

The structure and properties of $50\text{SnO}_2-(50-x)\text{P}_2\text{O}_5-x\text{B}_2\text{O}_3$ for component materials of PDP

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Abstract

Glasses in the $\text{SnO}_2-(50-x)\text{P}_2\text{O}_5-x\text{B}_2\text{O}_3$ system were examined as potential replacement for the PbO glass frits with low firing temperature for component materials of a plasma display panel. The glasses were evaluated for their structural and the thermal expansion coefficient, glass transition and glass softening temperatures and Vickers hardness as a function of the B_2O_3 content.

1. Introduction

Recently, flat panel displays (FPDs) have become widely used in many fields and commercial applications such as the plasma display panel (PDP). Glass frits are used in many parts of the PDP, such as the transparent dielectric, white dielectric, barrier rib, sealant and electrodes. PbO-based glasses are widely used in commercial glass frit owing to their low firing temperatures of below 580°C , which are necessary to prevent deformation of the glass substrate. However, the PbO component in these materials (50~85%) is deleterious to both health and the environment.

Therefore, new, low melting glasses without PbO are being evaluated. Generally, SnO, Bi_2O_3 , P_2O_5 , V_2O_5 and B_2O_3 are widely used in the development of low temperature melting, Pb-free glass.[1-2]. In this study, the thermal, mechanical and structural properties of $50\text{SnO}_2-(50-x)\text{P}_2\text{O}_5-x\text{B}_2\text{O}_3$ glasses were investigated in order to investigate their feasibility as a glass frit, component material of PDPs.

2. Experimental

Glasses were prepared with SnO_2 (99%, Junsei, Japan), H_3BO_3 (99%, Junsei) and H_3PO_3 (99%, Junsei). The glass compositions are shown in Table 1. The mixed batches in the reduction agent were melted in

an alumina crucible at $1000-1100^\circ\text{C}$ for 10-30min and quenched on a carbonate plate.

The bulk glass samples for measuring the thermal properties were polished to dimensions of $5\text{mm} \times 5\text{mm} \times 15\text{mm}$. The thermal properties of the glasses were measured on TMA equipment (Linseis DMA L77) at a heating rate of $10\text{K}/\text{min}$. From the obtained curves the linear coefficient of thermal expansion (α) was calculated as the mean value in the temperature range of $50-250^\circ\text{C}$. The glass transition temperature (T_g) was determined from the change in the slope of the elongation vs. temperature (Td) curve that was obtained from the maximum of the expansion trace.

Infrared spectra were recorded with an IR spectrometer (M2400-C-MJ, Simatzu, Japan) with the powder samples. The Raman spectra of the glasses were measured with a Raman spectrophotometer using the 514.5nm line of an Ar^+ laser as the exiting beam. The laser power was adjusted to 400mW . The Raman spectra were measured on bulk samples.

TABLE 1. Compositions of the melting samples

	SnO_2	P_2O_5	B_2O_3
A-1	50	50	0
A-2	50	45	5
A-3	50	40	10
A-4	50	35	15
A-5	50	30	20
A-6	50	25	25

3. Results and discussion

The prepared samples were checked visually for homogeneity. Most prepared samples were transparent glasses, but the samples with $x > 25$ had a milky appearance revealing crystallization. Fig. 1 shows the infrared spectral characterization of the $50\text{SnO}_2-(50-$

x)P₂O₅- x B₂O₃ glasses. The bands in the 720-800cm⁻¹ frequency range are assigned to symmetric stretching vibration ν_s (P-O-P) of the bridging oxygen atoms, those at 1300cm⁻¹ and 1400cm⁻¹ to (B-O) asymmetric stretching vibrations and those at 680cm⁻¹ to (O-B-O) symmetric stretching vibration. The broad band at 500cm⁻¹ is attributed to bending vibrations of the basic structural unit.

With increasing B₂O₃ content and decreasing P₂O₅ content, the high frequency bands corresponding to the stretching vibrations became weaker and broader. With 20-25mol.% B₂O₃, the band at 680cm⁻¹ is attributed to symmetric stretching vibrations ν_s (O-B-O) of the BO₄ structural units. With increasing content, the B₂O₃ replaced P₂O₅ in the glasses, and the stability of the glasses increased.[3] Other bands in the IR spectra at 1300⁻¹cm and 1400cm⁻¹ are ascribed to the asymmetric vibration (B-O) with 20-25mol.% B₂O₃.

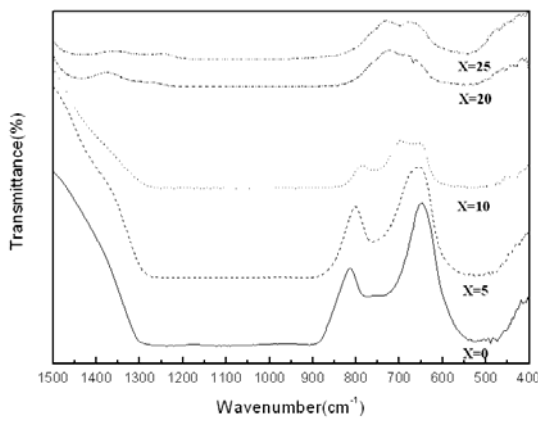


Fig. 1. Infrared spectra of the glasses of the SnO₂-(50-x)P₂O₅-xB₂O₃ glasses.

Fig. 2 shows the Raman spectra of the 50SnO₂-(50-x)P₂O₅-xB₂O₃ glasses. Several Raman bands are observed in two wave number regions: 650-750cm⁻¹ and 900-1200cm⁻¹. The former bands at around 650-750cm⁻¹ are due to P-O-P(bridging oxygen) stretching modes on the basis of the Raman spectra assignments for the Li₂O-P₂O₅[4] and ZnO-P₂O₅[5] glasses. The bands at 1150, 1050 and 970cm⁻¹ are assigned to meta-phosphate (PO₃⁻, Q²), pyro-phosphate(PO_{3.5}²⁻, Q¹), and ortho-phosphate(PO₄³⁻, Q⁰) species, respectively [6], where i in Q ^{i} represents the number of bridging oxygen per phosphate tetrahedral. For the 50SnO₂-(50-x)P₂O₅-xB₂O₃ glasses, the intensity of the Raman bands at around 650-750cm⁻¹ due to P-O-P(bridging oxygen) stretching modes became weaker and the band positions are shifted to higher wave numbers with increasing B₂O₃ content, as shown in

Fig. 2. The Raman spectra in the region from 900 to 1200cm⁻¹ suggest structural changes from Q² to Q¹ species with increasing B₂O₃ content.

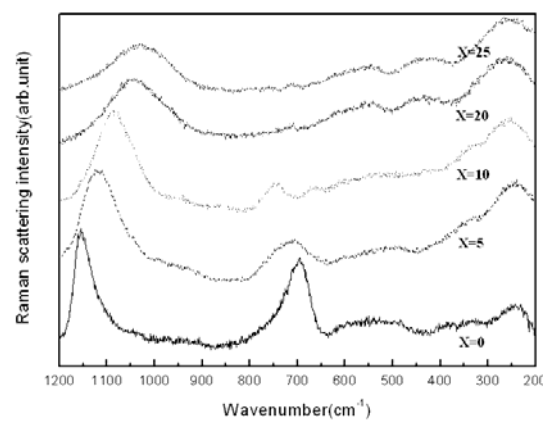


Fig. 2. Raman spectra of the 50SnO₂-(50-x)P₂O₅-xB₂O₃ glasses.

In Fig. 3, the α value decreased with increasing B₂O₃ content, whereas T_g and T_s both increased abruptly with small additions of B₂O₃ and reached a maximum at about 20mol.% B₂O₃ in the glasses. This behaviour was undoubtedly caused by changes in the structural network. This appear these B₂O₃ additions contents until 20mol.% increase from Fig. 3, 4. according to from BO₃ structure with BO₄ structures change to happen, the combination structure comes to be strong. B₂O₃ additions content of the above 20mol.% from BO₄ structure the change happens with BO₃ structures in other for the actual condition above boric acid where the combination structure becomes weak to happen.

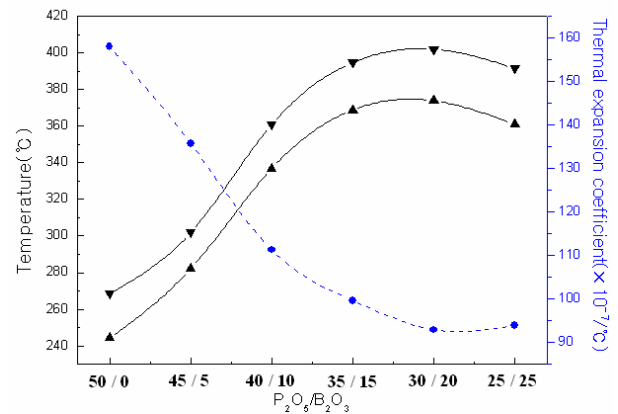


Fig. 3. Variation of the thermal expansion

coefficient(α), glass transition (T_g) and glass softening(T_s) temperatures vs. the B_2O_3 content in the $SnO_2-(50-x)P_2O_5-xB_2O_3$ glasses

The hardness increased with increasing B_2O_3 content up to 20mol.%, but then decreased with further increase in the B_2O_3 content (Fig. 4). In these results, the maximum hardness was obtained at the composition of 20mol.% B_2O_3 , which was also the composition where the largest amount of BO_4 was obtained. These results therefore indicate that the hardness of the glasses was correlated with the amount of the BO_4 structure.

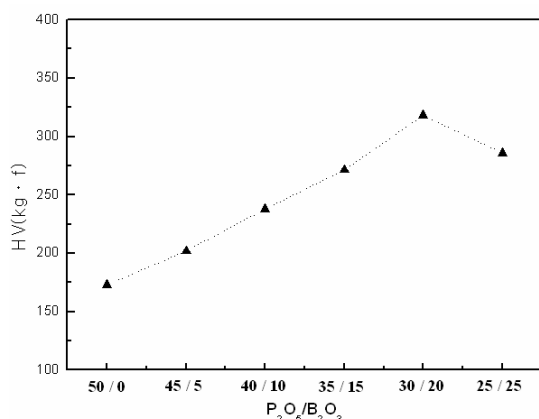


Fig. 4. Vickers hardness of the $SnO_2-(50-x)P_2O_5-xB_2O_3$ glasses

4. Summary

The structural and thermal properties of $50SnO_2-(50-x)P_2O_5-xB_2O_3$ glasses were examined. Increasing B_2O_3 content increased the glass transition and glass softening temperatures, but decreased the thermal expansion coefficient, and these changes were attributed to the structure of the glasses. The change of the local structure in the glasses suggested that the number of bridging oxygens decreased with increasing B_2O_3 content in the glasses, whereas the non-bridging oxygen concentration increased.

5. References

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