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硕 士 学 位 论 文

草酸沉淀法合成 YAG: Ce 和 YAG: Eu
荧光粉及性能研究

Preparation of YAG: Ce and YAG: Eu phosphors
by oxalic acid precipitation and their properties

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中文摘要

白光 LED 技术对于合理利用能源和绿色照明具有重要意义。它拥有广阔的应用前景,将成为替代白炽灯、荧光灯的新一代新型光源。蓝光 LED 与 YAG: Ce 荧光粉配合制备白光 LED,是当前白光 LED 的发展主流。使用性能优异的荧光材料可以有效提高白光 LED 发光效率。目前,制备 YAG: Ce 荧光粉公认最有效的方法是固相法;但该方法很难获得球形、无团聚的荧光粉,难以满足高效率白光 LED 对 YAG: Ce 荧光粉的要求。YAG: Eu 作为一种用于彩色投影电视及紧凑型荧光灯等领域中的高效红色荧光粉,已引起了人们越来越多的兴趣。

本研究用草酸沉淀法制备 Ce^{3+} 掺杂的 YAG: Ce 荧光粉和 Eu^{3+} 掺杂的 YAG: Eu 荧光粉;通过 TG-DTA、XRD、激光粒度仪、SEM、荧光分光光度计等进行表征,研究热处理温度、助熔剂、离子掺杂和滴加方法等制备条件对荧光粉的结晶过程、颗粒的显微形貌和发光性能的影响。主要研究结果和进展如下:

采用草酸沉淀法得到的前驱体,经过 1200°C 保温 2h 得到了单一物相、主晶体为 YAG 的荧光粉,粉末颗粒尺寸分布均匀,近似球形。随着热处理温度进一步升高,晶体逐渐完善,粉末粒径逐渐增大;YAG: Ce 的发光强度也逐渐增强,但 YAG: Eu 的发光强度提高并不明显。

研究了复合助熔剂中氟化物 (NaF 、 BaF_2 、 NH_4F) 的种类以及硼酸的用量对荧光粉的制备条件、颗粒形貌和发光性能的影响;发现助熔剂的加入可改善荧光粉颗粒形貌,促进晶体生长进而提高荧光粉激发和发射光谱的相对强度。

研究了离子掺杂对荧光粉性能的影响,观察了 YAG: Ce、YAG: Eu 的浓度猝灭现象;发现 Gd^{3+} 的掺杂使 YAG: Ce 荧光粉的发射光谱和激发光谱都有了有不同程度的红移,掺杂量越多红移越显著,这有利于降低白光 LED 器件相关色温和提高显色指数。

对比了反滴加和二次滴加对 YAG: Ce 发光性能的影响;发现当热处理温度高于 1315°C ,二次滴加制得的荧光粉有着更高的发光强度,这可能是由于二次滴加更有利于铈的掺杂,从而提高了荧光粉的发光强度。

选取本研究制备的、发光性能好的荧光粉和市场上的主流进口粉同步封装成白光 LED 灯,对两者的光学性能进行比较;结果表明,本研究制备的荧光粉有

更好的颗粒形貌、能有效地提高白光 LED 的性能。

关键词：草酸沉淀法；YAG 荧光粉；白光 LED

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Abstract

White LED (W-LED) technology is significant for appropriate utilization of energy and green lighting. It has a wide application prospect and consequently will become the new generation of illuminant as the substitute for the incandescent lamp and the fluorescent lamp. Nowadays it is the mainstream development trend that the W-LED consist of blue light GaN and yellow light YAG: Ce phosphor. Phosphors with high efficiency can improve the luminescent efficiency of W-LED. Now the solid-state reaction method is generally acknowledged as the most useful method of preparing YAG: Ce phosphor. Phosphors prepared by this method, however, are nonspheric and agglomerated. They are difficult to meet the requirement of high efficient W-LED. YAG: Eu as a kind of high efficient red phosphors which is applied to color projection TV and compact fluorescent lamp has aroused more and more interests.

YAG: Ce and YAG: Eu phosphors were synthesized by oxalic acid precipitation method in this investigation. To analyze the Effect of heat treatment temperature, fluxes, ion doping concentration and titration method on crystallization, morphology and luminescent properties, the phosphors were characterized with TG-DTA, XRD, laser particle sizing, SEM, fluorescence spectrophotometry and so on. The main results and achievements are as follows:

YAG phosphors with single phase and excellent luminous performance could be synthesized by oxalic acid precipitation method and heat treatment for 2h at 1200°C. Their particles were uniform in size, close to sphericity. With the increasing heat treatment temperature, the particles size increased. The fluorescence intensity of YAG: Ce was also enhanced steadily. This phenomenon, however, was un conspicuous in the case of YAG: Eu.

Effects of different fluorides such as NaF, BaF₂, NH₄F together with H₃BO₃, respectively, and concentrations of H₃BO₃ on preparation conditions, particulate morphology and the luminescent properties were studied in this dissertation. It is

confirmed that fluxes can improve particulate morphology, promote crystal growth and enhance relative intensity of excitation spectra and emission spectra of the phosphor.

Effects of ion doping on the properties of phosphors were studied. Concentration quenching phenomena of YAG: Ce and YAG: Eu was observed. Both excitation spectra and emission spectra of YAG: Ce phosphors showed a tendency of red-shift with increase of Gd^{3+} concentration, which was beneficial to reduce the correlated color temperat and enhance the color rendering index of W-LED devices.

Effects of inverse titration of chemical co-precipitation were compared with secondary titration for the luminescent properties. Results have showed that powders prepared by secondary titration method had higher emission intensity when heat treatment temperature was higher than 1315°C. This was probably relevant to the secondary titration method which might benefit to cerium homogeneous distribution at high heat treatment temperature.

The phosphors with good luminescent properties were chosen to be packaged to W-LED in synchrony with mainstream imported commercial phosphors. Effects of two kinds of phosphors on the optic properties of W-LED were compared. Results have showed that powders with better morphology can improve the optic properties of W-LED more effectively.

Key words: oxalic acid precipitation; YAG phosphor; white LED

第一章 绪论

1.1 白光 LED 照明

固体白光照明(solid state lighting, SSL)是指利用半导体发光二极管(light emitting diode, LED)产生白光,作为普通照明光源的技术。20世纪90年代初,随着日本日亚公司高效率蓝光LED的研制成功,高效、低能耗的白光LED得到了迅猛发展,预示着新的照明革命的到来。

白光LED作为一种非常有前景的无污染的绿色固体普通照明光源日益引起了各国科研机构的高度重视,纷纷由政府设置专项,编列预算与计划推行。如1998年日本政府拟定的“21世纪光照明计划”,2000年美国制定并实施的“国家半导体照明研究计划”及在2000年欧盟各国积极合作研发用于照明的LED的“彩虹计划”,其目的都是希望通过国家扶持以确保本国白光LED发展处于领先地位。另外,商用白光LED也得到了迅速发展。除日亚化学(Nichia)和住友电工(Sumitomo)外,还有丰田合成(Toyoda Gosei)、罗姆(Rohm)、东芝(Toshiba)和夏普(Sharp),美国科瑞(Cree),全世界3大照明厂通用电气(GE)、飞利浦(Philips)、欧司朗(Osram)以及惠普(HP)、西门子(Siemens)等企业也都投入了该产品的研发生产,对促进白光LED产品的产业化、市场化起了积极促进的作用。我国政府对发展蓝光、白光LED也高度重视,曾将此作为新材料领域的一个重点资助项目列入“863”资助计划,以促进LED产业的发展。国内的一些知名科研院所,如中国科学院物理所和长春光机与物理所、北京大学、北京有色金属研究院、石家庄电子十三所等单位也相继开展了这方面的研究工作。目前已取得了可喜的进步,正在缩短与国际先进水平的差距。

相对于已有的光源(白炽灯、荧光灯等),白光LED具有明显的优势,其特点大体总结为如下^[1]:

1. 发热量小,节能省电,耗电量只有白炽灯的12%(即为1/8),无热辐射;
2. 发光效率高;
3. 寿命长(1万~几万小时,约为日光灯的10倍);
4. 响应速度快;

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