$Y_3Al_3B_2O_{12}:RE^{3+}$ (RE = Tb, Eu): A promising material for the application of light emitting diode (LED)

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Abstract: $Y_3Al_3B_2O_{12}$ polycrystalline singly doped and co-doped with RE^{3+} ions (RE = Tb or/and Eu) have been synthesized by the solid-state interaction method at a temperature of 1250°C. The measurements of the luminescence excitation and luminescence spectra have been carried out at room temperature. The emission-color feature of materials was analyzed by CIE chromatic coordinates diagram and the correlated color temperature. The optimal concentration of RE^{3+} ions for emission of materials was found by studying the luminescence spectra. The rate and efficiency of the energy transfer process from Tb^{3+} to Eu^{3+} in $Y_3Al_3B_2O_{12}:Tb^{3+},Eu^{3+}$ polycrystalline have also been calculated based on the lifetime of the $^5D_4$ level of the Tb^{3+} ion.

Keywords: YAB polycrystalline, CIE diagram, energy transfer.

1. Introduction

During the last few decades, inorganic compounds doped with rare earth ions have been abundantly used for optical applications such as lighting, optical amplifier, laser, and scintillator (Ye, 2010, Ali, 2021). More recently, the invention of the white light emitting diodes (w-LEDs) has created a revolution in the lighting field and display systems (Ye, 2010). The prominent advantages of the w-LEDs are small volume, energy saving, low cost, environment-friendliness, and long persistence (Ye, 2010, Ali, 2021). Nowadays, the w-LEDs are gradually replacing traditional fluorescent lamps. At present, commercial w-LEDs usually are produced by the combination of the blue LED chip (GaN chip) with a yellow emitting phosphor (e.g. $Y_3Al_5O_{12}:Ce^{3+}$) embedded in the epoxy dome (Ye, 2010; Dierkes, 2015). White light is fabricated by a combination of blue and yellow lights. However, these w-LEDs indicate some weaknesses such as low colour rendering index and instability of color temperature. Moreover, the low luminous efficiency after a long period of working is also a limitation of blue-yellow LEDs (Singh, 2021). Thus, it is a pressing requirement to explore a white phosphor with high luminous efficiency using in the lighting field.

Trivalent rare earth (RE^{3+}) ions form an important class of activator ions which are commonly used in spectral devices. Due to the narrow characteristic of some emission bands, the RE^{3+} ions (e.g. Eu^{3+}, Nd^{3+}, and Tb^{3+}) have been used for laser action. Especially, the emission region of some RE^{3+} ions, for instance, Eu^{3+}, Dy^{3+}, Tb^{3+}, and Sm^{3+}, is in the visible region so these ions are applied in color display and lighting (Ye, 2010; Dierkes, 2015). It is noted that the Tb^{3+} ion emits strongly in the blue and green regions whereas the red band is characteristic emission of the Eu^{3+} and Sm^{3+} ions (Ali, 2021; Wang, 2017). The white light can be obtained due to the mixing of the blue, green, and red colors which are emitted simultaneously from the materials co-doped with Tb^{3+} and Eu^{3+} (or Sm^{3+}) ions (Ghosh, 2013; Do, 2019).

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Therefore, these materials have a high application potential for w-LEDs. The fabrication of white light by this way has been observed in some host matrices such as $KGdF_4:Tb^{3+},Sm^{3+}$ polycrystalline (Do, 2019), $CePO_4:Tb^{3+},Sm^{3+}$ nanocrystals (Sisira, 2019), $In_2O_3:Tb^{3+},Eu^{3+}$ nanocrystals (Ghosh, 2013), and $Ba_2P_2O_7:Tb^{3+},Eu^{3+}$ phosphors (Wang, 2017). It is known that yttrium aluminum garnet ($Y_3Al_5O_{12}$) is an efficiently optical material that has been widely used in the applications of laser, color display, and white light emitting diode (Kumar, 2017; Upasani, 2016). Due to the success in the lighting field of the $Y_3Al_5O_{12}:Ce^{3+}$ phosphor, many scientists hope to explore new materials for the applications of w-LED and laser based on the $Y_3Al_5O_{12}$ matrix doped with RE^{3+} ions. Some results have been published recently like $Y_3Al_5O_{12}:Sm^{3+}$ (Ali, 2021), $Y_3Al_5O_{12}:Tb^{3+}$ (Singh, 2021), $Y_3Al_5O_{12}:Ce^{3+},Yb^{3+}$ (Kumar, 2017), and $YAl_3(BO_3)_4:Eu^{3+}$ (Upasani, 2017). However, to the best of our knowledge, the optical properties of $Y_3Al_5O_{12}:Tb^{3+},Eu^{3+}$ polycrystalline have not been studied yet. To contribute knowledge about the spectroscopy of RE^{3+} ions in the inorganic compounds, in this work, we present the study results on the emission features of Eu^{3+} doped $Y_3Al_3B_2O_{12}$ ($YAB:Eu^{3+}$) phosphor as well as Tb^{3+} and Eu^{3+} co-doped in this material ($YAB:Tb^{3+},Eu^{3+}$). The energy transfer process from Tb^{3+} to Eu^{3+} also is discussed in detail. In this study, the partial substitute of aluminum in the $Y_3Al_5O_{12}$ matrix by boron aims to increase the solubility of rare earth doped into the material.

2. Experiment description

$Y_{3-x}Al_3B_2O_{12}:xEu^{3+}$ (x = 0.01, 0.02, 0.03, 0.04 and 0.05) and $Y_{2.98-x}Al_3B_2O_{12}:0.02Tb^{3+}xEu^{3+}$ (x = 0, 0.01, 0.02, 0.03, 0.04) phosphors were synthesized by the solid-state interaction. The starting chemicals include the oxides of Y_2O_3, Al_2O_3, H_3BO_3, Eu_2O_3, and Tb_4O_7 (Sigma Aldrich, 99.99%) which were weighed to the desired proportions. The precursors were thoroughly grounded with an agate mortar. The mixture was poured into a platinum crucible and pre-heated at 800 ^oC in an electric furnace for 6 h. Next, the powder product was cooled to room temperature and ground again. Afterward, the samples were heated one more time at 1250 ^oC for 8 h. It is noted that the samples containing Tb^{3+} ions were heated under CO gas and other samples were heated in air. In the following step, all products were washed with nitric acid solution to remove residual H_3BO_3 as well as YBO_3 which formed during heating. Finally, all samples were annealed at 300 ^oC for 12 h. The obtained products are in terms of white powder. The phase structure of samples was studied through X-ray diffraction (XRD) patterns. This measurement was carried out on an X-ray diffractometer SIMEMS D5005, Bruker, Germany using Cu–$K_{\alpha 1}$ irradiation. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra as well as the decay curves were measured at room temperature with a Fluorolog FL3-22 (Horiba Jobin-Yvon) with a 450 W Xe.

3. Results and discussion

3.1. Phase structure of materials

The XRD patterns of powder samples are presented in figure 1 and compared with the standard card of $Y_3Al_5O_{12}$ crystal (JCPDS 73–1370). It can be seen that the XRD patterns of YAB consist of some peaks that coincide with those of the standard PDF data. There are no peaks of other phases. This result indicates that our products are crystallized in single phase of cubic with space group of the Ia3d as reported in the standard data. For this structure, the lattice constant and unit cell volume are found to be 12.033 Å and 1742.29 $Å^3$, respectively.

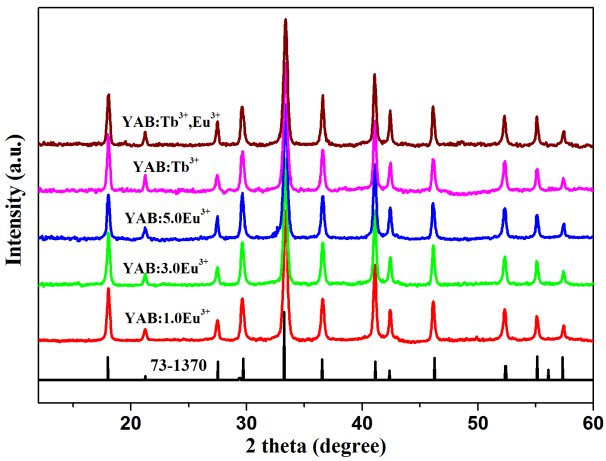

Figure 1. XRD patterns of the YAB:RE^{3+} polycrystalline

3.2. Spectral properties of the YAB polycrystalline doped with RE^{3+} ions

a) Spectroscopy of Eu^{3+} or Tb^{3+} singly doped into YAB polycrystalline

The PLE of Eu^{3+} in YAB:0.02Eu^{3+} sample was measured in the range from 350 to 550 nm by monitoring the emission wavelength at 612 nm (peak of the red band) and shown by curve a in figure 2. The PLE spectrum of other samples has the same structure as that of this sample. The spectrum includes some characteristic excitation bands of Eu^{3+} at wavelengths of 378, 394, 414, and 465 nm. Based on Carnall's report these bands are attributed to the transitions of $^7F_0 \rightarrow {}^5G_2$, $^7F_0 \rightarrow {}^5L_6$, $^7F_1 \rightarrow {}^5D_3$, and $^7F_0 \rightarrow {}^5D_2$, respectively (Carnall[a], 1968). Thus, the red luminescence of YAB:Eu^{3+} can be easily obtained upon excitation by light in the 370-535 nm region (near ultraviolet to green). These excitation bands are in the emission region of nUV, blue and green chips which are popularly used in optical devices.

The PLE of Tb^{3+} in YAB:0.02Tb^{3+} sample was recorded at the wavelength of 542 nm and indicated by curve b in figure 2. There are four excitation bands observed at the wavelengths of 352, 370, 378, and 485 nm. These bands are assisted to the transitions from ground level $^7F_6$ to the excited levels $^5L_9$, $^5L_{10}$, $^5G_6$, and $^5D_4$ in $4f^8$ configuration of Tb^{3+} ion, respectively (Carnall[b], 1968). Among them, the PLE band at 485 nm indicates the strongest intensity so it is usually used for exciting the luminescence of Tb^{3+} ion. As shown in figure 2, the excited band around 378 nm is recorded with both Tb^{3+} and Eu^{3+} ions. Consequently, the luminescence of both Tb^{3+} and Eu^{3+} will be observed upon this excitation wavelength. For this reason, the excitation wavelength of 378 nm was used for all luminescence measurements.

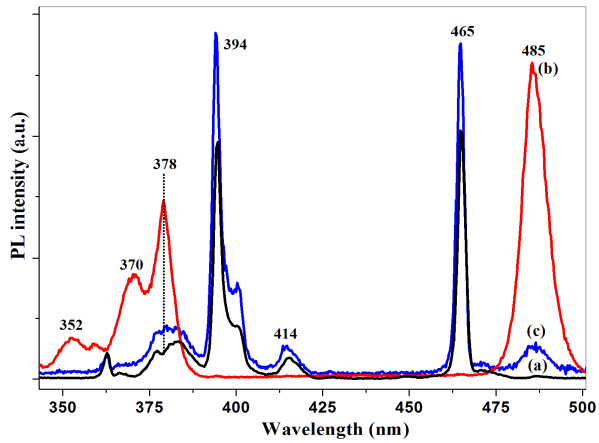

Figure 2. PLE spectra of: (a) Eu^{3+} in YAB:Eu^{3+}, (b) Tb^{3+} in YAB:Eu^{3+}, and Eu^{3+} in YAB:Tb^{3+},Eu^{3+}

The PL spectra of YAB:Eu^{3+} are observed under excitation by the wavelength of 377 nm and are illustrated in figure 3. These spectra include five emission bands originating from the $^5D_0$ excited level to the ^7F_J (J = 0-4) levels of the ground state in Eu^{3+} ion (Carnall[a], 1968). The peak of these bands is at the wavelength of 577, 589, 612, 652, and 701 nm. Among them, the $^5D_0 \rightarrow {}^7F_2$ transition indicates the dominant intensity in comparison with other transitions. The CIE chromatic coordinates diagram is shown in figure 4 which indicates that the color tone of YAB:Eu^{3+} is in the red region. The characteristic red-emission of phosphors doped with Eu^{3+} is generated by this band. This result suggests that the YAB:Eu^{3+} can be used for

producing red LEDs. As shown in figure 3, the intensity of luminescence depends on the concentration of Eu^{3+} ions. When increasing the Eu^{3+} concentration, the PL intensity increases and reaches a maximal value at a concentration around 4.0 mol%, then decreases. Thus, the optimum concentration for luminescence of YAB:Eu^{3+} phosphor is about 4.0 mol% of Eu^{3+}. The decrease of PL intensity after a specific concentration is called concentration quenching (Do, 2019). This phenomenon relates to the energy transfer process between Eu^{3+} ions.

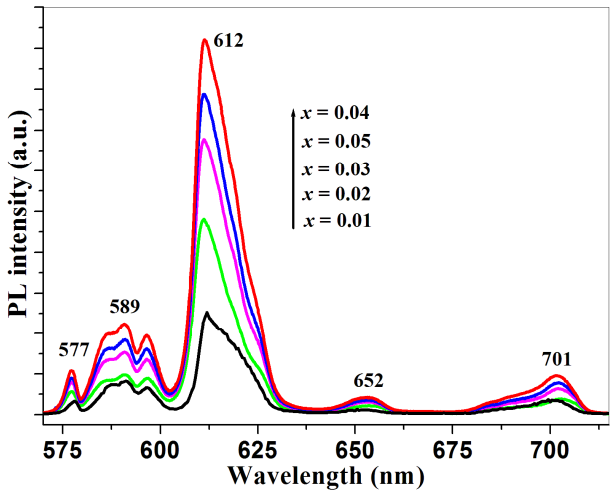

Figure 3. Emission spectra of YAB:xEu^{3+} polycrystalline (x = 0.01, 0.02, 0.03, 0.04 and 0.05).

The PL spectrum of YAB:Tb^{3+} polycrystalline, which was recorded under excitation at 377 nm, is expressed in figure 5 (emission spectrum with x = 0). There are four emission bands which are observed in the Tb^{3+} PL spectrum at the wavelengths of 488, 542, 585, and 620 nm corresponding to the transitions of $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$, respectively (Carnall[b], 1968). The $^5D_4 \rightarrow {}^7F_5$ emission band (green) indicates a significantly stronger intensity in comparison with other bands so this band is usually applied for laser and optical amplifier. Because of the dominant intensity of this band, the color tone of YAB:Tb^{3+} phosphor is in the green region of the CIE diagram (see figure 4).

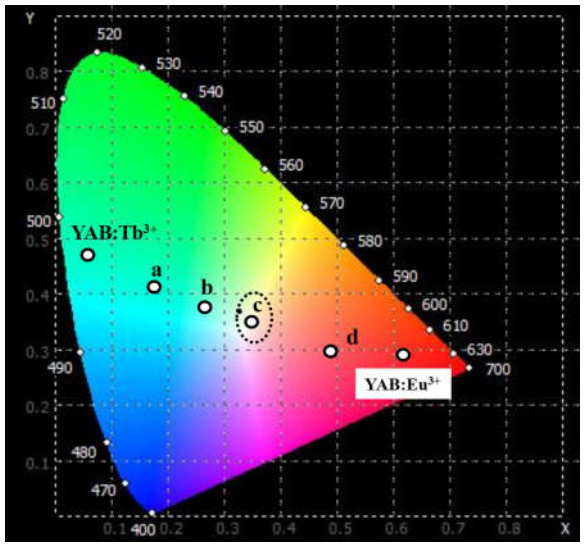

Figure 4. CIE Chromatic coordinates diagram of YAB:Tb^{3+}, YAB:Eu^{3+} and YAB:0.02Tb^{3+},xEu^{3+} where x = 0.01 (a), 0.02 (b), 0.03 (c) and 0.04 (d).

b) Luminescence of Tb^{3+} and Eu^{3+} co-doped YAB polycrystalline

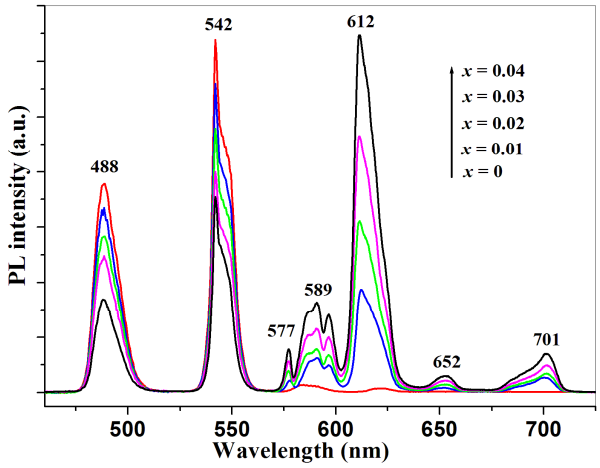

Figure 5. Emission spectra of YAB:0.02Tb^{3+},xEu^{3+} polycrystalline

The PL spectra of the YAB polycrystalline co-doped with 2.0 mol% Tb^{3+} and x mol % Eu^{3+} ions (x = 1.0, 2.0, 3.0, and 4.0) are shown in figure 5. These spectra consist of seven PL

bands centered at the wavelengths of 488, 542, 577, 589, 612, 652 and 701 nm. Two former bands are characteristic emissions of Tb^{3+} ion which correspond to the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions, respectively. The bands at 577, 652, and 701 nm are yielded by the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transitions in $4f^6$ configuration of the Eu^{3+} ion, respectively. Two emission bands centered at around 589 and 612 nm have the overlap between luminescence bands of Tb^{3+} and Eu^{3+}ions in which the band at 589 nm is overlap of $^5D_0 \rightarrow {}^7F_1$ (Eu^{3+}) with $^5D_4 \rightarrow {}^7F_4$ (Tb^{3+}) and the band at 612 nm is overlap $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}) with $^5D_4 \rightarrow {}^7F_3$ (Tb^{3+}).

Table 1. The color coordination (x, y), correlated color temperature (CCT, K), lifetime of the Tb^{3+}:$^5D_4$ level (τ_{exp}, ms), energy transfer rate (W_{ET}, s^{-1}) and efficiency (η_{ET}, %) for YAB:Tb^{3+},Eu^{3+}

Samples	x	y	CCT	τ_{exp}	W_{ET}	η_{ET}
YAB:0.02Eu^{3+}	0.612	0.291	3877	-	-	-
YAB:0.02Tb^{3+}	0.056	0.482	15310	3.35	-	-
YAB:0.02Tb^{3+},0.01Eu^{3+}	0.182	0.406	11953	2.75	64.24	17.69
YAB:0.02Tb^{3+},0.02Eu^{3+}	0.267	0.372	8354	2.32	131.79	30.60
YAB:0.02Tb^{3+},0.03Eu^{3+}	0.343	0.347	5070	2.09	198.23	37.36
YAB:0.02Tb^{3+},0.04Eu^{3+}	0.492	0.295	2692	1.79	259.79	46.50

The CIE chromatic coordinates diagram of the YAB:Tb^{3+},Eu^{3+} polycrystalline are illustrated in figure 4 (dots of a, b, c, d) and the color coordination (x, y) is displayed in Table 1. It can be seen that the color tone of the phosphor shifts toward the white light region with the increase of Eu^{3+} concentration. With the Eu^{3+} concentrations of 3.0 %, the color tone of the material is near the center of the white light region in the CIE diagram. It is noted that the human eye perceives the best with warm light sources having temperatures in the range from 5000 to 6500 K (Ye, 2010: Do, 2019). For the phosphor materials, their luminescence nature is usually evaluated based on the correlated color temperature (CCT) which is computed by using the following equation (Do, 2019):

$$CCT = -449n^3 + 3525n^2 - 6823n + 5520.33 \quad (1)$$

where $n = (x - x_e)/(y - y_e)$ and ($x_e = 0.332$, $y_e = 0.186$). Using the color coordination and the above equation, the CCT of YAB:Tb^{3+},Eu^{3+} samples were calculated and presented in Table 1. The calculated data indicates that the CCT of the YAB:Tb^{3+} is in the cold light region (high CCT). However, by co-doing the Eu^{3+} with Tb^{3+} ion in YAB polycrystalline, the CCT is shifted toward warm light and with the concentration of 3.0 mol% Eu^{3+} ions, the CTT is in neutral white light according to human vision. The calculated results of the color coordination and CCT show that the YAB phosphor co-doped with Tb^{3+} and Eu^{3+} has a high ability for w-LED application.

3.3. Energy transfer from Tb^{3+} to Eu^{3+} in YAB:Tb^{3+},Eu^{3+} polycrystalline

As shown in figure 2, the PLE band at 485 nm is recorded in the PLE spectrum of Tb^{3+} ion (curve a) but it does not occur in the PLE spectrum of Eu^{3+} ion (curve b). However, this band is clearly observed in the PLE of Eu^{3+} ions in YAB phosphor co-doped with Tb^{3+} and Eu^{3+} ions. This result indicates that there is an energy transfer process from Tb^{3+} to Eu^{3+} happening in YAB:Tb^{3+},Eu^{3+} phosphor. In order to affirm this presumption, the luminescence spectra of YAB:Tb^{3+},Eu^{3+} samples have been measured under excitation by 378 nm wavelength (see figure 5). It can be seen that the PL intensity of Tb^{3+} decreases whereas the PL of Eu^{3+} increases with the increase in the concentration of Eu^{3+}

ions. This result is clear evidence demonstrating the energy transfer process from Tb^{3+} to Eu^{3+} ion. This process leads to the luminescence enhancement of Eu^{3+} ion but luminescence quenching of Tb^{3+} ion. In another word, in YAB:Tb^{3+},Eu^{3+}, the Tb^{3+} ion plays a role as a sensitization center for luminescence of Eu^{3+} ions upon certain excitation conditions, for example, violet light with the wavelength of 378 nm.

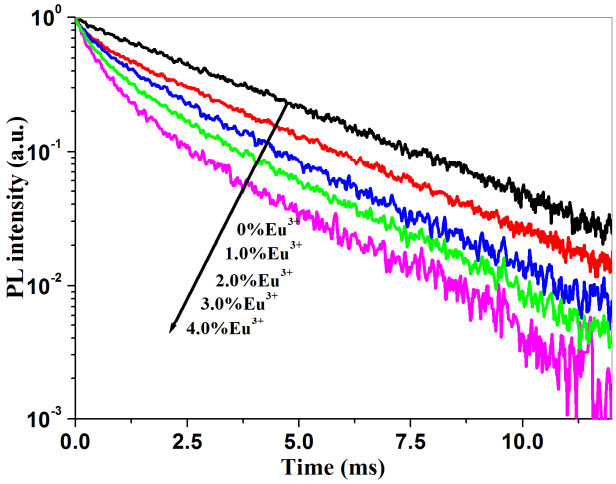

Figure 6. Decay curves of Tb^{3+}:$^5D_4$ level in YAB:0.01Tb^{3+},xEu^{3+} (x = 0.01, 0.02, 0.03 and 0.04).

The characteristic parameters of the energy transfer process from Tb^{3+} ion to Eu^{3+} in YAB:Tb^{3+},Eu^{3+} polycrystalline can be calculated based on the decay curve of the Tb^{3+}:$^5D_4$ level. These curves were measured by monitoring the luminescence signal at 542 nm under excitation at the wavelength of 378 nm. The obtained results of the decay curve are presented in figure 6. The experimental lifetime (τ_{exp}) of the Tb^{3+}:$^5D_4$ level was calculated by using the following formula (Do, 2019):

$$\tau_{exp} = \frac{\int tI(t)dt}{\int I(t)dt} \qquad (2)$$

The lifetime of the $^5D_4$ level was found to be 3.35, 2.75, 2.32, 2.09 and 1.79 ms for the Eu^{3+} concentrations of 0, 1.0, 2.0, 3.0 and 4.0 mol%, respectively. The lifetime decreases with the increase of Eu^{3+} concentrations in YAB:Tb^{3+},Eu^{3+} polycrystalline. For the YAB singly doped with Tb^{3+} ion, the obtained lifetime is the intrinsic lifetime of the $^5D_4$ level when the energy transfer can be ignored. Nevertheless, by co-doping the Tb^{3+} and Eu^{3+} ions in material, the lifetime of the $^5D_4$ level decreases. The decrease in lifetime results from the energy transfer from Tb^{3+} to the Eu^{3+} ions. The rate (W_{ET}) and efficiency (η_{ET}) of this energy transfer process are given by the following expressions (Do, 2019):

$$W_{ET} = \frac{1}{\tau(Tb,Eu)} - \frac{1}{\tau(Eu)} \qquad (3)$$

$$\eta_{ET} = 1 - \frac{\tau(Tb,Eu)}{\tau(Tb)} \qquad (4)$$

where τ(Tb,Eu) and τ(Tb) symbols are the lifetime of the Tb^{3+}:$^5D_4$ level in the absence and presence of Eu^{3+} ions in YAB polycrystalline, respectively. The values of W_{ET} and η_{ET} were calculated and displayed in Table 1. The obtained data shows that the energy transfer rate and efficiency increase with the increase of the Eu^{3+} ion concentration in the material. It is reported that the rate and efficiency of energy transfer from a donor to an acceptor depend strongly on the distance between these centers (Dierkes, 2015). For the increase of Eu^{3+} concentration in YAB:Tb^{3+},Eu^{3+}, the average separation Tb^{3+}-Eu^{3+} reduces. This causes an increase in interaction between the Tb^{3+} and Eu^{3+} ions. This is the main reason leading to the increase in the rate and efficiency of the energy transfer process from Tb^{3+} to Eu^{3+}.

4. Conclusion

$Y_3Al_3B_2O_{12}$ polycrystalline singly doped with Tb^{3+} or Eu^{3+} as well as co-doped with Tb^{3+} and Eu^{3+} were synthesized successfully by the solid-state interaction method. The investigation on structure indicates that the prepared material is crystallized singly phase in the cubic system.

Red emission of YAB:Eu^{3+} phosphor is easily obtained under excitation by the light in the UV-Vis region. The optimal concentration for luminescence of YAB:Eu^{3+} phosphor is around 4.0 mol% Eu^{3+} ion. The CIE coordinates and CCTs indicate that the luminescence of the YAB:0.01Tb^{3+},$x$$Eu^{3+}$ phosphor is in the neutral white light region when x = 3.0 mol%. This suggests that YAB:Tb^{3+},Eu^{3+} phosphor can be applied for w-LED. For YAB:Tb^{3+},Eu^{3+}, the Tb^{3+} ions play a role as the sensitizer centers for the luminescence of Eu^{3+} ions through the energy transfer. The rate and efficiency of the energy transfer process from Tb^{3+} to Eu^{3+} increase with the increase of Eu^{3+} concentration co-doping in YAB:Tb^{3+},Eu^{3+} phosphor.

Acknowledgments

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