Application of Phosphate Phosphor in Solid-State White Lighting of the Next-Generation

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White Light Emitting Diode

White Light Emitting Diode (WLED) has the advantages of a small size, low amount of heat, low power consumption, long life time, excellent response speed, environmental protection, planer packaged, and easily made for the products which are lighter, thinner, short, smaller and so on. Meanwhile, white LED has advantages such as lower power consumption and hardly broken than incandescent bulbs. Thus, white LED is the most optimistic product with a large potential in place of the conventional lighting equipment in the future. The characteristics of white LED have been compared with the conventional lighting equipment, as shown in Table 1 [1]. In fact, LED is a diode formed from semiconductor materials emitting light through a forward bias. Moreover, the materials of the LED diode usually were III-V group of the chemical elements, such as gallium phosphide , gallium arsenide, indium gallium aluminum phosphide (GaP), and indium gallium nitride (InGaN) used for high-brightness LED currently. The light-emitting principle of LED is applied a driving current to the semiconductor compound to promote the combination of electrons and holes. When the combination of electrons and holes were happen, the specific energy would be released in the form of light, as shown in Figure 1 [2]. The manufacturing of the white LED currently is using the above LED chip with converted-phosphor to emit white light.

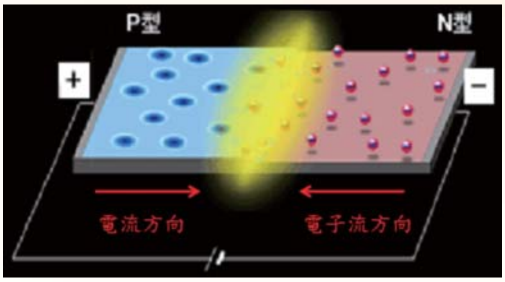

Fig.1 Schematic diagram of the light-emitting principle of LED [2]

	LED(1~2W)	Incandescent(60W)	Fluorescent(40W)	High-intensity Discharge Lamp(HID) (40W)
Luminous efficiency(lm/w)	15~20%	8~14%	25%	20~40%
Color	4,600K~15,000K	2,400~3,000K	4,200~6,500K	3,800~6,000K
temperature				
Reaction time	<100ns	0.15~0.25s	1~2s	Take severalminutes to stable
CRI	72(Ra)	100(Ra)	61~95(Ra)	65~70(Ra)
Life time	20,000~6,0000 hrs	1,000 hrs	12,000 hrs	12,000 hrs

Table.1 White LED V.S. Conventional lighting equipment[1]

Phosphor converted light-emitting diodes

In 1996, the white LEDs were fabricated by using the blue LED chip and yellow emitting phosphor such as cerium doped yttrium aluminum garnet (YAG: Ce) by Nichia, and further developed the major market age. The phosphor materials mainly combine a host lattice and a activator element, and sometimes can also be doped trace amounts of the sensitizer. Additionally, the activator and sensitizer always replace the specific locations in host lattice ions. Usually, the host lattice is only the one who plays the role of energy transfer in the excitation process, and does not absorb radiation energy. That is to say, activator is the main role to emit light. The phosphor applied in white LED has the following requirements [3]: (a) excellent absorb efficiency in blue light or ultraviolet light ; (b) excellent thermal stability; (c) physical stability, chemical stability and moisture resistance; (d) stability of phosphor under long-term irradiation by the UV light; and (e) fine particle size. Moreover, it is not suitable material for packaging.

Currently, the mainstream market on white LED is using blue LED chip combined with the yellow YAG converted phosphor to emit white light. However, although the conventional white LED has high brightness and efficiency, it still has some problems such as color variation and low reproducibility. Moreover, there is a problem with heat generated as the driving current increased due to the high power LED that has developed in recent years. That is to say, if heat problem cannot be improved effectively, luminous efficiency will be affected. To overcome the above shortcomings, it is necessary to take a way to improve the conversion efficiency and thermal stability. In recent years, the study using UV LED to excite red, green and blue color phosphors is a trend solution and its luminous diagram is shown in Figure 2. This type of white LED light is able to use UV LED chip to emit UV wavelengths to excite red, green and blue phosphor which were mixing in the appropriate amount of three of the phosphor components to form white light. Such manufacturing method provide excellent conversion efficiency, low cost, larger mass production , uniform color. It becomes one of the most promising manufacturing methods in the future [4]. On the other hand, regarding the heat problem, the phosphate oxide compound ($ABPO_4$, $A=Li^+$, Na^+, K^+, Rb^+, Cs^+ , B=Mg2+, Ca2+, Sr2+, Ba2+) as the host lattice of covalent nature of the phosphor have three dimensional rigid structure. The phosphate oxide is very suitable for carrier transport, and the thermal stability of the phosphate series is quite outstanding. Using phosphate as host lattice in the phosphor material can solve the thermal problem of the high power of white LED in effective way. Besides that, phosphate based phosphors have excellent color rendering, small color cast, low cost and low patents limit to be a great potential of development in the future. Figure 3 shows the diagram of the structure of the phosphate materials [5].

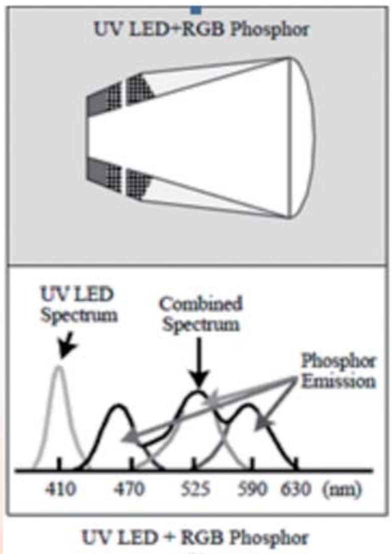

Fig.2 UV LED+RGB Phosphor [4]

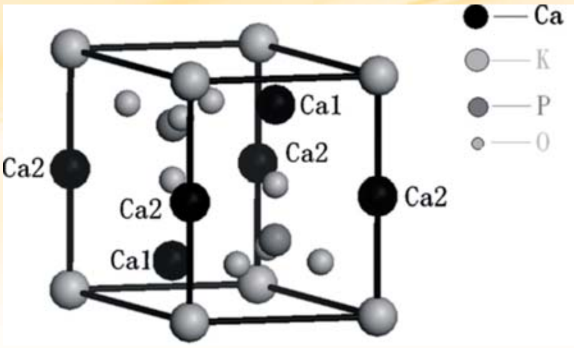

Fig.3 The host lattice of $KCaPO_4$ phosphate [5]

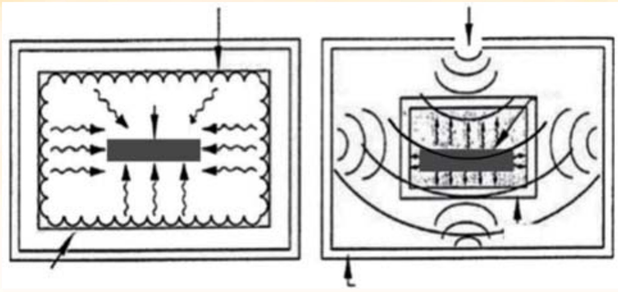

Fig.4 conventional sintering compare to microwave sintering [5, 6]

In recent years, our team has focused on using microwave sintering to reduce the particle size of phosphor. In fact, microwave sintering is a new method for synthesis of inorganic phosphor. By using the microwave sintering method, the sample can be heated and cooled quickly, it can also be heated simultaneously at different depths but with uniform heat, and it also has other advantages such as simple structure, low cost and high thermal conversion efficiency. In addition, by using the microwave sintering method, the sample can be synthesized and produced a phosphor having high purity, small particle size and uniform distribution in shorter time as well as lower temperature. However, the heat process not only affects the particle size of the phosphor, but also reduces the thermal stress. Figure 4 shows the comparison diagram of conventional sintering and microwave sintering [5, 6].

In our team's researches, we found that the particle size was 2μm on optimum doping concentration level by using microwave sintering, as shown in figure 5. Moreover, we also found that in the same sintering temperature of 1200°C, the sintering time of only 1 hour required to form the single phase of $YInGe_2O_7$ under microwave sintering which was rather low compared with conventional sintering. Since $YInGe_2O_7:Eu^{3+}$ phosphors were sintered under microwave, a pronouncedly smaller and more uniform grain size of less than 1 μm were obtained, as shown in figure 6.

On the other hand, in order to verify the thermal stability of phosphate phosphor, we used variable-temperature photoluminescence measurement. As shown in figure 7, the emission intensity is decreased as the temperature is increased since the probability of non-radiative transition caused by thermal activation and release of the luminescent center through the crossing point between the excited state and the ground state increases with increasing temperature, causing the luminescence being quenched. It is clearly found the emission intensity reduces slowly by only approximately 7% for the maximum emission peak with temperature increasing from 30°C up to 200°C. The thermal quenching temperature, T50, defined as the temperature at which the emission intensity is 50% of its original value, of commercially available $YAG:Ce^{3+}$ was lower than 200°C, indicating that the $KSrPO_4:Tb^{3+}$ phosphor prepared using microwave sintering had a good thermal stability as compared with those of the $YAG:Ce^{3+}$ phosphor prepared using conventional sintering and is suitable as luminescent material for white LED.

In summary, we believe that how to control particle size and distribution effectively in phosphor is a key technology for white LED. In addition, adding good thermal stability of phosphate phosphor as well as the combination of the plastic packaging will obtain the best advantage on the development of high-power white LED.

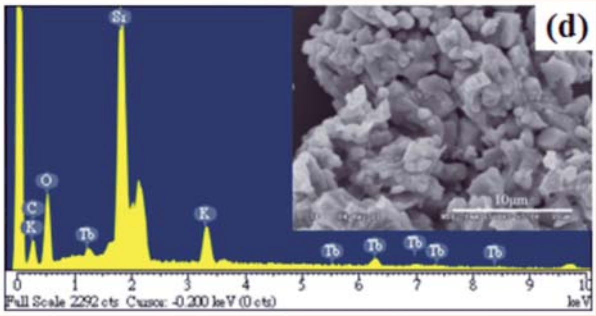

Fig.5 $KSrPO_4:Tb^{3+}$ phosphor formed by using microwave sintering [7]

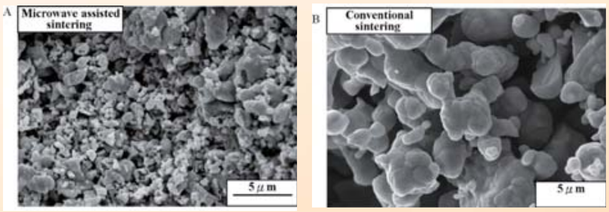

Fig.6 SEM images of $YInGe_2O_7$:50 mol% Eu phosphors prepared by (A)microwave assisted sintering at 1200°C for 1 h and (B) conventional sintering at 1200 °C for 10 h [8]

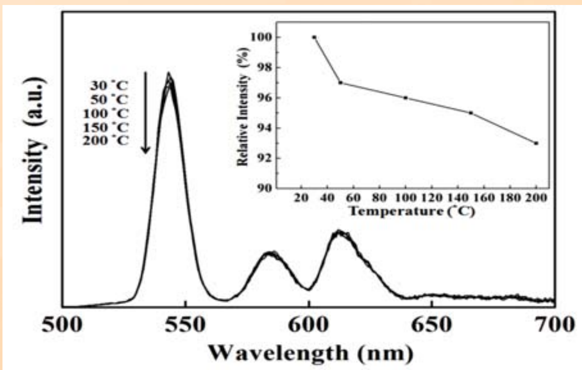

Fig.7 PL analysis of $KSrPO_4:Tb^{3+}$ phosphor

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