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Optical performance study of $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ ternary luminous fiber

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Abstract: In this study, down-conversion fluorescent powder of $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$, which were the common three primary colors materials with long afterglow, were synthesized by high temperature solid state method. The blends of rare earth (RE) luminescent materials have been of interest to reinvest the luminescent characteristics of polyethylene terephtahalate (PET) luminous fiber. The scanning electron microscopy (SEM) and an inversion fluorescence microscope were used to characterize the surface morphology and the dispersion of inclusion. Through analysis of microcosmic morphology, three typical dispersions of luminescent particles were summarized. The X-ray diffraction indicated that the phase structure of fiber samples and crystal structure of luminescence materials kept complete after prilling and spinning. From the fluorescence spectra and CIE 1931 coordinates, it could be found that different combinations of luminous fibers were desired to obtain divers colors emission luminous fiber. And the fiber samples were a light sensation which could induct different excitation wavelengths and convert it down to different colors. The afterglow decay curve and its differential curve were summarized indicating the three decay stages. The decay curve and decay rate curve showed that the contents of $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ had obvious influence on the afterglow of fiber samples.

Keywords: luminous fiber; $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$; $SrAl_2O_4:Eu^{2+},Dy^{3+}$; $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$; down-conversion; light sensation; rare earths

Since the rare earth (RE) co-doped long-lasting phosphors were discovered in 1960s, it has received much attention in the fields of chemistry, physics, biology and many kinds of applied science, because of their outstanding afterglow and high color purity[1–3]. Due to the special electronic structure of RE ion, the europium ion is usually treated as the activator in semiconductor materials. With doping of dysprosium ion and other metal ion, the semiconductor materials are endowed with long-lasting property[4–7]. The $SrAl_2O_4:Eu^{2+},Dy^{3+}$ with excellent initial brightness and long afterglow time is most widely used to obtain green light. There are several long-lasting phosphors materials to obtain blue and red emission, however, $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ which have prominent afterglow performance and high color purity. There are several long-lasting phosphor materials to obtain blue and red emission, especially $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ are the most prominent materials with blue and red emission[8–11]. Luminous fiber as a novel optical material is prepared by RE co-doped long-lasting phosphors and fiber-forming polymer. This functional fiber has attracted lots of research interests since 2005 because of itsusability on garment, architecture/decoration, road safety and emergency sign[12–16]. The $SrAl_2O_4:Eu^{2+},Dy^{3+}$ with green light emission is the host blend to prepare the luminous fiber which has green light emitting behavior. However, further study is still required to obtain full-color emission luminous fiber[17,18]. Hence, the luminous fibers with polychromatic light emission are very essential.

In this study, $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ were synthesized as the luminous host to prepare luminous fiber. The micro model of ternary luminous fiber is given in Fig. 1. The down-conversion occurred in fiber materials when the ultraviolet penetrated the polymeric membrane. The invisible radial was respectively converted in blue, green and red region at 480, 530 and 635 nm where the visual perception of human eye was better[19–21]. And with the process of down- conversion, the recombination of monochromatic lights which were emitted by RE luminescent materials were also available.

1 Experimental

1.1 Raw materials

Al_2O_3, $SrCO_3$, ZnO, SiO_2, Eu_2O_3, Dy_2O_3, H_3BO_3,

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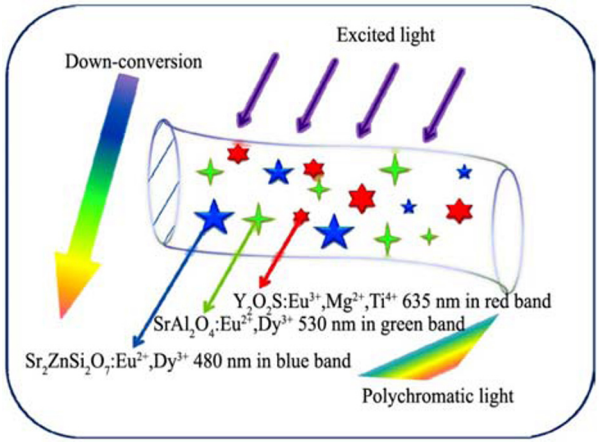

Fig. 1 Down-conversion process and recombination of monochromatic lights in microscopic view

Y_2O_3, S, TiO_2, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}6H_2O$, Na_2CO_3 of analytical reagent grade and as the starting materials were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The polyethylene terephthalate (PET) chips were produced by the Hengli Group Co., Ltd. The spinning additives were supplied by Jiangsu Gouda Complete Wiring Equipment Co., Ltd.

1.2 Preparation of rare earth luminescent materials

1.2.1 Preparation of $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$

$Sr_{1.95}ZnSi_2O_7:Eu^{2+}_{0.02},Dy^{3+}_{0.03}$ were synthesized using high temperature solid state method. After preliminary milling, these raw materials (ZnO, SiO_2, $SrCO_3$, Eu_2O_3, Dy_2O_3 and H_3BO_3) were dissolved in appropriate amounts of absolute ethanol, followed by ultrasonic dispersion for 30 min and mechanical mixing for 30 min in order to get the homogeneous mixture. The samples were heated by adding H_3BO_3 (the ratio of H_3BO_3 to $Sr_{1.95}ZnSi_2O_7:Eu^{2+}_{0.02},Dy^{3+}_{0.03}$ was 10 mol.%) to a high temperature of 1400 ºC for 3 h in a reducing atmosphere. The sintered products were re-milled in ball mill and sieved with 1000 mesh to get the desired size.

1.2.2 Preparation of $SrAl_2O_4:Eu^{2+},Dy^{3+}$

Al_2O_3, $SrCO_3$, Eu_2O_3, Dy_2O_3 and H_3BO_3 of analytical reagent grade as the starting materials were mixed and milled by the ratio in a mortar. After preliminary mill these raw materials were dissolved in appropriate amounts of absolute ethanol, followed by ultrasonic dispersion for 30 min and mechanical mixing for 30 min in order to get the homogeneous mixture. The samples were heated by adding H_3BO_3 (the ratio of H_3BO_3 to $Sr_{0.95}Al_2O_4:Eu^{2+}_{0.02},Dy^{3+}_{0.01}$ was 10 mol.%) to a high temperature of 1400 ºC for 3 h in a reducing atmosphere to sinter $Sr_{0.95}Al_2O_4:Eu^{2+}_{0.02},Dy^{3+}_{0.01}$. The sintered products were re-milled in ball mill and sieved with 1000 mesh to get the desired size.

1.2.3 Preparation of $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$

$Y_2O_2S:Eu^{3+}_{0.04},Mg^{2+}_{0.05},Ti^{4+}_{0.05}$ were synthesized using high temperature solid state method. The raw materials were weighed respectively by appropriate proportion (Y_2O_3, TiO_2, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}6H_2O$, S and Na_2CO_3). After preliminary mixing, the raw materials were ball milled in order to get the homogeneous mixtures. The mixtures were heated by adding Na_2CO_3 as flux (the ratio of Na_2CO_3 to $SrAl_2O_4:Eu^{2+},Dy^{3+}$ was 15 mol.%) to a high temperature of 1200 ºC for 4 h in the air atmosphere. The sintered products were re-milled in ball mill and sieved with 1000 mesh to get the desired size.

1.3 Preparation of luminous fiber

The schematic plot of preparation is given in Fig. 2. A definite amount of $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ were respectively mixed with PET chips and spinning additive in a mixer for blending well. Three kinds of PET-RE mixtures were processed into masterbatches at 270–290 ºC to obtain the PET-$Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$ masterbatches, PET-$SrAl_2O_4:Eu^{2+},Dy^{3+}$ masterbatches and PET-$Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ masterbatches respectively (the mass ratio of RE was about 15%–20%). The PET-RE masterbatches were mixed by the rate with PET chips and dried in the drying oven at 110 ºC for 24 h. The dried chips were melt spinning at 270–290 ºC to get the fiber samples. The mass ratios of $Sr_2ZnSi_2O_7:Eu^{2+},Dy^{3+}$, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ are shown in Table 1.

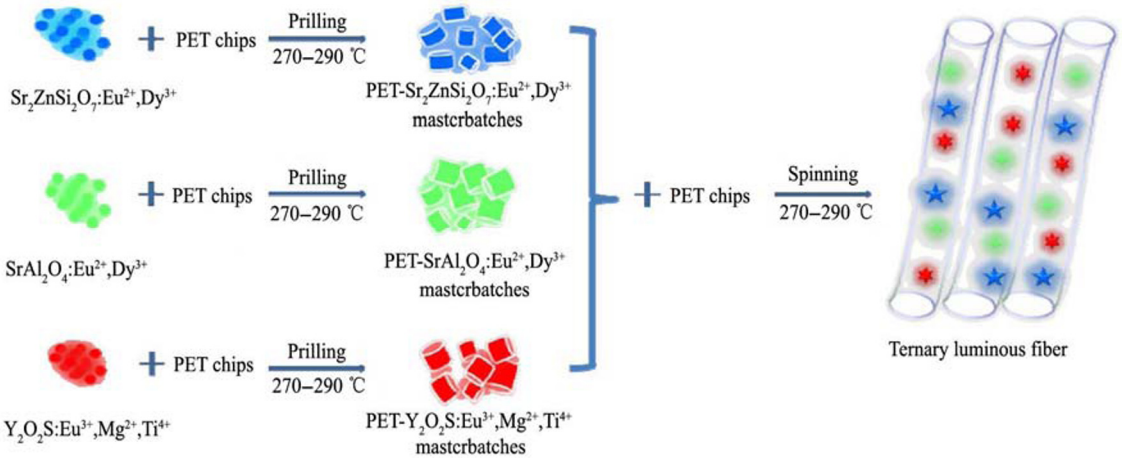

Fig. 2 Preparation diagram of ternary luminous fiber