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Fabrication of TiO_2 nanocrystallized glass

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Nanocrystallization of rutile and anatase was observed in a $CaO-B_2O_3-Bi_2O_3-Al_2O_3-TiO_2$ crystallized glass. The color of the present crystallized glass was changed by the heat-treatment temperature, and x-ray diffraction (XRD) patterns of the crystallized glass show that the apparent color change is correlated with the formation of titania nanocrystallites. The particle size of crystallites observed in the transmission electron microscope image is comparable to that measured by XRD pattern. In addition, a large change of refractive index between the rutile particles and glass matrix, 0.8 or larger, was obtained. The present titania crystallized glass will be not only a photocatalytic material but also a promising candidate for random lasing devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2679044]

Crystallized glass, usually obtained by heat treatment of the precursor glass, is superior to the mother glass in terms of strength, heat resistance, and thermal shock resistance, and it is used as photosensitive glasses,[1] low thermal expansion glasses,[2] and bioceramics[3] in industry. Since crystallized glass consists of both disordered glass regions and ordered crystalline regions, it can also possess not only merits of glass materials, such as high transparency, easy modeling, and wide chemical composition range, but also unique physical properties originating from the crystalline phase, such as ionic conductivity[4] and optical nonlinearity.[5,6]

Titanium oxide, titania, has attractive characteristics, such as chemical stability and high refractive index, and it is used in electronic devices or as a photocatalyst. In particular, the photocatalysis of titania is industrially applied in many fields owing to its strong oxidation capability and high hydrophilicity.[7–10] Titania-containing materials are usually prepared by vapor deposition,[8] sputtering deposition,[9] or by coating using a titania-containing sol.[10] However, the properties of titania produced by these deposition or coating techniques change over time by surface damage and thus a recoating process of the material is necessary. (In other words, there is the limitation of permanent performance in the titania deposition or coating materials.) On the contrary, if the titania crystallites exist in the glass matrix, the titania crystallites dispersed in the glass matrix will exhibit a stable characteristic property even with surface polishing.

However, literature on crystallization of glass containing titania crystallites by a heat treatment is scarce. Although a few studies of phase-separated titania glass have been reported, the obtained glass is usually heterogeneous with a mixture of titania crystallites and glassy regions even in the as-prepared samples without heat treatment.[11,12] Indeed, it is difficult to attain a high degree of transparency in a titania-crystallite-containing transparent glass because of light scattering by titania crystallites with a large refractive index. In addition, it is extremely difficult to obtain selective crystallization of titania, because a titania crystallite acts as a nucleus of other crystalline phases and also because it forms another crystal structure with other glass forming oxides, such as Al_2O_3 or SiO_2. On the other hand, the addition of titania is sometimes used to enhance the nucleation and crystal growth of other crystals,[13] where crystallization of titania is irrelevant.

There is only one report about a titania-containing crystallized glass material, a patent about the crystallized glass containing titania, in which rutile is crystallized by a heat treatment.[14] It reports that the obtained crystallized glasses, which contained fibrous crystals of rutile exhibiting high aspect ratios, presented improvements of mechanical strength compared with the original mother glass. The use of crystallized titania, however, is intended only for the physical improvement of the crystallized glass, not for its function, because the obtained crystallized glass consists essentially of rutile and $Al_4B_2O_9$. Moreover, there is a problem that most of glass compositions in this patent contains Pb, which is a pollutant element for the environment.

We can propose titania-nanocrystallized glass as a promising material for the following two applications. One is application as a photocatalytic transparent material and the other is as a lasing optical device. The titania crystallized glass will play a permanent photocatalytic property by titania crystallites dispersed fully in the glass matrix. Another application is use in an optical element. The titania nanocrystallites in the glass matrix can confine light, which is suitable and interesting for random lasing,[15] because the refractive index of titania is 2.52 (anatase)–2.728 (rutile). Cao and co-workers demonstrated laser oscillation in a polymer film containing titania particles and an organic dye.[16,17] If the host matrix of random media is an inorganic material, which has an advantage in terms of durability better than organic material, it will break through the wall for the practical application of random lasing devices. In this study, we examined TiO_2-crystallized glass with these points of view and report the crystallization behavior of $CaO-B_2O_3-Bi_2O_3-Al_2O_3-TiO_2$ (CaBBAT) glass.

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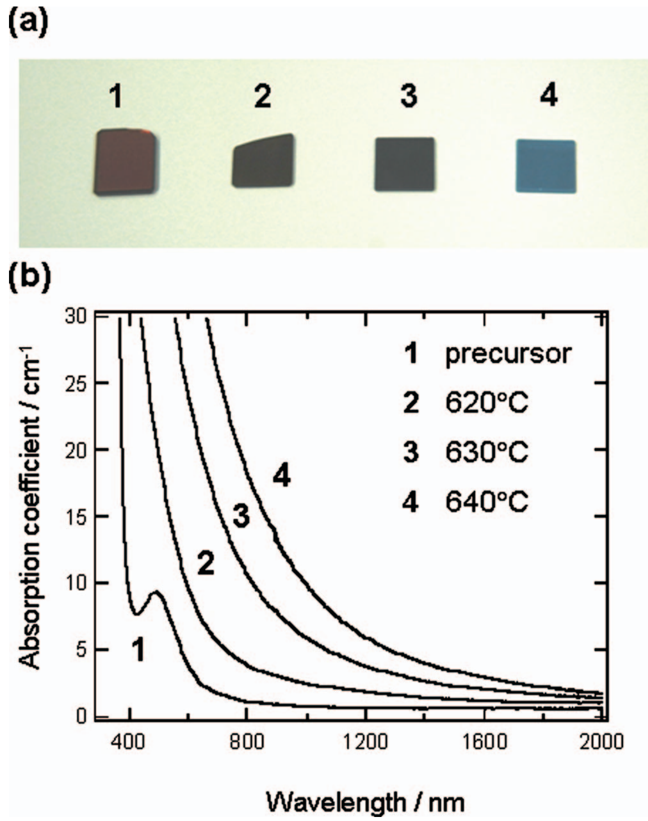

FIG. 1. (Color) (a) Photograph of the CaBBAT glasses heat treated at 620, 630, and 640 °C for 3 h together with the precursor glass. (b) Absorption spectra of the CaBBAT glasses heat treated at 620, 630, and 640 °C for 3 h together with the precursor glass.

The CaBBAT precursor glass was prepared by a conventional melt-quenching method. Batches consisting of $CaCO_3$ (5 mol %), Bi_2O_3 (10 mol %), TiO_2 (20 mol %), and B_2O_3 (65 mol %) were mixed and melted in an aluminum crucible (purity of 99.9%) in an electric furnace at 1300 °C for 40 min. Glass melt was quenched on a steel plate at 160 °C and then annealed at the temperature of glass transition, T_g, for 30 min. After mechanically polishing to obtain a mirror surface, the glass sample was heat treated on an alumina plate in an ambient atmosphere to obtain the corresponding crystallized glass. The temperatures of glass transition, T_g, crystallization onset, T_x, and crystallization peak, T_p, were measured by differential thermal analysis (DTA) operated at a heating rate of 10 K/min using TG8120 (Rigaku). The refractive index was measured with a prism coupler (Metricon) using a He–Ne laser ($\lambda = 633$ nm). The absorption spectra were measured with a spectrometer UV-3150 (Shimadzu). We used x-ray diffraction (XRD) and transmission electron microscopy (TEM) to examine the titania crystallites in the glass matrix, where TEM images were taken using JEM-2000FXII (JEOL).

The obtained transparent precursor glass was vinous in color of which T_g, T_x, and T_p measured by DTA were 569, 623, and 640 °C, respectively. On the other hand, the prepared glass melted in a platinum crucible was opaque because of crystallization of titania, whereas the samples with the same chemical composition melted in alumina crucible was transparent. It indicates that the contamination by Al_2O_3 was essential for the transparency and homogeneity of the glass. Figure 1(a) shows the photograph of the CaBBAT glasses heat treated for 3 h at 620, 630, and 640 °C together with the precursor glass, and Fig. 1(b) shows the absorption spectra of the corresponding glasses shown in Fig. 1(a). The absorption coefficient increases with increasing heat treatment temperature in the whole wavelength range covered. The apparent color of the sample drastically changes after the heat treatment above 625 °C from transparent vinous to translucent blue. Since the transmitted light is observable through these crystallized samples, this blue color is scattered light that originates from the microstructure consisting of nanoparticles. The absorption band around 490 nm in the precursor glass is attributed to Ti^{3+} but the effect of this absorption on color has not been clarified yet.

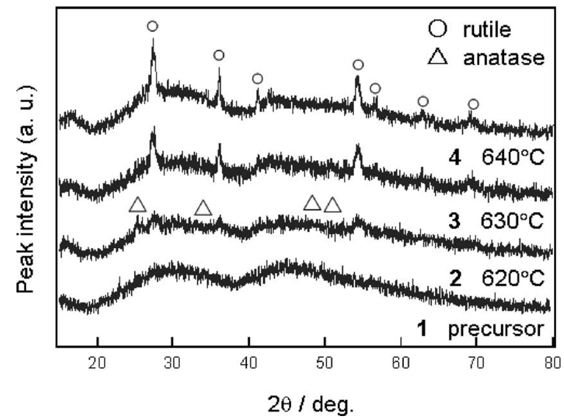

FIG. 2. XRD patterns of CaBBAT glasses heat treated for 3 h at different temperatures.

Figure 2 shows XRD patterns of CaBBAT glasses heat treated at 620, 630, and 640 °C for 3 h together with that of the precursor glass. The glasses with the heat treatment showed a mixture of the diffraction pattern of anatase[18] and rutile.[19] The obtained diffraction patterns show that titania crystallites were selectively formed as a single phase. The absence of diffraction peaks assignable to $Al_4B_2O_9$ indicates that a selective crystallization of titania has occurred. The average particle diameter measured from the Scherrer equation was 10–20 nm. Although the Aurivillius compound $CaBi_4Ti_4O_{15}$, which shows a large piezoelectric property,[20] can be crystallized from the chemical composition of the present glass, no diffraction peak assignable to $CaBi_4Ti_4O_{15}$ was observed. Since no apparent change of the XRD pattern was observed after surface polishing of 500 μm, we can conclude that the bulk crystallization took place by the heat treatment.

Figure 3 shows the TEM image of the CaBBAT crystallized glass heat treated at 630 °C for 3 h. The dashed circles show the domains that have less than 10 nm diameter, which is comparable to the particle size of titania crystallites estimated by the XRD patterns. The inset shows the electron diffraction pattern of the CaBBAT crystallized glass. The diffraction satellites attributable to rutile (110), (101), and (211) confirm the result of the XRD measurement. These domains, therefore, are attributed to the titania crystallites in the glass matrix and the titania domains with small size distribution are the origin of the blue scattering from the glass matrix. The fabricated microstructure consisting of titania nanocrystallites will work as a conventional photocatalytic material obtained by titania coating.

Since the refractive index of the CaBBAT glass was 1.754 at 633 nm, there is a difference of refractive index, Δn, 0.8 or larger, between the crystallized rutile and glass matrix.

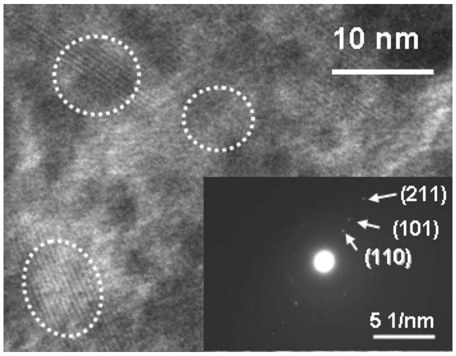

FIG. 3. TEM image of the CaBBAT crystallized glass heat treated at 630 °C for 3 h. Inset shows electron diffraction pattern of the CaBBAT crystallized glass heat treated at 630 °C for 3 h.

Although a value of the refractive index in a glass matrix remaining after crystallization is not known at present, it is suggested that the nanoscale crystallization is the dominant factor for the transparency of the titania-containing glass even in such a large Δn situation. The large Δn warrants the localization of photons, which is attractive as optical lasing devices.

In summary, we have fabricated TiO_2 nanocrystallized glass. The titania nanocrystallites in the glass, confirmed by XRD and TEM measurements, brought about the blue color due to scattering by the crystallites. In addition, a large Δn between rutile particles and the glass matrix, about 0.8 or larger, was obtained. The present bulk titania crystallized glass will open up an application field not only for a titania-containing photocatalyst but also for a random lasing device.

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