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Thermoresponsive scattering coating for smart white LEDs

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Abstract: White light emitting diode (LED) systems, capable of lowering the color temperature of emitted light on dimming, have been reported in the literature. These systems all use multiple color LEDs and complex control circuitry. Here we present a novel responsive lighting system based on a single white light emitting LED and a thermoresponsive scattering coating. The coated LED automatically emits light of lower correlated color temperature (CCT) when the power is reduced. We also present results on the use of multiple phosphors in the white light LED allowing for the emission of warm white light in the range between 2900 K and 4150 K, and with a chromaticity complying with the ANSI standards (C78.377). This responsive warm white light LED-system with close-to-ideal emission characteristics is highly interesting for the lighting industry.

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1. Introduction

Driven by advances in R&D in the field of light-emitting diodes (LEDs) [1–3], the lighting industry is expected to shift towards intelligent lighting systems in the coming years [4]. Controlling lighting by external stimuli such as temperature or electrical current is paramount for the development of these smart systems. An often experienced shortcoming of LEDs is the deviation of the emitted light spectrum from that of incandescent lamps, e.g. being perceived as warm when dimmed and more neutral at higher intensities. In this paper we present a thermoresponsive coating that, when applied on an LED, mimics the intensity-dependent behavior of a incandescent lamp. The intensity-related heat generated by white-light LEDs controls the correlated color temperature (CCT) of the LED-emitted light.

Addressing the CCT of emitted light, for instance switching between warm white and cold white light has attracted much attention. In order to achieve this switching, most systems use multiple LEDs [5,6]. The main disadvantage of such devices, however, is the need for a control system necessary for addressing all the LEDs separately. The concept of a smart single white light LED, on the other hand, is more appealing as this system would not require such a control system. A white light emitting LED package contains a blue light emitting LED embedded in a matrix material containing a photoluminescent material (with the lighting nomenclature addressed as the phosphor). The phosphor converts a part of the blue light to light of another color [2,3,7,8]. The CCT of the light emitted by the LED package depends on the type of blue LED and the type and quantity of phosphor in the package. As depicted in Fig. 1, a scattering coating on top of such an LED package facilitates more of the aforementioned light conversion from blue to another color by redirecting the emitted light back to the phosphor where it can be absorbed and subsequently re-emitted at another wavelength [9]. If the applied coating can be switched between a scattering and a transparent state, the CCT of the emitted light can be addressed [Fig. 1].

Fig. 1. Schematic depiction of the LED-package with the thermo-responsive coating on top. The picture on the left shows the device at low temperature/current, where the coating is in a scattering state. In the picture on the right the current/temperature is high and the coating is thus transparent. The color of the coating in this schematic depiction shows the color of the light leaving the device. For the sake of clarity the coating is depicted out of contact with the LED package; it should be noted, however, that the coating is brought into optical and thermal contact with the LED package.

2. Results and discussion

Non-aligned smectic liquid crystalline materials are known to be scattering, and when heated above their transition temperature to the isotropic state these materials become transparent [10,11]. This makes liquid crystalline materials ideal candidates for a thermoresponsive scattering coating [9]. Due to their appealing properties we have chosen to explore siloxane based liquid crystals [12]. Siloxanes are well-known to be temperature stable which is highly desirable during continuous LED operation at elevated temperature as well as in the curing step at elevated temperature during the coating procedure [13,14]. Moreover, due to the siloxanes' flexible main chain these materials tend to show fast response on temperature changes [15]. In order to devise a smart coated LED a liquid crystalline compound was designed with the clearing temperature matching the surface temperature of an operational LED [16,17]. The exact chemical structure and the preparation of the siloxane compound are described in the appendix (Fig. 7). The optical properties of the coating as well as the CCT of the light emitted by a coated LED can then be tuned by addressing the electrical current powering the LED.

Differential Scanning Calorimetry (DSC) measurements of the siloxane compound in the temperature range from -50 to 150 °C show a total of four phases with the corresponding transitions at -14 , 14 and 48 °C (Fig. 7 in the appendix). Aided by Polarization Optical Microscopy (POM) and Small-Angle X-Ray Scattering (SAXS) measurements (Figs. 7 and 8 in the appendix, respectively) the phases have been identified as a glassy state, smectic C, smectic A and the isotropic phase from low to high temperature. For the aforementioned application in lighting we would like to exploit the transition between the scattering smectic A phase and the transparent isotropic state at 48 °C.

In the temperature range of interest to the application, the material is either liquid crystalline or in the liquid state which makes the material sticky and pliable. With the goal of making a more mechanically robust coating the siloxane compound was mixed with ethoxylated bisphenol A diacrylate (BPADA), which can be photopolymerized after application on the LED. The refractive index of BPADA, as reported by the supplier, is similar to the assumed refractive index of compound **3** in the isotropic phase [18] causing the coating to appear transparent when the siloxane compound is in the isotropic phase and scattering when in the smectic phase. A photopolymerized mixture of the siloxane and BPADA in a 1:2 weight ratio was examined by Scanning Electron Microscopy (SEM) revealing domains of the siloxane with an average size of 120 nm in a matrix of BPADA. The experimental details and the SEM images are available in the appendix [Fig. 9].

The coating was applied to a cold white light emitting LED and the CCT of the emitted light was measured at different currents. The results are displayed in Fig. 2(a).

Fig. 2. a) Correlated color temperature (CCT) of the light emitted by the LED at different currents and temperatures applied to a cold white light LED coated with the thermo-responsive coating. The black diamond symbols show the uncoated LEDs. The red squares display the first run of increasing (closed symbols) and decreasing (open symbols) the current. The red circles display the second run. b) Demonstrator consisting of a row of coated cold white LEDs on the left-hand side and a row of bare cold white LEDs on the right-hand side. The top picture shows the demonstrator operating at a low current (~ 20 mA/LED) and the bottom picture at a high current (~ 60 mA/LED). In order to capture the switching of CCT on camera a diffuser is placed on top of the demonstrator at a large distance (approximately 5 cm).

As can be seen in Fig. 2(a), the CCT remains relatively constant at approximately 5500 K in the current range 0-35 mA. Around 45 mA the CCT increases rapidly with current to reach approximately 20000 K. In order to clarify the results described in Fig. 2(a), the temperature of the LED surface was measured at different currents (see the appendix for the experimental details and Fig. 10 for the correlation between the applied current and the surface temperature of the LED) and is displayed in Fig. 2(a). The transition of the CCT from approximately 5500 K to 20000 K occurs when the surface of the LED reaches 50-55 °C, which is just above the clearing temperature of the liquid crystalline material. This indicates that the change in CCT is caused by the transition of the coating from a scattering to a transparent state. As anticipated in the presence of a scattering coating [Fig. 1], at low currents the CCT of the light emitted by a coated LED is lower than that for a bare LED [Fig. 2(a)]. At higher currents, however, the CCT of the light emitted by a coated LED is observed to be significantly higher than that for a bare LED, as evident from Fig. 2(a). This can be explained by the fact that the coating is in optical contact with the LED package. Without the coating, a part of the light is reflected back into the LED package, increasing the path length of blue LED-emitted light through the phosphor and effectively increasing the chance for absorption by the phosphor. When the coating is applied, it will cause outcoupling of the light from the LED-package and thereby reducing the path length of the blue LED-emitted light through the phosphor.

In order to show the effect of the coating on the light emitted by the LEDs a demonstrator was built on a circuit board comprising a row of coated cold white LEDs on one side and a row of bare cold white LEDs on the other side. Figure 2(b) shows the demonstrator at a low current (~ 20 mA/LED, top picture) and at a high current (~ 60 mA/LED, bottom picture). Since the intensity of the light was too high for the photcamera to capture the effect of the coating a diffuser was placed on top of the demonstrator at a large enough distance not to affect the CCT. In the pictures it can be clearly seen that the CCT of the light emitted by the bare LEDs is approximately the same at both currents, while the row of coated LEDs emits a more blueish light at high current and a more yellow light at a low current. These pictures support the results from the CCT measurement.

The resulting LED system emits light of CCT tunable in the range from 5500 K to 20000 K. Lighting applications mostly feature LEDs emitting white light with a CCT between 2700 K and 5000 K, even though the American National Standards Institute's (ANSI) standards for LEDs [19] describe systems up to 6500 K. Another requirement for white light LEDs, described in the same ANSI standard, is the tolerance in chromaticity with respect to black body emitters. These defined tolerances can be approximated by 7-steps MacAdam ellipses [20] around the black body line in CIE color space.

White light LEDs consisting of a blue LED and a single phosphor [7–9] emit light of chromaticity along the line in the CIE color space diagram connecting the chromaticity of the blue LED to that of the phosphor. For the cold white light LEDs this is shown in Fig. 3. The purple line connects the chromaticities of the blue LED and the yellow phosphor in question, the data points (at different currents) corresponding to uncoated LEDs are depicted in black and the data points (at different currents) corresponding to the coated LEDs are shown in blue. The data points from both the coated and the uncoated LEDs are found on the purple chromaticity line for this type of LED. Figure 3 also displays the 5-steps MacAdam ellipses around the black body line (curve shown in black). The MacAdam ellipses show the tolerance in chromaticity of the smart LED with respect to the standards in the LED industry [19]. The chromaticity of the coated cold white light LED complies with the standards at low current (and thus low CCT) but significantly deviates from the black body line at high current (and thus high CCT). Due to the limited overlap between the chromaticity line of the cold white light LED and the black body line as well as due to the operation in the CCT range between 5500 K and 20000 K, a white light LED design of different properties should be used in order to obtain a responsive LED system that meets the ANSI requirements.

Fig. 3. The CIE 1931 diagram depicting the chromaticities of the light emitted by an uncoated cold white light LED (black data points) and a coated cold white light LED (blue data points), measured at different currents (5–60 mA). The right figure is an expansion of the relevant part of the left figure. The purple line represents the connection between the value in color space of the blue LED and the phosphor in question. The black curve represents the ideal black body emitter. The ellipses depict 5-steps MacAdam ellipses around black body emitters at a certain temperature.

As can be seen in Fig. 3, the black body line is not represented by a straight line in the range between 2700 K and 5000 K in the color space. A consequence of this is that the chromaticity line connecting the chromaticity points of the blue LED and a single phosphor, both comprising a white light LED, will display only limited overlap with the curved black body line. In order to achieve greater overlap between the black body line and the chromaticity line of the LED, the LED chromaticity line should display a certain curvature as well. To this end we opted for the use of multiple phosphors in one LED package with one

phosphor absorbing only the light emitted by the blue LED and the other phosphor absorbing both the light emitted by the blue LED and the light emitted by the first phosphor. The absorption and emission spectra of the components of such an LED are depicted in Fig. 4.

Fig. 4. Absorption (dashed lines) and emission (solid lines) spectra of the yellow (green lines) and the red phosphor (red lines) and the blue LED (blue line) present in a warm white light LED.

The thermoresponsive coating was applied to a warm white light LED (the LED package comprises two phosphors and a blue LED and their absorption and emission spectra can be seen in Fig. 4). The CCT and the chromaticity values of the light emitted by the coated and uncoated LEDs were measured at different electrical currents [Fig. 5(a)]. The CCT of the light emitted by the uncoated LED was measured to be approximately 3200 K (black symbols in Fig. 5(a)) and was found to be independent of the current applied (5 – 70 mA). At low current (5 mA) the CCT of the light emitted by a coated LED was measured to be around 2900 K and increased with current (red symbols in Fig. 5(a)). At currents exceeding 75 mA the CCT becomes constant at approximately 4150 K. Multiple cycles of increasing and decreasing current were carried out with hardly any fatigue [Fig. 5(a)]. This behavior is in agreement with measurements on the coated cold white light LEDs.

Fig. 5. a) Correlated color temperature (CCT) of the light emitted by the LEDs at different currents and temperatures. The black symbols display the uncoated LED and the red symbols the coated LED. The red squares depict the first run of increasing (closed symbols) and decreasing (open symbols) the current. The circles display the second run. b) Demonstrator consisting of a row of coated warm white LEDs (bottom) and a row of bare warm white LEDs (top). The top picture shows the demonstrator operating at a low current (~ 20 mA/LED) and the bottom picture at a high current (~ 80 mA/LED). In order to capture the switching of CCT on camera a diffuser is placed on top of the demonstrator at a large distance (approximately 5 cm).

In order to show the effect of the coating on the light emitted by the warm LEDs a demonstrator was built on a circuit board comprising a row of coated cold white LEDs on one side and a row of bare cold white LEDs on the other side. Figure 5(b) shows the demonstrator at a low current (~ 20 mA/LED, top picture) and at a high current (~ 80 mA/LED, bottom picture). The pictures show that the CCT of the light emitted by the bare LEDs is approximately the same at both currents, while the row of coated LEDs emits a more blueish light at high current and a more yellow light at a low current. The changes in the light upon changing the current are more subtle than in the case of cold white LEDs [Fig. 2(b)]. These pictures [Fig. 5(b)] support the results from the CCT measurement.

The chromaticities of the coated (blue symbols) and the uncoated (black symbols) LED systems were measured as well and the results are displayed in Fig. 6 along with the 5-steps MacAdam ellipses around the black body line. The presence of two phosphors in the LED package positions the chromaticity line between the separate lines connecting the chromaticities of the blue LED and each phosphor separately. Figure 4 shows that the red phosphor not only absorbs the blue LED light but the light emitted by the yellow phosphor as well which in turn causes the resultant chromaticity line to deviate from linearity as it comes closer to the chromaticity line connecting the chromaticities of the blue LED and the red phosphor [Fig. 6]. This deviation from linearity also keeps the chromaticity of the coated LED light within 5-steps MacAdam ellipses from the black body line at all currents. This means that the investigated LED system obeys ANSI standards at all operational currents which is a prerequisite for any real-life applications [19]. Various samples of coated warm white LEDs were prepared (the relative amount of compound **3** and the polymerization temperature of the coating were varied) and the emitted light was analyzed in color space for different electrical currents (Fig. 11 in the appendix). Although the color temperature ranges differed slightly from sample to sample, all corresponding chromaticities followed the black body line within the 5-steps MacAdam ellipses at all measured currents.

Fig. 6. CIE 1931 diagram depicting the chromaticities of the light emitted by an uncoated (black) and a coated LED (blue), measured at different currents (5-90 mA). The right figure is an expansion of the relevant part of the left figure. The red and yellow lines represent the connections between the chromaticity of the blue LED and the two different phosphors. The black curve represents the ideal black body emitter. The ellipses depict 5-steps MacAdam ellipses around black body emitters at a certain temperature. Several CCT lines are shown as black dotted lines.

3. Conclusion

In this paper we present a novel smart LED system, based on single white emitting LEDs, able to adjust the CCT of the emitted light in response to electrical current. The smart LEDs are based on a thermoresponsive material, coated on top of LEDs, that uses the heat generated by the LED to switch between a scattering and a transparent state, in turn causing a change in the CCT of the light emitted by the device. Furthermore, by tuning the design of the LED we were able to develop an LED system that automatically changes the CCT of the emitted light in the range between 2900 and 4150 K upon changing the current applied to the LED. Due to the presence of two different phosphors in the LED package, the chromaticity of the light emitted by the LED system remains within the 5-steps MacAdam ellipses from the black body line at all currents and CCTs, rendering this LED system applicable in the lighting industry.

4. Materials and experimental procedures

LEDs: The cold and warm white light LEDs used were models NSSW156 and NSSW157 from the company Nichia, respectively.

Application of the coating on top of the LED: A 50% solution by weight of a 1:2 mixture by weight of compound **3** and ethoxylated bisphenol A diacrylate (Sigma-Aldrich) containing 1% Irgacure 184 (Ciba Specialty Chemicals) as photoinitiator in toluene was stirred at room temperature for 3 hours. A total of 2 μ l of this mixture was dropcast on top of an LED with a concave top surface. The coated LED was dried in air overnight to allow the solvent to evaporate and then the LED was stored in a nitrogen atmosphere at 60 $^{\circ}$ C for 10 minutes prior to photopolymerization for 10 minutes.

CCT measurements: The CCT and the chromaticities of the emitted light at different currents was measured using a Konica Minolta CL500A spectrometer in a confined black space. The current was applied using a Keithley SMU2400 power source.

Appendix

Preparation and chemical characterization of the siloxane compound 3

The synthetic precursor **2** was prepared following a literature procedure [21] and coupled with **1** in a Pt-catalyzed hydrosilylation [22] reaction to afford the desired block co-polymer **3** (Fig. 7).

Fig. 7. Synthesis of 6-((4-methoxyphenoxy)carbonyl)phenoxy)hexyl-methylsiloxane dimethylsiloxane copolymer (compound **3**).

6-((4-methoxyphenoxy)carbonyl)phenoxy)hexyl-methylsiloxane dimethylsiloxane copolymer (compound 3): Compound **2** (250 mg, 0.78 mmol) and dichloro(1,5-cyclooctadiene)platinum(II) (catalytic amount; on the tip of the spatula, Sigma-Aldrich) were mixed at room temperature and under an argon atmosphere and dissolved in dry toluene with stirring. Siloxane **1** (105 μ l, 0.11 mmol, Sigma-Aldrich), was added in one portion and the mixture was stirred at room temperature for 10 min and then heated to 65 °C (oil bath temperature). The reaction could be followed by ^1H -NMR or IR and was typically completed within 15 minutes. The solvent was evaporated and the residue was thoroughly and repeatedly rinsed with methanol. Alternatively, the residue after evaporation can be dissolved in a minimum amount of toluene and then precipitated by the addition of methanol. These procedures were repeated until there was no residual monomeric species observed by NMR. The crude product was obtained as a grey to black viscous liquid and was further purified by repeated filtrations over a plug of silica using toluene and ethyl acetate in different ratios to flush the silica. The product is obtained as a white viscous liquid at room temperature (206 mg, 63%). ^1H NMR (400 MHz, CDCl_3): δ /ppm: 8.09 (br, 12), 7.08 (br, 12), 6.90 (br, 24), 3.98 (br, 12), 3.80 (br, 18), 1.79 (br, 12), 1.40 (br, 36), 0.55 (br, 12), 0.09 (br, 58). ^{13}C NMR (100 MHz, CDCl_3): δ /ppm: 165.3, 163.5, 157.3, 144.6, 132.3, 122.6, 121.8, 114.6, 114.3, 68.4, 55.7, 33.2, 29.3, 25.9, 23.1, 17.7, 1.4, -0.1.

Physical characterization of the siloxane compound 3

The DSC measurements were performed at a heating/cooling rate of 10 °C min^{-1} and the microscope images were taken between cross-polarizers (Fig. 8).

Fig. 8. The DSC and POM investigation of the phase behavior of compound **3**.

The Wide-Angle X-Ray Scattering (WAXS) and Small-Angle X-Ray Scattering (SAXS) measurements were performed on the thermo-responsive material sealed in a 1 mm thick glass capillary inside a custom-built heating stage equipped with a permanent magnetic field (1 T) needed to induce uniaxial alignment. The sample was irradiated with a 1.54 Å GeniX-Cu ultra-low divergence source. The material was heated to the isotropic phase prior to being cooled with a rate of 10 °C min⁻¹. Diffraction patterns were recorded upon cooling on a Pilatus 300K silicon pixel detector (Fig. 9).

Fig. 9. The WAXS (left) and SAXS (right) images for the a) higher-temperature smectic phase and b) lower-temperature smectic phase (see Fig. 8).

Characterization of the coating

Scanning Electron Microscopy (SEM)

In order to study the morphology of the thermo-responsive coating, Scanning Electron Microscopy (SEM) images have been made. The coating was printed on a thin (1 mm) glass slide and photopolymerized at 60 °C in a nitrogen atmosphere for 10 minutes; the same conditions as used for the coatings on the LEDs. The sample was cooled after polymerization, using liquid nitrogen and the sample was broken. The siloxane liquid crystal (compound **3**) was removed by treatment with ethyl acetate and the sample was dried afterwards. The material was made conductive by sputtering gold on the sample for 30 seconds at a current of 65 mA. SEM images were taken from the side of the coating at 5 keV (Fig. 10).

Fig. 10. SEM images of the thermoresponsive coating at different magnifications: a) 700x, b) 13000x, c) 50000x.

Thermal characterization of the cold white LED

Surface temperature of the LED

The surface temperature of the cold white LED was measured using a thermocouple, which was taped to the surface (phosphor) of the LED. The current applied to the LED was set using a Keithley SMU2400 (Fig. 11).

Fig. 11. Surface temperature of the LED as function of the applied current.

Color space analysis of the light emitted by coated warm white LEDs

The light emitted by various samples of coated warm white LEDs was analyzed in color space (Fig. 12).

Fig. 12. CIE 1931 diagram depicting the chromaticities of the light emitted by various samples of coated warm white LEDs measured at different electrical currents (5-60 mA). The data points shown in different colors were obtained by polymerization at different temperatures. All coatings contained 50% of compound **3**. The black curve represents the ideal black body emitter. The ellipses depict 5-steps MacAdam ellipses around black body emitters at a certain temperature. Several CCT lines are shown as black dotted lines.

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