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$Sr_{0.3}Ca_{0.7}MoO_4$:Tb^{3+}, Eu^{3+}荧光粉的颜色可调发光和温度传感特性

尹学爱[1,2]，吕树臣[1,3*]

（1. 哈尔滨工程大学 物理与光电工程学院，黑龙江 哈尔滨　150001；　2. 滨州学院 航空工程学院，山东 滨州　256603；
3. 哈尔滨师范大学 光电带隙材料教育部重点实验室，黑龙江 哈尔滨　150025）

摘要：采用共沉淀法合成了一系列颜色可调的单掺和共掺 $Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$, Eu^{3+}荧光粉。用X射线衍射和扫描电镜对荧光粉的晶体结构和形貌进行了表征。结果表明，Tb^{3+}和 Eu^{3+}的少量掺入无杂峰产生，对样品的晶体结构几乎没有影响。研究了样品的发光特性和温度传感特性。在样品的发光特性中，证实了 $Sr_{0.3}Ca_{0.7}(MoO_4)_2$荧光粉中 Tb^{3+}向 Eu^{3+}的能量传递。同时，通过温度依赖性发射光谱，证明所制备的 $Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$, Eu^{3+}荧光粉具有较好的热稳定性。计算了样品的绝对灵敏度和相对灵敏度，$Sr_{0.3}Ca_{0.625}(MoO_4)_2$:0.05$Tb^{3+}$, 0.025$Eu^{3+}$样品的相对灵敏度在514 K时最大值为0.861%·K^{-1}。此外，在紫外光激发下，通过调节 Eu^{3+}的掺杂浓度，$Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$, Eu^{3+}荧光粉的发光颜色可调谐。

关　键　词：荧光特性；能量传递；荧光粉；光学温度传感
中图分类号：O482.31　　**文献标识码：**A　　**DOI：**10.37188/CJL.20220376

Color-tunable Luminescence and Temperature Sensing Behavior of $Sr_{0.3}Ca_{0.7}MoO_4$:Tb^{3+}, Eu^{3+} Phosphor

YIN Xueai[1,2], LYU Shuchen[1,3*]

(1. *College of Physics and Optoelectronic Engineering*, *Harbin Engineering University*, *Harbin* 150001, *China*;
2. *Institute of Aeronautical Engineering*, *Binzhou University*, *Binzhou* 256603, *China*;
3. *Key Laboratory of Photoelectric Bandgap Materials*, *Ministry of Education*, *Harbin Normal University*, *Harbin* 150025, *China*)
* *Corresponding Author*, *E-mail*: *hsdlsc63@126.com*

Abstract: A series of Tb^{3+}/Eu^{3+} single-doped, co-doped $Ca_{0.3}Sr_{0.7}(MoO_4)_2$ phosphors with a tunable color were synthesized by the conventional co-precipitation method. The crystal structure and morphology of phosphors were characterized by X-ray diffraction and field emission scanning electron microscopy. The results showed that a small amount of Tb^{3+} and Eu^{3+} doped into the sample has no effect on the crystal structure of the sample, and there are no impurity peaks. We researched the luminescence properties and temperature sensing properties. The energy transfer from Tb^{3+} to Eu^{3+} in $Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$, Eu^{3+} phosphors was confirmed in the luminescence characteristics of the samples. The temperature-dependent emission spectra suggested that the as-prepared samples possessed good thermal stability. The absolute sensitivity and relative sensitivity of samples were calculated, and the maximum relativity sensitivity of $Sr_{0.3}Ca_{0.625}(MoO_4)_2$: 0.05$Tb^{3+}$, 0.025 Eu^{3+} sample was 0.861%·K^{-1} at 514 K. In addition, under near-ultraviolet light by adjusting the doping concentration of Eu^{3+}, the $Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$, Eu^{3+} phosphors realized tunability of emission color.

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Key words: photoluminescence properties; energy transfer; phosphors; optical temperature sensing

1 引 言

近几十年以来,稀土离子掺杂的发光材料在固态照明领域已经得到了广泛的应用,例如,荧光生物标记、光学温度传感、固体激光器和显示照明等[1-5]。荧光强度比(FIR)温度测量技术具有响应快、非接触性和灵敏度高等特点,因而是当前最有应用前景的测温方案[6-9]。稀土发光材料的灵敏度和相对灵敏度是评价发光材料温度传感性能的重要依据。

温度传感材料的性能不仅与掺杂的稀土离子有关,还与所选取的基质材料相关。由于MoO_4^{2-}的极化作用,稀土离子在钼酸盐中具有较强的跃迁吸收和发射;并且MoO_4^{2-}中的Mo^{6+}具有$4d^0$能级,能与Eu^{3+}和Tb^{3+}离子的4f能级相互作用,形成价电荷迁移带,给Eu^{3+}和Tb^{3+}离子提供有效的热猝灭能级,产生温度依赖性发光。因此,钼酸盐适合作为基质材料[10-14]。

为了适应不同应用的需求,设计和生产具有多色发射和可调色度的荧光体至关重要。因此,本文采用化学共沉淀法制备了具有优异热稳定性的$Sr_{0.3}Ca_{0.7}MoO_4$:Tb^{3+},Eu^{3+}系列荧光粉。系统地研究了$Sr_{0.3}Ca_{0.7}MoO_4$:Tb^{3+},Eu^{3+}的晶体结构、发光特性以及热稳定性和温度传感特性。利用323~563K的温度依赖性发射光谱,证明了$Sr_{0.3}Ca_{0.7}MoO_4$:Tb^{3+},Eu^{3+}系列荧光粉的热稳定性。研究了$Sr_{0.3}Ca_{0.7}MoO_4$:Tb^{3+},Eu^{3+}荧光粉的绝对灵敏度和相对灵敏度,在514 K时$Sr_{0.3}Ca_{0.625}(MoO_4)_2$:0.05$Tb^{3+}$,0.025 Eu^{3+}样品的相对灵敏度最大值为0.861%·K^{-1}。在274 nm光激发下,通过改变Tb^{3+}与Eu^{3+}的掺杂浓度比,发现随着温度升高样品的发光颜色逐渐由橙红色变为绿色。此外,随着Eu^{3+}掺杂浓度的增大,样品的发光颜色变化范围增大,因此Tb^{3+}和Eu^{3+}共掺的$Sr_{0.3}Ca_{0.7}MoO_4$荧光粉在温度传感材料上具有潜在的应用价值。

2 实 验

2.1 样品合成

采用化学共沉淀法制备了$Sr_{0.3}Ca_{0.7}MoO_4$:Tb^{3+},Eu^{3+}系列荧光粉,所有使用的试剂没有经过提纯处理。首先把一定摩尔百分数的Eu_2O_3溶于浓硝酸中,磁力搅拌均匀,经过排酸定容成$Eu(NO_3)_3$溶液。Tb_4O_7也经过同样的过程,制成$Tb(NO_3)_3$溶液。按照样品设计抽取适量的$Eu(NO_3)_3$和$Tb(NO_3)_3$溶液,将其滴加到$Ca(NO_3)_2$和$Sr(NO_3)_2$混合溶液中配制成40 mL硝酸盐溶液。将$Na_2(MoO_4)\cdot 2H_2O$溶于50 mL去离子水中,并加浓氨水配制成pH值为10的碱性溶液。然后将混合后的硝酸盐溶液滴加到Na_2MoO_4溶液中,搅拌40 min至反应完全。化学反应完成后,将得到的沉淀物用去离子水洗涤后,用离心机离心数次,最后将沉淀物放入干燥箱中烘干。最终的产物在800 ℃的温度下在空气中烧结2 h,慢慢冷却到室温。

2.2 样品测试和表征

采用Rigaku D/max2600/pc型X射线衍射仪(XRD)分析$Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$, Eu^{3+}荧光粉的晶体结构。测试范围10°~70°,扫描电压为40 kV,步长为0.02°。采用HitachiSU70扫描电镜(SEM)对样品进行形貌分析。采用Fluoromax-4型荧光光谱仪室温下测定样品的激发光谱和发射光谱,并且在323~563 K温度范围内对变温光谱进行了测试。

3 结果与讨论

3.1 样品的晶体结构分析

图1是$Sr_{0.3}Ca_{0.65}(MoO_4)_2$:0.05$Tb^{3+}$、$Sr_{0.3}Ca_{0.685}(MoO_4)_2$:0.015$Eu^{3+}$和$Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,

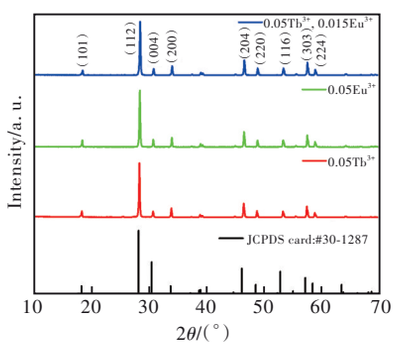

图1 $Sr_{0.3}Ca_{0.65}(MoO_4)_2$:0.05$Tb^{3+}$、$Sr_{0.3}Ca_{0.685}(MoO_4)_2$:0.015$Eu^{3+}$和$Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$荧光粉的XRD图。

Fig.1 XRD patterns for the $Sr_{0.3}Ca_{0.65}(MoO_4)_2$:0.05$Tb^{3+}$, $Sr_{0.3}Ca_{0.685}(MoO_4)_2$:0.015$Eu^{3+}$ and $Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$ phosphors.

0.015Eu^{3+}荧光粉的XRD图。从图1中可以看出，所有的XRD图谱与标准PDF卡片#30-1287相符，没有其他杂峰，说明所制备的样品是纯的体心立方晶相结构。这表明掺入少量的Tb^{3+}离子和Eu^{3+}离子对样品的晶体结构几乎没有影响。

用 MDI Jade 6 计算了 $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$, yEu^{3+}样品的晶格参数，结果如表1所示。结果表明，离子半径较小的Eu^{3+}离子成功取代了离子半径较大的Ca^{2+}离子，晶格体积随掺杂Eu^{3+}离子浓度的增加而逐渐缩小。

表1　$Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$($y$=0.01, 0.015, 0.025)晶格参数

Tab. 1　The lattice parameter of $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$($y$ = 0.01, 0.015, 0.025)

Samples	a/nm	b/nm	c/nm	Unit cell volume/nm^3
y = 0.010	0.530 93	0.530 93	1.169 31	0.329 6
y = 0.015	0.530 13	0.530 13	1.167 64	0.328 2
y = 0.025	0.529 27	0.529 27	1.165 11	0.326 4

3.2　样品形貌

为了观察样品的形貌，图2(a)给出了代表性样品 $Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$的扫描电镜图。从图中可看出，粉末颗粒近似球形。样品的元素Mapping如图2(b)~(g)所示，可以看出，样品包含Ca、Sr、Mo、O、Tb和Eu这几种元素。

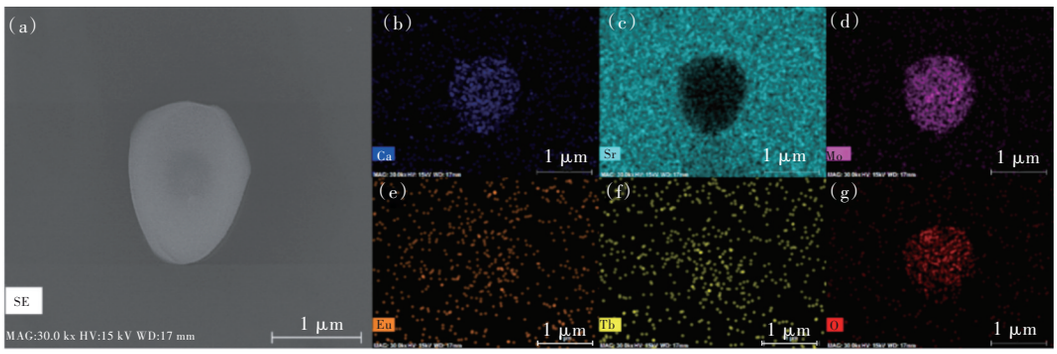

图2　$Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$样品表征。(a)SEM；(b)~(g)元素Mapping。

Fig.2　$Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$ sample. (a)SEM. (b)-(g)Element Mapping.

3.3　样品的激发光谱和发射光谱

图3为室温下不同样品的激发光谱。标记线(a)为 $Sr_{0.3}Ca_{0.65}(MoO_4)_2$:0.05$Tb^{3+}$荧光粉在监测波长为543 nm($Tb^{3+}$ $^5D_4$→$^7F_5$跃迁)的激发光谱。在220~340 nm范围内存在一个强激发宽带，对应于Tb^{3+} O^{2-}-Mo^{6+}和O^{2-}-Tb^{3+}的跃迁吸收[15]。此外，在487 nm处，有一个明显的激发峰，对应Tb^{3+}($^7F_6$→$^5D_4$)[16]。标记线(d)是$Sr_{0.3}Ca_{0.685}(MoO_4)_2$:0.015$Eu^{3+}$荧光粉在监测波长为615 nm($Eu^{3+}$ $^5D_0$→$^7F_2$跃迁)的激发光谱。在220~340 nm范围内有一个较强的激发带，对应于Eu^{3+} O^{2-}-Mo^{6+}和O^{2-}-Eu^{3+}的电荷迁移带[17]。在395 nm和465 nm处的弱激发峰来自于Eu^{3+}($^7F_0$→$^5L_6$)及Eu^{3+}($^7F_0$→$^5D_2$)[18]。标记线(b)和(c)为样品 $Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$在监测波长分别为543 nm和615 nm时的激发波谱。观察标记线(b)可见，在543 nm处监测Tb^{3+}离子的发光时，未见Eu^{3+}(395 nm，$^7F_0$→$^5L_6$)和(465 nm，$^7F_0$→$^5D_2$)的特征激发；但在标记线(c)中，当监测Eu^{3+}离子在615 nm处的发光时，出现基质宽带

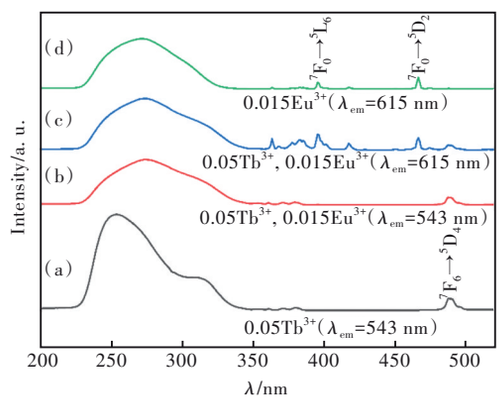

图3　不同样品的激发谱：(a)$Sr_{0.3}Ca_{0.65}(MoO_4)_2$:0.05$Tb^{3+}$($\lambda_{em}$=543 nm)，(b)$Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$, 0.015$Eu^{3+}$($\lambda_{em}$=543nm)，(c)$Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$, 0.015$Eu^{3+}$($\lambda_{em}$=615 nm)；(d)$Sr_{0.3}Ca_{0.685}(MoO_4)_2$:0.015$Eu^{3+}$($\lambda_{em}$=615 nm)。

Fig.3　Excitation spectra of different samples: (a)$Sr_{0.3}Ca_{0.65}(MoO_4)_2$: 0.05$Tb^{3+}$($\lambda_{em}$ = 543 nm), (b)$Sr_{0.3}Ca_{0.635}(MoO_4)_2$: 0.05$Tb^{3+}$, 0.015$Eu^{3+}$($\lambda_{em}$ = 543 nm), (c)$Sr_{0.3}Ca_{0.635}(MoO_4)_2$: 0.05$Tb^{3+}$, 0.015$Eu^{3+}$($\lambda_{em}$= 615 nm), (d)$Sr_{0.3}Ca_{0.685}(MoO_4)_2$: 0.015$Eu^{3+}$($\lambda_{em}$= 615 nm).

激发峰和 Tb^{3+}($^7F_6\rightarrow{}^5D_4$)特征激发带。这些表明从 Eu^{3+}到 Tb^{3+}没有能量传递,Tb^{3+}对 Eu^{3+}有能量传递。我们曾试图寻找能量传递效率与温度变化的关系[19],但结果不规律,可重复性差,如不同批次合成的同类样品并不完全遵守相同的规律。此外,基质对 Tb^{3+}离子和 Eu^{3+}离子都有能量传递。

图 4 为室温下激发波长为 274 nm 时,(a) $Sr_{0.3}Ca_{0.65}(MoO_4)_2$:0.05$Tb^{3+}$、(b) $Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$ 和 (c) $Sr_{0.3}Ca_{0.685}(MoO_4)_2$:0.015$Eu^{3+}$样品的发射光谱。标记线(a)是 Tb^{3+}的 4f-4f 跃迁发射峰,分别位于 487 nm($^5D_4\rightarrow{}^7F_6$)、543 nm($^5D_4\rightarrow{}^7F_5$)、587 nm($^5D_4\rightarrow{}^7F_4$) 和 622 nm($^5D_4\rightarrow{}^7F_3$)[20]。标记线(b)显示了 Tb^{3+}和 Eu^{3+}的 4f-4f 跃迁发射峰。标记线(c)显示 Eu^{3+}的 4f-4f 跃迁发射峰,分别位于 590 nm($^5D_0\rightarrow{}^7F_1$)、615 nm($^5D_0\rightarrow{}^7F_2$)、655 nm($^5D_0\rightarrow{}^7F_3$)和 701 nm($^5D_0\rightarrow{}^7F_4$)[21]。

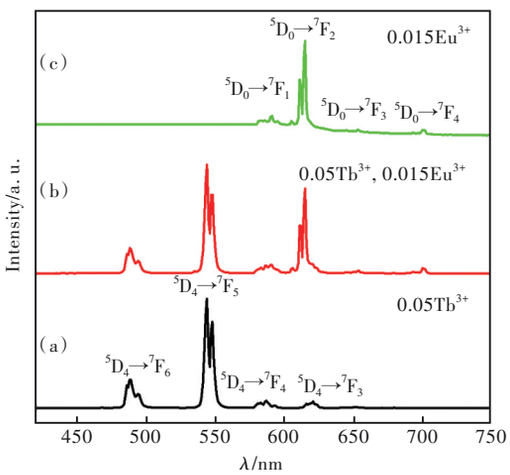

图 4 不同样品的发射谱(λ_{ex}=274 nm):(a) $Sr_{0.3}Ca_{0.65}(MoO_4)_2$:0.05$Tb^{3+}$,(b) $Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$,(c) $Sr_{0.3}Ca_{0.685}(MoO_4)_2$:0.015$Eu^{3+}$。

Fig.4 Emission spectra of different samples(λ_{ex}=274 nm): (a) $Sr_{0.3}Ca_{0.65}(MoO_4)_2$:0.05$Tb^{3+}$, (b) $Sr_{0.3}Ca_{0.635}(MoO_4)_2$:0.05$Tb^{3+}$,0.015$Eu^{3+}$, (c) $Sr_{0.3}Ca_{0.685}(MoO_4)_2$:0.015$Eu^{3+}$.

3.4 荧光粉的光学温度传感性质

为了研究材料的温度传感特性,我们测试了在 274 nm 激发下 $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$荧光粉在 323~635 K 温度范围内的温度依赖性发射光谱,如图 5(a)~(c)所示。可以看出,不同温度下样品的发射光谱波形和发射峰位置基本相同,Eu^{3+}和 Tb^{3+}的发射峰有不同的热猝灭趋势。随着温度的升高,Eu^{3+}的发光强度下降趋势比 Tb^{3+}更迅速。在该材料中,Tb^{3+}和 Eu^{3+}的热响应速度有明显差别,因此 Tb^{3+}和 Eu^{3+}的荧光强度比(FIR)将随温度发生显著变化。

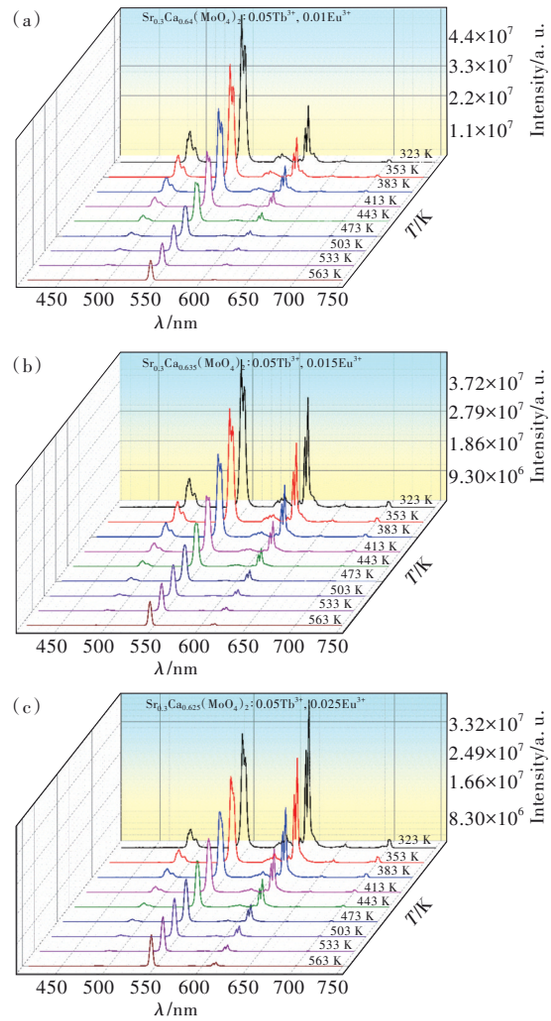

图 5 $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$荧光粉($\lambda_{ex}$ = 274 nm)的温度依赖性发射光谱。(a) y = 0.01;(b) y = 0.015;(c) y = 0.025。

Fig.5 Temperature-dependent emission spectra for $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$ phosphors(λ_{ex} = 274 nm). (a) y = 0.01. (b) y = 0.015. (c) y = 0.025.

对于单掺杂稀土离子的发光材料,发光强度与温度的关系由公式(1)表示[22-23]:

$$\frac{I_T}{I_0}=\left[1+Ae^{\left(-\frac{E}{K_BT}\right)}\right]^{-1}, \tag{1}$$

I_0是初始温度积分发光强度值,I_T是温度 T 下的积分发光强度值,常数 A 与基质材料相关,ΔE 是热猝灭活化能,K_B是玻尔兹曼常数。

随着温度升高,Tb^{3+}($^5D_4\rightarrow{}^7F_5$)和 Eu^{3+}($^5D_0\rightarrow{}^7F_2$)的荧光强度比值 FIR 有明显变化,适合温度测量[24]。在 $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$ (y = 0.01, 0.015, 0.025)荧光粉中,Tb^{3+}和 Eu^{3+}荧光强度比可简化为 R,用下列公式表示[23, 25]:

$$R = \frac{I_{Tb}}{I_{Eu}} = \frac{I_{0,Tb}}{I_{0,Eu}} \cdot \frac{1 + A_{Eu}\exp(-E_{Eu}/K_B T)}{1 + A_{Tb}\exp(-E_{Tb}/K_B T)}, \quad (2)$$

可以将公式(2)简化为[26]：

$$R = B + Ce^{-\Delta E/K_B T}, \quad (3)$$

其中，B、C和ΔE是与材料本身和掺杂的稀土离子有关的常数。将我们得到的数据与公式(3)进行拟合得到B、C和$\Delta E/K_B$的数值。图6是$Sr_{0.3}Ca_{0.65-y}(MoO_4)_2:0.05Tb^{3+},yEu^{3+}$样品$R$值与温度的关系(点为实验数据，线为拟合数据)。从图6中可以看出，样品的R值随温度升高而增大。样品的B、C和E/K_B数值如表2所示。

绝对灵敏度是反映材料温度传感性能的重要参数，绝对灵敏度越大，单位温度内R值变化越大，越适合用作测温材料。绝对灵敏度S可以用公式(4)表示[26]：

$$S = \frac{dR}{dT} = Ce^{-\Delta E/K_B T}\left(\frac{\Delta E}{K_B}\right)\left(\frac{1}{T^2}\right). \quad (4)$$

图7是$Sr_{0.3}Ca_{0.65-y}(MoO_4)_2:0.05Tb^{3+},yEu^{3+}$($y$ = 0.01, 0.015, 0.025)样品的绝对灵敏度和温度的关系。从图中可以看出，荧光粉的灵敏度S随温度的升高而增大。在563 K时，样品的灵敏度S最大值分别0.080 8，0.034 1，0.040 3 K^{-1}。

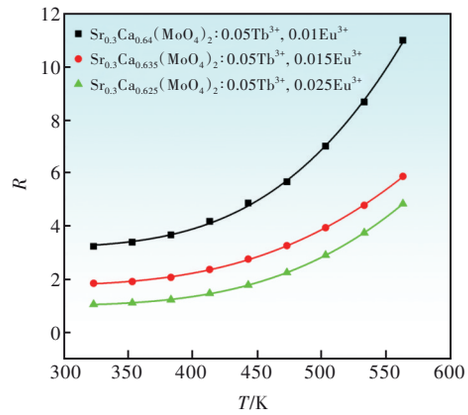

图6　$Sr_{0.3}Ca_{0.65-y}(MoO_4)_2:0.05Tb^{3+},yEu^{3+}$($y$ = 0.01, 0.015, 0.025)荧光粉的R值随温度变化曲线，点是实验数据，线是拟合结果。

Fig.6　Curve R *versus* temperature in $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2:0.05Tb^{3+},yEu^{3+}$ phosphors, the solid points and lines are experimental and fitting data, respectively.

表2　样品R值对应的B、C和$\Delta E/K_B$的数值及拟合度参数R^2

Tab. 2　The values of B, C, $\Delta E/K_B$ and their correlation coefficients R^2 of samples

Samples	B	C	$\Delta E/K_B$/K	R^2
y = 0.010	3.188±0.056	2 755.122±0.751	3 306.481±0.278	0.999 4
y = 0.015	1.748±0.016	792.650±0.302	2 961.431±0.714	0.999 8
y = 0.025	0.998±0.007	1 369.938±0.852	3 308.519±0.734	0.999 4

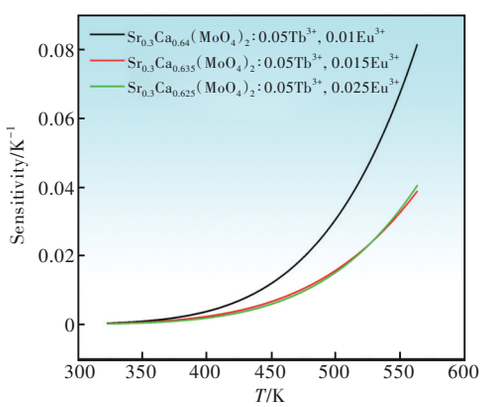

图7　$Sr_{0.3}Ca_{0.65-y}(MoO_4)_2:0.05Tb^{3+},yEu^{3+}$($y$ = 0.01, 0.015, 0.025)荧光粉中灵敏度随温度变化曲线

Fig.7　Sensitivity curve with temperature in $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2:0.05Tb^{3+},yEu^{3+}$($y$ = 0.01, 0.015, 0.025) phosphors

从公式(4)可以看出，绝对灵敏度随R值的变化而发生变化，不能精确评价不同测温材料的性能。相对灵敏度是温度变化单位值的R值的变化比率，不受R值变化的影响，更能反映材料对温度的敏感性。相对灵敏度可用公式(5)表示[26]：

$$S_R = \frac{1}{R}\frac{dR}{dT} = \frac{Ce^{-\Delta E/K_B T}\left(\frac{\Delta E}{K_B}\right)\left(\frac{1}{T^2}\right)}{B + Ce^{(-\Delta E/K_B T)}}. \quad (5)$$

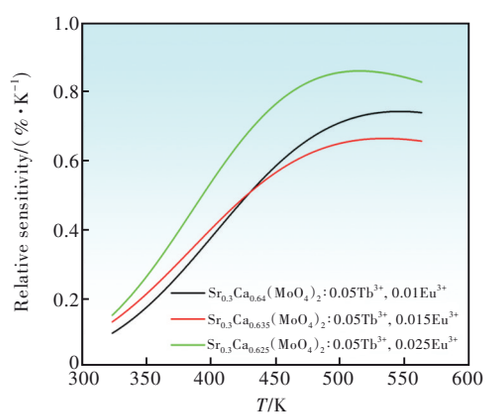

图8　$Sr_{0.3}Ca_{0.65-y}(MoO_4)_2:0.05Tb^{3+},yEu^{3+}$($y$ = 0.01, 0.015, 0.025)荧光粉的相对灵敏度与温度的关系

Fig.8　Curve of relative sensitivity *versus* temperature in $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2:0.05Tb^{3+},yEu^{3+}$($y$ = 0.01, 0.015, 0.025) phosphors

图 8 是样品的相对灵敏度与温度的关系。从图中可以看出,在 323~563 K 温度范围内,样品的相对灵敏度随温度的升高而增大。当 Eu^{3+}浓度为 0.01,0.015,0.025 时,最大相对灵敏度分别是 0.743%·K^{-1}(546 K)、0.664%·K^{-1}(534 K)和 0.861%·K^{-1}(514 K)。

3.5 样品的色坐标

在我们制备的 $Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$,$Eu^{3+}$荧光粉中,由于 Tb^{3+}($^5D_4\rightarrow{}^7F_5$)的绿光发射和 Eu^{3+}($^5D_0\rightarrow{}^7F_2$)的红光发射具有不同的热猝灭趋势,荧光强度随温度的升高而变化,发光颜色也会相应地发生改变。在 274 nm 激发下,我们计算了 $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$荧光粉在 323~563 K 温度范围内的 CIE 色坐标,如图 9(a)~(c)中。从图 9 可以看出,随着温度的升高,样品的发光颜色逐渐由橙红色变为绿色。此外,从图 9 中还可以发现,随着 Eu^{3+}掺杂浓度的增加,样品的发光颜色变化范围增大。

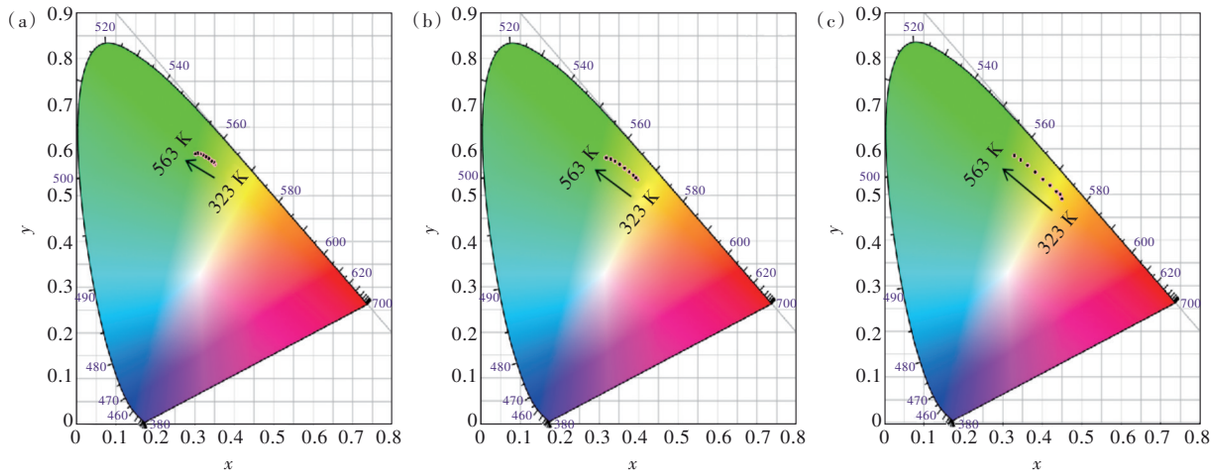

图 9 $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$荧光粉($\lambda_{ex}$ = 274 nm)的色坐标:(a)y = 0.01,(b)y = 0.015,(c)y = 0.025。

Fig.9 CIE coordinate diagrams for $Sr_{0.3}Ca_{0.65-y}(MoO_4)_2$:0.05$Tb^{3+}$,$yEu^{3+}$ phosphors(λ_{ex} = 274 nm): (a)y = 0.01, (b)y = 0.015, (c)y = 0.025.

4 结 论

本文采用共沉淀法制备了一系列 $Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$,$Eu^{3+}$荧光粉,利用XRD和SEM对样品的结构和形貌进行了表征,证实所得样品为体心立方的白钨矿结构。通过测试样品的激发光谱和发射光谱,分析了Tb^{3+}、Eu^{3+}掺杂浓度以及Tb^{3+}到Eu^{3+}的能量传递对荧光粉发光性能的影响。在 323~563 K 温度范围内,荧光粉的发光颜色从橙红色连续变化为绿色,可以用发光颜色直接表征温度。$Sr_{0.3}Ca_{0.7}(MoO_4)_2$:$Tb^{3+}$,$Eu^{3+}$荧光粉具有较高的相对灵敏度,因此该材料是一种具有潜在应用前景的温度传感材料。

本文专家审稿意见及作者回复内容的下载地址:http://cjl.lightpublishing.cn/thesisDetails#10.37188/CJL.20220376.

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尹学爱(1979-),女,山东滨州人,博士研究生,2007年于华中科技大学获得硕士学位,主要从事固体发光方面的研究。

E-mail: yinxueai08@163.com

吕树臣(1963-),男,黑龙江哈尔滨人,博士,教授,博士生导师,2002年于中国科学院长春光学精密机械与物理研究所获得博士学位,主要从事量子光学及固体发光方面的研究。

E-mail: hsdlsc63@126.com