



Yttrium Oxide doped Rear earth based afterglow phosphors, Synthesis and photoluminescence studies

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Abstract –

In this work, we developed a novel long afterglow material yttrium oxide doped rear earth by Combustion Method. The highlight of this work is the observation of bright red color tunable long afterglow of $Y_2O_3:Eu^{3+}, Ho^{3+}$. The structure information of the samples was studied in detail with X-ray diffraction. Photoluminescence and phosphorescence properties of the phosphor were investigated systematically. The reason why the photoluminescence and phosphorescence color can be tuned has been discussed. The bright long afterglow could be observed by naked eyes for 10s in the dark after ultraviolet irradiation was ceased. In this phosphor, Ho^{3+} , Eu^{2+} ions doped in Y^+ sites behave as luminescence centers, generate the defects serve as hole-trapping centers. In view of the experimental results, a feasible afterglow mechanism of $Y_2O_3:Eu^{3+}, Ho^{3+}$ was also proposed and discussed.

Key word- Afterglow phosphors, photoluminescence, phosphorescence

1. Introduction

Long afterglow phosphor is a kind of eco-friendly material, which could adsorb energy from the sunlight, fluorescent lamp or UV light, and store the absorbed energy, and then release the energy gradually in form of afterglow [1–13]. Because of the long afterglow properties, these materials have been used in many fields, such as illumination in darkness, emergency sign, artwork, luminescent paints, detection of radiation, display, and photocatalytic degradation [6–9]. Among the afterglow phosphors $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and $CaAl_2O_4:Eu^{2+}$, Nd^{3+} [1,10–13]. However, the duration and intensity of long afterglow phosphor are inferior in comparison with the former two phosphors [5, 14–16].

Therefore, the development of novel, high-intensity, long-duration, afterglow phosphor is required. Recently, Xu and co-workers reported a new NIR long-persistent $\text{SrGa}_{12}\text{O}_{19}:\text{Cr}^{3+}$ phosphor with the emission duration of more than 2 h with a broadband phosphorescence from 650 to 950 nm [17]. Duan et al. synthesized a novel long lasting phosphorescence phosphor $\text{La}_2\text{Zr}_2\text{O}_7:\text{Sm}^{3+}, \text{Ti}^{4+}$, and the color of afterglow/photoluminescence can be adjusted [18]. Besides the novel host, Y_2O_3 is a conventional host for rare-earth doping [19]. For example, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ was widely used as the phosphor in color display.

In recent years, the wide application in safety indication, emergency lighting, automobile instrument, luminous paint and optical data storage of long afterglow phosphors resulted in increased research in the field. Although efficient green and blue long afterglow phosphors have been investigated in detail, the progress on red phosphor is very slow.

The long afterglow red phosphor based on sulfide is very efficient and has about 180 min afterglow; nevertheless it is extremely sensitive to moisture and thus chemically unstable. $\text{CaTiO}_3:\text{Pr}^{3+}$, $\text{BaTiO}_3:\text{Pr}^{3+}$ and $\text{BaTiO}_3:\text{Cr}^{3+}$ are very stable, but have only a few minutes afterglow. $\text{MO}:\text{Eu}^{3+}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) phosphors with an afterglow of 120 min are not an ideal choice, because alkaline earth oxide is not very stable. Yttrium oxysulfide doped with europium ($\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$) red phosphor is a highly efficient material that is used extensively in display devices. Recently, the long afterglow phenomenon found in $\text{Y}_2\text{O}_2\text{S}:\text{Gd}^{3+}, \text{Eu}^{3+}$ doped with Ti^{4+} and Mg^{2+} ions has attracted attention on this material.

In this work, a red-emitting long afterglow material $\text{Y}_2\text{O}_3:\text{Eu}^{3+}, \text{Ho}^{3+}$ was synthesized and structure, photoluminescence and decay characteristics of the material were investigated, and the potential mechanism of the afterglow phenomenon was discussed.

2. Experimental Section

2.1 Synthesis of Phosphor:

In our preparative method Y_2O_3 (Sigma-Aldrich), Eu_2O_3 (Sigma-Aldrich) and Ho_2O_3 (Sigma-Aldrich) were dissolved in minimum volume of concentrated HNO_3 and boiled on water bath to get clear solutions of $\text{Y}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$ and $\text{Ho}(\text{NO}_3)_3$. The nitrate solutions were taken in a beaker according to the required stoichiometry. After that, TEA (triethanolamine) was added to that nitrate solution and the molecular ratio of metal salt:TEA was maintained 1:4. Then certain amount of concentrated HNO_3 solution was added to maintain the pH 3–4 to avoid any kind of metal hydroxide precipitation. TEA was used as it is an efficient chelating ligand and possesses good coordination properties with the metal ions. The clear solution of TEA complexed metal nitrate is evaporated on a hot plate at 180°C with constant stirring. Continuous heating of the solution causes foaming and puffing. During evaporation of the precursor solution, the TEA present in the system probably led to the formation of vinyl functional groups that cause polymerization. The black fluffy has been calcined and then annealed at 600°C to get the required phosphor.

3. Result and discussion

An X-ray diffraction pattern for the sample is shown in Fig. 2.1. The observed values of the diffraction pattern match quite well with the standard JNCPDS file (88-1040) and the patterns exhibit cubic symmetry [spacegroup Ia-3 (206)] of Y_2O_3 without any impurity which indicates that doping of Eu^{3+} and Ho^{3+} in Y_2O_3 lattice creates a solid solution.

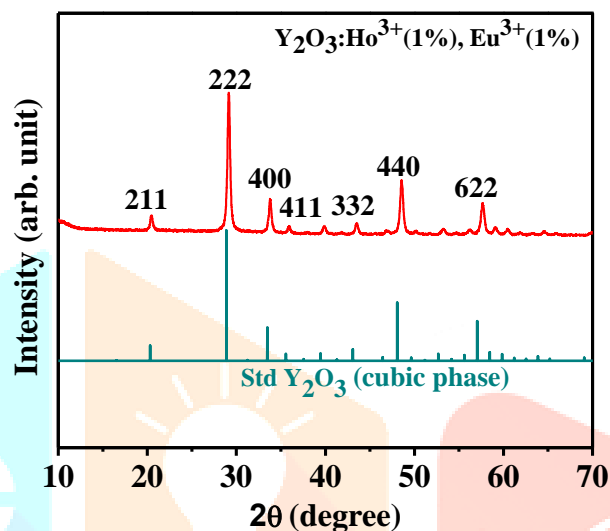


Fig. 1 XRD of Y_2O_3 doped with Eu^{3+} and Ho^{3+} phosphor

Fig. 2 shows the photoluminescence spectra of the phosphors excited by UV light at the wavelength of 254 nm. $Y_2O_3:Eu^{3+}, Ho^{3+}$ phosphors exhibited the strong red emission. Sharp emissions peaking at 582, 588, 594, 600 and 612 nm can be assigned to the ${}^5D_0 \rightarrow {}^7F_J$ (where J is 0, 1 and 2) transitions of Eu^{3+} ion (marked in Fig 2.2). No other emission can be observed in the $Y_2O_3:Eu^{2+}, Ho^{3+}$ sample, indicating that the doped Ho^{3+} ion do not show any significant emission under 254 nm excitation. The strongest red emission at 612 nm is due to the low symmetry position of Eu^{3+} ion with an inversion center and this forced-electric dipole transition is often dominant in the emission spectrum. So the strongest emission at 612 nm is ascribed to Eu^{3+} ion, which occupied on the C_2 site and these ions are dominant in the host. Moreover, $Y_2O_3:Eu^{3+}, Ho^{3+}$ samples were excited under UV 254 nm for 5 min, and then the excitation source was removed to examine whether the materials show long afterglow emission in the dark. $Y_2O_3:Eu^{2+}, Ho^{3+}$ sample exhibits an obvious red afterglow lasting for about 5 min, as can be seen in the left inset of Fig 3, the persistent luminescence of $Y_2O_3:Eu^{3+}, Ho^{3+}$ material can be observed by the naked eyes and it can last for 5 min.

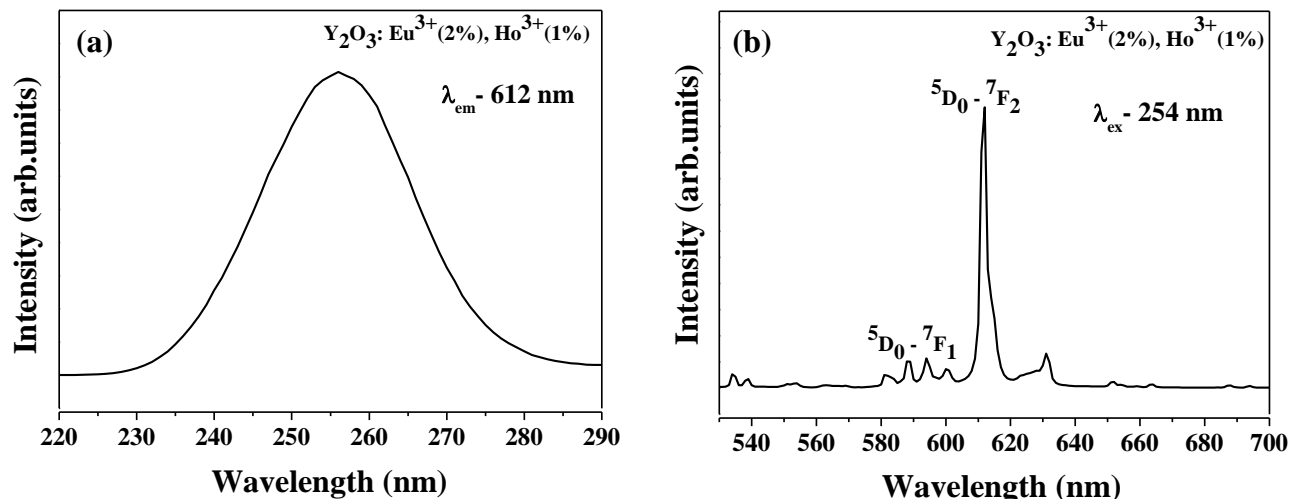


Fig. 2. Photoluminescence (a) excitation and (b) emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, Ho^{3+} samples

The lifetime curve of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, Ho^{3+} sample was recorded and shown in Fig. 2. It contains a rapid-decaying process and a slow-decaying process, the decay curve is similar to that of typical long afterglow materials. The decay characteristic of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, Ho^{3+} phosphor is similar to the rare-earth doping alkaline-earth aluminates long afterglow materials, which have drawn much attention from 1990s. One of the typical aluminates is $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, RE^{3+} ($\text{RE} = \text{Dy}$, Nd and Ho , etc.), which was successfully synthesized by Matsuzawa in 1996. Generally, the Eu^{2+} ion is the only luminescent center in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, RE^{3+} phosphors, and the doped RE^{3+} ions often generate the trap level in the host^[10,20]. In order to exhibit long afterglow phenomena, the phosphor should have suitable trap level and trap density and the trapped carriers do recombine in the luminescent centers occurred with the afterglow.

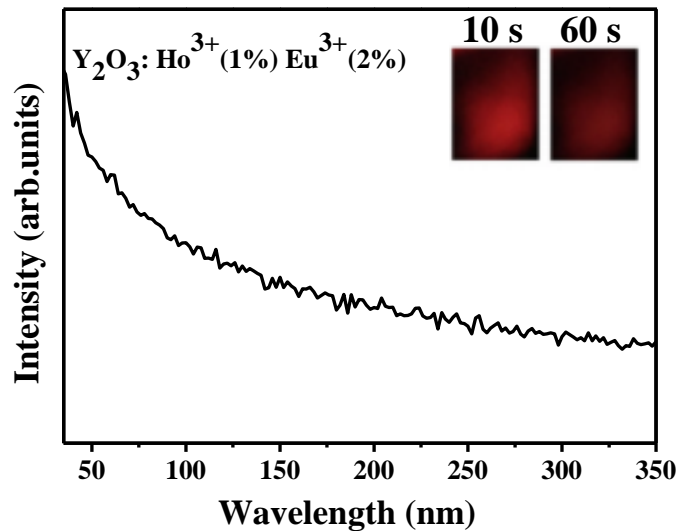


Fig. 3 The decay curve of the Y₂O₃:Eu³⁺, Ho³⁺ sample, the left inset is the afterglow photograph of Y₂O₃:Eu³⁺, Ho³⁺ phosphor which was examined at 2 min after the UV 254 nm light excitation for 5 min.

4. Conclusion

Y₂O₃ doped with Eu³⁺ and Ho³⁺ phosphor was synthesized by a complex based precursor solution method. The phase identification by XRD shows the formation of pure cubic phase of Y₂O₃. Y₂O₃:Eu³⁺, Ho³⁺ phosphor exhibits a red long afterglow phenomenon. The traps in the Y₂O₃:Eu³⁺, Ho³⁺ were generated by the addition of Eu³⁺ ions. The doped of Ho³⁺ shoaled the trap depth, which is beneficial for the carriers to escape from the trap as a result of which the afterglow appears sequentially.

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