白光LED用 $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:\text{Eu}^{3+}$ 荧光粉的红色发光及热特性

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2017-02-12 收稿, 2017-05-21 修回, 2017-05-22 接受, 2017-08-18 网络版发表

国家自然科学基金(11647306)和湖州师范学院校级科研项目(2016XJXM23)资助

摘要 采用简单的固相反应法制备了 $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:\text{Eu}^{3+}$ ($x=0, 2, 5, 10$)系列荧光粉. X射线衍射(XRD)分析证实 Li^+ 的电荷补偿有助于提升 Eu^{3+} 在 CaSnO_3 晶格中的溶解能力. 当 Li^+ 掺杂浓度为10%时, 8% Eu^{3+} 完全掺入 CaSnO_3 晶格, 结果显著提升 Eu^{3+} 的红色发光. 基于校对的发射谱, 讨论了这种荧光增强的原理. 此外, 在394 nm光波长激发下, 最佳样品 $\text{CaSn}_{0.9}\text{Li}_{0.1}\text{O}_3:8\%\text{Eu}^{3+}$ 显示了良好的热稳定性, 表明该材料可用于大功率白光LED的红色组分. 基于热特性的研究, 指出两个热布居过程主导 $\text{CaSn}_{0.9}\text{Li}_{0.1}\text{O}_3:8\%\text{Eu}^{3+}$ 的荧光猝灭.

关键词 白光LED, 电荷补偿, 红光发射, 热猝灭

目前, InGaN蓝光芯片结合YAG:Ce³⁺黄色荧光粉的光转换型白光LED已经广泛应用在照明、信号指示和显示等领域. 然而, 色温不稳定、显色性差等固有缺点的存在, 限制了它的实际应用^[1-3]. 类似于日光灯原理, 利用近紫外芯片激发蓝、绿、红三基色荧光粉可以有效解决上述问题. 因此, 许多研究小组已经致力于近紫外芯片激发的白光LED用荧光粉的开发, 其中又以红色荧光粉的研究最为广泛.

在众多的离子型发光中心中, 三价的 Eu^{3+} 特别适合用于白光LED用红色发光粉的开发^[4-6]. 然而, 由于宇称禁戒选率的限制, Eu^{3+} 的特征发射强烈依赖于基质晶格的选取. 虽然氟化物材料声子能量低, 可以有效抑制无辐射跃迁的发生, 但通常较差的热、化学稳定性并不利于大功率器件的应用. 根据文献报道, 当前的研究主要集中在 Eu^{3+} 掺杂各类氧化物材料^[2-5,7-12]. 例如, Zhang等人^[12]报道 $\text{CaSnO}_3:\text{Eu}^{3+}$ 是一

种非常有前途的白光LED用红色荧光材料. 遗憾的是, Eu^{3+} 较低的掺杂浓度制约了它的光致发光^[12,13]. 另一方面, 尽管目前已有一些关于 $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ 跃迁的热特性报道^[2,9,11,12,14-16], 但热猝灭机理的充分理解仍然非常必要.

本论文借助高温固相反应法制备了 $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:8\%\text{Eu}^{3+}$ ($x=0, 2, 5, 10$)系列荧光粉. 首先研究了 Li^+ 电荷补偿作用对 Eu^{3+} 溶解能力和发光效率的影响. 随后, 评估了最佳样品的热稳定性, 并基于热特性的分析阐明了可能的热猝灭机理.

1 实验

(i) $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:\text{Eu}^{3+}$ 系列荧光粉的制备. 简单的高温固相法用于 $\text{CaSnO}_3:\text{Eu}^{3+}$, Li^+ 荧光粉的制备. 按照化学计量比称取一定量的 CaCO_3 (AR), SnO_2 (CP), $\text{EuNO}_3 \cdot 6\text{H}_2\text{O}$ (4N)和 Li_2CO_3 (AR). 利用玛瑙研钵充分

引用格式: 庞涛. 白光LED用 $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:\text{Eu}^{3+}$ 荧光粉的红色发光及热特性. 科学通报, 2017, 62: 3783-3788

Pang T. Red emission and thermal properties of $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:\text{Eu}^{3+}$ phosphors for white LEDs (in Chinese). Chin Sci Bull, 2017, 62: 3783-3788, doi: 10.1360/N972017-00159

研磨后, 倒入氧化铝坩埚并置入高温炉中于 1300 °C 焙烧 3 h. 最后, 研磨获得白色粉末状荧光材料. 所有样品的化学组成详见表 1.

(ii) 表征. X 射线衍射谱(XRD)用于鉴别材料晶相和物相, 仪器型号为 Shimadzu-6000, 工作电压为 40 kV, 电流为 30 mA. 日立 F-4600 荧光光谱仪用于测量样品的光致发光光谱. 自制的控温装置用于热特性的研究, 测量误差小于 1 °C.

2 结果与讨论

2.1 XRD 分析

据文献[12]报道, Eu^{3+} 在 CaSnO_3 晶格中的最大溶解度不超过 2%. 然而, 本文在引入 Li^+ 后, Eu^{3+} 的掺杂浓度显著提升(图 1). 当 Li^+ 掺杂浓度为 10% 时, 杂质相 $\text{Eu}_2\text{Sn}_2\text{O}_7$ (JCPDS No. 70-1698) 完全消失. 换句话说, 此时 8% Eu^{3+} 全部掺入 CaSnO_3 晶格. 因为 Eu^{3+} 的半径(六配位下 $r=0.947$ Å)稍小于 Ca^{2+} (六配位下 $r=1$ Å) 的半径, 而远大于 Sn^{4+} (六配位下 $r=0.69$ Å) 的半径^[17], 所以基于固溶体理论可推知 Eu^{3+} 占据 Ca^{2+} 的格位.

为了阐明 Li^+ 在 Eu^{3+} 掺杂过程中所起到的作用, 图 1 也呈现了放大的谱图. 很明显, 随着 Li^+ 浓度由 0% 增加到 5%, 衍射峰逐渐向小角度移动. 根据布拉格衍射方程, 衍射角变小意味着晶面间距变大. 再考虑到 Li^+ 的半径(六配位下 $r=0.76$ Å)略大于 Sn^{4+} 的半径, 且在 XRD 谱中未观察到关于 Li 的杂相, 可以推断所有的 Li^+ 均掺入 CaSnO_3 晶格并占据 Sn^{4+} 的格位. 继续增加 Li^+ 的浓度达 10%, 观察到衍射角反而变大, 其原因在于更多的 Eu^{3+} 掺入晶格. 综上所述, 两种不同离子的共掺一起影响衍射峰的移动. 由于 Eu^{3+} 掺杂引入正电中心, 而 Li^+ 掺杂引入负电中心, 可推断 CaSnO_3 中 Eu^{3+} 掺杂能力的提升源自 Li^+ 的电荷补偿

作用.

2.2 增强的 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 发射

如图 2 所示, Eu^{3+} 的 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 跃迁在 Li^+ 掺杂后得到显著的增强. 而且, Li^+ 浓度越高, $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 跃迁的强度越大. 为了理解相关的原理, 将图 2 中的所有光谱按 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 跃迁的强度做归一化处理, 得到对应的校对谱(图 3)^[18]. 另根据公式^[18]

$$\frac{1}{\tau_R} = A_{\text{MD},0} n^3 \left(\frac{I_{\text{tot}}}{I_{\text{MD}}} \right), \quad (1)$$

式中, τ_R 是 $^5\text{D}_0$ 能级的寿命, $A_{\text{MD},0}$ 是真空中 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 跃迁的自发辐射几率 ($\sim 14.65 \text{ s}^{-1}$), n 是 CaSnO_3 的折射率 (~ 1.89)^[12], $I_{\text{tot}}/I_{\text{MD}}$ 是校对谱的总积分强度与 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 跃迁积分强度的比值, 我们计算了不同样品的 $^5\text{D}_0$ 寿命, 详见表 2. 进一步, 利用公式^[18,19]

$$\beta_J = A_J \tau_R, \quad (2)$$

式中, β_J 和 A_J 分别对应 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 跃迁的荧光分支比和辐射跃迁几率, 也计算了 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0, 1, 2, 3, 4$) 跃迁的几率(表 2). 由表 2 可知, 所有的 A_J ($J \neq 1$) 在 Li^+ 掺杂后均得到加强. 因为 A_J 是 $J-O$ 强度参数的函数, 且 $J-O$ 参数依赖于 Eu^{3+} 的局部环境, 所以 A_J 的增强必定源自 CaSnO_3 的晶格畸变以及相组成的改变(图 1).

2.3 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 发射的热猝灭

图 4 给出了最佳样品 $\text{CaSn}_{0.9}\text{Li}_{0.1}\text{O}_3: 8\% \text{Eu}^{3+}$ 在不同温度下的光致发光谱. 显然, Eu^{3+} 的 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 跃迁随着温度的升高而显著降低. 鉴于辐射几率与温度无关^[18-20], 荧光的猝灭必定源自 $^5\text{D}_0$ 能级粒子布居数的降低. 由于 $^5\text{D}_0$ 与 $^7\text{F}_6$ 之间的能隙 ($\sim 12300 \text{ cm}^{-1}$) 约为 CaSnO_3 声子能的 17.6 倍, 首先排除 $^5\text{D}_0$ 到 $^7\text{F}_6$ 的多声子弛豫^[13,21]. 此外, 考虑到 Eu^{3+} 的掺杂浓度保持不变,

表 1 所有样品的化学组成

Table 1 Chemical composition of all samples

样品	化学组成(原材料)			
	$\text{Ca}^{2+}(\text{CaCO}_3)(\text{mol}\%)$	$\text{Eu}^{3+}(\text{EuNO}_3 \cdot 6\text{H}_2\text{O})(\text{mol}\%)$	$\text{Sn}^{4+}(\text{SnO}_2)(\text{mol}\%)$	$\text{Li}^+(\text{Li}_2\text{CO}_3)(\text{mol}\%)$
0% Li^+	92	8	100	0
2% Li^+	92	8	98	2
5% Li^+	92	8	95	5
10% Li^+	92	8	90	10

图1 (网络版彩色)CaSn_{1-x}Li_xO₃:8%Eu³⁺(x=0, 2, 5, 10)的XRD谱
Figure 1 (Color online) XRD patterns of CaSn_{1-x}Li_xO₃:8%Eu³⁺(x=0, 2, 5, 10)

图2 (网络版彩色)CaSn_{1-x}Li_xO₃:8%Eu³⁺(x=0, 2, 5, 10)在 394 nm 光波长激发下的发光
Figure 2 (Color online) Photoluminescence of CaSn_{1-x}Li_xO₃:8%Eu³⁺(x=0, 2, 5, 10) under 394 nm excitation

离子间的能量传递也被排除^[16]。综上所述,必定存在其他以前很少被关注的过程主导着⁵D₀→⁷F_J跃迁的热猝灭。

由图5可知,⁵D₁→⁷F_J跃迁与⁵D₀→⁷F_J跃迁的积分

图3 (网络版彩色)不同样品中Eu³⁺的校正发射谱
Figure 3 (Color online) Corrected emission spectra of Eu³⁺ in different samples

强度比随温度的升高而增大。这意味着在升温过程中,发生了⁵D₀到⁵D₁的热布居过程。显然,该过程的发生可以降低⁵D₀能级粒子布居数。然而,根据公式^[12]

$$N(^5D_0) = \frac{N(^5D_1)g(^5D_0)}{g(^5D_1)\exp(-\Delta E/kT)}, \quad (3)$$

式中, $N(^5D_0)$ 和 $N(^5D_1)$ 是⁵D₀和⁵D₁的粒子布居数, $g(^5D_0)$ 和 $g(^5D_1)$ 对应能级的简并度, ΔE 是⁵D₀和⁵D₁之间的能隙,如果上述过程是主导⁵D₀→⁷F_J热猝灭的唯一过程,那么该跃迁的热稳定性应与激发波长无关。通过拟合 $\ln(I_0/I-1)$ 与 $10000/T$ 的关系曲线(图6),并将得到的斜率带入阿伦尼乌斯公式^[9]:

$$I = I_0 / [1 + C \exp(-\Delta E/kT)], \quad (4)$$

式中, I 和 I_0 是某给定温度和初始温度的强度, C 是常数, k 是波尔兹曼常数(8.62×10^{-5} eV/K), ΔE 是热猝灭激活能,确定394和464 nm激发下的热猝灭激活能分别为0.2760和0.3248 eV。显然,不同光波长激发下的不同热稳定性证实了其他热猝灭过程的存在。另外,

表2 ⁵D₀的辐射寿命和⁵D₀→⁷F_J的辐射跃迁几率

Table 2 Radiative lifetime of ⁵D₀ level and radiative emission probabilities of ⁵D₀→⁷F_J transitions

Li ⁺ 浓度(mol%)	τ_R (ms)	$A_J(s^{-1})$				
		⁵ D ₀ → ⁷ F ₀	⁵ D ₀ → ⁷ F ₁	⁵ D ₀ → ⁷ F ₂	⁵ D ₀ → ⁷ F ₃	⁵ D ₀ → ⁷ F ₄
0	1.53	4.64	98.89	363.99	15.49	156.54
2	1.42	5.21	99.15	385.63	16.69	183.24
5	1.47	5.44	99.05	382.65	16.19	162.99
10	1.45	5.86	98.97	395.17	16.76	158.48

图4 (网络版彩色)10% Li⁺样品在300, 400和500 K温度下的发射谱, 激发波长为394 nm

Figure 4 (Color online) Emission spectra of 10% Li⁺ sample excited by 394 nm at 300, 400 and 500 K

图5 (网络版彩色)最佳样品中⁵D₀, ⁵D₁→⁷F₂跃迁强度随温度的变化规律, 插图: ⁵D₁→⁷F₂跃迁与⁵D₀→⁷F₂跃迁积分强度比随温度的变化

通过与文献[6,8,9]所报道的结果进行对比, 发现CaSn_{0.9}Li_{0.1}O₃:8%Eu³⁺具有良好的热稳定性, 表明该材料可用于大功率白光LED器件的封装。

众所周知, 在394 nm光波长的激发下, Eu³⁺首先由⁷F₀态被激发到⁵L₆态, 随后经多声子弛豫衰减至⁵D₀态^[22]. 理论上, ⁵L₆态到⁵D₀态的多声子弛豫率随温度升高而增强, 因此温度升高应有助于提升⁵D₀态的粒子布居数, 但事实刚好相反. 这意味着温度的升高必定降低了⁷F₀态到⁵L₆态的激发效率. 为了证实上述推断, 图7给出不同温度下的激发谱. 很明显, 温度越高激发效率越低. 因此, 温度升高所导致的激发效率降低是⁵D₀→⁷F₂猝灭的另一个重要因素. 为了更

图6 (网络版彩色)CaSn_{0.9}Li_{0.1}O₃:8%Eu³⁺在394和464 nm光波长激发下的⁵D₀→⁷F₂跃迁的Ln(I₀/I-1)与10000/T的关系曲线

Figure 6 (Color online) Plot of or ⁵D₀→⁷F₂ transition of CaSn_{0.9}Li_{0.1}O₃:8%Eu³⁺ excited by 394 and 464 nm

图7 (网络版彩色)CaSn_{0.9}Li_{0.1}O₃:8%Eu³⁺在不同温度下的激发谱, 插图: 394和464 nm激发峰强度随温度的变化

Figure 7 (Color online) Excitation spectra of CaSn_{0.9}Li_{0.1}O₃:8%Eu³⁺ under various temperatures, inset: intensity of peaks at 394 and 464 nm versus temperature

好地理解这一过程, 列出下列稳态速率方程:

$$\rho\sigma N_0 - A_1 N_1 = 0, \quad (5)$$

式中, N_0 和 N_1 分别是基态(⁷F₀)和激发态(⁵L₆)的粒子布居数, ρ 是泵浦常数, σ 是激发截面, A_1 是⁵L₆态的衰减速率^[23]. 显然, N_1 的大小同时取决于 N_0 和 σ . 其中 σ 是温度的单调递增函数^[21], 因此 N_1 的减小必定源自 N_0 的减小, 即⁷F₀态的粒子布居数减少. 鉴于⁷F₀到⁷F_J($J>0$)的能隙很小, 有理由相信在加热过程中发生了⁷F₀到⁷F_J($J>0$)的热布居过程, 从而导致 N_0 和 N_1 的

降低。

3 结论

采用简单的固相反应法制备了 $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:8\%\text{Eu}^{3+}$ ($x=0, 2, 5, 10$) 系列荧光粉。XRD 分析表明 Li^+ 掺杂可以有效提升 Eu^{3+} 在 CaSnO_3 晶格中的溶解度。

当 Li^+ 浓度为 10% 时, 得到纯相的 $\text{CaSn}_{0.9}\text{Li}_{0.1}\text{O}_3:8\%\text{Eu}^{3+}$ 。与 $\text{CaSnO}_3:\text{Eu}^{3+}$ 和 $\text{Eu}_2\text{Sn}_2\text{O}_7$ 的混合物相比, 纯相的荧光粉产生更强的红光发射。通过加热最佳样品 $\text{CaSn}_{0.9}\text{Li}_{0.1}\text{O}_3:8\%\text{Eu}^{3+}$, 观察到猝灭的 $^5\text{D}_0 \rightarrow ^7\text{F}_J$ 跃迁。热特性的研究表明, 两个热布居过程 $^5\text{D}_0 \rightarrow ^5\text{D}_1$ 和 $^7\text{F}_0 \rightarrow ^7\text{F}_J$ ($J>0$) 起到主导作用。

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Summary for “白光 LED 用 $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:\text{Eu}^{3+}$ 荧光粉的红色发光及热特性”

Red emission and thermal properties of $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:\text{Eu}^{3+}$ phosphors for white LEDs

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Over the past ten years, white light emitting diodes (WLEDs) that combining the InGaN blue chip with $\text{YAG}:\text{Ce}^{3+}$ yellow-emitting phosphors have proverbially been applied in the fields of lighting, indicators and displays. However, there are also some problems with such “blue+yellow” WLEDs. For example, the color temperature is high and the color rendering index is low. Coating blue, green and red phosphors onto a near ultraviolet LED chips can potentially overcome the above problems. So far, many groups have focused on the development of tricolor emitting phosphors for the near ultraviolet chip excitation, especially the red emitting phosphors. Rare earth ions are widely used as emitting centers due to rich energy levels and metastable states with long lifetime. Among them, Eu^{3+} is particularly suitable for the red emission. The 4f-4f transitions of Eu^{3+} , however, are strongly dependent on its own local surrounding, and thus the selection of host materials is crucial. CaSnO_3 with low phonon energy and favorable thermal stability is a good choice. Unfortunately, the mismatch between Eu^{3+} and Ca^{2+} in charge and ions radii limits the doping level of Eu^{3+} . On the other hand, although some studies on thermal properties of $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions have been reported, there still exists a need to comprehensively understand the thermal quenching mechanism.

In this paper, $\text{CaSn}_{1-x}\text{Li}_x\text{O}_3:\text{Eu}^{3+}$ ($x=0, 2, 5, 10$) phosphors are synthesized by a simple solid state method. Firstly, the starting materials including CaCO_3 (AR), SnO_2 (CP), $\text{EuNO}_3 \cdot 6\text{H}_2\text{O}$ (4N) and Li_2CO_3 (AR) are mixed in stoichiometric ratio. After throughout grinding in agate mortar, the mixture are put into corundum crucible and then calcined in a silicon-molybdenum stove at 1300°C for 3 h. Finally, the white products are obtained. XRD analysis indicates that the solubility limit of Eu^{3+} in CaSnO_3 lattice is low, but the doping level of Eu^{3+} can be enhanced by introducing Li^+ ions. At 10% Li^+ doping, 8% Eu^{3+} ions are completely incorporated into CaSnO_3 lattice. On the basis of the shift of diffraction peaks, it is confirmed that the enhanced solubility limit of Eu^{3+} in CaSnO_3 is related to the charge compensation of Li^+ ions. More importantly, the enhanced $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions of Eu^{3+} are observed after introducing the Li^+ ions. When the Li^+ doping concentration is 10%, the strongest one is obtained. The related mechanism is discussed by using the corrected emission spectra. Take the optimal sample $\text{CaSn}_{0.9}\text{Li}_{0.1}\text{O}_3:8\%\text{Eu}^{3+}$ as an example, the thermal properties are also investigated. With increasing the temperature from 300 K to 500 K, the quenching of fluorescence is observed. Because the ratio of intensity for $^5\text{D}_1 \rightarrow ^7\text{F}_j$ to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ increases with the increase of temperature, the weaken emissions are related to the thermal population from $^5\text{D}_0$ to $^5\text{D}_1$. But due to the different activation energy for thermal quenching under 394 nm and 464 nm excitation, there must be some other thermal quenching processes. On the basis of the excitation spectra at various temperature, it is found that the weaken excitation efficiency is another key factor. Furthermore, it is clarified that the thermal population from $^7\text{F}_0$ to $^7\text{F}_j$ ($j>0$) is responsible for the decrease of excitation efficiency by using a steady-state luminescent rate equation.

white LEDs, charge compensation, red emission, thermal quenching

doi: 10.1360/N972017-00159