

The Color-Reversal Effect in Phosphors of WLED

Change of emission from green to blue in a Tb-activated phosphor is controlled by excitation with UV or VUV.

White-light-emitting diodes (WLED), compared with a traditional incandescent lamp and a mercury-vapor lamp, have attracted much attention because of their highly applicable value in our daily lives and wide feasibility in commercial products. The most common strategy to prepare a WLED is to combine blue InGaN chips with a $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) phosphor and to employ three light-emitting-diode (LED) chips, one each of red, green and blue light; the resulting LED partially converts the original blue radiation into its complementary yellow color, yielding cool white light. This cool white light generated from use of a single phosphor displays, however, a poor color rendition index (CRI) and highly correlated color temperature, which limit the application of WLED.^{1,2} It is difficult to obtain a large CRI with this approach, because the spectral components are inadequate to cover the entire visible region. A novel LED device containing red, green, and blue phosphors, was recently reported to achieve a CRI up to 90 on excitation with ultraviolet (UV) light. New phosphors with UV excitation bands are hence worthy of development.³

Oxonitridosilicates, $\text{Si}(\text{O},\text{N})_4$, are known to have excellent properties for application in the production of WLED. In this article, the study by Chun Che Lin (National Taiwan University), Ru-Shi Liu (National Taiwan University) *et al.* is reported that the photoluminescence of phosphor $\text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2:\text{Tb}$ is switchable between green and blue light on exciting the phosphor with UV and vacuum-UV (VUV) radiation; a configurational coordinate model is thus proposed for this observation of the color-reversal effect. According to this model, the dominant radiative decay results in a green emission under UV excitation in transitions from state $^5\text{D}_4$ to $^7\text{F}_j$ states in the Tb system. In contrast, blue emission via VUV excitation, comes from transitions from state $^5\text{D}_3$. This new mechanism is applicable to all Tb-doped phosphors and might be useful to adjust the optical properties against well-known cross-relaxation processes on varying the ratio of the green and blue contributions.

The emission spectrum of the Tb activator typically exhibits intense line systems in two typical sets from transitions $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 3-6$, 620-465 nm) and $^5\text{D}_3 \rightarrow ^7\text{F}_j$ ($j = 3-6$, 465-375 nm), emitting green and blue light, respectively, as Fig. 1 shows. In most cases, the green emission is dominant and the blue emission is weak, because the used excitation energy matches the energy gap between the $5d$ level and state $^5\text{D}_4$, which results in the depopulation of state $^5\text{D}_3$. Additionally, the cross-relaxation process between neighboring Tb activators results in considerable quenching from state $^5\text{D}_3$ to $^5\text{D}_4$. These two factors are responsible for the predominantly green emissions of numerous Tb-doped phosphors. In the present work,⁴ this unprecedented effect was further investigated on performing a color reversal between green and blue light through control of the relative contributions of both colors in a Tb-doped phosphor with UV and VUV excitation using synchrotron radiation.

A configurational coordinate model for the observation of this color-reversal effect is proposed. Phosphor $\text{Ba}_{2.89}\text{Si}_6\text{O}_{12}\text{N}_2:\text{Tb}_{0.11}$ is used to suppress the radiative decay from state $^5\text{D}_3$ to $^7\text{F}_{j=3-6}$ states. The green set remains the leading transition when the excitation energy matches the transition from the $5d$ level to state $^5\text{D}_4$, but the green transition gradually declines

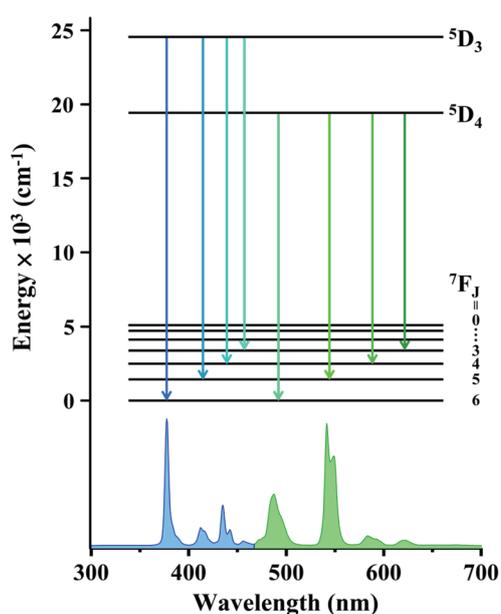
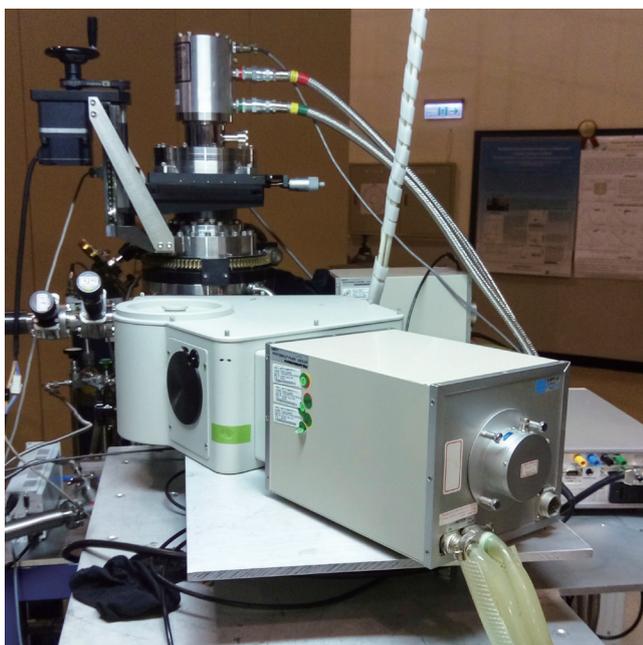


Fig. 1: PL spectrum of $\text{Ba}_{2.89}\text{Si}_6\text{O}_{12}\text{N}_2:\text{Tb}_{0.11}$ phosphor and corresponding energy levels (blue set: $^5\text{D}_{j=3}$ to $^7\text{F}_{j=3-6}$ transitions; green set: $^5\text{D}_{j=4}$ to $^7\text{F}_{j=3-6}$ transitions). [Reproduced from Ref. 4]

with energy of exciting radiation increasing from 254 to 147 nm; the blue transition concurrently grows in the opposite direction. Excitation energy increased from 254 to 211 nm leads to an enhanced probability of the excited electron to transfer to state 5D_3 on crossing the intersection between the $5d$ level and state 5D_3 . This mechanism is expected to be generally

applicable to Tb-doped phosphors and useful for the adjustment of the optical properties against well-known cross-relaxation processes on varying the ratio of the green and blue contributions. (Reported by Yu-Jong Wu)

This report features the work of Chun Che Lin, Ru-Shi Liu, and their co-workers published in Light-Sci. Appl. 5, e16066 (2016).



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- Photoluminescence
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Plasmon-Enhanced Catalysis: Design of Nanocatalysts with a Combination of Catalytic and Plasmonic Metals

A successful one-step strategy to grow monodispersed Au-Pd alloy and core-shell nanocrystals for electrochemical and plasmon-enhanced catalysis.

Pd is a catalysts widely studied for its notable catalytic properties.¹ The catalytic activity of Pd becomes further enhanced with electronic and strain effects through blending with other metal partners.² Incorporating a localized surface-plasmon resonance (LSPR) effect in the Pd-M bimetallic nanostructures is also a promising strategy. In a recent study of a Au-Pd alloy and core-shell nanoicosahedra with terraced shells reported by Chun-Hong Kuo (Institute of Chemistry, Academia Sinica) and his co-workers, they utilized the LSPR effect of Au to enhance the catalytic activity of Pd, whereas Au helps to convert radiant energy to electronic energy and hence stimulates the catalytic activity of Pd.³ A one-step strategy selectively

to synthesize alloy or core-shell Au-Pd icosahedral (IH) nanocrystals was developed in one pot.⁴ The procedure involved HAuCl_4 , H_2PdCl_4 , sodium citrate, CTAC and CTAB in a hydrothermal synthesis at 90 °C. The rate of reduction of HAuCl_4 and H_2PdCl_4 was tuned on varying the ratio $[\text{Br}^-]/[\text{Cl}^-]$, which plays the major role in a selective formation of alloy and core-shell IH nanocrystals. These nanocrystals display more than twice the activity for the electrooxidation of ethanol than commercial Pd catalysts, and they exhibit superior SPR-enhanced reduction of 4-nitrophenol. **Figures 1(a) and 1(d)** display the high-angle annular dark-field (HAADF) images of nanocrystals with a scanning transmission electron microscope (STEM), prepared