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Roles of doping ions in persistent luminescence of $SrAl_2O_4$:Eu^{2+}, RE^{3+} phosphors

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Abstract The polycrystalline Eu^{2+} and RE^{3+} co-doped strontium aluminates $SrAl_2O_4$:Eu^{2+}, RE^{3+} were prepared by solid state reactions. The UV-excited photoluminescence, persistent luminescence and thermo-luminescence of the $SrAl_2O_4$:Eu^{2+}, RE^{3+} phosphors with different composition and doping ions were studied and compared. The results showed that the doped Eu^{2+} ion in $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors works as not only the UV-excited luminescent center but also the persistent luminescent center. The doped Dy^{3+} ion can hardly yield any luminescence under UV-excitation, but can form a electron trap with appropriate depth and greatly enhance the persistent luminescence and thermo-luminescence of $SrAl_2O_4$:Eu^{2+}. Different co-doping RE^{3+} ions showed different effects on persistent luminescence. Only the RE^{3+} ion (e.g. Dy^{3+}, Nd^{3+}), which has a suitable optical electro-negativity, can form the appropriate electron trap and greatly improve the persistent luminescence of $SrAl_2O_4$:Eu^{2+}. Based on above observations, a persistent luminescence mechanism, electron transfer model, was proposed and illustrated.

Introduction

Eu^{2+}, RE^{3+} (RE: rare earth ions) co-doped alkaline earth aluminates xMO.$y$$Al_2O_3$: Eu^{2+}, RE^{3+} (M:Ca, Sr, Ba; RE: Nd, Dy rare earth ions) are functional inorganic materials with strong luminescence at the blue/green regions [1, 2]. They show high quantum efficiency, long afterglow lifetime, and good chemical stability, making them be potential persistent luminescence materials to replace the traditional ZnS-based phosphors. The effective mechanism of the persistent luminescence is not known, but it is supposed to involve the formation of both electron and hole trapping and the subsequent slow thermal bleaching of the traps followed by emission from Eu^{2+} ions [3–11]. The rather schematic mechanisms presented involved either a direct or a valence band assisted transfer of a hole from Eu^{2+} to a trap, and its eventual recombination with the emitting Eu^{2+} center after thermal excitation [3, 4]. However, these mechanisms involved the creation of Eu^{+} and RE^{4+} ions, which are highly dubious processes in solid state.

In the present work, a systematic investigation was carried out on the Eu^{2+} doped $SrAl_2O_4$ phosphors. Especially the roles of Dy^{3+} in persistent luminescence were clearly described. The possible mechanisms were presented and discussed.

Experimental

The polycrystalline Eu^{2+}, RE^{3+} co-doped strontium aluminates, $Sr_{1-x-y}Al_2O_4$:$Eu^{2+}{}_x$, $RE^{3+}{}_y$, were prepared by a high temperature solid-state reaction between stoichiometric mixtures consisting of $SrCO_3$ (AR), Al_2O_3 (AR), Eu_2O_3 (99.99%) and RE_2O_3 (99.99%), with H_3BO_3 (2 mol%) as a flux in a reducing atmosphere (5% H_2 + 95% N_2) at 1300 °C for 4 h. Prior to heating, the reagents were ground using a ball mill to form a homogeneous mixture. The phase and structural purity of all samples was checked by X-ray powder diffraction, but no additional phase or impurity was observed as showed in authors' previous work [12].

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Emission spectra, excitation spectra, afterglow spectra and afterglow decay curve were measured at room temperature with a Hitachi F-2500 fluorescent spectrometer. Prior to afterglow spectra and afterglow decay measurements, samples were irradiated with UV (365 nm) for 30 min. The thermoluminescence (TL) spectra were measured with a thermo-luminescent Spectrograph (F-J427A1) in the temperature range between 25 °C and 250 °C at a uniform heating rate of 2 °C/s. Prior to TL measurement, samples were irradiated with UV (365 nm) for 30 min.

Results and discussion

Roles of Eu^{2+} in persistent luminescence

Under UV-excitation $SrAl_2O_4$:Eu^{2+} and $SrAl_2O_4$:Eu^{2+}, Dy^{3+} yielded green luminescence (λ_{max} = 520 nm) at room temperature. The band shape and width of the emission spectra for both samples were found identical (Fig. 1) indicating that there are same luminescent centers in both samples. Emission bands could be fitted to a single Gaussian profile indicating that emission is from one site only. The fact of no emission detected for $SrAl_2O_4$ and $SrAl_2O_4$:Dy^{3+} verified that the Eu^{2+} ion is the one and only luminescent center in $SrAl_2O_4$:Eu^{2+}, Dy^{3+} (Fig.1). It also can be found in Fig. 1 that the UV-excited luminescence and the persistent luminescence occurred at a practically identical spectral range. The band shape and width of the emission spectra and afterglow (AG) spectra for Sr Al_2O_4:Eu^{2+}, Dy^{3+} were found identical too indicating that the emitting center in both cases is still the Eu^{2+} ion. So, it can be concluded that the co-doped Dy^{3+} ions don't change the UV-excited luminescence center and the persistent luminescence center as well. Eu^{2+} ion is not only the UV-excited luminescent center but also the persistent luminescent center (i.e. the afterglow center).

Roles of Dy^{3+} in persistent luminescence

Figure 2 shows the excitation and emission spectra of different phosphor samples. The co-doping of Dy^{3+} ions ($Sr_{0.97}Al_2O_4$:$Eu_{0.01}$, $Dy_{0.02}$) and the little change of composition ($Sr_{0.97}Al_2O_4$:$Eu_{0.01}$) were not found to change the UV-excited and persistent luminescence band position and the shape of the spectra (Figs. 1 and 2). But there is some difference for the excitation spectra at 220–250 nm after co-doping Dy^{3+} ions. This is maybe due to the effect of the changed crystal field after co-doping Dy^{3+}ions. Figure 3 shows the afterglow decay curves of different samples. The persistent luminescence of $SrAl_2O_4$:Eu^{2+} has a little dependence on composition but a strong dependence on the co-doped Dy^{3+} ions. However, it is still difficult to clarify the roles of Dy^{3+} in persistent luminescence, because the doping of Dy^{3+} ions would result in the creation of different defects, which are possible to form different defect levels. In the synthesis of phosphors, the introduce of ions and the composition change will create different crystal defects [13–15]. When Eu^{2+} and Dy^{3+} ions are introduced in crystal matrix, they will take the places of Sr^{2+} ions rather than Al^{3+} ions at enough high temperature, because the radii of Eu^{2+} and Dy^{3+} are similar to that of Sr^{2+}, but much bigger than that of Al^{3+}. The doping reactions for Eu^{2+}, Dy^{3+} in $Sr_{1\text{-}x\text{-}y}Al_2O_4$:$Eu^{2}$ + $_{x}$,$Dy^{3+}{}_{y}$ (x and y are the doping amount of Eu^{2+} and Dy^{3+} ions respectively) showed as below

$$\begin{aligned} &x/2Eu_2O_3 + y/2Dy_2O_3 + Al_2O_3 + x/2H_2 \\ &\quad + (1-x-y)SrO \rightarrow x/2H_2O + Sr_{1-x-y}Eu_xDy_yAl_2O_4 \\ &\quad [Sr^{\times}_{Sr}]_{1-x-y}[Eu^{\times}_{Sr}]_x[Dy^{\cdot}_{Sr}]_y[Al^{\times}_{Al}]_2[O^{\times}_{O}]_4[V''_{Sr}]_{y/2} \end{aligned} \quad (1)$$

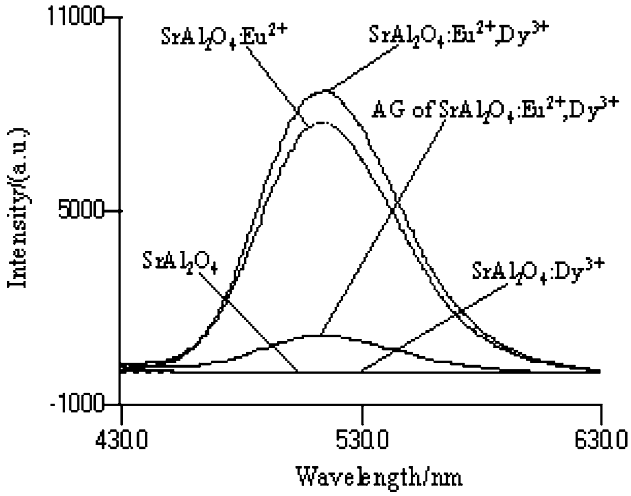

Fig. 1 Emission (UV-excited) and afterglow (AG) spectra

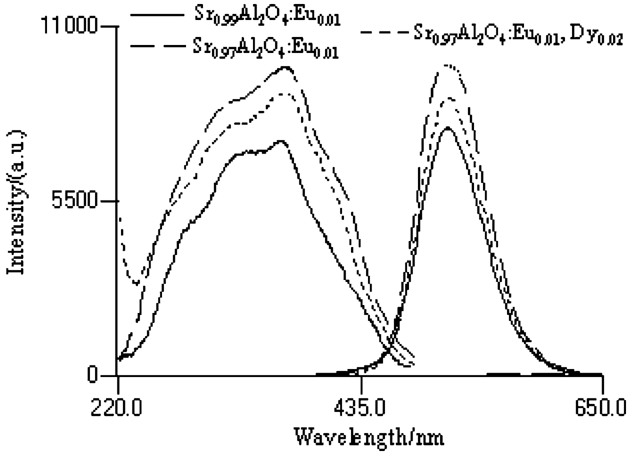

Fig. 2 Excitation and emission spectra of samples

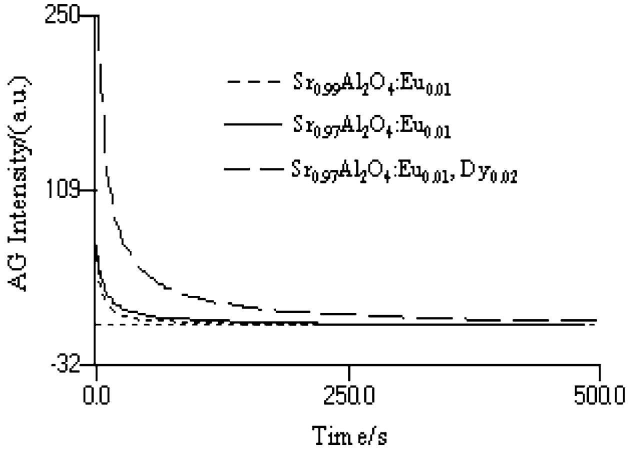

Fig. 3 Afterglow decay curves of different samples

The substitution between Eu^{2+} and Sr^{2+} is equivalent, from which a kind of point defect, $\mathrm{Eu}_{\mathrm{Sr}}^{\times}$, will be created. But the substitution between Dy^{3+} and Sr^{2+} is not equivalent, from which two kinds of point defects, $\mathrm{Dy}_{\mathrm{Sr}}^{\cdot}$ and vacancy of Sr^{2+} (V_{Sr}''), will be formed to keep charge balance.

Since there is always some difference between the radii of Eu^{2+}, Dy^{3+} and Sr^{2+}, so aberration of crystal matrix will exist to some extent after ions substitution. In fact, it is impossible for Eu^{2+}, Dy^{3+} to dope in crystal matrix completely according to stoichiometric ratio, so to some extent there actually exists the deficiency of SrO in the strictly quantified raw materials according to the stoichiometric ratio. Once SrO is deficient, the vacancies of Sr^{2+} and O^{2-} (V_{Sr}'' and $V\ddot{o}$) will be produced as below reaction (where x is the deficient amount of SrO):

$$(1-x)\mathrm{SrO} + \mathrm{Al_2O_3} \rightarrow \mathrm{Sr}_{1-x}\mathrm{Al_2O}_{4-x}[\mathrm{Sr}_{\mathrm{Sr}}^{\times}]_{1-x}[\mathrm{Al}_{\mathrm{Al}}^{\times}]_2 [\mathrm{O}_{\mathrm{O}}^{\times}]_{4-x}[V_{\mathrm{Sr}}'']_x[V\ddot{o}]_x \tag{2}$$

Thus, there always co-exist four main point defects $V\ddot{o}$, V_{Sr}'', $\mathrm{Eu}_{\mathrm{Sr}}^{\times}$ and $\mathrm{Dy}_{\mathrm{Sr}}^{\cdot}$ in $\mathrm{SrAl_2O_4{:}Eu^{2+}Dy^{3+}}$ crystal matrix. Since $\mathrm{Dy}_{\mathrm{Sr}}^{\cdot}$ has one positive charge, and $V\ddot{o}$ has two positive charges, it is possible for them to work as electron traps and capture free electrons. On the contrary, V_{Sr}'' has two negative charges and so can work as a hole trap and capture holes. Relative concentration of these point defects for different samples was listed in Table 1. Comparing with $\mathrm{Sr_{0.99}Al_2O_4{:}Eu_{0.01}}$, the co-doping of Dy^{3+} ions according to the stoichiometric ratio (in $\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01}}$, $\mathrm{Dy_{0.02}}$) would more or less increase the densities of $\mathrm{Eu}_{\mathrm{Sr}}^{\times}$, $V\ddot{o}$ and V_{Sr}''. The deficiency of Sr^{2+} ions (in $\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01}}$) would cause the obvious increase of $\mathrm{Eu}_{\mathrm{Sr}}^{\times}$, $V\ddot{o}$ and V_{Sr}''. But the afterglow decay property of $\mathrm{Sr_{0.95}Al_2O_4{:}Eu_{0.01}}$ is far worse than that of $\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01}}$, $\mathrm{Dy_{0.02}}$ (Fig. 3). So it can be concluded that it is the increase of Dy^{3+} ion ($\mathrm{Dy}_{\mathrm{Sr}}^{\cdot}$) rather than that of $V\ddot{o}$ and V_{Sr}'' that cause the big improvement of persistent luminescence. The existence of Dy^{3+} ($\mathrm{Dy}_{\mathrm{Sr}}^{\cdot}$) is a necessary condition for phosphor to show good persistent luminescence.

Table 1 Relative concentration of point defects in $\mathrm{SrAl_2O_4}$ crystal matrix (Normalized)

Item	$\mathrm{Eu}_{\mathrm{Sr}}^{\times}$	$\mathrm{Dy}_{\mathrm{Sr}}^{\cdot}$	V_{Sr}''	$V\ddot{o}$
$\mathrm{Sr_{0.99}Al_2O_4{:}Eu_{0.01}}$	100	100	100	100
$\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01}}$, $\mathrm{Dy_{0.02}}$	>100	0	>100	>100
$\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01}}$	>>100	0	>>100	>>100

Thermoluminescence spectra are an effective way to investigate the status of electron or hole traps in crystal matrix. The depth of each trap can be estimated from the thermal peak temperature by formula (1) [16–18]:

$$E = c_{\gamma}(kT_m^2/\gamma) - b_{\gamma}(2kT_m) \tag{1}$$

where T_m is the thermal peak temperature. k is the Boltzmann constant. γ is chosen as the full width (temperature) of the peak at its half-height ($\gamma = T_2 - T_1$; where T_2 and T_1 there the temperatures at half peak height). c_{γ} and b_{γ} are peak shape constants. It indicates from formula (1) that the higher peak temperature the deeper trap depth. Figure 4 shows the thermoluminescence spectra of $\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01},Dy_{0.02}}$, $\mathrm{Sr_{0.99}Al_2O_4{:}Eu_{0.01}}$ and $\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01}}$. Only one thermal peak appeared at about 51°C for $\mathrm{Sr_{0.99}Al_2O_4{:}Eu_{0.01}}$ and $\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01}}$. This means that the increase of $V\ddot{o}$ and V_{Sr}'' in the Sr-poor sample ($\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01}}$) doesn't create new thermal peaks and obvious increase of thermal peak temperature as well. But after Dy^{3+} co-doping ($\mathrm{Sr_{0.97}Al_2O_4{:}Eu_{0.01},Dy_{0.02}}$), a new thermal peak appeared at 70 °C, which is definitely corresponding to the electron trap of $\mathrm{Dy}_{\mathrm{Sr}}^{\cdot}$. The results of

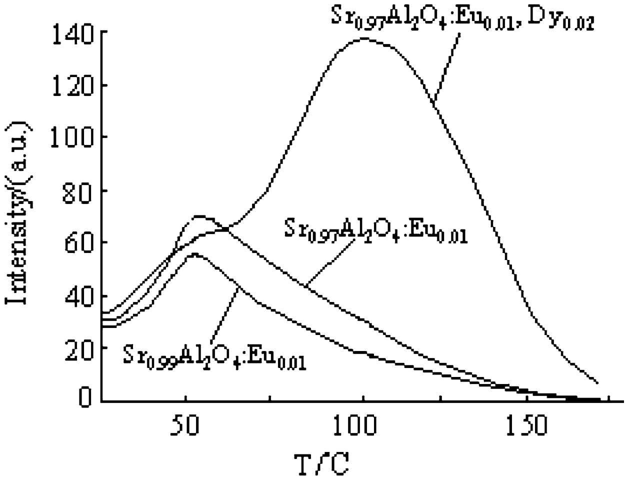

Fig. 4 Thermoluminescence spectra of samples

thermoluminescence spectra further verified that the doping of Dy^{3+} would create a new electron trap with appropriate depth.

Effects of different RE^{3+} ions on persistent luminescence

Except for the Sm^{3+}, the other doped RE^{3+} ions were not found to change the luminescence band position nor the shape of the spectra (Fig. 5). The emission can thus be concluded to originate from the same Eu^{2+} center. The persistent luminescence of the $SrAl_2O_4:Eu^{2+}$ has shown to be enhanced by co-activation with only some trivalent rare earth ions: Pr^{3+}, Nd^{3+}, Tb^{3+} and Dy^{3+} ions (Fig. 6). The Sm^{3+} ions caused a decrease in the persistent luminescence of $SrAl_2O_4:Eu^{2+}$ in agreement with previous studies [8, 9]. The best persistent luminescence was obtained by introducing either Dy^{3+} or Nd^{3+} ions in $SrAl_2O_4:Eu^{2+}$. The optical electro-negativities of those co-doping rare earth ions were listed in Table 2 [18]. All the RE^{3+} ions have big optical electro-negativities indicating that it is more possible for RE^{3+} ions to be electron traps rather than hole traps. The optical electro-negativities of RE^{4+} ions is much higher than that of RE^{3+} indicating that it is difficult for a RE^{3+} ion to lose an electron and become a RE^{4+} ion, which was regarded as a hole in the former mechanisms of hole transfer mode [3, 4]. It can be found from Fig. 6 that the persistent luminescence has a relationship with the optical electro-negativities of the co-doping RE^{3+} ions. Only the co-doping RE^{3+} (such as Dy^{3+} and Nd^{3+}) ions having a suitable optical electro-negativity can greatly enhance the persistent luminescence. Generally speaking, the bigger optical electro-negativity of the co-doping RE^{3+} ion, the deeper trap depth formed. But there is an exception for the Sm^{3+} ion. It has the highest optical electro-negativity, but $SrAl_2O_4:Eu^{2+}$,Sm^{3+} didn't show good persistent luminescence. This can be interpreted in such a way that the Sm^{3+} ions can be reduced to the divalent state in the weak reductive atmosphere and are thus unable to form effective electron traps. The several emission peaks at 520–600 nm were maybe yield by the Sm^{2+} or Sm^{3+} in the crystal lattice of $SrAl_2O_4:Eu^{2+}$,Sm^{3+} (in Fig. 6). Figure 7 shows the thermoluminescence (TL) spectra of $SrAl_2O_4:Eu^{2+}$,RE^{3+}. TL peaks were located at 72.5, 81.2, 94.6 and 102.1 °C depending on the RE^{3+} ions. This implied that the depth of trap for the RE^{3+} ions is $Dy^{3+} > Nd^{3+} > Pr^{3+} > Tb^{3+}$, which is in agreement with their afterglow decay properties given in Fig. 6.

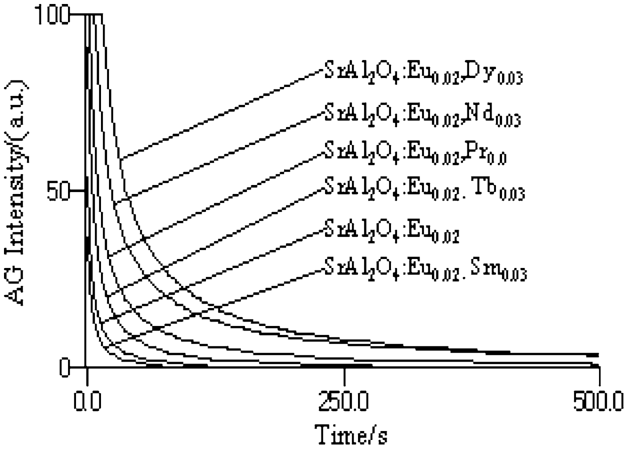

Fig. 6 Afterglow decay curves of RE^{3+} co-doped phosphors

Table 2 Optical electro-negativity (χ_{uncorr}) of co-doping RE ions

χ_{uncorr}	Dy^{3+}	Nd^{3+}	Pr^{3+}	Tb^{3+}	Sm^{3+}
RE^{3+}	1.21	1.20	1.18	0.95	1.45
RE^{4+}	3.03	2.99	2.6	2.55	3.03

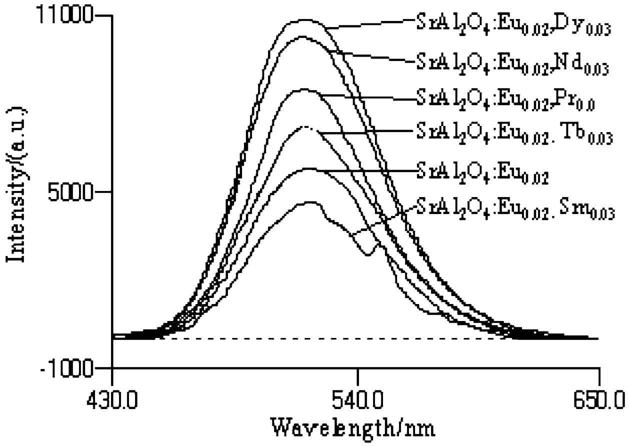

Fig. 5 Emission spectra of RE^{3+} co-doped phosphors

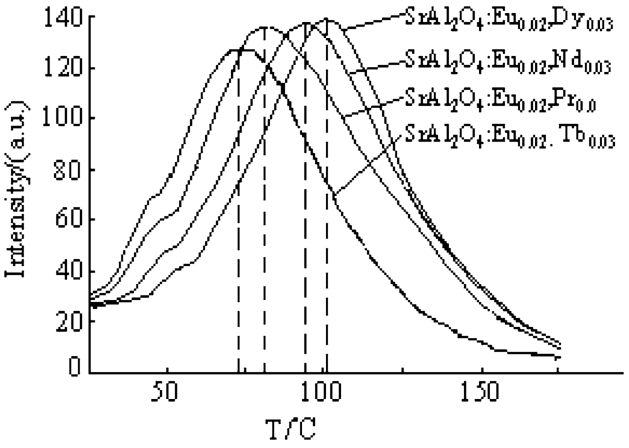

Fig. 7 Thermoluminescence spectra of RE^{3+} co-doped phosphors

Mechanism of persistent luminescence in $SrAl_2O_4$:Eu,Dy phosphors

In $SrAl_2O_4$:Eu,Dy phosphors, electron/hole pairs may be produced simultaneously under UV-light irradiation and trapped by electron traps ($\mathrm{Dy}^{\cdot}_{\mathrm{Sr}}$) and hole traps ($V''_{\mathrm{Sr}}$), respectively. The producing and trapping process of electron/hole pairs can be elucidated by the following equations:

Optical-ionization:

$$\mathrm{Eu}^{2+}(\mathrm{Eu}^{\times}_{\mathrm{Sr}}) + (h\nu)_a \rightarrow \mathrm{Eu}^{3+}(\mathrm{Eu}^{\cdot}_{\mathrm{Sr}}) + \mathrm{e} \qquad (3)$$

Trapping process of electrons:

$$\mathrm{Dy}^{3+}(\mathrm{Dy}^{\cdot}_{\mathrm{Sr}}) + \mathrm{e} \rightarrow \mathrm{Dy}^{2+}(\mathrm{Dy}^{\times}_{\mathrm{Sr}}) \qquad (4)$$

Trapping process of holes:

$$V''_{\mathrm{Sr}} + \mathrm{Eu}^{3+}(\mathrm{Eu}^{\cdot}_{\mathrm{Sr}}) \rightarrow \mathrm{Eu}^{\cdot}_{\mathrm{Sr}} + V''_{\mathrm{Sr}} \qquad (5)$$

In the case of electron trapping, two ways may be involved: one is the direct trapping (Fig. 8a), which occurs when the Eu^{2+} and the Dy^{3+} are very close in the matrix, another is the indirect trapping via conduct band (Fig. 8b), which occurs when the Eu^{2+} and the Dy^{3+} are isolated with each other. In the case of the hole trapping, the holes may be trapped by hole traps (V''_{Sr}) via the valence band (Fig. 8c). The persistent luminescence originates from the thermally stimulated recombination of trapped charge carriers. Some previous researches [15, 19] indicated that afterglow decay process for MAl_2O_4:Eu^{2+}, RE^{3+} at least includes one quick decay process and one slow decay process. This means that there possibly involve several recombination processes for the trapped charge carriers. When the electron trap ($\mathrm{Dy}^{\cdot}_{\mathrm{Sr}}$) and the hole trap ($V''_{\mathrm{Sr}}$) are located very close to each other, the electron traps are bleached thermally and directly feed electrons to the electron–hole recombination processes (Fig. 8d). When the electron trap ($\mathrm{Dy}^{\cdot}_{\mathrm{Sr}}$) and the hole trap ($V''_{\mathrm{Sr}}$) are isolated with each other, the electron traps indirectly feed electrons to the electron–hole recombination process via conduction band (Fig. 8e). The former needs lower excitation energy and corresponds to the quick decay process. The latter needs higher excitation energy and corresponds to the slow decay process. The recombination of the trapped charge carriers causes the excitation of the luminescence center (Eu^{2+}) by non-radiative energy transfer. The emission results from the normal de-excitation of the luminescence center (Eu^{2+}). The recombination processes of electrons and holes can be elucidated by the following equations:

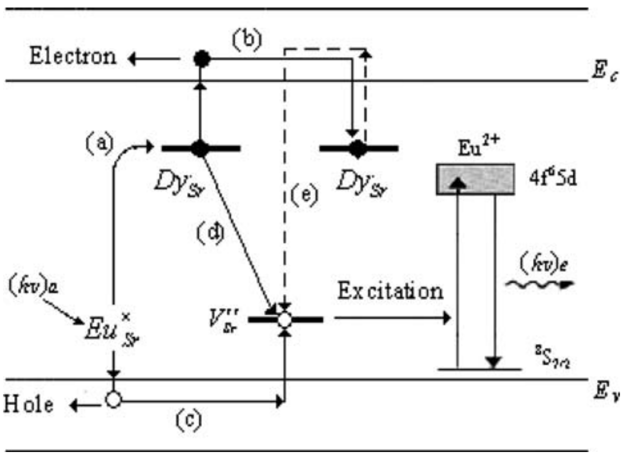

Fig. 8 Electron transfer mode (**a**,**b**) electron trapping; (**c**) hole trapping; (**d**) direct recombination; (**e**) indirect recombination)

Release of the trapped electrons:

$$\mathrm{Dy}^{2+}(\mathrm{Dy}^{\times}_{\mathrm{Sr}}) \rightarrow \mathrm{Dy}^{3+}(\mathrm{Dy}^{\cdot}_{\mathrm{Sr}}) + \mathrm{e} \qquad (6)$$

Recombination of electrons and holes:

$$\mathrm{Eu}^{3+}(\mathrm{Eu}^{\cdot}_{\mathrm{Sr}}) + \mathrm{e} \rightarrow \mathrm{Eu}^{2+}(\mathrm{Eu}^{\times}_{\mathrm{Sr}}) + (h\nu)_e \qquad (7)$$

Conclusion

The Eu^{2+} ion in $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors is not only the UV-excited luminescent center but also the persistent luminescent center. The Dy^{3+} co-doping would greatly enhance the persistent luminescence and thermoluminescence being of the creation of electron traps relating to the crystal defects of $\mathrm{Dy}^{\cdot}_{\mathrm{Sr}}$. Different RE^{3+} ions have different effects on persistent luminescence. Only the Dy^{3+}, Nd^{3+} ions, who have suitable optical electro-negativity, can effectively improve the persistent luminescence of Sr Al_2O_4:Eu^{2+}. A persistent mechanism proposed involves the producing, trapping and recombination of electron–hole pairs. The persistent luminescence is observed after a temperature controlled electron–hole recombination and subsequent energy transfer to the luminescent center (Eu^{2+}).

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