

Stability of Coated- $\text{Zn}_2\text{SiO}_4\text{:Mn}$ Phosphor for PDP Application

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1. Objective and background

PDP is the emissive display device which uses the visible rays from the phosphors excited by vacuum ultraviolet rays, which were generated by discharging He-Xe, Ne-Xe mixed gas in R, G, B, cells. Consequently, the R, G, B phosphors determines the quality images of PDP. Many options to select the phosphors are available for PDP application, depending on the manufacture. For typical application, $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$, $\text{YBO}_3\text{:Eu}$, $\text{Zn}_2\text{SiO}_4\text{:Mn}$ are used as blue, red, green phosphors, respectively. But critical problems of green phosphor are coming to the front among these. As for the $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphor, absorption of ultraviolet rays near 147nm and 173nm is good and color purity of green emission is known to be the most suitable among green phosphors for PDP application.

However, it has some problems. High operating voltage due to the discharge missing at green cell is one of examples, which ascribed to the negative charge at the phosphor surface. Another problem is an afterimage to be remained after new frame. Long decay time of this material is responsible for this. This also causes luminescence saturation at high frequency driving mode. Typical methodology to solve these problems is to blend

and use many green phosphors such as $\text{BaMgAl}_{14}\text{O}_{23}\text{:Mn}$, $\text{YBO}_3\text{:Tb}$, $\text{BaAl}_{12}\text{O}_{19}\text{:Mn}$, and $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors. As for the decay time of $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors, an option is possible with an adjustment of activator concentration, but it accompanies luminescence decrease and stability.

Another issue that is caused by phosphor is the discharging characteristics of Xe-Ne gas in the cell. It was reported that the $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ has a negative surface charge which is from the non-stoichiometric matrix of the host lattice, while red and blue phosphors have positive surface charges. The negative charge of the green phosphor may reduce the wall charge accumulated on the dielectric surface in PDP cell as shown in Fig. 1. Because the wall charges help to sustain the discharge in the cells that were subjected to the previous discharge, the reduction of wall charges can lead to non-uniform discharge or even non-discharge phenomenon in the PDP cell. As a consequence of this unstable discharge characteristic in the green cell, the efficiency of PDP device can be seriously reduced and a higher discharge voltage is required for driving the PDP device for compensating the reduced wall charges. One of the methods to solve this problem was, which had done by our group, to coat the surface

of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ by metal oxide which has the positive charge. It was observed that the discharging characteristics could be very stable and rising time for discharging could be dramatically decreased. However, negative effect of coating on the luminance and the stability has to be considered for panel application.

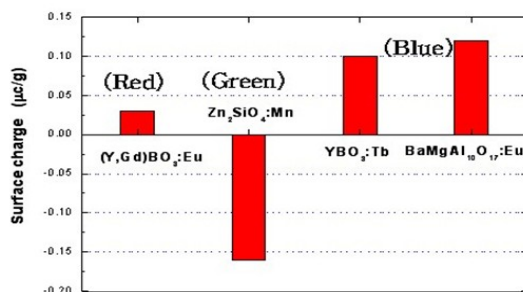


Fig. 1. surface charge of PDP phosphors.

In this work, we separated dominant effects to have influence on the longevity of phosphor into intensity of electron beam, ion beam, and VUV. Then, each independent variable was examined in terms of luminance as a function of time. Also, we examined what happened on the surface of phosphors after degradation.

2. Results

The host lattice of the $\text{Zn}_2\text{SiO}_4:\text{Mn}$ phosphor has the Willemite structure and each Zn and Si are surrounded by four oxygen atoms. Zn_2SiO_4 is achieving regular tetrahedron doing Zn or Si to the center, which is a little distorted. If host lattice structure is achieving perfect regular tetrahedron structure, union force between each element is strong. Therefore, substitution for other element is very hard. Mn^{2+} ion which is activator has a similar ionic size as Zn^{2+} . Doping of Mn^{2+} ions in Zn_2SiO_4 , makes it possible by a ${}^4\text{T}_{1g}({}^4\text{G}) \rightarrow {}^6\text{A}_{1g}({}^6\text{S})$ change of Mn ions which is responsible for green emission in the lowest excitation state

by a change for ground state. And, usually, Y_2O_3 and Al_2O_3 are known to be proper coating materials for phosphor stability. So, we experimented various metal oxide coating and mixed phosphors. $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, Y_2O_3 coated $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, La_2O_3 coated $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, Al_2O_3 coated $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, ZnO coated $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ and nano sized Y_2O_3 mixed $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphors were analyzed.

Figure 2 shows changing of luminescence of phosphors after exposing to electron beam. Damage to phosphor was observed and smaller particle and rougher surface was more influenced by electron.

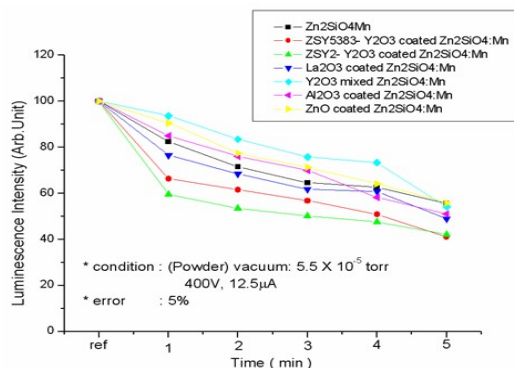


Fig. 2. The change of the luminescence after exposed to the electron beam

Figure 3 shows changing of chemical composition and binding energy after exposing to electron and ion beam on phosphor layer. The change of the binding energy of each element does not exist and the intensity of the peak just be altered. To be changed can be known the chemical composition after exposing to electron or ion beam on phosphor. It means that the ion or electron included in the plasma give the damage to the surface of the phosphor and that such damage gives the influence to the luminescence of the phosphor. SEM analysis was to see the change

of the surface state of the phosphor after exposing to electron and ion beam.

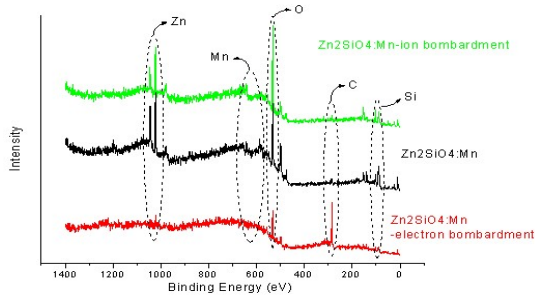


Fig. 3. The change of the chemical composition and binding energy after exposed to the ion beam

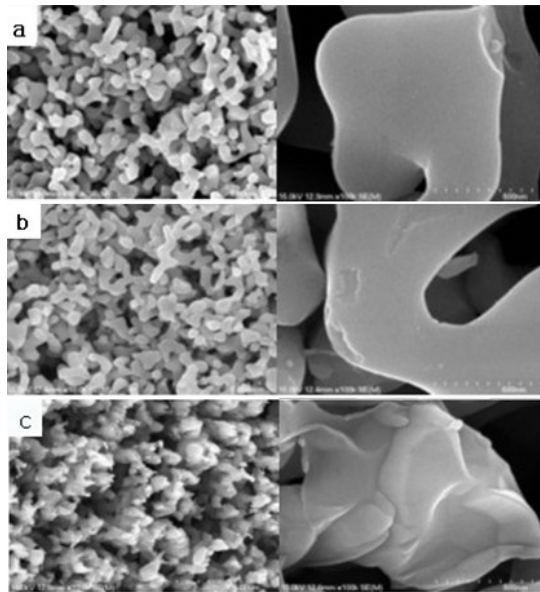


Fig. 4. The change of the SEM micrographs after exposed to the electron and ion beam.

(a) The surface state of raw $Zn_2SiO_4:Mn^{2+}$ phosphor, (b) The change of the surface state after exposed to the electron beam on $Zn_2SiO_4:Mn^{2+}$ phosphor, (c) The change of the surface state after exposed to the ion beam on $Zn_2SiO_4:Mn^{2+}$ phosphor

Figure 4 shows the surface image of $Zn_2SiO_4:Mn^{2+}$ phosphor after exposing to electron and ion beam. The case of the sample which exposed ion beam, surface of phosphor was

sputtered heavily and be change the chemical composition. It means that the damage of the surface state on phosphor connects the reason of the decrease of luminance and longevity. Based on these results, commercial green phosphors coated with metal oxide were exposed to the ion beam.

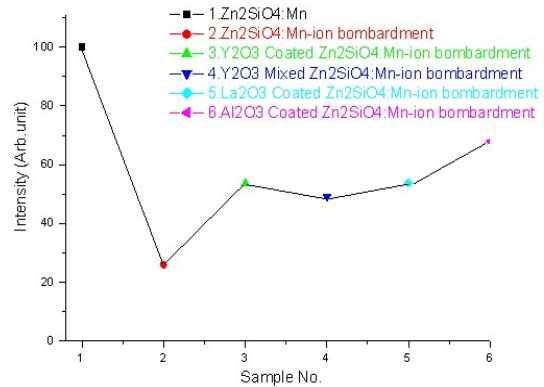


Fig. 5. The change of the luminance of the phosphors which were exposed to the ion beam

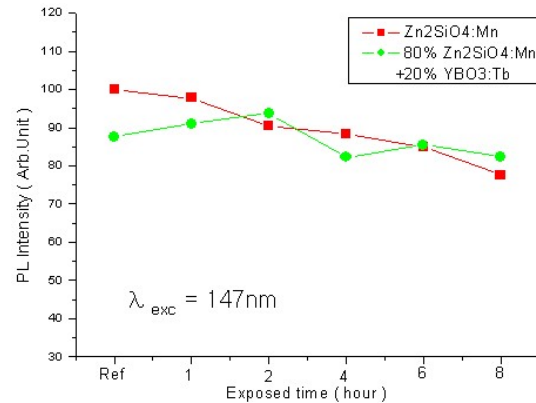


Fig. 6. The change of the luminance of the phosphors which were exposed to the VUV

Figure 5 shows the change of luminance of green phosphors which were exposed to the ion beam. The case of Al_2O_3 coated $Zn_2SiO_4:Mn^{2+}$ phosphor, range of decrease of luminance was the smallest because the Al_2O_3 are known to be proper coating materials for phosphor stability. Figure 6 shows the variation of luminance when they were exposed to the VUV. The case of coated

$\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor has not been examined, yet. More work is going on in this point..

3. Impact

In this study, aging characteristics specially electron and ion impact of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, nano sized metal oxide-coated and mixed $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ were examined for identifying the key attribute of green phosphor in PDP cell. Here, the PDP manufacturing processes were simulated in this experiment. More works had put on the checking the stability of coated-phosphors under our previous work that coated $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor with the positively charged metal oxide can be very helpful for uniform discharging in green cell. The surface of phosphor is damaged both metal oxide coated with $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ and raw $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ when it is exposed to electron or ion beam. But, in the case of metal oxide coated with $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, we could confirm the surface damage does less than the raw $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$. It means that the metal oxide coated with phosphor protects the damage to the surface from the electron and ion beam, and it also can increase the discharging stability.

As of now, Al_2O_3 coated $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ was found to be most suitable. We now believe that the coated green phosphor could be applied to the panel.

4. References

- [1] H. Tachibana, A. Mastuda, S. Haruk, N. Kosugi, K. Wani, and L. F. Weber, *IDW'00*, 2000, pp. 651-654
- [2] Korea patent 2001-0062387
- [3] A. Morell and N. El Khiati, *J. Electrochem. Soc.* 140(7), pp. 2019-2022(1993)
- [4] M. Tamatani, *J. Lumin.*, 100, 317 (2002)
- [5] S. J. Yoon, Y. K. Jung, J. W. Seo, B. H. Lee, Y. H. Kim and K.W. Whang, *Displays*, 23, 183 (2002)
- [6] G. Y. Hong, B. W. Jeoung, B. S. Jeon, C. H. Ha, K. W. Whang and J. S. Yoo, *J. Electrochem. Soc.* 151(10), pp. H205-H209 (2004) .
- [7] B. W. Jeoung, G. Y. Hong, B. Y. Han and J. S. Yoo, *Jpn. J. Appl. Phys.* Vol 43, No12 (2004), pp. 7997-8001
- [8] B. Y. Han, B. W. Jeoung, G. Y. Hong and J. S. Yoo: *IMID'04* (2004) p. 575-578
- [9] A. L. N Stevels and A. T. Vink, *J. Lumin.*, 8, pp. 443-451(1974)
- [10] H. K. Perkins and M. J. Soenko, *J. Chem. phys.*, 46(6), pp. 2398-2401(1967)
- [11] S. Shionoya and W. M. Yen, Phosphor handbook, p.194, *CRC press*. Boca Raton, Fl (1998)
- [12] J. J. Zhang, J. W. Ning, X. J. Liu, Y. B. Pan and L. P. Huang, *Mater, Lett.*, 57, p.3077 (2003)