Environmentally Friendly and New Generation Glasses for Plasma TV

Anal Tarafder, Shiv Prakash Singh and Basudeb Karmakar*

Glass Science & Technology Section, Glass Division, CSIR-Central Glass and Ceramic Research Institute, 196, Raja S.C. Mullick Road, Kolkata 700 032, India

---

Abstract: Glass plays an important role in the manufacturing of plasma display panel (PDP), that is, plasma TV. Glass is not only used there as front and back panel substrates, but also in its several components, such as front panel transparent dielectric (TD) layer, back panel opaque or white dielectric (WB) layer, barrier rib (BR) and sealing material in between front and back panels. In all the later cases, presently PbO is used in the tune of 60-80 wt% as a glass constituent. It is, therefore, essential to replace the PbO from glass compositions due to health and environmental issues keeping their existing properties unaltered. In this paper, an overview on the available PDP glasses and some of their key properties are reported. In addition, recent development carried at this institute on environmentally friendly lead-free dielectric glasses for plasma TV is briefly described. A low softening and dielectric constant lead-free $ZnO-P_2O_5$ based glass composition was also developed for manufacturing plasma TV in consideration of cost-effectiveness. We believe that this work will open up a new horizon in the plasma TV research and reduce its manufacturing cost significantly as well.

Keywords: *Plasma display panel (PDP), Plasma TV, Glass, Lead-free glass, Low softening point lead-free glass, Low dielectric constant glass*

---

* Corresponding author. Tel.: +91 33 2473 3496; fax: +91 33 2473 0957.

E-mail address: basudebk@cgcri.res.in (B. Karmakar).

1. Introduction

In recent past, the commercial uses of flat panel displays (FPDs) have increased enormously, especially in case of consumer electronics such as televisions, laptop computers, digital clocks, cell phones, telephones etc. In such cases, the most widely used flat panel displays are the liquid crystal display (LCD) and organic light emitting diodes (OLED's). OLED’s are mostly used for small displays in MP3 players and mobile phones and LCD is competing with plasma display (PDP) for sub 42 inch TV's and is being the display of choice for computer screens. But PDP is one kind of flat panel display which has emerged to be a potential display material for large dimension (>100 inches) high definition TV. Significant quality differences remain between PDP and other flat panel displays (LCD, OLED etc.) while they offer some shared benefits. It is true that with the advent of more affordable LCDs and the competition from the latest LED TVs, the plasma television market has shrunk recently. This is mostly as the sales representatives continue to favor LCD and now the latest LED TVs over plasma with their hype regarding burn-in and excessive power consumption. PDP has always remained the TV technology of choice for videophiles, home theater enthusiasts, sports fans and consumers desiring a larger screen size. PDPs are characterized by larger screen sizes (greater than 100 inches), wide viewing angle, more accurate image reproduction with better colour accuracy, contrast and brightness, superior ability to display moving images without motion artifacts and better pixel reliability over LCDs or LEDs. The share of 3D PDP TV is expected to represent over 86% of all PDP TVs in 2013. Depending on the type of voltage that is used to generate the plasma, AC and DC PDPs can be distinguished. Almost all the PDP companies have now adopted the AC PDP.

In plasma display panels, its front and back panels are made up of glass. Besides, some of its components are also composed of glass frits and ceramic fillers (e.g., TiO_2, SiO_2, ZrO_2, Al_2O_3, MgO and cordierite) reinforced glass microcomposites, viz., white back dielectric layer, barrier rib etc. Presently various glass powders such as PbO-ZnO-B_2O_3 and PbO-ZnO-SiO_2 [1-3] are being used which contain huge amount (60-80 wt%) of lead oxide (PbO). Lead oxide is used in glasses due to its low melting temperature and property tailoring ability. However, it creates hazardous effect on health and environment. The compositions and some key properties of PD200 glass substrate and different PDP glasses are presented in Table 1 and Table 2. As per the July 1, 2006 legislation European Commission (EC), all applicable products in the European Union countries must comply with Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS). The scope of the WEEE and RoHS legislations cover various households' appliances, information technology and telecommunication equipment, consumer equipment, lighting equipment, electrical and electronic tools, toys and leisure equipment, and automatic dispensers. Since the RoHS legislation came into effect, technological changes have continued and our understanding of the reliability questions associated with lead-free glasses has improved. However, these technologies have yet to reach a stage of reliability and technical viability.

In this paper, a brief overview of different types of glasses used in plasma TV is presented. In addition, environmentally friendly lead-free plasma TV component glasses recently developed by the authors are also discussed.

2. Brief History about PDP

The very first prototype for a plasma display monitor was invented in 1964 by Donald Bitzer, Gene Slottow, and Robert Willson. These three researchers at the University of Illinois concentrated their efforts on constructing the next generation of computer display screens. Donald Bitzer, H. Gene Slottow, and graduate student Robert Willson invented the original monochrome panels for Bitzer's PLATO Computer system, one of the first computer-assisted instruction systems in the world. The original neon orange monochrome Digivue display panels built by glass producer Owens-Illinois were very popular in the early 1970s because they were rugged and needed neither memory nor circuitry to refresh the images. A long period of sales decline occurred in the late 1970s because semiconductor memory made CRT displays cheaper than the US$2500 512 x 512 PLATO plasma displays. Nonetheless, the plasma displays' relatively large screen size and one inch thickness made them suitable for high-profile placement in lobbies and stock exchanges. The present major manufacturers of plasma display are Panasonic Corporation, Samsung Electronics, LG Electronics, etc.

3. Brief about PDP Structure

A sectional view of plasma display panel (PDP) structure is represented in Fig. 1. The PDP uses two panels of glass have been coated with the two different dielectric layers such as transparent dielectric, TD (in front panel glass) and rear dielectric (also known as white back, WB) layer that sandwich a thin layer of gas in several millions of tiny cells (fine discharge spaces). The plasma in each cell of an alternative current (AC) PDP is generated by dielectric barrier discharges (DBDs) operating in a glow regime in a rare gas mixture (typically 500 Torr, 100 μm gap). Each tiny cell is known as 'pixel' and each pixel is divided into three sub-cells. Phosphors in the three colours (red, green and blue (RGB)) are deposited on three sub-cells respectively. Varying the voltage of the signals to the cells thus allows different perceived colors. Especially in plasma display panels (PDPs) various types of glass powders are used for sealing purpose, barrier ribs, dielectric layers of front and back panels. Therefore, glass plays an important role in the manufacturing of plasma TV. Glass is not only used as front and back panel substrate of plasma TV, it is also used in PDP as front and back panel dielectric layer or as barrier rib in between front and back panel or as sealing material. The functions of the dielectric layer are to limit the discharge current and to stabilize the plasma in the discharge cell. This dielectric layer should have high dielectric strength and good transparency. These two glass substrates are separated by a material i.e. 'barrier rib', i. e., the partition. In PDP a rear glass dielectric layer (popularly known as white back) is used as the insulating film of the address electrodes on the rear glass substrate and also gives mechanical support to the barrier ribs (the partitions between the phosphor cavities). The dielectric layers (~30 μm thick) and barrier ribs (~120 μm height and ~80 μm thick) are formed by 'screen printing' on glass substrates in order to get the pattern. The dielectrics and barrier rib materials of PDP systems require a low dielectric constant (less than 15), low softening temperature (less than the strain point of PDP glass substrate which is 610°C for PD200) and low coefficient of thermal expansion (less than 83 x 10^{-7}/K) with respect to use of PD200 glass as substrate [4, 5].

4. Glasses and Its Microcomposites Used in Plasma Display Panels (PDPs)

Commonly three major components in PDPs other that two substrate plate glasses are made up of glass powders and its microcomposites. They are transparent dielectric, TD (front glass dielectric layer), white back, WB (rear glass dielectric layer) and barrier rib, BR (partition between phosphor cavities). It is technologically challenging to develop process technology as well as the befitting glass compositions to meet all the desired properties for PDP application.

4.1. Glass Substrate for Plasma Display Panel

In PDPs, the two substrate glasses are used to coat the transparent dielectric (in front panel glass) and rear dielectric (in back panel glass) layers that sandwich a thin layer of gas in several millions of tiny cells (fine discharge spaces). The $(Li_2O+Na_2O+K_2O)$-$(CaO+MgO+SrO+BaO)$-Al_2O_3-SiO_2 based glasses have been widely used for the substrate glass in PDP owing to its high strain point which is in excess of 600°C. There are several patents [6-15] in this regard which disclose the compositions and some key properties like strain point, glass transition temperature, coefficient of thermal expansion etc. A typical high strain point PDP substrate glass composition (PD200) developed by Asahi Glass Company Limited, Tokyo is presented in Table 1. The relevant properties are shown in Table 2. Therefore, it is important to develop the low softening point glass powders and its microcomposites without PbO so that the deformation of substrate glass could be avoided.

4.2. Transparent Dielectric (TD)

In PDPs, the transparent dielectric material is important since it maintains the discharge, and protects the electrodes of the device. Moreover, its transmission characteristics affect the image quality of the display. Such a dielectric layer is formed by screen printing repeatedly about three or four times. For the development of a reasonable dielectric layer for a PDP, several properties are required, such as: high transparency (above 80% after firing), low firing temperature of about 550-580°C, dielectric constant below 15, and a reasonable thermal expansion coefficient (8-9x10^{-6} K^{-1}) to match the glass substrate. Low melting and firing temperatures required for price competitiveness and may affect market share for PDPs since it is in competition with LCD technology. Therefore, it is important to obtain a low dielectric constant and firing temperature without impeding other requirements such as thermal, optical, and morphological properties. The PbO-B_2O_3-SiO_2-ZnO glasses have been widely used for the transparent dielectric layer in PDP owing to its low firing temperature below 580°C. However, the use of Pb should be terminated because of its toxicity to the human body and environment.

4.2. Rear Dielectric or White Back (WB)

In PDP white back dielectric (rear glass dielectric) is used as the insulating film of the address electrodes on the rear glass substrate and gives support to barrier rib. Glass powders are widely used as white back materials with addition of various types of ceramic oxide (e.g. SiO_2, TiO_2 etc) as filler for adjustment of its desired properties as well as improvement of its mechanical strength. Lead (Pb) based frits of PbO-B_2O_3-ZnO and $PbO-B_2O_3-SiO_2$ glasses are very popular as the commercial materials for PDP. For white back, reflection is another most important property other than other properties. Therefore, lead is used in this type of glass due to its low softening point (T_s) as well as high refractive index. Here, lead oxide (PbO) is used to the extent of 60-80 wt%.

4.3. Barrier Rib (BR)

Recently, glasses reinforced by ceramic fillers, such as Al_2O_3, SiO_2, TiO_2 etc. have been used as the barrier ribs of plasma display panels (PDP). The barrier rib, in essence, is a glass matrix composite reinforced with ceramic fillers. The compositions (wt%) of the glass matrixes used are generally in a range of (60-75)PbO-(2-25)SiO_2-(2-20)B_2O_3 with minor components, such as Al_2O_3, ZnO, TiO_2 and MgO. The ceramic fillers are added to the glass matrix primarily to prevent slumping of the ribs during sintering. The addition of filler generally improves the dimensional stability of the ribs during sintering but also influences the physical properties of the ribs, such as the dielectric constant, thermal expansion coefficient, and viscosity. As these properties affect the performance of PDP, it is crucial to select a proper combination of glass matrix and filler material for the ribs. As a filler material, Al_2O_3 powder is most commonly used because of its phase stability and chemical inertness. Al_2O_3 powder, however, has a moderately high relative dielectric constant (8.8-10.1) and thermal expansion coefficient ($8.0x10^{-6}$ K^{-1}). For a fast signal response characteristic of the PDP, the dielectric constant of the ribs needs to be 10. The dielectric constants of currently used lead borosilicate glasses fall in a range of 10 to 15. Therefore, a filler material with a lower dielectric constant is required to further reduce the dielectric constant of the ribs. It is well-recognized that the addition of inert fillers reduces the rate of sintering and increases the possibility of generating flaws in the sintered body. The sintering temperature of glass filled with inert ceramic powders is significantly higher that that of the glass matrix, which limits the use of the easily available and low-priced soda–lime glass substrates. The sintering temperature of glasses containing Al_2O_3 powder as the filler is in the range of 560° to 590°C, and the softening temperature of the soda–lime glass is 570°C. This demands the use of a glass substrate with a higher softening point, potentially increasing the cost of the PDP. Among the other oxide ceramics, fused quartz has a combination of desirable physical properties for a filler material. It has a dielectric constant of 4 and a thermal expansion coefficient of 11x 10^{-6} K^{-1}. The use of fused quartz as a filler should be more effective in reducing the dielectric constant of the barrier ribs. In addition, a reasonable difference in the thermal expansion coefficients between the filler and the matrix should make modification of the thermal expansion coefficient of the rib material more manageable.

There are several kinds of conventional manufacturing process for barrier ribs having each of shortcomings. Sandblasting method laminating selective protecting layer over glass paste takes severe material consumption rates. Screen printing method of laminating each glass paste layer is easy and common technique.

4.4. Sealing Glass

Sealing glass compositions is used for bonding the front and back plate substrate of PDP. For this purpose, high lead containing glasses are widely used for which the sintering temperature is leas than 400°C. The sealing glass prevents the deformation and cracking of a substrate caused by thermal and mechanical stress and reduces the sintering temperature to thereby enhance the air-tightness of the sealing glass.

5. Lead as an Environmental and Health Issue

Lead is one of the oldest industrial poisons. Contamination by industrial lead has occurred everywhere on the earth. Recently, the release of environmental contaminant PbO have increased enormously due to large production and uses of electrical and electronics gadgets which contain a large volume of lead components. A wide variety of adverse health effects arise from exposure to lead. It primarily affects the peripheral and central nervous systems, the blood cells and metabolism of vitamin D and calcium. There are many chronic effects like anaemia arising from inhibition of haem synthesis, chronic encephalopathy, cognitive impairment, sleeplessness, headaches, aggressive behaviours, convulsions, disruption of motor system and renal effects etc. arising from lead exposure.

6. CGCRI Contribution towards Lead Reduction from PDPs

Central Glass and Ceramic Research Institute, Kolkata recently developed the process and fabrication technology of some lead-free environmentally friendly glass frits for barrier ribs, transparent dielectric and white back of PDPs in collaboration with the M/s Samtel Color Limited, Ghaziabad under CSIR/NMITLI project.

6.1 Replacement of PbO from TD

Lead-free transparent dielectric (TD) layer attracted much attention of various researchers. In this context, Bi_2O_3, B_2O_3, BaO and ZnO are potential glass constituents to satisfy various requirements for TD. Recently, BaO-B_2O_3-ZnO, Bi_2O_3-B_2O_3-BaO-ZnO [16, 17] glasses were studied as a PbO free, low firing transparent dielectric layer for plasma display panels (PDP). The transparency of the Bi_2O_3-B_2O_3-BaO-ZnO glass system could be improved to a great extent by adding desirable amount of CuO and/or CeO_2 in these glass systems to eliminate yellowish or brownish color during PDP manufacturing. Table 3 shows the compositions of CGCRI developed lead-free TD glasses and Fig. 2 shows the TD coated PDP substrate (heat-treated).

6.2 Replacement of PbO from WB & BR

Recently, some Pb-free glasses in the systems BaO-ZnO-B_2O_3, Bi_2O_3-B_2O_3-BaO-ZnO, BaO-B_2O_3-SiO_2 [18-21] etc. have been reported as alternate white back and barrier rib materials for PDP. The effects of various types of crystalline fillers (e.g. SiO_2, TiO_2, Al_2O_3, ZrO_2, MgO, etc) in some of these lead-free glasses are reported. But only a very few glass compositions have been reported for white back and barrier rib application. Bismuth oxide based glass could be selected as a substitute of lead oxide based glasses as it is next to lead in the periodic table which has low melting temperature (820°C) and high refractive index (n = 2.5) as lead oxide (melting temperature = 880°C, n = 2.24). In this respect, CGCRI has developed the lead-free environment friendly low melting BaO-ZnO-B_2O_3 and Bi_2O_3-ZnO-B_2O_3 based glass systems which can be used for the development of opaque dielectric and barrier ribs glass microcomposites when added with some crystalline filler such as TiO_2, Al_2O_3 and SiO_2 etc. Table 3 shows the compositions of CGCRI developed lead-free WB and BR glasses and Fig. 3 and Fig. 4 show the WB and BR coated PDP substrate (heat-treated) respectively.

7. PDP-What Is Next?

Recently, it has been observed that there is growing interest to develop low softening point low dielectric constant transparent glass composition that can be used on the commercially available soda-lime silica glass substrate. Moreover, lower temperature processing helps achieve lower energy consumption leading to lower cost of production making the PDP more competitive in comparison to other flat panel displays like LCD. To develop the low softening point (<500°C) and dielectric constant dielectric glass layer and barrier rib on commercially available soda-lime silica PDP glass substrate, low melting $ZnO-P_2O_5$ based glass, $SnO-P_2O_5$ based glass, $SnO-ZnO-P_2O_5$, $SnO-B_2O_3-P_2O_5$, $MnO-SnO-P_2O_5$ and $ZnO-Sb_2O_3-P_2O_5$ [22-24] based glass systems are probable. In this respect, CGCRI has developed lead-free environmentally friendly low softening point (<500°C) and dielectric constant $ZnO-P_2O_5$ based glass system with some other minor oxides which can be used as dielectric layer and barrier rib for the front and back panels of PDP made of an ordinary soda lime silicate (SLS) sheet glass. Compositions and properties of CGCRI developed low softening (500°C) and dielectric constant glasses for low cost PDP is presented in Table 4.

8. Conclusions

In this paper, different types of glasses involved in manufacturing of plasma TV are briefly discussed. In addition, recent development carried at this institute on environmentally friendly lead-free dielectric glasses for plasma TV is also presented. A low softening and dielectric constant lead-free $ZnO-P_2O_5$ based glass composition was also developed for manufacturing PDP TV in consideration of cost-effectiveness. We believe that this work will open up a new horizon in the plasma TV research and reduce its manufacturing cost significantly as well.

Acknowledgements

This work has been supported by the NMITLI/CSIR, New Delhi under the sanctioned no. 5/258/49/2006-NMITLI. The authors gratefully thank Director of the institute for his kind permission to publish this paper.

References

1. W. Hiromitsu, O. Hiroyuki, O. Masahiko and H. Kazuo, US patent 6010973 (2000).

2. G-H Hwang, W-Y Kim, H-J Jeon and Y-S Kim, J. Am. Ceram. Soc. 85 (2002) 2961.

3. T. Shiro, M. Hideaki, U. Tadahiko and K. Koji, JP patent 10338547 (1998).

4. J. S. An, J. S. Park, J. R. Kim, K. S. Hong, H. Shin, J. Am. Ceram. Soc., **89,** 3658 (2006).

5. H. Shin, S. G. Kim, J. S. Park, J. S. An, K. S. Hong, H. Kim, J. Am. Ceram. Soc., **89,** 3258 (2006).

6. N. El Khiati, R. Gy, E. L. Bourhis, US6063718 **(**2000**).**

7. K. Maeda, S. Ohara, T. Nakashima, Y. Nakao, US6297182B1 (2001).

8. T. Nakashima, K. Maeda, Y. Nakao, US6313052B1(2001).

9. K. Nagai, T. Nakashima, K. Maeda, EP2202207A1 (2010).

10. K. Maeda, Y. Nakao, H. Kushitani, S. Ito, US5599754 (1997).

11. K. Maeda, H. Onoda, Y. Nakao, J. Sehgal, US5858897 (1999).

12. K. Maeda, H. Onoda, Y. Nakao, J. Sehgal, US5908794 (1999).

13. T. Nakashima, Y. Nakao, US6949485B2 (2005).

14. K. Nagai, T. Nakashima, K. Maeda, US2009/0137379A1 (2009).

15. K. Nagai, T. Nakashima, US2010/0210443A1 (2010).

16. R. R. Tummala, Borate Glasses: Structure, Properties and Applications, edited by L. D. Pye, et.al., Plenum Publishing Corp., 1978.

17. S. G. Kim, J. S. Park, J. S. An, K. S. Hong, H. Shin, H. Kim, J. Am. Ceram. Soc., **89**, 902 (2006).

18. E. S. Lim, B. S. Kim, J. H. Lee, J. J. Kim, J. Electroceram., **17**, 359 (2006).

19. S. G. Kim, H. Shin, J. S. Park, K. S. Hong, H. Kim, J. Electroceram., **15**, 129 (2005).

20. J. S. Park, J. H. Hwang, C. Y. Kim, T. Masaki, D. K. Choi and K. J. Hong, Proc. IDW/AD ’05, 1507-1510.

21. S. Lee, S. Hwang, M. Cha, H. Shin and H. Kim, J. Phys. Chem. Solids, 69 (2008) 1498-1500.

22. R. Morena, J. Non-Cryst. Solids, 263&264 (2000) 382-387.

23. R. K. Brow and D. R. Tallant, J. Non-Cryst. Solids, 222 (1997) 396-406.

24. B. Zhang, Q. Chen, L. Song, H. Li and F. Hou, J. Am. Ceram. Soc., 91 (2008) 2036-2038.

Table 1. Chemical Compositions (wt%) of PDP Glass Substrate and Existing Different Lead-Containing PDP Component Glasses

Component	High Strain Point PDP Glass Substrate	Barrier Rib (Opaque)	White Back	Transparent Dielectric
SiO_2	60	37.2	21.6	8.0
Al_2O_3	5	0.7		0.6
B_2O_3		6.8	6.8	16.2
ZnO				7.5
PbO		62.1	71.6	67.7
SrO	7			
CaO	8			
MgO	2			
ZrO_2	7			
Na_2O	4			
K_2O	7			
Total	**100**	**100**	**100**	**100**

Table 2: Some Key Properties of PDP Glass Substrate and Existing Different Lead-Containing PDP Component Glasses

Properties	High Strain Point PDP Glass Substrate	Barrier Rib (Opaque)	White Back	Transparent Dielectric
Strain Point (°C)	582	-	-	-
Annealing Point (°C)	626	450	461	495
Softening Point (°C)	836	484	492	580
CTE ($x\ 10^{-7}\ K^{-1}$)	83	73	78-80	75
Dielcetric Constant (ε / 1MHz)	10.3	9.5	14	9.5

Table 3: Composition and Properties of CGCRI Developed Lead-Free PDP Component (TD, BR and BR) Glasses

Component and property	Chemical composition (wt%)	
	TD Glass	**WB & BR Base Glass**
SiO_2	0-6	6-9.5
B_2O_3	17-33	17-29
ZnO	2-46	42-51
Bi_2O_3	0-72	0-22
Al_2O_3	0-2	1
K_2O	0	0-0.5
Li_2O	0	0.5-2.5
CaO	0-5	0-5
MgO	0	0-4
BaO	0-45	0-14
T_s (°C)	505-546	547-551
Exp.(α x 10^{-7}/K)	73-101	71-84
Transparency	76-84	-
D.C.	8.9-11.2	8.6-13.2

Table 4: Compositions and Properties of CGCRI Developed Low Softening (<500°C) and Dielectric Constant Lead-Free PDP Component Glasses for Low Cost PDP

Component and property	Chemical composition (mol%)
ZnO	40-45
P_2O_5	42-48
B_2O_3	0-5
SiO_2	0-6
Al_2O_3	0-5
Li_2O	0-5
Na_2O	0-5
K_2O	0-5
CaO	0-3
BaO	0-8
SrO	0-3
T_s (°C)	436-497
T_g (°C)	347-403
CTE (α) x 10^{-7}/K	82-103
D.C. (ε_r)	6.4-9.3
%T at 550 nm, t = 2 mm	80-90
Nature of glass coating applied on silver electrode coated panel substrate heat-treated at 470°C/30 min. (±20°C)	Yellow-free translucent

Figures

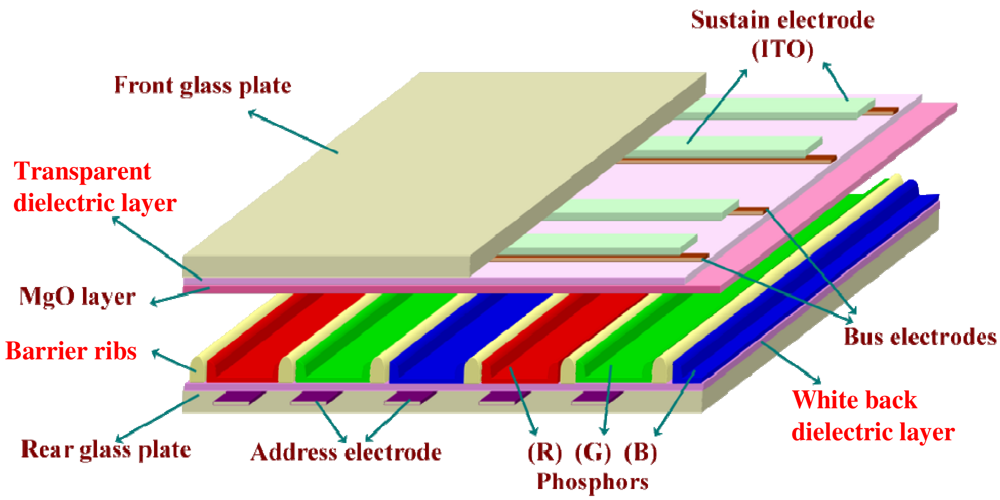

Fig. 1 Sectional view of a PDP discharge cells illustrating its structure

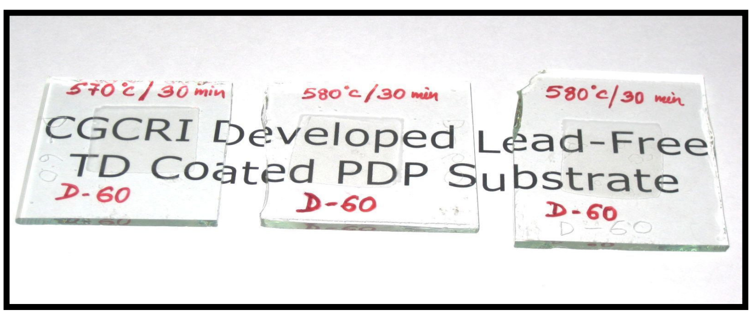

Fig. 2 CGCRI developed lead-free TD coated PDP substrate (heat-treated)

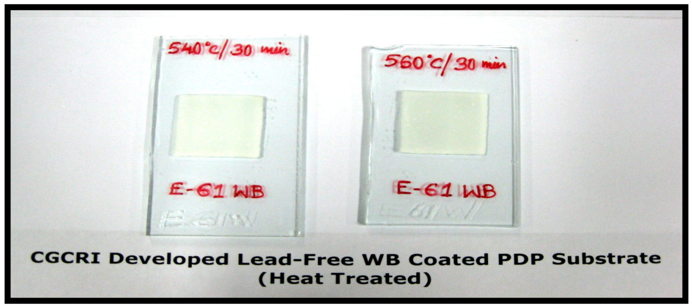

Fig. 3 CGCRI developed lead-free WB coated PDP substrate (heat-treated)

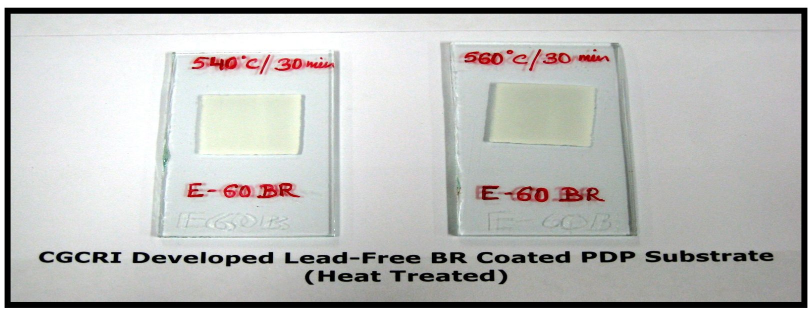

Fig. 4 CGCRI developed lead-free BR coated PDP substrate (heat-treated)