NJESR/December-2023/Volume-5/Issue-12 E-ISSN-2582-5836
DOI-10.53571/NJESR.2023.5.12.22-28

Advances In White Light Emission Materials: From Quantum Dots To Bismuth-Activated Phosphors

Anita Rai
Department of Chemistry
PPN PG College
Kanpur
Uttar Pradesh
India

(Received:26November2023/Revised:6December2023/Accepted:20December2023/Published:29December2023)

Abstract

White light emitting devices are widely used for domestic and commercial lighting; however, the commonly used InGaN blue LED coated with $Y_3Al_5O_{12}:Ce^{3+}$ phosphor produces light with strong blue emission and weak red components. This results in high correlated colour temperature (CCT > 5500 K), relatively low colour rendering index (CRI ≤ 85%), and possible eye strain during prolonged exposure. To improve color balance and achieve ideal CIE coordinates (0. 33 0. 33) a number of strategies have been investigated including rare-earth ion doping phosphor mixing and multi-LED configurations. However total success has not yet been attained. Recent developments focus on alternative strategies such as quantum dot based white light generation, graphite-like carbon nitride (g-C_3N_4) phosphors, and self-activated inorganic host materials that exhibit broad-band emission across the visible spectrum. In particular, materials containing defect states, oxygen vacancies, and charge transfer bands can produce wide spectral emissions suitable for white light generation. Bismuth-doped systems show significant promise due to their intrinsic broad-band luminescence and unique site-dependent emission properties, which help achieve balanced RGB emission. Compared to phosphors based on rare earth elements these materials are chemically strong thermally stable and possibly more affordable. Thus, the creation of bismuth-activated phosphors and self-activated host materials offers a viable and affordable route to the production of effective stable and aesthetically pleasing white light sources.

Keywords: White light emission; Bismuth-doped phosphors; Self-activated host materials; Quantum dots; Oxygen vacancies; Photoluminescence; CIE chromaticity coordinates; Solid-state lighting.

Introduction

The visible light coming from the sun consists of all colour radiations in which the colour red, green and blue (RGB) are the dominant one. The white light used in the houses and on streets, also called as Commercial white light, is produced using InGaN blue chip coated with yellow emitting $Y_3Al_5O_{12}:Ce^{3+}$. Though this light is very close to the white light coming from the Sun, however, it has weak red and intense blue colours. As a result, it has a high correlated colour temperature (CCT > 5500K), and relatively low colour rendering parameter (CRI <= 85%). The CIE coordinates are (0.30, 0.39). The ideal CIE coordinates are (0.33, 0.33). Moreover, a long time use causes headache and strain to eyes due to large intensity of blue colour. Attempts have been made by doping red emitting rear-earths / translation metal ions with Ce^{3+} such as Eu^{3+}, Sm^{3+}, Cr^{3+} etc. to compensate this red deficiency and also reducing the intensity of the blue chip. However, these efforts were not successful due to one or another reasons. People have also mixed rare-earth doped phosphors such as $Y_2O_3:Eu^{3+}$; $Y_2O_2S:Eu^{3+}$ with $Y_3Al_5O_{12}:Ce^{3+}$ to compensate this likeness but without any success.

Attempts have also been made to dope three rare-earths emitting red, green and blue colours in the same host to give white light. However, their intensity, excitation wavelength is a great problem to get perfect white light. Researchers have also used three independent LEDs coated with phosphors emitting green, red and blue colours and mix them to get white light. The current in the LEDs were varied to get white colour. As mentioned earlier the perfect white light has CIE coordinates (0.33, 0.33), however, in none of the above cases this value could be achieved of course the values are close to it. It is essential to mention that the source of white light should have high efficiency, long operational lifetime, high temperature tolerance and compact architecture. The white light emitted should be soothing to eyes. It should be warm white light (CCT < 5500K). Quantum yield is another important factor which is also taken in consideration for good white light source.

Several organic diets or polymers doped with different molecules all transition metal ions have also been tried. The disadvantages with these are that, in these cases, the pump wavelength are ultraviolet (UV) which is not good for eyes. It must be blue light or n-UV. The other problem with these are the low melting point, which reduces the lifetime. Several other new emerging white light emitting diodes (WLED) or quantum dots (QD-LED), perovskite LED (PE-LED) etc. are also being explored. Yet their practical use is still lacking by their intrinsic drawbacks such as their chemical instability, high production cost, mass production infeasibility, thermal instability, photo-degradation with time etc. Though the use of rare-earths are still in process it must be reduced to the extent possible due to their high cost. The high purity rare-earths are not available in India and they are imported from abroad. Moreover, in the light of the Prime

Minister's slogan “Swadeshi Movement”, Indian researchers working in this field are looking for alternative arrangements.

White Light from Quantum Dots

Quantum dots (QD) are the nano-size inorganic or organic molecules or materials which generally emit blue or n-UV light. White light from them can be achieved by carefully combining emission from quantum dots and the other material so that the overall emission covers the whole visible region (400-700 nm). The quantum dots exhibit size and composition dependent emission due to quantum confinement. Their peak position and overall emission can be tuned. The most widely adapted strategy uses a blue LED chip 450 nm to excite the red and green quantum dots embedded in a transparent matrix. A part of the blue light is absorbed by the two types of quantum dots and re-emitted at a longer wavelength (red and green regions) while the remaining blue light combines with the down-converted red and green emissions to generate white light. Core cell quantum dots such as cadmium selenide / zinc sulphide; indium phosphide / zinc sulphide are commonly used because of their high photoluminescence quantum yield (PLQI > 80-90%). Varying the quantum dot concentration and film thickness spectral emission can be optimised. Luk et al. have reported graphene quantum dots - agar on blue LED have white light emission with CIE coordinates (0.33, 0.38) CRI = 72 and CCT equivalent to 5532K. Luo et al. have shown white light emission in 10% graphene quantum dot spectral emission in 4-4 Bis (Carbazole=9Yl) biphenyl. Sekiya et al. developed white light in edge functionalized graphene quantum dots in dichloro-methane solutions.

White light emission can also be achieved using a single type of quantum dot that intrinsically produces broad band luminescence. In such systems white light arises from the coexistence of band edge emission and surface defect states recombination. Carbon quantum dots (CQD) are prominent example of this where multiple emissive centers generate a broad band spectrum covering blue to red emissions. Although single composition white quantum dots simplify the fabrication, it's long term stability is questionable compared to multi-quantum dot systems.

The quantum dot device is developed by integrating a thin layer of it on chip or remote phosphor architecture. In the on-chip design quantum dots are coated on the LED offering compact integration exposing them to higher thermal stress. In remote configurations the QD layer is kept away from the excitation source improving the thermal stability and operational lifetime. Encapsulation in silicon, epoxy or glass matrices are crucial to maintain high photoluminescence quantum yield and avoid photo-bleaching.

White Light Emission From Graphite Like Carbon Nitrides (g-C3N4)

g-C3N4 is a self-activated 2D semiconductor material which shows luminescent properties (450-650 nm) under suitable wavelength excitation. Recently Guo et al. developed a white light emitting phosphor by taking a combination of two self-activated phosphor g-C3N4 Cu3Cl(SR)2 material under 365 nm excitation. On 365 nm excitation the blue and the red emissions from the two combines and results a high quality white light with CRI (94.5) and quantum yield 20%.

White Light from Self Activated Host Materials

There are certain inorganic host materials which emit broad band emission in visible region on excitation with UV / n-UV / violet / blue light, such as vanadate, niobate, tantalate, molybdate, tungstate of some metals, zinc oxide, zirconium oxide, etc. The broad band emission covers whole visible region (400-700 nm) and therefore they emit white light. They are yet to be exploited. They can be synthesised easily using thermal or chemical methods. These oxides are highly thermally and chemically stable and environmentally resistive. On excitation, with charge transfer band (CTB) of phosphor materials they emit broad band. The broad band in them arise due to excitation of CTB band and defect levels due to oxygen vacancies (VO). The oxygen vacancies may be of two types (1) Interstitial oxygen vacancy (VOi) and (2) Surface oxygen vacancy (VOs). These oxygen vacancies result energy states in between valance band and conduction band. The defect states luminescence is influenced by several factors including phase composition, synthesis method, surface morphology, impurities, dopants etc. Generally, the oxygen vacancies are the main causes of defect levels, however, the reduction of cation, for example in ZrO2 the CTB (Zr4+O2-), Zr4+ is reduced to Zr3+ due electron trapping. This also gives it's own low lying energy state. The presence of defect levels have been studied by XPS, EPR and Photo-thermal spectroscopy. For example, Zn2V2O8 phosphor emits very intense white light (emission range 420-725 nm) on excitation with LED emitting at 405 nm. The emitted white light has CIE coordinates (0.33, 0.36) and internal quantum efficiency 36%. Bharat et al. developed self-luminescence Ca2KZn2(VO4)3 phosphor material which emits intense yellow-green light on excitation with n-UV chip. If this material is mixed with LiCaPO4:Eu2+ emitting blue light, it results white light. Hasegawa et al. synthesised LiCa3MV5O12 (where M is Zn, Mg) phosphor materials which emit bluish white light under 341 nm excitation. Ogi et al. synthesised Aluminium-boron-carbon-oxynitride (AlBCNO) single phosphor which emits white light with CIE coordinates (0.28, 0.35) and 25.1% quantum efficiency. Vaffuri et al. have reported Zinc-aluminium-borate (ZnAlB) white light emitting phosphor under n-UV (385 nm) excitation. MVO4, MNbO4 and MTaO4 (where M is La, Y, Gd, Ca, Sr, Ba etc.) phosphors emit broad emissions (380-600 nm) under 250-332 nm excitation. Doping of impurities in these shifts the emission wavelength towards the higher wavelength side which completes red emission. People have used bismuth as impurity in several cases. The Bi forms metal-metal charge transfer band (CTB) whose emission along with bismuth's own emission shifts the whole spectrum towards higher wavelength to give white light.

Broad Band Emission from Bismuth

Bismuth element shows a unique property of broad band emission from 380-600 nm due to 3p1 - 1s0 transition with maximum in blue region at 450 nm on excitation with 310 nm. The emission property strongly depends on the concentration of Bi. The peak shifts from blue to cyan region and the whole emission towards red at higher concentrations. Thus, Bi itself in a host emits white light on UV excitation. Bi3+ ions also transfer energy to activator / dopant to enhance their intensity. Thus, it behaves as sensitizer as well as activator. Bi3+ ion doped in a host also forms metal-metal charge transfer band (CTB) which also emits radiation in blue-green region. Interestingly in many reports it has been shown that Bi3+ has unique site dependent emission properties which can tune the emission as a whole and emit desirable white light. Very recently Ca3WO6 phosphor has been found to emit white light on UV excitation. In this case, the host tungstate emits blue emission whereas the Bi3+ 3p1 - 1s0 transition covers yellow-green region and the oxygen vacancies results red light. Thus, this completes the requirement of RGB to give white light. A similar thing is observed with bismuth doped metal vanadate, niobate, tantalate, molybdate, zirconate etc. and a thin layer of these coated on LED can be used to generate white light.

Conclusions

The commercial white light used in houses are not a complete replacement of sunlight. A continuous use for a long time causes strain to the eye and headache. The attempts to improve it using rare-earths / transition metals are not successful as of yet. Moreover, high purity rare-earths are very costly and not available in India. The self-activated host materials with bismuth may be a replacement of these. They are easy to develop in laboratory and much cheaper. Attempt must be made to develop white light sources using these.

References

1.Ye, S., Xiao, F., Pan, Y.X., Ma, Y.Y. and Zhang, Q.Y., 2010. Phosphors in phosphor-converted white light-emitting diodes: Recent advances in materials, techniques and properties. Materials Science and Engineering: R: Reports, 71(1), pp.1-34.

2.Berends, A.C., van de Haar, M.A. and Krames, M.R., 2020. YAG: Ce3+ phosphor: from icron-sized workhorse for general lighting to a bright future on the nanoscale. Chemical Reviews, 120(24), pp. 13461-13479.
3.Zhang, H., Zhang, H., Pan, A., Yang, B., He, L. and Wu, Y., 2021. Rare earth-free luminescent materials for WLEDs: recent progress and perspectives. Advanced Materials Technologies, 6(1), p.2000648.
4.Guo, H., Zhang, J., Ma, L., Chavez, J.L., Yin, L., Gao, H., Tang, Z. and Chen, W., 2015. A Non-rare-Earth ions self-activated white emitting phosphor under single excitation. Advanced Functional Materials, 25(44), pp.6833-6838.
5.Bharat, L.K., Jeon, S.K., Krishna, K.G. and Yu, J.S., 2017. Rare-earth free self-luminescent Ca2KZn2 (VO4) 3 phosphors for intense white light-emitting diodes. Scientific Reports, 7(1), p.42348.
6.Gaffuri, P, Salaun, M., Gautier-Luneau, I., Chadeyron, G., Potdevin, A., Rapenne, L., Appert, E., Consonni, V. and Ibanez, A., 2020. Rare-earth-free zinc aluminium borate white phosphors for LED lighting. Journal of Materials Chemistry C, 8(34), pp.11839-11849.
7.Hasegawa, T., Abe, Y., Koizumi, A., Ueda, T., Toda, K. and Sato, M., 2018. Bluish-white luminescence in rare-earth-free vanadate garnet phosphors: structural characterization of LiCa3MV3012 (M= Zn and Mg). Inorganic Chemistry, 57(2), pp.857-866.
8.Dang, P., Liu, D., Li, G., Al Kheraif, A.A. and Lin, J., 2020. Recent advances in bismuth ion-doped phosphor materials: structure design, tunable photoluminescence properties, and application in white LEDs. Advanced Optical Materials, 8(16), p. 1901993.
9.Luo, Z., Qi, G., Chen, K., Zou, M., Yuwen, L., Zhang, X., Huang, W. and Wang, L., 2016. Microwave-assisted preparation of white fluorescent graphene quantum dots as a novel phosphor for enhanced white-light-emitting diodes. Advanced Functional Materials, 26(16), pp.2739-2744.
10.Sekiya, R., Uemura, Y., Murakami, H. and Haino, T., 2014. White-light-emitting edge-functionalized graphene quantum dots. Angewandte Chemie International Edition, 53(22), pp.5619-5623.
11.Son, D.I., Kwon, B.W., Park, D.H., Seo, W.S., Yi, Y., Angadi, B., Lee, C.L. and Choi, W.K., 2012. Emissive ZnO-graphene quantum dots for white-light-emitting diodes. Nature nanotechnology, 7(7), pp.465-471.

12.He, P., Shi, Y., Meng, T., Yuan, T., Li, Y., Li, X., Zhang, Y., Fan, L. and Yang, S., 2020. Recent advances in white light-emitting diodes of carbon quantum dots. Nanoscale, 12(8), pp.4826-4832.