Aging Characteristics of the Green Phosphors for PDP Application

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Abstract

The picture quality of a plasma display panel is very sensitive to the phosphor characteristics such as decay time, surface state, and even longevity of phosphor material in itself. In this work, material characteristics of Zn_2SiO_4:Mn, Y_2O_3-coated Zn_2SiO_4:Mn, and YBO_3:Tb, which are dominant in commercial application, were examined for investigating the aging characteristics of green PDP phosphors. It was found that Y_2O_3-coated Zn_2SiO_4:Mn are easily degraded at high temperature. However, all the samples were very weak after vacuum annealing. The luminescence intensity was decreased by order of one magnitude.

1. Introduction

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 are available for PDP application, depending on the manufacturer. For typical application, $BaMgAl_{10}O_{17}$:Eu, Eu-doped yttrium borate, and Zn_2SiO_4: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 Zn_2SiO_4: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 example [1], 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 during operation. Typical methodology to solve these problems is to mix and use many green phosphors such as $BaMgAl_{14}O_{23}$:Mn, YBO_3:Tb, $BaAl_{12}O_{19}$:Mn, and Zn_2SiO_4:Mn phosphors.[2] As for the decay time of Zn_2SiO_4:Mn phosphors, an option is possible with an adjustment of activator concentration, but it accompanies luminescence decrease and stability.[3] The best way is to develop new materials or modify the phosphors. In these cases, we need to identify key attributes of each material.

In this study, the green phosphors which are available in commercial market were selected to identify the key attributes of each phosphor. We try to simulate the manufacturing process if possible and

more focus was put on the aging that phosphors were experiencing. Then we will discuss the effects of process parameters on the phosphor material. The objective of this work is to identify key attributes of green phosphors.

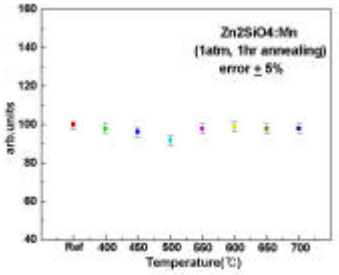
2. Experimental

Zn_2SiO_4:Mn, Y_2O_3 - coated Zn_2SiO_4:Mn, YBO_3:Tb, and $Sr_2Al_4O_6$:Mn were selected for the analysis. For paste, binder (Tokyo Kasei) and vehicle were mixed with phosphor at the ratio of 60:40. Complete mixing was carried out for more than 24 hours. Then, phosphor layer were made on the glass with the thickness of 120㎛. The experimental were carried out under two conditions. Each powder sample and corresponding phosphor layer on the glass were aged under muffle furnace at atmosphere. Condition was in the temperature range of 400℃~700℃ for 1 hour.

Aging characteristics of phosphor powder as well as phosphor film were examined. Temperature and pressure while aging were the main independent variables in our case. PL and CL were measured in each case. To examine the effects of process variable to phosphor, XRD, XPS, and SEM were taken. In this presentation, what happen in phosphor after aging will be discussed.

3. Results and discussion

The host lattice of the Zn_2SiO_4: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. [4,5] 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 $^4T_{1g}(^4G) \rightarrow {}^6A_{1g}(^6S)$ change of Mn ions which is responsible for green emission in the lowest excitation state by a change for ground state. [5.6], Another green phosphor, YBO_3 doped by Tb ion, has the excitation spectrum which a $^5D_4 \rightarrow {}^7F_5$ change transfer which is favorable to green emission.[7,8] Fortunately, the crystal face of YBO_3 has positive charge and high luminous efficiency. It also has short decay time. Therefore, it is a potential candidate of Zn_2SiO_4:Mn phosphor and be used with Zn_2SiO_4:Mn phosphors. However, YBO_3:Tb has low color purity, Specially, a deterioration characteristic is not good, and it needs additional treatment for PDP application.



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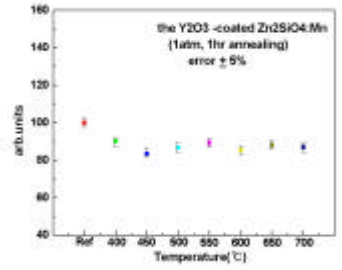

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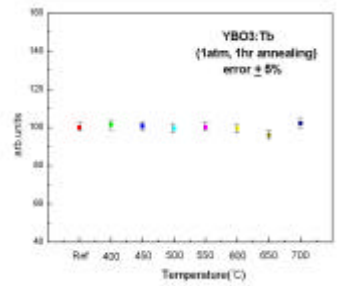

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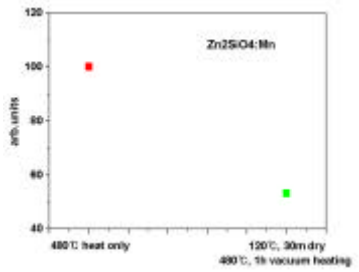
Figure.1. The luminescence variation along with the temperature in case of (a) Zn_2SiO_4:Mn (b) the Y_2O_3 – coated Zn_2SiO_4:Mn (c) YBO_3:Tb

For each sample, the luminescence was measured and compared with the original one, as shown in Fig. 1. All the data were obtained after more than 5 times measurement within a 5% error. Here, relative stability of YBO_3:Tb green phosphor was most strong, as expected. Usually, Y_2O_3 and Al_2O_3 are known to be proper coating materials for phosphor stability. However, in our case, Y_2O_3-coated Zn_2SiO_4:Mn shows rather poor aging characteristics. Theoretically, any reason can be ascribed to this phenomenon except poor coating quality.



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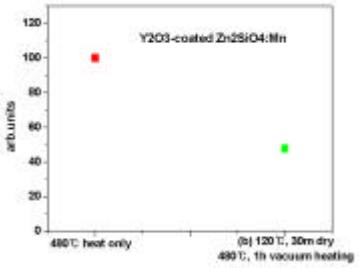

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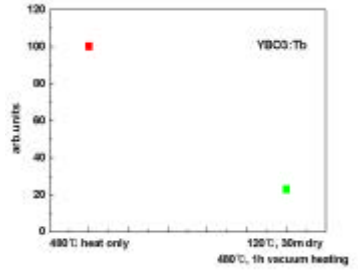

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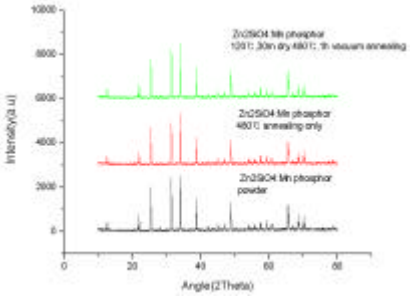
Figure.2. The luminescence after vacuum annealing in case of (a) Zn_2SiO_4:Mn (b), the Y_2O_3 coated - Zn_2SiO_4:Mn, and (c) YBO_3:Tb

Figure 2 shows how the luminescence of a phosphor film is influenced under vacuum annealing. In this experiment, phosphor film was exposed to 1 hour at 480℃ and 1 torr. Very severe damage to phosphor was observed in any sample that we dealt with. Zn ions evaporation was expected in Willmite structure and destruction of Zn_2SiO_4:Mn phosphors. However, more than 80 % decrease of YBO_3:Tb in luminance was observed.

We may expect that the decrease of a luminescence due to the structure broken while happening in high temperature and low pressure. The ZnO and the SiO_2 which are raw materials for composing the Zn_2SiO_4 lattice start a reaction at near 770℃ and 1 atm. Obviously, there is not observed the decrease of luminescence when annealed at 480℃ and an atmospheric pressure. But that temperature might be decreased at low pressure and it can have enough activation at vacuum level. Host lattice structure will be easily reliable to be broken.

Figure 3 shows XRD data. Any big variation from original lattice structure was not observed. However, subtle distortion can be observed. We may rely on the analysis of XPS or EDS for detail interpretation. We will discuss it at our presentation.



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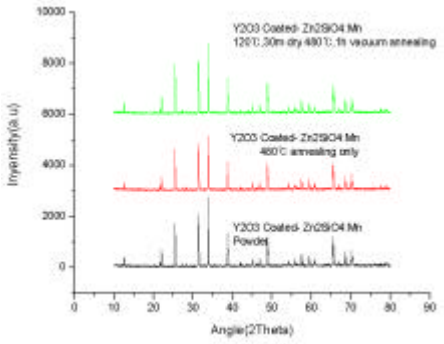

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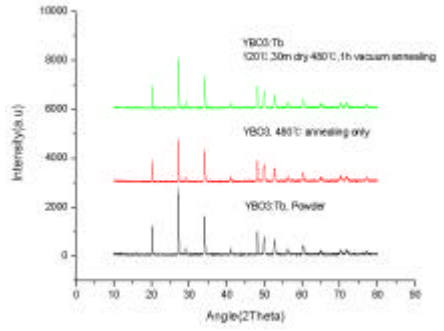

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Figure. 3. The XRD data after vacuum annealing for the phosphor of (a) Zn_2SiO_4:Mn (b) the Y_2O_3 coated-Zn_2SiO_4:Mn (c) YBO_3:Tb

4. Conclusion

In this work, aging characteristics of the Zn_2SiO_4:Mn, the Y_2O_3-coated Zn_2SiO_4:Mn, YBO_3:Tb were examined for identifying the key attribute of green phosphor in PDP cell. Here, the PDP manufacturing processes were simulated for analysis. In case of powder, phosphor coating could be found to be very cautious for guaranteeing the stability as well as surface modification. In atmospheric condition, phosphors could be durable till 600℃. However, in case of adopting the vacuum annealing, the luminescence was dramatically decreased in any case. The exact reason is remains unclear yet. In conference presentation, the cause of severe degradation and improving will be discussed based on the detail analysis.

5. Reference

[1] H. Tachibana, A. Mastsuda, 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] A. L N Stevels and A. T. Vink, J. Lumin., 8, pp. 443-451(1974)

[5] H. K. Perkins and M. J. Soenko, J. Chem. phys., 46(6), pp. 2398-2401(1967)

[6] D. T. Palumbo, J. J. brown Jr., J. Electrochem. Soc. 117, p. 1184(1970)

[7] S. Shionoya and W. M. Yen, Phosphor handbook, p.194, CRC press. Boca Raton, Fl (1998)

[8] J. J. Zhang, J. W. Ning, X. J. Liu, Y. B. Pan and L. P. Huang, Mater, Lett., 57, p.3077 (2003)