

白光发光二极管用单体白色荧光粉的研究进展

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摘 要: 近年来, 单体白色荧光粉, 尤其是基于能量传递原理构建的白色荧光粉成为发光领域的研究热点。简要评述了近 5 年紫外-近紫外基白光 LEDs 用单体白色荧光粉的研究进展。重点阐述了单掺杂体系, 以及基于能量传递原理构建的双掺杂及三掺杂等单体白色荧光粉的研究结果与最新进展; 同时, 分析和预测了该类材料的研究前景及发展方向。

关键词: 白光发光二极管; 单体白色荧光粉; 能量传递; 掺杂

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Recent Development on Single-phase White Emitting Phosphors for White LEDs

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Abstract: Recent work have focused on the development of single white emitting phosphor, in particular, based on the principle of energy transfer. This review represents the development on single white phosphor for white light emitting diodes during the past 5 years. The topic emphasized the co-activated and tri-activated white emitting phosphors obtained by the energy transfer from the sensitizer to acceptor. Moreover, the research prospect and future development of this material were discussed.

Keywords: white light emitting diode; single-phase white emitting phosphors; energy transfer; doping

目前, 商业化的白光发光二极管(LEDs)主要通过“蓝光 LED 芯片+YAG:Ce³⁺黄色荧光粉”的方式来发射白色光。虽然这种器件的发光效率很高(最新的记录已经突破 300 lm/W, 远高于传统白炽灯(约 16 lm/W)和日光灯(约 70 lm/W)的发光效率), 但是,

YAG:Ce³⁺的红色发光成分较少, 造成这种白光 LEDs 的色温较高、显色性较差^[1]。近年来, 随着近紫外芯片(370~410 nm)的发展, 利用“近紫外 LED 芯片+三基色荧光粉”获取白光 LEDs^[2], 能够有效地避免“蓝光 LED 芯片+YAG:Ce³⁺黄色荧光粉”型

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白光 LEDs 存在的缺陷。但是, 采用“三基色荧光粉”作为白光 LEDs 的主体材料时, 荧光粉混合物之间存在颜色再吸收和配比调控等问题。若以“单基质白色荧光粉”作为主体材料, 则能有效地避免这类问题, 提升白光的重现性, 因此, 单基质白色荧光粉成为白光 LEDs 用荧光粉领域的研究热点^[3]。研究人员不断总结和预测该方向的发展前景, 如李盼来等^[4]总结了硅酸盐、磷酸盐等白色荧光粉的发展进程, 同时展望了该方向的发展前景, 认为改进硅酸盐材料的合成条件, 进而得到纯相的材料将是一个研究重点。史强等^[5]阐述了焦硅酸盐及磷酸盐等单体白色荧光粉的发展现状。谢晔等^[6]重点总结了 $\text{Eu}^{2+}/\text{Mn}^{2+}$ 掺杂焦硅酸盐等白色荧光粉的发展情况。此外, 刘杰等^[7]较详细地分析和总结了双掺杂体系的发展情况, 预测了该方向的前景, 同时认为改善白色荧光粉在红色区域的发射强度, 以及控制材料的光色漂移等, 都是该方向的研究重点。

在上述实验研究结果和综述的基础上, 主要针对近 5 年来国内外白光 LEDs 用单体白色荧光粉的发展现状, 阐述单掺杂、双掺杂及三掺杂单体白色荧光粉的研究结果, 讨论其存在的问题, 并展望其未来的发展趋势。

1 单掺杂体系

目前, 总体而言, 可以通过两种方式在单掺杂体系中实现白光发射。一种方式是激活离子本身的跃迁发射位于红、绿(黄绿)和蓝色区域, 如, Dy^{3+} 在基质中主要表现其 ${}^4\text{F}_{9/2}-{}^6\text{H}_{15/2}$ (蓝)、 ${}^4\text{F}_{9/2}-{}^6\text{H}_{13/2}$ (黄绿)和 ${}^4\text{F}_{9/2}-{}^6\text{H}_{11/2}$ (红)特征跃迁发射, 当 3 个发射峰的强度, 尤其是蓝、黄发射峰强度合适时, 材料即可发射白色光^[8]。但是, Dy^{3+} 的发射为稀土 $4f-4f$ 跃迁, 谱带较窄, 光谱不饱满, 该材料用于照明时, 显色指数低, 因此, 必须改善其发光性能, 才能增强其在白光 LEDs 领域的应用价值^[9]。此外, 相对而言, Dy^{3+} 掺杂的材料余辉时间较长, 限制了该类材料在白光 LEDs 领域的应用。除了上述 Dy^{3+} 激活的一些单基质白色荧光粉, 还有其它的一些材料也能呈现白光发射, 2011 年, Hao 等^[10]采用 Eu^{3+} 激活 CaSc_2O_4 材料, 基于 Eu^{3+} 的特征发射, 可以使材料在红、绿和蓝各个区域出现多个锐峰, 使得材料整体发射白色光。Xu 等^[11]采用 Eu^{3+} 激活 $\text{Ca}_2(\text{Ca}_{2x/3}\text{In}_{1-x}\text{Nb}_{x/3})\text{NbO}_6$ 也获得了白色发光材

料。此外, Zhang 等^[12]通过调控 Eu^{3+} 的掺杂量, 在 $\text{BaCa}_2\text{In}_6\text{O}_{12}$ 中实现了白光发射, 测量了材料的温度光谱, 并将其与 395 nm 近紫外芯片组合, 获得了白光 LEDs, 相关光谱如图 1 所示。

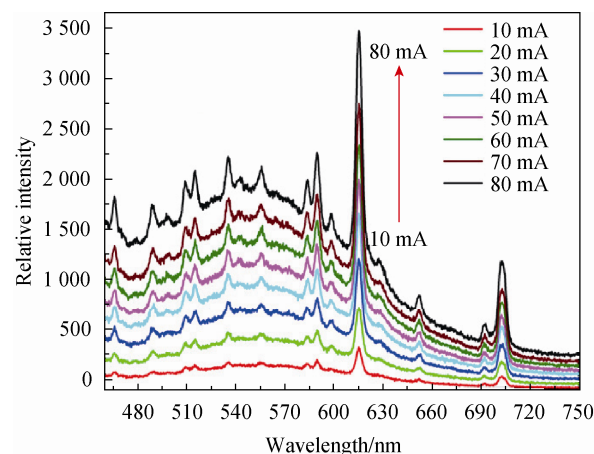


图 1 不同驱动电流下 GaN LED + $\text{BaCa}_2\text{In}_6\text{O}_{12}:\text{Eu}^{3+}$ 型白光 LEDs 的发光光谱^[12]

Fig. 1 Luminescence spectra of GaN LED + $\text{BaCa}_2\text{In}_6\text{O}_{12}:\text{Eu}^{3+}$ phosphor under different forward bias currents^[12]

通常, 发光材料由基质和激活剂构成, 基质组成对激活剂发光的影响是决定性的, 基质组成的任何变化都可能改变能量传递、晶场强度和共价性, 最终影响材料的发光效率和发光特性, 因此, 改变基质组分控制材料的发光特性, 进而获得白色光, 即成为另一种获取白色发光的方式。通过基质中都含有碱土金属阳离子 $\text{M}(\text{M}=\text{Mg}, \text{Ca}, \text{Sr}, \text{Ba})$, 其容易被 Eu^{2+} 或 Ce^{3+} 取代, 产生蓝和绿(黄绿)色发射带, 如果 Eu^{2+} 或 Ce^{3+} 取代 M^{2+} 占据基体中 2 个阳离子格位时, 将会产生峰值位于不同区域的宽带发射, 此时, 改变碱土化合物的组成, 就可以调节 Eu^{2+} 或 Ce^{3+} 的发射峰位置, 进而实现白色发光^[13-14]。如 Yu 等^[15]通过调控 Ba^{2+} 、 Sr^{2+} 的配比, 使 Eu^{2+} 在 $(\text{Ba}, \text{Sr})_{10}(\text{PO}_4)_4(\text{SiO}_4)_2$ 中实现了白色发光, 如图 2 所示。

Su 等^[16]通过调控基质组分, 也在 $\text{K}(\text{Ba}, \text{Sr}, \text{Ca})\text{BP}_2\text{O}_8:\text{Eu}^{2+}$ 中获得了白色光。总体而言, 通过调控基质组分, 可以使 Ce^{3+} 或 Eu^{2+} 在单基质中产生白色光, 但是, 由于 Ce^{3+} 或 Eu^{2+} 的发射峰多处于蓝和黄(绿)色区域, 使得该种白光与“ InGaN 芯片 + YAG:Ce 黄色荧光粉”模式白光存在类似的缺陷, 即缺乏红色发光成分, 造成白光 LEDs 的显色指数较低。因此, 只有提高材料在红色区域的发射强度, 才能改善材料的显色性。

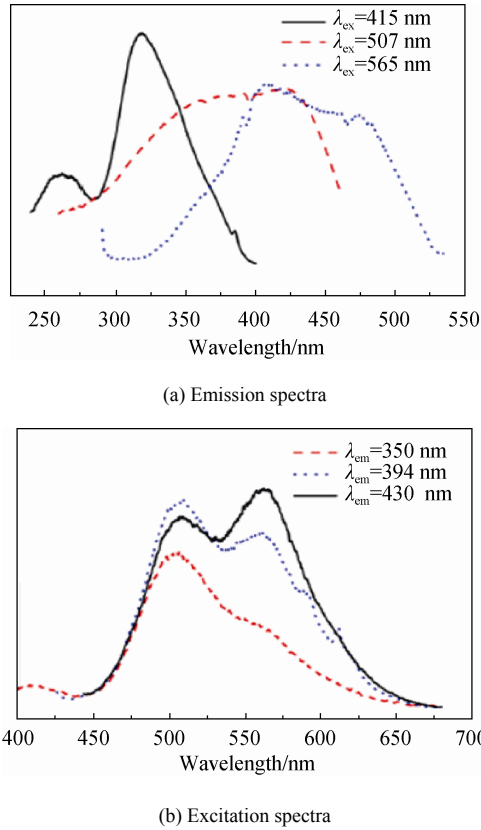


图2 (Ba,Sr)₁₀(PO₄)₄(SiO₄)₂:Eu²⁺的激发光谱与发射光谱^[15]
Fig. 2 Excitation and emission spectra of (Ba,Sr)₁₀(PO₄)₄(SiO₄)₂:Eu²⁺^[15]

2 双掺杂体系

2.1 Eu²⁺/Mn²⁺双掺杂体系

由于发光材料由基质和激活剂构成，就激活离子而言，Eu²⁺是一种重要的激活离子；对于基质而言，多含有碱土金属离子，由于碱土金属离子与Eu²⁺离子半径相似的特征使得Eu²⁺在这类基质中更加稳定，也更容易进入晶体格位，因此，表现出了极为活跃的应用特性。Eu²⁺的电子构型为4f⁷5s²5p⁶5d⁰，具有5d-4f发射，而5d轨道受晶场的影响较大，基于此，Eu²⁺在不同的基质组分及晶体环境中会发射不同颜色的光^[17]，如蓝、绿(黄绿)和红色光。过渡族元素Mn²⁺的3d电子组态中的⁴T₁(⁴G) - ⁶A₁(⁶S)是自旋禁阻的，对紫外吸收很弱，在不同的基质中，Mn²⁺的荧光性质差别较大。通常情况下，Mn²⁺取代碱土金属，如Ca²⁺、Sr²⁺和Ba²⁺等格位后，晶格畸变较大，不利于Mn²⁺的直接激发，很难实现直接发光^[18]。然而，若引入Eu²⁺作为共激活剂，Eu²⁺的发射光谱覆盖Mn²⁺的激发光谱，则构成了共振传递的必要条件，即施主的发射光谱和受主的激发光谱存在重叠，此时，可能存在能量施主和受主间的共振传递。基

于这种共振能量传递机理，通过Eu²⁺/Mn²⁺共激活基质化合物，即可获得呈白光发射的单体荧光粉。通过分析发现，以Eu²⁺/Mn²⁺作为激活离子，获取白色荧光粉的基质体系，主要涉及磷酸盐(卤磷酸盐)及硅酸盐(卤硅酸盐)，少量研究工作涉及硼酸盐、铝酸盐等^[19-29]。

早期，白色荧光粉主要是以硅酸盐作为基质来获得，主要的基质体系为焦硅酸盐和含镁正硅酸盐等，如(Ca, Sr, Ba)₃MgSi₂O₈^[30-32]，虽然这类材料的发光性能较好，但是，其合成条件较苛刻，物相结构较复杂，鉴于此，研究者尝试改进硅酸盐材料的性能^[33-35]。如尤洪鹏等^[36]在正硅酸盐Ba_{1.3}Ca_{0.7}SiO₄:Eu²⁺,Mn²⁺中实现了白色发射。而Maio等^[37]同样以Eu²⁺/Mn²⁺掺杂Ba_{1.55}Ca_{0.45}SiO₄材料，通过调控激活剂掺杂量，结合调控基质组分的配比，有效地调控了材料的光谱分布，进而获得了白色荧光粉，其发射光谱如图3所示。

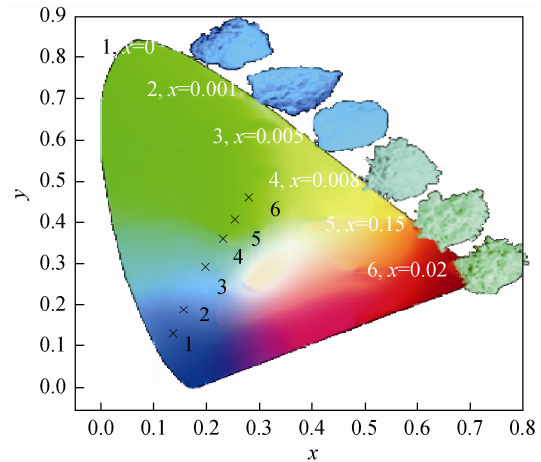


图3 Ca_{1.59}Sr_{0.35-x}SiO₄:0.03Li⁺,xEu²⁺ (x=0-0.20)的色坐标^[37]
Fig. 3 CIE chromaticity diagram and photographs of Ca_{1.59}Sr_{0.35-x}SiO₄:0.03Li⁺,xEu²⁺ (x=0-0.20)^[37]

目前，总体而言，单基质白色荧光粉的研究重点主要集中于磷酸盐体系，而磷酸盐的研究重点是A₃Ln(PO₄)₃(A=Ba, Sr等; Ln=Y, Gd, Lu等)、硅铈石结构的M₃^IM^{II}(PO₄)₃(M^I=Ca, Sr, Ba, Pb; M^{II}=La, Y, Sc, Bi, Tb, In等)、卤磷酸盐及其他一些正磷酸盐体系等^[38-44]。Guo等^[45]先后报道了多种Eu²⁺/Mn²⁺掺杂的硅铈石和A₃Ln(PO₄)₃等白色荧光粉，2012年报道了Eu²⁺/Mn²⁺掺杂的Sr₃Lu(PO₄)₃的材料白色发光特性，令人兴奋的是，该材料的色温位于暖白区域，加速了材料在室内照明领域的发展进程；而后利用Eu²⁺/Mn²⁺掺杂Sr₃Sc(PO₄)₃材

料, 同样获得了暖白发光材料, 在 355 nm 近紫外光激发下, 该材料的发射光谱覆盖 400~750 nm, 通过调控 Eu^{2+} 、 Mn^{2+} 配比, 材料表现出了很好的暖白发光特征, 其发射光谱如图 4 所示^[46]。

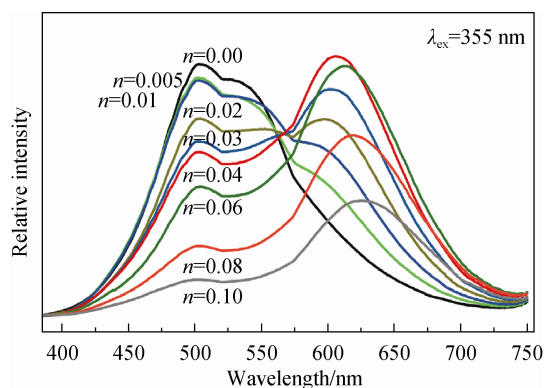


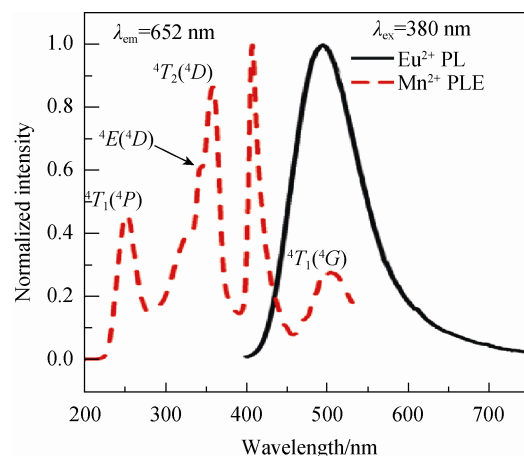
图 4 $\text{Sr}_3\text{Sc}(\text{PO}_4)_3:0.05\text{Eu}^{2+}, n\text{Mn}^{2+}$ 的发射光谱^[46]
Fig. 4 Emission spectra of $\text{Sr}_3\text{Sc}(\text{PO}_4)_3:0.05\text{Eu}^{2+}, n\text{Mn}^{2+}$ ^[46]

2014 年, Li 等^[47]报道了一种颜色可调型 $\text{Ca}_9\text{Mg}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$ 单基质白色荧光粉, 该材料具有较好的温度特性, 将材料与近紫外芯片组合, 所得器件的色坐标位于白色区域, 说明材料在单基质白色荧光粉领域有很好的发展前景。Liu 等^[48]报道了 $\text{Eu}^{2+}/\text{Mn}^{2+}$ 掺杂的正磷酸盐 $\text{KCaY}(\text{PO}_4)_2$ 材料, 通过调控 Eu^{2+} 、 Mn^{2+} 配比, 可以调控材料的发光颜色, 最终获得色坐标为(0.3001, 0.3102)的白色光。Huang 等^[49]报道 $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}, \text{Mn}^{2+}$ 白色荧光粉, 同样表现出了很好的应用前景, 其光谱如图 5 所示。

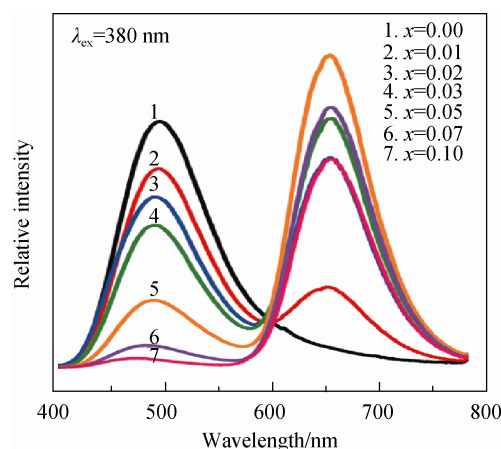
同期, 除了硅酸盐和磷酸盐体系获得了研究者的关注以外, 其他的一些 $\text{Eu}^{2+}/\text{Mn}^{2+}$ 掺杂的体系也得到了发展^[50-51]。Li 等^[52]报道了 $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}, \text{Mn}^{2+}$ 材料, 调控激活剂的用量及配比时, 可以改变材料的发光颜色, 进而获得白色光。总体而言, 这类材料是利用 Eu^{2+} 、 Mn^{2+} 间的能量传递, 通过调控 Mn^{2+} 的用量来改变 Eu^{2+} 、 Mn^{2+} 发射峰的强度比, 当配比合适时, 材料整体能发射白色光。

2.2 其他双掺杂体系

基于掺杂离子之间的能量传递, $\text{Ce}^{3+}/\text{Mn}^{2+}$ 、 $\text{Ce}^{3+}/\text{Eu}^{2+}$ 、 $\text{Ce}^{3+}/\text{Dy}^{3+}$ 、 $\text{Tm}^{3+}/\text{Eu}^{3+}$ 、 $\text{Dy}^{3+}/\text{Tm}^{3+}$ 、 $\text{Eu}^{3+}/\text{Bi}^{3+}$ 等掺杂的一些体系, 也可以发射白色光^[53-62]。王育华等^[63]报道了一种 $\text{Ce}^{3+}/\text{Mn}^{2+}$ 掺杂的 $\text{CaSr}_2\text{Al}_2\text{O}_6$ 白色发光材料, 并研究了 Ce^{3+} 、 Mn^{2+} 间



(a) Dotted line is excitation spectrum of $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Mn}^{2+}$, solid line is emission spectrum of $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}$



(b) Emission spectra of $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}, x\text{Mn}^{2+}$

图 5 $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Mn}^{2+}$ 的激发光谱、 $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}$ 和 $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}, x\text{Mn}^{2+}$ 的发射光谱^[49]
Fig. 5 Excitation spectrum of $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Mn}^{2+}$ and emission spectrum of $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}$ and $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}, x\text{Mn}^{2+}$ ^[49]

的能量传递过程及机理。Chen 等依据 Eu^{2+} 、 Ce^{3+} 分别在 $\text{Li}_2\text{SrSiO}_4$ 中分别发射黄、蓝光的特性, 结合“蓝光 LED+黄色荧光粉”构成白光 LEDs 的传统白光实现方式, 利用 Ce^{3+} 、 Eu^{2+} 间的能量传递, 实现了白光发射。通常 Dy^{3+} 的 $4\text{F}_{9/2}-6\text{H}_{15/2}$ 和 $4\text{F}_{9/2}-6\text{H}_{13/2}$ 跃迁位于蓝和黄色区域, 如果二者比例合适, 可以实现单基质白色发光, 但是, Dy^{3+} 在大多数基质中的发射相对较弱。鉴于此, 研究人员利用 Ce^{3+} 对 Dy^{3+} 的能量传递, 有效地提高了 $\text{Ca}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6:\text{Dy}^{3+}$ 的白色发光特征^[64], 研究结果如图 6 所示。从上述的研究可以得出, 调控激活离子配比及用量, 可以使一些体系发射白色光, 但是, 总体而言这种类型的基质体系较少。

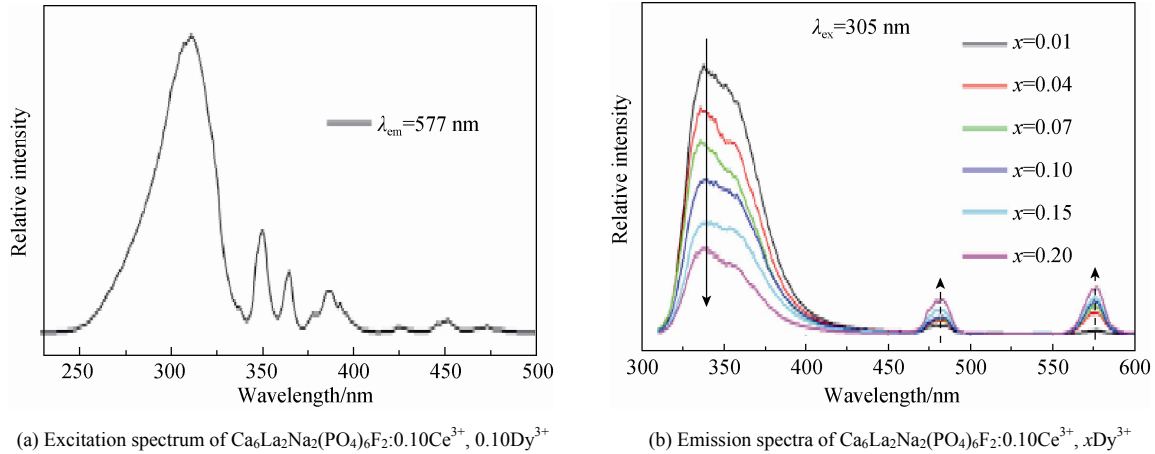


图 6 $\text{Ca}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2:0.10\text{Ce}^{3+}, 0.10\text{Dy}^{3+}$ 的激发光谱和 $\text{Ca}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2:0.10\text{Ce}^{3+}, x\text{Dy}^{3+}$ 的发射光谱($x=0.01\sim 0.20$)^[64]
 Fig. 6 Excitation spectrum of $\text{Ca}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2:0.10\text{Ce}^{3+}, 0.10\text{Dy}^{3+}$ and emission spectra of $\text{Ca}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2:0.10\text{Ce}^{3+}, x\text{Dy}^{3+}$ ($x=0.01\sim 0.20$)^[64]

3 三掺杂体系

从以上双掺杂体系可以看出, 在这些体系中, Eu^{2+} 或 Ce^{3+} 发射源于 $5d-4f$ 跃迁的蓝色光(对于 Ce^{3+} 和 Eu^{2+} 掺杂的体系, 一般来说, Ce^{3+} 发射紫光或蓝光, 而 Eu^{2+} 发射黄或黄绿色光), Mn^{2+} 发射源于 $\text{Mn}^{2+}(3d^5)$ 电子的激发态 4T_1 到基态 6A_1 跃迁产生的橙红或红色光, Tb^{3+} 发射对应 ${}^5D_4-{}^7F_5$ 跃迁的绿(黄绿)色光(图 7)。若 Mn^{2+} 或 Tb^{3+} 的激发光谱与 Ce^{3+} 或 Eu^{2+} 的发射光谱有明显的重叠, 则满足共振能量转移的必要条件, 此时, 激活离子间多存在能量转移现象。利用这种方式能够调控材料的发光颜色, 当二者比例合适时, 即可发射白色光。虽然合理地调整激活离子掺杂量及配比可以获得白色荧光粉, 但是, 这类材料在光谱分布上仍然存在一些缺陷, 如 $\text{Eu}^{2+}/\text{Mn}^{2+}$ 或 $\text{Ce}^{3+}/\text{Mn}^{2+}$ 掺杂的体系在绿色区域的发射相对较弱; 而 $\text{Ce}^{3+}/\text{Eu}^{2+}$ 或 $\text{Ce}^{3+}/\text{Tb}^{3+}$ 掺杂体系的红色发光成分较少, 这势必影响材料的整体发光效果。

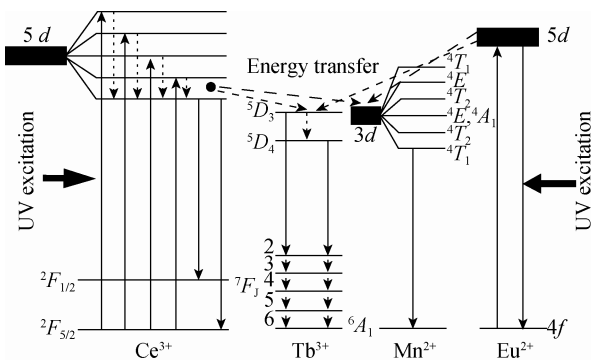


图 7 Eu^{2+} 和 Ce^{3+} 到 Tb^{3+} 和 Mn^{2+} 的能量传递示意图
 Fig. 7 Schematic diagram of energy transfers from Eu^{2+} and Ce^{3+} to Tb^{3+} and Mn^{2+}

基于双掺杂体系存在的一些问题, 研究者尝试用三掺杂的方式解决。三掺杂材料可以获得红、绿和蓝色区域均有较强发射的白色荧光粉, 这样可以避免材料发射光谱中的颜色缺失。这类体系的激活剂多是 $\text{Eu}^{2+}/\text{Tb}^{3+}/\text{Mn}^{2+}$ 和 $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Mn}^{2+}$, 这些激活剂之间可以依据图 7 所提供的方式实现能量传递, 从而可以在单基质中实现白色发光^[65-76]。Wang 等^[77] 以 $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Mn}^{2+}$ 激活 $\text{BaMg}_2(\text{PO}_4)_2$ (BMP), 通过 $\text{Ce}^{3+}-\text{Mn}^{2+}$ 和 Tb^{3+} 的能量转移, 获得了白色光, 如图 8 所示。

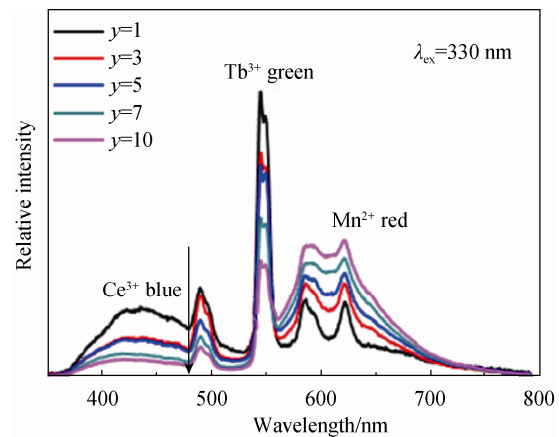


图 8 $\text{BaMg}_2(\text{PO}_4)_2:3\%\text{Ce}^{3+}, y\%\text{Mn}^{2+}, 3\%\text{Tb}^{3+}$ ($y=1\sim 10$) 的发射光谱^[77]
 Fig. 8 Emission spectra of $\text{BaMg}_2(\text{PO}_4)_2(\text{BMP}):3\%\text{Ce}^{3+}, y\%\text{Mn}^{2+}, 3\%\text{Tb}^{3+}$ ($y=1\sim 10$)^[77]

Liu 等^[78] 制备了 $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Mn}^{2+}$ 掺杂的 $\text{Sr}_{3.5}\text{Y}_{6.5}\text{O}_2(\text{PO}_4)_{1.5}(\text{SiO}_4)_{4.5}$ 白色发光粉, 并细致地研究了 $\text{Ce}^{3+}-\text{Tb}^{3+}$ 以及 $\text{Ce}^{3+}-\text{Mn}^{2+}$ 之间的能量传递过程及机理。Lü 等^[79] 以 $\text{Eu}^{2+}/\text{Tb}^{3+}/\text{Mn}^{2+}$ 激活

BaMg₂Al₆Si₉O₃₀ 材料，通过调整 Tb³⁺、Mn²⁺用量，获得了显色指数及色稳定性较好的白色荧光粉，结果如图 9 所示。Li 等^[80-83]用 Ce³⁺/Tb³⁺/Mn²⁺分别激活 Mg₂Y₈(SiO₄)₆O₂、Ca₃Gd₇(PO₄)(SiO₄)₅O₂、Ca₄Y₆(SiO₄)₆O 及 Ca₅(PO₄)₂SiO₄ 等，通过 Ce³⁺-Tb³⁺(Mn²⁺)的能量转移，也获得了白色或颜色可调型材料。

总体而言，在上述体系中，Ce³⁺(Eu²⁺)、Tb³⁺和 Mn²⁺的发射峰分别位于蓝、绿(黄绿)和红(橙红)色区域，通过调整激活剂用量及配比，可以较理想地控制各区域发射峰的强度，进而获得白光。以外，还有一些其他的三掺杂体系，图 10 为利用 Dy³⁺/Tm³⁺/Eu³⁺间的能量传递，来实现白色发光的方式^[84]。

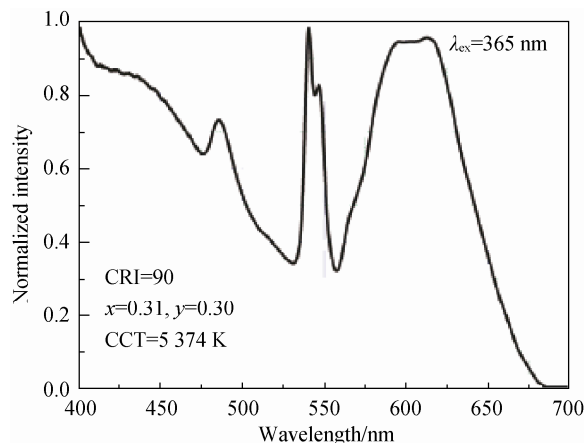
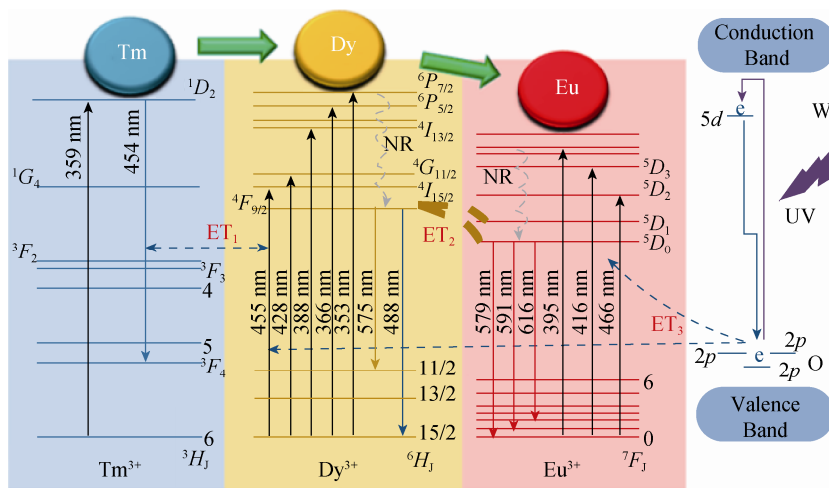


图 9 BaMg₂Al₆Si₉O₃₀:0.04Eu²⁺, 0.08Tb³⁺, 0.16Mn²⁺的发射光谱^[79]

Fig. 9 Emission spectrum of BaMg₂Al₆Si₉O₃₀:0.04Eu²⁺, 0.08Tb³⁺, 0.16Mn²⁺^[79]

CRI—Color rendering index; CCT—Correlated color temperature.



NR—Nonradiative; ET—Energy transfer; UV—Ultraviolet.

图 10 NaGd(WO₄)₂:Tm³⁺, Dy³⁺, Eu³⁺中激活离子 Tm³⁺, Dy³⁺和 Eu³⁺的激发与发射机理及其能量传递过程示意图^[84]

Fig. 10 Schematic energy-level diagram of excitation and emission mechanism and energy transfer from Tm³⁺ to Dy³⁺ and Eu³⁺ of NaGd(WO₄)₂:Tm³⁺, Dy³⁺, Eu³⁺^[84]

4 结论与展望

白光 LEDs 是一种全新的照明光源，白光 LEDs 用荧光粉亦是该方向的研究重点。目前，商业化的“蓝光 LED 芯片+黄色荧光粉”型白光 LEDs 存在色温较高，显色性较差等问题，同时，当前常用的几类荧光粉，如 YAG:Ce³⁺、硅酸盐和氮化物等，其制备温度很高，物相和结构确认比较困难，不容易制备纯相材料。近年来，随着紫外-近紫外芯片的发展，利用紫外-近紫外芯片+三基色荧光粉及单体白色荧光粉获得白光 LEDs。鉴于三基色型白光 LEDs 存在颜色再吸收和配比调控问题，单体白色荧光粉

成为发光领域的研究热点。总体而言，已报道的双掺杂白色荧光粉在光谱分布上仍然存在一些缺陷，如 Eu²⁺/Mn²⁺或 Ce³⁺/Mn²⁺掺杂的体系在绿色区域的发射相对较弱；而 Ce³⁺/Eu²⁺或 Ce³⁺/Tb³⁺掺杂体系的红色发光成分较少，这势必影响材料的整体发光效果。通常情况下，引入多种激活离子可以补偿这种光谱缺失，但是，这样的方式一定程度上可能会降低体系的发光强度及掺杂离子间的能量转移效率。因此，在不影响双掺杂体系发光效率等的情况下，如何改善双掺杂体系光谱分布的缺失问题，以及如何获得满足不同场合需求的白色荧光粉仍是该方向的研究重点。通常，荧光粉由基质和激活剂组成，

基于此, 可以通过调控基质的方式来改善双掺杂体系在光谱上的缺失, 进而获得所需特征参数的高效单基质白色荧光粉。

总之, 白光 LEDs 用单体白色荧光粉还处于方兴未艾的阶段, 需要改进的地方还很多, 如合理选择基质组分, 激活剂及其配比等, 以及如何提高材料的发光效率, 控制材料的显色性等, 均需要研究者做进一步深入、系统地研究。

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