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Crystallization behavior of bismuth oxide nano-glass studied via in situ transmission electron microscopy

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Abstract

The substitution of bismuth oxide for lead in glass and decreasing the particle size of glass powders to the nanoscale have both attracted considerable interest as techniques for decreasing the maximum firing temperature and alleviating environmental problems. However, crystallization during firing is an issue that needs to be solved. In this study, we investigated the sintering behavior of nanosized bismuth oxide glass and the mechanism of its crystallization. The crystallization behavior during sintering was analyzed by hot-stage microscopy. The microscopic sintering interaction between individual nanoglass particles was observed by in situ transmission electron microscopy. The glass softening and densification starting temperatures were dramatically decreased when decreasing the particle size from micro to nanoscale. Based on this study, the bloating of nanostructured bismuth oxide glass starts at 370 °C. This corresponds with the dissociation temperature of bismuth oxide. Therefore, the bloating phenomenon during the sintering of the nanoglass powder is attributed to the thermal dissociation of bismuth oxide.

Keywords: Nano-glass; Crystallization; In situ TEM; Bismuth oxide

1. Introduction

As the use of lead for electronics has been restricted by the Restriction of Hazardous Substances (RoHS) legislation due to its toxicity [1,2], studies have been performed with the purpose of replacing lead in glass with alternative materials. To achieve a low melting temperature, the composition is changed and the size of the particles is decreased [3–11]. Research about eco-friendly glass with low melting temperatures has been reported, with B_2O_3, TeO_2, P_2O_5, and Bi_2O_3 found to be suitable components for lead-free glass with a low softening temperature. Glasses containing these components are being used for display-panel sealings [4,5], thick-film conductors [12], frits for solar cell electrodes [13], and dye-sensitized solar cell sealings [14]. Among these suitable glass-forming compounds, Bi_2O_3–B_2O_3 has attracted the most attention.

In spite of the advantage of being a glass with a low melting temperature, Bi_2O_3–B_2O_3 glass exhibits problematic crystallization behavior during firing. Studies on the crystallinity and crystallization rate of bismuth borate glass have been reported [6,7]. The crystallization rate and behavior of Bi_2O_3–B_2O_3–ZnO glass has also been studied [8]. However, the underlying cause of nucleation and crystallization at the low temperature range of firing is still unclear. Furthermore, even though the synthesis of nanosized amorphous material has been reported, many problems arise if the firing temperature is decreased by a decreased particle size of the glass frits. These problems include dispersion [9], easy crystallization [10], and difficulties in the synthesis without compositional changes [11]. Moreover, the presence of dissociated bismuth causes problems by forming bonds with other components of the glass, thereby generating new compounds and inducing crystallization of other ceramics, such as $BiBO_3$, $BaBiBO_4$, or $ZnBi_4B_2O_{10}$.

To the best of our knowledge, there have been no previous studies on these problems or on how to prevent them. Also, no studies have been conducted on the negative effects of decreased

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particle size of Bi_2O_3-based glass powders on the glass forming process. In our study, we investigated the effect of the particle size on the sintering and crystallization behavior of the well-known Bi_2O_3–ZnO–B_2O_3 glass. The sintering and crystallization behaviors were studied using thermal analysis while being simultaneously observed by in situ transmission electron microscopy (TEM).

2. Materials and methods

Micro, sub-micro, and nanoglass samples were prepared using a commercial glass powder (Cera Co., Cheonan, Korea). It is based on the 38.06Bi_2O_3–33.7ZnO–22.9B_2O_3–4.44BaO–0.9Al_2O_3 (in mol%) glass, having a glass transition temperature of 370 °C and an average particle size of 15 μm. For the preparation of various glass powders, microsized glass was prepared first by sieving through a 500 mesh sieve. In the case of sub-micro and nanoglass preparation, dry milling and a non-transferred DC thermal plasma process were applied. Dry milling was performed using a planetary mono-mill (Pulverisette-7, Fritsch, Idar-Oberstein, Germany). The non-transferred DC thermal plasma system was operated under the following conditions: 7 kW power input, 15 L/min of argon-gas flow used as the plasma gas, and 0.5 L/min of oxygen acting as the reaction gas upon entering the reaction chamber. Using these techniques, we successfully obtained nanosized glass powder without compositional changes [11].

To determine the particle size of each glass powder, Field-Emission Scanning Electron Microscopy (FE-SEM, S-4300, Hitachi, Tokyo, Japan) was performed. Powders labeled Micro, Sub-micro, and Nano had average particle sizes (d_{50}) of 4.97 μm, 480 nm, and 40 nm, respectively. Micro and Sub-micro powders are irregular in shape, but the synthesized Nano powder is spherical in shape, as shown in Fig. 1. The glass transition temperature (T_g) and the crystallization temperature were measured by Differential Scanning Calorimetry (DSC, STA 449 F3, NETZSCH, Selb, Germany). The sintering behavior and the glass-softening temperature (T_s) of the powders were observed and analyzed by preparing cylindrical pellets (2 mm diameter and 3 mm height) with a metal mold under a constant pressure of 0.3 GPa. After preparation, the pellets were placed in the hot stage of a microscopy system (MISURA HSM, EXPERT SYSTEM SOLUTION, Viale, Italy) and fired at a heating rate of 10 °C/min. After sintering the pellets at temperatures up to 390 °C, the surface of the sintered pellets was observed using FE-SEM. In situ observation of the microscopic interactions between individual nano-glass particles during sintering was performed using a thermal stage (EM-SHH4 specimen holder, JEOL, Tokyo, Japan) at a heating rate of 10 °C/min in a TEM (JEM-3011 HR, JEOL, Tokyo, Japan) operated at 300 kV.

3. Results and discussion

The glass transition temperature of the Nano glass powder was measured to be 355 °C and was 15 °C lower than that of Micro and Sub-micro powders. Also, the temperature of the exothermal peaks decreased with decreasing particle size, and thus, the crystallization temperature decreased (Fig. 2). The temperature for the onset of densification (T_{ds}) decreased with decreasing particle size of the powders. In particular, the T_{ds} of the Nano glass dropped dramatically. The T_g of the Micro, Sub-micro, and Nano powders were measured to be 370 °C, 370 °C, and 355 °C, respectively, and the T_{ds} of the Micro, Sub-micro, and Nano glass powders were found to be 370 °C, 360 °C, and 315 °C, respectively (Fig. 3). From these results, it seems that a smaller size of glass particles strongly affects the glass-sintering rate in a favorable way. Mishra et al. calculated

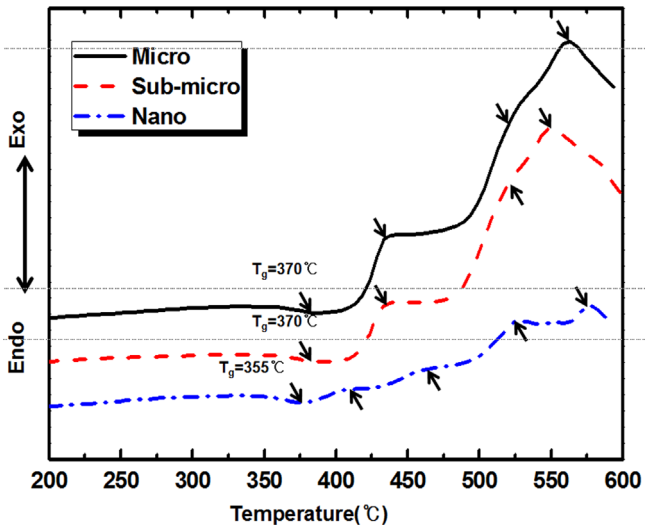

Fig. 2. DSC thermal analysis results of the various glass powders. The glass transition temperature of the Nano powder was 15 °C lower than Micro and Sub-micro powders. (Heating rate: 10 °C/min).

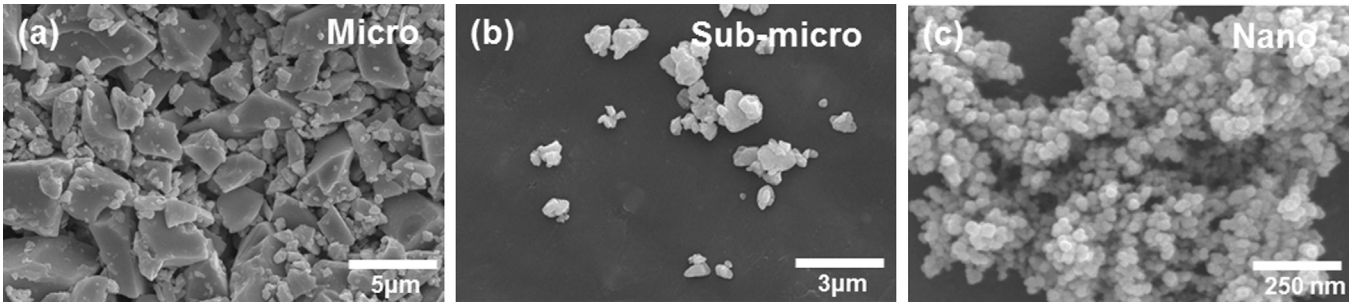

Fig. 1. SEM images of the as-prepared glass powders for the (a) Micro, (b) Sub-micro, and (c) Nano glass powders.