Synthesis and Luminescence of Nano Fluorescent Powder of 
$Y_4Al_2O_9: Eu^{3+}$

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Abstract: Nano fluorescent powder of $Y_4Al_2O_9: Eu^{3+}$ was synthesized by sol-gel method. The XRD shows that the product prepared at 900°C is pure-phase $Y_4Al_2O_9: Eu^{3+}$. The $Y_4Al_2O_9$ powder is nano-size crystal testified by BF and ED analysis of TEM. The grain diameter of $Y_4Al_2O_9$ is in the range between 20 and 50nm, and its average is 30nm. The luminescent spectra show that $Eu^{3+}$ ions occupy two kinds of sites in $Y_4Al_2O_9$ crystal lattice. One is in the strict inversion center, and the other is in off lying inversion center. When excited with UV light ($\lambda = 254nm$), $Y_4Al_2O_9: Eu^{3+}$ exhibits an orange emission band at $\lambda = 590nm$ due to the $5D_0\rightarrow 7F_1$ transition and a red emission band at $\lambda = 610nm$ due to $5D_0\rightarrow 7F_2$ transition.

Key words: rare-earth; sol-gel method; nano; fluorescent powders; synthesis; luminescence

1 Introduction

Nano luminescent material is an important branch of the research field of luminescent materials. There are many methods of preparing nano luminescent materials. In our study, the sol-gel method was applied to synthesize $Y_4Al_2O_9: Eu^{3+}$ fluorescent powder. There are three different phases in Y$_2$O$_3$-Al$_2$O$_3$ binary-system: YA103, Y$_3$Al$_5$O$_{12}$ and Y$_4$Al$_2$O$_9$ (YAO), which is reported in correlative literature. In the three phases of yttrium aluminates, YA103 and Y$_3$Al$_5$O$_{12}$ as matrixes of fluorescent materials are widely studied, while YAO as matrix of fluorescent materials is lesser studied. In this study, YAO phase has been obtained at 800°C by sol-gel method, and the single-phase obtained from xerogel sintered at 900°C. The particles of the fluorescent powder were observed through TEM, to be of nano-grade. The temperature of preparing YAO pure phase by sol-gel method was at 800°C and lower than that of high-temperature solid-state reaction method.

2 Experimental

2.1 Reagents

$Y_2O_3$ (4N), Al(NO$_3$)$_3$·9H$_2$O (A. R.), citric acid (A. R.), HNO$_3$(A. R.) and Eu$_2O_3$ (4N) were used in the experiments.

2.2 Methods

Solution of individual rare earth nitrates was blended with aluminium nitrate solution at the stoichiometric ratio of $Y_4Al_2O_9$: Eu$_{0.01}$. Then citric acid was added to the mixed solution at a molar ratio of 2:1, resulting in a citric complex solution. Finally, the resulting solution was evaporated for several hours in a water bath before it became sol. The sol was evaporated continuously before it became gel. The xerogel was prepared by baking the gel in an infrared dry box. The nano fluorescent powder was prepared from the xerogel sintered at different temperatures.

2.3 Instruments

A rigaku D/MAX ⅢB X-Ray diffractometer ($K_{Cu} = 1.540598\AA, 30$ kV/mA) was used to collect the powders diffraction data. The shape and diameter of particles were examined through a Philips CM12 TEM. The fluorescent spectra of specimens were measured using a Model F-4500 Fluorescence Spectrophotometer.

3 Results and Discussion

Samples were prepared from xerogel fired at different temperatures. XRD shows that YAO phase starts to form at 800°C. The samples sintered at 1000°C and 1200°C are still YAO single-phase as shown in Fig. 1. The particle shape and size were examined through TEM. The BF and ED of the sample prepared at 900°C are shown in Fig. 2. From Fig. 2, it is found the diameters of fluorescent sample powders are within the range of 20 to 50nm. The mean particle diameter is 30nm according to statistical analyses. We found that the mean particle diameter got bigger as the firing temperature got higher, and its size becomes above 1 µm when the firing temperature
was up to 1200°C.

In the experiments, the xerogel was sintered in a reducing atmosphere and in a non-reducing atmosphere, respectively. From the XRD analysis of the samples prepared in both atmospheres, it is discovered that they were of the same phase as shown in Fig. 3.

The fluorescent spectra of $Y_4A_1O_9:Eu^{3+}$ fluorescent powders were measured and shown in Fig. 4 and Fig. 5. Fig. 4 shows the excitation spectrum of $Y_4A_1O_9:Eu^{3+}$. In Fig. 4, there are three excitation peaks in spectrum 1 (394nm, 438nm, 471nm) and spectrum 2 (340nm, 395nm, 471nm), respectively. In these excitation spectra, there are two different peaks between spectrum 1 and spectrum 2. This is mainly attributed to the difference of the Eu$^{3+}$ ion sites in these two sample crystal lattices. These excitation peaks are attributed to the $f-f$ transition of Eu$^{3+}$. YAO crystallizes in the monoclinic system, and its space group is $Pnam$, point group is $C_{2h}$. When the Eu ion is doped into the YAO crystal lattices, it will be substituted for the $Y^{3+}$ because its radius is close to that of $Y^{3+}$ ($R_{Y^{3+}} = 0.088\text{nm}$). There are usually two kinds of ions of Eu element, i.e., Eu$^{3+}$ ($R_{Eu^{3+}} = 0.095\text{nm}$) and Eu$^{2+}$ ($R_{Eu^{2+}} = 0.109\text{nm}$), so the Eu element may suit the YAO lattice by these two forms. In view of the valence state and the ion radius, there should be only the Eu$^{3+}$ ion substituted for the $Y^{3+}$ in the crystal. Furthermore, by an-