Fabrication of transparent sintered ZnO-B$_2$O$_3$-Bi$_2$O$_3$ glass body by pressureless firing and hot isostatic pressing

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Abstract. The optimum conditions for the fabrication of transparent glass body in the ZnO-B$_2$O$_3$ (ZB) and ZnO-B$_2$O$_3$-Bi$_2$O$_3$ (ZBB) systems were examined by a pressureless firing and subsequent oxygen-supplied hot isostatic pressing (HIP). The pressurelessly-fired opaque ZB glass body possessed the maximum relative density (99.1%) when fired at 620°C for 15 min in air, and was hot isostatically pressed at 630°C for 12 h under the pressure of 150MPa (80%Ar - 20%O$_2$ atmosphere) to eliminate the residual pores; the light transmittance of this glass body was in the range of 35 to 51% (380 to 800 nm). In order to fabricate the transparent glass body at lower temperature, the fabrication conditions of ZBB glass body were examined. The pressurelessly-fired ZBB glass body possessed a maximum relative density (98.8%) when fired at 500°C for 2 h in O$_2$ atmosphere and hot isostatically pressed at 490°C for 12 h; the transmittance of the transparent ZBB glass body was in the range of 48 to 58% (500 to 800 nm).

1. Introduction

“Low melting glasses” are defined as glasses with lower softening points, as well as melting points, compared to the case of conventional glasses (e.g. the softening temperature of soda-lime glass being around 730°C), and the melting points being closer to the softening points. The low melting glasses are used in many fields, e.g., (i) the protection of thin dielectric layer between front glass of plasma display panels and electrodes of the devices [1], (ii) the sealing for the protection of metals/ceramics [2], and (iii) the sintering aids for the fabrication of ceramics [3]. Such glasses often contain lead oxide or environmentally restricted compound in order to lower the softening/melting points and sintering temperatures. The promising low melting glasses with no lead oxide addition but with properties comparable to lead oxide containing glasses would be the glasses in the ZnO-B$_2$O$_3$-Bi$_2$O$_3$ system, although the kinds of lead-free low melting glasses are limited until now.

The sealing of metals/ceramics is conducted by the melting operation of glasses; however, the sintering of glass powder is often required, because this operation is generally conducted at lower temperatures than the case of melting operation and minimizes the risk of damaging the properties of substrate. Nevertheless, the fabrication of transparent glass bodies by the conventional pressureless sintering technique is difficult, because the light scattering may occur at the residual pores. Since the sintering of glass powder is operated by the viscous flow mechanism [4], the high pressure application to the glass body seems to be effective to eliminate such residual pores. On the basis of such background, the present authors examined the fabrication conditions of transparent low melting glass body in the ZnO-B$_2$O$_3$-Bi$_2$O$_3$ system through the combination of pressureless firing and subsequent oxygen-supplied HIP treatment (O$_2$-HIP).
2. Experimental procedure

Two kinds of commercial glass powders, *i.e.*, ZnO-B$_2$O$_3$ (ZB) and ZnO-B$_2$O$_3$-Bi$_2$O$_3$ (ZBB), were used for the starting materials. The glass powder (approximately 1.0 ~ 1.5 g) was uniaxially pressed at 50MPa to form a disk with a diameter of 14 mm and a thickness of 2 mm. The cylindrical ZB powder compact was pressurelessly fired in air at a temperature between 590ºC and 670ºC for 15 min, and then was fired in 80% Ar - 20% O$_2$ atmosphere at a temperature between 620ºC and 640ºC for 12 h under the pressure of 150 MPa, using hot isostatic pressing (O$_2$-HIP). The cylindrical ZBB compact was pressurelessly fired at a temperature between 480ºC and 500ºC in the O$_2$ atmosphere, and hot isostatically pressed at a temperature between 480ºC to 500ºC for 12 h in 80%Ar - 20%O$_2$ atmosphere under the pressure of 150 MPa. The crystalline phases were checked using an X-ray diffractometer (XRD; RINT2100V/P, Rigaku, Tokyo, Japan) with CuKα radiation (40 kV, 40 mA). The chemical compositions were checked using an X-ray fluorescence spectrometer (XRF; ZSX-Primus II, Rigaku, Tokyo) and inductively-coupled plasma atomic emission spectroscopy (ICP-AES, SPS7700, Seiko Instruments, Tokyo). The particle morphology was studied using a field-emission scanning electron microscope (FE-SEM; S-4500, Hitachi, Tokyo). The bulk density of sintered glass body was measured by Archimedes method, using ethanol as an immersion liquid; the relative density was calculated on the basis of bulk density and true density, *i.e.*, 3.68 g·cm$^{-3}$ (ZB glass) and 6.08 g·cm$^{-3}$ (ZBB glass). The glass transition temperature ($T_g$) was examined using a differential thermal analyzer (DTA; Thermo Plus TG8120, Rigaku, Tokyo). The transmittance of glass body was measured using an ultraviolet–visible spectroscope (UV-Vis; V-660, JASCO, Tokyo).

3. Results and discussion

3.1 Properties of starting glass materials

The components and amounts determined by XRF and ICP-AES were: (i) ZB glass; 62.74 mass% ZnO, 30.14 mass% B$_2$O$_3$, 3.93 mass% Al$_2$O$_3$ and 2.86 mass% SiO$_2$, and (ii) ZBB glass; 15.78 mass% ZnO, 14.43 mass% B$_2$O$_3$ and 68.48 mass% Bi$_2$O$_3$. FE-SEM observation showed that ZB and ZBB powders consisted of infinite-shaped particles with sizes of approximately 5 μm. The transition temperatures ($T_g$) of ZB and ZBB glasses checked by DTA were 614.7 and 480.3°C, respectively.
occurred by the volume changes due to the crystallization. In order to eliminate the residual pores to show the transparency, the pressureless-fired ZB body was HIPed under the pressure of 150 MPa. The transmittances of HIPed glass bodies are shown in Fig. 3. The transmittance increased with increasing HIPing temperature but was in the range of 35 to 51% at 630°C (380 to 800 nm). The densification of glass body seems to be occurred by the viscous flow, because the viscosity of glass is reduced when the temperature exceeds $T_g (= 614.7°C)$ [4]. On the other hand, the lowering of transmittance with HIPing temperature from 630 to 640°C may be occurred by the creation of pores, due to the partial crystallization (see the XRD data in Fig. 2).

### 3.3 Fabrication of transparent ZBB glass body

The investigation on the sintering at lower temperature, compared to the case of ZB glass, was conducted using ZBB glass, because the $T_g$ of this glass is reduced down to 480.3°C, due to the introduction of Bi$_2$O$_3$ into the glass structure. The changes in relative density of ZBB glass body fabricated by the pressureless firing is shown in Fig. 4. Note that the oxygen (O$_2$) atmosphere during the firing was selected in order to avoid reducing the Bi$_2$O$_3$ [5]. The relative density of ZBB glass body attained 98.8% at 500°C, and then decreased on further firing. XRD patterns showed that no crystalline phases were present in the sintered ZBB glass bodies (no data shown here). This fact indicates that the glass state may be kept during the firing between 480°C and 520°C. Since the $T_g$ of ZBB glass powder is 480.3°C, the lowering of viscosity above $T_g$ [4] may contribute to enhancing the densification. On further increase in firing temperature, however, the pore size was enhanced by the coalescence of smaller pores (FE-SEM micrographs in Fig. 4); the swelling of glass body results in the decrease of relative density. This phenomenon may be enhanced by the release of vapor from the ZBB glass body, because the mass loss (1.3 mass%) was observed by thermogravimetry when the glass compact was fired up to 520°C. Further, the HIP treatment was conducted at a temperature between 480°C and 500°C for 12 h under the pressure of 150 MPa to fabricate the transparent ZBB glass bodies. The transmittance of ZBB glass body HIPed at 490°C for 24 h was in the range of 48 to 58% (500 to 800 nm) (see Fig. 5).
Overall, the transparent ZB and ZBB glass bodies could be fabricated using the combination of pressureless firing and subsequent HIP treatment.

4. Conclusion

The conditions for the fabrication of transparent ZB and ZBB glass bodies were examined by pressureless firing and HIP treatment. The results obtained were summarized as follows:

1) The pressurelessly-fired and opaque ZB body possessed the maximum relative density of 99.1% at 620ºC for 15 min in air, and then was further hot isostatically pressed under the pressure of 150 MPa (80%Ar - 20%O$_2$ atmosphere) in order to eliminate the residual pores; the transmittance of this glass body was 35 to 51% (380 to 800 nm).

2) In order to obtain the transparent glass body at comparatively lower temperature, the fabrication conditions of ZBB glass were examined, because the $T_g$ of ZBB glass was 480.3ºC and lower than the case of ZB glass (614.7ºC). The cylindrical ZBB compact was pressurelessly fired at a temperature between 480 and 520ºC in the O$_2$ atmosphere, and hot isostatically pressed at 490ºC for 12 h in 80%Ar - 20%O$_2$ atmosphere under the pressure of 150 MPa. Due to the HIPing treatment, the transparent ZBB glass body was obtained, and the transmittance of this glass body was in the range of 48 to 58% (500 to 800 nm).

References

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