

Zr⁴⁺ 掺杂 CsPbI₃ 钙钛矿量子点玻璃的光学性能

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摘 要: 钙钛矿量子点具有优异的光电性能, 有望应用于显示、光伏和光电探测等领域, 然而, 较差的稳定性限制其应用, 将钙钛矿量子点嵌入到玻璃中可以有效地提升其稳定性。采用高温熔融-热处理方法制备了 Zr⁴⁺ 掺杂 CsPbI₃ 量子点硼硅酸盐玻璃。结果表明: CsPbI₃ 量子点在玻璃内部析出, 并且随着 ZrO₂ 含量增加, 由于较小直径的 Zr⁴⁺ 取代了较大直径的 Pb²⁺, (200) 晶面的衍射峰向大角度偏移; 随着 ZrO₂ 含量的增加, 发光峰和吸收边均出现蓝移, 荧光强度和量子效率先增大后减小, 荧光寿命逐渐减小; 随着 ZrO₂ 含量增加, 玻璃中[BO₄]和[SiO₄]四面体网络结构增加, 导致玻璃三维网络结构增加, 从而抑制了 CsPbI₃ 量子点的析晶。本工作表明所制备的玻璃具有良好的热稳定性, 能够应用于显示、照明等领域。

关键词: 铅离子; 量子点; 硼硅酸盐玻璃; 析晶

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钙钛矿(CsPbX₃, X=Cl, Br, I)量子点因其具备良好的光电性能而受到广泛关注^[1-2]。它具备高量子效率(PLQY), 窄的半高宽(FWHM)以及宽光谱范围内可调谐发光等优点^[3-6], 广泛应用于激光器^[7-8]、发光二极管^[9-11]、太阳能电池^[12-13]、光电探测器^[14-16]等领域。然而, 它的缺点也是显而易见的, 一方面, CsPbX₃ 量子点的稳定性没有得到很好的解决; 另一方面, 量子点中铅元素的毒性引起了广泛的担忧, 这些问题对钙钛矿量子点未来的发展具有一定的制约性。

关于 CsPbX₃ 量子点稳定性不足的问题, 研究人员将量子点嵌入玻璃从而极大提高了量子点的热稳定性以及化学稳定性^[17]。通过改变玻璃组分以及热处理条件可以有效地控制量子点在玻璃中的尺寸大小和粒度分布^[18-20]。目前, CsPbX₃ 量子点已经成功在各种玻璃基质中析晶, 例如在硼硅酸盐玻璃^[21-22], 硼磷酸盐玻璃^[23]以及锗酸盐玻璃^[24]等。

值得注意的是, 在玻璃中掺杂金属离子可以改变其光学性能, 不同的金属离子对玻璃的调控途径大致可分为 3 方面: 一是改变钙钛矿量子点的析晶能力, 例如邹军团团队^[25]制备了 Bi³⁺ 掺杂 CsPbBr₃ 量子点玻璃, Bi³⁺ 进入空位从而促使 CsPbBr₃ 量子点粒径的减小, 光谱蓝移; 向卫东团队^[26]在 CsPbBr₃ 量子点玻璃中掺入 Ni²⁺, 消除了钙钛矿纳米晶体的结构缺陷, 提高了量子效率。二是取代钙钛矿量子点的 Cs⁺ 或 Pb²⁺ 并调控其光学性能, 例如 Mohammed 等^[27]在 CsPbI₃ 量子点玻璃中掺杂 Tb³⁺, Tb³⁺ 的掺杂占据了 Pb²⁺ 的位置, 增加了能带边缘的激发电子密度, 从而增强了量子点玻璃的荧光强度; 陈大钦团队^[28]在 CsPbCl₃ 钙钛矿纳米晶体中掺入锰离子, 证实了 Mn²⁺ 对 Pb²⁺ 的取代, 增加了 CsPbCl₃ 的带隙, 引起光谱蓝移, 实现了可调多色发光。三是稀土离子可以与钙钛矿量子点发生能量传递, 从而改善玻璃的光学性能, 例如许周速等^[29]在 CsPbBr₃ 量子点玻璃

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中掺入钕离子,研究了 CsPbBr_3 量子点到 Nd^{3+} 的能量转移,提高了量子点玻璃的光学性能;徐时清团队^[30]制备了 Dy^{3+} 掺杂的 CsPbBr_3 量子点玻璃,通过调节 Dy^{3+} 和量子点的能量传递关系,实现了量子点玻璃的可调谐发光。刘超团队^[31]在玻璃中嵌入了锰掺杂的 $\text{CsPb}(\text{Cl}/\text{Br})_3$ 纳米晶体,证实了锰离子和钙钛矿纳米晶体之间的能量转移,实现了可调双波段光致发光。目前, Zr^{4+} 对 CsPbI_3 量子点玻璃的光学性能影响鲜有报道,因此有必要开展 Zr^{4+} 掺杂对玻璃中 CsPbI_3 量子点的析晶影响。

本工作采用高温熔融-热处理法,在硼硅酸盐玻璃中制备了一系列掺杂 Zr^{4+} 的 CsPbI_3 量子点,通过改变 ZrO_2 的含量以及热处理温度和时间,可以有效的调节玻璃的发射波长(675~710 nm)以及发光性能,此外,适量 Zr^{4+} 的引入会增加玻璃网络中 $[\text{SiO}_4]$ 和 $[\text{BO}_4]$ 单元,导致玻璃中三维网络结构增加,从而抑制了量子点在玻璃中的析晶。最后对 Zr^{4+} 掺杂 CsPbI_3 量子点玻璃的热稳定性进行测量,所制备的玻璃样品在经历多次加热和冷却循环后依旧能保持初始的发射强度,表明其具备优异的热稳定性,在

照明、显示等领域具有潜在的应用价值。

1 实验

1.1 制备

采用高温熔融-热处理法制备了 Zr^{4+} 掺杂 CsPbI_3 量子点玻璃,玻璃的摩尔比例为:

$30\text{SiO}_2\text{-}30\text{B}_2\text{O}_3\text{-}20\text{ZnO}\text{-}7\text{Cs}_2\text{CO}_3\text{-}1.6\text{PbI}_2\text{-}6.8\text{NaI}\text{-}1\text{CaF}_2\text{-}x\text{ZrO}_2(x=0, 0.4, 0.8, 1.2, 1.6)$ 。

将所有原料准确称量(如表 1 所示)并依次放入玛瑙研钵中研磨 20 min, 样品混合均匀后放入干净的氧化铝坩埚当中并移至高温炉里在 1 200 °C 熔融 20 min, 之后将坩埚中的玻璃熔融液体迅速倒在不锈钢板上压制成形即可得到玻璃前驱体(PG)。最后,将玻璃前驱体放入小型箱式炉中分别以不同的温度(520~550 °C)保温 4 h 以及 530 °C 保温不同时间(2~12 h)进行热处理,玻璃样品命名为 $\text{Zr}_x\text{-}y\text{-}z$, 其中 x 表示 ZrO_2 浓度, y 表示热处理温度, z 表示热处理时间。待箱式炉冷却至室温后即可取出样品,将样品放在研磨机上打磨至表面平整光滑即可用于下一步的表征测试。

表 1 不同玻璃样品称取原材料的质量

Sample	SiO_2	B_2O_3	ZnO	Cs_2CO_3	PbI_2	NaI	CaF_2	ZrO_2
0-0-0	3.333 3	3.862 4	3.010 2	4.217 7	1.364 0	1.884 9	0.144 4	0.000 0
0.4-0-0	3.333 3	3.862 4	3.010 2	4.217 7	1.364 0	1.884 9	0.144 4	0.091 1
0.8-0-0	3.333 3	3.862 4	3.010 2	4.217 7	1.364 0	1.884 9	0.144 4	0.182 3
1.2-0-0	3.333 3	3.862 4	3.010 2	4.217 7	1.364 0	1.884 9	0.144 4	0.273 4
1.6-0-0	3.333 3	3.862 4	3.010 2	4.217 7	1.364 0	1.884 9	0.144 4	0.364 6

1.2 表征

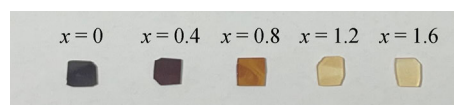
采用 FLS980 型荧光光谱仪(英国 Edinburgh Instruments 公司)表征玻璃样品的荧光光谱、荧光寿命以及热稳定性测试,荧光光谱(PL)和荧光寿命分别以 Xe 灯和 405 nm 的 ps 脉冲激光器作为激发光源。采用 UV-3600 UV-Vis-NIR 型分光光度计(日本 Shimadzu Instruments 公司)表征玻璃样品的吸收光谱。采用 Empyrean 型 X 射线衍射仪(荷兰 PANalytical 公司)记录玻璃的 X 射线衍射谱。采用 Nicolet 6700 型 Fourier 变换红外光谱仪(美国 Thermo Fisher Scientific 公司)和 532 nm 激光器作为激发光源的 InVia ReflexRaman 光谱仪(英国 Renishaw 公司)来分析玻璃的网络结构。

2 结果与讨论

2.1 玻璃颜色

掺杂不同浓度 ZrO_2 的玻璃样品同时在 530 °C

热处理 4 h, 可以发现随着 ZrO_2 含量的增多, 玻璃的颜色逐渐从黑色过渡到棕色, 如图 1a 所示。而在紫外灯的照射下, 随着 ZrO_2 的增多, 玻璃样品的荧光从深红色变为红色, 如图 1b 所示。



(a) Photograph of glasses under daylight



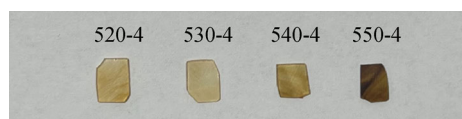
(b) Photograph of glasses under 365 nm UV lamp light

图 1 在 530 °C 热处理 4 h 的条件下, 不同浓度 ZrO_2 玻璃样品的照片

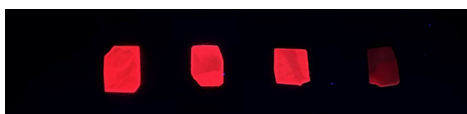
Fig. 1 Photographs of glass samples with different concentrations of ZrO_2 under the condition of heat treatment at 530 °C for 4 h

当 ZrO_2 的掺杂量为 1.2%(摩尔分数)时发光最

强, 选取这块玻璃分别在 520、530、540 °C 和 550 °C 的温度下热处理 4 h, 如图 2a 所示, 当热处理温度升高时, 玻璃从浅色过渡到深色。由图 2b 可见, 当热处理温度从 520 °C 升高到 550 °C 时, 玻璃的发光强度先增大后减小, 这是因为温度的升高会促进玻璃中 CsPbI₃ 量子点的成核和生长, 而当温度进一步升高时, 玻璃中的量子点浓度进一步增加, 从而引起荧光再吸收导致荧光强度减弱^[29]。



(a) Photograph of glasses under daylight



(b) Photograph of glasses under 365 nm UV lamp light

图 2 掺杂 1.2%(摩尔分数) ZrO₂ 玻璃样品在不同温度进行热处理后的照片

Fig. 2 Photographs of glass samples doped with 1.2% (in mole) of ZrO₂ after heat treatment temperatures at different temperatures

2.2 玻璃的物相及结构

图 3a 为未掺杂 ZrO₂ 的玻璃样品在不同热处理条件下的 X 射线衍射谱(XRD)。当在 530 °C 热处理温度处理 8 h 后, 在 28.5° 和 35.5° 附近出现了明显的衍射峰, 分别对应于 CsPbI₃ 量子点(JCPDS 01-080-4039)的(200)晶面和(211)晶面。随着热处理时间的进一步延长, 这 2 个衍射峰变得更加明显, 这是因为热处理时间的延长有利于 CsPbI₃ 量子点的析晶, 从而导致衍射峰的增强^[32]。由图 3b 可见, 在 CsPbI₃ 量子点玻璃中掺杂 Zr⁴⁺ 不会显著改变晶体结构, 随着 ZrO₂ 掺杂量的增加, (200)晶面的衍射峰向大角度略微偏移, 这是因为较小直径的 Zr⁴⁺ 取代了较大直径的 Pb²⁺ ^[33–34]。此外, 随着 ZrO₂ 含量的增加, 衍射峰的信号变得更弱, 这可能是由晶体浓度降低和结晶度变差引起。

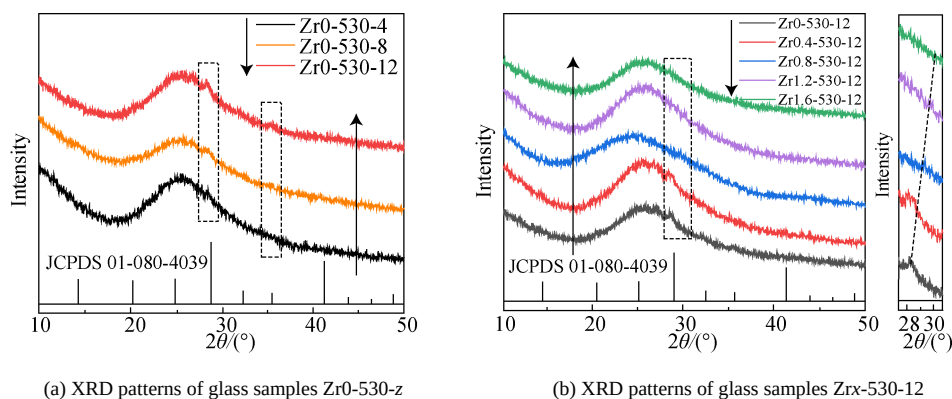
采用 Fourier 变换红外(FT-IR)光谱和 Raman 光谱分析了 ZrO₂ 对玻璃网络结构的影响。FT-IR 光谱如图 4a 所示, 可以观察到 480 cm⁻¹ 处[SiO₄]四面体单元的 Si—O—Si 弯曲振动^[35–36]、700 cm⁻¹ 处[BO₃]单元的 B—O 弯曲振动和[SiO₄]四面体单元的 Si—O 弯曲振动^[32, 37–38]、1 020 cm⁻¹ 处[SiO₄]单元的 Si—O—Si 弯曲振动和[BO₄]单元中 B—O 键的伸缩振动^[39–40]、1 250 cm⁻¹ 处硼氧环的振动^[39]以及 1 450 cm⁻¹ 处[BO₃]单元的 B—O 伸缩振动^[40]。Raman 光谱

如图 4b 所示, 在 532 nm 激发下, 玻璃样品存在 4 个明显的 Raman 强度峰, 分别是 500 cm⁻¹ 处[BO₃]单元的 B—O 振动^[32, 41–42]和[SiO₄]四面体单元的 Si—O—Si 伸缩振动^[29]、770 cm⁻¹ 处[BO₄]单元的 B—O—B 伸缩振动^[36, 43]以及 1 050 cm⁻¹ 处[SiO₄]单元的 Si—O—Si 反对称伸缩振动^[42–44]。此外, 在添加 ZrO₂ 后, 795 cm⁻¹ 处出现了特征峰, 对应[SiO₄]单元的 Si—O—Si 弯曲振动^[29]。从 FT-IR 和 Raman 光谱结果可以看出, 玻璃网络结构主要由[SiO₄]、[BO₄]和[BO₃]单元构成。随着 ZrO₂ 浓度的增大, Raman 光谱 770 cm⁻¹ 附近的[BO₄]单元以及 795 cm⁻¹ 附近的[SiO₄]单元明显增多, 有利于形成三维玻璃网络, 抑制 Cs⁺、Pb²⁺ 和 I⁻ 的迁移, 从而阻碍了玻璃中 CsPbI₃ 量子点的析晶^[40], 导致 XRD 衍射峰变弱, 如图 3b 所示。

2.3 玻璃的发光性能

不同 ZrO₂ 含量玻璃样品经过 530 °C 热处理 4 h 后的光学性能如图 5 所示。图 5a~图 5b 是在 450 nm 激发波长下记录的具有不同浓度 ZrO₂ 玻璃样品的吸收光谱和发射光谱, 可以观察到, 随着 ZrO₂ 浓度的增加, 吸收边和发光峰波长出现明显的蓝移, FT-IR 和 Raman 光谱的结果表明, 玻璃网络中[SiO₄]和[BO₄]单元随着 ZrO₂ 浓度的增加逐渐变多, 不利于玻璃中 CsPbI₃ 量子点生长, 这会导致量子点的尺寸减小, 从而引起光谱蓝移。此外, 随着 ZrO₂ 浓度的增加, 玻璃的荧光强度先增大后减小, 当 ZrO₂ 的浓度为 1.2% 时, 光致发光强度达到最大值。图 5c 为具有不同浓度 ZrO₂ 玻璃样品的激发光谱, 每个样品都以各自的发光峰值波长作为检测波长。由图 5c 可见, CsPbI₃ 量子点玻璃在可见光波段具备宽带激发特性。此外, 测试了不同浓度 ZrO₂ 玻璃样品的量子效率, 如图 5d 所示, 随着 ZrO₂ 浓度的增加, PLQY 先增大后减小, 当掺杂 ZrO₂ 的浓度为 1.2% 时, PLQY 最高为 32.6%。

从图 5 可见, 掺杂 1.2% ZrO₂ 时, 玻璃的发光性能最佳, 选取此玻璃进行后续研究。如图 6a~图 6d 所示, 改变不同的热处理温度和时间可以发现, 吸收边和发光峰波长随着热处理温度的升高或时间的延长均出现红移, 荧光强度先增大后减小。吸收边和发光峰的红移是因为随着热处理温度或时间的增加, 玻璃基质中生成的 CsPbI₃ 量子点尺寸半径增大, 导致量子点的带隙减小, 从而发生了红移^[44]。当热处理温度较低或热处理时间较短时, 玻璃中形成的 CsPbI₃ 量子点浓度较低, 玻璃的发光强度较弱, 随着热处理温度的升高或时间的延长, 量子点的浓度相应增加, 因此发光强度也进一步增强。然而当



Zr0.4-530-12 means glass sample doped 0.4% ZrO_2 heat treated at 530°C for 12 h, the same below.

图 3 (a)未掺杂 ZrO_2 玻璃样品在不同热处理时间下的 XRD 谱; (b)掺杂不同浓度 ZrO_2 玻璃样品在 530°C 热处理 12 h 后的 XRD 谱
Fig. 3 (a) XRD patterns of undoped ZrO_2 glass samples at different heat treatment times; (b) XRD patterns of glass samples doped with different concentrations of ZrO_2 after heat treatment at 530°C for 12 h

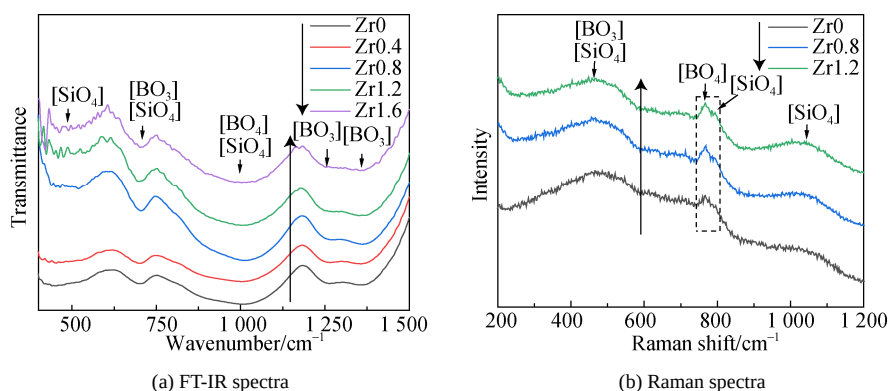


图 4 不同 ZrO_2 含量玻璃样品的 FT-IR 光谱和 Raman 光谱

Fig. 4 FT-IR spectra and Raman spectra of glass samples with different concentrations of ZrO_2

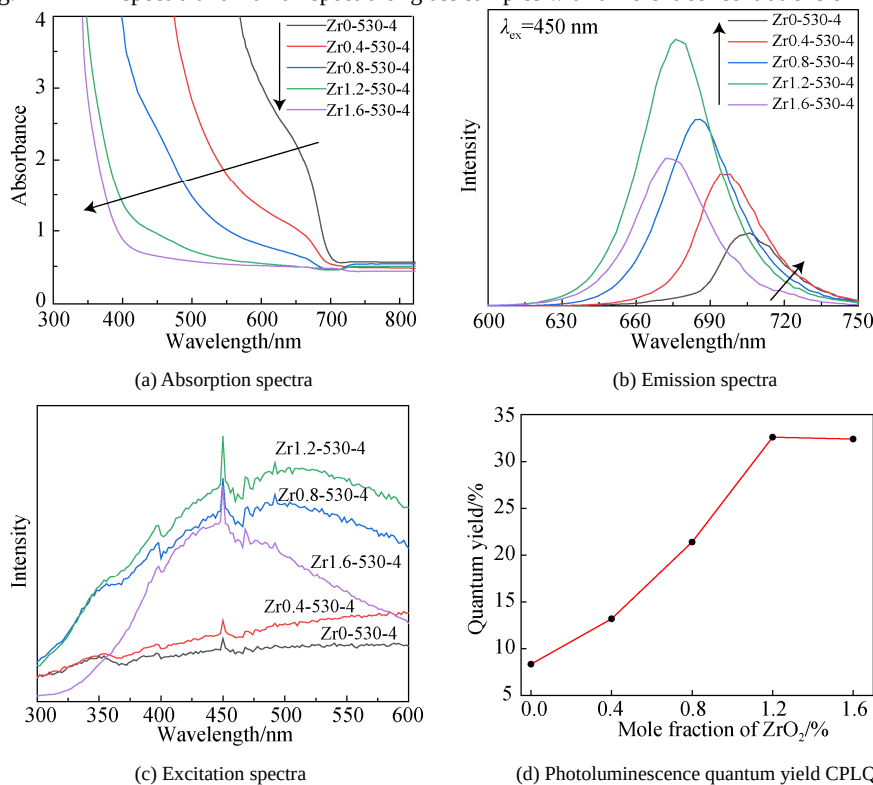


图 5 不同 ZrO_2 含量玻璃样品的吸收光谱、发射光谱、激发光谱和量子效率

Fig. 5 Absorption spectra, emission spectra, excitation spectra and PLQY of glass samples with different ZrO_2 concentrations

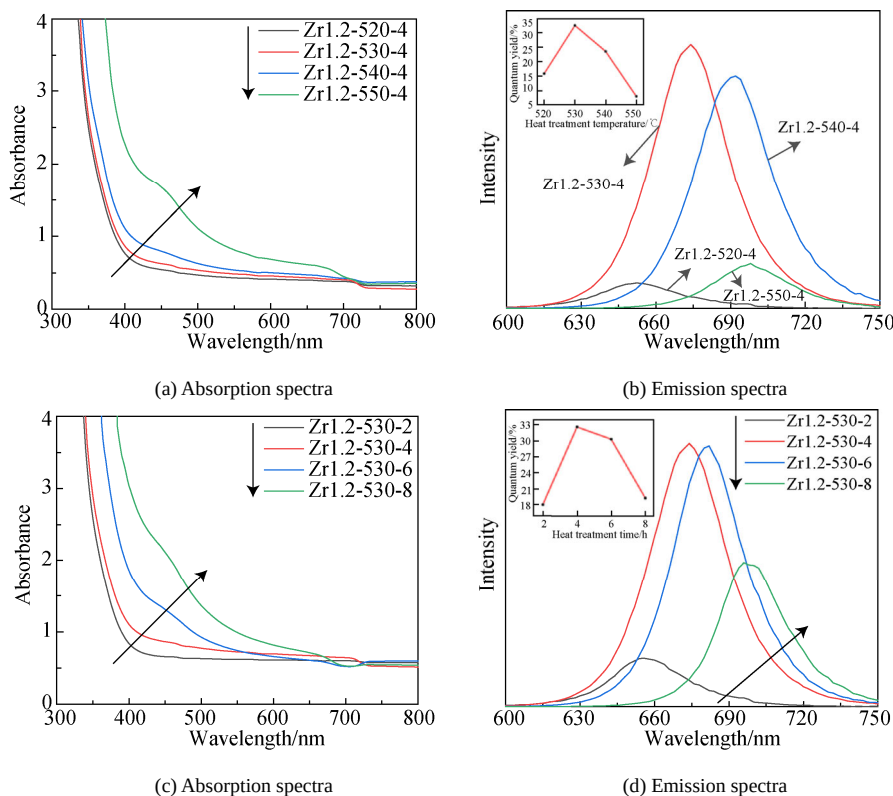


图6 掺杂 1.2% ZrO_2 玻璃样品在不同温度下热处理 4 h 后的(a)吸收光谱和(b)发射光谱(插图为热处理温度对量子效率的影响), 掺杂 1.2% ZrO_2 玻璃样品在 530 $^{\circ}\text{C}$ 热处理不同时间后的(c)吸收光谱和(d)发射光谱(插图为热处理时间对量子效率的影响)

Fig. 6 (a)Absorption spectra and (b)emission spectra (The insert shows the influence of varying heat treatment temperatures on the quantum yield) of glass samples doped with 1.2% of ZrO_2 after heat treatment for 4 h at different temperatures, (c)absorption spectra and (d)emission spectra (The insert shows the influence of varying heat treatment times on the quantum yield) of glass samples doped with 1.2% of ZrO_2 after heat treatment at 530 $^{\circ}\text{C}$ for different times

量子点浓度超过一定阈值, 将引发量子点荧光再吸收从而导致发光强度的下降。图 6b 和图 6d 插图展示了不同热处理温度和时间对应的 PLQY, 随着热处理温度的升高或时间的延长, PLQY 均是先增加后减小, 当热处理温度为 530 $^{\circ}\text{C}$, 热处理时间为 4 h 时, PLQY 最高为 32.6%。

表2 双指数拟合不同玻璃样品的荧光寿命

Table 2 Bi-exponential fitting of the fluorescence lifetime of different glass samples

Sample	τ_1/ns	τ_2/ns	$B_1/\%$	$B_2/\%$	χ^2	$\tau_{\text{ave}}/\text{ns}$
0-530-4	10.00	32.30	19.76	80.24	1.09	27.89
0.4-530-4	10.00	29.32	23.19	76.81	1.20	24.84
0.8-530-4	8.94	23.62	36.08	63.92	1.16	18.32
1.2-530-4	7.18	17.99	49.15	50.85	1.27	12.67
1.6-530-4	6.69	16.79	48.20	51.80	1.15	11.93
1.2-520-4	2.88	7.87	55.20	44.80	1.02	5.12
1.2-540-4	9.37	28.85	29.68	70.32	1.23	23.07
1.2-550-4	6.25	46.43	13.29	86.71	1.27	41.09

τ_1 is short PL lifetime. τ_2 is long PL lifetime. B_1 is the mass of τ_1 . B_2 is the weight of τ_2 . χ^2 is the fitting accuracy parameter. τ_{ave} is the average PL lifetime.

图 7a~图 7b 是不同玻璃样品在 ps 脉冲激光器(波长: 400.2 nm, 脉冲宽度: 57.3 ps)激发下的荧光衰减曲线, 各样品的荧光衰减寿命如表 2 所示。采用双指数函数拟合衰减曲线:

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

其中: $I(t)$ 表示荧光强度随时间的变化; A_1 和 A_2 是拟合参数; τ_1 和 τ_2 分别代表短寿命和长寿命。平均荧光寿命可通过下式计算:

$$\tau_{\text{ave}} = B_1 \tau_1 + B_2 \tau_2 \quad (2)$$

其中: B_1 和 B_2 分别代表 τ_1 和 τ_2 所占的比例, 它们可以通过下式计算得出:

$$B_1 = A_1 \tau_1 / (A_1 \tau_1 + A_2 \tau_2) \quad (3)$$

$$B_2 = A_2 \tau_2 / (A_1 \tau_1 + A_2 \tau_2) \quad (4)$$

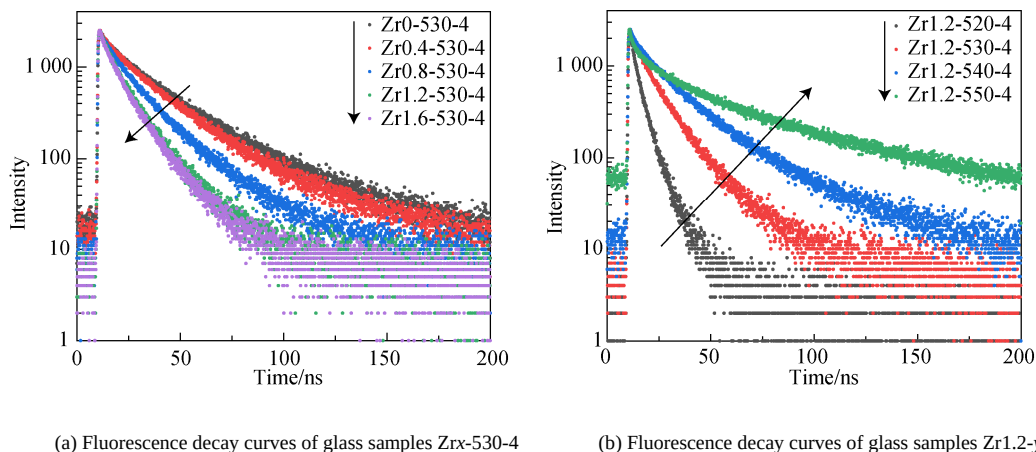
由表 2 可知, 随着 ZrO_2 浓度的增加, CsPbI_3 量子点尺寸减小, 量子点玻璃的荧光寿命逐渐减小。而当热处理温度增大时, CsPbI_3 量子点尺寸增大, 量子点玻璃的荧光寿命逐渐增加。可见, 量子点荧光寿命与量子点尺寸是正相关的。在量子点荧光衰减过程中, 受制于辐射跃迁与非辐射跃迁等多种因素的影响。量子点的尺寸增大, 一方面, 这会使量子限制效

应和电子-空穴波函数的相互作用减弱,从而降低了激子的复合速率,导致量子点荧光寿命的增加^[45];另一方面,量子点尺寸的增大时,其比表面积随之减小,导致量子点中表面缺陷的占比减少,从而降低了非辐射跃迁的比率,导致荧光寿命的增大^[46-47]。

2.4 玻璃的稳定性

所制备的 Zr^{4+} 掺杂 CsPbI_3 量子点玻璃的热稳定性,是制约其应用的一个重要因素。图 8a 为不同温度下掺杂 1.2% ZrO_2 玻璃样品的发射光谱,当温度

从 293 K 升高到 373 K 时,玻璃的发光强度不断下降,这是热猝灭导致的结果,当温度达到 353 K 时,PL 强度仅约为其室温下的 7.5%。此外,由图 8b 可见,将量子点玻璃逐渐加热至 373 K,然后逐渐冷却至室温,依次循环 5 次,并记录不同温度下的 PL 强度,结果显示,玻璃样品的光致发光强度在多次循环后几乎没有变化,制备的玻璃样品具备出色的热稳定性,表明其在照明、显示等领域具有潜在的应用价值。

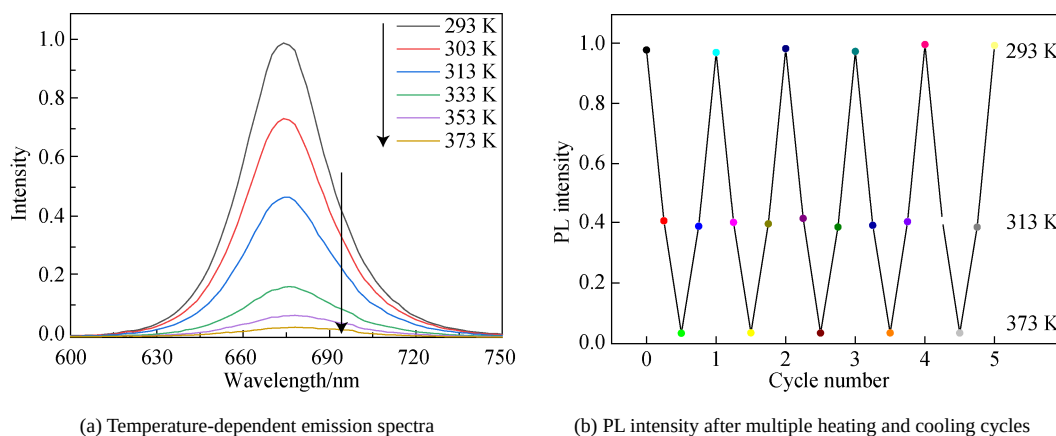


(a) Fluorescence decay curves of glass samples Zrx-530-4

(b) Fluorescence decay curves of glass samples Zr1.2-y-4

图 7 不同浓度 ZrO_2 玻璃样品和不同热处理温度掺杂 1.2% ZrO_2 玻璃样品的荧光衰减曲线图

Fig. 7 Fluorescence decay curves of the glass samples with different ZrO_2 concentrations and with 1.2% of ZrO_2 after heat treatment at different temperatures



(a) Temperature-dependent emission spectra

(b) PL intensity after multiple heating and cooling cycles

图 8 (a)掺杂 1.2% ZrO_2 玻璃样品在 293~373 K 温度范围内随温度变化的发射光谱, (b)掺杂 1.2% ZrO_2 玻璃样品在 293 K 和 373 K 之间多次加热和冷却循环后的光致发光强度

Fig. 8 (a)Temperature-dependent emission spectra for the glass sample doped with 1.2% of ZrO_2 in the temperature range of 293~373 K, (b) PL intensity of the glass sample doped with 1.2% of ZrO_2 after multiple heating and cooling cycles between 293 K and 373 K

3 结论

采用高温熔融热处理法成功制备了 Zr^{4+} 掺杂 CsPbI_3 量子点玻璃,通过表征玻璃样品的 XRD,证明了 CsPbI_3 量子点从玻璃中析出。在相同的热处理

条件下,荧光强度和量子效率随着 ZrO_2 含量的增加先增大后减小,最高量子效率为 32.6%。此外,发射光谱和吸收光谱均发生蓝移,这是因为随着 ZrO_2 浓度增加玻璃网络中 $[\text{SiO}_4]$ 和 $[\text{BO}_4]$ 单元逐渐增多,使得玻璃三维网络结构增加,不利于 Cs^+ 、 Pb^{2+} 和 I^-

的迁移,从而抑制了 CsPbI₃ 量子点的析晶。在经过 293~373 K 多次加热和冷却循环后,玻璃样品依旧保持初始的发射强度,表明了 Zr⁴⁺ 掺杂 CsPbI₃ 量子点玻璃具有出色的热稳定性,有望应用于照明、显示等领域。

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Optical Properties of Zr^{4+} Doped CsPbI_3 Perovskite Quantum Dots Glass

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Extended Abstract

Introduction In recent years, all-inorganic halide perovskite (CsPbX_3 , $\text{X}=\text{Cl}, \text{Br}, \text{I}$) quantum dots (QDs) have attracted widespread attention due to their excellent optical and electrical properties. They exhibit high photoluminescence (PL) efficiency, narrow emission bandwidth and tunable emission energy at a wide spectral range. However, the poor stability of CsPbX_3 QDs under ambient conditions strongly limit their applications. In this work, CsPbI_3 QD-doped borosilicate glasses were prepared by high-temperature melting-quenching followed by heat treatment. ZrO_2 is employed as the network modifier, which effectively modifies the local network structure of glass. By optimizing the concentration of ZrO_2 and the heat treatment temperature or time, the PL efficiency of the glass can be effectively improved. PL intensity of the QDs glass sample demonstrates high stability, which is almost unchanged after multiple heating and cooling cycles between 293 K and 373 K.

Methods The CsPbI_3 QD-doped glasses were prepared by high-temperature melting-quenching followed by heat treatment. All raw materials with the designed ratios were accurately weighed and mixed in an agate mortar for 20 min. After the raw materials were thoroughly mixed, they were placed in a covered alumina crucible and transferred to a muffle furnace for melting at 1200 °C for 20 min. Afterwards, the glass melt was quenched onto a steel plate and pressed into a glass plate. Finally, the precursor glass were heat-treated at different temperatures (520–550 °C) for 4 h and at 530 °C for different times (2–12 h) to precipitate the CsPbI_3 QDs.

PL spectra, PL decay curves and thermal stability of glass samples were examined with a FLS 980 fluorescence spectrometer. Optical absorption spectra were recorded by using a UV-3600UV-Vis-NIR spectrometer. X-ray diffraction patterns were recorded by

using an X'Pert PRO powder diffractometer. The network structure of glass was analyzed by using a Nicolet 6700 spectrometer and an InVia Reflex Raman spectrometer. The photoluminescence quantum yield (PLQY) was measured with an absolute PLQY measurement system.

Results and discussion From the XRD results, as the heat treatment time increases, two diffraction peaks at angles (2θ) of 28.5° and 35.5° become stronger in intensity, corresponding to the (200) and (211) planes of CsPbI₃ QDs, respectively. With increasing the ZrO₂ concentration, the diffraction peak of (200) crystal plane shifts to a larger angle, which is attributed to the replacement of larger Pb²⁺ ions by smaller Zr⁴⁺. Based on FTIR and Raman spectra characterizations, the network structure of glass is mainly composed of [BO₄], [SiO₄] and [BO₃] units. As the ZrO₂ concentration increases, the fraction of tetrahedral network structure formed by [BO₄] and [SiO₄] units in the glass increases, leading to an increase in the fraction of the three-dimensional network structure of the glass, therefore inhibiting the crystallization of CsPbI₃ QDs and reducing the size of QDs. This results in the blue shift of the absorption edge and emission peak wavelength. From the emission spectra, with increasing the ZrO₂ concentration, the PL intensity of the glass samples first increases and then decreases. Both the absorption edge and emission peak wavelength show a clear redshift with increasing the heat treatment temperature or time, which is mainly attributed to the increased size of QDs. According to the PL decay curves, as the ZrO₂ concentration increases, the PL lifetime of glass gradually decreases; as the heat treatment temperature increases, the PL lifetime of glass gradually increases. Finally, after multiple heating and cooling cycles at 293–373 K, there was no significant decrease in the PL intensity of the glass.

Conclusions The CsPbI₃ QD-doped borosilicate glass was prepared successfully by high-temperature melting-quenching followed by heat treatment. X-ray diffraction shows that CsPbI₃ QDs are precipitated in the glass. With increasing the ZrO₂ concentration, the PL intensity of the glass samples first increases and then decreases, and the highest PLQY reaches 32.6%. In addition, the emission peak wavelength and absorption edge show a blue shift, which is attributed to the increased fraction of tetrahedral network structures formed by [BO₄] and [SiO₄] units in the glass at higher ZrO₂ concentrations. Consequently, the increase in the fraction of the three-dimensional network structures of the glass impedes the movement of Cs⁺, Pb²⁺ and I⁻, inhibiting the crystallization of CsPbI₃ QDs. After multiple heating and cooling cycles at 293–373 K, there was no significant decrease in the PL intensity of the glass, indicating that Zr⁴⁺ doped CsPbI₃ perovskite QDs glass has good thermal stability, which may find applications in display, lighting and other fields.

Keywords zirconium ions; quantum dots; borosilicate glass; crystallization