melted at 1350 °C and quenched on a steel plate. The glass sample having a mirror surface was heat treated in an ambient atmosphere to obtain the corresponding crystallized glass. The absorption spectra of the samples were measured with a spectrometer. We used x-ray diffraction (XRD) to examine TiO_2 crystallites in the glass matrix. The image of the glass surface was obtained by atomic force microscopy (AFM).

Figure 1(a) shows the photographs of the CaBBAT glasses (a) and the SnO-containing CaBBAT glasses (b), (c), and (d), where the amount of SnO is 0.1 mol % for (b), 0.5 mol % for (c), and 1.0 mol % for (d). The colors of the samples changed with increasing amount of SnO, and transparent glasses were obtained with SnO contents ranging

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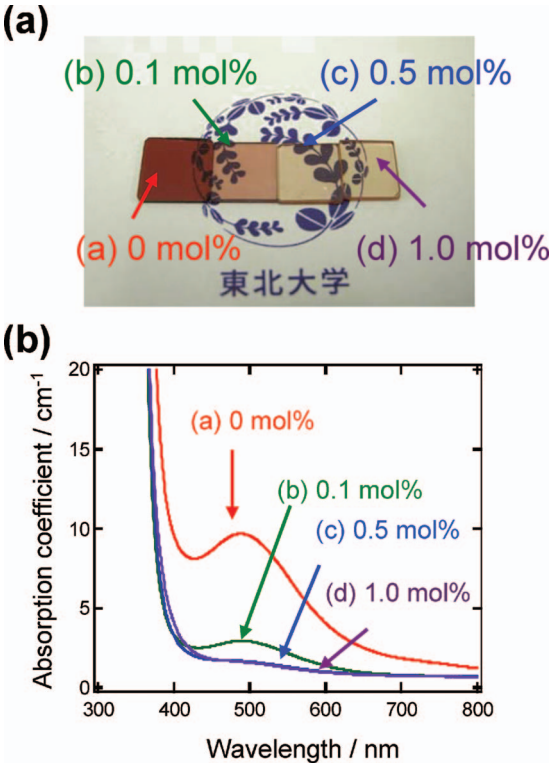

FIG. 1. (Color) (a) Photographs of the CaBBAT glasses with SnO addition of (a) 0, (b) 0.1, (c) 0.5, and (d) 1 mol %. (b) Absorption spectra of the CaBBAT glasses with SnO addition of (a) 0, (b) 0.1, (c) 0.5, and (d) 1 mol %.

from 0.1 to 1 mol %. On the other hand, precipitation of SnO_2 crystallites was observed in the sample containing 2 mol % of SnO, suggesting a limitation of SnO content. Figure 1(b) shows the absorption spectra of the glass (a) and the SnO-containing samples (b), (c), and (d). The absorption coefficient in the visible region drastically decreases with addition of SnO and saturates with 0.5 mol % of SnO. The absorption edge of the glass with SnO addition of 1 mol % shifts to a longer wavelength and the absorption in the visible region remains nearly the same as that of 0.5 mol % of SnO, indicating that the addition of 0.5 mol % of SnO can attain the minimum optical absorption coefficient of the present glass in the visible region. The transmittance of the sample (a) was 10%, whereas that of sample (c) was about 70%, showing a clear improvement in the transparency. If the change of valence of the Sn ion, from divalent to tetravalent in a glass melt or glass matrix, is responsible for the suppression of optical absorption, addition of oxides of multivalent transition metals is expected to be also effective in improving the transparency. However, no improvement of transparency was observed in the CaBBAT glass containing such metal oxides as CeO_2, Cu_2O, and Sb_2O_3 in which the valences of the metals are changeable. This indicates that the effect of SnO addition is not a simple redox reaction. Murata and Mouri attributed the absorption in the visible region to Bi-radical-like species.[9] Since an absorption band depends on the chemical composition of a bismuth-based glass, a structural change consisting of several ions should be considered for clarification of the mechanism. Further discussion on the absorption coefficient of the glass will be given in a separate paper.

Figure 2 shows the XRD patterns of the CaBBAT crystallized glass with and without addition of SnO. The heat-

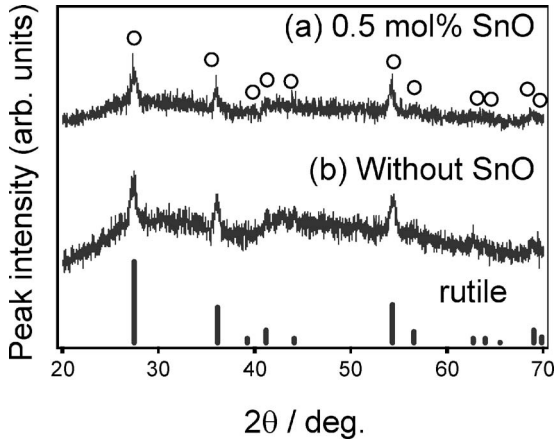

FIG. 2. XRD patterns of CaBBAT glasses with 0.5 mol % SnO (a) and without SnO (b) together with rutile (TiO_2, Ref. 11). The ○ marks are assigned to the diffraction peaks of rutile. The glasses were heat treated for 3 h at 630 °C.

treatment condition was at 630 °C for 3 h, and the amount of SnO was 0.5 mol %. The diffraction pattern of rutile is also shown in the same figure for reference.[11] The circles in the figure show the diffraction peaks of rutile. The XRD pattern indicates that a selective TiO_2 nanocrystallization has occurred independently of the addition of SnO. The average diameter of TiO_2 crystallites in the crystallized glass estimated using the Scherrer equation is about 10 nm, which is comparable to that of the CaBBAT crystallized glass without addition of SnO. The addition of SnO in the present study, therefore, improves the transparency of the CaBBAT glass without affecting the selective crystallization of TiO_2.

We examined the photocatalytic property of the TiO_2 crystallized glass with and without addition of SnO by using a conventional decomposition reaction of methylene blue. Seven pieces of bulk TiO_2 crystallized glasses ($10\times10\times1$ mm^3) were immersed in a 10 μM methylene blue solution, and then, the sample was placed in a dark place for over 18 h to remove the effect of surface adsorption. After the immersion, the solution was irradiated with UV light of 365 nm wavelength for 120 h.

The reaction rate is generally proportional to the concentration of materials associated with the reaction. The decomposition rate can be determined using the optical absorption coefficient before and after irradiation, A_0 and A, respectively. Since the optical absorbance is proportional to concentration, we can express the decomposition reaction coefficient k of TiO_2 as

$$k = \ln(A_0/A)t^{-1}S^{-1}, \quad (1)$$

where S is the surface area of the sample (7×10^{-4} m^{-2}) and t is the UV irradiation duration.The decomposition reaction coefficients k of the TiO_2 crystallized glass with SnO and that without SnO were 3.62 and 0.59 h^{-1} m^{-2}, respectively. Therefore, the reaction coefficient of the crystallized glass with SnO is about six times as large as that of the glass without SnO. The reaction coefficient usually depends on the surface area of the sample and on the amount of the precipitated crystallites. However, the AFM images of the surface of these crystallized glasses show no remarkable difference of surface state between the glass with SnO and that without SnO. For example, the root-mean-square roughness of the surface of the former was 9–16 nm, whereas that of the

latter was 12–14 nm. Moreover, the diffraction intensities of TiO_2 crystallites in the XRD patterns of the TiO_2 crystallized glass with SnO and that without SnO addition are similar (see Fig. 2). Considering the fact that the present XRD pattern reflects the precipitated crystalline phase located several microns from the surface, the photocatalytic results indicate that the addition of SnO to the CaBBAT glass composition affects the fine nanostructure at the very surface of the TiO_2 crystallized glass. Since the nanostructure that is expected to dominate the photocatalytic property of the matrix is still unclear, another measurement to analyze the critical structure at the surface of the TiO_2 crystallized glass will clarify this aspect.

In summary, we have prepared TiO_2 nanocrystallized glass with an improved photocatalytic property using an addition of SnO. The obtained results show that the SnO addition enhances both the transparency and the photocatalytic activity without any derogatory effect on the selective nature of TiO_2 precipitation. Although the underlying mechanisms for the above mentioned effects remain to be clarified, the present TiO_2 nanocrystallized glass, therefore, will be a promising transparent photocatalytic material without any coating process.

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[1]Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, Nature (London) **432**, 84 (2004).
[2]H. Masai, T. Fujiwara, Y. Benino, and T. Komatsu, J. Appl. Phys. **100**, 023526 (2006).
[3]S. Kondo, K. Takeda, and Y. Yamamura, Solid State Ionics **53-56**, 1183 (1992).
[4]A. Fujishima and K. Honda, Nature (London) **238**, 37 (1972).
[5]H. Hosono, Y. Sakai, M. Fasano, and Y. Abe, J. Am. Ceram. Soc. **73**, 2536 (1990).
[6]W. T. Brydges III and D. W. Smith, U.S. Patent No. 3,948,669 (April 6, 1976).
[7]T. Kokubo, M. Shigematsu, Y. Nagashima, M. Tashiro, T. Nakamura, T. Yamamuro, and S. Higashi, Bull. Inst. Chem. Res., Kyoto Univ. **60**, 260 (1982).
[8]H. Masai, T. Fujiwara, H. Mori, and T. Komatsu, Appl. Phys. Lett. **90**, 081907 (2007).
[9]T. Murata and T. Mouri, J. Non-Cryst. Solids **353**, 2403 (2007).
[10]Y. Fujimoto and M. Nakatsuka, Jpn. J. Appl. Phys., Part 2 **40**, L279 (2001).
[11]JCPDS Card No. 01-084-1283.