Photoluminescence and energy transfer of YAG: Ce³⁺, Gd³⁺, Bi³⁺

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In this study, Gd³⁺ and Bi³⁺ ions act to redshift the emission band to orange region, and to enhance significantly the maximum emission of YAG: Ce³⁺. On account that size mismatch between the host and the doped Gd³⁺ ion, the crystal structure turns soft, and the emission spectra are not tuned from 540 to 570 nm but decreased the emission intensity. Accordingly, an effective way to increase emission intensity is to introduce Bi³⁺ ion into the YAG: Ce³⁺, Gd³⁺ phosphors. Experimental results show partial overlapping between the emission band of Bi³⁺ ion and the excitation band of Ce³⁺ ion, indicating that the energy transfer from Bi³⁺ to Ce³⁺ ions exists in the (Y_{1.94}Ce_{0.06}Gd)Al₅O₁₂: Bi³⁺ phosphor. Bi³⁺ ion can serve as the activator to provide energy for Ce³⁺ ion via cross relaxation phenomenon. Therefore, the (Y_{1.94}Ce_{0.06}Gd)Al₅O₁₂: Bi³⁺ phosphor could have potential applications in warm white LEDs.

Keywords: YAG: Ce³⁺, Gd³⁺, Bi³⁺ phosphor; energy transfer; reabsorption.

1. Introduction

Yttrium aluminum garnet (Y₃Al₅O₁₂, YAG) has been familiar as one of the most general phosphor host materials. Various rare earth elements doped YAG phosphors are useful in many display applications including low voltage field emission display, cathode ray tube, and back light source.^{1–4} Among them, white light emitting diodes (LEDs) based on YAG yellow phosphor plus a blue LED chip have many disadvantages, for instance, blue/yellow color separation, poor color rendering index property and lacking red component in visible spectra. Besides, white LEDs exhibit a limited color range less than 80% according to National Television Standards Committee. For the goal of widening the color range of white LEDs, some researchers proposed to add a red-emitting phosphor layer to the surface of the yellow-green emitting phosphor layer.^{5,6} For the YAG: Ce³⁺ phosphor, it does not work well, because resin silicones have to be used, and then it loses the initial idea of resin-free package. The other solution is that the emission of the YAG:Ce³⁺ phosphor may be tailored by the additional co-doping elements, such as Cr³⁺, Pr³⁺, Eu³⁺, Sm³⁺, and Mn³⁺.^{7–10} Many earlier researches have indicated that one of the most effective way to produce

multicomponent compounds is that Y³⁺ ions are substituted by Gd³⁺ ion, i.e., (Gd, Y)AG: Ce³⁺.^{11–14} Royal Philips Electronics firstly produced a white LED product,¹⁵ a direct bonding of a polycrystalline (Gd, Y)AG: Ce³⁺ ceramic plate combined with the blue-emitting LED. The white LED products showed that the emission wavelength can be shifted toward red region with co-doping Gd³⁺ ions, but accompanied by a 30% decrease of luminous efficacy.¹²

Bi³⁺ ion is popular as post transition metal ion result from a configuration of 6s², which consists of a strong broad absorption owing to ¹S₀→³P₀ transition in the UV region. Based on the survey in the literatures, Bi³⁺ ion can be used as a sensitizer to improve the emission intensity of some materials.^{16,17} Actually, some previous work reported about the luminescent properties that Bi³⁺ ion was co-doping with other RE³⁺ ion activators, and energy transfer between Bi³⁺ and RE³⁺ ions occurred, like YSiO₅: Bi³⁺, YSiO₅: Bi³⁺, Eu³⁺,¹⁸ Dy³⁺,¹⁹ YVO₄: Bi³⁺, Sm³⁺,²⁰ and CaSrS: Bi³⁺, Tm³⁺.²¹ It is clear from these literatures that the Bi³⁺ ion can strongly absorb excitation energy, then transfer efficiently to lower excited states of RE³⁺ ions. However, Bi³⁺ ion influence on the luminescence characteristics of YAG: Ce³⁺ phosphor has rarely been studied in the literature.

The aim of present work is to improve the color component of the YAG-based white LED. Gd^{3+} ions were doped into the YAG: Ce^{3+} phosphor via the co-precipitation method, which showed that the spectra of $(\text{Y}_2\text{Gd})\text{Al}_3\text{O}_{12}$: Ce^{3+} phosphor was redshifted from yellowish-green to orange emission. In addition, the Bi^{3+} ion effects on the luminescence properties of $(\text{Y}_{1.94}\text{Ce}_{0.06}\text{Gd})\text{Al}_5\text{O}_{12}$ phosphor and the energy transfer from Bi^{3+} to Ce^{3+} ions in YAG host, which were studied in detail.

2. Experimental Details

The YAG powders doped with Ce^{3+} ions were prepared by a co-precipitation method. Y_2O_3 , Gd_2O_3 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as starting materials. Nitrate salts were synthesized by dissolving Y_2O_3 and Gd_2O_3 in HNO_3 , and surplus HNO_3 was removed by evaporation. After that, yttrium nitrate, gadolinium nitrate, cerium nitrate, and aluminum nitrate were dissolved in distilled water according to the formula of $(\text{Y}_{1.94}\text{Ce}_{0.06}\text{Gd})\text{Al}_5\text{O}_{12}$ with stoichiometry. It should be mentioned here that ammonium hydrogen carbonate (AHC) solution was used as precipitator, while appropriate amounts of $(\text{NH}_4)_2\text{SO}_4$ and sodium dodecyl sulfate (SDS) were added as dispersants in order to alleviate agglomeration. Furthermore, nitrate salts solution was dropped into the NH_4HCO_3 solution which was mixed by distilled water and ethanol with volume ratio (2:1). The concentration ratio of nitrate salts solution and NH_4HCO_3 was 1:2.5. During the titration process, pH value of the mixed solution was kept at 7.2–7.8. The whole preparation process was conducted at room temperature with vigorous stirring. After the preparation process was finished, the final solution was aged at room temperature for 24 h so that Ce^{3+} ions were totally entered into YAG lattice. After that, the precipitate was collected by centrifuging and washing with distilled water and ethanol three times. Finally, precursor powders were obtained by drying the precipitate at 75°C .

The YAG: Ce^{3+} , Gd^{3+} phosphor powders were prepared by calcining the precursors at 950°C for 2 h. To dope with Bi^{3+} ions, different amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in distilled water with a small quantity of HNO_3 to restrain hydrolysis of $\text{Bi}(\text{NO}_3)_3$. The solutions were added into the as-prepared YAG: Ce^{3+} , Gd^{3+} phosphor powders. The $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ powder's weight ratios were 0.00, 0.75, 1.5, 2.25, 3, and 3.75 wt.%. Then the suspensions were evaporated and dried at 75°C for several hours to get the precursor powders. Finally, these samples were calcined at 750°C for 2 h.

Phase compositions of the as-prepared phosphor powders were characterized by using X-ray diffraction (XRD) analysis, $\text{CuK}\alpha$, at 40 kV and 100 mA, with scanning speed of 15°min^{-1} at a step of 0.02° . Thermal behaviors of the phosphor powders were analyzed by using differential scanning calorimetry and thermogravimetry (DSC/TG) analysis,

with a thermal analyzer (NETZSCH STA 449C, Germany) in air at a heating rate of $10^\circ\text{C}/\text{min}$. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the as-obtained samples were measured by using an FLS-920T fluorescence spectrophotometer (Edinburgh, UK) equipped with a 450 W Xe light source and double excitation monochromators.

3. Results and Discussion

The XRD patterns of the $(\text{Y}_{2.94}\text{Ce}_{0.06})\text{Al}_5\text{O}_{12}$, $(\text{Y}_{1.94}\text{Ce}_{0.06}\text{Gd})\text{Al}_5\text{O}_{12}$, and $(\text{Y}_{1.94}\text{Ce}_{0.06}\text{Gd})\text{Al}_5\text{O}_{12}: x\text{Bi}^{3+}$ ($x = 0, 0.75, 1.5, 2.25, 3, 3.75$ wt.%) phosphors were shown in Fig. 1. The XRD pattern of the $(\text{Y}_{2.94}\text{Ce}_{0.06})\text{Al}_5\text{O}_{12}$ is coincident with JCPDS card (No. 33-0040),²² manifesting that Ce^{3+} ions are incorporated into the YAG host lattice without altering the primary structure of YAG. As Gd^{3+} ion substitutes for Y^{3+} ion with the normal stoichiometric ratio, all the diffraction peaks agree well with the standard card, but a slight peak shift to lower angle is observed as shown in Fig. 1(b). The lattice distortion is the result of the ionic radius difference of Gd^{3+} ion ($1.05 \text{ \AA}$) and Y^{3+} ion ($1.02 \text{ \AA}$). Although the co-doping of Ce^{3+} and Gd^{3+} ions have no clear influence on the crystal structure of host, the shift impacts the following luminescent behaviors. Figures 1(c) and 1(d) show the XRD patterns of $(\text{Y}_{1.94}\text{Ce}_{0.06}\text{Gd})\text{Al}_5\text{O}_{12}$ samples doped with different Bi^{3+} ion concentrations. It is noticeable that the diffraction peaks of all samples can be exactly ascribed to pure cubic phase of YAG when the Bi^{3+} ion content is $x \leq 2.25$ wt.%. The change of diffraction band intensity and full width at half maximum is not significant. The distinct shift of peak is identified until $x = 3.75$ wt.%, which is speculated that a Bi_2O_3 -YAG solid solution is formed.

Figure 2 presents the DSC/TG curves of the YAG: Ce^{3+} , Gd^{3+} phosphor. It can be seen that a broad endothermic peak at about 161.6°C is accompanied by a mass loss corresponding to the evaporation of water.²³ When temperature is increased to 927°C , there is an exothermic peak, which corresponds to a crystallization of the precursor. It is also displayed in Fig. 2 that the mass loss is about 35% from room temperature to 800°C , which is attributed to the water evaporation and the precursor decomposition. There is almost no mass loss above 930°C .

The room-temperature PLE and PL spectra of the $(\text{Y}_{2.94}\text{Ce}_{0.06})\text{Al}_5\text{O}_{12}$ and $(\text{Y}_{1.94}\text{Ce}_{0.06}\text{Gd})\text{Al}_5\text{O}_{12}$ phosphors are depicted in Fig. 3(a). The shape of excitation curve of $(\text{Y}_{1.94}\text{Ce}_{0.06}\text{Gd})\text{Al}_5\text{O}_{12}$ phosphor does not vary much compared to that of $(\text{Y}_{2.94}\text{Ce}_{0.06})\text{Al}_5\text{O}_{12}$ phosphor, which shows two excitation peaks of Ce^{3+} ion at 340 nm and 460 nm, respectively. The emission spectrum peak of $(\text{Y}_{2.94}\text{Ce}_{0.06})\text{Al}_5\text{O}_{12}$ phosphor at 540 nm is a yellow-green broad band. It can be observed that the emission peak of $(\text{Y}_{1.94}\text{Ce}_{0.06}\text{Gd})\text{Al}_5\text{O}_{12}$ phosphor shifts from 540 nm to 570 nm, which redshifts up to about 30 nm. This obvious

Fig. 1. (a) XRD patterns of $(Y_{2.94}Ce_{0.06})Al_5O_{12}$, $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$, $Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$: 2.25 wt.% Bi phosphors calcined at 950°C for 2 h. (b) Detailed XRD patterns from 32° to 34.5° for $(Y_{2.94}Ce_{0.06})Al_5O_{12}$, $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$, $Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$: 2.25 wt.% Bi phosphors. (c) XRD patterns of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$: x.% Bi samples. (d) The detailed XRD patterns from 32° to 38° for $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$: x.% Bi samples calcined at 750°C for 2 h.

red-shift spectrum is also reflected on the change of phosphors' body color from yellow green to orange. The reason for the red-shift can be explained by the mechanism discussed below.

Fig. 2. DSC-TG curves of the as-prepared precursor.

As we know, Ce^{3+} replaces Y^{3+} sites in dodecahedral of YAG crystal structure where the symmetrical characteristic is D_2 . Ce^{3+} ion obtains one $4f$ electron, i.e., ground state electronic configuration is $4f^1$. The ground state level splits into two spectroscopic branched terms of $^2F_{5/2}$ and $^2F_{7/2}$ due to spin coupling. Excited state $5d$ can be divided into five energy levels by crystal field degeneracy. Hence, the electronic configuration of the excited state of Ce^{3+} reaches $5d_1$ and $5d_2$ states in the crystal environment. Figure 3(b) shows the electron transitions from the ground state of Ce^{3+} ($^2F_{5/2}$ and $^2F_{7/2}$) to the excited states of Ce^{3+} ($5d_1$ and $5d_2$) because of the different crystal field splitting components. The electrons at $5d_2$ state reach to $5d_1$ state by the relaxation process, then return to the $4f^1$ state accompanied by the yellow-greenish emission.

Gd^{3+} ion has a steady electronic structure in the $4f^7$ electronic configuration. Therefore, the host environment has hardly any effect on the energy levels of Gd^{3+} ions. In addition, considering that the lowest excitation energy of Gd^{3+}

Fig. 3. (a) PLE ($\lambda_{em} = 550$ nm) and PL spectra ($\lambda_{ex} = 460$ nm) of the $(Y_{2.94}Ce_{0.06})Al_5O_{12}$ and $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$ phosphors. (b) Energy levels diagram of $(Y_{2.94}Ce_{0.06})Al_5O_{12}$. (c) $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$.

ions is very high, the immediate energy transfer from Ce^{3+} ion to Gd^{3+} ion is almost impossible in the YAG system.²⁴ In this condition, the decreased PL intensity can be attributed to the lattice distortion on account of a substitution of Y^{3+} ion with large ionic size. When larger Gd^{3+} replaces Y^{3+} , the substitution of Gd^{3+} ion causes that the Ce–O distance is shortened, and thus the crystal field around Ce^{3+} ion becomes stronger. It is perceived that the crystal field splitting (D_q) is proportional to $1/R^5$, which R is the bond length of activator cation-ligand anion.²⁵ This larger crystal field splits the lowest energy level of Ce^{3+} ion, i.e., $5d$ state band, and eventually induces a red-shift emission of Ce^{3+} ion as shown in Fig. 3(c).

The PL properties of Bi_2O_3 modified $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$ phosphors are to reveal the effects of Bi^{3+} ion, as shown in Fig. 4. It can be seen that an introduction of Bi_2O_3 can obviously improve the emission intensity of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$ phosphor in Fig. 4(a). The optimum concentration of Bi_2O_3 is 2.25 wt.%, and then the emission intensity decreases with the increase of Bi^{3+} ion content (x). Especially, as x value reaches 3 wt.%, it leads to concentration quenching. Besides, there are a trace partial overlapping between the emission band and the excitation band of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$. The sharp increase of overlapping of the $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}: xBi^{3+}$ luminescence spectra when the Bi^{3+} ion content is $x \leq 2.25$ wt.% indicates that Bi^{3+} ion can serve as the activator to provide energy for Ce^{3+} ion, and the energy transfer exist in the $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}: Bi^{3+}$ phosphor.

The luminescence intensities rise caused by Bi^{3+} ions can be clarified via energy level diagram in Fig. 4(b). The ground state of a free Bi^{3+} ion with ns^2 configuration is the 1S_0 state. The excited states come from the $nsnp$ configurations, which are 3P_0 , 3P_1 , 3P_2 , and 1P_1 states in order to increase energy.²⁶ Earlier works on the luminescence of Bi^{3+} ion in oxide host lattice have shown that the excitation band attributes to

the $^1S_0 \rightarrow ^1P_1$ transition and the emission band attributes to the $^3P_1 \rightarrow ^1S_0$ transition. The $^1S_0 \rightarrow ^3P_1$ electronic transitions were partially allowed because of the mixing of the triplet 3P_2 state with the singlet 1P_0 state by the spin–orbit interaction. Besides, the radiative transitions from the 3P_0 -related state can occur, because the mixing of the 3P_2 - and 3P_0 -related states have the vibronic interaction, including the nontotally symmetric vibrations or the hyperfine interaction.²⁷ The spectra of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}: xBi^{3+}$ are strongly overlapped between the $4f \rightarrow 5d$ excitation and emission bands. The Bi^{3+} ion emission via the $^3P_1 \rightarrow ^1S_0$ transition can be absorbed by the ground state of Ce^{3+} ion, and the additional energy is available to excite Ce^{3+} ion. That is, the $Bi^{3+} \rightarrow Ce^{3+}$ energy transfer occurs. So the increase of the PL intensity is mainly attributed to the fact that the Ce^{3+} ions reabsorb energy from the emission band of Bi^{3+} ions. It can be concluded from above results and discussion that the introduction of Bi^{3+} ion can improve the emission intensity of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$ phosphor significantly.

Thermal quenching property is a crucial parameter in evaluating the luminescent properties of the phosphor. Plentiful investigations have studied the thermal quenching behaviors.^{28–31} The temperature-dependent luminescent property of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}: 2.25$ wt.% Bi^{3+} was measured at temperature range 20–230°C, and the results are shown in Figs. 4(c) and 4(d). The thermal quenching temperature, T_{50} , is identified as the temperature at which the emission intensities is half of its primal value. It can be seen that the emission intensity of the measured phosphor decreases more rapidly with increasing temperature than that of YAG: Ce^{3+} , and the measured phosphor has inferior T_{50} than YAG: Ce^{3+} , which suggests that the co-doping of Gd^{3+} , Bi^{3+} ions have a negative effect on the thermal stability for the reason given below luminescence explanation. As Gd^{3+} , Bi^{3+} ion concentrations are enough, the crystal field splitting of Ce^{3+} $5d$ level becomes large but the crystal structure turns

Fig. 4. (a) PLE ($\lambda_{em} = 550$ nm) and PL spectra ($\lambda_{ex} = 460$ nm) of the $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}: x\% Bi$ samples. (b) Energy level diagram of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}: Bi$. (c) Temperature-dependent emission intensities of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}: 2.25$ wt.% Bi. (d) Temperature-dependent relative emission intensity of $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}: 2.25$ wt.% Bi and commercial YAG: Ce^{3+} .

soft. Hence, the electrons are easily excited to a state far away from the ground state equilibrium position, especially at a high temperature as seen in Fig. 4(c).³² Actually, that is also partly why Gd^{3+} -doping can lead to a red-shift of the emission spectra of the $(Y_{2.94}Ce_{0.06})Al_5O_{12}$, but weaken the luminescence intensity of the $(Y_{1.94}Ce_{0.06}Gd)Al_5O_{12}$.

4. Conclusions

YAG: Ce^{3+} and YAG: Ce^{3+} , Gd^{3+} and YAG: Ce^{3+} , Gd^{3+} , Bi^{3+} phosphors were synthesized via a co-precipitation method. The PLE spectra spans the UV to blue region, and the PL spectra ranges from yellowish-green to orange. In the various crystal environments of the YAG: Ce^{3+} , Gd^{3+} , Bi^{3+} structures, the emission intensities fluctuate and emission peak shifts from 540 nm to 570 nm via adjusting the doped cation concentration of phosphors, with energy transfer. Because the crystal structure turns soft, the emission intensity weakens relatively, especially at a high temperature. The results show that an introduction of Bi^{3+} ion can markedly

enhance the emission intensity of YAG: Ce^{3+} , Gd^{3+} because of cross relaxation between Ce^{3+} and Bi^{3+} ions. Consequently, the orange-red emitting phosphors YAG: Ce^{3+} , Gd^{3+} , Bi^{3+} could have potential application in blue or n -UV LEDs.

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