Possible Glass Systems for Non-Pb Dielectric Layers, Barrier Rib and Sealant in PDP

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Abstract

It is inevitable that reconsideration of the use of lead oxides in the electronics industry be undertaken as long as detrimental effects to the environment remain. To solve this problem, many recent studies on Pb-free compositions for PDP (plasma display panel) dielectric layers and also sealing glass compositions have been made. The present study was conducted to investigate whether the alternative systems for lead-free low firing glasses, detailed below, are available for use in PDP materials. The results suggest that low-melting phosphate glasses would be suitable as an alternative material for the Pb-based dielectric layer, sealants and barrier ribs in PDP.

1. Introduction

With the growth of information technology, flat, thin and wide displays were introduced. The world market demand for frits (for dielectric layers, ribs and sealing glasses) for the plasma display panels (PDP) industry will be approximately 400 tons by 2005. Accompanying the demands for materials, there remains the problem of waste treatment in terms of environmental pollution to soil and water.

Regarding solders for welding electronic parts, the European Union (WEEE/RoHS) has decided to prohibit the use of lead-containing solder by the year 2008 [1]. In normal cases, lead contained in glass has no risk of leakage and is harmless, but there is a risk of leakage from glass powders generated during the processing and in waste treatment. Since glass is used, collected and recycled widely in society, any adverse effect during the collection and recycling process may have a great impact on society. Therefore, lead-free glass is in demand in order to eliminate such a possibility. In terms of materials and components for production of PDP, the main target is a low-cost replacement for Pb, as well as reducing power consumption. It is therefore timely to develop Pb-free materials for dielectric layers, barrier ribs and sealing materials.

In this paper, the factors influencing the selection of Pb-free materials for future applications are discussed. The experience obtained by Sunchon National University in developing each of the materials is summarized and some thoughts on the direction of future developments are given.

2. Future dielectric layer, barrier rib and sealing materials requirements.

For transparent and white dielectric layers, the current process is based on the screen-printing method, using $PbO\text{-}B_2O_3\text{-}SiO_2\text{-}Al_2O_3$ system for frit composition. Recently a blade coating has been introduced for a transparent dielectric layers to form a dry film. Screen-printing, sandblasting and photo process methods have been used for barrier ribs. The materials are composed of a matrix of the PbO based system and fillers (TiO_2, ZrO_2, Al_2O_3).

For dielectric layer materials in PDP, $SnO\text{-}P_2O_5$, $ZnO\text{-}P_2O_5$, $V_2O_5\text{-}P_2O_5$ and $B_2O_3\text{-}SiO_2$ systems have been studied for use in low temperature applications [2-3]. Regarding the design of the composition of frits for PDP, the following have been considered: 1) breakdown voltage of above 3.5kV, 2) transmittance of above 80% (transparent dielectric layers), 3) low dielectric layer constant (for transparent dielectric layers) and high dielectric layer constant (for white dielectric layers,10-20), 4) surface smoothness of below 200 nm, 5) a thermal expansion coefficient of $80\text{-}90\times10^{-7}$ /K, 6) low porosity and small pore size, and 7) low firing temperature glasses (<550°C). In addition to the main requirements, no reaction should occur between electrodes (ITO, bus) and dielectric layers during the firing process, meaning special attention is needed on the design of the composition of the dielectric layers [4].

For the barrier ribs, including black barrier ribs, white barrier ribs and hybrid ribs type, treatment of waste materials (3/4 mixture of paste and sand) and the use of a Pb-free composition need to be investigated. Low firing temperature (<400℃) and Pb-free composition are related to the sealing of the frits. With regard to the processes, the green sheet laminate process and the capillary filtration process have been introduced to the fabrication of dielectric layers and barrier ribs [5]. Also vehicles have been studied for dry film and complicated cell types, which have the characteristic of a low firing temperature.

3. Current research works.

For transparent dielectric layers, BaO-B_2O_3-ZnO-RO, and P_2O_5-ZnO-RO are being investigated as alternatives. Glasses in the P_2O_5-RO's systems plus additives have been examined as potential replacements for PbO glass frits for part materials (dielectric layers, barrier rib and sealant) in PDP, namely P_2O_5-ZnO-BaO-Al_2O_3-SiO_2 and P_2O_5-ZnO-SnO-SiO_2-B_2O_3; B_2O_3-ZnO-BrO_2-SiO_2-CaO; B_2O_3-ZnO-SiO_2-Al_2O_3-CaO and BrO_2-B_2O_3-Al_2O_3-CaO. The phosphate glass system has a strong advantage for low firing temperature glass but it has been known to be soluble in water. However, we have recently developed a phosphate glass system which overcomes the low water-solubility of phosphate glasses. In general, the CTE and Tg of materials (single oxide and element) have an inverse relationship. Based on our results as shown in Fig. 1, in a narrow range of temperature, the multicomponent oxide system indicated that the CTE's showed a scattered band as a function of Tg.

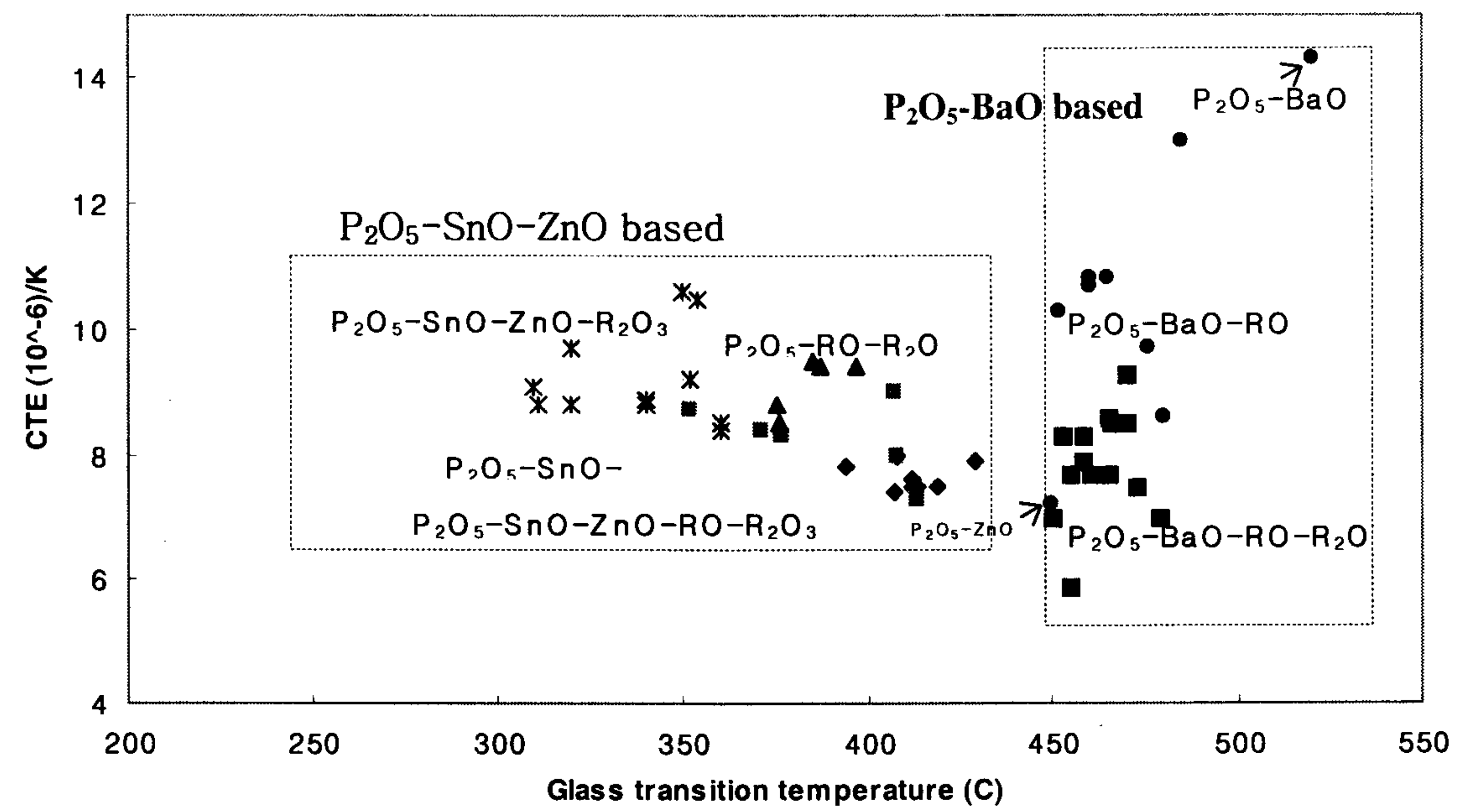

Fig. 1 Coefficient of thermal expansion (CTE) and glass transition temperature (Tg) of phosphate glasses

For white dielectric layers, there are several glasses with fillers designed to improve the refractivity: B_2O_3-ZnO-SiO_2-CaO, ZnO-B_2O_3-SiO_2-CaO-Al_2O_3, P_2O_5-ZnO-$Al_2O_3(SiO_2)$, P_2O_5-B_2O3-SiO_2-CaO, and B_2O_3-BaO-ZnO. As for barrier ribs, it was found that ZnO-B_2O_3-SiO_2-RO, ZnO-B_2O_3-BaO, P_2O_5-B_2O_3-ZnO, P_2O_5-SiO_2-ZnO, P_2O_5-SnO-ZnO, and Bi_2O_3-B_2O_3-SiO_2-BaO-SnO glasses with fillers [6-7] , ZrO_2, TiO_2 and Al_2O_3 have been used. Sealants with compositions of P_2O_5-SnO-ZnO [3] and others are being used: P_2O_5-

$ZnO\text{-}SnO\text{-}R_2O$, $P_2O_5\text{-}ZnO\text{-}SnO\text{-}B_2O_3\text{-}Al_2O3$, and $ZnO\text{-}B_2O_3\text{-}SiO_2\text{-}Bi_2O_3\text{-}RO\text{-}R_2O$.

In Table 1, several possible compositions for unleaded glasses for PDP are summarized

Table 1 Summary of compositions for lead-free glasses for parts of PDP

P_2O_5	B_2O_3	ZnO	SiO_2	Al_2O_3	RO	R_2O	Parts
oo*		oo	o	o	o		dielectric layer
	oo	oo	o	o	o	o	dielectric layer
o	oo	oo			o	o	dielectric layer
oo	o	oo		o	o	o	barrier ribs
	oo		o		o	o	barrier ribs
	oo	oo	oo	o	o	o	barrier ribs
oo	-	o		o	o		sealant

* oo and o mean major and minor components, respectively

4. Discussion

The direction in which research and development needs to proceed in the transition from lead-based to lead-free materials is through incorporation of new techniques (spray, spin, die and blade coating processes) and consideration of various combinations of materials with frit size, size distribution, vehicle type (hybrid type) as well as composition as shown in Fig. 2.

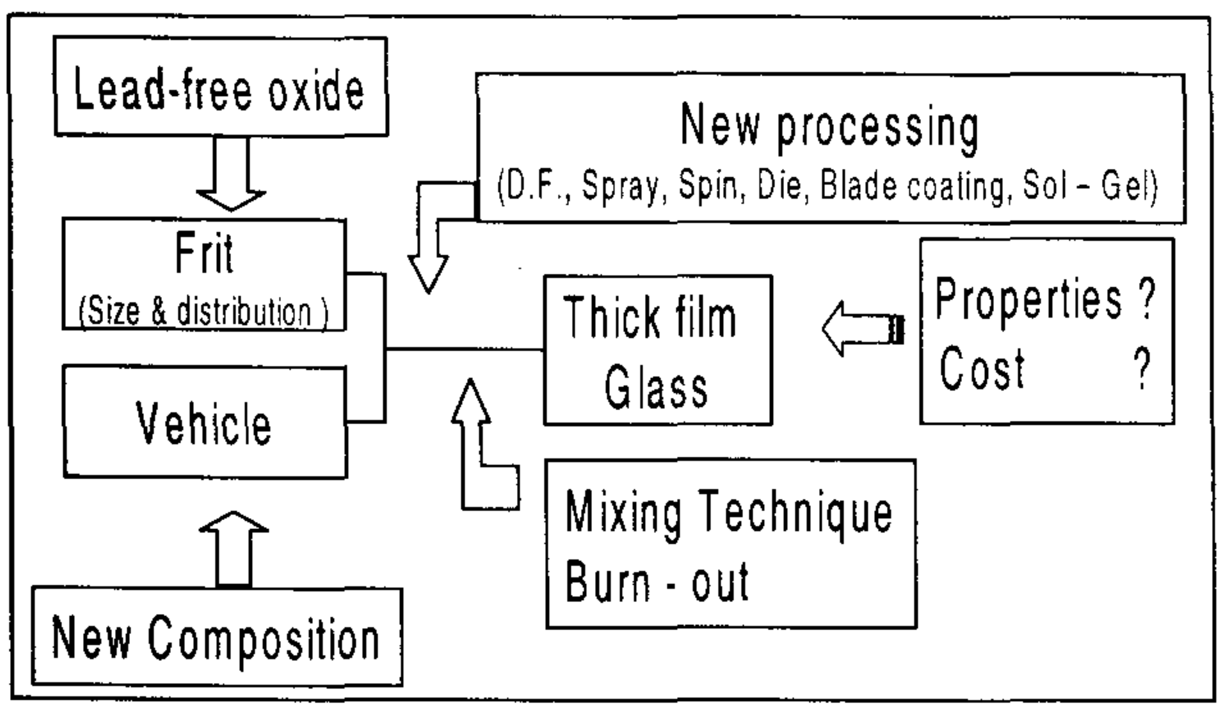

Fig. 2 Future research and development direction on lead-free oxides in PDP

As potential replacements for PbO glass, B_2O_3, P_2O_5 and Bi_2O_3 glasses could be feasible. However, environmental concerns should be of paramount consideration when discussing the selection of lead-free glass systems. Elements that thus far have been known to cause toxic problems are Hg, Cd, Pb. Ag, Bi, and Zn have also been discussed as candidates to replace Pb, but their effects on human health are still under investigation. Through in Vitro testing, many experiments have been reported on the effect of Bi on the human body [8]. Bi is close to Pb in the periodic table of elements, therefore the properties would be very similar to the more undesirable Pb, which is recognized as having environmental and health concerns. Unfortunately the information on bismuth – related toxicity is unclear. With regards to the environment, it is known that bismuth is a safe, non-carcinogenic, environmentally suitable alternative to Pb [9]. On the other hand, toxicity in humans from Bi depends on the type of bismuth compounds [8]: toxicity is seemingly not directly related to the dose or duration of bismuth exposure [10]. It should be noted however, that the use of bismuth has economic drawbacks. Bismuth is made as a byproduct of lead, copper, tin, silver, and gold plants and the final step involves an oxidation of molten bismuth to form bismuth oxide. This process means that the price is at present seven times higher than lead. In terms of production, the one of third of the total production of

Bi is provided from other sources of lead production. Thus, increased use of Bi could increase the production of toxic Pb waste.

Borate and phosphate glasses are of interest in the application of Pb-free glasses. As shown in Fig.1, P_2O_5-SnO-ZnO-RO-RO_2 and P_2O_5-BaO-ZnO-RO-RO_2 are in the range of low firing temperature. However $BaCO_3$ as a raw material is classified as a toxic substance. Barium and its water-soluble compounds belong to the 1st group in the PRTR (Pollutant Release and Transfer Register), Japan [11]. From a practical point of view therefore, when considering long-term usage of the product, BaO cannot be considered as a suitable component in non-Pb glass systems [12].

As a conclusion, it is necessary to study new, environmentally friendly, Pb-free glasses for dielectric layers in order to add to our fundamental knowledge in the field and development of these materials.

5. Acknowledgement

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6. References

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