Accelerated life time testing and optical degradation of remote phosphor plates

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\textbf{Abstract}

In this investigation the thermal stability and life time of remote phosphor encapsulant plates, made from bisphenol-A polycarbonate (BPA-PC), are studied. Remote phosphor plates, combined with a blue-light LED source, could be used to produce white light with a correlated colour temperature (CCT) of 4000 K. Spectral power distribution (SPD) and photometric parameters of thermally-aged phosphor plates were measured by Integrated-Sphere. Results show that thermal ageing leads to a significant decrease in the luminous flux and chromatic properties of plates. The photometric properties of thermally-aged plates, monitored during the stress thermal ageing tests, showed a significant change both in the correlated colour temperature (CCT) and in the chromaticity coordinates (CIE \(x, y\)). It is also observed that there is a significant decay both in the phosphor yellow emission and in the blue peak intensity. The decrease in the luminous flux is strongly correlated to the deterioration of the chromatic properties of the phosphor plates. The results also show a significant decay of CCT, postulating that the degradation of the remote phosphor plates affects the efficiency of light and the colour of emitted light as well. The decrease of CCT takes place with almost the same kinetics as the lumen depreciation.

1. Introduction

The introduction of white LEDs to the lighting market was a revolutionary achievement in this market domain. Excellent optical quality, high efficiency, high reliability, and eco-environmentally of LEDs are main advantages, which make them superior than traditional light sources. Among different techniques of producing white light, phosphor-converted white LEDs is more common because of its price and colour rendering index. The wavelength-converting phosphors in combination with InGaN blue LED are commonly used in white LEDs, since they have less problematic issues during service. For example, the RGB 3-chip LED requires complex control of electronics in order to guarantee a defined colour over operating time. Although LEDs are more reliable than conventional light sources, several reports \([1–5]\) have shown that package and phosphor layer of white LEDs can degrade, resulting in the reduction in the light efficiency. The main reason for phosphor damage is radiation of light and the generated heat by LED chip during operation. In order to reduce the effects of generated heat on the degradation reaction, the idea of using phosphor layer far from the chip, called remote phosphor, was introduced \([6,7]\). Remote phosphor produces light with high extraction efficiency and lower operating temperature \([6–8]\). In this configuration, the phosphor layer is deposited onto the lens. Lens materials, used in LEDs, are mainly silicon, epoxy resins, and bisphenol A polycarbonates (BPA-PC), among which BPA-PC more widely used due to its optimum combination of high impact strength, heat resistance and high modulus of elasticity.

Since remote phosphor is a new technology to produce white light, there are not many reports dealing with the reliability of remote phosphor in the literature \([9,10]\). The aim of this paper is to investigate the effect of heat on the optical properties and the reliability of remote phosphor. For this reason a set of accelerated thermal stress tests were applied with temperature level between 100 and 140 °C. The reliability studies and life time assessment at temperatures lower than 100 °C can be done by extrapolation.

2. Materials and methods

Two types of 3 mm-thick remote phosphor plates with correlated colour temperature (CCT) of 5000 and 4000 K are used in this study hereafter named A and B with the colour rendering index of...
(CRI) 80. There are some differences in the amount/type of additives, are used in the substrate (BPA-PC) of remote phosphor. Normal additives, used in plastic lens in LED applications, contain optical brightener, scatter agent, flame retardant, and heat stabilizer. The specimens are kept in a furnace at 100, 120, and 140 °C up for 3000 h. Testing temperatures for accelerated lumen depreciation test is determined in such a way that the temperature does not exceed the glass transition temperature of the plastics. Glass transition temperature (\(T_g\)) of BPA-PC is 150 °C, so the maximum accelerated temperature is chosen 10 °C below the \(T_g\). A few trial experiments were performed at temperatures close to glass transition temperature and it was observed that plates started to bend and deform. So, it is not possible to do any characterization on these deformed plates. On the other hand, experiments below 100 °C will take a very long time due to slower kinetics of reaction. So, the idea is to do accelerated experiments at this temperature range and then extrapolate the results to lower temperature. We have measured the temperature of the remote phosphor following the standard in preparation [11]. Optical properties of thermally-aged plates, i.e. luminous flux depreciation, were studied at room temperature, using an integrated sphere. In addition to lumen depreciation, colour shifting in thermally-aged specimens is also studied. Every LED colour is represented by unique \(x\)-\(y\) coordinates. The Commission International de l’Eclairage (CIE) system is the common method to characterize the composition of any colour in terms of three primaries [12]. Artificial colours shown by the common method to characterize the composition of any colour nates. The Commission International de l’Eclairage (CIE) system is the deprecation rate parameter, and heat stabilizer. The specimens are kept in a furnace at 100, 120, and 140 °C up for 3000 h. Testing temperatures for accelerated lumen depreciation test is determined in such a way that the temperature does not exceed the glass transition temperature of the plastics. Glass transition temperature (\(T_g\)) of BPA-PC is 150 °C, so the maximum accelerated temperature is chosen 10 °C below the \(T_g\). A few trial experiments were performed at temperatures close to glass transition temperature and it was observed that plates started to bend and deform. So, it is not possible to do any characterization on these deformed plates. On the other hand, experiments below 100 °C will take a very long time due to slower kinetics of reaction. So, the idea is to do accelerated experiments at this temperature range and then extrapolate the results to lower temperature. We have measured the temperature of the remote phosphor following the standard in preparation [11]. Optical properties of thermally-aged plates, i.e. luminous flux depreciation, were studied at room temperature, using an integrated sphere. In addition to lumen depreciation, colour shifting in thermally-aged specimens is also studied. Every LED colour is represented by unique \(x\)-\(y\) coordinates. The Commission International de l’Eclairage (CIE) system is the common method to characterize the composition of any colour in terms of three primaries [12]. Artificial colours shown by \(X, Y, Z\), also called tristimulus values, can be added to produce real spectral colours. The \(x, y, z\) are the chromaticity coordinates [12] which are the ratios of \(X, Y, Z\) of the light to the sum of the three tristimulus values. It is necessary only to consider the quantity of two of the reference stimuli to define a colour since the three quantities \((x, y, z)\) are made always to sum to 1. \((x, y)\) is usually used to represent the colour.

Colour temperature is the absolute temperature at which a blackbody radiator radiates a light which has a chromaticity equal to that of the light source [12]. Correlated colour temperature (CCT) is the temperature of a blackbody whose chromaticity resembles that of a light source. Low colour temperature implies warmer (more yellow–red) light, while high colour temperature appears to be a colder (more blue) light.

There are several reliability models, which could potentially be applied for thermal-stress and lumen depreciation of LED system. These models can be divided in three main categories; (i) linear, (ii) logarithmic, (iii) exponential or any combination of these formula’s [12]. Linear and logarithmic models can certainly NOT be used for remote phosphor, since it has an exponential decay behaviour [7, 13]. The reliability model for the life time assessment of remote phosphor plate is based on an exponential luminous decay equation, where the time-to-failure can be calculated as [13]

\[
\Phi(t) = \beta \exp(-\alpha t),
\]

where \(\Phi(t)\) represents the lumen output, \(\alpha\) is the rate of reaction or depreciation rate parameter, \(t\) is time and \(\beta\) is a pre-factor. When lumen output, \(\Phi\), is equal to 70%, \(t\) is time-to-failure [13]. The rate of reaction, \(\alpha\), is related to the activation energy of the reaction and to the ageing temperature as follows [13, 14]

\[
\alpha = A \exp \left( \frac{-E_a}{KT} \right),
\]

where \(A\) is a pre-exponential factor, \(E_a\) is the activation energy (eV) of the degradation reaction, \(K\) is the gas constant, and \(T\) is the absolute temperature (K).

3. Results

3.1. Thermal degradation test

Stress at high temperature levels can induce thermal ageing and consequently a strong optical power lowering and depreciation of light output, as is shown in Fig. 1 for the case of thermal ageing at 140 °C for sample B (as an example). Reduction of light output with increasing thermal ageing time for samples, aged at 100 and 120 °C, show the same trend in both samples. It is noticeable that there is a significant decay both in the phosphor yellow emission and in the blue peak. As is shown in our previous work the yellowing of BPA-PC plates leads to the reduction in the light transmissivity of plates [15]. Reduction in yellow emission also illustrates the decay of phosphor conversion efficiency.

A more quantitative description of the effects of thermal-ageing on the performance of remote phosphor A and B is given in Fig. 2. This Figure illustrates the evolution of the normalized flux intensity and therefore the degradation kinetics of the phosphor plates. Clearly, the degradation rate shows a significant dependence on the stress temperature level; the higher the ageing temperature, the higher the lumen depreciation and the degradation kinetics.

Based on the alliance for solid state illumination system and technology (ASISST) standard, lifetime of LEDs is defined as time to reach 70% of its initial lumen output [13]. The experiments at 100 °C were performed up to 20% reduction in light output. Therefore the extrapolation of experimental data at 100 °C is needed. The lumen output is extrapolated to higher depreciation by the model that is explained in our previous paper [13]. Table 1 illustrates the calculated values for the reaction rate (\(\alpha\)) for each temperature for remote phosphor plates A and B.

![Image](image.png)

Fig. 1. The evolution of spectral power distribution (SPD) of sample B at 140 °C.
kinetics as the luminous flux decay and can therefore be ascribed to the thermally activated degradation mechanism discussed above.

The reduction in colour temperature suggests that the degradation of the remote phosphor plates has consequences not only on the light extraction efficiency but also on the colour of the emitted light. Colour shifting of light is determined by variation of Chromaticity Coordinate (CIE $x$, $y$). The direction of the change in the Chromaticity Coordinates of both plates A and B during thermal ageing is illustrated in Fig. 5. As is illustrated in this graph, the light turns towards yellow region of the chromaticity diagram in remote phosphor A and B.

Fig. 6a shows the change in the intensity of the blue and yellow luminescence peaks during ageing time, obtained from the SPD of a white LED. Obviously the decrease in the intensity of the blue takes place with a faster kinetics compared to that of the yellow peak, which is in agreement with the fact that there is a shift of the chromatic coordinates of the analysed LEDs towards yellowish light. Fig. 6b depicts the ratio of the intensity of the yellow to the blue peak with ageing time.

3.2. Prediction of time-to-failure at lower temperatures

The real working temperature of LEDs depends on the working conditions (whether it is outdoor or indoor application). The LED
temperature in a sunny day in a hot summer at currents as high as 700 mA can reach 90 °C [9,10]. However in this paper the mentioned temperature is more an average over the whole year. Therefore, the kinetics of lumen depreciation to 30% of its initial value by using exponential luminous decay model and Arrhenius equation should be extrapolated to temperatures lower than 100 °C. This can be done using Eq. (1) by equating \( \Phi \) to 0.7, knowing that \( a \) can be obtained from Eq. (2). The values of \( a \), calculated for 40, 60 and 80 °C, are given in Table 2. As is seen the higher the temperature the faster the lumen depreciation.

Fig. 7 illustrates time-to-failure (70% lumen decay) of remote phosphors A and B, calculated at different temperatures. It is seen that at 40 °C the light output from lens A reduces to 70% of its initial value after 25 kh, while for remote phosphor B time-to-failure is 30 kh. This slight difference in lifetime of these two LED lens materials is due to the difference in the type of lens/substrate and amounts of phosphors in remote phosphors.

4. Discussions and conclusions

The excitation sources, used for phosphors in LEDs, are different from those of phosphors in conventional lighting. The excitation sources for phosphors in LEDs are UV (360–410 nm) or blue light (420–480 nm), whereas those for conventional inorganic phosphors in cathode-ray tubes (CRTs) or fluorescent lamps are electron beams or mercury gas (254 nm). Therefore, the phosphors in LEDs should have high absorption of UV or blue light. Conventional incandescent and fluorescent lamps rely on either heat or discharge of gases. In addition, they should also have high conversion efficiency, high stability against chemical, oxygen, carbon dioxide, and moisture, low thermal quenching, and appropriate emission colours. Different phosphor, such as orthosilicates [15,16], aluminates [17], and sulfides [17,18], have been used in white LEDs. However, some oxide-based phosphors can be excited efficiently by blue InGaN chip such as YAG:Ce and other garnet phosphors [17]. On the other hand, sulfide-based phosphors are thermally unstable and very sensitive to moisture, and their luminescence degrades significantly under ambient atmosphere without a protective coating layer [17]. For the time being, YAG:Ce is the best option and the most widely applied phosphor in white light LEDs because YAG:Ce has the best performance in terms of efficiency [18]. However, the main disadvantage of YAG:Ce is poor colour rendering index and serious thermal quenching of luminescence.

Temperature is a very significant controlling parameter in LED reliability. High temperature levels can damage the optical

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.63E-05</td>
<td>1.03E-05</td>
</tr>
<tr>
<td>60</td>
<td>3.19E-05</td>
<td>2.15E-05</td>
</tr>
<tr>
<td>80</td>
<td>5.79E-05</td>
<td>4.12E-05</td>
</tr>
</tbody>
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Fig. 6. (a) Variation of the integral of the blue and yellow luminescence for a sample B thermally-aged at 140 °C and (b) variation of the ratio of the intensity of the yellow to the blue peak measured on a white LED submitted to stress at 140 °C.

Fig. 7. Time-to-failure (70% lumen decay) of remote phosphor at different temperatures for sample (a) A and (b) B.
properties of the package and of the material used for the encapsulation [1–5]. This can result in a significant reduction in the luminous flux, emitted by the devices. Spectral power distribution (SPD) method is used to study the effect of high temperature stress test on the optical degradation of remote phosphor. The aim was to investigate the effect of temperature on the lumen depreciation of LED-based products and on their CCTs. It is shown that the degradation mechanisms is thermally activated and has activation energy of 0.33 eV (Fig. 3). As it is published already in our previous paper [14] the main reason of the decreasing intensity of blue light is the yellowing and discolouration of the lens. Comparing the results of this paper and our previously published paper, one can see that the activation energy of the yellowing reaction in commercial lens plates (substrate plates) are slightly higher than that of remote phosphor plates, inferring that the proposed activation energy for remote phosphor plates has contributions both from the worsening of substrate plates and the reduction in the phosphor conversion efficiency. In another words, presence of phosphor would accelerate the degradation kinetics or slightly decrease the activation energy.

It is clearly seen that the lower the depreciation rate, the better the performance a remote phosphor could have. The results also show that there is a direct relation between the temperature and kinetics of degradation. It is also shown that decreasing the transmittance of PC plates together with the reduction in phosphor efficiency limits the reliability of remote phosphor light sources and there is a colour shift towards yellow.

It is already reported that in normal operating conditions remote phosphor plate can reach temperature level of around 40 °C [13]. So, lumen depreciation up to 30% reduction is extrapolated to temperatures lower than 100 °C. It is shown that the lifetime, defined as 30% lumen depreciation at 40 °C, is around 35 k h, which is in agreement with previous works [14]. It is also shown that the agreement rate, $\alpha$, and the colour shifting for samples A and B are slightly different. This could be attributed to the differences in their chemical compositions and amount of phosphors.

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