Thermal and electrical properties of Bi_2O_3-B_2O_3-ZnO glasses for the application to plasma display panel

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Abstract

In this study, Bi_2O_3-B_2O_3-ZnO glass system, which was expected to have similar properties with PbO containing glass system, was selected as a PbO replaceable potential composition because the atomic weight and ionic radius of Bi is similar to those of Pb. Glasses with different modifier/former ratio were prepared by melting the raw ingredient mixtures in Bi_2O_3-B_2O_3-ZnO system, and the thermal and electrical properties of the sintered samples were examined. The glass transition temperatures and the dielectric constant of the glass pellets were between 350 ℃~500 ℃ and 15-35, respectively.

1. Objectives and Background

Plasma display panels (PDPs), which are already competing effectively against cathode ray tubes (CRT) and liquid crystal display (LCD), are one of the most promising devices for large-size HDTV receivers, especially for home wall-hanging display units in spite of their high price range.

The front glass of PDP is covered with thin (20~40 ㎛) dielectric layers and MgO protective layer is deposited on the dielectric layer. For transparent dielectric layers, which limits current and acts as a capacitor, the process is based on the screen printing method. For use in low temperature applications, glass paste that has low melting temperature has been used. Followings are the things to be considered in compositional design of the transparent dielectric layer for PDP[1,2]: 1) breakdown voltage of above 2 kV when the thickness is 30 ㎛, 2) transmittance above 80% in the visible light wavelengths, 3) surface smoothness, 4) chemical stability with respect to electrode (Ag) migration, 5) low dielectric layer constant, 4 below 200 nm, 6) a thermal expansion coefficient around $8\sim9\times10^{-6}\ K^{-1}$ which is almost the same with that of the substrate glass, etc.

PbO containing glass system has been popular which is advantageous in the sintering at low temperature. However, recent nature protection issues restrict the wide use of PbO. It is therefore timely to develop Pb-free materials for dielectric layers, barrier ribs and sealing materials. P_2O_5, B_2O_3, V_2O_5 have been employed for the development of the Pb-free glasses[3,4]. However, no many Pb-free glasses have been examined for the application to the PDP except BaO-B_2O_3-ZnO system[5].

In this study, Bi_2O_3-B_2O_3-ZnO system is investigated for the application to the dielectric layer of PDP. The glass transition temperature (T_g), was measured and the dielectric properties of the samples was also evaluated using an impedance analyzer.

2. Experimental procedure

High purity raw materials of Bi_2O_3 (99.6%), B_2O_3 (99.9%) and ZnO (99.9%) were weighed to the compositions with different molar ratios as shown in Table 1, and melted for 30 min. at 1100℃ after mixing. The molten glass was quenched on a platinum plate. The glass was dry-crushed with a planetary ball mill for 2 h at 400 rpm. The crystallization of the glass was analyzed with an X-ray diffraction (Material Analysis and Characterization, M03XHF, Japan). The glass transition temperature of the glass was measured by using differential scanning calorimetry (DSC). Glass powders with different compositions were cold-isostatic-pressed (CIPed) under the pressure of 100MPa in order to form pellets. The pellets were sintered at 390-550℃. The density of pellet was measured by the Archimedes method. Dielectric characteristics of the pellets were analyzed by using an impedance gain phase analyzer (HP4194, U.S.A.).

Table1. Employed Composition of Glasses and the Results of X-ray Diffraction after quenching.

No.	Bi_2O_3	B_2O_3	ZnO	Notes
1	40	20	40	Glass
2	35	30	35	Glass
3	30	40	30	Glass
4	25	50	25	Glass
5	20	60	20	Glass
6	15	70	15	Partially crystallized

3. Results

On the basis of X-ray diffraction analysis shown in Fig. 1, every composition except No. 6 showed glass characteristics with broad diffraction peaks, which signifies that Bi2O3-B2O3-ZnO system possess wide compositional range of glass such as the PbO containing glass system.

Fig. 2 shows the glass transition temperature (Tg) of the glasses obtained from the DSC analysis.[6] The molar ratio of Bi2O3 and ZnO was fixed and the amount of B2O3 was changed. Because the role of B_2O_3 is glass former and Bi_2O_3 and ZnO play the role of modifier, the result shows a relationship between the amount of glass former and the glass transition temperature.

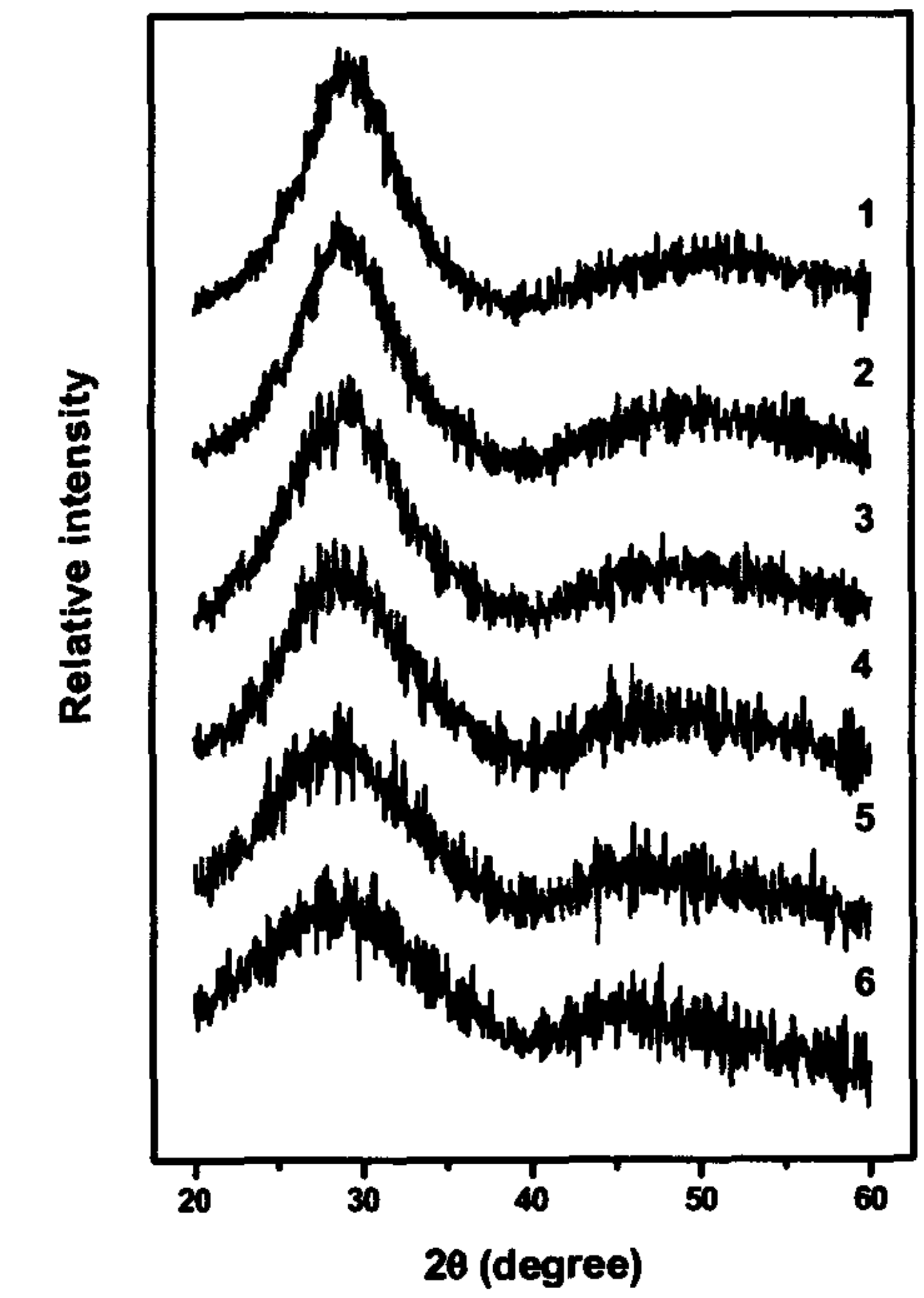

Fig. 1 XRD result of glasses after quenching

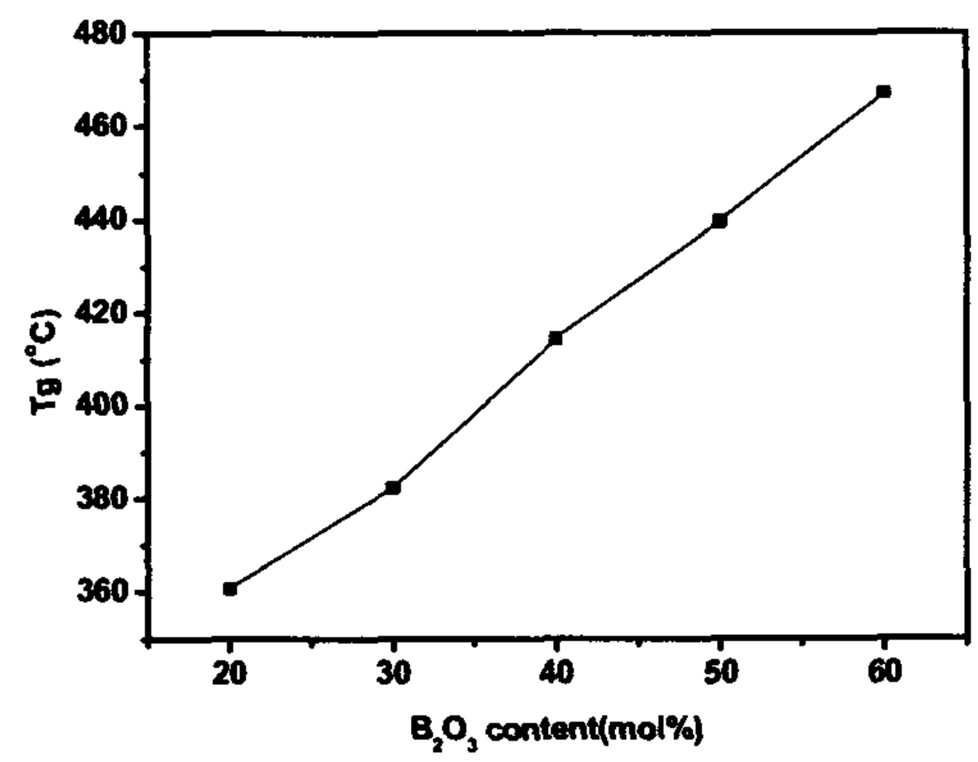

Fig. 2 Tg of various as a function of B_2O_3 amount.

The Tg was in the range of 360~470℃ and it increased as the amount of B_2O_3 increased, which implies that the eutectic temperature of the glasses is proportional to the amount of B_2O_3.

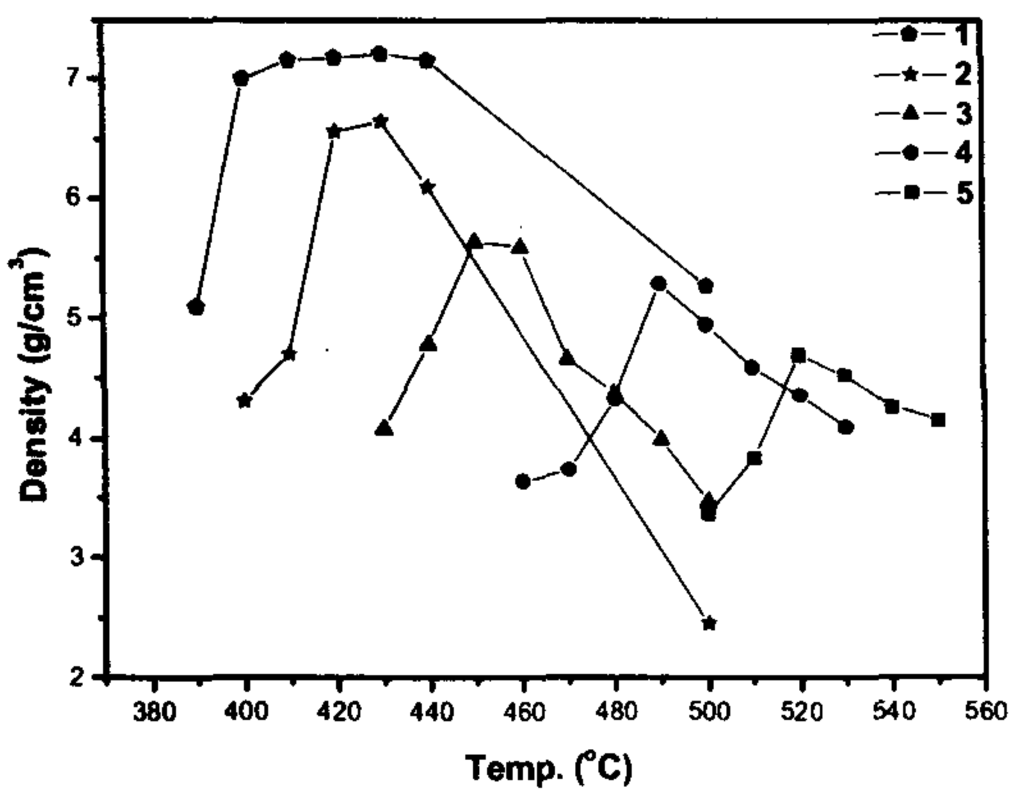

Fig.3 Bulk densities of glass after sintering at various temperatures.

Fig. 3 presents the sintered density of the glass pellets as a function of sintering temperature. After sintering at optimum temperature where highest density was achieved, the glass state was still maintained on the basis of the X-ray analysis shown in Fig. 4.

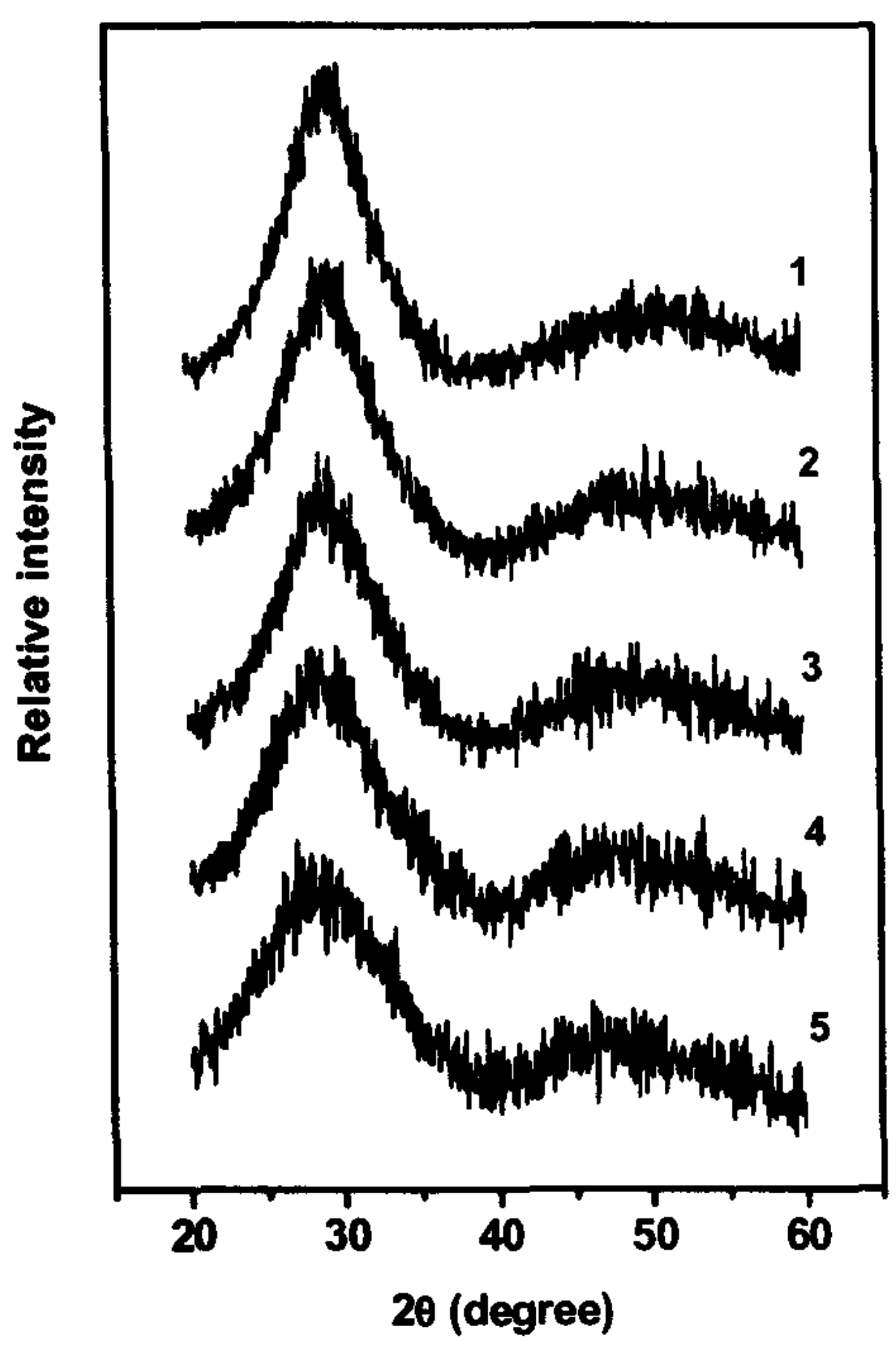

Fig.4 XRD result of glasses after sintering at optimum temperature.

The microstructures of the $20Bi_2O_3$-$60B_2O_3$-$20ZnO$ which is thought to the most appropriate composition among various compositions is revealed in Fig. 5. When the pellet is sintered above the optimum temperature, many spherical pores are observed in the matrix. The number and size of the pores were increased as the sintering time increased, which is different from the pore coalescence phenomena that usually observed at the final stage of sintering. This result could be indirect evidence that the pores are created by the gas generated from the inside of the pellet during sintering.[7]

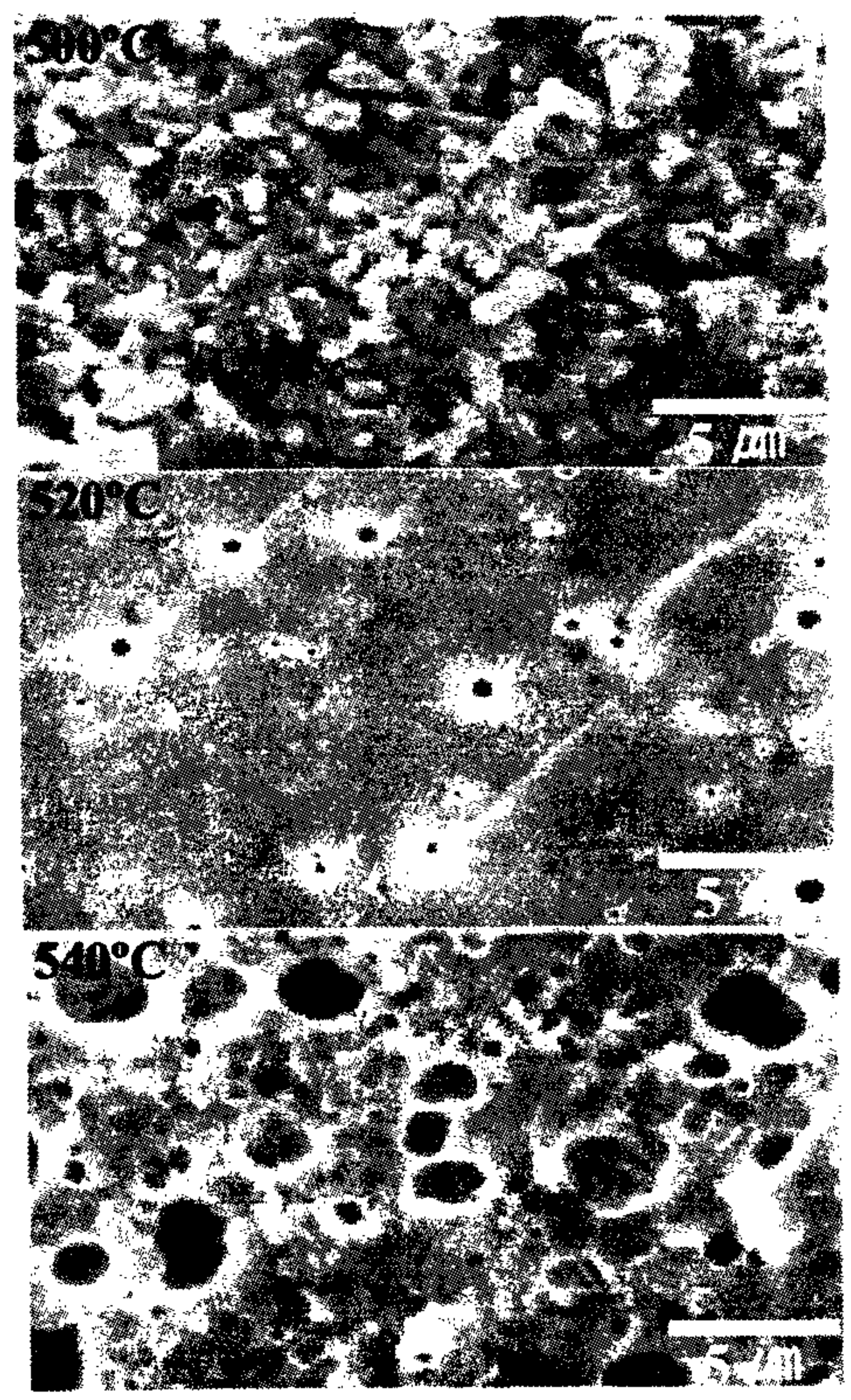

Fig.5 SEM micrograph of $60B_2O_3$-glass after sintering at various temperatures.

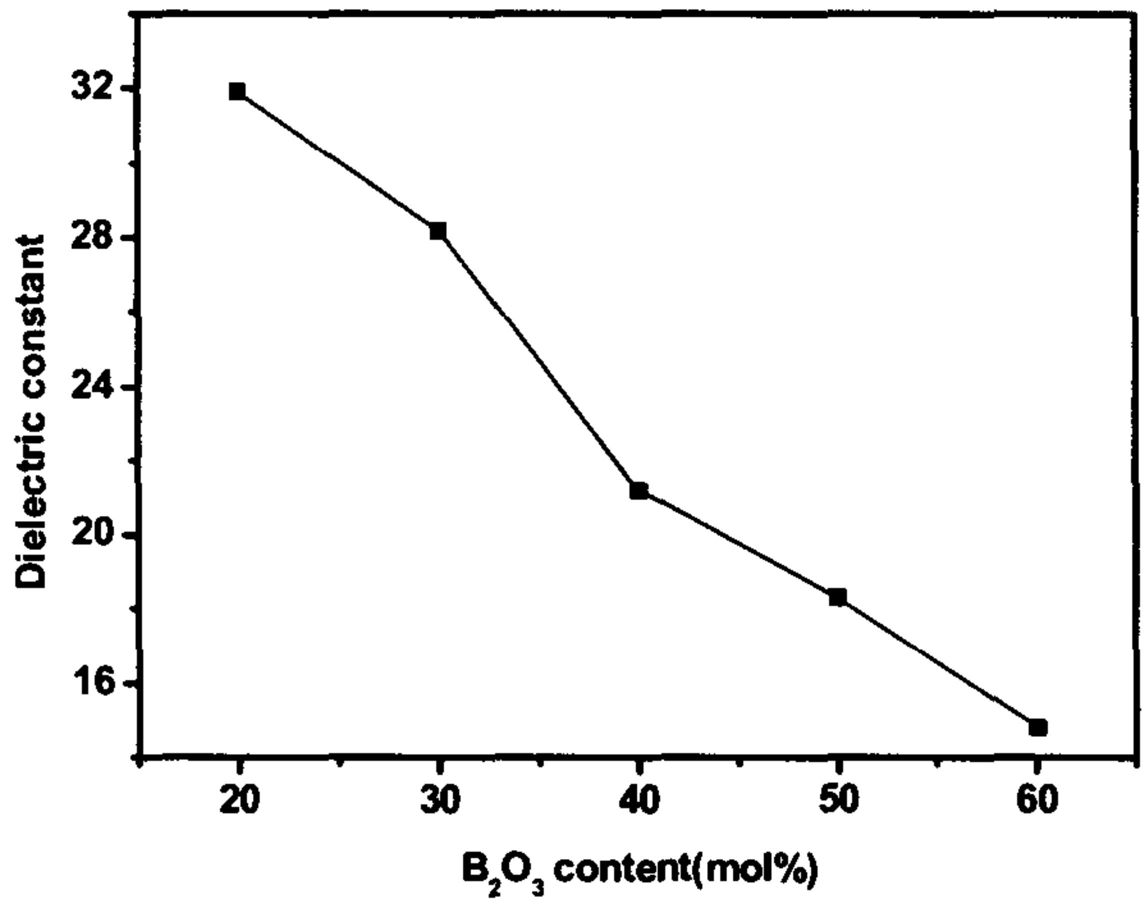

Fig.6 Dielectric constant of glasses after optimum sintering.

It is generally known that the oxygen ion has the highest dielectric polarizability among the various ions in oxide glasses.[8] When glass modifier ions are added to glasses, non-bridging oxygen is formed which contributes to an increase of dielectric constant. As shown in Fig. 6, the dielectric constant was decreased as the amount of B_2O_3 increased. It is thought due to the decrease in the amount of glass modifiers (Bi_2O_3 and ZnO) as well as the non-bridging oxygen ions. The required dielectric constant for the application of the transparent dielectric layer was satisfied in the 50-60 mol% of B_2O_3 content.

4. Conclusion

1) Tg of the glasses was increased as the amount of B_2O_3 increased when the molar ratio of Bi_2O_3 and ZnO was fixed.

2) Dielectric constant was linearly decreased when the amount of B_2O_3 increased.

3) A powerful candidate material with suitable dielectric constant and sintering temperature, which can replace the PbO containing system, was found in the Bi_2O_3-B_2O_3-ZnO system.

5. Acknowledgements

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6. References

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