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BaLaGa₃O₇:Bi³⁺ 荧光粉的制备及发光性能研究

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摘 要:采用高温固相法合成了 BaLa_{1-x}Ga₃O₇:xBi³⁺ (0.01≤x≤0.13) 系列荧光粉。X 射线衍射数据和 Rietveld 精修结果表明, BaLa_{1-x}Ga₃O₇:xBi³⁺ 荧光粉具有黄长石结构。扫描电镜图像显示, 荧光粉的颗粒为不规则形状, 尺寸在 5~30 μm 之间。漫反射光谱表明, BaLaGa₃O₇ 基体对于 Bi³⁺ 离子掺杂发光具有合适的光学带隙。在 348 nm 紫外光激发下, BaLa_{1-x}Ga₃O₇:xBi³⁺ 荧光粉呈现出中心波长位于 475 nm 的宽带发射。随着 Bi³⁺ 离子掺杂浓度增加, 荧光粉的发射强度出现先增加后减少的趋势, 该浓度猝灭发光现象源于偶极-偶极相互作用。其中, BaLa_{0.89}Ga₃O₇:0.11Bi³⁺ 荧光粉的发射强度达到最大, 量子产率为 19.2%, 且在 150℃ 时的发射强度仍能保持 25℃ 时的 69.2%, 说明 BaLa_{1-x}Ga₃O₇:xBi³⁺ 荧光粉在近紫外激发白光 LED 领域具有潜在的应用价值。

关键词: Bi³⁺ 离子; 镓酸盐; 荧光粉; 发光性能; 白光 LED

中图分类号: O482.31

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0 引言

当前, 白光发光二极管(Light-Emitting Diode, LED)在照明、显示等领域发挥着不可估量的作用。由于封装工艺简单、经济成本较低等特点, 蓝光 LED 芯片与黄色、红色荧光粉组合成为工业界主流的封装技术^[1]。为了满足高显色性的照明需求, 紫外 LED 芯片与三基色荧光粉的组合也是一种较佳的选择。目前, 能够被紫外 LED 芯片激发的商业荧光粉大多数以稀土离子(Ce³⁺、Tb³⁺、Eu³⁺等)作为激活剂^[2-4]。由于稀土离子具有丰富的能级结构, 蓝色荧光粉的发射光谱会与绿色、红色荧光粉的激发光谱部分重叠, 从而造成严重的重吸收, 导致白光 LED 器件在工作时出现发光效率较低和发射颜色失真的现象。如何避免光谱重吸收, 已成为当前提高照明效率和品质的重要研究方向。

三价铋离子(Bi³⁺)是一种典型的非稀土离子激活剂, 仅对紫外光有较强的吸收能力, 可有效避免因光谱重吸收而影响器件发光性能的问题。Bi³⁺的电子构型为[Xe]4f¹⁴5d¹⁰6s², 其裸露在外的 6s 和 6p 电子对配位环境(如晶体场强、配位数、占位对称性等)非常敏感。当 Bi³⁺离子掺杂到不同类型的基质(如硼酸盐、硅酸盐、锆酸盐、钨酸盐等)时, 可以实现从紫外到红色不同颜色的发光^[5]。例如, Cs₃Zn₆B₉O₂₁:Bi³⁺ 蓝色荧光粉^[6]、NaGd₉(SiO₄)₆O₂ 蓝色荧光粉^[7]、Ca₃Lu₂Ge₃O₁₂:Bi³⁺ 青色荧光粉^[8]、Ba₂Ga₂GeO₇:Bi³⁺ 青色荧光粉^[9]、Ca₂MgWO₆:Bi³⁺ 黄色荧光粉^[10]。此外, 通过阳离子取代调控配位环境, 在 BaSrGa₄O₈:Bi³⁺ 荧光粉中实现了从橙黄色到绿色的发光颜色调整^[11]。目前, 就 LED 照明和显示需求而言, 开发一种能被近紫外 LED 芯片激发的 Bi³⁺ 掺杂新型荧光粉引起了人们的兴趣。

BaLaGa₃O₇ 是黄长石结构 ABC₃O₇ (A=Ca, Sr, Ba; B=镧系元素; C=Al, Ga)中的一员。迄今为止,

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以稀土离子为激活剂的BaLaGa₃O₇荧光粉相继报道,如BaLaGa₃O₇:Tm³⁺, Dy³⁺[12], BaLaGa₃O₇:Pr³⁺, Tb³⁺[13] 荧光粉。然而,以Bi³⁺离子为激活剂的BaLaGa₃O₇荧光粉尚未见研究。本文选择具有良好稳定性的BaLaGa₃O₇作为基质材料,采用高温固相法合成了BaLa_{1-x}Ga₃O₇:xBi³⁺荧光粉,通过相关表征手段对其晶体结构、微观形貌和发光性能进行了研究。

1 实验

1.1 样品制备

采用高温固相法合成了BaLa_{1-x}Ga₃O₇:xBi³⁺(0.01≤x≤0.13)系列荧光粉。根据化学计量比称取BaCO₃(99.99%)、La₂O₃(99.99%)、Ga₂O₃(99.99%)、Bi₂O₃(99.99%)等原料,置于玛瑙研钵中,加入适量无水乙醇后研磨30 min,使其混合均匀。将混合物置于氧化铝坩埚中,在1100℃马弗炉中预烧12小时。冷却至室温后,将前驱体研磨成粉,置于氧化铝坩埚中,在1300℃马弗炉中煅烧8 h。将冷却至室温后的样品研磨成粉末以进行表征。

1.2 样品表征

使用PANalytical Empyrean型X射线衍射仪对样品的晶体结构进行X射线衍射(X-ray diffraction, XRD)测量,测量条件为Cu Kα1辐射(λ=1.540 59 Å, 1 Å=0.1 nm),管电压为40 kV,电流为40 mA。使用晶体结构分析软件(General Structure Analysis System, GSAS)对XRD图谱进行Rietveld精修,分析样品的晶体结构参数。使用配备能量色散X射线能谱(Energy Dispersive X-ray Spectroscopy, EDS)的扫描电子显微镜(Scanning Electron Microscope, SEM)测量样品的形貌和元素分布。使用UV3600型紫外-可见-近红外分光光度计记录样品的漫反射光谱(Diffuse Reflectance Spectra, DRS)。使用QuantaMaster 8000型荧光光谱仪记录样品的激发光谱(Photoluminescence Excitation, PLE)、发射光谱(Photoluminescence, PL)和荧光衰减曲线,通过积分球测试粉末样品的量子产率。此外,通过上述光谱仪与THMS 600型精确温度控制的加热制冷台配合测试样品的变温光谱。

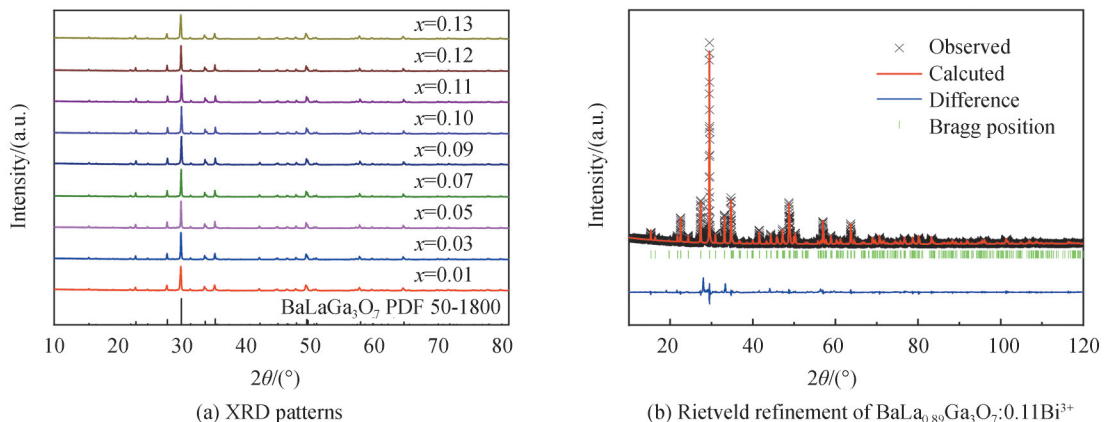
2 结果与讨论

2.1 结构与形貌分析

图1(a)为BaLa_{1-x}Ga₃O₇:xBi³⁺(0.01≤x≤0.13)样品的XRD图谱。所有样品的衍射峰均与BaLaGa₃O₇标准卡片(No.50-1800)吻合,未观察到其他杂质峰的存在,说明合成的样品均为纯相,Bi³⁺离子的引入并未破坏BaLaGa₃O₇基体的晶体结构。通常而言,掺杂离子与晶格离子之间的半径百分比不超过30%时,掺杂离子能够置换晶格离子;半径百分比越小,越容易产生置换。半径百分比计算公式为^[14]

$$D_r = \left| \frac{R_m(\text{CN}) - R_d(\text{CN})}{R_m(\text{CN})} \right| \quad (1)$$

式中, D_r 代表半径百分比, $R_m(\text{CN})$ 代表基质晶体中离子半径, $R_d(\text{CN})$ 代表掺杂离子半径。在BaLaGa₃O₇晶体中,存在Ba²⁺、La³⁺和Ga³⁺三种阳离子,离子半径分别为1.42 Å(CN=8),1.18 Å(CN=8)和0.47 Å(CN=4),



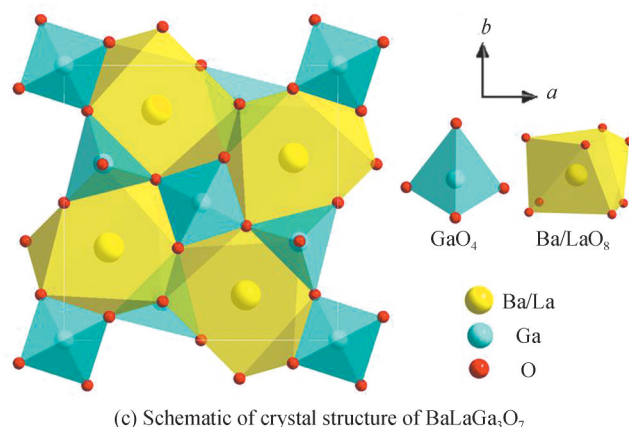

 图1 BaLa_{1-x}Ga₃O₇:xBi³⁺ (0.01 ≤ x ≤ 0.13)样品的XRD图谱和BaLaGa₃O₇的晶体结构示意图

 Fig.1 XRD patterns of BaLa_{1-x}Ga₃O₇:xBi³⁺ (0.01 ≤ x ≤ 0.13) samples and schematic of crystal structure of BaLaGa₃O₇

而Bi³⁺离子的半径为1.11 Å (CN=8)。经计算,La³⁺离子的D_r值(5%)远小于Ba²⁺离子的D_r值(21%),根据离子半径相近易于取代的原则,确定Bi³⁺离子取代La³⁺离子的晶格位置。为了准确获取样品的晶体结构信息,对BaLa_{0.89}Ga₃O₇:0.11Bi³⁺样品的XRD图谱进行Rietveld精修。如图1(b)所示,样品的衍射峰与精修结果非常吻合。表1展示了Rietveld精修的主要晶体结构参数,其中R_{wp}=5.49%,R_p=6.18%,χ²=7.37,说明精修结果较为准确,进一步证实了BaLa_{0.89}Ga₃O₇:0.11Bi³⁺样品的黄长石结构。图1(c)为BaLaGa₃O₇的晶体结构示意图,晶胞由沿c四方轴的多面体层交替形成,其中四面体位点被Ga³⁺离子占据,Ba²⁺和La³⁺离子以1:1的比例随机占据十二面体位点。

 表1 BaLa_{0.89}Ga₃O₇:0.11Bi³⁺样品Rietveld精修的主要参数

 Table 1 Main parameters of Rietveld refinement of the BaLa_{0.89}Ga₃O₇:0.11Bi³⁺ sample

Formula	BaLa _{0.89} Ga ₃ O ₇ :0.11Bi ³⁺
Space group	P-421m
a=b/Å	8.165 6(6)
c/Å	5.402 4(1)
V/Å ³	360.219 4(8)
Z	2
R _{wp} /%	5.49
R _p /%	6.18
χ ²	7.37

图2为BaLa_{0.89}Ga₃O₇:0.11Bi³⁺样品的SEM图像。样品颗粒呈现出不规则的形状,尺寸在5~30 μm之

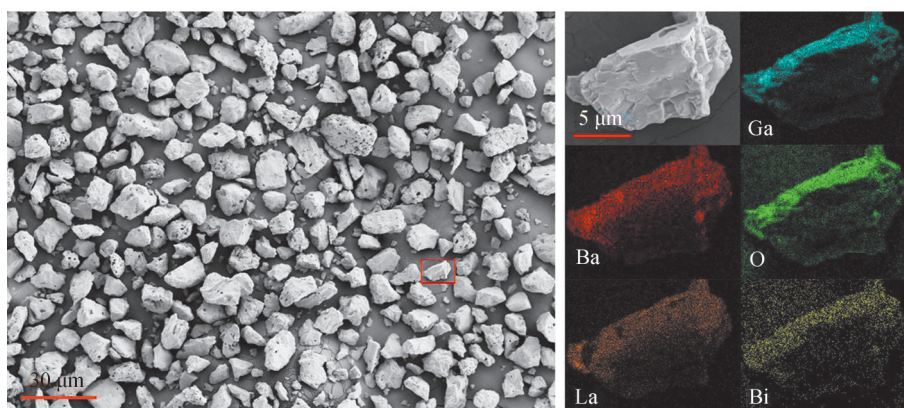

 图2 BaLa_{0.89}Ga₃O₇:0.11Bi³⁺样品的SEM图像和EDS元素分布

 Fig.2 SEM image and corresponding elemental mappings of BaLa_{0.89}Ga₃O₇:0.11Bi³⁺ sample

间。另外,图中展示了单个颗粒的EDS图像,进一步证实了 $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ 样品由Ba、La、Ga、O和Bi元素组成,各元素在样品中均匀分布,未观察到元素团聚和相分离的现象。

2.2 光学性能分析

图3(a)为 $\text{BaLaGa}_3\text{O}_7$ 和 $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ 样品的漫反射光谱。可以看出,未掺杂样品的吸收截止边缘位于240 nm左右,源于 $\text{BaLaGa}_3\text{O}_7$ 基体的本征吸收。当 Bi^{3+} 离子掺入 $\text{BaLaGa}_3\text{O}_7$ 基体后,样品在270 nm和350 nm处各有一个吸收峰,这分别归因于 Bi^{3+} 离子的 $^1\text{S}_0 \rightarrow ^1\text{P}_1$ 和 $^1\text{S}_0 \rightarrow ^3\text{P}_1$ 跃迁。此外, $\text{BaLaGa}_3\text{O}_7$ 基体的光学带隙 E_g 可根据Kubelka-Munk吸收函数计算^[15]

$$\alpha = (1 - R)^2 / 2R \quad (2)$$

$$(ah\nu)^2 = A(h\nu - E_g) \quad (3)$$

式中, α 代表吸收率, R 代表漫反射率, $h\nu$ 代表光子能量, A 代表比例常数。如图3(b)所示,通过外推 $[ah\nu]^2$ vs. $h\nu$ 曲线的线性部分可知 $\text{BaLaGa}_3\text{O}_7$ 基体的 E_g 值为5.12 eV。对于 Bi^{3+} 离子发光而言, $\text{BaLaGa}_3\text{O}_7$ 基体具有合适的光学带隙。

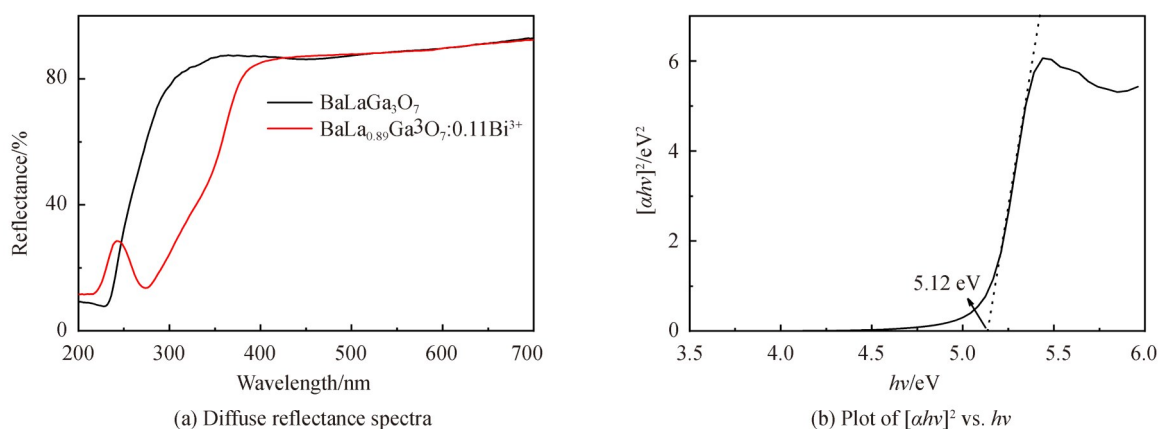


图3 $\text{BaLaGa}_3\text{O}_7$ 基体和 $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ 样品的漫反射光谱
Fig.3 Diffuse reflectance spectra of $\text{BaLaGa}_3\text{O}_7$ host and $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ sample

图4(a)为 $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ ($0.01 \leq x \leq 0.13$)样品的激发光谱和发射光谱。可以看出, $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ 样品具有一个归因于 $\text{Bi}^{3+}:^1\text{S}_0 \rightarrow ^3\text{P}_1$ 跃迁的宽激发带,峰值位于350 nm左右,与近紫外LED芯片能够较好地匹配。此外,随着掺杂离子浓度的增加, $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ 样品激发带的峰值位置发生了微小红移,即从340 nm红移到350 nm处。这是因为较大的 Bi^{3+} 离子取代 La^{3+} 离子后,会降低该晶格位点周围的晶体场强度,引起晶体场劈裂导致最低的激发能级下降,从而引起激发带的峰值位置红移^[16]。在348 nm紫外光激发下, $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ 样品呈现覆盖375~650 nm波长的宽带发射带,峰值位于475 nm,归因于 $\text{Bi}^{3+}:^3\text{P}_1$

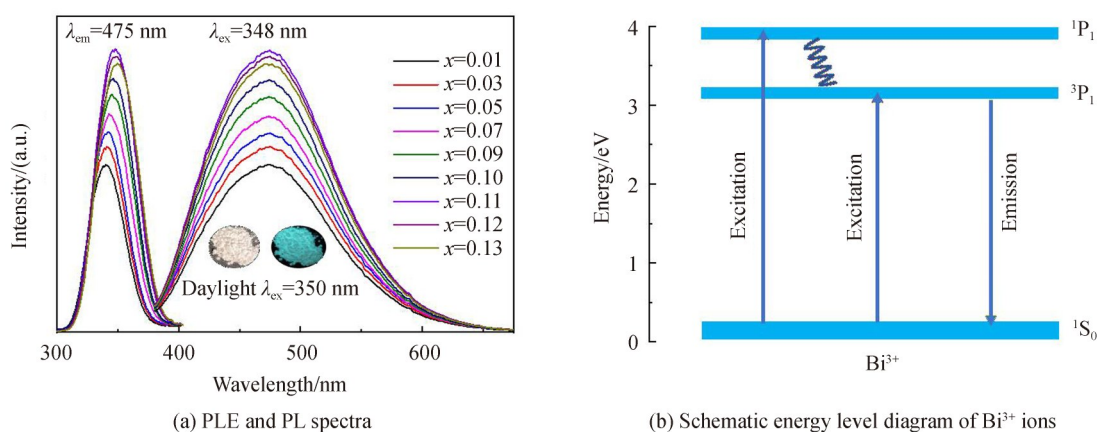


图4 $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ ($0.01 \leq x \leq 0.13$)样品的荧光光谱和 Bi^{3+} 离子的能级示意图
Fig.4 Fluorescence spectra of $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ ($0.01 \leq x \leq 0.13$) samples and schematic energy level diagram of Bi^{3+} ions

→¹S₀跃迁。图4(b)展示了Bi³⁺离子发光的能级示意图。当被紫外光激发时,位于基态¹S₀能级的电子一部分跃迁到¹P₁能级,另一部分跃迁到³P₁能级,其中¹P₁能级的大部分电子会通过自旋-晶格弛豫跃迁到³P₁能级,因此样品的青光发射来自位于³P₁能级的电子返回到基态。

随着Bi³⁺离子的含量增加,样品的发射强度逐渐增强,当掺杂含量为0.11时达到最大值,之后发射强度逐渐减弱。这种发光现象归因于浓度猝灭效应。为了究其原因,引入掺杂离子之间能量的临界距离 R_c ,公式为^[17]

$$R_c = 2 \times \left(\frac{3V}{4\pi X_c N} \right)^{1/3} \quad (4)$$

式中, X_c 代表最佳掺杂浓度, N 代表单位晶胞中La³⁺离子的数量, V 代表单位晶胞的体积。对于BaLaGa₃O₇:Bi³⁺, $X_c=0.11$, $N=2$, $V=357.05 \text{ \AA}^3$ 。经计算, R_c 值约为 14.58 \AA ,远远大于交换相互作用距离($\sim 5 \text{ \AA}$)。因此,Bi³⁺离子之间的浓度猝灭效应不太可能是由交换相互作用引起的,所以可推测电多极相互作用在浓度猝灭现象中起主要作用。电多极相互作用有三种类型,即偶极-偶极相互作用、偶极-四极相互作用和四极-四极相互作用。根据Dexter理论,通过以下式(5)分析电多极相互作用的类型^[18]。

$$\log(I/x) = A - (\theta/3)\log x \quad (5)$$

式中, I 代表发射强度, x 代表掺杂浓度, A 代表基质在相同激发条件下的常数, θ 代表电多极特性($\theta=6,8$ 和 10 分别对应于偶极-偶极、偶极-四极和四极-四极相互作用)。如图5所示,通过对 $\log(I/x)$ 和 $\log(x)$ 的关系进行线性拟合,得到直线的斜率($-\theta/3$)为 -1.66 , $\theta=4.98$,接近于数值6,表明BaLa_{1-x}Ga₃O₇:xBi³⁺样品的浓度猝灭机理是偶极-偶极相互作用。

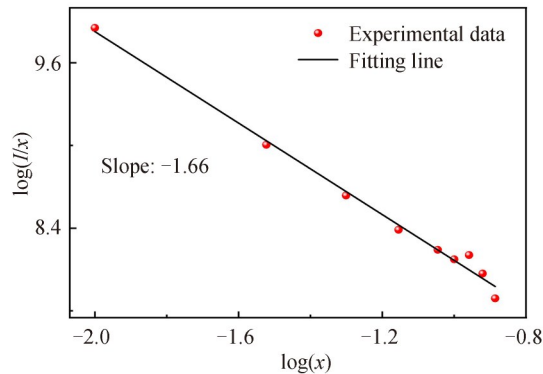


图5 BaLa_{1-x}Ga₃O₇:xBi³⁺(0.01≤x≤0.13)样品中 $\log(I/x)$ 与 $\log(x)$ 的关系
Fig5 Relationship between $\log(I/x)$ and $\log(x)$ for BaLa_{1-x}Ga₃O₇:xBi³⁺(0.01≤x≤0.13) samples

为了更进一步确定Bi³⁺离子对样品发光的影响,在激发波长348 nm、发射波长475 nm下测试BaLa_{1-x}Ga₃O₇:xBi³⁺(0.01≤x≤0.13)样品的荧光衰减曲线,以及对Bi³⁺的荧光寿命进行分析。如图6(a)所示,样品的衰减曲线可通过双指数函数进行很好地拟合^[19]。

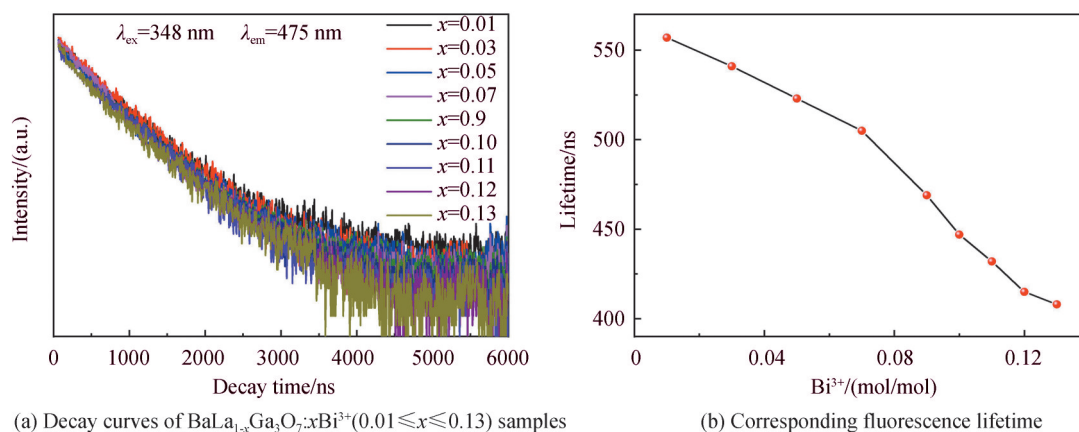
$$I(t) = A_1 \exp^{-t/\tau_1} + A_2 \exp^{-t/\tau_2} \quad (6)$$

式中, $I(t)$ 代表在时间为 t 时的发射强度, A_1 和 A_2 代表该条件下的拟合常数, τ_1 和 τ_2 代表寿命的指数成分。因此,荧光寿命 τ 计算公式为^[20]

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (7)$$

根据图6(b)的计算结果分析可知,随着Bi³⁺离子浓度增加,BaLa_{1-x}Ga₃O₇:xBi³⁺样品的荧光寿命逐渐减小。此种变化趋势说明掺杂离子Bi³⁺之间存在着能量转移,非辐射跃迁因掺杂离子浓度增加而逐渐变强,最终引起样品的荧光寿命减小。

量子产率(Quantum Yield, QY)是评估荧光粉性能优劣的关键光学性能之一。选择以发光强度最强的BaLa_{0.89}Ga₃O₇:0.11Bi³⁺样品为代表,对它的量子产率进行测量,计算公式为^[10]

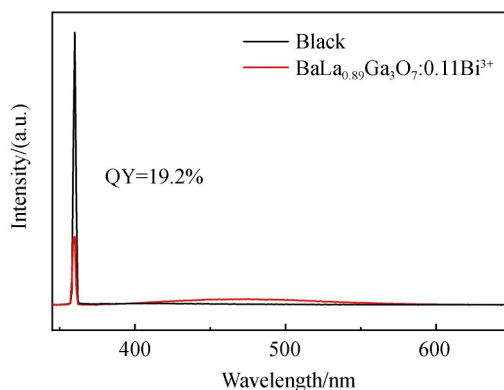
(a) Decay curves of $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ ($0.01 \leq x \leq 0.13$) samples

(b) Corresponding fluorescence lifetime

图6 $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ ($0.01 \leq x \leq 0.13$)样品的衰减曲线以及对应的荧光寿命Fig.6 Decay curves of $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ ($0.01 \leq x \leq 0.13$) samples and corresponding fluorescence lifetime

$$\eta = \frac{\int L_{\text{direct}}}{\int L_{\text{direct}} - \int L_{\text{without}}} \quad (8)$$

式中, η 代表量子产率, L_{direct} 代表待测样品的积分强度, L_{without} 代表空白样品的积分强度。根据图7的测试数据计算分析可知, $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ 样品的 η 值为19.2%, 其值相对较低, 因此还需进一步提高才能获得应用。

图7 $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ 样品的量子产率Fig.7 Quantum yield of $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ sample

白光LED长时间工作时, 一部分电能会转换成热能, 致使器件的内部温度升高, 影响荧光粉的发光效率。因此良好的热稳定性是荧光粉实现商业化的一项基本性能要求。图8(a)为 $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ 样品在25~200 °C温度范围内的变温光谱。可以看出, 随着温度的升高, $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ 样品的发射强度逐渐下降。如图8(a)中的插图所示, $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ 样品在150 °C时的发射强度仍能保持25 °C时的69.2%, 说明荧光粉具有一定的热稳定性。与表2中列举的同类荧光粉相比, 其热稳定性相对稳定。为了进一步理解这一热淬灭现象, 可以通过式(9)计算样品的活化能 E_a [21]。

$$\ln\left(\frac{I_0}{I} - 1\right) = \ln(A) - \frac{E_a}{KT} \quad (9)$$

式中, I_0 代表初始温度下的发射强度, I 代表其它温度下的发射强度, A 代表常数, K 代表玻尔兹曼常数, T 代表热力学温度。如图8(b)所示, 根据 $\ln(I_0/I - 1)$ 和 $1/KT$ 之间的线性关系进行拟合, 得到其斜率为-0.258 5, 活化能 E_a 值可以计算出为0.258 5 eV。

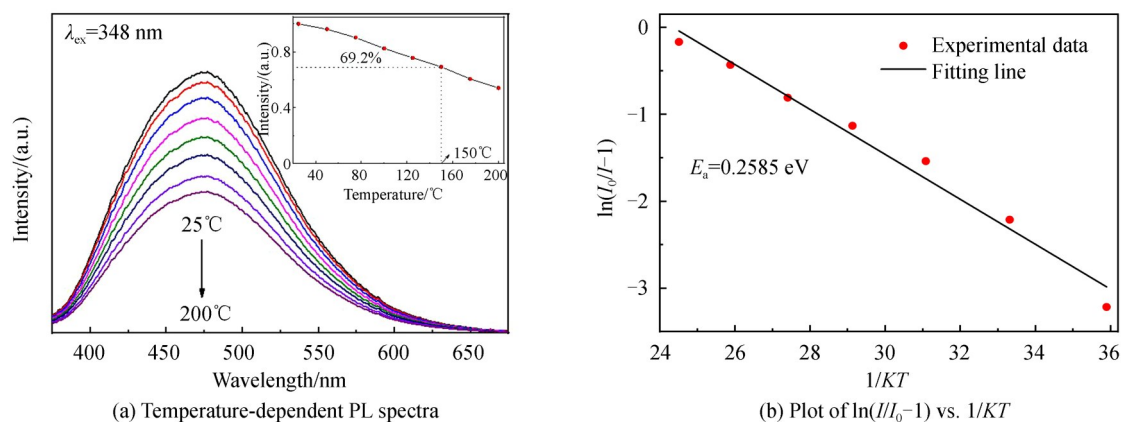


图8 BaLa_{0.89}Ga₃O₇:0.11Bi³⁺样品的变温光谱
Fig.8 Temperature-dependent PL spectra of BaLa_{0.89}Ga₃O₇:0.11Bi³⁺ sample

表2 Bi³⁺掺杂荧光粉的光学性能

Table 2 Luminescence properties of some phosphors activated with Bi³⁺

Sample	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	PL Intensity at 423 K	Reference
Cs ₃ Zn ₂ B ₉ O ₂₁ :Bi ³⁺	322	436	100%	[6]
NaGd ₉ (SiO ₄) ₆ O ₂ :Bi ³⁺	340	465	76%	[7]
Ca ₃ Lu ₂ Ge ₃ O ₁₂ :Bi ³⁺	380	477	75%	[8]
Ba ₂ Ga ₂ GeO ₇ :Bi ³⁺	365	497	35%	[9]
Ca ₂ MgWO ₆ :Bi ³⁺	340	550	33%	[10]
K ₂ MgGeO ₄ :Bi ³⁺	335	614	85%	[22]
BaLaGa ₃ O ₇ :Bi ³⁺	348	475	69%	This work

4 结论

采用高温固相法合成了BaLa_{1-x}Ga₃O₇:xBi³⁺ (0.01≤x≤0.13)系列荧光粉。荧光粉样品为黄长石结构,属于四方晶系,具有P-421m空间点群结构。荧光粉颗粒呈现不规则形状,尺寸在5~30 μm之间。漫反射光谱表明BaLaGa₃O₇具有合适的光学带隙。BaLa_{1-x}Ga₃O₇:xBi³⁺具有较宽的单一激发带和发射带,峰值分别位于348 nm和475 nm左右,归因于Bi³⁺:¹S₀↔³P₁跃迁。随着Bi³⁺离子掺杂浓度的增加,样品的激发带峰值从340 nm逐渐红移到350 nm处;样品的发射带峰值位置不变,发射强度呈现先增加后减少的趋势,这一浓度猝灭现象是由偶极-偶极相互作用引起的;样品的荧光寿命呈现逐渐下降的趋势,归因于Bi³⁺离子之间相互作用的增强。BaLa_{0.89}Ga₃O₇:0.11Bi³⁺样品的发射强度最高,量子产率为19.2%;随着温度的升高,其发射强度逐渐下降,在150 °C时的发射强度仍能保持为25 °C时的69.2%,热淬灭的活化能为0.258 5 eV,具有一定的热稳定性。综上所述,BaLa_{1-x}Ga₃O₇:xBi³⁺荧光粉在紫外激发白光LED中具有潜在的应用价值。

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Synthesis and Luminescent Properties of $\text{BaLaGa}_3\text{O}_7$: Bi^{3+} Phosphors

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Abstract: At present, with the increasingly serious environment and energy, the research and development of green and low energy consumption technology has attracted extensive attention. In the field of lighting, as a green light source in the 21st century, phosphor-converted White Light-Emitting Diodes (WLEDs) are expected to become an indispensable generation of comfortable and healthy lighting system due to its

obvious advantages of high luminous efficiency, low environmental pollution and low energy consumption. The two key materials for commercially available WLEDs are yellow YAG:Ce phosphors and blue LED chips. In this scheme, the lack of red component results in only a low color rendering index (<80), high related color temperature ($>4\ 500\ \text{K}$) cold white light, which are not conducive to the application of indoor lighting. Generally speaking, adding efficient red phosphors on this basis can obtain a higher color rendering index and a lower color temperature. However, one of the costs of adding such phosphors is that the device becomes significantly less efficient. From a more comprehensive and humanized perspective, the combination of ultraviolet LED chip with red, blue and green phosphors has undoubtedly attracted the attention of the majority of scientific researchers. As far as we know, rare earth ions (such as Eu^{2+} and Ce^{3+}) are used as activators for most of the phosphors that can be excited by ultraviolet LED chips and tricolor phosphors in the lighting scheme. However, the mixture of three primary phosphors can easily cause spectral reabsorption. In addition, an imbalance between supply and demand makes rare earths expensive, which is a major impediment to their commercialization. In view of this situation, choosing phosphors with non-rare earth ions as activators can effectively solve the above problems of rare earth doped phosphors. Nowadays, as another type of activator, bismuth (Bi), has been extensively studied and reported because of the potential optical properties related to the strong interaction with surrounding coordination environments and abundant valence states. In this paper, a series of $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ ($0.01 \leq x \leq 0.13$) phosphors were synthesized through traditional high temperature solid state method. The X-ray diffraction patterns and rietveld refinement results indicate the pyrite structure of above samples. Scanning electron microscope images show that the phosphor particles are irregular in shape with the size of $5\sim 30\ \mu\text{m}$. Diffuse reflectance spectra of $\text{BaLaGa}_3\text{O}_7$ matrix indicate a suitable optical band gap for Bi^{3+} luminescence. When Bi^{3+} substitutes La^{3+} , the excitation wavelength has a red shift from 340 to 350 nm. Under the excitation of 348 nm ultraviolet light, $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ phosphors exhibit one evident emission peak at 475 nm. With the increase of Bi^{3+} concentration, the emission intensity firstly increased and then decreased, and this optical phenomenon is generally considered to be related to the concentration quenching. Among them, the emission intensity of $\text{BaLa}_{0.89}\text{Ga}_3\text{O}_7:0.11\text{Bi}^{3+}$ phosphor reaches the maximum with a quantum yield of 19.2%, and the emission intensity at 150 °C still maintains 69.2% of that at 25 °C. It indicates that the $\text{BaLa}_{1-x}\text{Ga}_3\text{O}_7:x\text{Bi}^{3+}$ phosphors have potential application value in the field of near ultraviolet excited white LEDs.

Key words: Bi^{3+} ion; Gallate; Phosphors; Photoluminescence properties; White LEDs

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