文章编号: 1000-324X(2016)10-1009-04 DOI: 10.15541/jim20160901

发光材料及其新进展

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发光材料也称为发光体, 是能够把从外界吸收的各种形式的能量转换为电磁辐射的一类功能材料。这种电磁辐射是一种非平衡辐射, 在本质上不同于黑体辐射。发光材料通常发出可见光, 也可以是紫外光和红外光。按照不同激发方式, 发光材料可分为光致发光、阴极射线发光、电致发光、化学发光、摩擦发光、X射线发光等。热释光也是材料的一种发光特性, 虽然它不是非热辐射, 但热释光谱是研究发光材料的重要手段。发光材料种类繁多, 应用广泛, 主要集中在固态发光、显示技术、医学诊断、成像分析、安全标签、能量转换以及各种探测器、激光器、放大器等领域。由于巨大的应用需求, 发光材料研究受到了广泛重视, 主要热点有LED荧光材料、量子点发光、光伏转换材料以及闪烁材料等[1-4]。

LED荧光粉通常由近紫外光或蓝光激发发光, 其发光中心多为稀土离子或过渡金属离子, 基质材料主要有硅酸盐、铝酸盐、石榴石、磷酸盐和氮化物等体系[5-7]。不同基质对荧光粉的寿命、显色指数等参数影响很大。迄今为止, YAG: Ce一直是最重要的商用荧光粉, 广泛用于半导体照明, 由发蓝光的GaN芯片与发黄光的YAG: Ce荧光粉共同产生白光。YAG: Ce商用荧光粉存在两大问题: 1)YAG: Ce红光成分偏弱, 导致显色指数差, 通常需要添加硫化物或硫氧化物红色荧光粉补色, 比如, $Y_2O_2S:Eu^{3+}$和$SrY_2S_4: Eu^{3+}$。与氧化物、硫化物荧光粉相比, 氮化物荧光粉以其高显色指数和高亮度等优点也受到极大关注, 主要有AlN: Eu^{2+}、$CaSiO_2N_2: Ce^{3+}$、$LaSiO_2N: Ce^{3+}$等; 2)荧光粉封装时通常采用环氧树脂和有机硅等溶剂, 传热性差, 容易老化, 对于大功率器件来说问题更突出。采用单晶荧光体不仅能够避免荧光粉自身带来的热导性和稳定性等缺陷, 提高LED的发光效率, 延长使用寿命, 而且单晶自身作为透明的光学衬底材料, 有望带来LED封装技术的革命[8]。另一种替代荧光粉的块体材料——玻璃荧光体也值得关注, 已发展出多种玻璃荧光体及其制备技术, 如PiG方法[9]。

量子点是具有独特光学和电学性质的纳米尺寸半导体颗粒材料, 其光电性质由纳米尺度上颗粒的尺寸、形状和量子物理决定[10], 有些量子点还具有光致发光特性。相比普通有机荧光材料, 量子点具有更宽的吸收带、更长的荧光寿命、更好的光稳定性和更好的发光带调制性, 在生物医疗、LED、光催化、能源等领域有着巨大的应用潜力。过去十多年来, II-VI族化合物如CdS、CdTe、HgSe等量子点已得到广泛研究。近年来研究发现, 碳材料量子点因具有发光效率高、化学稳定、水分散性好、低光漂白特性、高生物相容性、低成本和低毒性等特点而备受瞩目[11-14]。这些碳材料量子点通常是近似于球形的纳米颗粒, 由非晶态和晶态两部分组成, 主要包括石墨烯量子点和碳量子点等[12]。石墨烯量子点可用于LED, 产生具有极高颜色纯度的绿、橙、红等多色发光; 空心碳球是基于碳量子点发光的三维多色荧光纳米材料。碳量子点的发光机理仍有待探讨, 而高质量碳量子点的实用制备技术是未来发展方向[12]。

尽管光伏技术应用已有半个多世纪, 但是太阳能的利用仍然价格较为昂贵, 这很大程度上是由于太阳能电池转换效率不高。硅基太阳能电池由于只能吸收太阳光很窄波段的能量, 大约损失 50%太阳光。近年来, 将一些光谱转换材料应用到太阳能电池上, 主要包括上转换、量子剪裁和下转换等发光材料[15-16]。利用上转换发光材料把红外光转化成易吸收的可见光, 最大转化效率可以提高到 47.6%。通过在太阳能电池前表面增加一层下转换材料, 其转换效率可提高到 38.6%。目前, 掺杂澜系三价离子 Er^{3+}和 Ho^{3+}的上转换发光材料和 Tb^{3+}-Yb^{3+}共掺窄隙下转换材料已用在 C-Si(晶体硅)太阳能电池上[15]。最近, 钙钛矿铅卤化物 $CH_3NH_3PbX_3$(X 代表 Cl、Br 或 I)以其迁移率高、扩散长度长、光吸收系数大等优点成为新一代光电材料, 特

别在太阳能电池上有重要应用，太阳能电池转换效率可提高到 20%以上[17-19]。由于单晶相对于薄膜具有更好的完整性, $CH_3NH_3PbX_3$ 晶体可能会有更为优良的光电性能。因此, $CH_3NH_3PbX_3$ 晶体的生长广受关注，最近陕西师范大学已报道生长出直径 2 英寸的 $CH_3NH_3PbX_3$ 晶体[20]。

闪烁体是由高能射线激发产生可见光的一类发光材料，在核医学成像、高能物理、核物理、安全检查等领域有着广泛应用。光输出、衰减时间、密度等是衡量闪烁材料的主要参数, CsI、BGO、PWO、$LaBr_3$、Lu_2SiO_5 都是重要的闪烁晶体，至今还应用在各个领域。近年来，一些新闪烁晶体以其独特性能而备受关注，比如 $SrI_2:Eu^{3+}$晶体表现出优异的闪烁性能[21], $ZnO:Ga^{3+}$是一种超快闪烁体[22], $Bi_4Si_3O_{12}$ 是双读出量能器的候选材料[23], $Li_6Gd(BO_3)_3$、Cs_2LiYCl_6 则是中子探测材料[24]。自从 GE 公司推出 Gemstone 闪烁体以来，透明陶瓷闪烁体成为一个新的研究热点。稀土掺杂 YAG、LuAG、LuO_2 等成为重点关注的透明闪烁陶瓷，其制备、性能和应用得到广泛研究，但发光机理、反位缺陷等科学问题仍值得探讨[25-26]。

此外，发光材料在材料种类上已拓展到有机发光材料[27]和有机–无机杂化材料[28]等；在发光机理上还有缺陷发光[29]和应力发光等效应[30]；在应用领域上荧光标记材料也是一类重要发光材料。到目前为止，发光材料已发展成为一门跨学科的热门研究领域，它涉及到化学、物理学、器件技术和材料科学等诸多学科，这种跨学科特性必将带来更多激动人心的新发现、新材料和新应用[4]。

Recent Developments of Luminescent Materials

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Luminescent materials, also called phosphors, are generally characterized by the electromagnetic radiation with energy beyond thermal radiation. That means the luminescence is different from black-body radiation. The luminescent material usually emits visible light, but ultraviolet (UV) and infrared (IR) light are also included. Thermo-luminescence is a luminescence but not a cold light which generates light in a non-thermal way. However, the thermo-luminescence (TL) spectrum is an important way to study luminescent materials. Luminescence can occur as a result of many different kinds of excitation, which is expressed as photo-, cathode-, electro-, chemi-, tribo-, X-ray, or sono-luminescence. Luminescent materials have been widely used in solid-state lighting, display, medical diagnostics, security labeling, energy conversion, detectors, lasers, and amplifiers. Recently, luminescent materials have been paid much attention due to its huge application demands, especially in the fields of LED phosphors, quantum dots, perovskite solar cells, and scintillators[1-4].

Phosphors on light emitting diodes (LED) are generally excited by near UV or blue light and consist of an inert host doping with activator ions, usually transition (3d) or rare earth (4f) metals. The transparent host materials may include silicates, aluminates (garnet), phosphates, and nitrides[5-7]. The fluorescent life and color rendering index greatly depand on the host materials. Up to now, YAG: Ce^{3+} powders are the most successful phosphors which are commercially used in semiconductor lighting. The YAG: Ce^{3+} yellowish phosphors are used to convert monochromatic light from a blue or UV LED to broad-spectrum white lights. However, there are still some drawbacks for commercial phosphors. Lack of red emission for $YAG:Ce^{3+}$ phosphors may result in poor color-rendering index, so it is necessary to add some red phosphors, such as $Y_2O_2S:Eu^{3+}$ and SrY_2S_4: Eu^{3+}. Beside oxides, nitrides are another kind of luminescent materials due to their advantages of stable structure, suitable doping and multi-states. The main nitride phosphors include $CaSiO_2N_2$: Ce^{3+}, $LaSiO_2N$: Ce^{3+} and AlN: Eu^{2+}. Epoxy resin and organic silicone are common packaging materials for LEDs with $YAG:Ce^{3+}$ phosphors, but heat performance and aging are trouble problems, especially for high powder LEDs. Compared with $YAG:Ce^{3+}$ phosphors, single crystals show good thermal performance and stability which can improve the luminescent effect and life time of the LED lamps. Furthermore, the combination of transparent crystal and flip chip technology leads a revolution in LED fields[8]. Recently, luminescent glass attracted much attention as potential phosphors replacing $YAG:Ce^{3+}$ phosphors and several glasses and preparation techniques have been developed [9].

Quantum dots (QDs) are nanometer sized semiconductor particles with unique optical and electrical properties dictated by their size, shape, and the quantum physics that arises at the nano-scale[10]. Some quantum dots showed photo-luminescence characteristics. Compared to organic fluorophores, quantum dots can emit photoluminescence (PL) with much improved characteristics, including a wider absorption band, longer fluorescence life-time, good photostability and spectral tuneability of the PL band *etc.*, making them promising candidates for biomedicine, LED, photocatalyst and energy-related applications. In past decades, the QDs of II-VI compounds, such as CdS, CdTe, and HgSe, have been investigated extensively. Recently, carbon QDs attracted much attention due to its merits of high luminescent efficiency, chemical stability, dispersibility in water, low photo bleaching, biocompatibility, low cost, and low toxicity[11-14]. Carbon dots, including graphene quantum dots (GQDs) and carbon quantum dots (CDs), are generally quasi spherical nanoparticles consisting of amorphous and crystalline parts. GQDs can emit high color-purity green, orange and red light for LED application. Hollow Carbon Spheres (HCSs) were reported as the first examples of three-dimensional multicolor fluorescent nanomaterials based on carbon dots (CDs). Conclusive evidence and convincing explanation is still absent for the photoluminescence mechanism and facile synthesis of CDs and GQDs with high quality are still challenges[12].

Despite photovoltaic (PV) technologies being available for more than half a century, the production of solar energy remains costly, largely owing to low power conversion efficiencies of solar cells. Each PV material responds to a narrow range of solar photons and leads the loss of approximately 50% of the incident solar energy in silicon-based solar cell conversion to electricity. Some spectral converters have been developed for PV applications, mainly including lanthanide-based upconversion, quantum cutting and down-shifting materials[15-16]. The upconversion luminescent materials can transform two (or more) transmitted sub-bandgap photons into photon in visible light and the maximum efficiency was calculated to be 47.6%. Modified with a downconverting layer on the front surface, a solar cell can achieve a conversion efficiency of up to 38.6%. So far, Er^{3+} and Ho^{3+} doped upconversion materials and Tb^{3+}/Yb^{3+} codoped downconversion materials have been applied in crystalline Si solar cells[15]. Recently, methylammonium lead trihalide perovskites ($CH_3NH_3PbX_3$, where X is Cl, Br or I) have emerged as new generation optoelectronic materials duo to high carrier mobility, long carrier diffusion length and large light absorption coefficient in the UV-Vis range. It was reported that the conversion efficiency of perovskite solar cells has achieved 20%[17-19]. Because single crystals have no grain boundaries, it is anticipated that perovskite single-crystal-based devices will have much better optoelectronic performances. There have been a lot of efforts to grow $CH_3NH_3PbX_3$ single crystals and a crystal up to 2 inches has been grown in China[20].

Scintillators are one kind of luminescent materials excited by high energy particles and widely used in the fields of nuclear medicine imaging, high energy physics, safety inspection. Light yield, decay time and density are the main parameters to characterize scintillation materials and a lot of important scintillation crystals have been developed in the past decades, such as CsI, BGO, PWO, $LaBr_3$, and Lu_2SiO_5. Recently, some new scintillation crystals have been studied for different applications, for example, SrI_2:Eu^{3+} crystal is a high performance scintillator[21], ZnO:Ga^{3+} crystal is super fast scintillator[22], $Bi_4Si_3O_{12}$ crystal is a potential scintillator for dual readout calirometer[23], $Li_6Gd(BO_3)_3$ and Cs_2LiYCl_6 crystals can be used for nutron detecting[24]. Scince Gemstone scintillator was developed in GE company, tranparent ceramics scintillators become a hot topic. Most research work was focused on preparation, properties and applications of Re-doped YAG, LuAG, LuO_2 ceramics. However, the luminescent mechanism and anti-site defects have not yet been deciphered[25-26].

In addition, many organic or organic-inorganic luminescent materials have been developed and applied in OLED, fluorescent labeling, homeland security, and environmental cleaning[27-28]. Some materials show luminescent characteristics due to defects, stress and so on[29-30]. Up to now, luminescent materials have become a hot topic through materials research fields as well as interdisciplinary fields. The interdisciplinary character of this research discipline, which includes different aspects of chemistry, physics, device technology, and materials science, will lead to many exciting discoveries, new materials and new applications in future.

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