J Electroceram (2006) 17:331–334
DOI 10.1007/s10832-006-9736-0

Thermal and mechanical properties of lead-free transparent dielectric materials for plasma display panels

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Received: 2 August 2005 / Revised: 3 February 2006 / Accepted: 10 July 2006

Abstract The transparent dielectric materials for front panel in PDPs require good thermal expansion matching to glass substrate. Lead oxide (PbO) has been broadly utilized in transparent dielectric layers for low-temperature firing process. According to environmental and human health problem, however, Pb-based glass ceramics are no longer suitable for transparent dielectric layers. Glass with the Bi-based system was examined as a potential replacement for Pb-based glass. Softening point and coefficient of thermal expansion of the glass were at 520°C and $8.5 \times 10^{-6}/{}^{\circ}C$, respectively. Optimum sintering temperature for the highest densification was at 560°C, which indicated the highest flexural strength value derived from the lowest pore volume fraction. In addition, transmittance of specimen sintered at 560°C was about 90% in a visible light region. These results suggested that Bi-based glass would be suitable as an alternative to Pb-based dielectric layer in PDPs.

Keywords Transparent dielectric materials · Lead-free · Thermal property · Mechanical property · Plasma display panels

1 Introduction

Plasma Display Panels (PDPs) are type of flat panel display, which have merits of large display area and wide viewing angle suitable for the wall-hanging TVs [1]. Dielectric layer is formed on a front glass substrate to cover the display electrodes in a PDP. It is necessary for the dielectric layer to maintain discharge, to have a high dielectric strength, and to have good transparency. For the development of a reasonable dielectric layer for a PDP, several properties are required such as high transparency (above 80% after firing), high break down voltage (above 9 kv at 20 μm), a low firing temperature of about 550–600°C, a dielectric constant below 15, and a reasonable coefficient of thermal expansion (8–9 $\times 10^{-6}$/K) to match the glass substrate [2].

Pb-based frits have been utilized in transparent dielectric layers for low-temperature firing process. However, there are a number of problems associated with their use due to a component deleterious to health and the environment.

Recently, it has been reported that Bi-based glass systems were examined as a potential replacement for Pb-based glass with low firing temperature for the dielectric layer of plasma display panel. However, it has been scarcely reported to investigate on their thermal and mechanical properties behavior for sintered layer with pore-free. In this study, Bi-based glass was investigated for the application to the dielectric layer of PDP depending on its sintering behavior.

2 Experimental procedures

All compositions were prepared from chemically pure 60wt% Bi_2O_3(Junsei chemical co. LTD, Japan, 99%), 18w% B_2O_3(Junsei chemical co. LTD, Japan, 95%), 3wt% CaO (Junsei chemical co. LTD, Japan, 98%), 15wt% ZnO(Junsei chemical co. LTD, Japan, 99%), and 7wt% SiO_2(Wako Pure Chemical Industries, Japan, 92.8%). The weighed batch mixed with a ball mill for 1 h, and then the mixed powders were melted in an aluminum crucible at 1100°C for 1 h. The melt was quenched into stainless plate to make glass flakes and quenched glass was crushed in an agate mortar.

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The specific surface area of glass frit was conducted using Brunauer-Emmett-Teller (BET, ASAP2010, U.S.A) with nitrogen-gas adsorption method, and density of frit was measured using pyconometer (Micromertitics Accupyc 1330, U.S.A) with He-gas adsorption method. The coefficient of thermal expansion (CTE) and softening point of glass ceramics with the dimension of $\Phi 7 \times 4$ mm were measured by dilatometer (Netzsch DIL 402, Germany). Bulk glasses were made by steel mold to form rectangular bars with the approximate dimensions of $20 \times 10 \times 3$ mm, which were sintered at 540°C - 600°C for 1h, respectively. In order to measure mechanical property of sintered bodies, flexural strengths of all specimens were examined by a three-point bending test with a support distance of 10 mm using a Universal Testing Machine (UTM, Shimadzu AGS-500D, Japan). Five specimens were tested to obtain the average strength. The microstructures of cross sections for sintered bodies were observed by a scanning electron microscope (SEM, Hitachi S-3000H, Japan). The transmittance of sintered specimen was measured in the wavelength range from 300 to 800 nm using an ultraviolet – visible spectrophotometer (UV-VIS, HP8453, U.S.A.).

3 Results and discussion

It has been reported that the coefficient of thermal expansion (CTE) of material is dependent on its densification, crystalline phases, and additives [3]. Especially, densification behavior strongly affect on thermal and mechanical properties of ceramic materials. Densification behavior can be reversely investigated by mechanical property of material depending on viscous flow and pore generation mechanism.

During sintering in the presence of liquid phase, three separate densification process occur. These are: first, rearrangement of solid particles to give increased density; secondly, solution-precipitation in which material is dissolved away from contact points, allowing the centers of particles to approach; and finally, coalescence of solid particles with a cessation of sintering [4]. The sintering of glass and amorphous powder was proceeded by viscous flow, and this enhances densification rate related to the decreasing viscosity of the liquid phase with increasing temperature.

Figure 1 shows flexural strengths of sintered bodies at various sintering temperatures for 1 h. Sintered body at 560°C has the highest strength value, which means that there was enough energy for densification of glass through viscous flow. Beyond optimum temperature (560°C), however, strength values decreased with increasing sintering temperature. There are many factors that influence on the strength of porous and dense ceramic bodies. For example, strengths of ceramic materials increase with decreasing grain size and pores volume fraction, and major effect on the structure in most ceramics are resulted in porosity. The mechanical be-

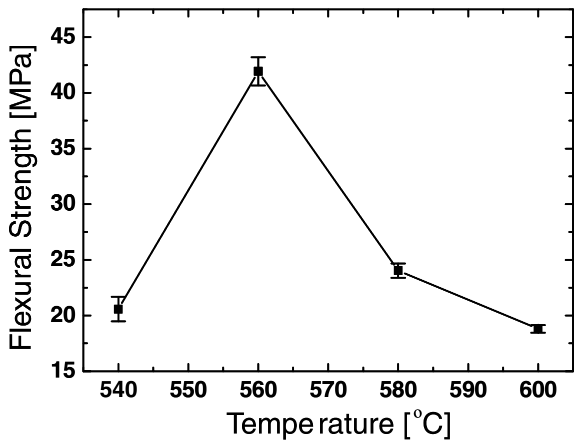

Fig. 1 Flexural strengths of specimens sintered at various temperatures for 1 h

haviors of the sintered bodies at various temperatures for 1 h were investigated depending on defects originated by reduction reaction of Bi ions and insufficient viscous flow for densification during sintering process. It was known that higher temperature accelerates evaporation rate through reduction reaction of Bi ions [5, 6, 8]. Therefore, decreased strength with increasing temperature meant increasing pore volume fraction derived oxygen gas generated by reduction reaction of Bi ions. The reason for low strength of specimen sintered at 540°C may be related to insufficient viscous flow for densification.

Mechanical property of ceramic materials is dependent on the fundamental relationship between strength(S) and porosity, which is expressed as follows:

$$S = S_o e^{-kP}$$

where S_o is the strength at zero porosity, P is the porosity and k a constant. In this study, the inverse relationship between strength and porosity was found, and this is closely in a good agreement with microstructure observation shown in Fig. 2.

Figure 2 shows SEM images of the cross sections of specimens sintered at various temperatures for 1 h. In microstructure observation of specimens sintered at 540°C, it could be confirmed that pores among the particles caused by insufficient viscous flow for densification, which was directly related to mechanical property of material. However, specimens sintered at 560°C presented nearly pore-free, which revealed that optimum sintering temperature for densification was 560°C in Bi-based glass. Beyond optimum temperature, the number of pores increased with increasing temperature, which could be strong evidence that the pores were created by the evaporation of gases generated from the inside of the pellet during sintering [7]. Also, pore size increased with increasing temperature due to coalescence of pores generated by violent reduction reaction of Bi ions [8]. Consequently,

Table 1 Physical, thermal, and optical properties of Bi-based glass used in this study

Surface area (m^2/g)	Density (g/cm^3)	Thermal expansion coefficient ($^{\circ}C^{-1}$)	Softening point ($^{\circ}$C)	Transmittance (%)
3.214	4.9697	8.5×10^{-6}	520	≈90

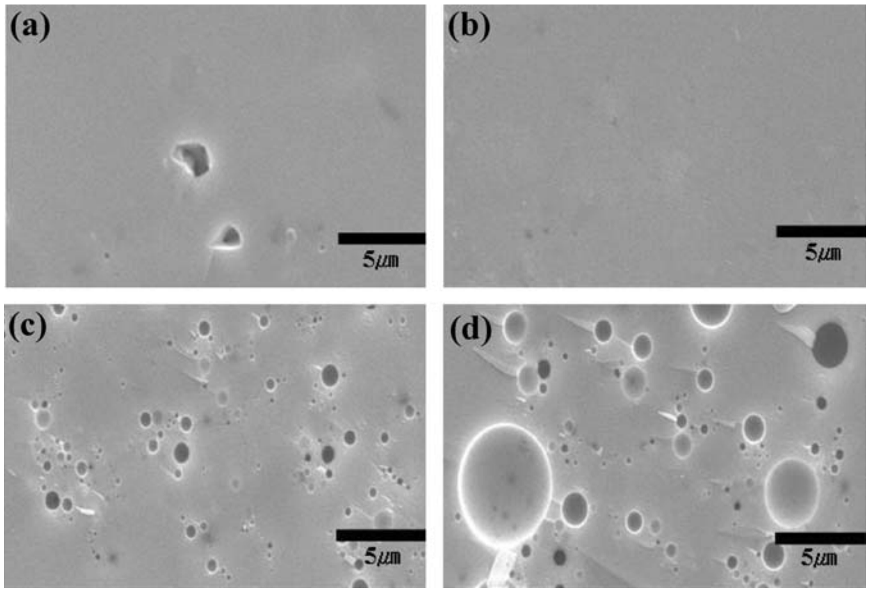

Fig. 2 SEM images of cross sections for specimens sintered at various temperatures for 1 h; (a) 540, (b) 560, (c) 580, and (d) 600°C

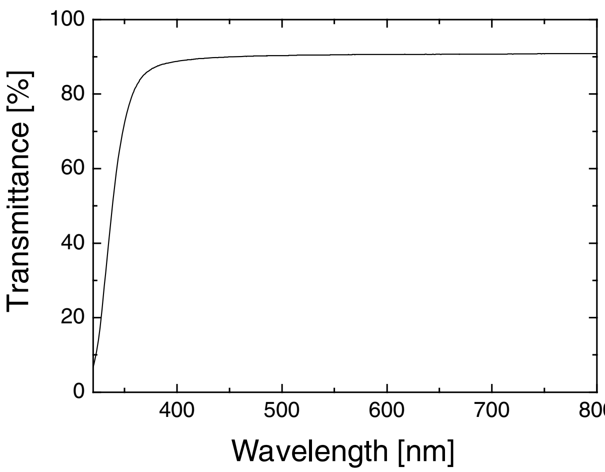

Fig. 3 Optical transmission spectrum of the specimen sintered at 560°C for 1 h

sintering temperature of Bi-based glass strongly affected on thermal and mechanical properties depending on densification and pore generation behavior. Decrease of mechanical property caused by pore generation would influence on degradation of transparency and thermal property such as CTE.

Figure 3 shows the transmission spectra of the specimen sintered at 560°C, the sample exhibits a high transmittance (>90%) in the visible region. The transmittance is expected to depend on several factors, such as oxygen deficiency, surface roughness, and impurity centers [9]. The reason for high transmittance of the specimen is mainly attributed that the defects such as pore and oxygen deficiency is relatively free.

Table 1 summarizes physical, thermal, and optical properties of Bi-based glass such as the specific surface area, density, CTE, softening point, and transmittance. These results indicate that Bi-based glass used in this study is suitable for transparent dielectric materials of PDPs due to relatively low softening point. Since transparent dielectric layer in a PDP requires sintering temperature in a range of 550°C–600°C.

4 Conclusions

Bi-based glass system for low-temperature firing process was investigated as one candidate for replacement of Pb-based glass in transparent dielectric materials of PDPs. Coefficient of thermal expansion, softening point, and optimum sintering temperature for densification of the glass were $8.5 \times 10^{-6}/^{\circ}$C, at 520°C and 560°C, respectively. Additionally, transmittance of specimen sintered at 560°C was about 90% in a visible light region. Sintering behavior strongly affected on thermal, mechanical and optical properties of Bi-based glass depending on densification rate and evaporation rate of oxygen resulted from reduction reaction of Bi ions.

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