Change of Optical Properties in Zinc Oxide-Based Glasses including Metal Oxides for Transparent Dielectric

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(Received September 19, 2009: Received in revised form October 6, 2009: Accepted October 8, 2009)

Abstract This paper presents a new method for the improvement of color temperature without the change of the driving scheme using transparent dielectric layers with various metal oxides (CeO_2 , Co_3O_4 , CuO, Fe_2O_3 , MnO_2 , NiO) in plasma display panels (PDP). In this study, we fabricated $ZnO-B_2O_3-SiO_2-Al_2O_3$ glasse with various metal oxides and examined the optical properties of these glasses. As the metal oxides were added to the glasses, the visible transmittances of the dielectric layers decreased and the transmittances in special wavelength regions were reduced at different rates. The change of the transmittance in each wavelength range induced the variation of the visible emission spectra and the change of the color temperature in the PDP. The addition of Co_3O_4 and CuO slightly decreased the intensity of the blue light, but the intensities of the green and the red light were significantly decreased. Therefore, the color temperature can be improved from 6087K to 7378K and 7057K, respectively.

Key words transparent dielectric layer, metal oxide, transmittance, color temperature, plasma display panel.

1. Introduction

In the recent years, the flat panel display (FPD) market has been growing fast with the technological advance of the large screen size and high definition. AC plasma display panels (ac PDPs) are expanding rapidly in this market through the competition with liquid crystal displays (LCDs) and organic light emitting diodes (OLEDs). Whereas, the PDP must overcome some drawback, such as brightness, efficiency, contrast ratio and color temperature. 1-5) Especially, it is necessary to improve the low color temperature of the PDP. The lower color temperature in the PDP is essentially caused by the lower blue luminance compared to the red or green luminance. As a result, the blue luminance needs to be increased significantly to enhance the color temperature of the PDP. Many researchers and manufacturers have been studying to improve color temperature of the PDP, such as optimization of the color filter, the design of the driving scheme, asymmetric barrier rib, and new phosphor. ⁶⁻⁸⁾

Currently, the research activities for the improvement of the color temperature in the transparent dielectric layer focus on the change of the glass color and the control of the yellowing phenomenon by transition metal ions in the PDP. The thermal, optical and morphological properties of CuO-doped Bi₂O₃-B₂O₃-BaO-ZnO glass and Bi₂O₃-B₂O₃-ZnO glass were investigated. ^{9,10)} The change of the state of the cobalt ions and copper ions in Bi₂O₃-B₂O₃-BaO-ZnO glass and Bi₂O₃-B₂O₃-ZnO glass, respectively, with various contents were reported. ^{11,12)} But, these investigations did not included the change of the optical property by other various metal oxides in the transparent dielectric layer and the changes of the color temperature in the PDP are not researched.

In this paper, we examined the optical property of ZnO- B_2O_3 -SiO₂-Al₂O₃ glass with various metal oxides such as CeO₂, Co₃O₄, CuO, Fe₂O₃, MnO₂, and NiO in these dielectric layers of the PDP. The changes of the spectrum intensities in red (R), green (G), and blue (B) were studied under the variety of metal oxides. We also demonstrated the change of the color temperature from the chromaticity coordinates obtained by the simulation, which was computed from the relations between the measured visible light spectrum of the PDP and the visible light transmittance curves of dielectric layers.

2. Experimental procedure

All the compositions were prepared from high pure 88mol% ZnO-B₂O₃-SiO₂-Al₂O₃, 10mol% K₂O, and 2mol%

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Na₂O-Li₂O, to which CeO₂, Co₃O₄, CuO, Fe₂O₃, MnO₂, and NiO were exceeded at the concentration of 2mol%, respectively. The mixture of raw materials was melted in a platinum crucible at 1300 °C for 1 h in air and then quenched on a ribbon-roll to obtain a cullet. Quenched cullet was ground in a ball mill for 15h to obtain glass powders. The glass powders were then mixed using a three-roll-miller for 30 min with an organic vehicle to make paste. The glass paste was coated onto the ITO coated PD200 glass (2.8 mm thickness, Asahi Glass, Japan) plate by the screen-printing method. The dried paste coated glass was fired at 585 °C for 15min. The thickness of the transparent dielectric layer was ~25 μ m after firing.

The optical transmittance characteristics of the fired layers on the PD200 glass substrate in the visible region (from 380 to 780 nm) were measured using an ultraviolet-visible-near infrared light spectrophotometer (Cary 5000, Varian, Inc., Australia). The visible emission spectrum data of the PDP were measured on the spectroradiameter (Konica Minolta Sensing, Inc., CS-1000A, Japan). The color temperature and CIE chromaticity coordinates are calculated from the simulation.

3. Results and discussion

Fig. 1 shows the optical transmittance spectra of the

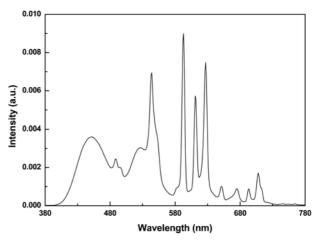


Fig. 2. Visible spectra of white color emitted from R, G, B cells in the PDP.

dielectric layers with CeO₂, Co₃O₄, CuO, Fe₂O₃, MnO₂, and NiO, respectively, between 380 and 780 nm in comparison with the dielectric not containing the metal oxide. With the addition of the metal oxides in the dielectric layers, the visible transmittance decreased in special wavelength regions with an overall reduction. When Co₃O₄, MnO₂, and NiO were added, the transmittance decreased at 430-690 nm, 400-600 nm, and 390-580 nm, respectively. Adding Fe₂O₃ and CeO₂ reduced the transmittance of the transparent dielectric layer when the wavelengths were below 450 nm and 500 nm, respectively. As CuO was included, the trans-

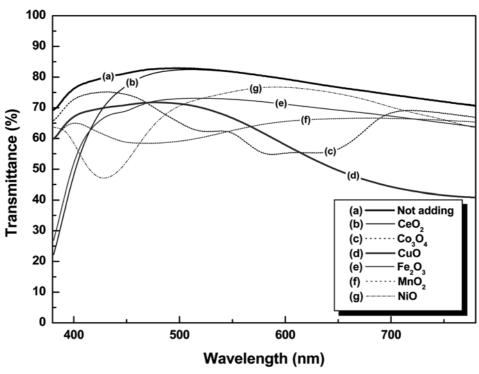


Fig. 1. Optical transmittance spectra of dielectric layers as a function of metal oxide addition.

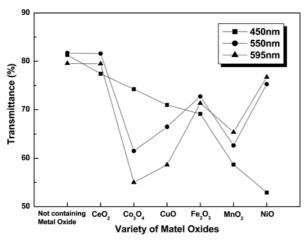


Fig. 3. Transmittance at 450 nm, 550 nm, and 595 nm as a function of metal oxide addition.

mittance decreased when the wavelengths were above 500 nm. ¹³⁻¹⁶⁾

Fig. 2 represents the visible spectrum of the white color emitted from the red (R), green (G), and blue (B) cells in the PDP. The intensity of the red light had three peaks with the representative peak at 595 nm, and two other peaks at 610 nm and 630 nm. The green light showed a high intensity at 550 nm with a slight range and the intensity of the blue light occurred broadly at 450 nm.

The optical transmittance values of dielectric layers at 595 nm, 550 nm, and 450 nm, which are the representative wavelengths of R, G, and B, are shown in Fig. 3. The transmittance of dielectric layer without the metal oxide at 450 nm, at 550 nm, and 595 nm had the similar values,

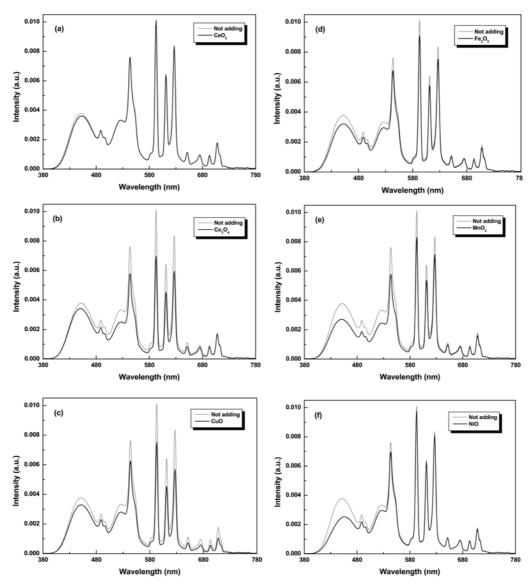


Fig. 4. Visible emission spectra with CeO_2 (a), Co_3O_4 (b), CuO (c), Fe_2O_3 (d), MnO_2 (e), and NiO (f) by comparison with not adding metal oxide.

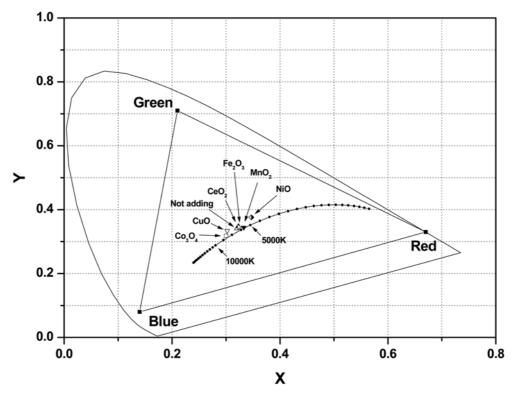


Fig. 5. Changes of color temperature related to the black body locus on CIE (1931) chromaticity coordinates from the simulation.

81.3%, 81.7%, and 79.6%, respectively. When CeO_2 was contained, the transmittances changed with a little reduction by 4% in the blue region. As the Co_3O_4 was added, the transmittance at 450 nm decreased to 74.2%. However, the remarkable reduction of transmittance by 20% and 25% appeared in the green region (550 nm) and the red region (595 nm), respectively.

When the dielectric layer included CuO, the transmittance at 595 nm and 550 nm decreased by 21% and 15%, respectively, but a decrease of 10% occurred at 450 nm. On the other hand, while NiO was contained, the decrease of the transmittance by 28% at 450 nm happened with a little diminution of the transmittance by 6% and 3% in the green and the red region, respectively. As Fe₂O₃ was added, the similar decrease of the transmittance in all regions occurred. On the whole, the addition of NiO and MnO₂ in the dielectric layers reduced the transmittance considerably within the blue wavelength range. However, the inclusion of Co₃O₄ and CuO decreased the transmittance massively at the 550 nm and 595 nm with a little reduction of the transmittance at 450 nm.

Fig. 4 shows the changes of the white emitted luminance in the PDP with variety of metal oxides using the simulation. With the addition of CeO₂, the luminance intensity was

similar to the value of the dielectric layer not containing the metal oxide. The addition of Co_3O_4 and CuO in the dielectric layer decreased the intensity of the blue light slightly in the range of 400 nm to 500 nm, but the intensities of the green and the red light in the range of 500 nm to 640 nm were significantly decreased. However, when NiO and MnO_2 were added in the dielectric layer, the intensity of the blue light was extremely reduced. The addition of Fe_2O_3 in the dielectric layer decreased the intensity of the blue, the green, and the red by the similar amount.

Fig. 5 illustrates the changes in the color temperature related to the black body locus on the Commission Internationale de l'Eclairage (CIE) 1931 (x, y)-chromaticity coordinate by simulation. The solid square marks denote the National Television System Committee (NTSC) standard coordinates, and the linked solid circles indicate the black body locus with the related color temperature.

As Co_3O_4 and CuO were added, the coordinates of the color temperature were moved toward the blue region from (0.320, 0.341) to (0.300, 0.318) and to (0.302, 0.334), respectively, because of the significant reduction of the green and the red light intensity. Compared with the results of the dielectric layer not containing the metal

Table 1. Color temperature as a variation of metal oxides.

Metal oxide	CIE 1931		Color
	X	У	Temperature (K)
Not adding	0.320	0.341	6087
$\mathrm{Co}_3\mathrm{O}_4$	0.300	0.318	7378
CeO_2	0.323	0.348	5889
CuO	0.302	0.334	7057
Fe_2O_3	0.324	0.346	5889
MnO_2	0.333	0.344	5464
NiO	0.347	0.376	5011

oxide, the PDP with the dielectric layer containing Co_3O_4 and CuO shows an enhancement of the color temperature from 6087K to 7378K and to 7057K, respectively. However, when MnO_2 and NiO were added, the color temperature decreased from 6087K to 5464K and to 5011K, respectively, and the coordinates of the color temperature moved from (0.320, 0.341) to (0.333, 0.344) and to (0.347, 0.376), respectively. Table 1 shows the CIE chromaticity coordinate and their correlated color temperatures in various metal oxides. The color temperature of the PDP can be controlled within a wide range by the addition of the transition metals in the transparent dielectric layer.

4 Conclusion

In this study, we have prepared the metal oxides included ZnO-B₂O₃-SiO₂-Al₂O₃ system glasses and examined their optical properties. The effect of the metal oxides in the transparent dielectric layer of the PDP on improving the color temperature was reported. With addition of the metal oxides in the glasses, the visible transmittance of the dielectric layers decreased in the specific wavelength regions with an overall reduction. The independent change of the optical transmittances in different wavelength ranges

generated the variation of the R, G, and B emissions and the change of the color temperature in the PDP. Especially, it is found that the addition of Co₃O₄ and CuO in the dielectric layers could enhance the color temperature from 6087K to 7378K and 7057K, respectively.

References

- 1. J. P. Boeuf, J. Phys. D, Appl. Phys., 36(6), R56 (2003).
- M. F. Gillies and G. Oversluizen, J. Appl. Phys., 91(10), 6315 (2002).
- G. Y. Hong, B. W. Jeoung, B. S. Jeon, J. S. Yoo, C. H. Ha and K. W. Whang, J. Electrochem. Soc., 151(10), H205 (2004).
- 4. G. Oversluizen and T. Dekker, IEEE Trans. Plasma Sci. **34**(2), 305 (2006).
- Y. Hirano, K. Ishii and Y. Murakami, in Proceedings of 12th
 Int. Display Workshops, Institute of image information and Television Engineers (Takamatsu, Japan 2005), p.1539.
- T. Okamura, S. Fukuda, K. Koike, H. Saigou, M. Yoshikai, M. Koyama, T. Misawa and Y. Matsuzaki, J. Vac. Sci. Technol.A, 19(4), 1090 (2001).
- K. D. Cho, H. S. Tae and S. I. Chien, IEEE Trans. Elec. Dev., 50(2), 359 (2003).
- 8. H. Tachibana, A. Matsuda, S. Haruki, N. Kosugi, K. Wani and L. F. Weber, in Proceedings of the International Display Workshops Digest (Kobe, Japan, November 2000), p.651.
- J. Y. Song, T. J. Park and S. Y. Choi, J. Non-Cryst. Solids, 352, 5403 (2006).
- S. W. Lee, S. J. Hwang, M. L. Cha, H. W. Shin and H. S. Kim, J. Phy. Chem. Solid, 69, 1498 (2008).
- Y. T. An, B. H. Choi and H. S. Kim, Kor. J. Mater. Res., 18(12), 678 (2008).
- 12. J. Y. Song and S. Y. Choi, Displays, 27, 112 (2006).
- 13. C. R. Bamford, Phys. Chem. Glasses, 3, 189 (1962).
- 14. I. Fanderlik, J. Kocik and J. Nebrensky, Colouring of Glass. 2nd ed., SNTL, Prague, (1978).
- 15. M. B. Volf, Chemical Approach to Glass, p. 141, Elsevier, New York, (1984).
- 16. H. Scholze, Glass, Nature, Structure, and Properties, 3rd ed., p. 234, Springer, New York, (1991).