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Tunable emission from green to red in the GdSr₂AlO₅:Tb³⁺,Eu³⁺ phosphor *via* efficient energy transfer

Herein, a series of $GdSr_2AlO_5:Tb^{3+}$, Eu^{3+} phosphors were successfully synthesized through a high temperature solid-state reaction, and their crystal structures as well as photoluminescence properties were investigated in detail. Compared to the intense emission of ${}^5D_0 \rightarrow {}^7F_1$ or ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} , another strong emission corresponding to ${}^5D_0 \rightarrow {}^7F_4$ was observed. Concentration quenching is not obvious in Tb^{3+} or Eu^{3+} -doped $GdSr_2AlO_5$ because structure isolation and energy transfer (ET) of $Gd^{3+} \rightarrow Eu^{3+}$ and $Gd^{3+} \rightarrow Tb^{3+}$ were found. Moreover, the energy transfer process from Tb^{3+} to Eu^{3+} was verified by the overlap of luminescence spectra and the variation of lifetime. Energy transfer mechanism was determined to be a dipole–dipole interaction, and ET efficiency as well as quantum efficiency were also obtained. Moreover, the emission color of $GdSr_2AlO_5:Tb^{3+}$, Eu^{3+} can be tuned from green to red by altering the ratio of Tb^{3+}/Eu^{3+} . These results indicate that the $GdSr_2AlO_5:Tb^{3+}$, Eu^{3+} phosphor is a promising single-component white light-emitting phosphor.

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Introduction

White light-emitting diodes (w-LEDs) with superior advantages, such as high energy efficiency, good physical and chemical stability, long lifetime, and environment friendliness, have been drawing attention and are regarded as the next generation of illumination sources. 1-4 The most available material for light devices involves Ce³⁺-doped yttrium aluminum garnet (YAG:Ce³⁺) with blue-LED chips, which has been commercialized.5,6 Because of the scarcity of red component, it encounters a low color rendering index ($R_a < 80$) and a high color temperature (CCT > 7000 K).7,8 To overcome these drawbacks, the combination of a UV LED chip with red (Ca₄(PO₄)O:Eu²⁺), green $(Na_2Y_2B_2O_7:Ce^{3+},Tb^{3+})$, 10 and blue $(Na_rCa_{1-r}Al_{2-r}Si_{2+r}O_8:Eu^{2+})$ 11 to achieve white-light with high Ra and appropriate CCT is another approach. However, the mixture of different phosphors brings about an inevitable problem of fluorescence reabsorption, resulting in the loss of luminous efficiency. 12,13 Therefore, it is obligatory to develop a single-phase white lightemitting phosphor.

Rare earth ion-doped aluminate phosphors, such as LaSr₂-AlO₅:Ce³⁺/Eu²⁺, ^{14,15} (La,Gd)Sr₂AlO₅:Ce, ¹⁶ and (La,Gd)Sr₂(Al,B) O₅:Ce, ¹⁷ have been studied extensively due to their cheap raw materials and good chemical and physical stability. The structural properties of this aluminate-based phosphor and the

However, the luminescence of Ce³⁺ and Eu²⁺ belong to the f-d transition.¹⁸ Upon reviewing the literature, it is observed that it is difficult to find other rare-earth ions with f-f transition for doping into the GdSr₂AlO₅ phosphor. As is well known, codoping of different rare ions as a sensitizer and activator plays a significant role in obtaining emission *via* energy transfer processes.¹⁹

effect on the luminescence properties have been investigated.

Tb³⁺ and Eu³⁺ with characteristic green^{20,21} and red^{22,23} emissions are widely used in luminescent materials, respectively. Compared to most Eu³⁺-doped phosphors with the dominant emission corresponding to ${}^5D_0 \rightarrow {}^7F_1$ or ${}^5D_0 \rightarrow {}^7F_2$, the Eu³⁺-doped GdSr₂AlO₅ phosphor shows an intensive emission related to ${}^5D_0 \rightarrow {}^7F_4$. It is clear that Tb³⁺ functions as a good sensitizer to improve the luminescence efficiency of Eu³⁺ ions in Sr₂MgSi₂O₇,²⁴ Na₃La(PO₄)₂,²⁵ CaYAlO₄,²⁶ and Y₂O₃ (ref. 27) phosphors. In this study, a single-phased GdSr₂AlO₅:-Tb³⁺,Eu³⁺ phosphor was synthesized by a conventional solid-state method. The efficient energy transfer from Tb³⁺ to Eu³⁺ was systematically investigated with steady state fluorescence, lifetime measurement, and the energy transfer efficiency. Moreover, the color of the total emission can be tuned by altering the ratio of Tb³⁺/Eu³⁺ in the GdSr₂AlO₅ host.

2. Experimental method

A series of phosphors with the composition of GdSr₂AlO₅:Tb³⁺, GdSr₂AlO₅:Eu³⁺, and GdSr₂AlO₅:Tb³⁺,Eu³⁺ were prepared by a conventional high temperature solid-state method under

Guangdong Provincial Engineering Technology Research Center for Optical Agricultural, College of Materials and Energy, South China Agriculture University, Guangzhou 510642, P. R. China. E-mail: tleibf@scau.edu.cn

a reductive atmosphere (5% $\rm H_2$ + 95% $\rm N_2$) at 1500 °C. SrCO $_3$ (A. R.), Al $_2$ O $_3$ (A. R.), Gd $_2$ O $_3$ (A. R.), Tb $_4$ O $_7$ (99.99%), and Eu $_2$ O $_3$ (99.99%) were used as raw materials. They were stoichiometrically weighed and mixed by grinding in an agate mortar for 30 min. After this, they were transferred into ceramic crucibles and calcined in a high-temperature tubular furnace at 1500 °C for 4 h at a heating rate of 3 °C min $^{-1}$. Finally, the samples were cooled down to room temperature in the furnace and ground into powders for subsequent use.

Bruker D8 (voltage 40 kV and current 40 mA) over the 2θ range from 10° to 70° with $\text{CuK}\alpha$ radiation ($\lambda=1.54178~\text{Å}$) was used to obtain the XRD patterns of $\text{GdSr}_2\text{AlO}_5\text{:Tb}^{3+},\text{Eu}^{3+}$ samples. Hitachi F-7000 spectrophotometers with a 150 W xenon lamp light source were used to obtain the excitation and emission spectra. The morphology of the prepared phosphor was examined by a field-emission scanning electron microscope (Hitachi S-4800). The decay curves were obtained using the Hamamatsu Quantaurus-Tau C11367 fluorescence spectrophotometer. The chromaticity data were calculated by the CIE1931 software. Photoluminescence absolute quantum efficiency (QE) was determined νia Hamamatsu Quantaurus-QY C11347 using an integrated sphere. All the measurements were conducted at room temperature.

3. Results and discussion

3.1 XRD analysis

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Fig. 1(a) shows the XRD patterns of the as-prepared $GdSr_2AlO_5$ host and Tb^{3+} , Eu^{3+} -doped phosphor as well as the standard patterns of $EuSr_2AlO_5$ (JCPDS 70-2197). The patterns agreed with the crystallographic structure of the JCPDS card 70-2197, and impurity peaks were not found. This result illustrates that the obtained samples are in single phase, and doping of Tb^{3+} and/or Eu^{3+} ions at low concentrations does not change the crystal structure. In addition, it can be observed from Fig. 1(b) that the diffraction peak positions of the samples are shifted slightly to a higher angle as compared to those of the standard patterns of $EuSr_2AlO_5$ (JCPDS 70-2197); this can be due to the replacement of large-size Eu^{3+} sites by the smaller-size trivalent ions. Hence, RE^{3+} ions were effectively doped into the lattice; this could be confirmed by the slight change in the diffraction peaks.

Fig. 1(c) displays a partial structure of GdSr₂AlO₅. As reported previously, the crystal structure of GdSr₂AlO₅ is isostructural with the standard file of EuSr₂AlO₅ (JCPDS no. 70-2197, tetragonal, space group *I4/mcm*).²⁸ Gd atoms will occupy the half 8h sites, and the other half is occupied by the Sr atoms. The cell also contains 4a sites, which are fully occupied by the Sr atoms, and the Al atoms will occupy the 4b sites. The 4c sites and 16l sites are occupied by O, denoted as O₁ and O₂, respectively. The GdO₈ polyhedron consists of two O₁ atoms and six O₂ atoms, where the latter are shared by four AlO₄ tetrahedral on the adjacent layers, forming an isolated structure. Fortunately, isolation in space weakens the interaction between the paired ions. To some extent, the concentrating quenching effect would be avoided.²⁹

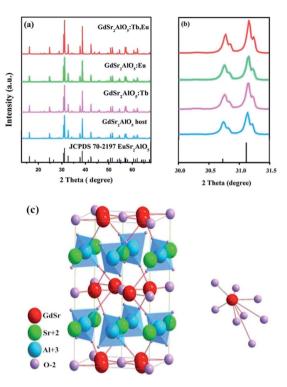


Fig. 1 (a) Representative XRD patterns of the samples. (b) Magnified XRD patterns between 30° and 31.5° . (c) Crystal structure of the $GdSr_2AlO_5$ and the coordination environment of GdO_8 .

3.2 SEM with energy dispersive X-ray analysis

Fig. 2(a) displays the morphology of the $GdSr_2AlO_5$: Tb^{3+} , Eu^{3+} sample. The surface image shows irregular particles with a size range of 5–10 μ m. Moreover, as shown in Fig. 2(b), EDS is used to analyze the chemical composition of the $GdSr_2AlO_5$: Tb^{3+} , Eu^{3+} phosphor, and the result confirms the presence of Gd, Sr, Al, O, Tb, and Eu elements in the phosphor. Compared with the abovementioned XRD results, the EDS results demonstrate that Tb/Eu ions have been successfully incorporated into the $GdSr_2AlO_5$ lattice.

3.3 Luminescence properties

The excitation spectrum of $GdSr_2AlO_5$:2% Tb^{3+} is shown in Fig. 3(a). The excitation spectrum monitored at 548 nm exhibits a broad band and several weak peaks. The broad band from

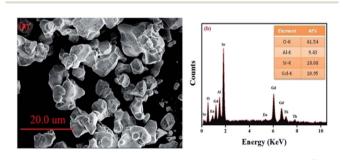


Fig. 2 SEM image (a) and EDS spectrum (b) of $GdSr_2AlO_5$:2%Tb³⁺,2% Eu^{3+} .

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200 nm to 250 nm centered at 220 nm is ascribed to the fd transitions of the Tb³⁺ ions, whereas the excitation peaks at 275 and 310 nm originate from the transitions of ${}^8S_{7/2} \rightarrow {}^6I_{7/2}$ and ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ of the Gd³⁺ ions, respectively.^{30,31} The appearance of strong excitation sharp bands of Gd³⁺ ions confirms that there is an efficient energy transfer from Gd³⁺ to Tb³⁺. The emission spectra of the phosphor under 220, 275, and 310 nm excitation in the wavelength range from 400-650 nm are also depicted in Fig. 3(a). There are two groups of lines in the emission spectrum: one group in the region from 400 to 480 nm is derived from the ${}^5D_3 \rightarrow {}^7F_I (J = 5, 4, \text{ and } 3)$ transitions of Tb³⁺. The second groups of lines in the wavelength range from 480 to 650 nm originate from the ${}^5D_4 \rightarrow {}^7F_I (J=6, 5, 4, \text{ and } 3)$ transitions. Among these emissions, the ${}^5D_4 \rightarrow {}^7F_5$ transition with a maximum at about 548 nm exhibits the strongest emission intensity. The emission intensity increases with the increasing concentration of Tb3+, as presented in Fig. 3(b). Concentration quenching does not occur in GdSr₂AlO₅:Tb³⁺.

Fig. 3(c) and (d) present the excitation and emission spectra as well as concentration-dependent luminescence intensity of GdSr₂AlO₅:yEu³⁺. The excitation spectrum of the Eu³⁺-activated sample monitoring the emission wavelength at 705 nm contains a broad band in the wavelength range from 220 to 350 nm, corresponding to the charge transfer transition of Eu³⁺ $(O^{2-} \rightarrow Eu^{3+})$ and several characteristic narrow peaks at 383 nm and 393 nm. They are attributed to ${}^7F_0 \rightarrow {}^5G_2$ and ${}^7F_0 \rightarrow {}^5L_6$ electronic transitions of the Eu3+ ions. In this band, there should be absorption of transitions from ${}^8S_{7/2}$ to ${}^6I_{7/2}$ level of Gd³⁺, which is too weak and is overlapped with the strong CTB of the $O^{2-} \rightarrow Eu^{3+}$. 32,33 The emission spectrum consists of multiple band emissions at 587, 607, 622, 657, and 705 nm, which are assigned to the ${}^5D_0 \rightarrow {}^7F_I (J = 0, 1, 2, 3, \text{ and } 4)$ transitions of Eu³⁺ ions,³⁴ respectively. Among these emission peaks, the two most intense lines are the emissions located at

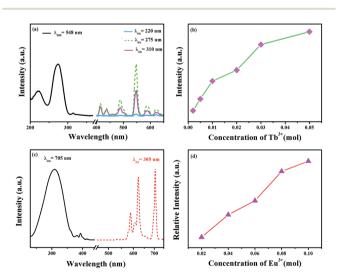


Fig. 3 (a) Excitation and emission spectra of the GdSr₂AlO₅:2%Tb³⁺ phosphor. (b) Concentration-dependent luminescence intensity of GdSr₂AlO₅:xTb³⁺. (c) Excitation and emission spectra of the GdSr₂-AlO₅:2%Eu³⁺ phosphor and (d) concentration-dependent luminescence intensity of GdSr₂AlO₅:yEu³⁺

622 and 705 nm. Obviously, the magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$ is stronger than the $^5D_0 \rightarrow {}^7F_2$ electronic transition; this indicates that Eu³⁺ ions in the GdSr₂AlO₅ host occupy a site with a non-inversion symmetry; this is consistent with its structure. Compared to other Eu³⁺ phosphors, GdSr₂AlO₅:Eu³⁺ provides more red components to improve R_a . Similarly, there is no evident concentration quenching with the change in the Eu³⁺ concentration.

The foundation of energy transfer is the spectral overlapping Tb³⁺ emission and the Eu³⁺ excitation. As is clearly shown in Fig. 4, there are some overlaps between the emission of ${}^5D_3 \rightarrow$ $^{7}\text{F}_{6}$ (Tb³⁺) and the excitation of $^{7}\text{F}_{0} \rightarrow {}^{5}\text{G}_{2,3,4,5}$, $^{5}\text{L}_{8}$ (Eu³⁺). Moreover, the excitation of ${}^{7}F_{0} \rightarrow {}^{5}D_{3}$, ${}^{5}L_{6}$ (Eu³⁺) overlaps with the emission of ${}^5\mathrm{D}_3 \to {}^7\mathrm{F}_5$ (Tb³⁺). 35

To further investigate the energy transfer process, a series of samples of $GdSr_2AlO_5:2\%Tb^{3+},x\%Eu^{3+}$ (x = 0, 0.5, 1, 2, 3, and 5) were prepared whose emission spectra under the excitation at 275 nm are presented in Fig. 5(a). The characteristic sharp emission peaks of Tb³⁺ and Eu³⁺ are observed. The tendency in the variation of Tb³⁺ and Eu³⁺ differs significantly. The emission intensity of Tb3+ at 548 nm decreases remarkably with an increase in the concentration of Eu3+, whereas the emission intensity of Eu³⁺ increases monotonously. Fig. 5(b) depicts the contribution of different ions in the corresponding emission spectra. The G/R (green to red) ratio continuously decreases notably. Based on the prerequisite of the concentration of Tb³⁺ being a constant value, explanation for this phenomenon should be the evidence of energy transfer from Tb³⁺ to Eu³⁺.

In spite of steady-state spectra, kinetic spectra are necessary to better analyze the energy transfer mechanism of $Tb^{3+} \rightarrow Eu^{3+}$ in GdSr₂AlO₅. Fig. 6(a) shows the fluorescence decay curves of Tb³⁺ emissions, which are obtained under 275 nm excitation and detected at 548 nm. The luminescence curves can be fitted well with the double-exponential expression:36,37

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$
 (1)

where I and I_0 represent the luminescence intensity at time t and 0, A_1 and A_2 are equal to constants, t is the time, and τ_1 and τ_2 are the rapid and slow lifetimes for exponential components, respectively. As a function of these parameters, the average luminescence lifetime (τ) was determined by the following equation:

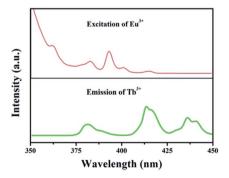


Fig. 4 Spectral overlapping of the PL spectrum of GdSr₂AlO₅:Tb³⁺ and the PLE spectrum of GdSr₂AlO₅:Eu³⁺.

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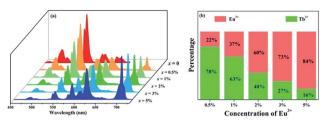


Fig. 5 (a) Emission spectra of $GdSr_2AlO_5$:2%Tb³⁺,x%Eu³⁺ (x = 0, 0.5, 1, 2, 3, and 5) under 275 nm excitation. (b) Variation tendency of the green emission of Tb³⁺ and the red emission of Eu³⁺.

$$\tau = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2) \tag{2}$$

The values of τ are calculated to decrease when the Eu³⁺ concentration increases; this indicates that energy transfer occurs from Tb³⁺ to Eu³⁺, as expected. Furthermore, the energy transfer efficiency is calculated by the expression as follows:³⁸

$$\eta_{\rm T} = 1 - I_{\rm s}/I_{\rm so} \tag{3}$$

where η_T represents the energy transfer efficiency, and I_s and I_s represent the luminescence intensity of Tb^{3+} in the presence and absence of Eu^{3+} , respectively. The results of η_T are shown in Fig. 6(b). It can be found that the efficiencies from Tb^{3+} to Eu^{3+} increase with the increasing Eu^{3+} concentration, which can reach the maximum value of 83%. Therefore, the energy transfer from Tb^{3+} to Eu^{3+} ions is efficient to improve Eu^{3+} luminescence.

3.4 Energy transfer mechanism

The type of energy transfer should depend on either the exchange interaction or the multipolar interaction. It relies on the critical distance between the Tb³⁺ (sensitizer) and Eu³⁺ (activator), and the critical distance is expressed by the following formula:³⁹

$$R_{\text{Tb-Eu}} = 2 \left[\frac{3V}{4\pi x_{\text{c}} N} \right]^{1/3}$$
 (4)

where *V* represents the cell volume, *N* is equal to the number of cations in the unit cell, and x_c is the total concentration of Tb³⁺ and Eu³⁺. In this case, N = 4 and V = 498.64 Å³. The

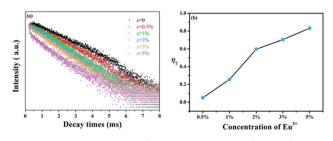


Fig. 6 (a) Decay curves of Tb³⁺ in GdSr₂AlO₅:2%Tb³⁺,x%Eu³⁺ (x = 0, 0.5, 1, 2, 3, and 5). (b) Energy transfer efficiencies ($\eta_{\rm T}$) in GdSr₂AlO₅:2% Tb³⁺,x%Eu³⁺ as a function of different Eu³⁺ concentrations.

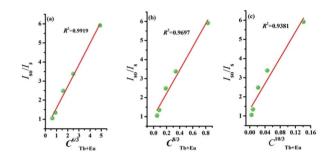


Fig. 7 Dependence of I_{so}/I_s of Tb³⁺ on (a) $C^{6/3}$, (b) $C^{8/3}$, and (c) $C^{10/3}$.

corresponding distance is calculated to be more than 5 Å, indicating that ${\rm Tb}^{3+} \to {\rm Eu}^{3+}$ energy transfer would tend to be a multipolar interaction. On account of energy transfer mechanism for multipolar interaction, the following expression can be given:^{40,41}

$$I_{so}/I_s \propto C^{n/3} \tag{5}$$

where $I_{\rm so}$ and $I_{\rm s}$ are the luminescence intensity of the sensitizer without and with activator. C represents the doping concentration of ${\rm Tb}^{3+}$ and ${\rm Eu}^{3+}$ ion. The values for n=6, 8, and 10 correspond to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions. Results are illustrated in Fig. 7. The best linear fit was obtained when n=6, which confirmed energy transfer through dipole–dipole mechanism.

The detailed $Gd^{3^+} \to Tb^{3^+}$, $Gd^{3^+} \to Eu^{3^+}$, and $Tb^{3^+} \to Eu^{3^+}$ energy transfer processes are shown in Fig. 8. The electrons were excited from the $^8S_{7/2}$ ground state to the 6I_J excited state of Gd^{3^+} under 275 nm excitation. Because the energy levels 5D_3 of Tb^{3^+} and 5D_1 state of Eu^{3^+} are lower than the 6I_J state of Gd^{3^+} in the diagram, the energy transfer processes from $Gd^{3^+} \to Tb^{3^+}$ and $Gd^{3^+} \to Eu^{3^+}$ occur simultaneously. In addition, the electrons absorbing energy were excited from the 7F_6 ground state to the 5D_3 excited state of Tb^{3^+} . The energy transfer process occurs between Tb^{3^+} and Eu^{3^+} activators since the 5D_3 state of Tb^{3^+} lies higher than the 5D_1 state of Eu^{3^+} . Then, the electrons from the excited state of 5D_3 (Tb^{3^+}) and 5D_1 (Eu^{3^+}) relaxed to 5D_4 and 5D_0 , respectively. Finally, green to red emission is yielded by electrons returning to their respective ground states.

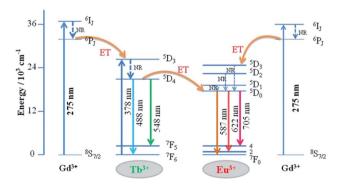


Fig. 8 Schematic of energy transfer from Tb³⁺ to Eu³⁺ in GdSr₂AlO₅.

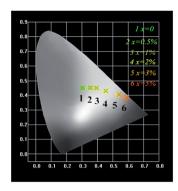


Fig. 9 CIE chromaticity diagram for $GdSr_2AlO_5$:2% Tb^{3+} ,x% Eu^{3+} (x = 0, 0.5, 1, 2, 3, and 5) samples.

3.5 CIE chromaticity coordinate and QE

The Commission Internationale de L'Eclairage (CIE 1931) chromaticity coordinates of $GdSr_2AlO_5$:2%Tb³⁺,x%Eu³⁺ phosphors under the excitation at 275 nm are presented in Fig. 9. The CIE coordinates shifted from (0.320, 0.466) to (0.574, 0.403) for the samples x = 0 to x = 5% correspond to green, yellow-green, and red. It is clear that the coordinate Y changes linearly with the X, the expression of which can be shown as below:

$$Y = 0.7541 - 0.6109X \tag{6}$$

The equation proves that the range of chromaticity coordinates can be obtained by adjusting the ratio of Tb^{3+} and Eu^{3+} mathematically. The as-prepared phosphor emits bright tunable visible light, implying its potential application in multicolor displays, and meets the requirement for application in n-UV LEDs.

For photo-luminescence application, the importance of quantum efficiency (QE) should be considered. According to the method described by De Mello *et al.*, QE can be calculated by the following equation:⁴²

$$\eta_{\rm QE} = \frac{\int L_{\rm S}}{\int E_{\rm R} - \int E_{\rm S}}$$
 (7)

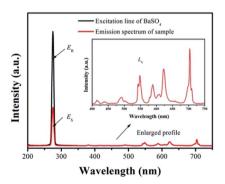


Fig. 10 Excitation line of $BaSO_4$ and emission spectrum of the sample. Inset shows the magnification of the emission spectrum.

where $L_{\rm S}$ is the emission of the sample, $E_{\rm S}$ equals to the spectrum of the sample excited by the light, and $E_{\rm R}$ represents the spectrum of the excitation light without the sample. The results are listed in Fig. 10. Under 275 nm sexcitation, the calculated QE of GdSr₂AlO₅:2%Tb³⁺,2%Eu³⁺ is 78.5%, which demonstrates a high QE.

4. Conclusions

The GdSr₂AlO₅:Tb³⁺,Eu³⁺ phosphors were prepared by a high temperature solid-state reaction method, and their luminescence properties were investigated in detail. Due to REO₈ structure isolation, damping of the concentration quenching would occur. Energy transfer from $Gd^{3+} \rightarrow Eu^{3+}$ and $Gd^{3+} \rightarrow Tb^{3+}$ was found in the excitation spectrum. Moreover, the luminescence properties and the transient spectra confirmed the efficiency energy transfer from Tb^{3+} to Eu^{3+} . The mechanism it demonstrated is dipole–dipole interaction. $GdSr_2AlO_5$:- Tb^{3+} , Eu^{3+} phosphors were able to provide multi-color emission from green, yellow, orange, and finally to deep red by the different ratios of Tb^{3+}/Eu^{3+} . Additionally, the QE can reach about 78.5%. All the results indicate that the series of $GdSr_2-AlO_5$: Tb^{3+} , Eu^{3+} phosphors can be a candidate for color tunable luminescence materials used for n-UV LEDs.

Conflicts of interest

There are no conflicts to declare.

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