

蓝宝石基光色可调荧光玻璃陶瓷的发光性能

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摘要 荧光玻璃陶瓷是高功率白光照明器件的重要材料之一,然而,红色荧光粉易与玻璃粉在共烧结时发生反应,制约了荧光玻璃陶瓷的发展。本课题组将(Ca,Sr)AlSiN₃:Eu²⁺红色荧光粉与Y₃Al₅O₁₂:Ce³⁺黄色荧光粉复合,在高热导率的蓝宝石基质上以硼硅酸玻璃粉为黏结剂,采用丝网印刷技术制备了荧光玻璃陶瓷,研究了样品共烧结过程中材料结构、形貌、元素比等的变化,模拟了实验过程,分析了发光性能。结果表明:在制备玻璃陶瓷的共烧结过程中,两种荧光粉均未与粘结玻璃发生明显的反应;随着红粉掺杂量增加,玻璃陶瓷的发射光谱红移且强度逐渐降低,量子效率呈现下降趋势;玻璃陶瓷具有优异的热稳定性,150℃下的发光强度为室温下的89%;随着红粉掺杂量增加,样品表现为由冷白光向暖白光转变的光色可调性,最佳光电参数为流明效率147.70 lm/W、色温4915 K、显色指数73.3。

关键词 材料; 发光材料; 玻璃陶瓷; 红色荧光粉; 蓝宝石; 光色可调性

中图分类号 TB34 **文献标志码** A

DOI: 10.3788/CJL220951

1 引言

固态照明广泛存在于户内、室外、景观、汽车大灯等人们生产生活的各个领域,固态照明用发光材料的研究和发展,对于促进社会进步和经济发展具有重要意义。目前,市场上照明主流使用的白光LED器件因有机物封装导致的“热稳定性差、易老化”等缺陷,限制了其在高功率领域的应用和发展。利用玻璃的热稳定性、热导率均高于有机物的特性,采用“荧光玻璃陶瓷+远程封装+芯片(或激光)”方式组装器件,是解决上述问题的有效途径之一^[1-2]。在荧光玻璃陶瓷方面,研究人员已利用Y₃Al₅O₁₂:Ce³⁺/LuAG:Ce³⁺荧光粉的高热稳定特性制备出了发光性能良好的黄(绿)光材料^[3-7];但在红光材料方面,目前有效匹配蓝光激发的商用氮化物或氟化物红色荧光粉的热稳定性与氧化物粉体相比均相对较差,在制备玻璃陶瓷的共烧结过程中容易分解或与玻璃粉发生反应,降低了材料的发光性能。因此,在荧光玻璃陶瓷中补充红光改善发光器件的显色性,成为了近年来的研究热点^[7-8]。红光补充型荧光玻璃陶瓷的制备大致可分为三种方式:一是在基质玻璃或粘结玻璃中掺杂发光离子(如Eu³⁺)补充红光^[9-10];二是在黄(绿)光玻璃陶瓷表面通过有机物黏附红色荧光粉(CaAlSiN₃:Eu²⁺,Ca₂S₅N₈:Eu²⁺,K₂SiF₄:

Mn⁴⁺等)来增加红光发射^[11-12];三是直接在黄(绿)粉中掺入一定比例的红粉(CaAlSiN₃:Eu²⁺,Ca₂S₅N₈:Eu²⁺,MGF:Mn⁴⁺等),通过二次熔融烧结、放电等离子烧结、丝网印刷烧结等方法制备双荧光粉相玻璃陶瓷^[13-18]。相比较而言,第三种方式对显色性的改善效果相对明显,且不会出现红色荧光体脱落的现象。然而,采用该方式制备样品时,通常需要超过600℃的温度,在此温度下,红色荧光粉易与液化的基质玻璃(粘结玻璃)发生反应从而降低发光性能,使得玻璃陶瓷的综合发光效率总体表现相对不高。基于蓝宝石高热导率和高透过率的优点^[14],本团队将其作为基质衬底材料,利用Y₃Al₅O₁₂:Ce³⁺黄粉和(Ca,Sr)AlSiN₃:Eu²⁺红粉均能被蓝光芯片(商业蓝色激光)有效激发以及其热稳定性相对良好的特点,采用丝网印刷-共烧结技术模拟了荧光粉与玻璃粉的共烧结过程,并通过调整荧光粉中红色粉体的含量,制备了光色可调、综合发光性能相对优异的双相荧光玻璃陶瓷。

2 实验

2.1 样品制备

样品制备分为粘结玻璃制备和玻璃陶瓷制备两部分。粘结玻璃采用传统的高温熔融冷却法制备,玻璃成分为SiO₂-B₂O₃-ZnO-Al₂O₃-CaO,其原料是纯度均为

收稿日期: 2022-06-06; 修回日期: 2022-07-01; 录用日期: 2022-07-08; 网络首发日期: 2022-07-18

基金项目: 国家自然科学基金(52062017)

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99.9% 的 H_3BO_3 、 SiO_2 、 ZnO 、 Al_2O_3 、 CaO 。准确称取原料约 50 g, 将其置于玛瑙研钵中充分研磨, 研磨均匀后装入刚玉坩埚, 而后放入 1300 °C 马弗炉中熔制 90 min。倒玻璃液时, 将一小部分倒入石墨模具中成型, 然后在 680 °C 马弗炉中退火 2 h (消除内部应力), 冷却至室温后取出样品打磨抛光, 进行相关测试; 其余部分直接倒入去离子水中淬裂成玻璃碴, 将玻璃碴放入 80 °C 烘箱中直至完全烘干后取出, 再放入玛瑙研钵中充分研磨, 过 200 目筛网后制备成粘结玻璃粉。荧光玻璃陶瓷采用丝网印刷工艺制备, 制备过程分印刷浆料制备和玻璃陶瓷印刷两步。印刷浆料制备: 将 1% (质量分数, 下同) 乙基纤维素加入盛有 99% 松油醇有机液体的烧杯中, 将烧杯置于 60 °C 恒温水浴槽中, 充分搅拌烧杯内的溶液, 直至两者完全相溶后制成黏结剂, 再将黏结剂、粉体 (17% 荧光粉 + 83% 粘结玻璃粉) 按比例混合, 充分搅拌后调制成油漆状混合物, 制成印刷浆料。玻璃陶瓷印刷: 先将蓝宝石平放至印刷机基板上, 再用刮刀将印刷浆料在 200 目印刷网板上来回印刷 5 次左右 (样品的印刷次数应一样, 以保证印刷厚度相同); 印刷后的样品放入真空抽滤机中抽真空 10 min, 然后将样品放入马弗炉中按一定的升温制度烧结, 自然冷却后制备成玻璃陶瓷样品。升温制度如下: 室温下升温至 200 °C 烧结 90 min (除去松油醇) → 升温至 680 °C 烧结 60 min (除去乙基纤维素) → 升温至 750 °C 烧结 30 min, 升温速率均为 5 °C/min。按照玻璃陶瓷原料中不同种类荧光粉的比例, 将 $x=0\%$, 1%, 2%, 3%, 17% 的 (Ca, Sr) AlSiN_3 : Eu^{2+} 红色荧光粉 (简称“CSASN”) 与 17% - x 的 $\text{Y}_3\text{Al}_5\text{O}_{12}$: Ce^{3+} 黄色荧光粉 (简称“YAG”) 混合制备的玻璃陶瓷分别命名为 Y-GC、Y-R1-GC、Y-R2-GC、Y-R3-GC 和 R-GC。

2.2 测试表征

基于阿基米德排水法, 利用自制的密度测试仪测定粘结玻璃的密度, 利用宝石数字折射仪测定玻璃的折射率。密度和折射率的取值分别为 3 个不同测量点的平均值。粘结玻璃的转化点温度测定以及玻璃陶瓷样品的 DSC 模拟实验均采用热重及同步热分析仪 (Mettler TGA/DSC3+) 进行, 其中: 测试转化点温度时的升温速率为 10 °C/min, 温度测试范围为 400~800 °C; DSC 模拟实验条件为 750 °C 停留 30 min, 观察样品的吸放热情况。采用 X 射线粉末衍射仪 (Bruker, D8 Advance) 测试样品的结构, 测试条件: Cu K_α 辐射, 2θ 扫描范围为 $10^\circ\sim 80^\circ$, 扫描速率为 $10^\circ/\text{min}$ 。采用配备能谱分析 (EDS) 系统的扫描电子显微镜 (Sigma 500, SEM) 分析样品形貌和元素组成。采用荧光光谱仪 (FIS980) 测定样品的激发光谱、发射光谱和量子效率, 激发光源为 450 W 氙灯。样品的热稳定性采用热猝灭分析系统 (EX-1000) 进行测定, 温度测试范围为 25~200 °C, 升温速率为 10 °C/min, 以 25 °C 作为间隔点, 每个点上停留 5 min, 待温度稳定后再进行光谱测

试。样品的光电性能采用配备有积分球的光电测试系统 (HAAS-2000) 进行测定, 测试蓝光芯片的型号为兆驰 FB1128B。

3 结果与讨论

3.1 粘结玻璃的基本性质

粘结玻璃的 DSC 曲线如图 1 所示。样品热分析结果显示, 样品的玻璃转化温度 (T_g) 为 702 °C, 且在 700~800 °C 之间没有明显的放热峰。这表明实验选取的 750 °C 的二次烧结温度是相对适宜的温度, 在此温度下烧结不会出现析晶, 不会影响样品的透明度。图中插图 (实物图和 XRD 图谱) 均进一步表明制备的粘结玻璃呈现明显的非晶体特征, 成玻性能良好。通常来说, 荧光粉与基质 (粘结) 玻璃之间的密度差、折射率差是影响荧光玻璃陶瓷发光性能的两个较为关键的因素^[19]。小的密度差有利于荧光粉颗粒在玻璃中均匀分布, 相近的折射率可以减少光的散射, 从而提升玻璃陶瓷样品的透明度和出光效率。图 1 插图中给出了粘结玻璃样品的密度 (ρ) 和折射率 (n), 其值分别为 $\rho=2.937\text{ g}\cdot\text{cm}^{-3}$ 和 $n=1.595$, 与 YAG 荧光粉的值 ($\rho=4.54\text{ g}\cdot\text{cm}^{-3}$, $n=1.83$) 相比^[20] 尽管有一定距离, 但作为硼硅酸盐玻璃, 其密度和折射率俨然已相对较高^[21-22], 从而在一定程度上保证了制备相对透明的玻璃陶瓷的可行性, 后续的实物照片和 SEM 图像也证实了这一点。

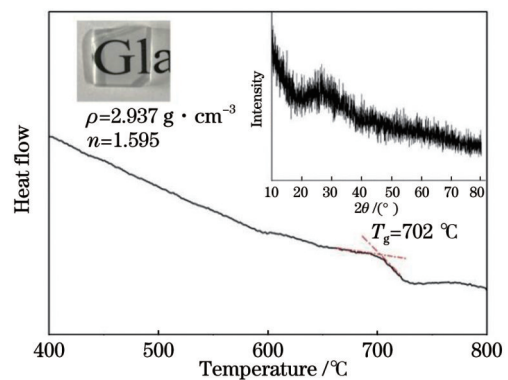


图 1 粘结玻璃的 DSC 曲线 (插图为玻璃的实物图和 XRD 谱)
Fig. 1 DSC curve of frit-seal glass (the insets are physical photo and XRD pattern of frit-seal glass)

3.2 结构分析

图 2 所示为掺杂纯 YAG 黄粉 (Y-GC)、纯 CSASN 红粉 (R-GC) 和两者共掺 (Y-R2-GC) 玻璃陶瓷的 XRD 图谱。显而易见, 对于单掺黄粉的 Y-GC 玻璃陶瓷, 其衍射峰与 YAG 荧光粉原料相比, 既没有生成新峰, 原峰也没有消失, 两者的吻合度极高。这表明 YAG 荧光粉与粘结玻璃粉在烧结过程中没有发生任何反应, 荧光粉的晶相保持完好。相比 CSASN 红色荧光粉原料, 单掺红粉的 R-GC 样品的衍射峰具有以下特点: 1) 衍射强度发生了变化, 在 18° 、 37° 、 56° 衍射角附近, R-GC 样品的衍射峰强度比红色荧光粉原料有一定增强 (或者

其他角度峰减弱)。2)玻璃陶瓷样品中的部分衍射峰(如 26° 、 39° 、 47° 、 63°)消失。以上两方面可能是由荧光粉掺入玻璃陶瓷时择优取向导致的(荧光粉掺入玻璃粉烧结成型后,无法完整地由XRD仪器从各个角度收集信息)^[23];另外,在红色荧光粉与玻璃粉烧结过程中,荧光粉的微结构可能部分发生了一定的扭曲和改变,导致部分面的衍射峰增强或消失,这也是一个可能的原因。3)玻璃陶瓷没有出现与荧光粉原料不同的新相,也没有出现峰位移动(虽然衍射强度变化和部分峰消失),这说明红色荧光粉制备成玻璃陶瓷时,粘结玻璃粉与荧光粉之间基本没有发生大的侵蚀反应。对于同时掺杂黄粉、红粉制备的Y-R2-GC玻璃陶瓷来说,其所有衍射峰都能与Y-GC黄粉或CSASN红粉对应,没有新的衍射峰生成。这表明在制备两相荧光玻璃陶瓷过程中,不仅荧光粉与玻璃粉没有发生明显的化学反应,而且两种荧光粉之间也没有发生化学反应,从而保证了玻璃陶瓷的出光效率。

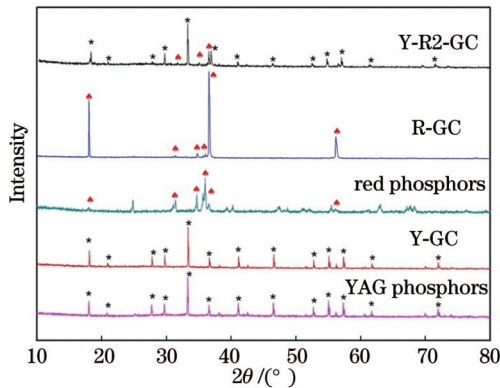


图2 玻璃陶瓷的XRD图谱

Fig. 2 XRD patterns of glass ceramics

为进一步研究荧光粉在共烧结过程中是否与粘结玻璃发生了反应,本课题组采用DSC仪器按照实验条件对玻璃陶瓷的制备进行了实验模拟,测试其在 750°C 下共烧结30 min(1800 s)过程中体系的吸放热情况,测试结果如图3所示。由图3可知,无论是单掺

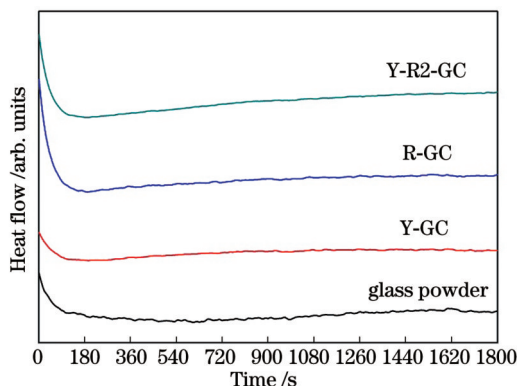


图3 实验模拟的玻璃陶瓷的DSC曲线图

Fig. 3 DSC curves of glass ceramics prepared with experimental simulation

杂YAG黄粉的Y-GC、单掺杂CSASN红粉的R-GC,还是双掺的Y-R2-GC玻璃陶瓷,在约100 s后的保温阶段,均表现出与粘结玻璃粉一样的平坦曲线,体系没有吸热也没有放热。这表明在上述3个样品的制备过程中,YAG黄粉、CSASN红粉均没有与粘结玻璃发生交互反应。这一结论与前述XRD的分析结果一致。如图3所示,在约100 s之前,所有样品均呈现出吸热现象,这是仪器加热停止后到保温期间经过了一段过渡期,或者仪器自身的程序设计导致热量发生了变化,与样品自身的吸放热无关。

3.3 形貌与元素分析

图4所示为不同荧光粉掺杂玻璃陶瓷的SEM图像和EDS扫描分析图。图4(a)为纯粘结玻璃粉在蓝宝石基质上二次烧结后的SEM平面图,可见,粘结玻璃经过二次熔融烧结后呈现出良好的玻璃态,这也证实了烧结过程中粘结玻璃没有发生析晶行为。图4(b)~(d)分别展示了Y-GC、R-GC以及Y-R2-GC三个样品的SEM平面图。图4(b)中的圆形颗粒为YAG荧光粉,其相对均匀地分布在粘结玻璃中。图4(c)中的方形颗粒是CSASN荧光粉,其相对均匀地分布,但相对而言,其分布均匀性低于YAG荧光粉。这是由于CSASN荧光粉为氮化物,其在粘结玻璃粉(氧化物)中的润湿性小于其在同为氧化物的YAG荧光粉中的润湿性^[24-25],润湿性的不足导致其分散程度降低。图4(d)中粉体分布的相对不均匀性也很可能是这个原因。另外,图4(d)中方形CSASN荧光粉的可见度很小,这是由红粉的掺杂比例(2%)较小导致的。图4(e)中Y-GC的横截面形貌显示:YAG颗粒紧密嵌入玻璃中(YAG与粘结玻璃之间的密度差小且浸润性好),在粘结玻璃与蓝宝石的界面处没有任何断层和裂缝。这表明粘结玻璃与蓝宝石之间的黏结性能良好,这得益于实验选取的硼硅酸盐粘结玻璃的膨胀系数与蓝宝石差异较小,两者在受热时的尺度、体积变化同步。图4(e)还显示,样品的印刷厚度在 $210\ \mu\text{m}$ 左右,结合后续实物图显示的良好透过性以及光电指标分析中表现出的良好性能(图8),可知该印刷厚度较为适宜。

为进一步探究玻璃陶瓷制备过程中荧光粉颗粒与粘结玻璃之间的相互作用,对相关样品进行了EDS点扫描和线扫描分析。图4(g)给出了Y-GC样品中点1处的扫描结果,可见,Al、Y元素的原子数比 $n_{\text{Al}}:n_{\text{Y}}=1.58$,该数值与YAG荧光粉分子式中Al、Y元素的比值1.67接近。图4(i)给出了该样品的线扫描结果,可见,YAG荧光粉中Al、Y元素含量快速下降,与粘结玻璃中Si、Zn、Ca元素的快速上升同时交汇。上述结果均表明YAG荧光粉没有与粘结玻璃发生明显的反应。图4(f)所示的R-GC样品中点2的点扫描结果证实该样品中只存在Zn、Al、Si、Ca、O等元素(Au元素为样品喷金带入),没有发现CSASN荧光粉中的Sr、N等独有元素,这与粘结玻璃的成分是一致的。图4(h)给

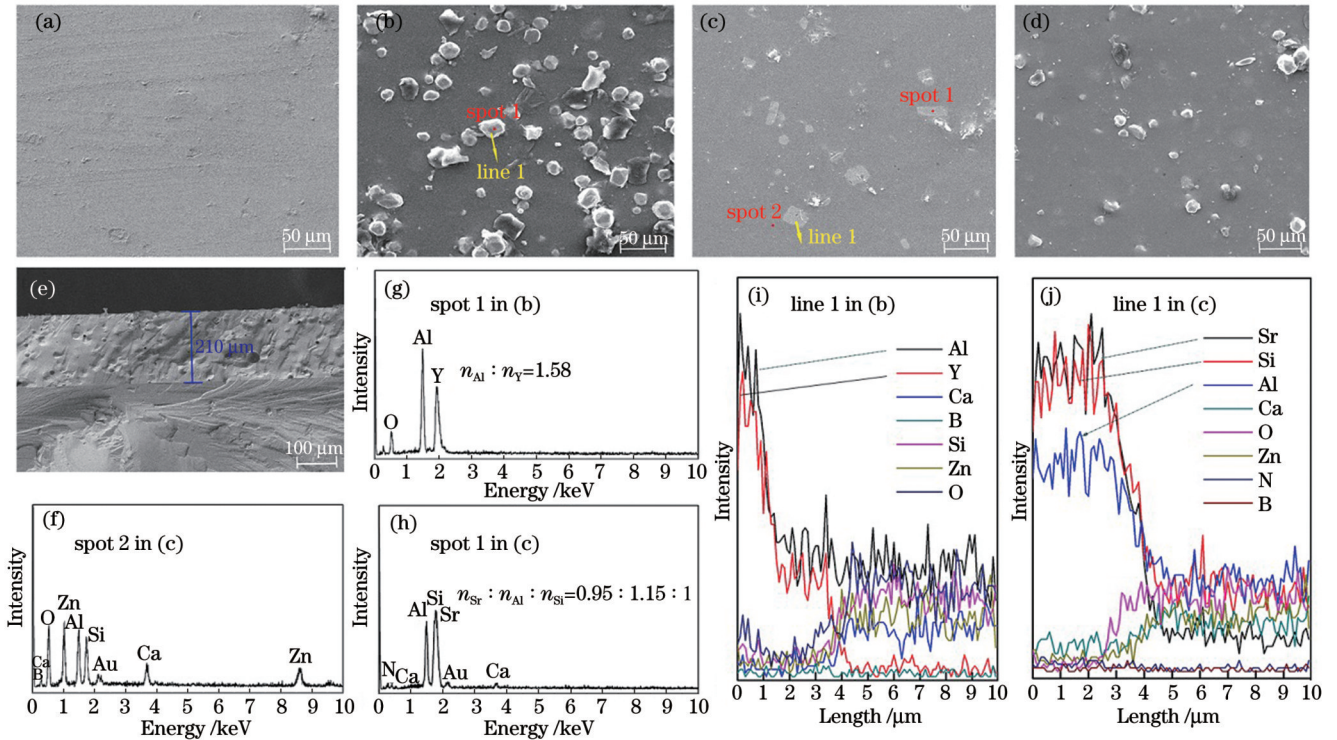


图4 玻璃陶瓷的SEM形貌及EDS扫描分析。(a)~(d)粘结玻璃原片、Y-GC、R-GC、Y-R2-GC样品的平面形貌；(e)Y-GC样品的横截面形貌；(f)~(j)EDS点扫描和线扫描分析曲线

Fig. 4 SEM morphologies and EDS analysis of glass ceramics. (a)~(d) Plane morphologies of original frit-seal glass, Y-GC, R-GC, and Y-R2-GC samples; (e) cross-section morphology of Y-GC sample; (f)~(j) EDS analysis of spot/line scanning

出了R-GC样品中荧光颗粒上点1处的点扫描结果,可见,Sr、Al、Si元素的原子数比 $n_{Sr} : n_{Al} : n_{Si} = 0.95 : 1.15 : 1$,与(Ca, Sr)AlSiN₃红色荧光粉中Sr、Al、Si元素的原子数比接近(粉体中 $n_{Ca} : n_{Sr} = 0.05 : 0.95$)。图4(j)显示,荧光粉中Sr、Al、Si元素的快速下降与粘结玻璃中元素的快速上升同时交汇。上述R-GC的分析结果给出了另一个CSASN荧光粉没有与粘结玻璃发生明显相互作用的有力证据。

3.4 发光性质分析

在450 nm蓝光激发下,不同CSASN荧光粉含量的玻璃陶瓷的发射光谱如图5所示。Y-GC样品的以约540 nm为中心的宽带谱源于YAG荧光粉中发光中

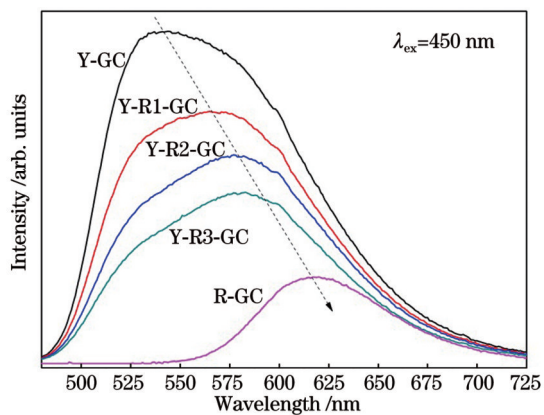


图5 玻璃陶瓷的发射光谱图

Fig. 5 Emission spectra of glass ceramics

心 Ce^{3+} 从5d到4f的典型能级跃迁,R-GC样品中的以约625 nm为中心的宽带发射来自CSASN荧光粉中 Eu^{2+} 的5d到4f能级跃迁,其余Y-R1-GC、Y-R2-GC、Y-R3-GC样品的光谱则来源于 Ce^{3+} 和 Eu^{2+} 的发射光的复合。随着CSASN红粉的质量分数从1%增加到3%,光谱出现了明显的红移,这是由于红粉含量增加提高了发射红光的比例,也正因为如此才能实现样品的光色可调。图5还显示发射强度随着红粉比例增大而逐渐下降,这可能是由CSASN红粉的蓝光转换效率低于YAG黄粉导致的。CSASN红粉掺入玻璃陶瓷后,其本身微结构的改变、粉体缺陷增多、界面光散射增加等也是导致其发光强度下降的可能因素^[26]。

图6展示了Y-GC、R-GC、Y-R2-GC样品及相应原料的量子产率。Y-GC样品的量子产率可达90.42%,仅比其粉体原料的量子产率(92.10%)降低了1.68个百分点。这是因为YAG荧光粉在制备玻璃陶瓷时未被粘结玻璃侵蚀,晶体结构得以保存完好,从而使得发光效率几乎未受影响。另外,YAG荧光粉与粘结玻璃之间较小的折射率差以及YAG荧光粉与蓝宝石之间良好封接等,使得样品的缺陷减少和光散射降低,这也是其保持高量子效率的原因之一。相比于Y-GC样品,R-GC样品的量子产率仅为54.80%,相较于其粉体原料的量子产率(89.11%)下降了34.31个百分点。这可能是由于CSASN红粉在与玻璃粉共烧结过程中,其微结构部分发生了一定的扭曲和改变,减

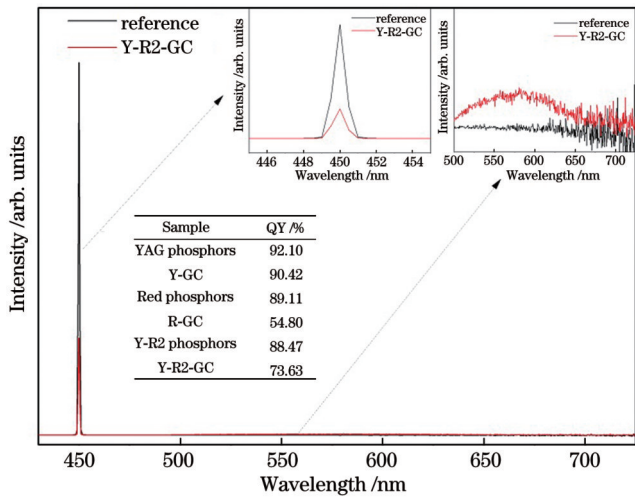


图6 玻璃陶瓷的量子效率(插图为局部放大图,表格为各样品的量子效率)

Fig. 6 Quantum yield (QY) of glass ceramics (the insets are local enlarged drawings and the table is QY of each sample)

小了光子的跃迁概率,从而降低了发光强度。这一结论与图2所示的结构分析相吻合。另外,红粉与粘结玻璃之间较差的润湿性会导致缺陷和光散射增加,因此也有可能降低红光玻璃陶瓷的量子产率。Y-R2-GC的量子产率为73.63%,虽然相比其粉体原料降低了14.84个百分点,但红粉的加入会改善样品的显色性和色温等发光性能,一定程度上相对较小的量子效率降低也相对可以接受。

热稳定性是衡量发光材料能否推广应用的最重要指标之一。图7所示为Y-R2-GC样品在450 nm光激发下的变温光谱。随着温度升高,光谱的发射峰位置基本保持不变,表明所制备的玻璃陶瓷材料的光色稳定性高;同时,发射强度随着温度升高而缓慢下降,这是由于在激光提供的能量作用下,发光中心(Ce^{3+} 、 Eu^{2+})的无辐射跃迁光子数增多,辐射光子数减少。虽

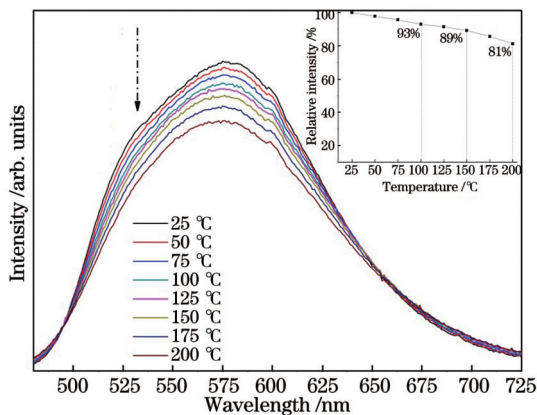


图7 Y-R2-GC样品的变温光谱图(插图为光谱相对强度的变化)

Fig. 7 Temperature-dependent PL spectra of Y-R2-GC (the inset is relative intensity of spectrum)

然温度升高会导致发光强度下降,但从插图显示的相对发光强度值可以看出Y-R2-GC样品表现出了优异的热稳定性:100 °C时,其发光强度只比初始时的发光强度降低了7个百分点(为93%);150 °C时,发光强度也仅衰减至初始值的89%;200 °C时仍能保持初始值的81%,该数值高于有机物封装的白光LED的发光强度^[9,27]。上述结果表明,本课题组将蓝宝石作为衬底制备的荧光玻璃陶瓷具有优异的热稳定性能,有望在高功率照明领域推广应用。

3.5 封装器件的性能

图8所示为玻璃陶瓷样品的发光图和色坐标图。由图8(a)可以发现:在自然光下,未添加CSASN红色荧光粉的Y-GC样品呈现亮黄色(这与YAG荧光粉的本征颜色是一致的),未添加YAG荧光粉的R-GC样品与CSASN红色荧光粉的颜色也基本一致;随着红色荧光粉含量增加,样品的颜色从亮黄色逐渐变成深黄色(这是红色、黄色荧光粉复合的表现)。图8(b)显示,在紫光照射下,样品更加清晰地呈现了从黄色到红色的逐渐改变。另外,不难发现,除R-GC样品的透过性比较差(可能是由红色荧光粉与粘结玻璃浸润性相

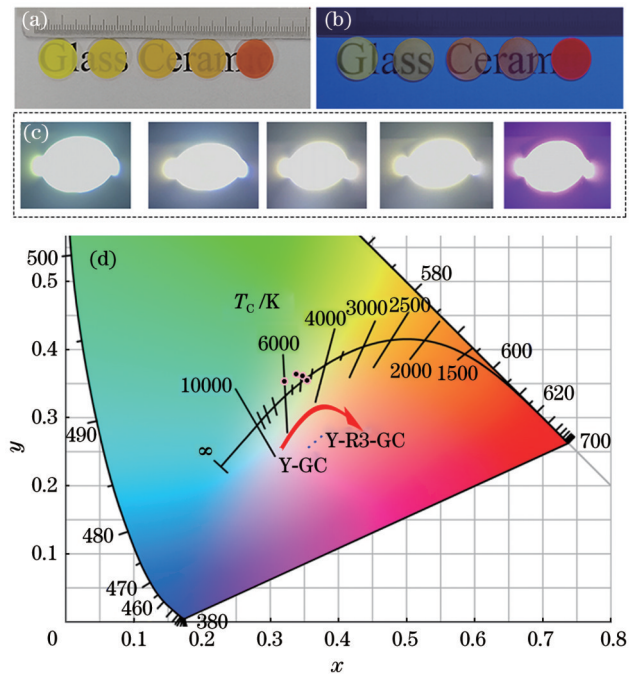


图8 玻璃陶瓷的发光图(从左向右依次为Y-GC、Y-R1-GC、Y-R2-GC、Y-R3-GC、R-GC样品)及色坐标图。(a)自然光下的发光图;(b)365 nm紫光下的发光图;(c)封装450 nm蓝光芯片下的发光图;(d)色坐标图。

Fig. 8 Luminescence pictures of glass ceramics (samples are Y-GC, Y-R1-GC, Y-R2-GC, Y-R3-GC and R-GC from left to right) and CIE color coordinates. (a) Luminescence picture under natural light; (b) luminescence picture under light of 365 nm; (c) luminescence pictures of samples encapsulated with 450 nm blue chip; (d) CIE color coordinates

对较差导致的)之外,其他样品均具有良好的透过性。上述结果均表明,添加的不论是黄色荧光粉还是红色荧光粉,它们均未与粘结玻璃发生明显的反应,保证了荧光粉原有的颜色和荧光玻璃陶瓷相对较高的透明度,有利于提升后续玻璃陶瓷的出光效率。图 8(c)为各玻璃陶瓷样品简单封装蓝光芯片后的发光效果图,可知,发光颜色从冷白光到暖白光逐渐改变。这表明随着制备玻璃陶瓷样品中 CSASN 红色荧光粉的含量增加,可以实现光色可调的发光。图 8(d)所示的色坐标图中色温逐渐降低也能很好地说明这一点。

为了更好地证实样品的光色可调性,表 1 列出了所制备的玻璃陶瓷的相关光电性能参数。在相同的电流下(20 mA),从 Y-GC 到 Y-R3-GC,随着红粉含量增加,除了色温(CCT)逐渐降低外,显色指数(CRI)逐渐增大

(从 68.8 增大到 76.2),这是由于红光的补充提升了 R9 的数值;但随之而变的是流明效率(LE)从 180.69 lm/W 逐渐降低到 123.98 lm/W,这是由对光通量贡献大的黄粉含量降低而对光通量贡献小的红粉含量增大引起的,同时含红粉量多的样品的量子效率低也是一个重要原因(如图 6 所示)。在不同电流下点亮芯片时,同一玻璃陶瓷样品的发光效率逐渐降低,这是由于芯片本身的效率骤降效应引起了强度降低^[28-30]。分析表 1 所列各样品的光电指标可以发现,综合性能指标相对较优的样品为 Y-R2-GC 样品(流明效率为 147.70 lm/W,显色指数为 73.3,色温为 4915),与其他研究成果的性能指标(尤其是流明效率)相比,处于相对较高的水平。这表明本课题组制备的玻璃陶瓷样品在高功率暖白光 LED 照明领域有着更广阔的应用前景。

表 1 玻璃陶瓷的光电性能参数

Table 1 Photoelectronic parameters of glass ceramics

Sample name	Current /mA	CIE		CCT /K	CRI	LE /(lm·W ⁻¹)
		<i>x</i>	<i>y</i>			
Y-GC	20	0.320	0.354	6019	68.8	180.69
Y-R1-GC	20	0.342	0.371	5166	69.1	165.14
Y-R2-GC	20	0.348	0.355	4915	73.3	147.70
Y-R3-GC	20	0.336	0.328	4627	76.2	123.98
R-GC	20	0.448	0.229	1398	23.3	23.15
Y-R2-GC	60	0.341	0.346	4952	73.6	139.45
Y-R2-GC	150	0.339	0.342	4970	73.8	121.43
Sample in Ref. [31]	500	-	-	4019	82.6	50.4
Sample in Ref. [13]	100	0.348	0.363	4929	73.0	77.58
Sample in Ref. [14]	-	0.451	0.469	3000	66.0	131
Sample in Ref. [15]	350	0.319	0.257	6896	76.0	102

4 结 论

选用蓝宝石衬底基质、硼硅酸粘结玻璃,通过丝网印刷法成功制备了一系列 Y₃Al₅O₁₂:Ce³⁺黄色荧光粉和(Ca,Sr)AlSiN₃:Eu²⁺红色荧光粉共掺杂的荧光玻璃陶瓷。研究表明,粘结玻璃的密度、折射率分别为 2.937 g/cm³和 1.595,且具有优异的抗析晶性,这些特性保证了后续玻璃陶瓷良好的发光性能。共烧结样品中黄色和红色荧光粉的结构、元素比以及元素分布等结果均表明,两种荧光粉均未与粘结玻璃发生明显的反应。随着红粉掺杂量增加,玻璃陶瓷的发射光谱红移且强度逐渐降低,量子效率也呈现下降趋势。制备的玻璃陶瓷具有优异的热稳定性,150 °C 下的发光强度为室温下的 89%,200 °C 下的发光强度为室温下的 81%,远高于目前商用有机物封装 LED 的发光强度。随着红粉掺杂量增加,玻璃陶瓷表现为显色指数升高、色温和流明效率降低,并表现出由冷白光向暖白光转变的光色可调性。发光性能相对较优的样品(其光电参数如下:流明效率为 147.70 lm/W,色温为 4915 K,

显色指数为 73.3)处于同类研究的中高水平。

综上所述,本课题组制备的荧光玻璃陶瓷具有光色可调性,并具有优异的热稳定性和良好的综合发光性能,有望应用于高功率白光照明领域。

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Luminescence Properties of Sapphire-Based Color-Tunable Glass Ceramic Phosphors

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Abstract

Objective Solid-state lighting (SSL) has been widely used in indoor and outdoor lighting, including landscape lighting and

automobile headlights. As mainstream SSL devices, phosphor-converted WLEDs (pc-WLEDs), exhibit many advantages such as low energy consumption and environmental friendliness. However, the applications of pc-WLEDs in high-power fields have been restricted because of their poor thermal stability, which originates from organic encapsulation. Glass ceramic phosphor (GC) is an important material required to resolve the problems resulting from high thermal stability by the means of remote encapsulation. Unfortunately, the chemical reaction between the red phosphors and glass powders during the co-sintering process significantly hinders the development of GCs. In this study, GCs are prepared by a screen-printing technique using a binder of borosilicate glass powder and a sapphire matrix with superior thermal conductivity. The phosphors used for the preparation of GCs are compounded with (Ca, Sr) AlSiN₃ : Eu²⁺ (CSASN) and Y₃Al₅O₁₂ : Ce³⁺ (YAG). The experimental processes of the GCs are simulated, and their optical properties are analyzed. Superior optical properties and color-tunable GCs are obtained. All results reveal that the as-prepared GCs are promising candidates for high-power white illumination.

Methods GC preparation was divided into two parts. The first was the preparation of frit-seal glass, which was prepared by a rapid melt-quenching technique with a composition of SiO₂-B₂O₃-ZnO-Al₂O₃-CaO. One part of the glass melt was poured into a graphite mold and annealed to remove the thermal stress. After natural cooling, the sample was polished into a small cube for detection. The other part was poured directly into deionized water to quench the cullet, which was then dried and milled into glass powder. The second part was the preparation of the GC, using a screen-printing technique utilizing slurries, substrates, and screens. The slurries, consisting of CSASN, YAG, frit-seal glass powder, and an organic binder solution, were manually printed on the sapphire substrate using a screen. The printed samples with mass fractions of 17% YAG + (17% - x) CSASN + 83% glass powders (where $x=0\%$, 1%, 2%, 3%, and 17%) were marked as Y-GC, Y-R1-GC, Y-R2-GC, Y-R3-GC, and R-GC series, respectively. After drying in an oven, the printed samples were sintered in a muffle furnace and allowed to cool naturally. Further, a series of GCs were prepared, and related characterization was performed.

Results and Discussions The pattern of Y-GC corresponds well to that of YAG phosphor. Compared with the pattern of the CSASN phosphor, the intensities of some peaks of R-GC become higher or lower and some diffractions disappear, which originates from the preferential orientation when CSASN phosphors are prepared into R-GC (Fig. 2). The experimental GC processes are simulated using a DSC device. All GC samples show flat lines, similar to the results for glass powder (Fig. 3). As shown in the SEM images of the GCs (Fig. 4), the YAG and CSASN particles exhibit an acceptable homogeneous distribution in the glass, and the thickness of the samples is approximately 210 μm . The values of $n_{\text{Y}} : n_{\text{Al}}$ (atomic ratio) and $n_{\text{Sr}} : n_{\text{Al}} : n_{\text{Si}}$ in the EDS spectra of the GCs correspond to those of the phosphors, and no additional elements appear in the glass regions. Meanwhile, distinct boundaries appear between the elements of CSASN and the glass powder in the EDS spectra. The above results, shown in Fig. 2 to Fig. 4, indicate that the two phosphors have no obvious chemical reactions with the sealing glass during the co-sintering process for GC preparations. With an increase in the red phosphor content, the PL spectra of the GCs exhibit a red shift (Fig. 5), and the intensities and quantum yields decrease gradually (Fig. 6). The results are ascribed to the changes in the microstructure of CSASN during GC preparation. The thermal stability of the GCs decreases gradually, but the rate of decline is small. The PL intensity at 150 °C is maintained at 89% of the initial value (Fig. 7), which is attributed to the high thermal conductivity of the frit-seal glass and sapphire substrate. With the increase in red phosphor content, the GC samples show a color change from yellow to red and a color-tunability from cool white to warm white encapsulated with a blue chip (Fig. 8). GCs exhibit a decrease in luminous efficiency (LE), a decline in correlated color temperature (CCT), and an increase in the color rendering index (CRI). The results are due to the small luminous flux of red light and the QY decrease in the GC. The LE gradually decreases as the operation current increases from 20 to 150 mA, which is ascribed to the phenomenon of “efficiency droop” (Table 1).

Conclusions GCs containing YAG and CSASN phosphors are prepared using a screen-printing technique on a sapphire substrate. The results indicate that the two phosphors have no obvious chemical reactions with the sealing glass during the co-sintering process for the GC preparation. With increasing red phosphor content, the PL spectra exhibit a red shift. Meanwhile, the intensities and quantum yields gradually decrease. The GCs show superior thermal stability, and the PL intensity at 150 °C is maintained at 89% of the initial value. The GC samples exhibit color tunability from cool white to warm white with increasing red phosphor content. The optimal photoelectronic parameters of the GCs are a luminous efficiency of 147.70 lm/W, color temperature of 4915 K, and color rendering index of 73.3. These results indicate that the as-prepared GCs have a wide range of applications in the field of high-power white illumination.

Key words materials; luminescent materials; glass ceramic; red phosphor; sapphire; color tunability