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Effects of RE^{3+} as a co-dopant in blue-emitting long-lasting phosphors, $Sr_3Al_{10}SiO_{20}:Eu^{2+}$

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Abstract A series of novel long-lasting phosphors, $Sr_3Al_{10}SiO_{20}:Eu^{2+},RE^{3+}$, were prepared and studied. Under UV irradiation, broad-band emission long-lasting phosphorescence located at 466 nm was observed in all of these phosphors at room temperature. The effects of RE^{3+} as a co-dopant in $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ were discussed in conjunction with the afterglow decay curves and thermoluminescence (TL) spectra. Quantitative TL spectra revealed that the introduction of RE^{3+} ions into $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ host produces a highly dense trapping level at appropriate depth (335 K), which is considered to be responsible for the long-lasting phosphorescence at room temperature.

Introduction

Since the reports by Palilla et al. [1] and Abbruscato [2], long-lasting phosphors based on aluminates have been investigated by many researchers. Till now, the most efficient long-lasting phosphors are still based on alkaline-earth aluminates, e.g. $SrAl_2O_4$:Eu,Dy (green) and $CaAl_2O_4$:Eu,Nd (deep blue) [3]. However, those aluminosilicate-based long-lasting phosphorescence materials have attracted much more attention because of their stability, visible light transparency and practical application [4–6].

Strontium aluminosilicate $Sr_3Al_{10}SiO_{20}$, which crystal structure was determined by XRD and solid-state NMR, revealing that double AlO_6 octahedra chains interconnected with AlO_4 and SiO_4 tetrahedra to from a three dimensional network where the strontium cations are located [7]. In this kind of structure, it is very easy to implant rare-earth luminescent ions into host lattice. Recently, Eu^{2+} or Tb^{3+}-doped $Sr_3Al_{10}SiO_{20}$ phosphors have been reported and used as PDPs (plasma display panels) and FEDs (field emission displays), due to theirs excellent luminescent performance [8, 9]. However, long-lasting phosphorescence properties have not been reported in this kind of strontium aluminosilicate host.

In this work, we prepared a series of Eu^{2+} and RE^{3+} co-doped $Sr_3Al_{10}SiO_{20}$ long-lasting phosphors, and discussed the effects of RE^{3+} as a co-dopant in $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ in conjunction with the afterglow decay curves and thermoluminescence (TL) spectra.

Experimental

Phosphor samples were prepared by firing mixtures of high-purity $SrCO_3$, Al_2O_3, SiO_2, Eu_2O_3 and another rare-earth oxide in a reducing atmosphere at 1500–1600 °C for several hours. The nominal compositions of all samples were $Sr_{2.98}Eu_{0.01}RE_{0.01}Al_{10}SiO_{20}$. For comparison, single -doped $Sr_{2.99}Eu_{0.01}Al_{10}SiO_{20}$ was also prepared by this method.

Crystal structure of all synthesized powder phosphors were checked by D/max-IIB X-ray diffractometer. The excitation and emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Long-lasting phosphorescence spectra were measured on the same instrument. The afterglow decay curve measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer. Quantitative TL spectra were measured on a model FJ-427A1 TL meter (made by Beijing Nuclear Instrument Factory, China) with a heating rate of 2 K/s

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in the temperature range from 293 to 673 K. Before measurement, 0.03 g power samples were pressed into pellets (5 mm diameter and 1 mm thickness), and then exposed for 5 min to a standard UV lamp peaking at 365 nm with a power of 15 W. All measurements were carried out at room temperature (RT) except for the TL spectra.

Results and discussion

Among all RE^{3+} co-doped $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ samples, $Sr_3Al_{10}SiO_{20}:Eu^{2+},Ho^{3+}$ presented the longest phosphorescent decay time of these materials. Hence, $Sr_3Al_{10}SiO_{20}:Eu^{2+},Ho^{3+}$ was chosen as illustration. Figure 1 gives the emission and excitation spectra of $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ and $Sr_3Al_{10}SiO_{20}:Eu^{2+},Ho^{3+}$. Independently of the existence or nonexistence of auxiliary activators Ho^{3+}, those phosphors exhibit broad-band emission spectra peaking at 466 nm of Eu^{2+} transition and no characteristic luminescence of the Ho^{3+} auxiliary activators. It is worthy of noting that, other RE^{3+} as a auxiliary activator co-doped into $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ host also gave the only blue broad-band emission and no characteristic emission of the auxiliary activators themselves. As shown in Fig. 1, the excitation spectra of $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ and $Sr_3Al_{10}SiO_{20}:Eu^{2+},Ho^{3+}$ are wide (200–450 nm), containing at least three bands located at 280, 348 and 408 nm. All the emission and excitation bands can be attributed to the 4f–5d transition of Eu^{2+} [10].

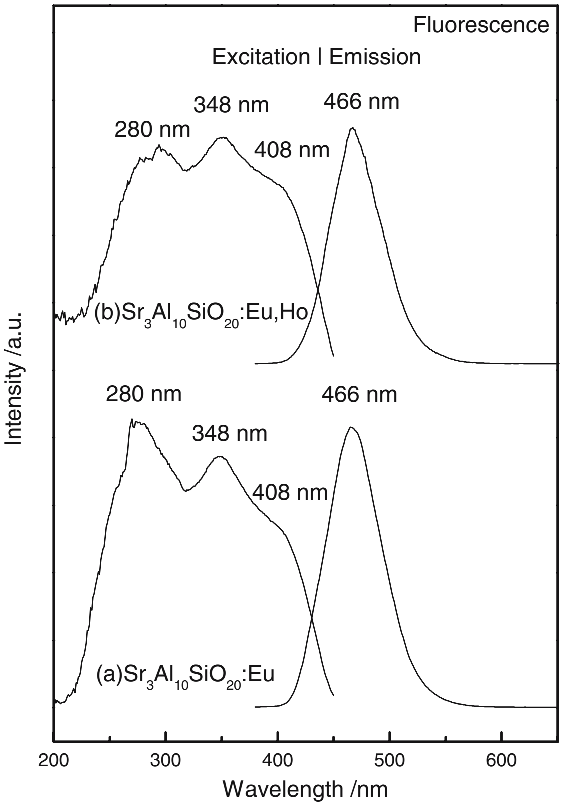

Fig. 1 Emission and excitation spectra of (**a**) $Sr_3Al_{10}SiO_{20}:Eu^{2+}$; (**b**) $Sr_3Al_{10}SiO_{20}:Eu^{2+},Ho^{3+}$

An important result of the present work is that we have observed obvious blue phosphorescence when RE^{3+} co-doped into $Sr_3Al_{10}SiO_{20}:Eu^{2+}$. Figure 2 shows the long-lasting phosphorescence spectra of some samples at 10 min after stopping the excitation source. Long-lasting phosphorescence spectra of all samples are identical in wavelength position and shape. Moreover, the shape and bandwidth of the long-lasting phosphorescence spectra and the steady-state UV-excited luminescence spectra were found identical as well. These properties point out that the radiation centers in both cases are the same, which can be attributed to the characteristic emission of Eu^{2+}.

Figure 3 gives the afterglow decay curves of Eu^{2+}, RE^{3+} co-doped $Sr_3Al_{10}SiO_{20}$ phosphors in double logarithmic scale format. These decay curves were measured by a Varian Cary Eclipse fluorescence spectrophotometer. The excitation light of the samples were blocked when the samples had been exposed for 5 min under 365 nm UV light and the emitted afterglow from them were recorded over a time period of 30–1200 s in the kinetic analysis mode of the spectrometer system. The scan interval is set to 30 s. The afterglow emission intensity of all samples decreases quickly at first and then slowly. The afterglow intensity for these samples decreases as follows: (a) > (b) > (c) > (d) > (e). The phosphorescence for the $Sr_3Al_{10}SiO_{20}:Eu^{2+},Ho^{3+}$ phosphor can be seen with the naked eye in the darkroom clearly for more than 6 h even after the 365 nm UV irradiation source have been removed.

It is well-known that trapping centers play an essential role for photo energy storage in persistent, photostimulable, and thermostimulable phosphors [11, 12]. Usually,

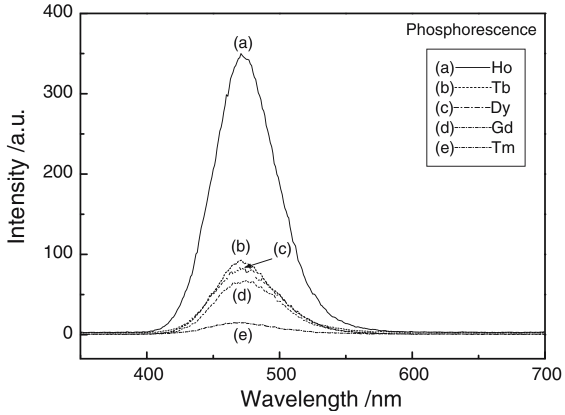

Fig. 2 Long-lasting phosphorescence spectra of (**a**) $Sr_3Al_{10}SiO_{20}:Eu^{2+},Ho^{3+}$; (**b**) $Sr_3Al_{10}SiO_{20}:Eu^{2+},Tb^{3+}$; (**c**) $Sr_3Al_{10}SiO_{20}:Eu^{2+},Dy^{3+}$; (**d**) $Sr_3Al_{10}SiO_{20}:Eu^{2+},Gd^{3+}$; (**e**) $Sr_3Al_{10}SiO_{20}:Eu^{2+},Tm^{3+}$. These samples were irradiated by 365 UV light for 5 min before measurement

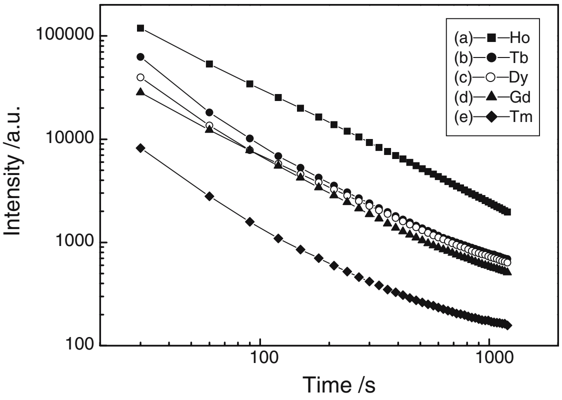

Fig. 3 Afterglow decay curves of (**a**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Ho^{3+}; (**b**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Tb^{3+}; (**c**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Dy^{3+}; (**d**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Gd^{3+}; (**e**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Tm^{3+}

information of trap depth can be obtained by TL measurements. The shallower the charge trap depth is, the lower the temperature of TL peak is [13]. To the best of our knowledge, the dominant peaks are situated slightly above room temperature if materials show high long-lasting phosphorescence performance [14]. Moreover, the long-lasting phosphorescence performance is proportional to the trap density ρ.

Figure 4 shows the quantitative TL spectra of the co-doped $Sr_3Al_{10}SiO_{20}$:Eu^{2+},RE^{3+} phosphors and the single-doped $Sr_3Al_{10}SiO_{20}$:Eu^{2+} phosphor. As shown in Fig. 4, the trap depths of all phosphors have the appropriate peak at 335 ± 2 K. It is important to note that all the TL intensity of the co-doped phosphors is stronger than the single Eu^{2+}-doped phosphor. From Fig. 4, it can be also seen that the ability of trapping electrons/holes by these defects created via introducing both Eu^{2+} and RE^{3+} into the host $Sr_3Al_{10}SiO_{20}$ seem to be much higher than that of the single Eu^{2+}-doped $Sr_3Al_{10}SiO_{20}$. Figure 5 gives the relative trapping density ρ of all the rare earth co-doped samples.

On the basis of the above afterglow decay curves and quantitative TL spectra, we found that, in a series of Eu^{2+} and RE^{3+} co-doped $Sr_3Al_{10}SiO_{20}$ long-lasting phosphors, $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Ho^{3+} phosphor was the longest phosphorescent materials of this system and the neighborhood of Ho^{3+} ions, such as Tb, Dy and Er ions etc. co-doped $Sr_3Al_{10}SiO_{20}$:Eu^{2+} also present good phosphorescence performance. And their phosphorescence performances are better than the away Ce, Pr, Nd ions etc. co-doped counterparts. For the case of Sm, Tm and Yb, their phosphorescence performances are not acceptable, while the case of Ce, Pr and Tb give good phosphorescence result. The partly reducible of Sm^{3+}, Tm^{3+}, Yb^{3+} to Sm^{2+}, Tm^{2+}, Yb^{2+} under the prepared process should take charge of this result, which is agreement with the results of quantitative TL spectra (Fig. 4). While for the case of Ce, Pr, Tb, the valency of Ce, Tb, Pr is mainly +3 under the prepared atmosphere. Accordingly, it is feasible to suggest that the ionic radii and valences of the RE^{3+} species have an key effect on the phosphorescence performance of RE^{3+} as a co-dopant in $Sr_3Al_{10}SiO_{20}$:Eu^{2+} phosphors. That is, the ionic radius in the neighborhood of Ho^{3+} and the valences of +3 are more suitable as a co-doped auxiliary activator in this system.

The detailed description of long-lasting phosphorescence mechanism is not yet known. Long-lasting phosphorescence was observed in Eu^{2+} and Dy^{3+} co-doped spinel-type strontium aluminate phosphor and the cause of such phenomenon was believed to the thermostimulated recombination of holes and electrons which enhanced by the incorporation of Dy^{3+} to forms a highly dense trapping level [3]. When the highly dense trapping level is thermally released with a proper rate at room temperature, the intense

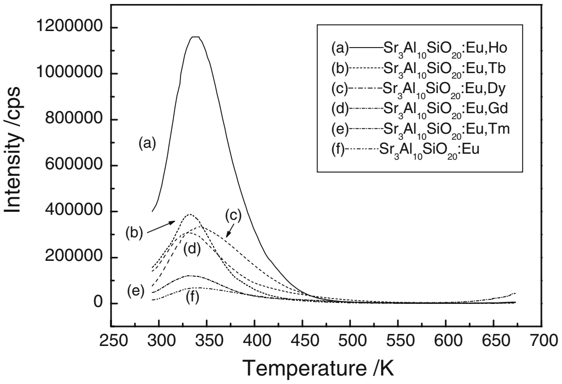

Fig. 4 TL spectra of (**a**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Ho^{3+}; (**b**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Tb^{3+}; (**c**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Dy^{3+}; (**d**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Gd^{3+}; (**e**) $Sr_3Al_{10}SiO_{20}$:Eu^{2+},Tm^{3+}. The heating rate is 2 K/s

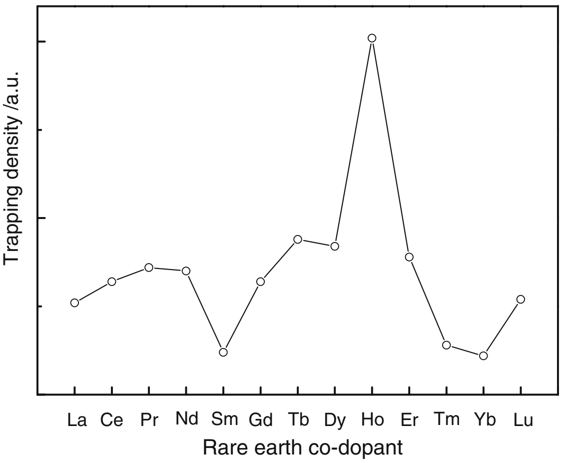

Fig. 5 Relative trapping density ρ of $Sr_3Al_{10}SiO_{20}$:Eu^{2+}, RE^{3+} phosphors

green long-lasting phosphorescence is available. In our case, the introduction of RE^{3+} ions into the $Sr_3Al_{10}SiO_{20}$:Eu^{2+} also produces a highly dense trapping level at appropriate depth, especially for the Ho^{3+} ions, and the recombination of trapped electrons and holes delayed the Eu^{2+} emissions, which resulted in the blue long-lasting phosphorescence.

Conclusions

Long-lasting phosphorescence phenomenon was observed Eu^{2+} and RE^{3+} co-doped $Sr_3Al_{10}SiO_{20}$ phosphors. The luminescence properties, including fluorescence spectra, long-lasting phosphorescence spectra and TL spectra, as well as the afterglow decay curves, were studied. The results revealed that the Ho^{3+} ions are the most suitable auxiliary activators in this system to give long-lasting phosphorescence.

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References

1. Palilla FC, Levine AK, Tamkus MR (1968) J Electrochem Soc 115:642
2. Abbruscato V (1971) J Electrochem Soc 118:930
3. Matsuzawa T, Aoki Y, Takeuchi N, Murayama Y (1996) J Electrochem Soc 143:2670
4. Qiu J, Miura K, Inouye H, Kondo Y, Mitsuyu T, Hirao K (1998) Appl Phys Lett 73:1763
5. Qiu J, Kawasaki M, Tanaka K, Shimizugawa Y, Hirao K (1998) J Phys Chem Solids 59:1521
6. Kinoshita T, Yamazaki M, Kawazoe H, Hosono H (1999) J Appl Phys 86:3729
7. Capron M, Fayon F, Coutures J, Massiot D, Douy A (2002) J Solid State Chem 169:53
8. Kubota S, Shimada M (2002) Appl Phys Lett 81:2749
9. Kubota S, Yamane H, Shimada M (2002) Chem Mater 14:4105
10. Blasse G, Bril A (1968) Philips Res Rep 23:201
11. Jia D, Jia W, Evans DR, Dennis WM, Liu H, Zhu J, Yen WM (2000) J Appl Phys 88:3402
12. Yamamoto H, Mastusuzawa T (1997) J Lumin 72:287
13. Mckeever SWS, Chen R (1997) Radiat Meas 27:625
14. Zhang TZ, Su Q, Wang SB (1999) Chin J Lumin 20:170