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Synthesis and characterization of $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphors prepared by sol–gel–combustion processing*

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A type of red luminescent $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphor powder is synthesised by sol–gel–combustion processing, with metal nitrates used as the source of metal ions and citric acid as a chelating agent of metal ions. By tracing the formation process of the sol–gel, it is found that it is necessary to reduce the amount of NO_3^- by dropping ethanol into the solution for forming a stable and homogeneous sol–gel. Thermogravimetric and Differential Scanning Calorimeter Analysis, x-ray diffractionmeter, scanning electron microscopy and photoluminescence spectroscopy are used to investigate the luminescent properties of the as-synthesised $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+}. The results reveal that the $Sr_3Al_2O_6$ crystallises completely when the combustion ash is sintered at 1250 °C. The excitation and the emission spectra indicate that the excitation broadband lies mainly in a visible range and the phosphors emit a strong light at 618 nm under the excitation of 472 nm. The afterglow of $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ phosphors sintered at 1250 °C lasts for over 1000 s when the excited source is cut off.

Keywords: $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphors, red luminescence, sol–gel–combustion method
PACC: 7855, 7865P, 8116

1. Introduction

Strontium aluminate phosphors activated by europium have attracted much attention since they showed excellent properties such as high quantum efficiency, long persistence of phosphorescence, and good stability.[1] Commercial strontium aluminates powders with large size particles are usually prepared by a solid-state reaction,[2] and smaller particles must be obtained by grinding the larger phosphor particles, which can easily induce additional defects and greatly reduce the luminescence efficiency. With the development of technologies on materials, several kinds of chemical synthesis techniques such as chemical precipitation,[3] combustion synthesis,[4,5] sol–gel process,[1,6,7] and sol–gel–combustion process[8] have been used to prepare strontium aluminate phosphors. Among them, sol–gel–combustion process is an efficient technique for synthesizing phosphors due to the efficient mixing of starting materials and a relatively low reaction temperature, resulting in more homogeneous products than those obtained by the solid-state reaction method. In this process, citric acid is generally used as a chelating agent of metal cations. The polymerising ability of citric acid is effectively utilised for the formation of sol, where the metal ions are uniformly distributed. Apart from that, citric acid also serves as a fuel and induces the exothermic combustion reaction during the calcinations of the dried gel.[9,10] Sol–gel–combustion process involves three steps: preparation of stable and homogeneous sol, formation of gel and combustion of gel. Among these steps, the preparation of stable and homogeneous sol is similar to that of sol–gel process. Usually, the pH value of sol should be adjusted with ammonia solution[1] or other additive[7] to stabilise the raw materials.

In recent years, the different phases of strontium aluminates doped with rare earths have been developed like $Sr_2Al_6O_{11}$:Eu^{2+}, $Sr_4Al_{14}O_{25}$:Eu^{2+}, $SrAl_2O_4$:Eu^{2+}, $SrAl_{12}O_{19}$:Pr^{3+}, etc. By changing the crystal structure of the matrix in which Eu^{2+} ions reside, visible light emitting at different wavelengths can be obtained. Examples that had been reported included emission at 520 nm for $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and 480 nm for $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+}.[11,12] However, the progress in the study of red phosphor $Sr_3Al_2O_6$ is very slow.

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In the present work, we use sol–gel–combustion method to synthesise $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphors. There are two objectives for this investigation. One is to find a preparation method of obtaining a stable and homogeneous sol of strontium aluminate sol without adjusting its pH value requested, and the other is to improve luminescent properties through adjusting phase compositions of $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphors prepared by sol–gel–combustion method.

2. Experiment

Eu_2O_3(99.99%), Dy_2O_3(99.9%), $Al(NO_3)_3{\cdot}9H_2O$ (99%), $Sr(NO_3)_2$ (99%), and $C_6H_8O_7{\cdot}H_2O$ (99%) were used as raw materials, and they were weighted according to the composition of $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$. One solution was prepared by dissolving $Sr(NO_3)_2$ into deionized water, and another one was made by using Eu_2O_3 and Dy_2O_3 dissolved in concentrated nitric acid. Two solutions were then mixed. The following step was to add citric acid into the aqueous solution to chelate metal ions. The amount of citric acid in mole was two times that of the metal ions. The mixed solution was heated to 85–90 °C under magnetic stirring until the color of the sol turned straw yellow, then a little amount of ethanol was slowly dropped into the solution until no rufous gases evaporated out and the sol turned colorless again. The resulting colorless sol was further heated with stirring at 85–90 °C until a highly viscous wet gel was formed. Subsequently, the sol was poured into a crucible, which was transferred to a muffle furnace preheated at 600 °C. Initially, the wet gel boiled, followed by decomposition with the evolution of large amounts of gases (oxides of carbon and nitrogen). Then, spontaneous ignition occurred and underwent combustion with enormous swellings occurring. The entire combustion process would last a few minutes. To obtain white combustion ash, the muffle furnace was then heated to 850 °C for 1 h to remove the residual carbon. The porous and loose combustion ash was milled and subsequently annealed at 900–1250 °C for two hours in an active carbon atmosphere to produce $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphors. In order to investigate the influence of the doped Eu and Dy ions on the structures of luminescent materials, $Sr_3Al_2O_6$, $(Sr_{0.97}Eu_{0.03})_3Al_2O_6$ samples were prepared in a similar process. To understand the role of Dy^{3+} in $Sr_3Al_2O_6$ phosphors, four $(Sr_{0.97-x}Eu_{0.03}Dy_x)_3Al_2O_6$ samples with different values of x, i.e. $x = 0$, 0.02, 0.03 and 0.04, were synthesised according to the experimental procedures mentioned above. The details about sol–gel–combustion process is summarized in a flow chart shown in Fig.1.

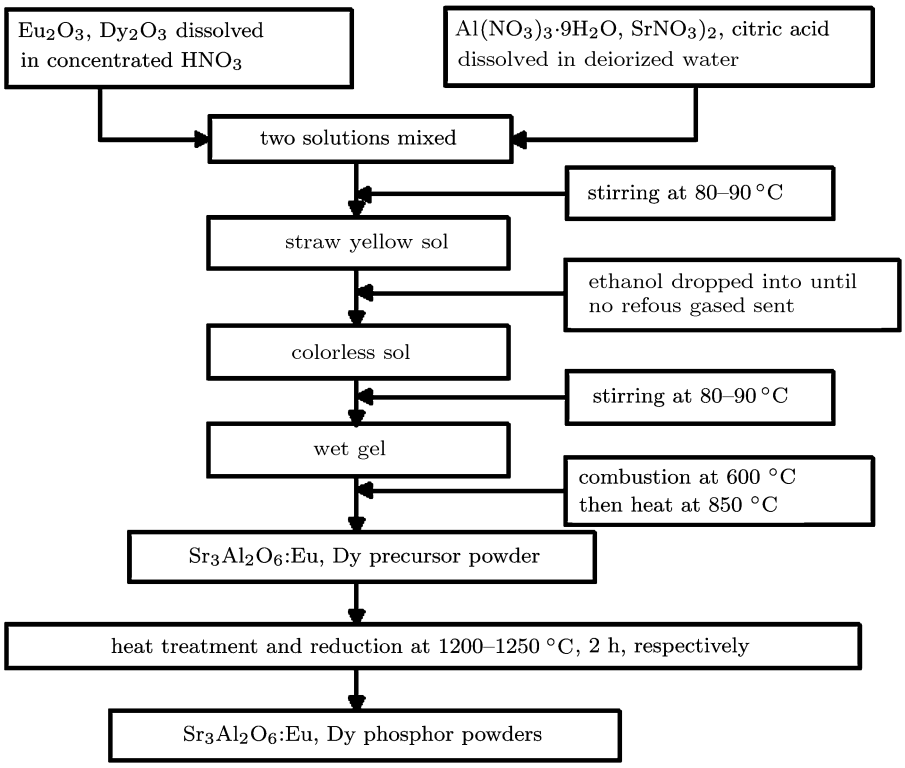


Fig.1. Schematic diagram for the synthesis of $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphor powders via a sol–gel–combustion route.

The crystalline structure of the phosphors powders was analysed by x-ray diffractometer (XRD, Rigaka D/Max 2500v/pc). The thermal decomposition behaviour of the wet gel was examined by means of Thermogravimetric and Differential Scanning Calorimeter Analysis (TG–DSC, Netzsch STA 449C) in air from 35 °C to 1100 °C at a heating rate of 10 °C/min. The morphology and the size of phosphors powders were observed using scanning electron microscope (SEM) (HITACHI X-650). The excitation and the emission spectra of the powder samples were recorded by using a fluorescence spectrophotometer (RF-540). The decay curve of afterglow was measured by using the brightness meter (ST-86LA). All the measurements were performed at room temperature.

3. Results and discussion

3.1. Formation of sol and gel

In the preparation of stable sol, the pH value of sol was not adjusted with ammonia solution or other additive in the present work. In the heating process, with the evaporation of water, some precipitates formed gradually if the ethanol was not dropped into the solution. The XRD pattern of precipitates shown in Fig.2 is entirely the same as that given in the literature (PDF No. 76-1375) and no peak of any other phase is detected, indicating that $Sr(NO_3)_2$ is formed with cubic lattice. Due to a low solubility of $Sr(NO_3)_2$ in water, $Sr(NO_3)_3$ crystals are easily separated from the solution after water evaporation. Therefore, NO_3^- coming from $Al(NO_3)_3$, $Sr(NO_3)_2$, and concentrated nitric acid, which was introduced as a solvent of Eu_2O_3 and Dy_2O_3, has a great effect on the sol–gel process. It is necessary to reduce the amount of NO_3^- in the solution for the formation of transparent gel.

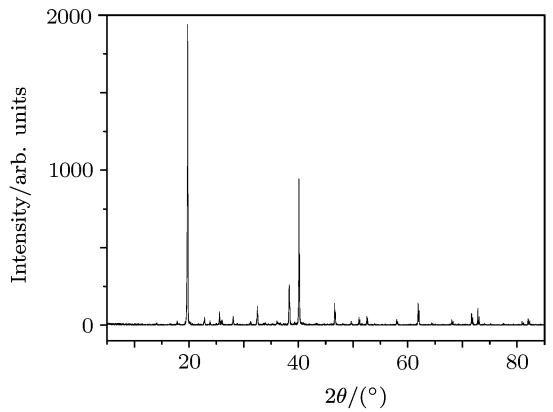


Fig.2. XRD pattern of $Sr(NO_3)_2$ separated from the aqueous solution.

In this experiment, the ethanol was dropped into the precursor solution to reduce the amount of NO_3^-. The esterification of ethanol with nitric acid is given as follows:

$$CH_3CH_2OH + HNO_3 \Leftrightarrow CH_3CH_2 - O - NO_2 + H_2O. \quad (1)$$

Because the boiling point of ethyl nitrate is 88.7 °C, and the precursor solution was maintained at 80∼90 °C, the ethyl nitrate transpired out immediately from solution as soon as the ethanol was dropped into the precursor solution, and the amount of NO_3^- in the solution decreased.

In the above process, citric acid was used as a chelating agent in preparing the gel. In order to illustrate the reaction of citric acid with other materials, the reactions of $Al(NO_3)_3{\cdot}9H_2O$ with citric acid (H_3Cit) are given as follows:[13]

First, when $Al(NO_3)_3{\cdot}9H_2O$ is dissolved in water, it is easy to hydrolyze and chemical reactions occur as follows:

$$Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_3 + 3H^+. \quad (2)$$

Then,

$$Al(OH)_3 + 3H_3Cit \Leftrightarrow Al(H_2Cit)_3 + 3H_2O, \quad (3)$$

$$2Al(OH)_3 + 3H_3Cit \Leftrightarrow Al_2(HCit)_3 + 6H_2O, \quad (4)$$

$$Al(OH)_3 + H_3Cit \Leftrightarrow AlCit + 3H_2O. \quad (5)$$

In the heating process at 85∼90 °C, the volume of the solution was slowly reduced and then a transparent sol formed. When the NO_x gas from the nitrate was gradually evolved, the color of the sol turned straw yellow. When a few of $Sr(NO_3)_2$ precipitates formed in the solution, the ethanol was slowly dropped into the solution, so a certain amount of NO_3^- in the solution decreased and the precipitates dissolved again. As most of the NO_x gas was exhausted, the sol turned colorless again. Further heating led to dehydration and caused the condensation reaction between –COOH groups with the concurrent formation of water. When most of the excess water was removed, the sol turned into a transparent gel.

3.2. Self-combustion behaviour of $Sr_3Al_2O_6$:Eu, Dy wet gel

Usually, when transparent $Sr_3Al_2O_6$:Eu, Dy wet gel forms, Xerogel can be prepared by baking the wet gel at about 90 °C. Because the high water absorbency of citrate–gel, this process usually lasts more than 24 h.[14] In order to shorten the preparation time of $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphor, wet gel can be introduced into a muffle furnace that has been preheated at 600 °C. In this process, Citric acid performed as a fuel leads to an exothermic combustion reaction during the calcination of wet gels.

The behaviour of the combustion process of citrate gels was studied by thermal analysis (TG and DSC) of the wet gel. A TG–DSC plot for the sample obtained is shown in Fig.3. The TG curve exhibits four distinct weight loss steps. The first weight loss step with a gradual weight loss of ∼8% takes place in a temperature range of 80–150 °C due to moisture vaporisation from wet gel. The second weight loss step with a loss about 7% happens between 150–200 °C corresponding to the desorption of H_2O from the hydroxyl group of wet gel. Correspondingly, two endothermic peaks at 106 °C and 190 °C in DSC curve are attributed to the release of water. The third weight loss step from 450 °C to 550 °C corresponds to the decomposition and the oxidation of the metal-citric acid compounds. As expected, the sharp and intense exothermic peak is observed at 510 °C in the DSC curve. A weight change associated with this step is approximate 30%. In this step, a great quantity of gases such as CO, CO_2 and NO are produced. A little weight loss (∼5%) is observed from 850 °C to 970 °C and the endothermic peak at 946 °C can be ascribed to the decomposition of $SrCO_3$ and the formation of $Sr_3Al_2O_6$.

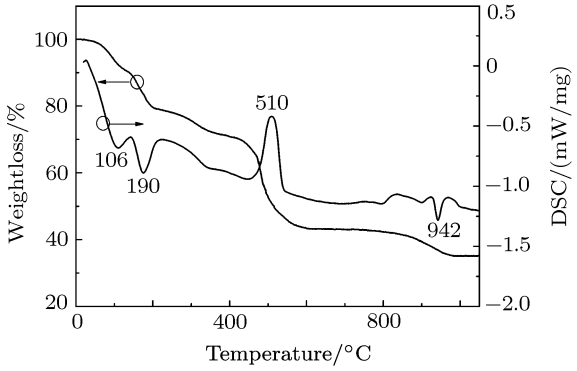


Fig.3. TG–DTA curves of precursor wet gel.

3.3. Formation of $Sr_3Al_2O_6$:Eu, Dy phosphor in the sintering process

Figure 4 shows x-ray diffraction spectra of the $Sr_3Al_2O_6$,$(Sr_{0.97}Eu_{0.03})_3Al_2O_6$ and $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ phosphors prepared at 1200 °C for two hours. No significantly different XRD patterns are observed from these samples. It suggests that doped Eu and Dy ions have little influence on the structure of the luminescent materials.

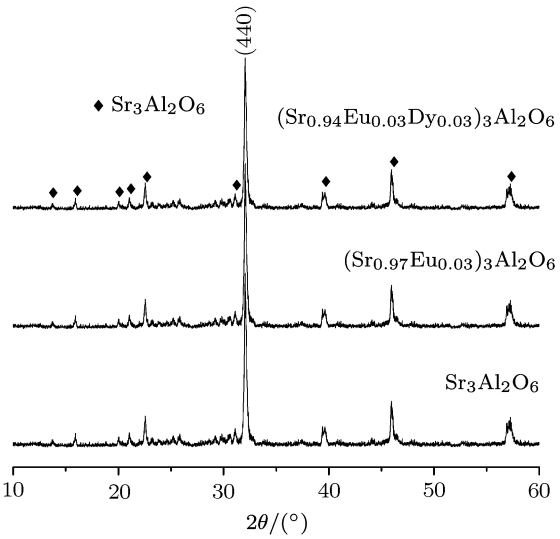


Fig.4. XRD patterns of $Sr_3Al_2O_6$,$(Sr_{0.97}Eu_{0.03})_3Al_2O_6$ and $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ phosphors obtained at 1200 °C.

Figure 5 gives x-ray diffraction patterns for the $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ phosphors prepared at different temperatures for two hours under the same conditions. After heating the combustion ash at 900 °C for two hours, the powders become a mixture of $SrCO_3$, SrO and $Sr_3Al_2O_6$, in which $SrCO_3$ is a major phase. The XRD patterns of the powders obtained at 1000 °C for two hours are similar to those produced at 900 °C. Heating the resulting combustion ash at 1100 °C for two hours produces a mixture of $Sr_3Al_2O_6$, $SrCO_3$ and SrO, in which $Sr_3Al_2O_6$ and $SrCO_3$ become major phases. When calcinations temperature rises to 1200 °C and 1250 °C, the diffraction peaks of $SrCO_3$ and SrO vanish, and pure $Sr_3Al_2O_6$ phase is obtained, which is confirmed to be in accordance with powder data in PDF card No. 24-1187. According to that, the sample is cubic lattice $Sr_3Al_2O_6$ without impurity. These results confirm that sol–gel–combustion method provides a satisfactory condition for forming $Sr_3Al_2O_6$ with a single phase. However, the crystallinity of $Sr_3Al_2O_6$ prepared at 1200 °C is very low. When sintering temperature increases up to 1250 °C, $Sr_3Al_2O_6$ crystallises

completely. This temperature is much lower than that used in a conventional solid-state reaction reported somewhere (above 1505 °C).[15] This is because the homogeneous precursors prepared by using this method increase the reactivity of staring materials, thereby reducing the calcining temperature compared with the solid-state method. Although actual synthesis temperature 1250 °C is still high if the advantages of sol–gel–combustion method are considered, there is no H_3BO_3 added into the system in our experiment.

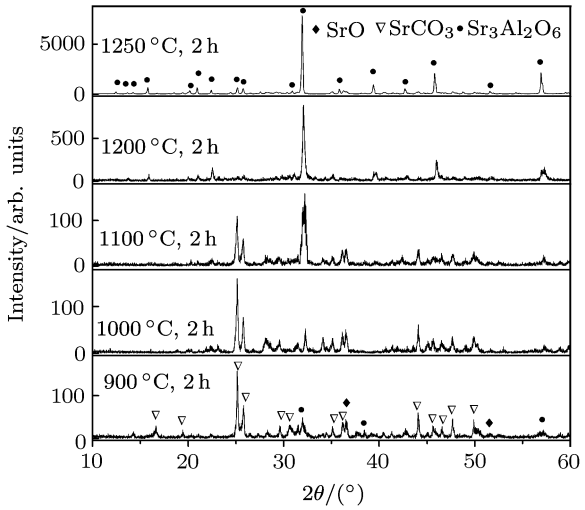


Fig.5. XRD patterns of $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ phosphors obtained at different calcinations temperatures.

Figure 6 displays an SEM micrograph of $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ powders prepared at 1250 °C for two hours in which are shown whisker-like crystallites with nanorod leaves. The average size of whisker-like crystallites is about 1 μm–1.5μm. The formation mechanism of whisker-like $Sr_3Al_2O_6$ crystallite is under consideration.

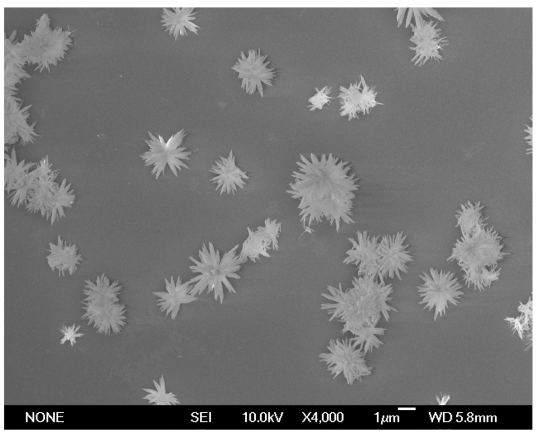


Fig.6. SEM image of $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ phosphor calcinated at 1250 °C.

3.4. Luminescent property of the phosphor

Figure 7 shows the excitation and the emission spectra of $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ phosphor prepared at 1250 °C for two hours. From 400 nm to 535 nm, the excitation spectrum of the phosphors shows two wide bands with their peaks at about 440 nm and 472 nm, separately. These can be attributed to crystal field splitting of Eu^{2+} d-orbital. The emission spectrum excited by visible light (λ_{ex} = 472 nm) includes a broad and symmetric band peaked at 618 nm with a half width about 83 nm, indicating only one luminescent centre, belonging to the emission of $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions in $Sr_3Al_2O_6$. Although $4f$ electrons of Eu^{2+} are not sensitive to crystal lattice environments due to the shielding function of outer shell, $5d$ electrons can be easily coupled with crystal lattice, thus $4f5d$ hybridisation state can be split by the influence of crystal field and coupled fiercely with crystal lattice phonon, which leads to a broad emission band.

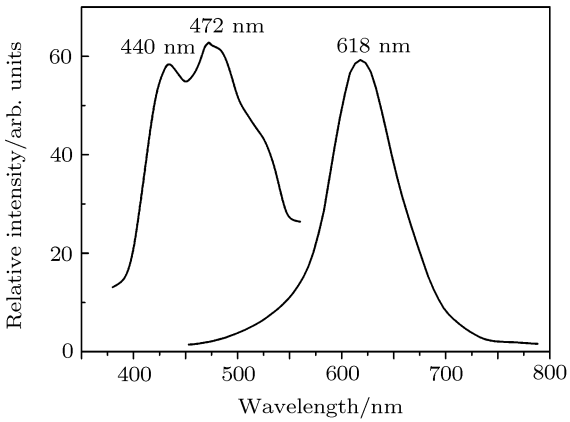


Fig.7. Excitation and emission spectra of $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ prepared at 1250 °C by sol–gel–combustion process.

The peak positions in the emission spectra depend strongly on the nature of Eu^{2+} surroundings, therefore, Eu^{2+} ions can emit different visible lights in various crystal fields. It is known that crystal field strength can be represented by the parameter D_q, which is inversely proportional to the 5-th power of the bond length R[16]

$$D_q \propto 1/R^5. \tag{6}$$

A shorter bond length implies a stronger crystal field strength. The average bond length of Sr–O in $Sr_3Al_2O_6$ is 2.5598 Å and that in $SrAl_2O_4$ is 2.6166 Å

(1 Å = 0.1 nm), thus it is believed that the crystal field strength at the Sr^{2+} site in $Sr_3Al_2O_6$ is stronger than that in $SrAl_2O_4$. As is known, a strong crystal field can lower the energy level of the excitative state of $4f^6 5d^1$ for Eu^{2+}. The Sr site in $Sr_3Al_2O_6$ has a stronger crystal field than that in $SrAl_2O_4$, thus the energy level of the excitation state of $4f^6 5d^1$ for Eu^{2+} in $Sr_3Al_2O_6$ is lower than that in $SrAl_2O_4$ (effect of nephelauxetic). Moreover, the stronger crystal field can also result in a bigger split of the $4f5d$ hybridization state.[17] The lower energy level and the bigger split of the excitative state of the $4f^6 5d^1$ directly lead to a red shift of the emission peak of $Sr_3Al_2O_6$. The effects of nephelauxetic and crystal the field on the $4f^6 5d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ions in $Sr_3Al_2O_6$ and $SrAl_2O_4$ host are shown in Fig.8, which can give a reasonable explanation to the changes of the emitting peaks with the host.

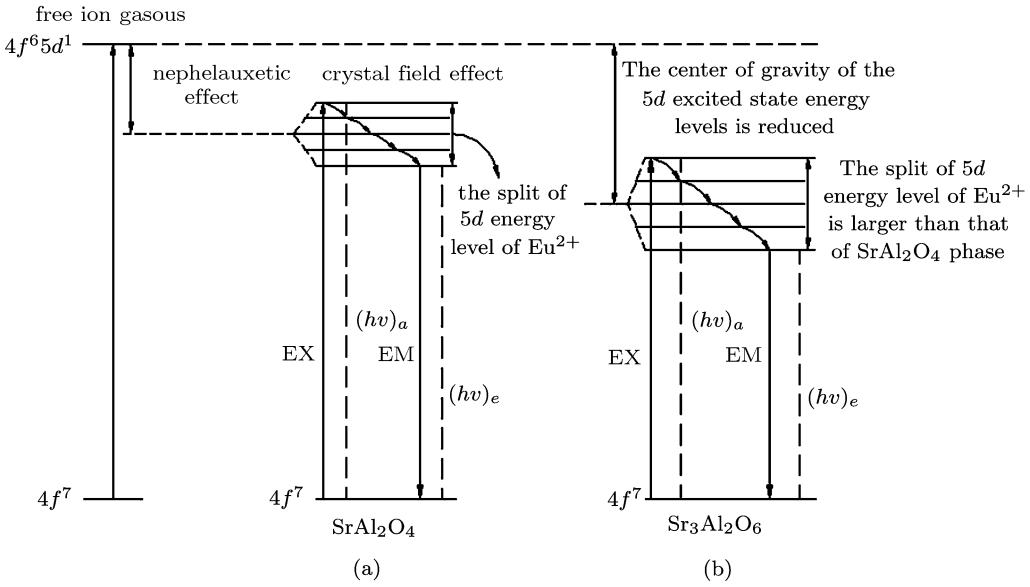


Fig.8. Effects of nephelauxetic and crystal field on the $4f^6 5d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ions in $SrAl_2O_4$ (a) and $Sr_3Al_2O_6$ (b) hosts.

The spectral features are drastically different between Eu^{2+} and Eu^{3+} ions, i.e. a broad band featureless emission of Eu^{2+}[1] and sharp line-like emissions of Eu^{3+} ions.[18] As is well known, the emission of Eu^{2+} ion in a solid state compound generally shows a broad band character from $4f^6 5d$ to $4f^7$ (except the f–f line emission at about 360 nm in some special compounds[19]); while that of Eu^{3+} ion always gives a series of typical emission lines in a spectral region of 570–750 nm corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) transitions. This offers us a very convenient way to determine the valence state of Eu ions in solid state compounds. The wide bands of excitation and emission spectra of $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphor, and the Eu^{3+} emission peak[18] do not appear in the emission spectra, indicating that Eu^{3+} in the crystal matrix has been reduced to Eu^{2+}. The special Dy^{3+} emission peak is not present, which can be ascribed to the function that the hole-trapping centre Dy^{3+} serves as.

In the $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphor, the doped materials are rare earth elements Dy^{3+} and Eu^{3+}. Eu^{3+} in the crystal matrix can be reduced to Eu^{2+}, but Dy^{3+} cannot be reduced to Dy^{2+} in a weak reductive atmosphere. Using thermodynamic relations and under the assumption of reduction process, oxide states of rare earth elements react with CO and change into a reduced state. Thus, the following relations can be considered to take place in the reaction:

$$Eu_2O_3 + CO \rightarrow 2EuO + CO_2, \quad (7)$$

$$Dy_2O_3 + CO \rightarrow 2DyO + CO_2. \quad (8)$$

Using Gibbs free energy, it can be given

$$\Delta G = \Delta G^{\circ} + RT \ln K, \tag{9}$$

where $R = 8.314$ J/mol·K is the universal gas constant, T is the temperature measured in Kelvin. K is the equilibrium constant, ΔG° is the standard Gibbs free energy of reaction, and ΔG is the free energy. $K_{\mathrm{Eu1200\ ^{\circ}C}} = 2.16 \times 10^{-8}$, and $K_{\mathrm{Dy1200\ ^{\circ}C}} \cong 0$.[20] Based on expression (9), because of $K_{\mathrm{Dy1200\ ^{\circ}C}} \cong 0$, it is not possible to reduce Dy^{3+} into Dy^{2+}. Thus it could be considered that this element exists only in a trivalent form (Dy^{3+}). Considering non-zero equilibrium constant of Eu^{2+} production, there is a possibility of having Eu^{2+} in the reaction.

It has been reported that the optical electronegativity of Eu^{3+} is 1.74 eV,[21] and the optical electronegativity of Dy^{3+} is 1.37 eV.[22] From the values of optical electronegativity, it can also explain why Eu^{3+} in the crystal matrix can be reduced into Eu^{2+}, but Dy^{3+} cannot be reduced into Dy^{2+}.

Figure 9 shows the emission spectra ($\lambda_{\mathrm{ex}} = 472$ nm) of $(Sr_{0.97-x}Eu_{0.03}Dy_x)_3Al_2O_6$ prepared at 1250 °C with different amounts of Dy^{3+} ($x = 0$, 0.02, 0.03, 0.04). It can be seen that co-doped Dy^{3+} ions do not change the wavelength of luminescence. It implies that the crystal field, which affects 5*d* electronic states of Eu^{2+}, is not dramatically changed by the variation of doped Dy^{3+}. The luminescence of $Sr_3Al_2O_6$:Eu^{2+} is improved largely by co-doping with Dy^{3+}. However, if the doped amount of Dy^{3+} is too large ($x > 0.03$), the concentration quenching will take place and the luminescent effect will weaken.[23]

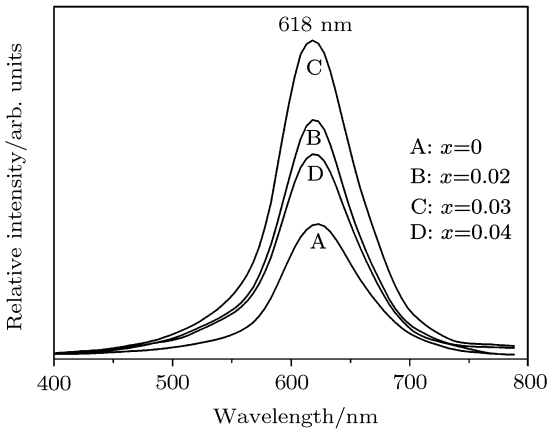


Fig.9. Emission spectra of $(Sr_{0.97-x}Eu_{0.03}Dy_x)_3Al_2O_6$ prepared at 1250 °C by sol–gel–combustion process ($\lambda_{\mathrm{ex}} = 472$ nm).

Figure 10 shows an afterglow decay curve of $(Sr_{0.97-x}Eu_{0.03}Dy_x)_3Al_2O_6$ phosphor at room temperature after it has been excited by sunlight for 10 min. The decay process contains a rapid-decaying process and a slow-decaying processe. The decay speeds of afterglow of phosphors are different from each other when they are co-doped with various amounts of Dy^{3+} (see inset in Fig.10).

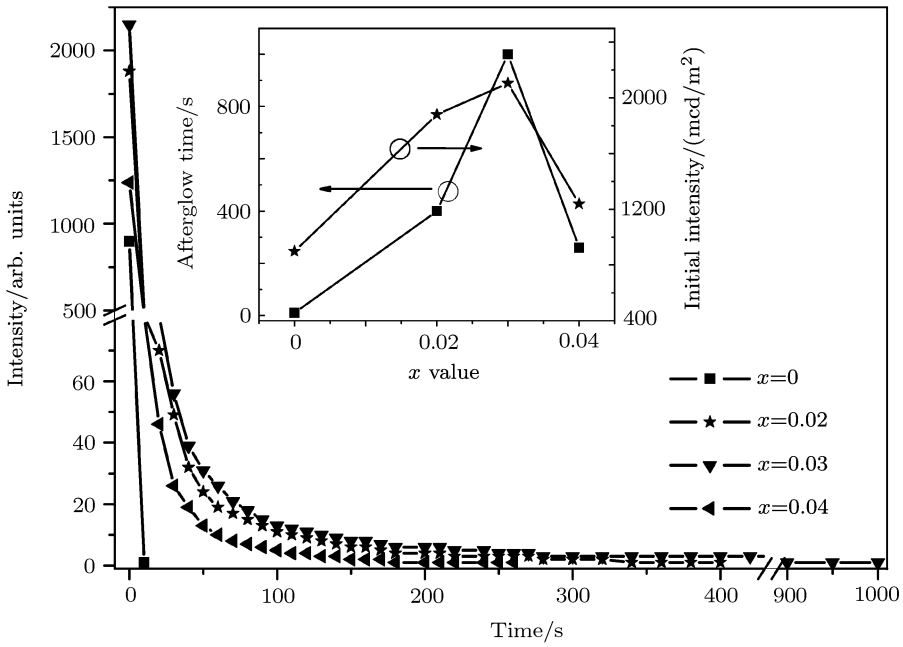


Fig.10. Afterglow decay of $(Sr_{0.97-x}Eu_{0.03}Dy_x)_3Al_2O_6$ prepared at 1250 °C by sol–gel–combustion process. The inset shows the effect of Dy^{3+} content on initial intensity of afterglow and persistence time in $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} powers excited by sunlight for 10 min.

If the doped amount of Dy^{3+} is too low to form enough trapping defects in the matrix materials, the time for afterglow will increase with Dy^{3+} content increasing. When the ratio of Eu/Dy is 1:1, the afterglow time, which allows the time to be recognized by the brightness meter ($\geq$ 1 mcd/m^2), lasts for over 1000 s when the excited light source is cut off. However, if the doped amount of Dy^{3+} is too high ($x > 0.03$), the concentration quenching will take place and the luminescent effect will weaken.

The mechanism of the long afterglow can be hole trapped–transported–detrapped process.[24] The Dy^{3+} works as a trap of holes (trap levels). The trap levels are in between the excited state and the ground state of Eu^{2+}. After excitation by sun light, electron and hole pairs are produced and some free holes transported in the conduction band are captured by the Dy^{3+} traps. When the excitation source is cut off, some holes captured by the Dy^{3+} traps are then thermally released slowly and relax to the excited state of Eu^{2+}, finally return to the ground state of Eu^{2+} accompanied with emitting light. This is the reason why the afterglow of $(Sr_{0.97-x}Eu_{0.03}Dy_x)_3Al_2O_6$ ($x = 0.02$, 0.03, 0.04) phosphor can last a long period at a relatively low luminescent intensity level.

4. Conclusions

The red long afterglow $Sr_3Al_2O_6$:Eu^{2+}, Dy^{3+} phosphors have been synthesised by sol–gel–combustion synthesis processing, along with heating the resulting combustion ash precursor powder at 1250 °C in a weak reductive atmosphere containing active carbon. During the formation of sol and gel, the dropping of ethanol into the precursor solution can reduce the amount of NO_3^- in the solution and ensure the formation of stable and homogeneous sol and gel. The phosphors prepared at 1250 °C have pure cubic $Sr_3Al_2O_6$ phase, and exhibit a broad excitation band mainly in visible range and a red broad emission band of main peak at 618 nm under the excitation of 472 nm. The afterglow of phosphor $(Sr_{0.94}Eu_{0.03}Dy_{0.03})_3Al_2O_6$ prepared at 1250 °C lasts for over 1000 s after the excited source has been cut off.

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