

# A facile and effective strategy to synthesize orthorhombic $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$ with blue-green persistent luminescence

Juan Han<sup>1</sup>, Ziqiu Jiang<sup>1</sup>, Wenyan Zhang<sup>1,4</sup>, Lingyun Hao<sup>1</sup>, Yaru Ni<sup>2,3</sup>, Chunhua Lu<sup>2,3</sup>, and Zhongzi Xu<sup>2,3</sup>

<sup>1</sup> College of Material Engineering, Jinling Institute of technology, Nanjing, China

<sup>2</sup> Jiangsu Collaborative Innovation Center for Advanced Inorganic Function

Composites, Nanjing Tech University, Nanjing, PR China

<sup>3</sup> State Key Laboratory of Materials-Oriented Chemical Engineering, College of Materials Science and Engineering, Nanjing Tech University, Nanjing, PR China

E-mail: wiseyanyan@jit.edu.cn

**Abstract.**  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  is known as a high efficient material for generating persistent luminescence. Due to its low structural stability, it is a challenge to prepare such orthorhombic material in large scale. In this work, a facile and effective strategy was designed for the preparation of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  with high purity by combining the advantages of solid state reaction and chemical vapor deposition method. The prepared  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  could effectively store the UV light energy and emit blue-green luminescence for 240 min by slow liberation of photo-excited electrons. Its blue-green afterglow was composed of two luminescent emissions which released from the Eu centers located in different crystal fields.

## 1. Introduction

Afterglow materials have attracted a great deal of interest since ancient years. Owing to its special ability to store and release light energy, such material could be applied widely for the rewritable optical memory media, security signs, traffic signage, dial markers and medical diagnostics[1, 2]. Persistent luminescence of materials depends not only on their crystal structure but on the distribution and concentration of luminescent centers inside the materials. Consequently, the development of afterglow material was rather slow until the discovery of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{2+}$  in 1996, which made a significant breakthrough in this field as it extended the afterglow duration from minutes to tens of hours[3]. From then on, people found it the key to enhance the persistent luminescence is to construct appropriate trap levels inside the materials to realize effective capturing, storing and slowly releasing of excited carriers (electron and hole). After that, extensive research was triggered on inventing new persistent phosphors as well as bringing out reasonable mechanism models of long-lasting luminescence. Silicates, germanate, gallate and titanate materials were also found to be promising hosts for storing and releasing photo-generated carriers with high efficiency[1-6]. However, the aluminates phosphors are still recognized to be the most effective afterglow material at present due to its high brightness, long phosphorescence time, suitable chemical stability, non-toxicity, and low cost.

$\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  is a “mysterious” species in the family of aluminates afterglow phosphors. Due to its low structural stability, such material could only be prepared in narrow and strict synthesis conditions. Smets et al. firstly reported the synthesis of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}$  and suggested that it was a single phase with similar crystal structure like  $\text{Sr}_{1.33}\text{Pb}_{0.67}\text{Al}_6\text{O}_{11}$ , which could yield high efficient



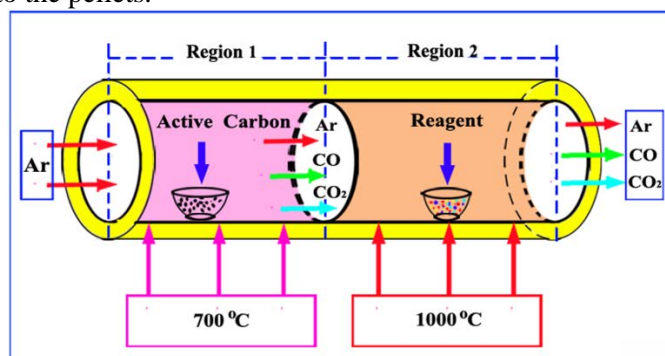
luminescence [7]. Wang et al. named such material as “so-called  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}$ ” because their work indicated that the  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}$  was not a single-phase crystal but a mixture of  $\text{SrAl}_2\text{O}_4$  and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  [8]. Furthermore, it is ambiguous that whether  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  is an appropriate matrix for the generation of persistent luminescence. Takashi et al. studied the optical properties of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  and found that the material could not yield persistent luminescence [9]. Song et al. also reported that the  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}$  didn't show obvious persistent luminescence whereas the  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Er}^{3+}$  could emit blue phosphorescence longer than 14 h [10]. Xue et al. investigated the effects of sintering temperature on the phase formation and luminescent properties of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  [11]. However, as the phosphor they synthesized was a mixture of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ ,  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  and  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ . Though  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  was main phase in the mixture, the afterglow luminescence they reported was actually a mingled emission of those three phosphors [11]. After that, little progress was got about the structure and optical property of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$ .

To make clear about the optical property of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$ , it is necessary to obtain such “mysterious” species with high purity and favorable quality. In this work, an effective and moderate strategy was proposed for the synthesis of such phosphor.  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  with high purity could be obtained by that strategy which combined the advantages of solid state reaction and chemical vapor deposition method. The prepared  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  exhibited favorable persistent luminescence at room temperature.

## 2. Material and Experiments

$\text{Al}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$  (99.9%),  $\text{Dy}_2\text{O}_3$  (99.9%),  $\text{H}_3\text{BO}_3$  (99.5%),  $\text{SrCO}_3$  (99.5%), urea (99.5%) and active carbon (99.5%) were purchased from Guoyao Corporation. Reactant ratio for  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  were  $0.01\text{Eu}_2\text{O}_3+0.02\text{Dy}_2\text{O}_3+0.97\text{SrCO}_3+1.5\text{Al}_2\text{O}_3+0.4\text{H}_3\text{BO}_3+1\text{urea}$  (mol%). A blank sample, the  $\text{Sr}_2\text{Al}_6\text{O}_{11}$ , was prepared by the same reactant ratio of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  but without the addition of  $\text{Eu}_2\text{O}_3$  and  $\text{Dy}_2\text{O}_3$ . Then the reactants were ground in an agate mortar to mix them together, and pressed into pellets.

As shown in Figure 1, solid state reaction was carried out in a tubular oven. The tubular hearth is made up of two regions which were regulated by independent temperature-control system. Active carbon particles were placed at the first region and heated at  $700\text{ }^\circ\text{C}$  to produce large amount of thermal CO gas ( $2\text{C}+\text{O}_2\rightarrow\text{CO}$ ). The pellets were located at the second region and the second region was then heated at  $1000\text{ }^\circ\text{C}$  for 2h. Ar gas flew from the first region to the second region continuously to deliver the CO gas to the pellets.

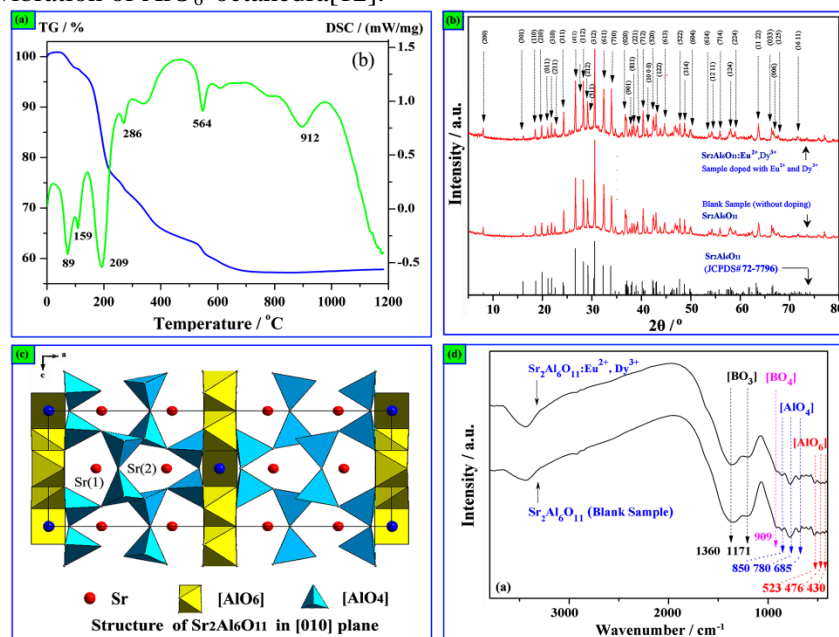


**Figure 1.** Scheme of synthesis process.

Material structures were investigated by X-ray diffraction (Thermal ARL X'TRA) and Fourier transforming infrared spectra (FTIR, Nicolet IS-10,  $4000\text{--}400\text{ cm}^{-1}$ ). Photo-luminescence (PL) and afterglow spectra were analyzed by fluorescence spectrometer (Edinburghinstruments FS5). Optical properties were also studied by incident reflection (UV-Vis-NIR spectrometer, Shimadzu, UV 3101PC). Thermal behavior was analyzed by the DSC-TG characterization (NETZSCH STA 409 PC).

### 3. Results and discussion

DSC-TG curves indicated the  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  could be obtained at  $1000^\circ\text{C}$  as there were neither weight loss nor thermal variation above that temperature (Figure 2(a)). XRD pattern shows the prepared  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  has high purity as all the diffraction peaks matched well with the crystal planes of orthorhombic  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  (JCPDS#72-7796, Figure 2(b)). The orthorhombic  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  structure was made up by two kinds of planes: the  $\text{AlO}_4$  plane which was connected by corner-shared  $\text{AlO}_4$ -tetrahedra groups, and the  $\text{AlO}_6$  plane which was connected by edge-shared  $\text{AlO}_6$ -octahedra groups (Figure 2 (c))[7, 9]. The  $\text{AlO}_4$  and  $\text{AlO}_6$  planes are cross-linked by  $\text{AlO}_4$ -tetrahedra. FTIR spectra reveal the existence of the two planes, as shown in Figure 2(d). The FTIR bands at  $850, 780$  and  $643\text{ cm}^{-1}$  corresponds to the stretching vibration of  $\text{AlO}_4$ -tetrahedra. The  $523, 476$  and  $430\text{ cm}^{-1}$  bands are assigned to the vibration of  $\text{AlO}_6$ -octahedra[12].



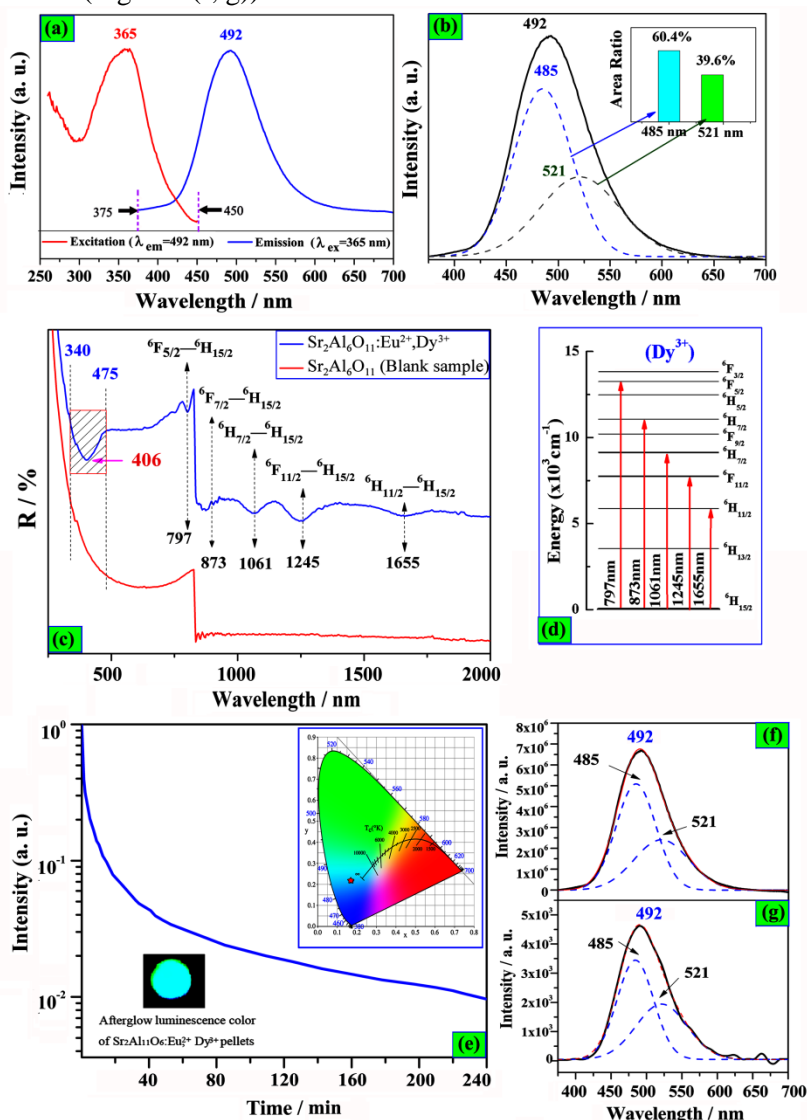
**Figure 2.** (a) DSC-TG curves of reactants; (b) XRD patterns of products; (c) Scheme of  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  structure; (d) FTIR spectra of products

In fact, the orthorhombic  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  is fairly unstable as its zigzag  $\text{AlO}_4$  planes tends to transform spontaneously to release its structural stress[9]. That enhanced the difficulty in stabilizing the  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  structure during the synthesis process. So the  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  structure could only be synthesized in narrow and strict conditions. Herein, as the CO gas was produced from the oxidation of carbon, they provided the pellets with not only a reductive atmosphere but high thermal energy to accelerate the crystallization of  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  phase (Figure 1). Intermediate products, such as  $\text{CO}_2$  and volatile boric acid, have little influence on the crystallization of  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  as they were removed from the reaction system with the flow of CO gas. Thus the preparation strategy in this work could facilitate the formation of high purity  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  by taking advantages of solid state reactions and CVD method. The  $909\text{ cm}^{-1}$  band is assigned to the vibration of residual amorphous boron oxygen compounds, indicating that the boric acid could help to prevent the structure transformation of orthorhombic  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  and improve its stability during the reaction.

Under  $365\text{ nm}$  excitation,  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  exhibited a broad emission band in  $375\text{-}650\text{ nm}$  (Figure 2(a, b)). The blue-green emission band centered at  $492\text{ nm}$  is mainly attributed to the  $4f^65d-4f^7$  electron transition of  $\text{Eu}^{2+}$  ions. Excitation band of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  overlapped with the emission band at  $375\text{-}450\text{ nm}$ , indicating the emission light at  $375\text{-}450\text{ nm}$  could be applied by the  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  to excite second emission lights (Figure 2(a)). That was supported by the reflection spectra, which show that the  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  could absorb  $340\text{-}475\text{ nm}$  light whereas

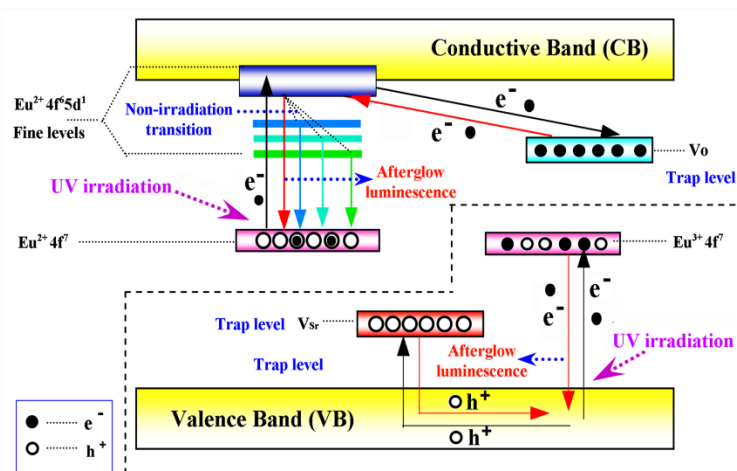
the  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  without doping have no absorption at that range (Figure 2(c)). Those absorbed light was captured by the  $\text{Eu}^{2+}$  ions to generate its  $4f^65d-4f^7$  electron transitions. In addition, the weak absorption at 797-1655 nm are assigned to the  $\text{Dy}^{3+}$  f-f electron transitions and confirms the doping of  $\text{Dy}^{3+}$  ions (Figure 2(c,d)).

The 492 nm emission band is asymmetric and could be de-convoluted into two Gaussian bands at 485 and 521 nm (Figure 2(b)). The splitting of 492 nm band originated from the variation of crystal fields around the Eu(1) and Eu(2) sites, as the  $4f^65d-4f^7$  electron transitions of  $\text{Eu}^{2+}$  ions are very sensitive to coordinate environments. The 492 nm emission of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  could still be detected after 240 min (Figure 2(e)) [7,9,13]. The profile of 492 nm emission did not change with the decay of emission intensity, indicating the Eu(1) and Eu(2) sites both contribute to the blue-green persistent luminescence (Figure 2(f, g)).



**Figure 3.** Excitation and emission spectra of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  ( $\lambda_{\text{ex}}=365\text{nm}$ ,  $\lambda_{\text{em}}=492\text{nm}$ ); (b) Gaussian fitting of 492 nm emission band; (c) UV-vis-NIR spectra of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  and  $\text{Sr}_2\text{Al}_6\text{O}_{11}$ ; (d) Scheme for the electron levels of Dy ions; (e) Persistent luminescence as a function of time for  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  (Inset, CIE chromaticity diagram of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$ ); (f) Emission spectrum of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  (1 min after excitation); (g) Emission spectrum of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+},\text{Dy}^{3+}$  (240 min after excitation)

Modified Clabau theory is recognized to be a reasonable model to explain the afterglow mechanism of  $\text{Eu}^{2+}, \text{Dy}^{3+}$  doped aluminates [14-16]. According to that theory, the afterglow emission process of  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}, \text{Dy}^{3+}$  could be speculated as follows (Figure 4): (1) the doping of  $\text{Eu}^{2+}$  and  $\text{Dy}^{3+}$  ions generated  $\text{V}_\text{o}$  and  $\text{V}_\text{Sr}$  defects; (2) Under UV irradiation, the electrons excited from  $\text{Eu}^{2+} 4f^7$  to  $4f^65d^1$  level could move into conductive band (CB), while some electrons were excited from valence band (VB) to  $\text{Eu}^{3+} 4f^7$  level; (3)  $\text{V}_\text{o}$  defects trapped the electrons released from CB, while  $\text{V}_\text{Sr}$  defects trapped the holes from VB; (4) The trapped electrons and holes were released slowly from  $\text{V}_\text{o}$  and  $\text{V}_\text{Sr}$  to yield the blue-green persistent luminescence.



**Figure 4.** Proposed afterglow mechanism for  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}, \text{Dy}^{3+}$

#### 4. Conclusion

In this work, we report the synthesis and optical properties of a distinctive afterglow material  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}, \text{Dy}^{3+}$ . It was simple and effective to synthesize the orthorhombic  $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Eu}^{2+}, \text{Dy}^{3+}$  with high purity. Under UV excitation, the special aluminates exhibits broad emissions at 375–650 nm and the 375-450 nm emission lights could be utilized by the material to excite second emission. The Eu(1) and Eu(2) sites in  $\text{Sr}_2\text{Al}_6\text{O}_{11}$  lattice both contribute to the blue-green persistent luminescence.

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