Thermal Property of Phosphate Glasses for Low Firing Temperature in PDP

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Abstract

Replacing Pb-free glass composition for the dielectric materials is expected in PDP industry. In this study, phosphate glasses, P_2O_5- ZnO- SnO (PZS), P_2O_5-ZnO-BaO (PZB) were selected for a new transparent dielectric. Thermal properties (Tg, CTE) were measured with differential thermal analyzer and thermal mechanical analyzer. The glass transition of the glasses was ranged at 365~405 ℃ for the PZS system and $5.9\sim9.5\times10^{-6}$/K of thermal expansion were found. The PZB system showed 445~470 ℃ of glass transition. Thus, the glass compositions would be a potential candidate for a transparent dielectric layer in plasma display panel.

1. Introduction

For the environmental issue, every potential environmentally contaminating component including lead-oxide (PbO) has been restricted. Especially, in the electronic and dielectric materials, though PbO was commonly used for the distinct advantage of cutting down the firing temperature that is essential for the application, the definite harmfulness on the nature limited its further usage[1]. With in the same context, Pb-free glass systems have brought much interest in many electronic fields-no exception in PDP (plasma display panel)[2]. For the application of Pb-free glass into PDP, specifically, transparent dielectric part, the glass is supposed to be sintered under 580℃ and more importantly there should be no premature crystallization before the sintering temperature. In order to meet these two critical conditions, several compositions based on phosphate glasses, were considered and experimented based on previous works because the glasses have a applicable advantage as low-melting glasses[3,4]. However their results showed some disagreement especially on the thermal results.

In this study, mainly two phosphate glasses were used: P_2O_5- ZnO - SnO (PZS), P_2O_5-ZnO-BaO (PZB) to further explore thermal part of diverse phosphate glasses. Actually the first system was already studied by Morena focusing on the application of sealing glasses[5]. He found that this system has a low Tg of below 400℃ and a good aqueous durability compared with PbO system when P_2O_5 contents do not exceed 30~33mol%[5]. For the second system glass system, BaO was used to compensate the water soluble properties of phosphate glasses.

The main purpose is to study the thermal property mainly in two glass systems-PZS, PZB and to invent an applicable Pb-free glass composition for the transparent dielectric material in PDP. In this work, the influence of glass transition temperature and thermal expansion system on the glass system as a function of the SnO/ZnO ratio will be discussed. For the second, further experiments with different component are necessary.

2. Experimental method

Chemical reagent-grade, $NH_4H_2PO_4$, ZnO, SnO, $BaCO_3$, Al_2O_3 and SiO_2 were mixed well with a mortar and a pestle for 20min. The batches (Table 1) were preheated at 500℃ for 30min in an alumina crucible to evaporate ammonia and water in the batch and minimize the tendency of subsequent phosphate loss. Then, batches were melted for 1h at 1100℃. Each glass melt was quickly poured on a copper plate. After confirming formation of glass, these bulk were ground by a vibration mill for 4h to make them glass powder of below 10*um*.

Glass transition temperatures(Tg) were studied by DTA(Differential Thermal analysis, DTA-TA 1600, USA) with Al_2O_3 as a reference material. Softening temperature (Td) and coefficient of thermal expansion (CTE) were measured in thermal mechanical analyzer (TMA, Rhometric U.K) at a heating rate of 5 /min up to 300 with bulk specimen, which were removed residual stress at the temperature of 10℃ above Tg of each glass for 1h then it cooled very slowly in furnace. The glass removed from a mold for the measurement of CTE was carefully polished to have the required size.

Table.1 Compositions of melts in the P_2O_5-ZnO-SnO/BaO system (in wt%)

Glasses	P_2O_5	ZnO	SnO	BaO	Notes
S1	40	50	10	-	Crystallized
S2	40	40	20	-	Glassy
S3	40	30	30	-	Glassy
S4	40	20	40	-	Glassy
S5	40	10	50	-	Glassy
P1	48	32	-	20	Glassy
P2	50	30	-	20	Glassy
P3	72	28	-	-	Glassy

3. Results and Discussion

Figure 1 shows the glass formation region of the P_2O_5-SnO-ZnO glass system to compare with a previous work [5]. The shade area in the ternary diagram is a glass formation region found by Morena. The S2~5 of composition included in the glass formation region were clear glass after pouring on a copper plate at RT., while S1 out side of Morena zone was crystallized.

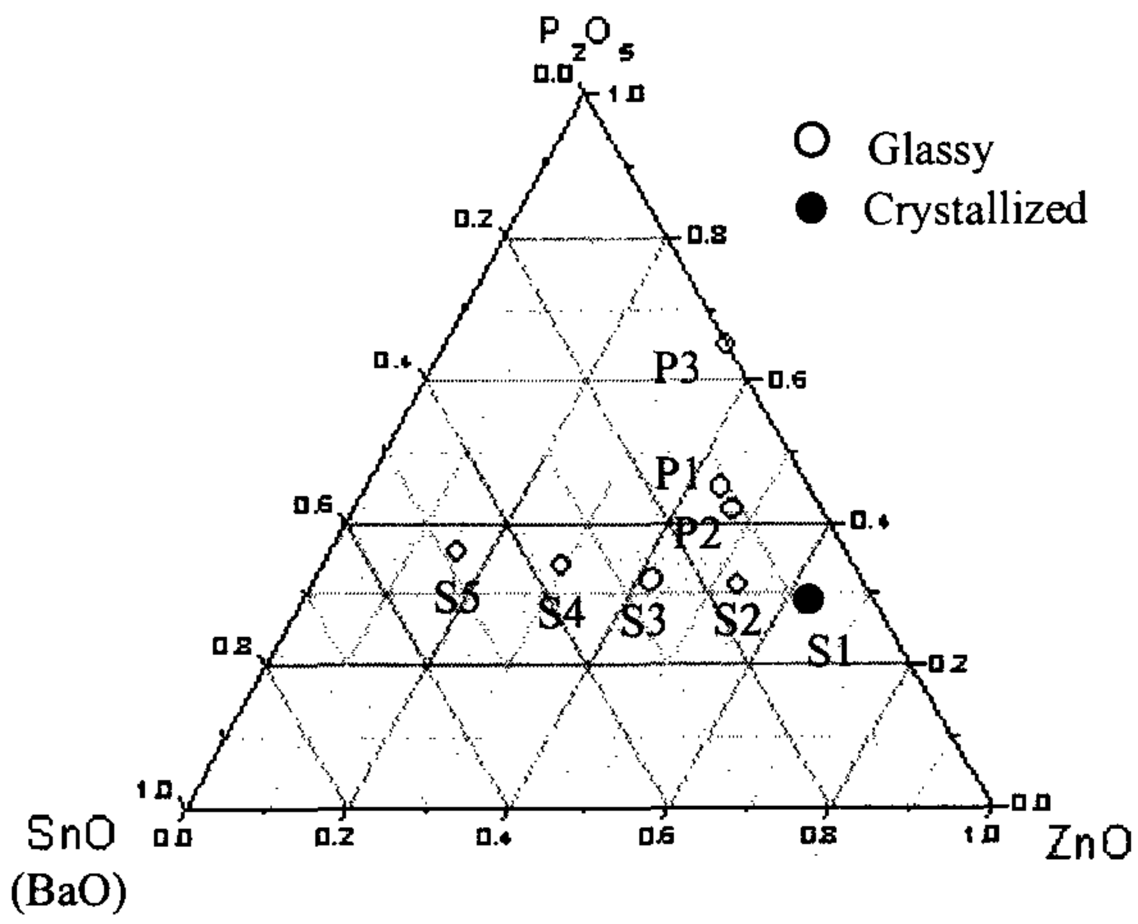

Fig.1 Glass formation region of P_2O_5-ZnO-SnO/BaO system(in mol%)

When glass frit on a substrate was fired, the composition and glass formation region of P_2O_5-SnO-ZnO/BaO as well as several thermal properties such as Tg, onset of exothermic temperature (To), maximum peak of exothermic temperature (Tc) and coefficient thermal expansion (CTE) of the glasses should be considered. As an optimum glass composition known glass frit in transparent dielectric, the glass should be amorphous up to firing temperature. During process of PDP, glass firing for transparent dielectric is generally performed at 580 . Therefore, Tg is required at least below 500 to be amorphous and to form a uniform glass thick layer.

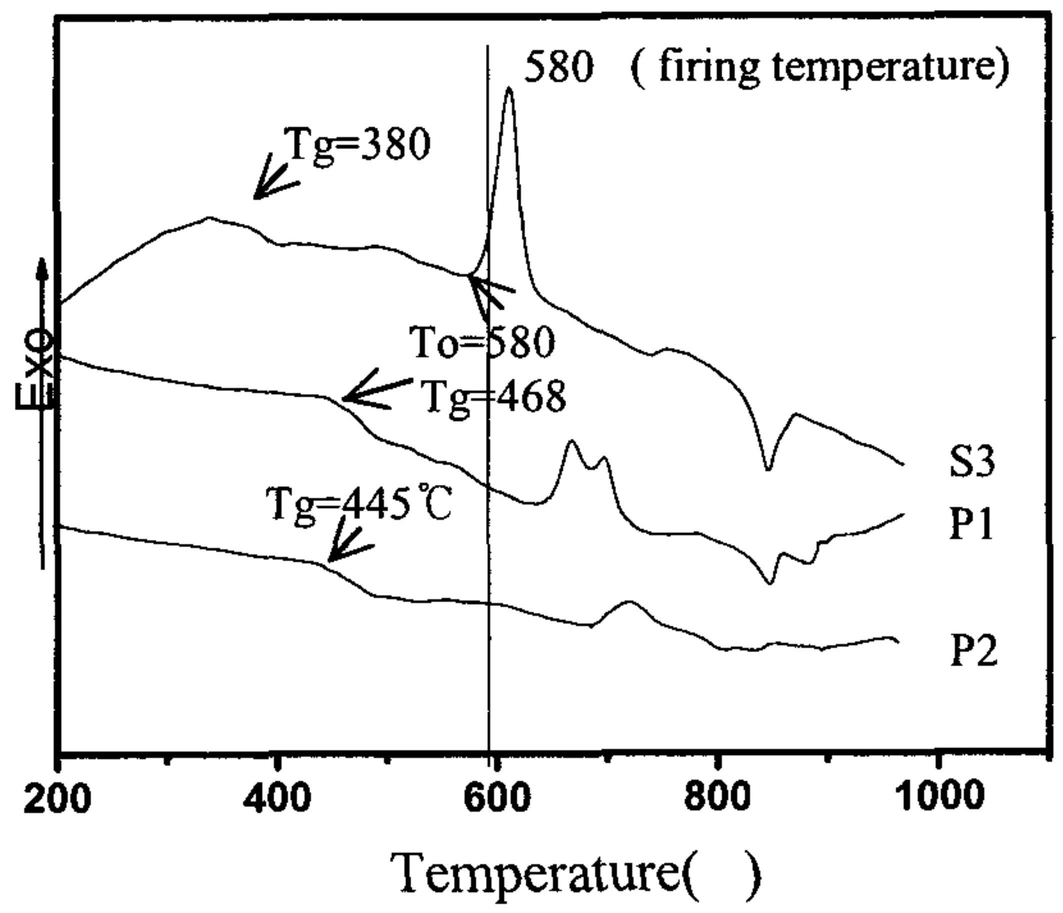

Fig.2. DTA curves of S3, P1 and P2

Figure 2 represents DTA results showing that Tg of S3, P1 and P2 is 380, 468 and 445 , respectively. When considered for a low temperature glass firing at below 500 , we could expect a transparent layer on a substrate because of having a low glass transition temperature. To be amorphous, the exothermic temperature(To) should be avoided because crystallization can be occurred during baking in the range of firing temperature. It was investigated that glass firing should be performed below onset exothermic temperature for avoiding crystallization. Thus, we thought that P1 and P2 with To of above 600 have a possibility to complete glass firing at 580 for PDP, while there was a crystallization peak around at 580 so in the case of S3, it will be difficult to expect a transparency when sintered.

As shown in Fig.3 and 4, Tg and Td were in the range of 325~380℃ and 365~405℃, respectively. Note that Tg and Td are highest at the smallest SnO/ZnO ratio(S2) and decreases with increasing the ratio of SnO/ZnO because the effect of SnO on glass was more active than that of ZnO as a modifier. Especially, it was found the Tg and Td were decreased rapidly when the ratio of SnO/ZnO became 2 but the change of Tg and Td was a little when the ratio of SnO/ZnO was above 2. This result was identical with the previous work but the reason has not been revealed. When glass firing performed, CTE was also important thermal property to match with a substrate. In the glass system, the CTE showed 5.9~9.1× 10^{-6}/K and increased with increasing the ratio SnO/ZnO (Fig. 5). The CTE of soda-lime glass used as a substrate in PDP is in the range of 7.5~8.5× 10^{-6}/K, so that S4 and 5 are suitable for that of soda-lime glass. For the change of Tg, Td and CTE, the effect of SnO on the glass composition was more active than that of ZnO.

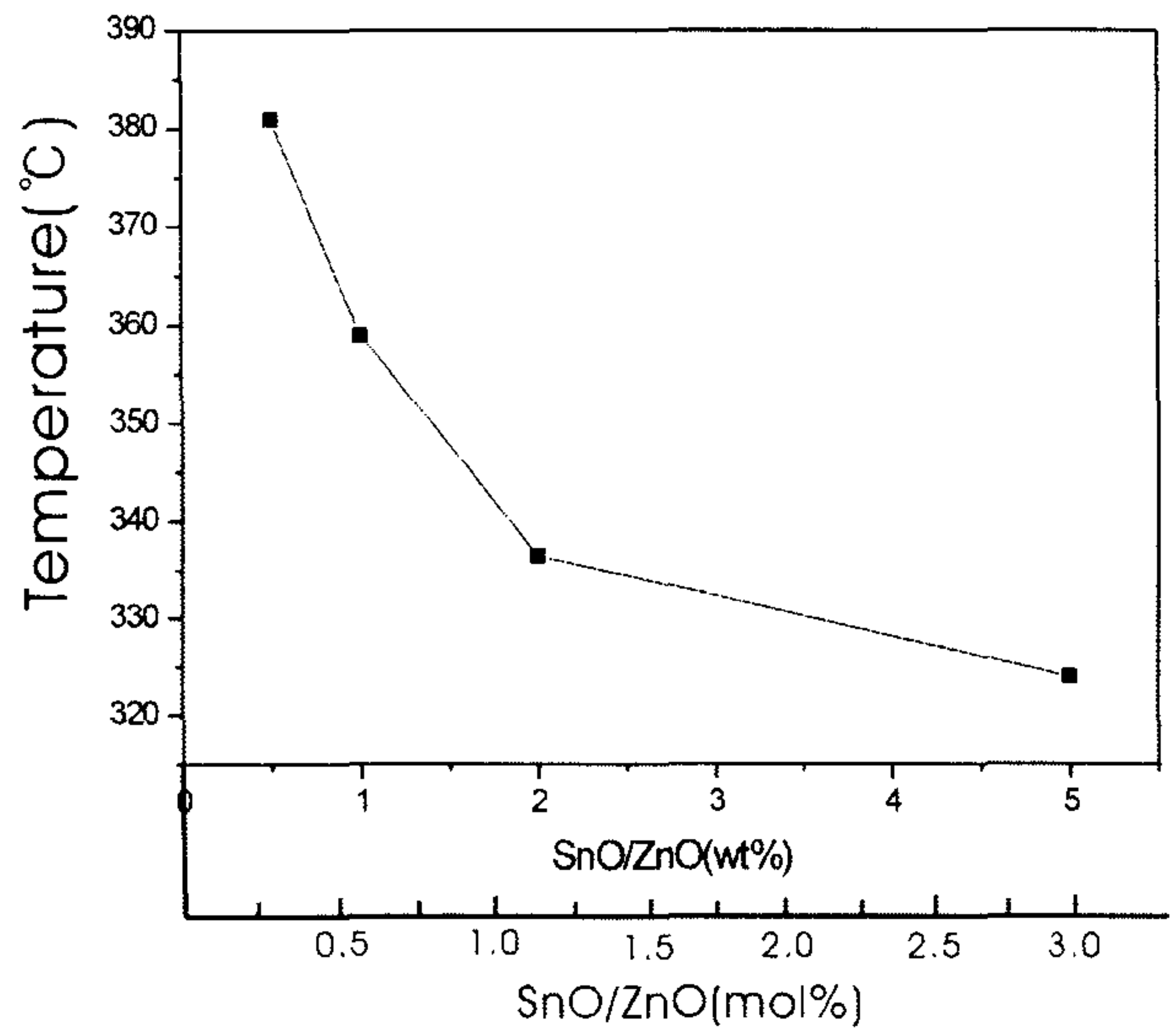

Fig.3. Change of the glass transition temperature(Tg) with increasing the ratio of SnO/ZnO

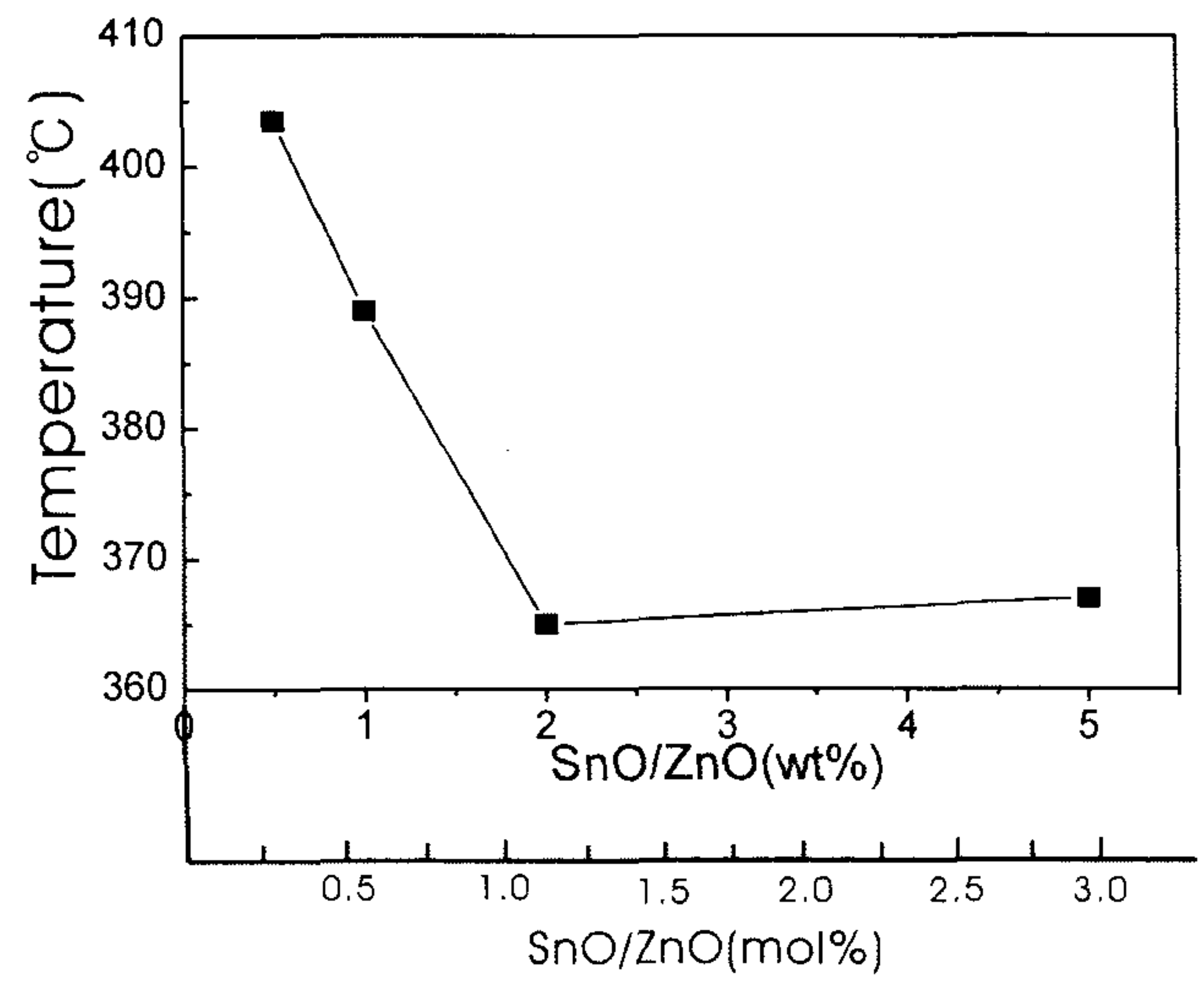

Fig.4. Softening temperature (Td) with increasing the ratio of SnO/ZnO.

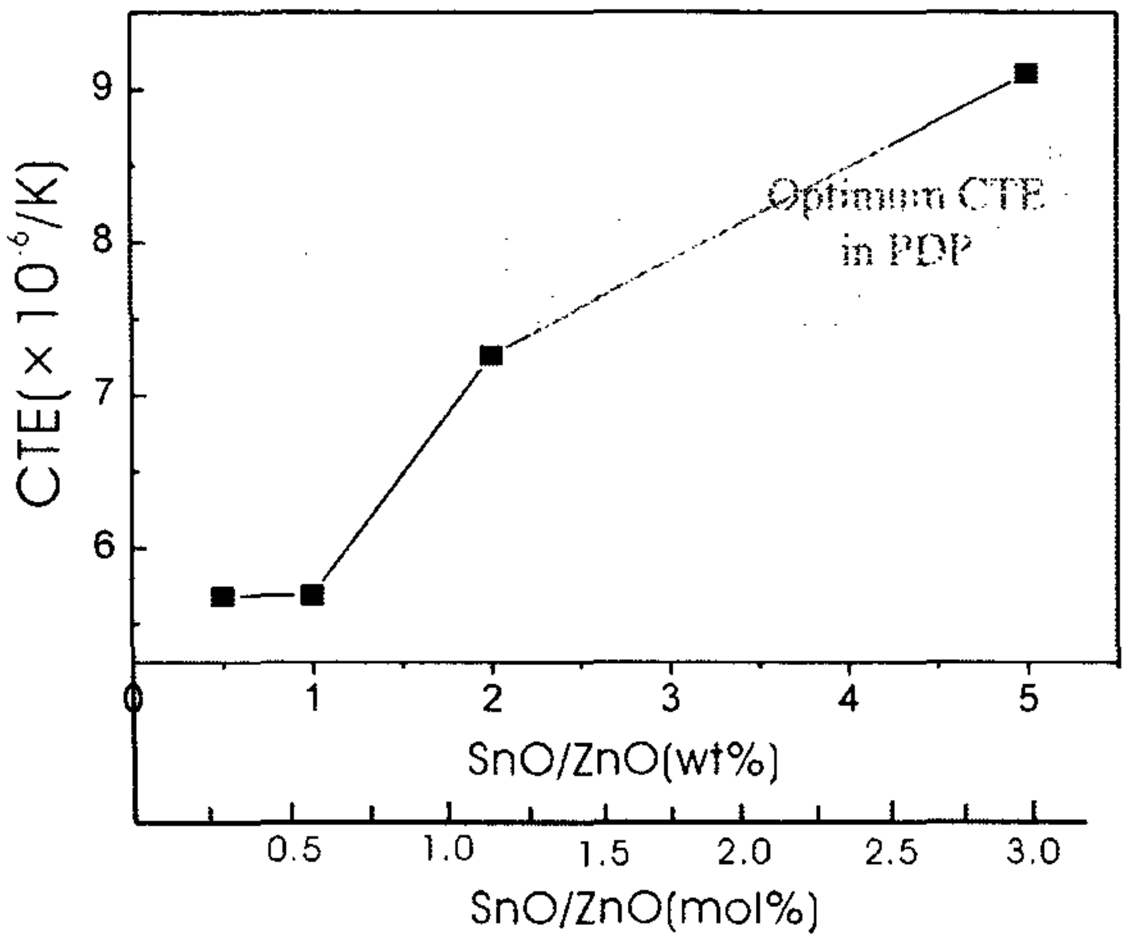

Fig.5.Change of the coefficient of thermal expansion (CTE) with the ratio of SnO/ZnO

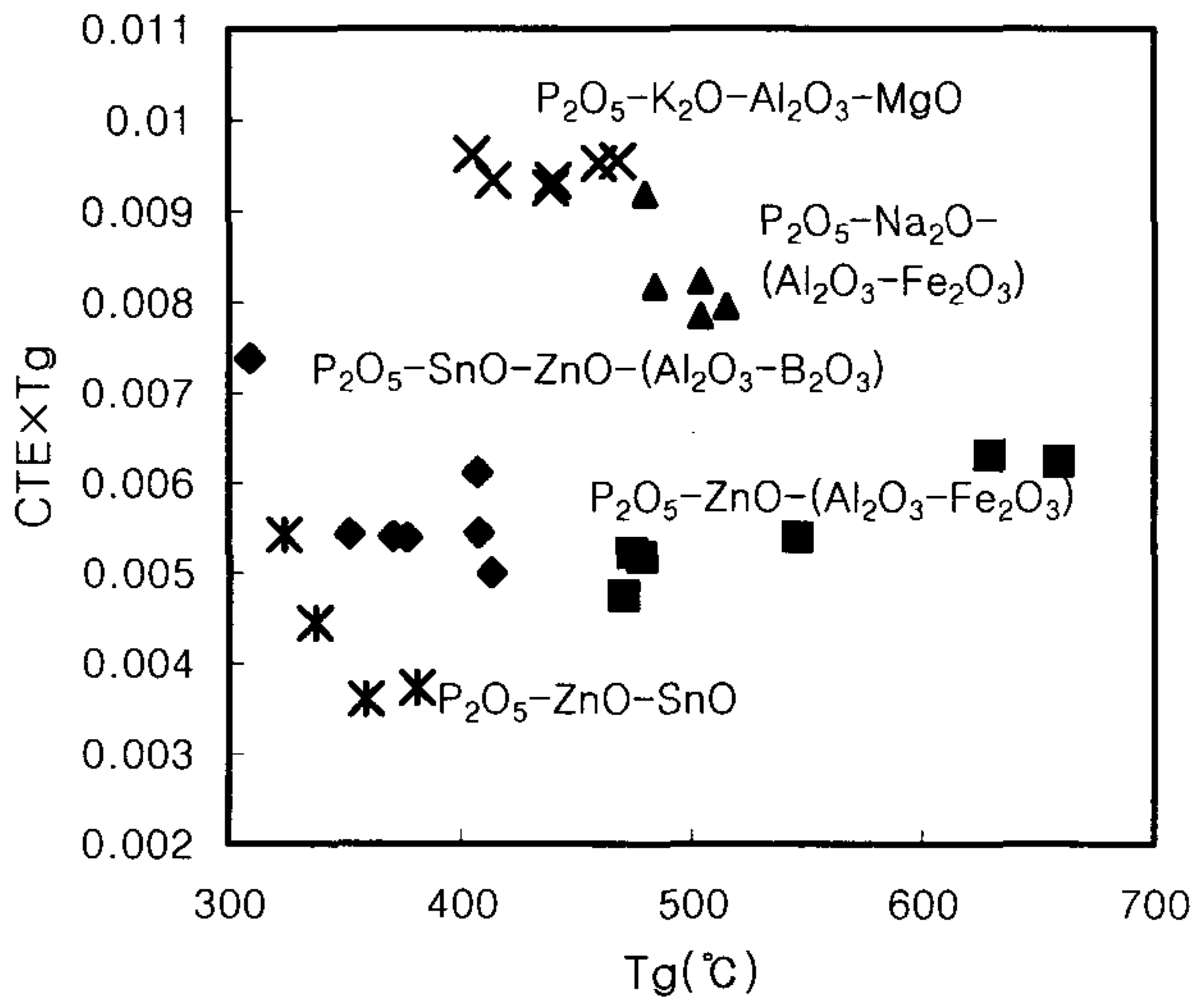

Fig. 6 Product of thermal expansion coefficient (CTE) and glass transition temperature (Tg) versus glass transition temperature on phosphate glasses[7,8]

On the other hand, the data of Fig. 3 and 5 give the prediction of CTE for phosphate glasses (P_2O_5-SnO-ZnO) based on an empirical approach suggesting a relationship between CTE and Tg, which is a product CTE(α)×Tg[6]. For several phosphate glass compositions, it is found that CTE×Tg is in the range 0.005 to 0.01 depending phosphate glass shown in Fig .6. The experimental values of CTE×Tg in PZS fall just below 0.0054 (the average value in P_2O_5-ZnO glasses). Thus, for low firing temperature glasses, a proper CTE of glass is able to be predicted by Tg, which varies as a function of SnO/ZnO ratio.

4. Conclusion

It was investigated that 30~50P_2O_5, 30~50SnO, 30~50wt%ZnO system had 325~380℃ of glass transition temperature, 365~405℃ of softening temperature and 5.9~9.5× 10^{-6}/K of coefficient of thermal expansion. The Tg and CTE increased with increasing the ratio SnO/ZnO. The PZB system showed 445~470℃ of glass transition and To above 600℃ Thus, two kinds of the glass composition as a frit would be a potential candidate for Pb–free transparent dielectric layer in ac-PDP.

5. Acknowledgements

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6. References

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